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Broad diversity of near-infrared single-photon emitters in silicon

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The boom of silicon in semiconductor technologies was closely tied to the ability to control its density of lattice defects [1]. After being regarded as detrimental to the crystal quality in the first half of the 20th century [2], point defects have become an essential tool to tune the electrical properties of this semiconductor, leading to the development of a flourishing silicon industry [1]. At the turn of the 21st century, progress in Si-fabrication and implantation processes has triggered a radical change by enabling the control of these defects at the single level [3]. This paradigm shift has brought silicon into the quantum age, where individual dopants are nowadays used as robust quantum bits to encode and process quantum information [4]. These individual qubits can be efficiently controlled and detected by all-electrical means [4], but have the drawback of either being weakly coupled to light [5] or emitting in the mid-infrared range [6] unsuitable for optical fiber propagation. In order to isolate matter qubits that feature an optical interface enabling long-distance exchange of quantum information while benefiting from well-advanced silicon integrated photonics [7], one strategy is to investigate defects in silicon that are optically-active in the near-infrared telecom bands [8, 9].

In this talk, I will present our latest results on the isolation of single optically-active defects in silicon [10,11]. Despite its small band gap, this semiconductor hosts a large variety of emitters that can be optically detected at single scale at 10K. We have identified individual emitters in silicon belonging to seven different families of fluorescent defects, including the common carbon-complex called the G-center [12]. These artificial atoms have been created by carbon implantation of a commercial silicon-on-insulator wafer usually employed for integrated photonics. Single-photon emission is demonstrated over the $1.1-1.55 \mu m$ range, spanning the O and C telecom bands. We have further observed that some single defects exhibit additional appealing properties, such as a small spread of the ZPL energies or a strong PL intensity well above the liquid nitrogen temperature. Given the advanced control over nanofabrication and integration in silicon, these individual artificial atoms are promising systems to investigate for Si-based quantum technologies, including integrated quantum photonics and quantum communications.

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NV centres in diamond as local probes of fields, strain and temperature

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The nitrogen-vacancy (NV) defect in diamond is being increasingly used as a quantum sensor to probe condensed matter systems. In this talk, I will discuss specifically how ensembles of NV centres in a single-crystal diamond can be employed to image vector magnetic and electric fields simultaneously [1] as well as the full strain tensor [2]. I will present applications of these imaging capabilities to studies of the diamond itself (via probing of internal or surface fields), and to studies of external samples such as 2D ferromagnets [3]. Finally, I will discuss the case of temperature sensing, drawing conclusions from imaging experiments performed in a cryogenic environment [4].

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Rydberg excitations of the neutral Silicon Vacancy center in diamond and their role in the spin selective decay

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Impurities in diamond is of interest due to their broad range of applicability. Various point defects embedded in diamond and realized as a solid-state quantum bit, bioimaging agent, or ultrasensitive electric or magnetic field sensor. The negative SiV was demonstrated to be indistinguishable single photon source in diamond with addressable electron spin. However, milikelyin temperatures are required for actual spin manipulation that limits its applicability.

Recently, it has been found that the neutral SiV as a S=1 system has a long coherence time and is very promising for quantum communication applications [1]. However, the electronic structure of SiV⁰ is not yet completely understood. Towards the foundations of our recent previous work [2,3], we employ plane-wave supercell calculations on SiV(0) by means of density functional theory to map the Rydberg-like bound exciton states above the Jahn-Teller coupled ${}^{3}A_{2g} \rightarrow {}^{3}A_{2u} \oplus {}^{3}E_{u}$ 1.31-eV localized zero phonon optical transition [4]. According to our *ab-initio* results, an electron hole can localize around a SiV that provides 1s, 2s, 2p... series starting at 1.4-eV (Fig. 2.).

In collaboration with the Nathalie P. de Leon group we report the realization of optically detected magnetic resonance and coherent control of SiV⁰ centers at cryogenic temperatures, enabled by efficient optical spin polarization via previously unreported higher-lying excited states (Fig. 1.). We assign these states as bound exciton states using group theory and density functional theory. These bound exciton states enable new control schemes for SiV⁰ as well as other emerging defect systems.

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Figure 1. (a) Photo-luminescence excitation (PLE) and optical spin-polarization (OSP) spectra of SiV centers. (b) Scaling of peak positions extracted from PLE. The fit uses $E_n = E_l - E_v/n^2$. $\Delta_{1,2}$ are the deviations from the model (central cell correction). (c) Proposed bound exciton model for the higher lying excited states in the hole picture.



Figure 2. Schematic overview of the bound exciton model. (a) Depiction of orbitals and energy levels associated with ground and excited states of SiV^0 . (b) Depictions of the bound exciton excitations, where the model is a SiV^- with a weakly bound positively charged hole that is orbiting around the negative defect. We model these bound holes by means of DFT calculations in supercells hosting up to 8000 carbon atoms.

Stacking fault-spin defect complexes for quantum technology applications

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Defect-based quantum systems in wide bandgap semiconductors are strong candidates for scalable quantum-information technologies. With spin-active defects, it is possible to encode and manipulate quantum information under optical excitation. In addition to the identification and characterization of such defects, it is essential to improve their optical and thermal stability for robust communication. Indeed, the systems based on point defects in semiconductors are often complicated by charge-state instabilities and interference by phonons, which can diminish spin-initialization fidelities and limit room-temperature operation. We have identified a pathway around these drawbacks by showing that an engineered quantum well can stabilize the charge state of a qubit [1]. Using density-functional theory (DFT), we have demonstrated robustness against photoionization and room temperature stability of a near-stacking fault axial divacancy. Experimental verification of theoretical results has provided a materials-based solution to the optical instability of color centers in semiconductors.

Here, we extend our theoretical simulations towards a family of stacking fault-spin defect complexes in SiC (Fig.1). We perform high accuracy calculations using semi-local (PBE) and in select cases, hybrid (HSE06) level of DFT. We present results on the structural, excited state, and magneto-optical properties of stacking fault-spin defect complexes that will assist in experimental identification. We argue that stacking fault-spin defect complexes are promising materials systems for the development of robust single-photon sources and spin qubits.



Figure 1: Stacking fault in 4H-SiC (yellow) with multiple defect sites (encircled in red)

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Wavelength Dependence of the Electrical Readout of NV Centers in Diamond

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The nitrogen-vacancy center in diamond is one of the most attractive and best investigated quantum systems used. Owing to its exceptionally stable spin state that is accessible by microwave and laser irradiation, it can be easily initialized, manipulated and read out even at room temperature. Various applications of these color centers in the areas of quantum computing, quantum communication and quantum sensing have already been implemented and tested. However, the optical readout of the NV center's spin state is quite inefficient and does not lend itself easily to miniaturization. Alternatively, as suggested by Bourgeois et al. [1] and demonstrated by Hrubesch et al. two years later [2], the spin state can also be read out electrically measuring the spin-dependent photocurrent. However, compared to the standard optical detection method, its electric analogue has been barely investigated up to now.

In the present work we address the wavelength-dependence of the electrical readout of NV centers. For this, electrically and optically detected magnetic resonance experiments (EDMR and ODMR, resp.) are performed simultaneously on as-grown type IIa CVD diamonds, equipped with Ti-Pt-Au contacts to extract the photocurrent. To investigate the wavelength dependence of both photoluminescence and photocurrent as well as of the actual ODMR and EDMR contrast, we use two different approaches: Firstly, we provide excitation pulses of wavelength width $\Delta \lambda \approx 10$ nm from a pulsed supercontinuum source, covering the spectral range between 490 and 630 nm. We then repeat these experiments with pulsed laser diodes at selected wavelengths between 440 and 640 nm.

For both readout techniques, we find optimal ranges of excitation wavelengths, which are different for EDMR and ODMR. This difference can be understood with the help of the NV photoluminescence excitation spectrum and the wavelength-dependent ionization rates of both, NV centers and substitutional nitrogen donors. Based on these, we develop a model considering the dominant contrast-limiting processes for ODMR and EDMR.

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Photoionization of negatively charged NV centers in diamond: theory and *ab-initio* calculations

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The negatively charged nitrogen-vacancy (NV⁻) center in diamond has become one of the leading platforms to test and implement various quantum technologies [1]. Most of these applications rely on optical spin polarization and read-out. However, optical excitation can lead to the photoionization process, whereby NV⁻ is converted to NV⁰. For many applications this is a detrimental process. However, *deliberate* ionization of NVs can also be very beneficial [2,3]. The experimental measurements of photoionization thresholds and cross-sections for the NV center are challenging. This is especially true for the photoionization from excited ³*E* state, as it competes with the stimulated emission.

In this work we present *ab-initio* calculations of photoionization thresholds of NV⁻ center from the ground ${}^{3}A_{2}$ and excited ${}^{3}E$ states. We show that after the ionization from ${}^{3}E$ state the NV center transition to metastable ${}^{4}A_{2}$ electronic state, providing an explanation of electron spin resonance experiments [4]. In addition, we present a new *ab-initio* methodology to calculate absolute photoioization cross-sections and apply it to the photoionization processes of NV⁻. These calculations provide complete picture of photoionization mechanisms and explain recent spin-to-charge conversion experiments [5,6]. The main results of our work are summarized in Figure 1.



Figure 1. Calculated cross sections as a function of photon energy. Solid blue: photoionization from the excited state ${}^{3}E$, σ_{ph} ; dark red: stimulated emission, σ_{st} ; orange: intra-defect absorption, σ_{intra} ; dashed blue: photoionization from the singlet state ${}^{1}E$.

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Atomic Scale Investigation of Point and Extended Defects in

Gallium Oxide

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Point defects are at the heart of the important properties of novel wide band gap and oxide semiconductors, and therefore understanding the details of the defects and their role in determining the properties becomes imperative. β -Ga₂O₃ has received significant attention recently due to its unique advantages, including high breakdown voltage and availability as bulk substrates, which make it a viable candidate for next-generation power device applications [1]. Here we present the first direct microscopic observation of the formation of interstitialdivacancy complexes within β -Ga₂O₃ lattice using atomic resolution scanning transmission electron microscopy (STEM) [2]. We directly observed that cation atoms, such as Ga and Sn dopants, can be present in multiple interstitial sites, and each interstitial atom is paired with two adjacent vacancies. The observed interstitial-divacancy complexes are consistent with the calculation using density functional theory (DFT), which predicts them to be compensating acceptors. The number of the observed complexes increase as a function of Sn doping concentration, which is consistent with the increase in the concentration of the trap state at E_c -2.1 eV measured using deep level optical spectroscopy. This strongly suggests that the defects are correlated with that trap level. Our finding provides new information on the exact origin of the properties of β -Ga₂O₃ that has been unobtainable using other methods. The results also provide new important insight on the material's unique response to the impurity incorporation that can impact their properties, which can ultimately guide the development of growth and doping of new-generation materials for power electronics.

Based on the finding, we have extended our study to investigate the growth characteristics and electronic properties of β -(Al_xGa_{1-x})₂O₃. The main benefits of β -(Al_xGa_{1-x})₂O₃ include the high channel mobility at the interface, as well as being able to achieve a tunable band gap, which may overcome some of the barriers existing in the fabrication of β -Ga₂O₃ based devices. Despite the promises, the growth and application of β -(Al_xGa_{1-x})₂O₃ films and heterostructures still remain at a nascent stage. Using quantitative STEM, we have identified the dominant mechanism of the Al atom incorporation into β -Ga₂O₃, and determined the detailed structure of point and extended defects in these films that affect the growth characteristics and properties of the heterostructure devices [3]. Our analysis showed that the Al atoms occupy both octahedral and tetrahedral sites, with an approximate ratio of (54:46), which highlights the growth mechanism of the film in a non-equilibrium condition, in contrast to the bulk growth at equilibrium where Al atoms occupy the octahedral sites only. DFT simulation showed that the

occupancy may be governed by the kinetics of the surface diffusion during the growth. In addition, the formation of planar extended defects is commonly observed, especially at high Al concentration in β -(Al_xGa_{1-x})₂O₃ films. Quantitative analysis of the STEM images reveals that the Al composition decreases near the planar defect, suggesting that the formation of the planar defect is due to the fluctuation in Al concentration during the growth, and that the formation of the defects can therefore be the limiting factor for the epitaxy to continue beyond a certain critical film thickness [4].

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First-principles studies of band alignments and doping of AlGaO alloys

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Gallium oxide has emerged as a promising ultrawide-bandgap semiconductor for power electronics applications, partly due to its ability to be *n*-type doped. Alloying Ga₂O₃ with Al₂O₃ can further widen its band gap, potentially enabling novel device designs. But this alloying quickly leads to an increase in the band gap and in the position of the conduction-band minimum, and it is not clear whether (Al_xGa_{1-x})₂O₃ ("AlGO") alloys will also be dopable. It is also unclear how this behavior extends to other polymorphs of AlGO alloys, whose band offsets are less well known.

Acceptor doping is unlikely to lead to *p*-type conductivity in AlGO alloys, as common dopants are afflicted by polaronic hole trapping [1]. Similar behavior is expected in other oxide polymorphs, as these phases of Ga_2O_3 share similar electronic structures [2]. Moreover, since the valence-band edge of AlGO alloys does not vary considerably, it is also likely to extend over the full (Al_xGa_{1-x})₂O₃ alloy range.

In this talk, the properties of group-IV (C, Si, Ge, and Sn) and transition metal (Hf, Zr, and Ta) substitutional dopants in AlGO alloys are systematically exploreed using first-principles hybrid functional calculations. In Ga_2O_3 , all dopants act as shallow donors. However, in Al_2O_3 all are deep defects, characterized by DX behavior or the emergence of positive-U (+/0) levels. Combining our calculations of dopant charge-state transition levels with information of the AlGO alloy band structure, the critical Al composition at which each dopant transitions from being a shallow to a deep donor is estimated. Si is identified as being the most efficient dopant to achieve *n*-type conductivity in high Al-content AlGO alloys, acting as a shallow donor over the entire predicted stability range for AlGO solid solutions [3].

The band alignments of alternative polymorphs of Ga₂O₃ with Al₂O₃ and AlGO alloys and their relationship with electronic properties will also be discussed. In orthorhombic alloys, which are of interest for their spontaneous polarization, Al alloying causes an increase in the band gap and the energetic position of the conduction-band minimum, and a decrease in the lattice parameters [4]. Interestingly, 50% Al-content ordered alloys show especially low formation enthalpies.

This work was performed in collaboration with Joel Varley, Darshana Wickramaratne, Sierra Seacat, and Hartwin Peelaers, and was supported by the ONR/NRL 6.1 Base Program.

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The Ga(1) vacancy in β -Ga₂O₃ and its family of trapped impurities

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It now seems well established that neighboring Ga(1) atoms adjacent to the Ga(1) vacancy in β -Ga₂O₃ undergo large displacements, leading to the formation of one of two shifted configurations of the form of a Ga interstitial adjacent to two Ga(1) half-vacancies. These two configurations[1-3] are illustrated in Fig. 1 (with potential H trapping sites shown); we choose the labels "Varley"[1] and "Kyrtsos"[2] to denote their first appearances in the literature. Both of these configurations for the isolated vacancy are considerably deeper in energy than the unshifted one (for which no direct evidence has to date been obtained).

In the (-3) charge state for the isolated vacancy, the Varley configuration is favored, while after trapping a hole[4,5] or one or more protons the Krytsos configuration is favored[6-8]. The primary O-H vibrational absorption arises from two H trapped at the Kyrtsos configuration[6], while thermal treatments can lead to other features arising from one or more H trapped at the Varley configuration[7,8]. Subsequent work has yielded methods to obtain the dipole directions of such defects[9,10] and is suggesting additional versions of defects with these two shifted configurations, but perturbed by lattice defects such as O vacancies or atomic impurities such as Si and Fe. Vacancy motion along the c axis from Varley to Kyrtsos to Varley, etc., may generate these perturbed vacancy defects. We are using the hybrid DFT CRYSTAL17 code[11] to assess candidates for these possible configurations and the constraints imposed on their existence by our experimental results.

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O-H centers that contain Si and Fe impurities in Ga₂O₃

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Si and Fe are common contaminants in Ga_2O_3 [1,2]. Furthermore, the intentional introduction of Si is used to dope Ga_2O_3 n-type [3], and Fe is used to make the material semi-insulating [4,5]. Hydrogen is also a common contaminant in oxide semiconductors that can interact with other defects to make them electrically inactive. We have introduced H and D into samples of Ga_2O_3 , some of which were undoped and some of which were intentionally doped with Si or Fe to investigate the possible interaction of H and D with these impurities that affect electrical properties.

The Si doped material was a 0.5 μ m thick epitaxial layer grown by MBE on an Fe-doped substrate. This material was subsequently treated in hydrogen and deuterium plasmas. SIMS results (Fig. 1) show a D profile that tracks the Si dopant profile in a way that is characteristic of the compensation or passivation of the Si shallow donor by D. The Fe-doped sample was a (010) wafer doped with Fe to be semi-insulating. This sample was annealed in H₂ and D₂ ambients at elevated temperature to introduce H and D.

We have found O-H (O-D) vibrational lines at 3477 (2577) [Fig. 2(a)] and 3490 (2585) cm⁻¹ [Fig 2(b)] that are present in both Si- and Fe-doped samples. The 3477 (2577) cm⁻¹ line is stronger for the Si-doped epilayer and the 3490 (2585) cm⁻¹ line is stronger for the Fe-doped bulk sample. We attribute the former O-H (O-D) line to a complex that includes a Si impurity and the latter O-H (O-D) line to a complex that contains Fe. Undoped Ga₂O₃ treated in D₂ also exhibits weak O-D lines at 2577 and 2585 cm⁻¹ that arise from Si and Fe impurities that are unintentionally present in the host crystal. The polarization properties [6] of these lines have also been investigated to provide structure-sensitive information for the defects. Theory suggests microscopic models for the Si-H and Fe-H complexes.

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Fig. 1. SIMS profiles for Si and D in a Si-doped Ga_2O_3 epitaxial layer grown by MBE that was subsequently treated in a D-plasma.



Fig. 2. (a) IR spectrum (77 K) of a Si-doped epitaxial layer of Ga_2O_3 treated in a D-plasma. (b) IR spectrum (77 K) of an Fe-doped Ga_2O_3 sample annealed in a D_2 ambient at 900 °C

Exploring donor dopant candidates in (AI,Ga)₂O₃ alloys through hybrid functional calculations

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Gallium oxide and related alloys are rapidly developing as promising material platforms for next-generation power electronics owing to their large, tunable band gaps, controllable electrical conductivity, and commercially-available single-crystal substrates that can be grown via a number of industrially-scalable processes. Analogous to the AlGaN system, the incorporation of Al into Ga_2O_3 to form $(Al_xGa_{1-x})_2O_3$ (AlGO) alloys can lead to a significant increase of the band gap, but spanning a much larger rage of ~4.8 eV-8.6 eV.[1,2] AlGO also exhibits the possibility of different crystal structures and lattice constants, leading to a number of possible epitaxial relationships beyond the wurtzite AlGaN system. Despite this promise, a number of questions remain as to the effectiveness of donor doping and how to overcome the possibility of compensation in the limit high Al-contents, similar to that in AlGaN. Here we assess *n*-type doping of Ga₂O₃ and consider the prospects of doping in the larger-gap Alcontaining alloys using first-principles modelling approaches based on hybrid functional calculations. We consider a number of conventional dopants such as Si, Ge and Sn, as well as lesser-explored transition-metal donor dopants that have been identified as effective alternatives.[3-5] We additionally consider the role of native cation vacancies, which are known to be potentially problematic sources of compensation. Our results identify composition regimes in AlGO alloys that may be most effectively targeted for increased band gaps and effective donor doping, with composition regimes specific to particular dopant species. These results provide guidance for doping in Ga₂O₃ and related alloys incorporated into heterostructure devices.

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Figure 1. (a) Illustration of when certain dopants on the tetrahedral or octahedral sites introduce localized states in the band gap, shown relative to the conduction band edge of β -(Al_xGa_{1-x})₂O₃ alloys (yellow shaded region) as a function of Al content. The transition from a shallow donor to a deep acceptor at Al concentrations unique to each dopant is illustrated for Si_{Al} in Al₂O₃, showing the charge-density isosurface associated with delocalized charge of a shallow donor configuration in (b) and of the localized charge of the acceptor state in (c).

Defects in gallium oxide, in the bulk and on the surface

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Monoclinic gallium oxide (β -Ga₂O₃) is an ultra-wide bandgap semiconductor with potential applications in power electronics [1-3]. The bandgap of ~4.8 eV results in a predicted breakdown field of 8 MV/cm, higher than currently used materials such as GaN (3.5 MV/cm) and 4H-SiC (3.2 MV/cm). Semi-insulating substrates are required for most practical devices such as metal-oxide-semiconductor field effect transistors. Defect properties [4] of these substrates will affect the performance of device structures grown on them.

This presentation will discuss recent experimental studies on Czochralski-grown β -Ga₂O₃ single crystals doped with Mg or Zn acceptors [5,6]. These dopants result in semi-insulating material and are likely compensated by oxygen vacancies and shallow donors. Iridium impurities originating from the crucible form deep donors that also compensate acceptors. The Ir⁴⁺ oxidation state gives rise to an absorption threshold in the visible/UV part of the spectrum and an IR absorption peak at 5148 cm⁻¹ [7,8].

Recent results for Zn-doped β -Ga₂O₃ show that Zn is a deep acceptor and, similar to Mg, forms IrZn pairs. Figure 1 shows a low-temperature IR spectrum of β -Ga₂O₃:Zn. The main peak at 5148 cm⁻¹ is due to an isolated Ir⁴⁺ donor. Smaller sidebands are also observed, which are attributed to Ir⁴⁺ impurities perturbed by a nearby Zn acceptor. These sidebands have slightly different frequencies than those seen in β -Ga₂O₃:Mg, consistent with the idea that the small peaks are due to Ir pairing with the respective acceptor (Zn or Mg).

Acceptors are passivated by hydrogen, an omnipresent contaminant, resulting in IR absorption peaks corresponding to O–H vibrational modes near 3500 cm⁻¹. An IR spectrum of deuterated β -Ga₂O₃:Zn is shown in Fig. 2. The frequency of the vibrational modes suggest that the ZnH structure is similar to that of MgH complexes, where the O–H bond is oriented along the *a* axis.





Fig. 1. IR spectrum of Ir^{4+} in β -Ga₂O₃:Zn. The main peak at 5148 cm⁻¹ is due to isolated Ir^{4+} while the smaller sidebands are assigned to IrZn pairs.

Fig. 2. IR spectrum deuterated β -Ga₂O₃:Zn. The O-D peak at 2583 cm⁻¹ is attributed to a zinc-deuterium complex.

In addition to defects in the bulk, spectral microscopy has revealed several specific defects on the surface. Some of these localized centers are very bright UV emitters, much brighter than ZnO [9]. By combining photoluminescence and Raman spectroscopy, intriguing clues are being found about the identity of these mysterious surface defects.

Figure 3 shows a PL map of a bulk, hydrogenated sample. The defect emission was observed everywhere, but especially bright regions were detected as well. Some emitters are so bright, low laser power (<0.6 mW delivered to the sample) and short integration times (10 ms) had to be used to avoid saturating the spectrometer. To obtain a useful benchmark comparison, we collected PL maps of hydrogenated β -Ga₂O₃ and bulk ZnO under the same experimental conditions. From this comparison, we found that the β -Ga₂O₃ emitters have an intensity 50 times that of ZnO. We are currently performing Raman experiments to determine the identity of these very bright centers.



Fig. 3. Map of the PL intensity of bright emitters (3.27 eV) in hydrogenated β -Ga₂O₃.

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Imaging defects in silicon carbide

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Many defects induce energy levels within the forbidden band gap of a semiconductor. Electronic transitions between these levels or the band edges can be accompanied by radiative recombination producing a unique fingerprint of the defect. Mapping these defect optical signatures is a versatile, non-contact tool to characterise defect distributions in semiconductors [1].

Defects photoluminescence in wide band gap semiconductors, such as silicon carbide and diamond, has been of great recent interest for a range of emerging quantum technologies. The ability to optically address single defects is an exciting route towards solid state quantum computing, communication and sensing [2]. Significant progress has been made with the nitrogen-vacancy centre in diamond and a broad range of defects in SiC including the silicon vacancy [3] and the divacancy [4].

There are now opportunities to leverage these quantum measurement techniques to gain insight into defect formation and evolution during semiconductor device fabrication and how these defects may impact device performance. The defects themselves may be thought of as atomic size probes used to gauge device characteristics [5-6]. In particular, optically active defects are prevalent on the surface of SiC after oxidation (see Fig. 1) which is a key step in SiC device fabrication [7-9]. These defects appear to exist at or close to the SiC/SiO₂ interface and can be resolved on the single defect level as confirmed with photon correlation experiments. They can be in electrical communication with the substrate and may therefore be involved in charge carrier trapping in SiC devices.

In this talk I will review defect imaging in SiC. In particular, single defect spectroscopy and its application to defects associated with the SiC/SiO₂ interface will be considered. The properties of these defects determined from such optical measurements will be summarised as well as opportunities for their use in quantum applications. I will also allude to other materials systems where this technique is employed.



Figure 1. Confocal photoluminescence mapping of the Si-face of 4H SiC (a) after SiO_2 etching and (b) after annealing in an oxygen ambient resulting in a 14 nm thick SiO_2 surface layer. Bright isolated spots are associated with single defects.

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Optical and microwave control of spin-1/2 transition metal defects in SiC

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Solid-state based spins with strong optical interfaces are an ideal platform for the development of quantum networks. These systems enable long-distance communication between remote centers due to their favorable spin properties and optical addressability. Notably, several transition-metal defects in SiC, a wide-bandgap semiconductor with well-established fabrication techniques, offer compatibility with telecom and semiconductor industries [1-3]. This has led to intense scrutiny of the spin and optical properties of these defect centers. We show that, for spin-1/2 defects, a combination of the defect symmetry and the strong spin-orbit coupling restricts the allowed spin transitions, leading to spin lifetimes above seconds at cryogenic temperatures, but limiting the possibility of addressing the spins via resonant microwave driving [4]. The interaction with a central nucleus with non-zero spin opens forbidden transitions, enabling microwave driving via oscillating magnetic or electric fields. Our results show that this spin-1/2 defects can be efficiently addressed optically and via microwaves in a variety of device architectures, and the strong hyperfine coupling can be used to indirectly control the central nuclear spin.



Figure 1 (a,b) Color map of matrix elements between electronic spin-1/2 states with hyperfine substructure. Turning on the hyperfine coupling leads to efficient spin-driving with an oscillating field parallel to both the symmetry axis of the defect and to the static magnetic field B₀. This is enabled via the dipolar coupling between the nuclear and the electronic spin, which leads to a non-trivial quantization direction. (c) View along c-axis of the electronic wavefunction. Dipolar field at points of high electron density point parallel or antiparallel to black arrows.

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Defect analysis in 4H-SiC using low-energy muons

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Silicon carbide (SiC) has received increasing attention as a wide-bandgap semiconductor suitable for advanced high-power, high-temperature and quantum applications. Despite the many similarities to established Si process technologies, SiC-based power electronics require a number of modified fabrication steps, and fundamental understanding of the material properties and the reliability of state-of-the-art SiC devices are still poor [1].

There exist a variety of characterization methods – either on material or on device level - which are used to investigate processing-induced defects both in the SiC epitaxial layer and at the oxide/SiC interface, however, most of them lack the ability to resolve shallow defects close to the SiC surface. A powerful technique for a depth-resolved analysis of electronic or magnetic properties in thin-film systems is low-energy muon spin rotation (LE- μ SR). In μ SR, spin-polarized muons (μ^+) are implanted into the target material where they live for a mean lifetime of 2.2 μ s before decaying into a positron and two neutrinos. By measuring the direction of the emitted positrons in a time-resolved fashion with detectors placed around the sample, conclusions on the muon's interaction with its local environment can be drawn. At the low-energy muon (LEM) facility at the Paul Scherrer Institute, Switzerland, implantation energies in the keV range can be achieved, providing a valuable extension of conventional bulk μ SR techniques and allowing depth-resolved studies of thin films and multilayered structures in the first 300 nm of the target material. Previously, LE- μ SR was proven successful in studying defect profiles in thin films [2,3] and has also been deployed to investigate band bending and charge-carrier profiles as well as their manipulation in semiconductors [4,5].

In this talk, the potential of LE- μ SR for the investigation of device-relevant defects in 4H-SiC is discussed using the example of vacancy defects. Experiments on proton-irradiated and subsequently annealed 4H-SiC show a distinct difference in the muon response to silicon (V_{Si}) and carbon (V_C) vacancies [6,7], suggesting that LE- μ SR is sensitive to the different relaxation mechanisms driven by the vacancy nearest-neighbor dangling bonds. For this study, low-doped n-type 4H-SiC was irradiated with protons to varying fluences and subsequently annealed leaving either V_{Si} and V_C (annealed at 300°C, "V_{Si} samples") or predominantly V_C (annealed at 1200°C, "V_C samples"). Vacancy concentrations were confirmed by DLTS and PL and ranged from 10¹⁴-10¹⁵ cm⁻³ for the V_{Si}, and from ~10¹⁷-10¹⁹ cm⁻³ for the V_C samples. Experimental measurements were supported by density-functional theory calculations using hydrogen as a substitute for the muon.

The implantation of μ^+ into insulators or semiconductors leads to the formation of a hydrogenlike bound state called Muonium [Mu = (μ^+e^-)] which can be easily distinguished from unbound μ^+ by their different precession frequencies in an external magnetic field. The so-called dia- and paramagnetic decay asymmetries A_D (μ^+) and A_{Mu} (Mu) are determined by the amplitudes of the corresponding precession signals and are proportional to the fraction of muons (F_D , F_{Mu}) in the particular state. In Fig. 1, F_D and F_{Mu} are shown as a function of the muon implantation energy, measured at 200 K and 0.5 mT. At energies >10 keV, samples with very large V_C concentrations (> 10^{17} cm⁻³) exhibit an increased diamagnetic fraction at the expense of F_{Mu} compared to the non-irradiated reference sample. Based on DFT calculations, this behavior can be explained by either a trapping of Mu⁰ at V_C where it captures an electron to form Mu⁻ or the trapping of Mu⁺ at V_C, where a two-electron capture process leads first to the formation of Mu⁰ and finally to Mu⁻.

Samples with V_{Si} , on the other hand, show smaller diamagnetic fractions compared to the nonirradiated reference sample, indicating that hardly any Mu⁺ or Mu⁻ is formed. Here, fielddependent measurements (not shown here) and DFT calculations suggest an attraction of the implanted μ^+ to the negative V_{Si} , where it captures one electron and forms the paramagnetic Mu⁰ state. As this Mu⁰ formation is delayed, it is not observed in the F_{Mu} fraction at 0.5 mT, and the V_{Si} and reference samples show similar F_{Mu} . Interestingly, a change in the diamagnetic signal is already observed at very low V_{Si} concentrations around 3×10^{14} cm⁻³, much lower compared to the V_C samples. We attribute this difference partially to the larger Si void compared to V_C , but mainly to its electrical properties: the strong attractive force of negatively charged V_{Si} for the positive muon and the larger energy gain by formation of V_{Si} -Mu compared to V_C -Mu.



Fig. 1: (a) Diamagnetic and (b) muonium fractions of proton-irradiated 4H-SiC measured at 200 K and 0.5 mT [7].

Our results demonstrate the exciting possibilities of LE- μ SR to distinguish between high-spin (such as V_{Si}) and negative-U behavior (such as V_C) of defects in semiconducting materials and its potential application to similar systems, such as e.g. SiGe. In addition to vacancy defects, we have initiated LE- μ SR investigations to identify and distinguish defects close to the SiC surface, which is a key aspect for many electronic and quantum technology applications. First results of this new extension of LE- μ SR will be discussed.

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Resolving the vibronic fine structure of silicon vacancy emission in silicon carbide

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Point defects in silicon carbide (SiC) have recently risen to prominence as single-photon emitters (SPEs) suitable for quantum technology applications, with the silicon vacancy (V_{si}) in 4H-SiC at the forefront [1]. Simultaneously, SiC is an important material platform for power device technology, but its utilization is hindered by the detrimental impact of point defects such as the carbon vacancy (V_c) on device performance [2]. As such, understanding the interaction of defect states with the semiconductor electronic structure is vital.

The negatively charged V_{si} in 4H-SiC (V_{si}) emits into three zero-phonon lines (ZPLs) at 858 nm (V1'), 861 nm (V1) and 916 nm (V2), where V1/V1' arise from V_{si} at a hexagonal (*h*) lattice site and V2 is assigned to the pseudo-cubic $V_{si}(k)$ [3]. Single-photon emission from V_{si} in 4H-SiC is characterized by sharp ZPLs and a broad phonon side-band (PSB), where the fraction of light channeled into the ZPL amounts to approximately 6-9 % for the two V_{si} configurations [4]. Although the V_{si} is a reliable and high-fidelity SPE, it is important to understand the influence of environmental effects on the Si vacancy emission spectrum in order to ensure optimal single-photon purity, indistinguishability and brightness. Indeed, emission from V_{si} (and comparable color centers) can be modified by interactions between defect states and external perturbations such as electric fields [5,6] and strain [7], while coupling to lattice vibrations can strongly impact the signature of a color center.

In this study, we investigate the near-infrared (NIR) portion of photoluminescence (PL) spectra from irradiated n-type 4H-SiC samples. A family of narrow peaks (labeled the L-lines) emerge close to the V1 and V1' emission lines attributed to $V_{Si}(h)$. We report on formation



conditions, electric field dependence and thermal response of the L-lines, and discuss potential origins.

Emission spectra were collected from samples holding 10 μ m epitaxial layers and showing the (0001)-face (Cree, Inc). The

Figure 1: PL spectra from a He-irradiated (2.7 MeV) sample, (a) before and (b) after subtracting the background emission.

epi-layers were n-doped (nitrogen) to net carrier concentrations of $\sim 1 \cdot 10^{15}$ cm⁻³. The samples were irradiated with 1.8 MeV protons or 2.7 MeV He ions to fluences in the range

 $1 \cdot 10^{12}$ - $8 \cdot 10^{13}$ cm⁻², and subsequently annealed at temperatures between 300 and 800 °C for 30 minutes in nitrogen flow. PL spectroscopy was conducted at 10-300 K and using either continuous wave lasers having excitation wavelengths of 405 nm or 806 nm, or a pulsed Ti:sapphire tunable laser operating at 740 nm.

Figure 1(a) displays PL spectra from He-irradiated 4H-SiC samples where L1-L7 are labeled. Importantly, several properties observed for the L-lines indicate a shared origin with that of V1/V1': The L-lines (i) appear after irradiation (regardless of ion species) in immediate

proximity to the V1 and V1' ZPLs, (ii) increase linearly in intensity with proton fluence, and (iii) are only observed when Vsi is present. Another point in favor of the L-lines' association with V_{Si} is the electric field dependence. Intensity enhancement beneath a Schottky diode, Stark shifts and field-dependent intensity modulation are all found for V1' and at least one of the L-lines, and individual differences between L1 and L2 prompt the hypothesis that the L-lines can energy be sub-divided into at least two groups. Finally, the thermal responses of V1/V1' and the L-lines also indicate a pairing trend, where steady thermal quenching (TQ) occurs for V1 and L1 while V1' and L2-L4 exhibit negative TQ features.

The results give support for a tentative assignment of the L-lines to the Si vacancy, and we now turn to the question of how the L-lines arise. The periodic nature

of the L-lines is evidenced by equidistantly spaced Figure 2: Example energy distribution markers (vertical dashed lines) in Figure 1(b). Once associated with dJT distortion of defect the markers are superimposed over the spectra, the states, in three (top) and two (bottom) existence of two distinct subsets of different line dimensions.



periodicity becomes apparent. Note that the energy separation between adjacent peaks is different for line groups V1-L4 and L1-L3. meV the i.e., 1.45 and 1.59 meV, respectively. Immediately, the regular and oscillatory appearance of the L-lines brings to mind the possible involvement of phonons in the optical transitions. However, although Huang-Rhys modeling is able to capture the shape and spacing of the observed features, the energy separation between neighboring peaks of ~1.5 meV is considerably smaller than the local vibrational modes of V_{Si} [8]. Instead, we propose a model for a vibronic origin of the L-lines where the degeneracy of the V_{si} orbitals is lifted by a dynamic Jahn-Teller (dJT) distortion mediated by moderate electron-phonon coupling. The potential energy surface accordingly transforms from one to more minima, for instance three, as schematically illustrated in Figure 2. To account for the close-lying and periodically spaced emission lines the minima cannot be identical, but instead separated by some small energy barrier.

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Dipolar Spin Relaxation of Divacancy Qubits in Silicon Carbide

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Divacancy point defect spins in silicon carbide (SiC) implement qubits with outstanding characteristics and capabilities, including but not limited to, 64 ms coherence time, spin-tophoton interfacing, and sizable, 10-30% room-temperature read-out contrast, all of these in an industrial semiconductor host. Despite these great demonstrations, there are still numerous open questions on the physics of divacancy spin qubits. In particular, spin relaxation, which sets the fundamental limit for the spin coherence time, has yet to be thoroughly studied. In this work, we carry out theoretical simulations of environmental spin-induced spin relaxation processes of different divacancy configurations in 4H-SiC, using a novel method for defect spin system relaxation [1]. We study the magnetic field dependence of the longitudinal spin relaxation time, T_1 . In particular, we reveal magnetic field values where the T_1 time drops resonantly due to coupling to either ²⁹Si and ¹³C nuclear spins or electron spins associated with other defects and dopants. We also provide a quantitative analysis of the dependence on the defect spin concentration of the defect spins and the applied magnetic field in the most relevant cases and provide a simple analytical expression allowing either for estimation of the T_1 time in samples with known spin defect concentration or for estimation of the local spin defect concentration of an ensemble or a single divacancy qubit, from the measured relaxation rates. Online preprint may be found at [2].



Figure 1: Magnetic field dependence of the longitudinal spin relaxation rate $1/T_1$ due to a) nuclear spins of natural abundance and b) spin-1/2 point defects of various concentrations. a) Relaxation due to ²⁹Si (solid dark blue line) and ¹³C (solid light blue line) nuclear spins are considered separately. For ²⁹Si, we also depict the largest (dashed dark blue line) and the smallest (dotted dark blue line) relaxation rate found in ensemble calculations.

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SO₄ complexes in CdTe and CdSe

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Oxygen, sulfur, and their complexes with native defects play an important role in the performance of CdTe- and CdSe-based semiconductor devices. Of particular examples are CdTe and CdTe_xSe_{1-x} thin-film solar cells whereby oxygen can be introduced during multiple steps of the cell fabrication process. As a part of the post-growth chloride `activation step' it proved to be beneficial for grain boundary nucleation and passivation. Sulfur, on the other hand, may out-diffuse from CdS window layers and add to the well-established phenomenon of intermixing at the CdS/CdTe interface. The cumulative impact of both elements, oxygen and sulfur, on the solar cell performance, however, is unclear without conclusive understanding of the fundamental properties of these impurities and their complexes in the host material.

The subject of the present work are sulfur-oxygen complexes (SO^{*}_n), which cause a double feature at 1097 and 1108 cm⁻¹ [1-3] and a triple one at 1094, 1107, and 1126 cm⁻¹ [4,5] in single-crystalline CdTe and CdSe, respectively. While the involvement of sulfur and oxygen in SO^{*}_n was convincingly evidenced by the spectroscopic identification of weak ³⁴S isotope analogues of the main ³²S features [3,5] and in-growth oxygen doping experiments [1,4], the microscopic structure of the complexes remains unidentified. The original model of a `SO₂ molecule' [3,5] turned out to be not fully consistent with recent first-principles calculations [6].

Here, we combine infrared absorption spectroscopy and first-principles theory to study SO_n^* in CdTe and CdSe. Temperature- and polarization-sensitive measurements performed on ¹⁶O- and ¹⁸O-enriched samples show that the above-mentioned IR absorption lines are due to v₃-like stretching vibrations of a disturbed SO₄ tetrahedron. The v₁ symmetric stretching, v₄ bending and v₁ + v₃ combination modes of the sulfate units are identified. A slightly-disturbed nearly axially oriented sulfate ion substituting for regular Cd atom is proposed as a most plausible model for the complex in CdTe and CdSe, respectively.

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Rapid Recombination by Cadmium Vacancies in CdTe

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The ability to accurately model, understand and predict the behaviour of crystalline defects would constitute a significant step towards improving photovoltaic device efficiencies and semiconductor doping control, accelerating materials discovery and design. In this work, we apply hybrid Density Functional Theory (DFT) including spin-orbit coupling to accurately model the atomistic behaviour of the cadmium vacancy (V_{Cd}) in cadmium telluride (CdTe).¹ In doing so, we resolve several longstanding discrepancies in the extensive literature on this species.

CdTe is a champion thin-film absorber for which defects, through facilitation of non-radiative recombination, significantly impact photovoltaic (PV) performance, contributing to a reduction in efficiency from an ideal detailed-balance limit of 32% to a current record of 22.1%. Despite over 70 years of experimental and theoretical research, many of the relevant defects in CdTe are still not well understood, with the definitive identification of the atomistic origins of experimentally observed defect levels remaining elusive.^{1–3}

In this work, through identification of a tellurium dimer ground-state structure for the neutral Cd vacancy, we obtain a single negative-U defect level for V_{Cd} at 0.35 eV above the VBM, finally reconciling theoretical predictions with experimental observations. Moreover, we reproduce the polaronic, optical and magnetic behaviour of V_{Cd} ⁻¹ in excellent agreement with previous Electron Paramagnetic Resonance (EPR) characterisation.⁴ We find the cadmium vacancy facilitates rapid charge-carrier recombination, reducing maximum power-conversion efficiency by over 5% for *untreated* CdTe—a consequence of tellurium dimerisation, metastable structural arrangements, and anharmonic potential energy surfaces for carrier capture.

The origins of previous discrepancies between theory and experiment, namely incomplete mapping of the defect potential energy surface (PES) and approximation models, are highlighted and discussed. Importantly, these results demonstrate the necessity to include the effects of both metastability and anharmonicity for the accurate calculation of both charge-carrier recombination rates in emerging photovoltaic materials and the efficiency limits imposed by both native and extrinsic defect species.

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Dopability and Defect Tolerance in Antimony Selenide

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With the global demand for energy increasing year on year, diversification beyond current technologies and materials is crucial to meeting this demand by accessing more sustainable materials in a wider variety of device architectures and applications. In photovoltaics, while silicon is the dominant technology, its poor absorption puts severe restrictions on device thinness and flexibility, while established 'thin-film' materials such as CdTe allow strong absorption from nanometre-thin films and flexible devices but suffer from toxicity and low abundance of constituent elements.^{1,2}

Antimony Selenide, on the other hand, is a highly promising candidate chalcogenide photovoltaic absorber, possessing a very high absorption coefficient, near-ideal band gap and relatively abundant constituent elements. Solar cells utilising it as the absorber layer are nearing 10% in efficiency,³ and the pseudo-1D nature of the material, held together by van der Waals interactions, has been highlighted as a potential reason for benign grain boundaries.⁴ Our recent theoretical work, however, has found that despite a high dielectric constant and a ns² 'lone-pair' cation configuration, both characteristics that have been associated with the concept of defect tolerance in photovolatics, Sb₂Se₃ possesses multiple low formation energy intrinsic defects with mid-gap transition levels that could severely hinder future improvements in open circuit voltage without passivation.⁵

In this work, we discuss these hybrid density functional theory calculations of the intrinsic defects of Sb₂Se₃ with a focus on examining how the amphoteric behaviour of antimony and selenium allows for such problematic antisite defects. Further, we attempt to calculate carrier capture properties of these defects and accurately assign the defect levels seen in DLTS experiments, to guide future device construction. Finally, we examine the effect of extrinsic doping in Sb₂Se₃, including our collaborations with experimental physicists and device engineers at the University of Liverpool, looking at potential n-type contaminants that may be leading to unintentional and unconventional device architectures,⁶ as well as strategies for p-type dopability. Through these results, our study examines the specific effects at play within Sb₂Se₃ but also explores the consequences on the applicability of 'defect tolerance' within post-transition metal chalcogenide materials.

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Carrier Dynamics Near a Crack in GaN Microwires with AlGaN Multiple Quantum Wells

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In order to establish the relationship between luminous efficiency and material characteristics, it is essential to precisely measure the relative contribution of radiative and non-radiative recombinations. This is usually obtained through the measurements of the luminescence decay time as a function of temperature. To do so, the commonly used technique is time-resolved photoluminescence spectroscopy [1]. However, this technique does not allow nanoscale resolution, which is the relevant scale for defect characterizations.

To go beyond this limitation, fast electrons can be used as a highly localized excitation source for luminescence measurements. This technique is called cathodoluminescence (CL) spectroscopy. Recently, picosecond time-resolved CL technique has been developed to reach at the same time high spatial and high temporal resolutions [2,3]. However, it is difficult to obtain a high brightness pulsed electron gun, which leads to reduced spatial resolution, low CL intensity or photocathode aging issues.



Figure 1 (a) SEM image of a full wire and (b) the corresponding mapping of the CL spectra along the wire. (c) Close-view SEM image near a crack on a different wire and its corresponding CL spectra map (d). The horizontal axis corresponds to the c-axis. The color bars indicate the normalized CL intensity.



Figure 2 Normalized CL intensity of the MQW (black squares) and CL lifetime (red circles) as a distance to the crack acquired at T = 5K

In this work, to circumvent these limitations, we took advantage of the specific statistics of electron/hole pair generation by fast electrons. Indeed, in a secondary electron microscope, the interaction of the incident electron with the semiconductor generates almost instantaneously (< 1 ps) a bunch of electron/hole pairs (typically > 300). These electron/hole pairs can then radiatively recombine with a probability that decreases with time, according to their carrier lifetime. Hence, by studying the autocorrelation function of the CL intensity ($g_2(\tau)$), a strong

bunching is expected at $\tau = 0$ ($g_2(\tau = 0) >> 1$). More importantly, by fitting $g_2(\tau)$, we access to the local carrier lifetime without the need for an expensive pulsed electron gun [4].

Thus, to measure the $g_2(\tau)$ of the CL signal, we built a Hanbury Brown and Twiss (HBT) interferometer to analyze the CL photon statistics. We applied this technique to the study of AlGaN/GaN core-shell quantum wells on GaN microwires grown by metalorganic vapor phase epitaxy [5]. Due to the lattice mismatch between the GaN core and the AlGaN shell, there is a formation of cracks. Near a crack, we observe that the CL blueshifts by about 100meV (Figure 1). By performing 6 x 6 k.p simulations in combination with transmission electron microscopy analysis, we ascribe this shift to the strain relaxation by the free surface near cracks. To quantify the impact of cracks on the nanoscale luminous efficiency, we recorded the carrier lifetime and the CL intensity in this region. As expected, we observe a reduction of crack region, while at the same time the intensity increases due to an improvement of the light extraction efficiency (Figure 2).

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Shallow and deep states of beryllium acceptor in GaN: why photoluminescence experiments do not reveal small polarons for defects in semiconductors

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Currently, only one shallow acceptor (Mg) has been discovered in GaN. Here, using photoluminescence (PL) measurements combined with hybrid density functional theory, we demonstrate that a shallow effective-mass state also exists for the Be_{Ga} acceptor. PL band with a maximum at 3.38 eV reveals a shallow Be_{Ga} acceptor level at 113 ± 5 meV above the valence band, which is the lowest value among any dopants in GaN reported to date. Calculations suggest that the Be_{Ga} is a dual-nature acceptor with the "bright" shallow state responsible for the 3.38 eV PL band, and the "dark", strongly localized small polaronic state due to the difference in the hole capture efficiency between the two states [1].

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Photoluminescence study of point defects in ammonothermal GaN

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Ammonothermal growth is a promising method for obtaining high-quality bulk GaN crystals. The crystals demonstrate outstanding structural properties, yet contain a high concentration of point defects [1]. In this work, we investigate point defects in basic ammonothermal GaN by using steady-state and time-resolved photoluminescence (PL) techniques.

We reported recently [2] that the low-temperature PL spectrum from basic ammonothermal GaN contains three defect-related PL bands: The Mg-related ultraviolet luminescence (UVL) band with the zero-phonon line at 3.27 eV, the Zn-related blue luminescence (BL1) band with a maximum at 2.9 eV, and a new yellow luminescence (YL2) band with a maximum at 2.3 eV. Figure 1(a) shows the PL spectra at two temperatures, where the shapes of the broad BL1 and YL2 bands are fitted with an expression obtained from a one-dimensional configuration-coordinate model. The PL analysis revealed that the concentrations of the Mg and Zn responsible for the UVL and BL1 bands are in mid-10¹⁶ cm⁻³, in agreement with secondary-ion mass-spectrometry measurements. A small blue shift of these PL bands with increasing excitation intensity or a slight red shift with a time delay after a laser pulse (both up to 10 meV) could be explained by the donor-acceptor-pair (DAP) nature of electron transitions at low temperatures, where the donor is presumably O_N – the typical shallow donor in GaN.



Fig. 1. PL spectra from as-grown ammonothermal GaN (a) and after annealing at 1100 C in nitrogen ambient (b). The dashed lines show the shapes of the broad PL bands composing the spectra. The shapes are simulated using a one-dimensional configuration-coordinate model. The annealing leads to the reduction of the YL2 band and the emergence of the YL4 and RL4 bands.

While the UVL and BL1 bands are common for GaN grown by other techniques, such as MOCVD or HVPE, the YL2 band is a new defect PL band. Its position and shape are different from the omnipresent C_N -related YL1 band (with the ZPL at 2.59 eV and band maximum at 2.17 eV). The YL2 band shifts significantly (by up to 0.1 eV) with excitation intensity or time after a laser pulse. From the analysis of the PL band shape and position at different experimental conditions, we concluded that the transition level of the defect responsible for the YL2 band is located at 0.6 ± 0.1 eV above the valence band. The YL2 band is preliminarily attributed to a defect complex containing the gallium vacancy (V_{Ga}). First-principles calculations predict that several complex defects involving the V_{Ga} can cause PL bands in the red-yellow region of the PL spectrum [3]. It is also known that ammonothermal GaN crystals contain a high concentration of the V_{Ga} [1].

To identify the defect responsible for the YL2 band, we annealed GaN samples in a nitrogen ambient at different temperatures. It is expected that complexes containing V_{Ga} and H, such as $V_{Ga}O_NH$ and $V_{Ga}O_N2H$, would dissociate with increasing temperature. Preliminary results are shown in Fig. 1(b). At annealing temperatures above 1000 °C, the intensity of the YL2 band started decreasing, and another yellow band with a maximum at 2.06 eV (tentatively labeled YL4) could be resolved (Fig. 1(b)). A red band with a maximum at 1.6 eV (RL4) appeared and became very strong even at lower temperatures (already at 850 °C). If the intense RL4 band results from dissociation of some complex, the complex is likely nonradiative.

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Nitrogen vacancy-acceptor complexes in GaN

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Understanding and identifying point defects in GaN is important for improving the material quality and increasing GaN-based devices' efficiency. GaN can also serve as a case study to understand the properties of point defects in semiconductors and compare them with first-principles calculations. In this process, photoluminescence (PL) is one of the most valuable experimental tools. A number of PL bands are identified in GaN, yet several puzzles remain unsolved [1]. Among them is the attribution of the red luminescence (RL) band in undoped GaN and GaN doped with acceptor impurities.

Several RL bands with different properties and belonging to different defects have been discovered in GaN [1]. One of them is the RL2 band observed in semi-insulating GaN grown under Ga-rich conditions. This band (with a maximum at about 1.8 eV) usually appears together with the green luminescence band (with a maximum at 2.35 eV) labeled GL2 and attributed to the isolated nitrogen vacancy (V_N) [2]. The characteristic feature of the RL2 and GL2 bands is an exponential decay of PL after a laser pulse at temperatures down to ~15 K. The PL lifetime is sample-independent, indicating that these PL bands are caused by internal transitions (from an excited state to the ground state located in the gap). For the V_N, the ground state (the +/2+ charge transition level) is located at 0.4-0.5 eV above the valence band, and the excited state is located at about 0.1 eV below the conduction band [2]. In semi-insulating GaN with the Fermi level located between the ground and excited states of the V_N⁺, a photogenerated electron is first captured by the excited state, after which the defect captures a hole, with the following electron-hole annihilation producing the GL2 band. The GL2 band is often strong in semi-insulating GaN due to the fast capture of electrons by the excited state. However, the PL lifetime is long (about 250 µs for temperatures between 15 and 100 K).

We propose that the RL2 band in semi-insulating GaN samples is the V_NA complex, where A is a single acceptor, such as Mg_{Ga} , Zn_{Ga} , Be_{Ga} , Ca_{Ga} . The V_NMg_{Ga} complex was proposed earlier as a source of the red PL band in Mg-doped GaN [3]. Our preliminary calculations indicate that several V_NA complexes may cause PL bands in the red part of the spectrum, with not much different PL maximum and expected zero-phonon line positions.

We observed the RL2 band in undoped GaN, as well as in GaN doped with Be, Mg, or implanted with Ca. The undoped, Mg- and Be-doped GaN samples were grown by molecular beam epitaxy, and Ca was implanted into GaN grown by hydride vapor phase epitaxy. In all the cases, the RL2 band coexisted with the GL2 band. After subtraction of the known shape [2] of the GL2 band, the shape of the RL2 band can be studied (Fig. 1(a)). For the four samples, the shapes are different, although the peak position is about the same (1.7-1.8 eV). The characteristic feature of the RL2 band in these samples is an exponential decay of PL in a wide range of temperatures, down to 18 K. Such behavior indicates that the transition is internal: from an excited state to the ground state of the same defect.

The temperature dependences of the RL2 band in the four GaN samples are shown in Fig. 1(b). The PL lifetime τ and its temperature dependence are drastically different for samples with different acceptor species. The results were reproduced for several samples from each group. The dependences can be fitted with the following equation:

$$\tau = \frac{\tau_0}{1 + C_1 \exp(-E_1 / kT) + C_2 \exp(-E_2 / kT)},$$
(1)

where τ_0 is the PL lifetime in the limit of low temperatures, and E_1 and E_2 are two activation energies. The larger activation energy E_2 may correspond to thermal emission of electrons from the excited state to the conduction band. The small activation energy E_1 (3 and 7 meV for Bedoped and undoped GaN, respectively) corresponds to a possible temperature dependence of the characteristic time of the internal transition. A similar low-temperature dependence with E_1 = 2 meV was observed for the GL1 band caused by unknown donor-like defect [4].

We attribute the RL2 band with the exponential decay to the V_NA complexes. In Mg-, Bedoped and Ca-implanted samples, the acceptor A is Mg_{Ga} , Be_{Ga} , and Ca_{Ga} , respectively. In undoped GaN, Mg may be present as a contaminant, but no Be or Ca impurities are expected. However, the temperature dependences of PL lifetime and the shapes of the RL2 bands are not the same in undoped and Mg-doped GaN samples. The identity of the acceptor in the V_NA complex responsible for the RL2 band in undoped GaN remains unknown.



Fig. 1. The RL2 band in GaN. (a) PL spectra at T = 18 K after the subtraction of the GL2 band. (b) The temperature dependence of the RL2 lifetime. The lines are calculated using Eq. (1) with the following parameters: $E_1 = 0$ and $E_2 = 250$ meV for GaN:Ca, $E_1 = 7$ meV and $E_2 = 80$ meV for undoped GaN, $E_1 = 3$ meV and $E_2 = 100$ meV for GaN:Be, and $E_1 = 0$ and $E_2 = 30$ meV for GaN:Mg.

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Silicon Colour Centres

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Abstract:

The future global quantum internet will require high-performance matter-photon interfaces. The highly demanding technological requirements indicate that the matter-photon interfaces currently under study all have potentially unworkable drawbacks, and there is a global race underway to identify the best possible new alternative. For overwhelming commercial and quantum reasons, silicon is the best possible host for such an interface. Silicon is not only the most developed integrated photonics and electronics platform by far, isotopically purified silicon-28 has also set records for quantum lifetimes at both cryogenic and room temperatures [1]. Despite this, the vast majority of research into photon-spin interfaces has notably focused on visible-wavelength colour centres in other materials. In this talk I will introduce a variety of silicon colour centres and discuss their properties in isotopically purified silicon-28. Some of these centres have zerophonon optical transitions in the telecommunications bands [2], some have long-lived spins in their ground states [3], and some, including the newly rediscovered T centre, have both [4]. [1] K. Saeedi, S. Simmons, J.Z. Salvail, et al. Science 342:830 (2013). [2] C. Chartrand, L. Bergeron, K.J. Morse, et al. Phys. Rev. B 98:195201 (2018). [3] K. Morse, R. Abraham, A. DeAbreu, et al. Science Advances 3:e1700930 (2017). [4] L. Bergeron, C. Chartrand, A.T.K. Kurkjian, et al. PRXQuantum 1 020301 (2020).

Bio

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Formation Behavior of Oxygen Precipitates in Silicon Wafers Subjected to Ultra-High-Temperature Rapid Thermal Process

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Gettering technology for silicon (Si) wafers with high purity in device active layers is necessary for the manufacture of image sensors and logic devices. The oxygen precipitates, referred to as bulk micro-defects (BMDs), in Si wafers is known to serve as an exceptional gettering site. Falster et al. reported that a rapid thermal process (RTP) using a non-oxidation ambient generates an excess vacancy (*V*) concentration in Czochralski (CZ) Si wafers [1]. Excess *V* enhances the oxygen precipitation during thermal treatment after RTP [1-3]. In addition, we studied the ultra-high-temperature RTP technology for CZ-Si wafers [4-6]. We discovered for the first time that RTP temperatures higher than 1300°C in an oxygen ambient enable us to achieve both an effective annihilation of void defects in CZ-Si wafers as well as a well-controlled generation of excess *V* simultaneously [5]. The RTP wafers formed BMDs in the bulk region when heat treatments were included. This RTP technology allows the production of CZ-Si wafers with a well-designed structure of a denuded zone and intrinsic gettering zone (DZ-IG), which is expected to have an impact on semiconductor manufacturing.

In our study, we clarified that BMD density is dependent on the residual V concentration in Si wafers owing to RTP [6]. However, the activation temperature that promotes the generation of BMDs is still unclear. Therefore, in this study, to clarify the nucleation and growth behaviors of BMDs owing to residual V, we investigated the effect on BMD density under variations of the temperature and duration of heat treatment after RTP.

CZ-Si wafers with diameters of 300 mm were used. The oxygen and nitrogen concentrations in the wafers were 1.17×10^{18} cm⁻³ (old ASTM) and 7.8×10^{14} cm⁻³, respectively. The soak condition in the RTP was set to 1350° C for 30 s in oxygen ambient, and the cooling rate was set to 120 K s⁻¹ to leave excess V in the bulk region. The heat treatment after RTP was configured in two temperature stages. The temperature in the first stage ranged from 750°C to 950°C, and the duration of this stage was 0.5–16 h. Meanwhile, the second stage was fixed at 1000°C for 16 h. The ramp-up rate in the first stage was fixed at 10 K min⁻¹, whereas in the second stage, it was fixed at 5 K min⁻¹. Infrared (IR) tomography (Raytex, MO441) was used to measure the BMD density.

The BMD densities reached 8×10^9 cm⁻³ (upper detection limit by IR tomography) at depths greater than 150 µm under all heat treatment conditions. Therefore, we focused on BMD densities at depths lesser than 150 µm to clarify the difference in BMD densities under each heat treatment condition. Figure 1 depicts the relationship between the depth from the wafer surface at which the BMD density reaches 1×10^9 cm⁻³ and the temperature in the first stage of heat treatment. The plots represent the experimental data, whereas the lines represent the simulation results. When the temperature in the first stage was 850°C, the depth was the shallowest; that is, it was found to be the temperature at which the BMD density was the highest. Furthermore, the BMD density was dependent on the duration of the heat treatment at

temperatures lower than 850°C; however, its influence was weak at temperatures higher than 850°C.

As the temperature increased, the nucleation rate and growth rate of BMD also increased. Thus, the nucleation stopped earlier at higher temperatures because the residual *V* concentration in the wafers was consumed owing to the pair annihilation of the interstitial Si atoms generated by the BMD growth [7]. As a result of reproducing the experiment through simulation, it was concluded that the heat treatment temperature of 850°C resulted in the highest BMD density in consideration of the BMD size and residual *V* concentration in accordance with the BMD nucleation rate and growth rate.

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Temperatures for first stage (°C)

Figure 1. Relationship between the depth from the wafer surface at which the BMD density reaches 1×10^9 cm⁻³ and the temperatures for the first stage of the heat treatment.

Defect control and Si/Ge core-shell heterojunction formation on silicon nanowire surface formed by top-down method

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One-dimensional semiconductor nanowire structures are focused as important building blocks of next-generation devices [1]. As the growth of nanowires, vapor-liquid-solid (VLS) growth using a metal catalyst, which is one of the bottom-up methods, is well known. However, in view of future device applications, a top-down approach capable of controlling the position and size of nanowires is important. Although there are advantages described above, defects are introduced on the nanowire surfaces during the formation of nanowires, which affects the device performance [2].

Here, we formed silicon nanowire (SiNW) arrays on p-type (100) Si substrates by nanoimprint lithography and reactive ion etching (RIE) methods. A thin Cr layer was patterned on the Si substrates for UV-nanoimprint lithography and lift-off processes. The RIE method using SF_6 and C_4F_8 plasma was used for deeply etching the Si substrates to form the SiNW array structures. ESR measurements were performed to investigate surface defects of SiNWs. Chemical polishing etching (CPE) and thermal oxidation were also performed to remove the surface damage and reduce the diameter of the SiNW arrays.

Figure 1 (a) shows SEM images of well aligned SiNWs formed by the top-down method. However, the surface of SiNWs became very defective after annealing in N_2 at 900 °C as shown in Figure 1 (b). due to the damage induced by etching. The ESR measurements clearly showed an ESR signal with a g-value of 2.006 which is attributed to dangling bond-type surface defects. To remove the surface damages, we performed thermal oxidation and chemical etching processes. This technique was found to be effective in removing the surface damage layer and simultaneously achieving a reduction in the nanowire diameter (Figure 1(d)).



Figure 1. SEM images of SiNW arrays (a) before and (b) after N_2 annealing at 900 °C. (c) An ESR signal observed for SiNWs after N_2 annealing. (d) A SEM image of SiNW array after chemical polishing etching (CPE) and thermal oxidation

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Characterization of grain boundaries' electrical activity by conductive atomic force microscopy in mc-Si wafers

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Multicrystalline silicon (mc-Si) is a widely used material for photovoltaic applications. The presence of metallic contaminated grain boundaries strongly affects the material's electronic properties enhancing electron-hole recombination, thus reducing the solar cell performance. The present study aims to investigate the electrical activity of metallic contaminated grain boundaries in mc-Si [1].

Two sets of mc-Si wafers, contaminated with iron and aluminium, respectively, were analyzed. The wafers presented grain boundaries whose density and character were characterized by Electron Backscatter Diffraction (EBSD), while their electrical activity was analyzed using Conductive Atomic Force Microscopy (c-AFM). The grain boundary density decreases along the ingot height and the most common coherent grain boundaries have the character $\Sigma 3^n$. The grain boundary electrical activity is mostly due to metallic precipitates located at the grain boundaries. In particular, iron precipitates enhance the current contrast at the grain boundaries. Both fixed voltage maps and current-voltage characteristics at the grain boundaries decorated with metallic impurities. As shown in Figure 1, the current profiles measured by c-AFM across a grain boundary were modelled by assuming the contribution of a Coulombic potential introduced by the positively charged precipitate. Quantitative parameters regarding the segregated iron-related precipitates are estimated from the model.



Figure 1: a) Schematic of the tip-sample system in a region close to a GB. The iron precipitate (yellow) with charge Q and radius R_p that decorates the GB introduces a Coulombic potential that induces a charge redistribution and changes the current flowing between tip (red) and sample. (b) Experimental current profile across a grain boundary and fit. Inset: distribution of R_p calculated from 50 current profiles.

The results of this study, based on local electrical characterization and appropriate modelling, will contribute to improving the understanding of the recombination at iron precipitates at grain boundaries in mc-Si.

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Experimental and theoretical investigation of the stoichiometry and morphology of oxide precipitates in silicon

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The stoichiometry of oxide precipitates (SiO_x) was the subject of a decades lasting debate. Values for x ranging from 1 to 2 were obtained by different methods and different samples. Electron energy loss spectroscopy (EELS) is a method which is very suitable to determine the stoichiometry of oxide precipitates. The local electron energy loss (EEL) spectra obtained using scanning transmission electron microscopy (STEM) can be deconvoluted into the spectra of pure Si, SiO, and SiO₂ and from the proportion of the pure phases it is possible to determine stoichiometry profiles by taking EEL spectra across the interface between oxide precipitate and silicon matrix.

An important recent finding, obtained by EELS carried out by STEM, was that the center of oxide precipitates consists of oxygen-rich SiO_x being in most cases SiO_2 surrounded by suboxide with decreasing x towards the edges meaning the oxidation state of silicon changes from Si^{4+} via Si^{3+} , Si^{2+} , Si^{1+} , to Si^0 [1].

It is not yet clear if oxide precipitates always possess such a suboxide shell. This is important because the suboxides surrounding oxide precipitates act as gettering sinks for Cu impurities [2]. Oxide precipitates need a certain size and nearly no silicon above or below it for successful deconvolution of EEL spectra. This makes the analysis of very small oxide precipitates impossible

We tried to further clarify this issue by theoretical investigation of the phase composition of oxide precipitates and the corresponding emission of self-interstitials at the minimum of the free energy and their evolution with increasing number of oxygen atoms in the precipitates [3].

Applying the model to spherical oxide precipitates, we found that for low numbers of precipitating oxygen atoms the composition is SiO₂ accompanied by a high emission of self-interstitials which relieve the strain [3]. The emission of self-interstitials just slightly decreases up to a critical number of precipitated oxygen atoms. Then, the minimum free energy suddenly drops to low values of x, the stoichiometry changes into a suboxide, and the emission of self-interstitials becomes very low. The critical number of precipitated oxygen atoms increases with increasing temperature and decreases with increasing density of oxide precipitates. This means that the availability of suboxides for gettering of Cu impurities depends on both the annealing temperature and the density of oxide precipitates.

Applying the model to oblate spheroidal precipitates for low numbers of precipitating oxygen atoms the composition is also SiO_2 , the self-interstitial emission relieving the strain is very high, and the morphology remains spherical [3]. However, when a critical number of oxygen atoms is reached the precipitate changes its shape from sphere to platelet, stops the emission of self-interstitials while maintaining a composition of SiO_2 . The optimum aspect ratio of the platelets lies between 0.02 and 0.03.

It is important to know that the results of modeling refer to homogeneous oxide precipitates

under quasi-equilibrium conditions. The kinetics of morphology change is much more slowly than a change of stoichiometry in reality. This would mean, when the octahedral morphology gets unstable suboxides can be expected to form as well.

It was found by STEM investigations that the morphology change starts at octahedral morphology. Then the growth into $\langle 110 \rangle$ directions starting at the edges of the octahedron is enhanced until a platelet evolves from the octahedron and the original octahedron remains as fins on the platelet before it vanishes completely [3].

The formation of suboxides at the edges of oxide precipitates after reaching a critical size can explain several phenomena like gettering of Cu by segregation to the suboxide region, lifetime reduction by recombination of minority carriers in the suboxide, and improved detectability by preferential etching.

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Hydrogen in anatase TiO₂

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Titanium dioxide or titania (TiO₂) has attracted a great deal of attention since the discovery of photocatalytic splitting of water under ultraviolet light exposure [1]. TiO₂ in nature occurs as rutile, anatase, or brookite, of which only rutile is a stable polymorph of bulk titania. Contribution of the surface free energy causes a reversal in the relative stabilities of the three polymorphs for nano-sized TiO₂: rutile is stable at sizes above 35 nm, brookite at sizes between 11 and 35 nm, and anatase at sizes below 11 nm.

Bulk anatase substrates are currently not available except those prepared from natural crystals which suffer from high amount of impurities, defects, and crystal imperfections. The lack of good quality synthetic bulk anatase single crystals seriously hinders the progress in understanding of its electrical and optical properties which is prerequisite for efficient applications of titania because it is this polymorph that shows the best performance in energy-related applications and optoelectronics [2,3].

Hydrogen is a common impurity in oxides—of which titania by no means is an exception with a strong impact on their electrical and optical properties. In wide band gap metal oxides hydrogen preferentially binds to oxygen and acts either as an amphoteric defect or as a shallow donor [4,5]. The latter is the case in anatase [6,7], where according to theory, interstitial hydrogen (H_i) forms an O–H bond pointing along the a(b) axis [8].

Vibrational mode spectroscopy is an important experimental approach providing a wealth of information about chemical composition of defects, their symmetry, thermal stability, etc [9]. Here, IR absorption and Raman scattering are employed to probe vibrational modes of hydrogen-related complexes in anatase titania. The properties of H_i [10], the nature of "hidden" species, invisible for the standard IR absorption spectroscopy, as well as complexes of hydrogen with Fe and Cr are addressed.

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Fe-Li complex emission in ZnO

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We report on three new extremely sharp emission lines in zinc oxide (ZnO) related to Fe-Li complexes. The identification is based on a comparison of a sample co-doped by both iron and Li, and a lithium-free sample doped by iron only. Both samples were implanted with iron and annealed under oxygen-rich conditions as described in detail in ref. [1]. The newly observed emission lines at 705nm (1.75873eV, C1), 712nm (1.74153eV, C2), and 732nm (1.69283eV, C3) are slightly red-shifted as compared to the ${}^{4}T_{1}$ to ${}^{6}A_{1}$ transition at 693nm (1.78734eV) ascribed to isolated Fe³⁺ in ZnO (see Fig. 1) [2]. All emission lines were characterized by temperature-dependent high resolution cw and time-resolved photoluminescence spectroscopy, as well as photoluminescence excitation spectroscopy. Different from the ${}^{4}T_{1}$ to ${}^{6}A_{1}$ transition of Fe³⁺ with its at least three excited states, we find only a single thermally activated excited state for each of the new complex-related emission lines. Whereas we find for the undisturbed spin-forbidden ${}^{4}T_{1}$ to ${}^{6}A_{1}$ transition at 693nm a lifetime of (24.9 ± 0.5)ms, the lifetimes are reduced for the new complex emission lines to (8.5 ± 1.0) ms. We ascribe this reduction to a stronger mixture of the internal Fe 3d states with surrounding p-orbitals. We present Zeeman spectroscopy measurements up to 15T for the complex emission lines, for which the splitting is very similar to the splitting of the undisturbed ${}^{4}T_{1}$ to ${}^{6}A_{1}$ transition. Therefore, we ascribe the new lines also to internal ⁴T₁ to ⁶A₁ transitions, but red-shifted due to a slightly modified crystal field splitting and stronger admixture of the surrounding p-orbitals. As concluded from EPR/ENDOR spectroscopy [3], the incorporation of iron and lithium atoms located on nextnearest zinc lattice sites leads to an elongation of the bond between lithium and the intermediate oxygen atom. As a consequence, the oxygen atom is expected to move closer to the iron atom. This shorter distance between the surrounding oxygen atom and the central iron atom leads to an increased local crystal field, resulting in a down-shift of the excited ⁴T₁ state. For these Fe-Li complexes three different geometrical configurations are possible in the hexagonal ZnO lattice, which we consider as the origin of the three different emission lines observed by us.



Figure 1: Low temperature PL spectra of the Fe-Li co-doped sample (bottom), showing the ${}^{4}T_{1}$ to ${}^{6}A_{1}$ emission of Fe³⁺ and the Fe-Li complex emission lines C1-C3, and the lithium free iron doped sample (top) without the complex emission lines.

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Frenkel pairs versus secondary defects balance in ion irradiated semiconducting oxides

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Intrinsic point defects and their complexes are of paramount importance for functionalization of materials [1]. In semiconductors, the defect formation energy depends on the charge state, in its turn affected by the Fermi level (E_F) [2]. Moreover, the charge state of the defects determines the energy position of the corresponding carrier traps in the band gap [2]. In return, changing intrinsic defect contents results in the E_F -shifts and, eventually, E_F -pinning, as predicted theoretically [3-5]. These phenomena arrest significant attention in semiconducting oxides, since intrinsic defects play prominent donor/acceptor roles in these materials.

Studying defects under irradiation has a long tradition; if the sample is irradiated at low enough temperatures and the measurements performed in-situ, direct signatures of the Frenkel pairs, i.e. vacancies and selfmeasurable interstitials. are [6]. Spectroscopic measurements are, of course, preferable, but not always Specifically, possible. studying the practically phenomena in a wide E_F-range, i.e. from highly resistive to highly conductive material, sets severe limitations for the applicability of the spectroscopic techniques. Alternatively, in-situ resistance measurements are possible, and collecting resistance data at low temperatures as a function of the irradiation dose has recently unveiled interesting correlations [7-9].

In the present contribution, we summarize the data of 50K in-situ resistance measurements as a function of the irradiation dose in systematically selected oxide samples [8-9] as shown in Fig.1. Notably, all irradiations were performed using 3MeV Si²⁺ ions so that the ballistic production rate for the Frenkel pairs was comparable in all samples (for simplicity, the same displacement energy, 15 eV, was used for all elements in ballistic simulations). The samples were in form of crystalline thin films grown on sapphire substrates, so that the projected range of the ions was well within the substrate for these samples. The resistance evolution in Fig.1 demonstrates systematic trends, interpreted in terms of the E_F -governed point defect balance, consistently with theoretical predictions [3-5, 8, 10].

More specifically, the data in Fig.1 were explained considering the formation of isolated Frenkel pairs and



Fig.1. Resistance evolution as a function of the 3MeV Si²⁺ ion irradiation dose at 50 K for several systematically selected groups of samples: (a) comparing different oxides, (b) varying initial E_F in In₂O₃, and (c) investigating the alloy effect in the In₂O₃-Ga₂O₃ system. The upper scale plots total Frenkel pair generation as calculated from a ballistic model. The flat high-resistivity segments of the data correspond to the outof-sensitivity range for our equipment.

secondary defects at low- and high dose ranges, respectively. As an example, we discuss the resistance evolution trend for the undoped In_2O_3 below, while similar explanation scenarios hold for other samples too. Indeed, the non-monotonic resistance trend suggests a sub-division for the low- and high dose ranges, see the data for the undoped In_2O_3 sample in Fig.1. It is reasonable to assume that for low doses the irradiation induce Frenkel pairs - vacancies and self-interstitials in both In- and O-sublattices, i.e. in the form of V_{In}/In_i and V_o/O_i , respectively; as such, the low temperature and low Frenkel pair concentration prevent the secondary defect complexes buildup. In contrast, for high doses, the buildup of secondary defects, e.g. antisites in In- and O-sublattices (i.e. In_O and O_{In}) and larger complexes is plausible, because of increasing defect concentration.

Fig.2 guides through a more quantitative analysis accounting for multiple charge contributions from each of the Frenkel pair configurations. In theory, if no other type of defects (except those in Fig.2(b)) are introduced, E_F might be pinned at $V_0(0/+)$ position, since after reaching this level the total charge of the Frenkel pairs generated in both sublattices is zero. In correlation with this prediction, we observe a characteristic "turning point" in Fig.1, labelled as R_{max}; however, E_F does not remain pinned. Indeed, keeping the E_F-level pinned would result in a constant resistance; however, further dose



Fig.2. Guidance for quantitative explanations of the low dose data for the undoped In_2O_3 sample in Fig.1. Panel (a) plots E_F as a function of the carrier concentration (n) for In_2O_3 at 50 K (solid line) and sets two characteristic data points (symbols) for n, as converted from the resistance data in Fig.1. Panel (b) shows the band gap positions for the Frenkel pairs in different charge states in In_2O_3 as calculated in Ref.10. The arrows interconnect panels (a) and (b), in particular explaining the turning point for the resistance evolution (R_{max}) for the undoped In_2O_3 , because at that E_F the total charge of the Frenkel pairs generated in both sublattices is zero. Notably, the resistance to carrier concentration conversion was done accounting for the low temperature carrier mobility measurements before and after the irradiation. The high dose part of the data were explained applying a similar "charge counting" approach for the antisites.

accumulation leads to the resistance decrease for the undoped In_2O_3 sample in Fig.1; which was explained in terms of the charges induced by the antisites. By comparing the number of newly generated carriers (corresponding to the R_{max} in Fig.1) and the ballistic Frenkel pair generation, we estimated the efficiency of the dynamic annealing for the Frenkel pairs in In_2O_3 too.

In conclusion, we made consistent interpretations of the Frenkel pairs versus secondary defects balance in ion irradiated semiconducting oxides systematically varying the oxide parameters. The present data may be of practical use in a variety of device applications requiring predictions of the oxides radiation tolerance. In a more general perspective, the present methodology may be highly valuable to benchmark the defect simulation data in variety of semiconductors.

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Designer Dopants for Improved Transparent Conducting Oxides

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The combination of electrical conductivity and optical transparency in a single material gives transparent conducting oxides (TCOs) an important role in modern optoelectronic applications such as in solar cells, flat panel displays, and smart coatings. The most commercially successful TCO so far is tin doped indium oxide (Indium Tin Oxide - ITO), which has become the industrial standard TCO for many optoelectronics applications; the ITO market share was 93% in 2013. Its widespread use stems from the fact that lower resistivities have been achieved in ITO than in any other TCO; resistivities in ITO have reached as low as $7.2 \times 10-5\Omega$ cm, while retaining >90% visible transparency. In recent years, the demand for ITO has increased considerably, mainly due to the continuing replacement of cathode ray tube technology with flat screen displays. However, indium is quite a rare metal, having an abundance in the Earth's crust of only 160 ppb by weight, compared with abundances for Zn and Sn of 79000 ppb and 2200 ppb respectively, and is often found in unstable geopolitical areas. The overwhelming demand for ITO has led to large fluctuations in the cost of indium over the past decade. There has thus been a drive in recent years to develop reduced-indium and indium-free materials which can replace ITO as the dominant industrial TCO. In this talk I will outline the strategies that we use in the Materials Theory Group to look beyond the current TCO materials, highlighting the interplay of theory and experiment

Identification of Li_{Ni} and V_{Ni} acceptor levels in doped nickel oxide

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Nickel oxide (NiO) is a versatile *p*-type semiconducting oxide with applications in solar cells [1-4], LEDs [5], electrochromics [6], UV photodetectors [7,8], and many more. While insulating in the pure stoichiometric form, semiconducting NiO thin films can be obtained by doping with lithium (leading to the formation of the Li substitutional defect, Li_{Ni}) or by inducing nickel deficiency during film growth (resulting in formation of the Ni vacancy defect, V_{Ni}). These two methods have been widely used in device fabrication. However, the energetic position of the charge transition levels (CTLs) belonging to these two defects have been unknown up to now. This is mainly the result of a previous lack of rectifying structures introducing carrier depletion into NiO. The knowledge of CTLs belonging to defects is crucial, for example for developing heterostructure devices, as high doping can lead to Fermi level pinning which impacts band alignment.

In this work [9], we show that heterostructures of NiO grown on top of SnO₂:F (FTO)-coated substrates reproducibly exhibit the formation of a space charge layer in NiO thin films. We fabricated both Li-doped and Ni-deficient thin films in this heterostructure configuration to perform capacitance-voltage (CV) measurements and thermal admittance spectroscopy (TAS), to study the two main acceptors Li_{Ni} and V_{Ni} . Using TAS, we found clear signatures of exactly one defect level per sample/ dopant type (Figure 1), which we attribute to the (-/0) CTLs of the Li_{Ni} and the V_{Ni} . The former is located at approximately 190 meV, the latter typically around 400 meV above the valence band edge. The estimated hole capture cross sections amount to $6 \cdot 10^{-17}$ cm² for Li_{Ni} and $2 \cdot 10^{-15}$ cm² for V_{Ni} .



Figure 1: Thermal admittance spectroscopy (TAS) results obtained on FTO/NiO heterostructures. NiO doped with Li (purple) and by oxygen excess (gray lines). (a) TAS spectra for various measurement frequencies, (b) Arrhenius plots of the extracted emission rates.

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Single-photon emitters in hexagonal boron nitride

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Hexagonal boron nitride (h-BN) is best known as an atomically thin two-dimensional material with an ultra-wide band gap and excellent stability. These properties also make h-BN a promising candidate to host quantum defects, and there has been much excitement over reports of single-photon emission from h-BN crystals. Despite extensive experimental and theoretical characterization, the microscopic origin of the reported single-photon emission is still the subject of debate.

In this work, we employ first-principles computational techniques to demonstrate that boron dangling bonds [1] are a compelling candidate for the microscopic origin of the observed single-photon emission. We utilize density functional theory with a hybrid functional to obtain accurate energetics and atomic geometries. The boron dangling bond possesses an optical transition with an energy of 2.06 eV and a Huang-Rhys factor of 2.3. We will discuss the level structure of the dangling bond that leads to optical dipole misalignment and magnetic field dependence.

We have further extended our understanding of the boron dangling bond by studying its properties in a single monolayer of h-BN, as opposed to bulk material [2]. We have also studied the influence of out-of-plane distortions on the dangling bond [3]. This work highlights an important feature of two-dimensional materials: the bending and twisting of the plane can give rise to important physics.

Lastly, we will briefly discuss our recently released python code Nonrad, which enables the evaluation of nonradiative transition rates [4]. Nonradiative transitions are important not only for studying bulk recombination mediated by point defects, but also for evaluating the quantum efficiency of a given quantum defect.

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Boron vacancy pair as a new quantum bit in hexagonal boron nitride with feasible decoherence protection and fabrication possibilities

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Point defect qubits in semiconductors have already demonstrated their capabilities and outstanding potential as minuscule sensors. In particular, the NV center in diamond is about to revolutionize sensing in medicine, biology, and material science. On-demand fabrication of point defect qubits close to the surface of their host material is of major importance for nanoscale sensing, since the sensitivity as well as the spatial resolution depend considerably on the distance between the qubit and the target. Qubits in layered semiconductors provide an alternative way to overcome this issue, owing to mature exfoliation possibilities and premising the formation of qubits either directly on the surface or even in monolayer samples. In this talk, we theoretically investigate the stability and magneto-optical properties of a neutral bonded pair of boron vacancies in hexagonal boron nitride and demonstrate that this system can operate as an optically addressable spin qubit with unprecedented characteristics. The stress absorption capabilities of the vacancy complex allow tailoring of the electronic structure and consequently enable control over all the magneto-optical properties of the qubit. We discuss several feasible ways of the realization of this newly proposed qubit and the possibilities of efficient decoherence protection that may result in a highly functionable point defect qubit even in a dense nuclear spin environment.



Coherent Control of Spin Defects in hexagonal Boron Nitride

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Optically active defects in solids with accessible spin states are promising candidates for quantum applications. While several candidates in 3D crystals including diamond and silicon carbide have been extensively studied, the coherent control of color centers in 2D materials is still an open issue. We recently investigated a bright 850nm fluorescence in irradiated hexagonal boron nitride (hBN) and found it spin-dependent. Using magnetic resonance techniques such as optically detected magnetic resonance (ODMR), we identify this fluorescence associated with a particular defect, a negatively charged boron vacancy $V_{\rm B}$, possessing a spin triplet (S=1) ground state and a zero-field splitting D/h of 3.48 GHz [1]. Moreover, we realized a coherent control of these defects by applying pulsed ODMR protocols [2]. In particular, we measured spin-lattice relaxation time (T_1) of 18 µs and spin coherence time (T₂) of 2 μ s at room temperature. T₁ increases by three orders of magnitude at cryogenic temperature following a T^{-5/2} power law, while T₂ remains almost unaffected. Employing electron spin-echo envelope modulation (ESEEM) we were able to separate the quadrupole and hyperfine interactions with the surrounding nuclei. Finally, by applying a two-frequency "holeburning" technique, we partially decoupled the electronic spin state from its inhomogeneous nuclear environment, which prolonged the spin coherence time by a factor of three. Our results can be important for employment of spin-decorated hBN layers as local probes in hybrid quantum systems including artificial van der Waals heterostructures, nanoscale devices and emerging atomically thin magnets, which, however, requires careful defect and heterostructure engineering.

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Thermodynamics of carbon defects in hexagonal boron nitride

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Carbon is often present in hexagonal boron nitride (hBN) samples as an unintentional impurity. In particular, recent experiments on bulk hBN samples produced by high-pressure high-temperature (HPHT) synthesis with Ba-BN as a solvent, which is one of the most popular growth method, showed the existence of carbon-rich domains, where the density of C atoms exceeds 10¹⁸ cm⁻³ [1]. Point defects in hBN have recently attracted a lot of interest due to observations of single-photon emitters (SPE) in visible and UV ranges [2,3]. The intensity of at least some of them is correlated with the amount of carbon related defects (carbon dimers, trimers or complexes with vacancies) are in good accordance with experimental characteristics of SPEs [5,6]. This calls for a detailed investigation of carbon chemistry in hBN.

In this contribution we present results of *ab initio* modeling of carbon defects in hBN. We analyzed their formation energies and concentrations as a function of temperature and growth conditions. The studied defects are: carbon monomers, dimers, trimers, and larger carbon clusters (up to C_{10}), as well as complexes of carbon with vacancies, antisites, and substitutional oxygen. To understand formation of defects in hBN samples with non-equilibrium amount of carbon, we introduce effective chemical potential of carbon. We analyze the applicability of the formation energy formalism, determining the solubility limit of carbon in hBN.

Among all investigated defects, the lowest formation energies correspond to carbon complexes of up to three atoms. Assuming T = 2000 K, which is a typical temperature of HPHT process, densities of carbon monomers, dimers and trimers exceed 10^{17} cm⁻³. In Fig. 1 we show the concentration of carbon-related defects on the growth temperature under N-rich conditions in the absence of additional oxygen. Apart from monomers, dimers, and trimers, other defects that can be present at concentrations larger than 10^{14} cm⁻³ are C₄, C₆, and star-like complexes C_B(C_N)₃ and C_N(C_B)₃. Formation energies of carbon complexes with vacancies and antisites are higher than 4 eV for physically achievable Fermi energies.

The presence of oxygen strongly modifies the results, but only under N-poor conditions. C_N - O_N becomes one of the most important defect with density exceeding 10^{17} cm⁻³ at 2000 K. This complex, together with the carbon dimer, is considered a candidate to explain the ubiquitous 4.1 eV luminescence [7]. Our calculations show that the abundance of C_N - O_N strongly depends on the growth condition, in contrast to the dimer which does not. Under N-poor conditions C_N - O_N occurs in larger concentrations than the dimer.

Above considerations present carbon chemistry in the carbon-rich limit. In addition, we developed the methodology which enables to determine the densities of different carbon defect species for a fixed amount of carbon in the system. In particular, we found out the maximal amount of carbon above which the clustering of carbon in big complexes starts. At typical temperatures of the growth, under intermediate conditions (between N-rich and N-poor), the maximal amount of carbon is 10^{18} - 10^{19} cm⁻³ (Fig. 2). This value can be considered a solubility limit. As the formation energy refers only to the equilibrium amount of impurities, we introduced the effective chemical potential of carbon to find densities of carbon complexes in

the presence of non-equilibrium amount of carbon. The applicability of the formation energy formalism above and below the solubility limit will be discussed.



Fig. 1. Densities of carbon defects as a function of temperature under N-rich conditions



Fig. 2. Solubility limit of carbon in hBN (intermediate conditions). *N_C* stands for the density of carbon atoms

In general, our calculations present important new results about the carbon chemistry in hexagonal boron nitride. These results will be useful for continued identification of single-photon emitters in hBN.

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Room-temperature optically detected magnetic resonance of single defects in hexagonal boron nitride

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Optically addressable spins in materials are important platforms for quantum technologies, such as repeaters and sensors. Identification of such systems in two-dimensional (2d) layered materials offers advantages over their bulk counterparts, as their reduced dimensionality enables more feasible on-chip integration into devices. Here, we report optically detected magnetic resonance (ODMR) from previously identified carbon-related defects in 2d hexagonal boron nitride (hBN)¹. We show that single-defect ODMR contrast can be as strong as 6% and displays a magnetic-field dependence with both positive or negative sign per defect. This bipolarity can shed light onto the low contrast reported recently for ensemble ODMR measurements for these defects. Further, the ODMR lineshape comprises a doublet resonance, suggesting either low zero-field splitting or hyperfine coupling. Our results offer a promising route towards realising a room-temperature spin-photon quantum interface in hexagonal boron nitride.



Figure: (a) Integrated PL spectrum of a single defect under 532-nm optical excitation. (b) ODMR spectra for the same defect as a function of in-plane magnetic field. The black crosses mark the saturated contrast at that magnetic field strength, i.e. 1.1 % and 1.9% at 7 mT and 14 mT, respectively, saturating at ~4% at 25 mT and beyond. (c) ODMR resonance central frequency against magnetic field, fit to a linear function. The g-factor extracted from the linear extrapolation is 1.98(1).

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First-principles calculations of shallow impurities

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Shallow impurities are central to semiconductor technology. The ability to accurately predict their properties can greatly aid experimental identification and device design. A thorough understanding of the physics of shallow impurities has also taken on new urgency in the context of quantum information science, where they form key components of qubits. Because of the large spatial extent of the wave function, first-principles calculations of shallow centers have traditionally been very challenging. In addition, the "central cell corrections" that are crucial for accurately describing binding energies and hyperfine parameters are not adequately captured by traditional semi-local functionals in density functional theory, requiring advanced approaches that have proven too computationally demanding. We have developed a methodology that is capable of accurately predicting properties of shallow impurities [1]. It is based on a combination of extrapolating results from supercell calculations carried out using a semi-local functional with performing select calculations using a hybrid functional. We will illustrate the power of this approach with results that provide an explanation for an observed unexpected strain dependence of the hyperfine properties of shallow donors in silicon, a system with applications in atomic clock transitions for silicon-based spin qubits.

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First-principles assessment of defect tolerance in halide perovskites

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Halide perovskites are strong material candidates for next-generation photovoltaic and light emitting devices, with the latest solar conversion efficiency greater than 25%. Motivated by the impressive optoelectronic performance, halide perovskites have been commonly proposed as "defect tolerant"; i.e., defects are present in these materials with high concentrations, but do not impact the device performance. However, this notion has not been rigorously assessed before. Based on accurate first-principles calculations, we demonstrate that defect-assisted nonradiative recombination in halide perovskites is actually strong [1], but the strong lattice coupling and anharmonicity need to be treated with a sophisticated methodology [2]. The iodine interstitials [3] and hydrogen vacancies [4] are detrimental nonradiative recombination centers in the prototypical halide perovskite MAPbI₃ (MA=CH₃NH₃), and could substantially impact the device performance. In addition to intrinsic point defects, extrinsic impurities should also be concerned. For instance, Bi incorporation could induce drastic nonradiative recombination as well. Even though Bi impurity itself is not a nonradiative recombination center, it could promote the formation of recombination centers such as the iodine interstitial by shifting the Fermi level [5].

We explicitly show that the defect-assisted nonradiative recombination in halide perovskites is comparable to or even stronger than that in more conventional semiconductors. What makes halide perovskite relatively distinct is that they can be grown with low defect densities using low-cost deposition techniques. However, phrasing halide perovskites as "defect tolerant" lacks fundamental basis, and is potentially misleading. Similar to the case in other conventional semiconductors, suppressing the formation of defects that act as nonradiative recombination centers is still key to further enhancing the optoelectronic performance of halide perovskites.

This work was done in collaboration with Mark E. Turiansky, Jimmy-Xuan Shen, and Chris G. Van de Walle at the University of California, Santa Barbara.

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Assessing the Impact of Defects on Lead-Free Perovskite-Inspired Solar Cells via Photo-Induced Current Transient Spectroscopy

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Lead-free perovskite-inspired materials (PIMs) are receiving ever-growing attention in photovoltaics, optoelectronics, and beyond, due to their similarity with mainstream lead-based perovskites while being free of the toxicity concerns associated with the latter [1–3]. In the search of PIMs with high optoelectronic potential, the identification of defect-tolerant compounds has been recognized as a key priority, given that their low-temperature processing is generally conducive to compositional and structural defects [4,5]. However, a comprehensive experimental characterization of the defect properties of such semiconductors has not been pursued to date, thereby hampering the rational development of defect-tolerant PIMs. Indeed, the application of mainstream defect-level characterization techniques (e.g., deep-level transient spectroscopies and thermal admittance spectroscopy) to PIMs would be problematic [6–8] or impracticable [8] due to the near-intrinsic nature of many such semiconductors [9].

Overcoming the limitations of mainstream defect-level spectroscopies, herein we demonstrate the wide applicability of photo-induced current transients as a probe into the defect parameters of PIMs [9]. We apply this approach to six representative antimony- and bismuth-based PIMs (i.e., Cs₃Sb₂I₉, Rb₃Sb₂I₉, and four embodiments of the Ag_aBi_bI_x system, with x = a + 3b) while also deriving the relevant model equations. This allows us to reveal that photo-induced current transient spectroscopy (PICTS) can detect the deep levels in such PIMs, which possess energy depths in the range of 0.2–0.7 eV and have varying concentrations and capture crosssections [9].

Building on the PICTS-determined defect levels, we present a methodology called One-Center Defect Tolerance Analysis (OCDTA) that allows the quantitative assessment of the defect tolerance of PIMs in the photovoltaic context [9]. This reveals that solar cells based on some of the PIMs studied herein would be rather tolerant to the defect levels detected. Further, we show that PICTS applied to PIMs could potentially probe defect levels down to mid-gap and could reach a sensitivity in the part-per-trillion range [9].

In view of its wide applicability to lead-free PIMs, our findings demonstrate that PICTS offers a versatile platform to further the understanding of the defect properties of PIMs and could thus catalyze the development of environmentally-friendly, high-performance PIM photovoltaics and optoelectronics.

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Role of Hydrogen in Defect Passivation of Cesium Lead Halide Perovskites Thin Films

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Cesium lead halide perovskites (CsPb X_3 with X = Cl, Br, I) are semiconductors that are receiving a great interest in the field of photonics and optoelectronics thanks to their electronic properties [1,2]; the highly efficient radiative recombination, the fine tuning of the emission in the range UV-VIS by changing the material composition -and, thus, its band gap- and the high carrier mobility make them the perfect candidate for light emitters. Moreover, they are known to be defects tolerant [3-5]. To further improve the quality of the emission, several kinds of treatments were applied to halide perovskites, such as annealing or chemicals additives addition. A successful strategy used in the last decades for III-V semiconductor compounds and alloys is the hydrogen implantation with optimal dose. In fact, hydrogen has been demonstrated to passivate both deep and shallow defects [6,7].

In this contribution we present results concerning hydrogen treatment realized for the first time on CsPbCl₃ thin films (500 nm) obtained by RF magnetron sputtering [8]. Different doses of hydrogen have been used from 2×10^{18} to 2×10^{19} ions/cm². The samples characterization has been mainly conducted at the micro and macro scale in a temperature range from 10 to 300 K. Exciton and carrier recombination dynamics have been studied by picosecond time resolved photoluminescence (PL) measurements.

Room temperature micro-PL spectrum of the untreated sample compared to samples treated with different hydrogen doses are reported in Figure 1. All the treated samples show a red shift of the PL peak energy of around 30 meV compared to the untreated one. Such shift is also observed in the transmittance curves (Figure 1b). Similar PL peak energy shift has been observed in macro-PL spectra acquired at room temperature.

XRD (X-Ray Diffraction) analysis has been also performed to investigate the hydrogen effect on the lattice crystalline phase. The XRD spectrum reveals the presence of a compressive strain in the untreated CsPbCl₃ sample, shown by a shift of the XRD peak at lower angle. Such strain (and therefore shift) is removed when the sample is treated with hydrogen. The role of hydrogen is therefore both to remove the compressive strain and to shift the PL peak at lower energy.



Figure 1. a) Room temperature micro-PL spectrum of the untreated sample compared to samples treated with different hydrogen doses; b) Room temperature transmittance spectra of the untreated sample and the one treated with the intermediate hydrogen dose.

At 10 K an increase of PL lifetime (Figure 2a) and a significant enhancement of the micro-PL and macro-PL intensity peak (Figure 2b) are found to be dependent with increasing hydrogen dose. Moreover, the Arrhenius plot changes in treated samples as shown in Figure 2c.



Figure 2. a) Comparison of PL decay at 10 K among untreated and hydrogen treated samples; b) Macro-PL spectra of the same samples reported in (a); c) Spectrally integrated PL intensity (normalized at the value at 10 K) as a function of the inverse of temperature for the untreated sample and for the treated sample with the highest hydrogen dose.

Our results indicate that the hydrogen treatment has a twofold effect: on the one hand it passivates defects leading to an increase of the PL lifetime, on the other hand it can induce a strain variation in the crystalline structure as already observed in dilute nitrides compounds [9].

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The Urbach tail in inorganic halide perovskites

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The structural and dynamical disorder in semiconductors represents a topic of fundamental relevance because of its contribution to the spectral lineshape of the photoluminescence (PL) and its major role in ruling the carrier transport properties at the band-edge. To this regard the halide perovskites family, a currently deeply investigated class of semiconductors extremely interesting for innovative applications spanning from energy harvesting to high brilliance incoherent and coherent light emitters, shows a peculiar degree of disorder, which is only recently under investigation. Among the inorganic metal halide perovskites, CsPbBr₃ is one of the most interesting because of its energy gap value ($E_g = 2.3 \text{ eV}$) that makes it suitable for efficient light emitters in the green spectral region instead of nitride-based LED. However, despite these perovskites are considered "defect tolerant" [1-3] and definitely more stable respect the hybrid perovskites, they still suffer of a limited radiative efficiency and of relevant aging issues. These deficiencies are usually ascribed to defects which are not only related to the presence of elements different from the constituent ones, but also to structural and compositional disorder (i.e. vacancies, deviation from stoichiometry, domains formation, lattice distortion, possibly combined with local strain). In addition to this kind of disorder, essentially static, the intrinsic dynamical disorder due to thermal fluctuations and phase transitions must be considered. Both kind of disorder, object of experimental and theoretical investigations [4,5], affect the carrier dynamics and the optical and transport properties, but in different ways, becoming relevant to distinguish between them. As far as the carrier dynamics, the radiative efficiency and the spectral properties are concerned, the disorder, independently from its nature, manifests itself mainly in two striking ways: a reduction of the carrier lifetime and mobility and a spectral broadening of the PL spectrum. While deep traps and recombination centres, arising from static disorder, affect only the carrier lifetime, the shallow states related to static and/or dynamic disorder play a major role in the carrier dynamics and in the spectral shape, giving rise to a broadening and a low energy exponential tail in the joint density of states (JDOS), the so-called Urbach tail (UT) [6,7]. In particular, the UT affects the conduction and photovoltaic performances of devices and its steepness is considered a figure of merit. It is commonly found that halide perovskites exhibit a rather steep UT but a not-negligible broadening, and a deeper understanding of the origin and the kind of disorder giving rise to these features is therefore of relevance.

In this work we focus on CsPbBr₃ samples but, provided that all halide perovskites show a similar behaviour, our analysis can be extended to the whole class of these semiconductors.

The physical information concerning the JDOS and the disorder, i.e. mainly the inhomogeneous broadening and the UT, are extracted from the analysis of spectrally and picosecond time resolved PL as a function of temperature and excitation power; the PL spectra on a macro and micro scale are also considered.

A wide set of $CsPbBr_3$ samples, prepared with different synthesis/deposition methods [8,9], i.e. bulk and nanocrystalline samples deposited by spin-coating or RF magnetron sputtering, was analysed, reporting for all the samples a very similar behaviour independent of morphology (bulk, thin nanocrystalline films), thickness, substrate and growth/deposition technique.

The results show that the contribution of static disorder to the broadening of PL emission is around 6 meV and almost negligible as far as the UT is concerned; in addition, from spatially resolved PL, it turns out that this kind of disorder involves sub-micron length scales. The increase with the temperature (T) of the Urbach Energy E_u , i.e. the inverse of the exponential tail slope, follows the expected dependence related to the lattice thermal fluctuations assessing its intrinsic origin, as already confirmed by power dependent measurements and time resolved PL spectra. In addition, in the low temperature range, E_u turns out to be linearly related to the T-dependent shift of the band edge, as expected for an intrinsic origin of the UT. As T exceeds 150 K, E_u follows the expected almost linear increase with T while the band edge energy shift exhibits relevant deviations from this dependence, as already reported in several papers. These deviations turn out to be sample dependent and can be attributed to changes in the strain. Finally, from the analysis of the PL spectra it comes out that the temperature dependent broadening has mainly an inhomogeneous origin rather than a homogeneous one: for this latter the values turn out to be lower than those commonly reported but in agreement with the measured dephasing times. The similar T-dependence of E_u and the inhomogeneous broadening suggests that at high temperature they have a common origin that can be ascribed to the disorder related to the random tilt of the unit cell octahedron, typical of these materials.

Therefore, the disorder that originates the PL broadening and the shallow states exponential tail in $CsPbBr_3$ has an intrinsic, dynamical origin related to lattice fluctuations and instabilities.

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Mitigation of LID and LeTID in Photovoltaics - Facets of Hydrogen Introduction

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The terms LID and LeTID describe problematic bulkj lifetime degradation effects that given rise to worries and intensive research activity in the silicon photovoltaics for decades. Just when Light-Induced Degradation (LID) due to the activation of Boron-Oxygen defects was regarded a solved problem there were first reports of yet another degradation phenomenon occurring upon illumination at elevated temperatures [1, 2]. This degradation effect termed Light and elevated Temperature-Induced Degradation (LeTID) has been investigated thoroughly by many groups in recent years since it would significantly reduce the potential of silicon-based solar cells. While the precise mechanism is still under debate it has become consensus that the effect is related to the high amounts of hydrogen [3–5] that are often incorporated in the silicon bulk during solar cell processing to facilitate interface and bulk defect passivation – in part to allow for efficient mitigation of LID.

This contribution will give an overview on the key studies linking incorporated hydrogen to occurrence and magnitude of LeTID. The studies will be used to derive general findings and aspects of the degradation phenomenon. A tentative model for the defect is suggested based on these findings and will be discussed in the presentation.

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A family of defects with negative-U properties in Czochralski-grown silicon doped with AI, B, Ga, or In: complexes of a group-III substitutional atom with the oxygen dimer

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It has been recently argued that a complex consisting of a substitutional boron atom and two oxygen atoms (B_sO_2) is a center with negative-U properties, and it is responsible for minority carrier trapping effects, persistent photoconductivity and light induced degradation of lifetime in Czochralski-grown silicon (Cz-Si) crystals doped with boron [1,2]. Depending on the position of the Fermi level, the B_sO_2 defect is either a deep donor or in several different configurations with a shallow acceptor level. The E(-/+) occupancy level of the defect has been found to be at $E_v + 0.32$ eV. Transitions between the different states associated with hole/electron emission or capture by the defect could be monitored with the use of junction capacitance techniques. From an analysis of temperature dependencies of rates of carrier emission and capture by the B_sO_2 defect in Cz-Si:B samples with different hole concentrations, electronic characteristics of the defect have been determined and its configuration coordinate diagram constructed [1,2].

We have detected a hole emission signal similar to that due to the B_sO_2 defect in Schottky diodes on p-type Si crystals doped with either Al, Ga, or In impurities. Fig. 1 shows conventional DLTS spectra recorded on as-manufactured Schottky diodes prepared on slices of p-type silicon doped with different group-III atoms. It appears that nearly identical hole emission signals with their maxima at about 391-392 K occur in all the spectra. The hole emission rates have been measured in these diodes in the temperature range from 360 K to 420 K with the use of high-



Fig. 1. Conventional DLTS spectra recorded in the temperature range 300-420 K on as-manufactured Schottky diodes from Cz-Si materials doped with either B, Al, Ga, or In impurity atoms during growth. All the spectra were recorded with the emission rate window of 10 s^{-1} and filling pulse of 200 ms.

resolution Laplace DLTS technique. Fig. 2 shows Arrhenius plots of the measured hole emission rates in four Si samples doped with either B, Al, Ga, or In impurity atoms. It is found that the emission rates and the derived values of activation energy for hole emission are very close for the differently doped samples.

We have carried out measurements of temperature dependencies of equilibrium occupancy and hole capture kinetics for the detected traps in samples doped with the different acceptor impurities. It is found from the analysis of the changes in magnitude of the DLTS signals with temperature that in all the samples the equilibrium occupancy function of the traps are characteristic for a defect with negative-U properties [3]. Further, it is revealed that positions of the E(+/-) occupancy level are very close in different samples, $E(+/-) \approx E_v + 0.32$ eV. Fig. 3 shows Arrhenius plots of the hole capture rates for the detected negative-U



Fig. 2. Arrhenius plots of hole emission rate measured in the temperature range 300-420 K on as-manufactured Schottky diodes from Cz-Si materials doped with either B, Al, Ga, or In impurity atoms during growth. The emission rates have been measured with the use of Laplace DLTS technique. The derived values of activation energies for emission and pre-exponential factors are given in the graph.



Fig. 3. Temperature dependencies of hole capture rates in diodes from Cz-grown Si doped with B, Al, Ga, and In impurity atoms. Solid lines were calculated with the use of equations from Ref. [3] and values of energy barriers and frequency factors as fitting parameters. Concentrations of holes in the samples have been determined from CV measurements at different temperatures and the [p] values at T = 300 K are given in the plot.

defects in four diodes doped with different group III impurities. The obtained experimental data have been treated with the use of non-equilibrium occupancy statistics for defects with negative-U properties proposed in Ref. [3]. Solid curves in Fig. 3 have been calculated with the use of equations from Ref. [3] and fitted to the experimental data. The decay rates depend on hole concentration [p], and the values of [p] used for fitting the data in Fig. 3 have been derived from CV measurements. The energy barriers for the transformations between the different defect states have been derived and compared for the samples doped with different acceptors.

We have checked the presence of inadvertent boron impurity atoms in the samples doped with either Al, Ga, and In impurities with the use of secondary ion mass spectroscopy, low-temperature photoluminescence, and admittance spectroscopy measurements, and boron has not been detected in significant concentrations. We suggest that the observed negative-U defects in Cz-Si samples doped with different acceptor impurities are associated with the complexes incorporating a substitutional group-III impurity atom and two oxygen atoms (A_sO₂, where A can be B, Al, Ga, or In). According to the model proposed in Ref. [1], transformations between the deep donor and shallow acceptor configurations of the B_sO₂ center are related to a transformation of the oxygen dimer in the vicinity of a Bs atom from a "square" to a staggered configuration. It appears that the presence of different group-III atoms in the A_sO₂ complex does not result in significant changes of the O₂ transformation processes. However, the $(B_sO_2)^- \Rightarrow$ $(B_sO_2)^+$ reaction is enhanced compared to that for other group-III atoms probably because of local tensile strain induced in the lattice by a relatively small substitutional boron atom.

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Electron- and proton irradiation of strongly doped silicon of p-type: formation and annealing of boron-related defects

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Boron impurity is widely used as a dominant dopant in silicon crystals of p-type. Interactions of impurity atoms with intrinsic point defects, vacancies and self- interstitials whose generation in crystals can be related to external conditions such as heat-treatment, plastic deformation, and irradiation with nuclear particles bring up an acute problem of semiconductor materials science. Various impurity-related complexes can be formed and they may be responsible for variations in electrical, optical and other properties of studied material. In contrast to commercial n-type silicon doped with phosphorus, boron impurity atoms display complicated behavior in p-type material. By way of example, phosphorus-vacancy complexes are stable in n-Si at room temperature, whereas it has long been known that such simple complexes like boron-vacancy pairs and boron interstitials turned out to be unstable at this temperature [1,2]. As a result, electrical properties of p-Si subjected, say, to fast electron irradiation and energetic protons under normal conditions should be determined by other boron-related complexes. However, the annealing behavior of such defects is as yet little understood.

This paper is aimed at investigating the electrical properties of boron-doped p-Si irradiated with 3.5 MeV electrons and 15 MeV protons at room temperature and then annealed. Samples were cut from a floating-zone Si crystal with a boron concentration of $4 \cdot 10^{16}$ cm⁻³. To trace formation and annealing processes of boron-related defects Hall effect and conductivity measurements over a wide temperature range of 20 to 300 K were taken. This allows us to separately determine marked changes in the total concentration of the shallow states of substitutional boron, N_A , and the total concentration of all compensating donors, N_D , making a quantitative analysis of relevant equations of charge balance. The initial material was weakly compensated, so the compensation ratio N_D^0/N_A^0 was about a few percent. Irradiated samples were subjected to isochronal anneals.

After electron irradiation a vast amount of the shallow acceptor states of substitutional boron of about 90 percent was lost and their removal rate at the beginning of the irradiation was found to be equal to $\eta_A = 0.79$ cm⁻¹. In sharp contrast, the total concentration of all compensating donors increased only by a small fraction of the boron loss. This is a conclusive evidence that the most boron-related complexes are electrically neutral in the irradiated p-type Si. They may be deep acceptors, since no significant concentration of radiation-produced acceptors were found between E_v +0.04 eV and E_v +0.2 eV where E_v is the top of the valence band.

These boron-related complexes turned out to be very stable. Our annealing study revealed only one prominent stage of the restoration of the shallow acceptor states of substitutional boron between $T \approx 500^{\circ}$ and 700° C, with a small fraction of boron-related defects also

annealed around $T \approx 350^{\circ}$ C. Interestingly, a similar marked annealing stage of radiationproduced defects we observed earlier in electron-irradiated p-Si heavily doped with boron, $p \approx 8 \cdot 10^{17}$ cm⁻³, too. Among the known boron-related complexes a substitutional boron atom B_s^- paired with an interstitial boron atom B_i^+ produced via the Watkins replacement mechanism is considered as a plausible defect model. Isolated neutral vacancies simultaneously produced in irradiated samples are believed to form neutral multi-vacancy complexes with deep acceptor states whose annealing may not be detected by Hall effect measurements.

The properties and behavior of boron-related complexes in proton-irradiated p-Si appears to be very similar to those observed in electron-irradiated p-Si. As expected, the removal rates of the shallow acceptor states of substitutional boron in the 8 MeV and 15 MeV proton-irradiated p-Si turned out to be $\eta_A = 260 \text{ cm}^{-1}$ and $\eta_A = 110 \text{ cm}^{-1}$, respectively, i.e. much larger than that for the electron-irradiated p-Si. A clearly defined annealing stage of boron-related defects takes place over a temperature range between $T \approx 500^{\circ}$ and 700°C. Such similarities of the annealing processes of boron-related complexes in electron- and proton-irradiated p-Si are in contrast to what is known about electron- and proton-irradiated phosphorus-doped n-Si where the properties and behavior of phosphorus-related defects appear to be rather different for the both kinds of irradiation [3].

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Characterization of LPCVD Polycrystalline Silicon Trap-Rich Based Substrates for RF Applications

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A category of engineered Silicon-on-Insulator (SOI) substrates suitable for radio-frequency (RF) applications relies on the introduction of a trap-rich (TR) polycrystalline silicon (polySi) layer to prevent the formation of a parasitic surface conduction (PSC) sheet beneath the buried oxide (BOX), detrimental for RF performances (Figure 1) [1], [2]. Figures of merit (FoM) for such applications are insertion loss, linearity and crosstalk. The substrate's contribution to those FoM can be related to the effective resistivity ρ_{eff} [3] and the second harmonic power H2 [4] measured on coplanar waveguide (CPW) line structures (inset of Figure 2(a)). Though this measurement provides a way to assess the substrate suitability for RF applications, it does not give direct information about introduced traps; whose properties are difficult to characterize due to the combination of high resistivity and large trap density. In the TR layer Fermi-level pinning occurs, preventing the use of capacitive measurement techniques.



Figure 1 – Impact of the TR layer on the RF substrate for the suppression of the PSC layer, detrimental for RF applications. In that case, the PSC is represented by a conductive layer of electrons. But it can be made of holes instead depending on V_{DC}, the fixed oxide charges and so on. For each structure, the metal depicts the circuit fabricated on the engineered SOI wafer. The base substrate is a high resistivity (HR) silicon ($\rho > 1 \ k\Omega$.cm).

For this study, we associated both RF and trap characterization. Because of the mentioned difficulties, deep level transient spectroscopy (DLTS) [5] is not suitable to characterize such substrates. Instead, we used a variant of this technique called photo-induced current transient spectroscopy (PICTS) [6]. In this method, free carriers are provided by sample illumination. A transient current, due to thermal de-trapping after light extinction, was measured between t₀ and T_w. The time t₀ is the cut-off time of the first part of the transient while T_w is the period in which the transient is measured. The signal was then processed to obtain, over a temperature range, a spectrum depending on the trap energy levels and capture cross-sections. Three RF substrates (called structures A, B and C) were fabricated to study both the impact of the introduction of a TR layer and the impact of the substrate anneal. Structure A is a highresistivity (HR) silicon wafer. For structures B and C, 1.65 µm of undoped polySi was deposited by low-pressure chemical vapor deposition (LPCVD) of silane, on HR substrates. For each structure, the HR silicon is p-type and has a resistivity of 3-8 k Ω .cm. Finally, structure C undergoes an anneal of 900°C during 2 hours in N2 ambient. For RF measurement, a 400 nmthick SiO₂ film was deposited by plasma-enhanced chemical vapor deposition (PECVD), using tetraethoxysilane (TEOS) as a precursor, to provide electrical insulation between the studied structure and the deposited CPW lines. Concerning PICTS measurements, Schottky barrier diodes were fabricated by the evaporation of semi-transparent Ti metal on the top of the studied structures (inset of Figure 2(b)).



Figure 2 – Measured second harmonic power H2 as a function of V_{DC} (a) on structures A, B and C (described in the text). Measured PICTS spectra (b) on structures A, B and C for λ = 940 nm, V_R = 10 V, t₀ = 5 ms and T_w = 100 ms. Each spectrum was measured for saturation conditions. For clarity, the PICTS signal was normalized to its maximum value. Tested structured for each measurement was depicted in the inset of each figure.

H2 measurements as a function of applied bias V_{DC} were performed on structures A, B and C. Obtained results are shown in Figure 2(a). It can be noticed that the presence of the TR layer allows a reduction of the second harmonic power by 35 dB while the substrate anneal increases it by 10 dB. Level of harmonics for structure A is higher because of the formation of the PSC layer, making the semiconductor surface highly conductive. In the case of structures B and C, it can be noticed that H2 is nearly independent on applied voltage V_{DC}. This is due to Fermi level pinning preventing band curvature at the surface of the semiconductor and formation of the PSC layer (see Figure 1). PICTS spectra, measured at saturation conditions on structures A, B and C, are shown in Figure 2(b) for an illumination wavelength λ of 940 nm and a reverse voltage V_R of 10 V. For structure A (HR substrate), the signal decreases as a function of T and a peak is located at 180 K. Concerning structures B and C, the dominant part of the spectrum is present near ambient temperature with a peak lying at 270 K. The effect of the anneal was the reduction of the normalized PICTS signal intensity between 100 and 225 K. By studying the PICTS spectrum under several conditions, such as the illumination wavelength λ or the filling pulse t_p, we were able to see that the signal detected in structure A originates from the surface, likely interface states between the deposited metal and the semiconductor. Concerning the peak observed in structure B and C, its variation with λ shows us that it is present in the volume, has an activation energy of 0.45 eV and captures preferentially electrons. We associated it with the presence of the polySi layer. Moreover, by performing complementary secondary ion mass spectroscopy (SIMS) and scanning resistance profiling (SRP) measurement we were able to highlight the presence of boron contamination inside polySi for structure C, partly responsible for the 10 dB increase of H2.

To conclude, we highlight two important parameters for the understanding of TR RF properties: information on introduced traps (density and signature) and contamination level. PICTS allows us to bring information about the first one. However, for a more complete comprehension of the TR layer, it has to be associated with techniques giving complementary information about introduced contamination (SIMS, SRP, ...).

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Computational spectroscopy for point defects

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First-principles calculations based on density functional theory (DFT) play a crucial role in the identification and characterization of point defects in materials. However, the miniaturization of devices, use of new types of semiconducting and wide-band-gap materials in electronics, and advancement of quantum technologies motivates the further development of computational methods for defects. Specifically, the utility of such calculations can be enhanced by: (i) improving the general quantitative accuracy of the methods, (ii) increasing the range of defect properties that can be addressed, and (iii) including aspects that make calculations more directly comparable to experiment. This talk will discuss several examples of recent theoretical developments aimed at each of these directions. I will give an overview of methodologies for defect-related transitions, including how the effects of temperature can be included for direct comparison to electrical measurements [6], and how these properties relate to defects for quantum technologies [7]. Also, I will discuss how quantum embedding has emerged as a promising way of combining DFT with many-body methods for correlated excited states of defects [8].

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Finite-Size Corrections of Defect Energy Levels Involving Ionic Polarization

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Interest in optical transitions involving defect states has been growing in recent years for their potential in the identification of qubit systems [1]. In this context, density functional theory calculations subject to periodic boundary conditions represent the method of choice for studying defect properties. However, in a supercell, the long-range nature of the electric field associated to a localized charge leads to spurious interactions that need to be corrected [2, 3]. In this regard, we develop a scheme for finite-size corrections of vertical transition energies and single-particle energy levels involving defect states with built-in ionic polarization in supercell calculations [4]. The method accounts on an equal footing for the screening of the electrons and of the ionic polarization charge arising from the lattice distortions. We demonstrate the accuracy of our corrections for various defects in MgO and in water by comparing with the dilute limit achieved through the scaling of the system size. The general validity of our formulation is also confirmed through a sum rule that connects vertical transition energies with formation energies of structurally relaxed defects.

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Silicon Carbide for Integrated Quantum Photonics

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A decade of focused research on silicon carbide color center spintronics and photonics has demonstrated that these systems can be used to build out the quantum technology backbone [1, 2]. The integration of color centers into nanophotonic devices is a crucial step in ensuring high fidelity and scalability of quantum processes, enabled by high light and matter interaction. However, due to the high chemical inertness of the substrate, as well as the lack of suitable heteroepitaxial growth techniques, the fabrication of nanodevices is challenging. Our recent collaboration reports the highest Purcell enhancement of color center emission in 4H-SiC enabled by the development of the silicon carbide on insulator platform [3]. Looking into nanofabrication approaches with optimal scalability for quantum technologies, we design triangular photonic devices and explore their propagation and resonant mode characteristics [4]. Furthermore, we study the formation and character of polaritons in the multi-emitter-multicavity systems suitable for all-photonic quantum simulators of solid-state phenomena.

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Computics Approach to Dislocation-Impurity Complexes and Interface Characteristics of GaN Devices*

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I report first-principles large-scale density-functional calculations which clarifies structural and electronic properties of dislocation-impurity complexes and device interfaces of GaN. "Computics" is the word which represents interdisciplinary collaboration between material science and computer science (http://computics-material.jp/index-e.html). After brief explanation of such close collaboration, I will explain the results for line and planar defects in GaN.

First, the dislocation-impurity complex [1]. The *pn*-junction diodes of GaN occasionally show leakage currents under inverse-bias voltage. Amano and his collaborators at Nagoya University have identified a leakage position of the *pn*-junction diodes as the position of the screw dislocation crossing the junction structure. Then the issue is why screw dislocation causes the leakage current in the *pn* diodes. We even don't know what the screw dislocation is in the atomic scale. We have resolved this issue. Based on the desnity-functional theory, we have examined all possible structures for the core of the screw dislocations in GaN, determined their atomic structures and revealed the dislocation energetics. Then we have found that the energetically favorable dislocation cores attract Mg acceptor impurities and passivate their acceptor functions due to quantum mechanical interference among electron states. This leads to the local n-type area around the dislocation and the leakage current in the GaN *pn*-diodes. A role of hydrogen ubiquitous in GaN devices is also discussed.

Second, the interface of the gate insulator and GaN [2]. Gate insulators which produce good performance of devices, in particular Metal-Oxide-Semiconductor (MOS) devices as a heart of current technology, is crucial in semiconductor technology. For GaN, Al₂O₃ and SiO₂ are candidate insulators. But they have pros and cons. We have explored a possibility of mixed oxides of Al₂O₃ and SiO₂, $(Al_2O_3)_{1-x}(SiO_{2)x}$ which we call AlSiO, and found its high potential. We have found that the oxygen vacancy which occasionally induces stress induced leakage current (SILC) in SiO₂ is less harmful in AlSiO and that the interface of GaN/AlSiO is intrinsically trap-free. The latter is due to the atomic diffusion in amorphous AlSiO layers which is clarified in the melt-quench technique in our molecular-dynamics simulations.

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Strain control for p-type doping of haeckelite GaN

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Despite of high demand for efficient blue light emitting diode (LED) for optoelectronics, low efficiency of p-type doping of GaN remains hindering its light emission performance. While several crystallographic phases of GaN have been considered for blue LEDs, the haeckelite phase (4|8-GaN) emerges as the stable phase for atomically thin GaN (from $2 \sim 18$ atomic layers of GaN) to challenge the wurtzite phase (w-GaN) [1,2] in the nanoscale. Regardless of the importance of 4|8-GaN for nanophotonics, the ptype doping of 4|8-GaN is still unexplored. Here, we present a theoretical study of p-type doping of 4|8-GaN with Mg and Be acceptors using selfinteraction corrected density functional theory (DFT) [3-5]. We find that Mg and Be acceptors in 4|8-GaN exhibit a dual nature i.e., the hole state exhibits a polaronic ground state (hole bound to a single nitrogen atom) and а metastable delocalized state (widely extended over many atoms). The polaronic states of Mg and Be acceptor are more stable than the respective delocalized states by 33.4 meV and 263.2 meV. We then show that tensile strain applied along the z axis (perpendicular to the basal plane) changes the ground state of Mg acceptor between the polaronic state and the delocalized state, which paves the way for effective p-type doping of 4|8present We also the GaN. simulated photoluminescence (PL) spectra of Mg acceptor



Figure 1. Polaronic (Z-1D, Z and X) and delocalized hole (D) state of Mg acceptor in 4|8-GaN under various c axis strain and their photoluminescence spectra predicted by *ab initio* calculation.

in 4|8-GaN for three different polaronic states, which directly reflects the type of polaronic state controlled by lattice strain. Our work provides a practical guideline to the effective p-type doping of 4|8-GaN, and thus opens the possibility of practical realization of atomically thin blue LED for nanophotonics.

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Do N vacancies exist in III-nitrides?

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N vacancies were hypothesized to be abundant and responsible for the residual *n*-type conductivity in GaN and the other III-nitrides in the earliest days of GaN research [1]. Optical spectroscopy combined suggested that N vacancies would act as shallow donors in GaN [2–4]. State-of-the-art theoretical calculations seem to nowadays agree that the N vacancy should be both a deep donor and not that abundant in *n*-type material due its high formation energy [5]. Detecting, identifying and characterizing nitrogen vacancies in GaN and the other III-nitrides is challenging to say the least, as they appear to be elusive to most structure-sensitive defect spectroscopies and microscopies.

Reports on direct detection of N vacancies in GaN with positron annihilation spectroscopy [6] are also scarce, as generally they are too small to localize a positron. In heavily Mg-doped material, experimental evidence suggests that they may occur at relatively high concentrations as $Mg_{Ga} - V_N$ pairs [7]. Importantly, this complex is neutral and the open volume sufficiently large for positron localization thanks to the small size of Mg (compared to Ga) and suitable atomic relaxation. N vacancies have also been suggested to be observed in relatively low-energy electron irradiated GaN [8] similarly as in the optical experiments [3, 4], but predominantly in the neutral charge state and hence not shallow donors. Also, the observed effect was minute and the identification of the N vacancies only tentative. Interestingly, in InN there is strong evidence of the N vacancies being particularly abundant at the InN/GaN growth interface, but they were observed only through the existence V_{In} -n V_N (n = 1 – 3) complexes thanks to the V_N -induced modification of the V_{In} positron annihilation signal [9].

Polar III-nitride heterostructures provide a setting where positrons can be driven and semilocalized (at least in two dimensions) at selected interfaces thanks to the built-in electric fields [10]. By performing positron experiments on a large set of N- and Ga-polar GaN/AlGaN/GaN heterostructures, and augmenting these experiments by state-of-the-art theoretical calculations of the positron state and annihilation signals, we are able to show that positrons detect N deficiency at the net negative polarization interface [11]. This finding is in line with the N vacancies at the interface acting as hole traps with deep donor character, responsible for detrimental phenomena in high electron mobility transistors. N vacancies do exist.

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A luminescence band related to carbon complexes in GaN:C observed by below bandgap excitation

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In order to exploit the full potential of carbon doping for application in Gallium nitride (GaN) based high-power devices, a detailed understanding of the doping behavior of carbon in GaN is desirable. Recently, the presence of tri-carbon complexes was proven in heavily carbon-doped GaN [1]. Furthermore, it was suggested that these tri-carbon defects induce charge state transition levels in the GaN bandgap [2,3].

In the study presented here, carbon-doped GaN grown by HVPE was investigated by photoluminescence (PL) and PL excitation spectroscopy. The carbon concentration varied over a range of two orders of magnitude from 3×10^{17} cm⁻³ to 3.5×10^{19} cm⁻³ as determined by secondary ion mass spectrometry. Compared to a nominally undoped reference sample, additional defect-related PL emission bands emerge under above bandgap excitation in carbon-doped GaN, as shown in Figure 1. A band around 3.0 eV is commonly attributed to C_N-H_i defect complexes and transforms into the C_N related band around 2.2 eV under prolonged UV illumination [4,5,6]. The overall PL intensity decreases with increasing carbon concentration due to the formation of nonradiative defects. Particularly, the quenching of carbon-related transitions can be explained by the formation of defect complexes containing more than one carbon atom [1,2]. PL spectra excited below the GaN bandgap reveal a near-infrared emission band around 2.7 eV with onset at 2.4 eV. The intensity of the 1.62 eV PL transition follows the carbon concentration.

We tentatively assign this additional band to the presence of defect complexes containing more than one carbon atom which were proven in [1,2] for the same set of samples investigated here. This 1.62 eV PL gives additional evidence for the presence of deep charge state transition levels in the GaN bandgap by tri-carbon defects. These should be taken into account for understanding and engineering the electrical properties of highly resistive layers in GaN devices.

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Figure 1: PL spectra recorded at 15 K with above bandgap excitation and $P_{\text{exc}} = 0.036 \text{ W cm}^{-2}$ for a) an undoped reference sample, and b) selected carbon doped samples covering a range of [C] = 3.2×10^{17} to 3.5×10^{19} cm⁻³.



Figure 2: PL spectra recorded at 15 K with below bandgap excitation and $P_{\text{exc}} = 0.028$ W cm⁻². The arrow indicates the emission emerging around 1.62 eV with increasing carbon concentration.

The mechanism for the emanation of a-type threading dislocations by stacking fault overlapping in III-nitride heterostructures

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The introduction of high densities of edge type threading dislocations (TDs) in III-nitride hetero-epitaxy is still not clearly understood regarding the possible operating mechanisms. TD densities exceeding 10^{10} cm⁻² are often observed while there is no resolved shear stress on the primary slip systems. Matthews-Blakeslee glide on pyramidal systems and TD introduction due to island coalescence are so far the principal mechanisms suggested to explain the phenomenon. Based on extensive transmission electron microscopy (TEM) observations on various ternary and quaternary InAlGaN epilayers, we propose a concise mechanism for TD introduction caused by the superposition of intrinsic basal stacking faults (BSFs) of I1 type (Figure 1)[1]. The I1 BSFs are often introduced during growth and are likely to be surrounded by prismatic stacking faults (PSFs), since in this way the high energy fault vector component c/2 is avoided. The eventual closure of the domain requires introduction of a second I1 BSF terminating the PSFs. Formation of zonal dislocations surrounding such a closed domain depends on the number of monolayers between the two BSFs. Our proposed crystallographic model imposes the introduction of the TDs as geometrically necessary defects for the coexistence of crystallographically equivalent morphological variants of the PSFs around the domain (Figure2). The mechanism appears to be energetically favorable, particularly for the case of Drum-type PSFs, and to explain well all the experimentally observed configurations of BSF domains.

The structural models of such domains, their delimiting partial dislocations and the crystallographic mechanism explaining the TD introduction from them is detailed based on TEM, HR(S)TEM, and EELS analysis. The proposed topological model is consistent with the bicrystalline symmetry and explains all the observed morphologies of these domains [2]. Elasticity theory was employed to estimate energetically the favorability of the proposed mechanism. The influences of misfit strain and local compositional inhomogeneities in the domains were also considered. The generality of this mechanism of defect introduction is supported by several experimental observations of BSF domains acting as TD nucleation sites in InGaN, AlGaN, and InAlGaN films, as well as in multiple quantum wells.

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Figure 1: Cross sectional HRTEM images along [-1-120] superimposed with colored GPA phase maps of (a) an I₃ and (b) an I₄ stacking fault domain. Phase maps were obtained using g1-100. Stacking sequences are indicated. All BSFs are of I₁ type. In (b) the lower BSF is stepped. (c) & (d) Corresponding Bragg-filtered images showing (2-200) lattice fringes. Extra half-planes are indicated by arrows in (d).



Figure 2: (a) Schematic view of a stacking fault domain consisting of two II BSFs connected by Drum prismatic stacking fault (PSF), the dislocation reactions at the nodal 1 and 2 of the domain leading to the introduction of the TD (bL) are given; (b) and (c) bright field TEM plan view image of the domains, showing hexagonal shape SF domain giving rise to six TDs(b) and rhombic SF domain giving rise to 4 TDs, which may form half-loops.

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Differences in deep levels spectra of proton irradiated bulk Ga₂O₃ crystals as affected by orientation changing from (010) to (-201)

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Electrical properties and deep traps spectra of Ni Schottky diodes on β-Ga₂O₃(Sn) crystals grown by Edge-defined Film-fed Growth (EFG) were studied before and after irradiation at room temperature with 5×10^{14} cm⁻² 20 MeV protons. Before irradiation the shallow donors concentrations deduced from C-V profiling were 3.2×10^{17} cm⁻³ for the (010)-oriented sample and 2.7×10^{17} cm⁻³ for the (-201) sample with respective Schottky barrier heights close to 1.75 eV and 1.5 eV. Proton irradiation led to a strong (by about 10^{17} cm⁻³) decrease of the density of uncompensated shallow donors. Electron traps spectra in the starting samples of both orientations were dominated in both cases by the Fe related E2 centers near Ec-0.8 eV and native defects related E3 centers near E_c-1 eV. The concentrations of these centers were close for both orientations of the samples before irradiation. After exposure to protons the Fe densities remained virtually the same, the densities of the E3 traps slightly increased, similarly for both samples. However, very prominent differences were observed in the low energy part of the deep electron traps spectra. For the (-201) sample irradiation introduced low concentrations of shallow traps with levels near E_c -0.2 eV (center A) and E_c -(0.45-0.5) eV (center B) with approximately uniform spatial distribution. In the (010) sample the result of irradiation was the introduction of very prominent traps with a low electron capture cross section and the level near Ec-0.23 eV (center C). DLTS spectra measurements with different bias/pulsing settings showed that these traps were located in the top $\sim 0.1 \,\mu\text{m}$ of the irradiated (010) sample, while in the bulk the shallow centers spectra were similar to the ones detected in the (-201) sample (Fig. 1 compares the DLTS spectra of the two types of samples when probing the near surface region, mind that the subsurface C centers are manifestly absent in the (-201) sample). C-V profiling at low temperatures done after cooling the sample at reverse bias with the voltage sweep preceded or not preceded by application of the high forward bias indicated that the C centers in question were acceptor s with the concentration of high 10¹⁶ cm⁻³. The presence of this prominent trap resulted in an interesting hysteretic behavior in low temperature I-V characteristics and was clearly detected in current DLTS spectra.

Deep acceptors spectra were dominated by centers with optical ionization threshold near 2.3 eV and 3.1 eV, with similar concentrations for both types of studied samples before irradiation (Fig. 2(a), (b)). The concentration of deep acceptors increased much stronger for the (010) orientation (Fig. 1(a), (b)) with the optical threshold 3.1 eV increased by about 3 times in both cases, whereas the amount of increase for the acceptors with the optical threshold 2.3 eV was very much more pronounced for the (010) sample, particularly in the case of the deep acceptor traps with optical ionization threshold near 2.3 eV often attributed to Ga vacancy-interstitial Ga acceptors.



Fig. 1. DLTS spectra of the samples with (010) and (-201) orientations measured before and after proton irradiation for the near surface region of the samples



These results point to considerable impact of the Ga_2O_3 crystals anisotropy on the effects produced by irradiation with high energy particles.

Magnetic Resonance and Magneto-optical Properties of Cr^{3+} in β -Ga₂O₃

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 β -Ga₂O₃ is a wide bandgap semiconductor that is attractive for various applications, including power electronics, as transparent conductive electrodes, etc. The key to the realization of device applications is to achieve control over conductivity by doping and mitigation of trap states, as most of the electronic properties of β -Ga₂O₃ are affected by the presence of dopants/contaminants and/or intrinsic defects. Here, transition metals are of special importance, since they are unintentionally present during the growth, used as intentional dopants or used for ohmic contacts. Therefore, it is of crucial importance to understand the electronic structure of those impurities.

In this work we investigate the electronic structure of Cr^{3+} which is a common impurity in β -Ga₂O₃ as was demonstrated by electron paramagnetic resonance (EPR) and secondary ion mass spectroscopy in the past. Cr^{3+} was also linked to the R₁ and R₂ PL lines at approx. 1.79 eV due to a similarity in emission energy with an internal Cr^{3+} transition in Al₂O₃. In other works, however, the same emission in β -Ga₂O₃ was linked to Fe. In order to unambiguously determine the origin of this emission and study the electronic structure of the defect causing it, we performed a combined EPR and magneto-optical study. We prove that the R₁ and R₂ PL lines originate from an internal Cr^{3+} transition from the first excited state (²E) to the ⁴A₂ ground state, by comparing the spin-Hamiltonian parameters of the ground state measured by EPR and magneto-PL, which are in perfect agreement. Furthermore, we determine the spin-Hamiltonian parameters of the first excited state to be $g_a = 1.7$, $g_b = 1.5$ and $g_{c^*} = 2.1$.

Identifying vacancy defects in β-Ga₂O₃

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We have applied slow positron beams and fast positron spectrometers to study vacancy-type defects in a wide variety of β -Ga₂O₃ materials: unintentionally doped and Si and Sn doped hetero- and homo-epitaxial thin films grown by metal-organic chemical vapor deposition (MOCVD) and halide vapor phase epitaxy (HVPE), as well as Mg, Fe and Sn doped bulk crystals grown by the Czochralski (CZ) and edge film-fed growth (EFG) methods [1,2,3]. The data can usually be interpreted as the presence of varying concentrations of Ga vacancy related defects in some of the samples. However, the colossal anisotropy of the positron annihilation signals makes quantitative interpretations cumbersome, as the magnitude of the anisotropy is comparable to the changes produced by annihilation at vacancy defects [1]. We report on a detailed experimental and theoretical investigation of the positron annihilation signals in β -Ga₂O₃ and provide an approach for identifying different kinds of vacancy defects based on the signal anisotropy.

I will mainly focus on our computational studies of the vacancy defects and the associated "fingerprints" present in their expected positron annihilation data that allow us to link the observed anisotropy to the underlying defect structures. Interestingly, when the modeling results and experiments are compared, it appears that bulk-like positron signals might not be observed in any of the studied β -Ga₂O₃ samples. The main vacancy-type defects observed with positrons are most likely split Ga vacancies [4] where a next-nearest-neighbor Ga atom relaxes strongly, half of the way towards the vacancy, creating a structure with two "half-Ga vacancies". This suggests that all the β -Ga₂O₃ samples studied so far contain high concentrations of split Ga vacancies, irrespective of doping or conduction type.

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Charge state transition levels of cobalt in β -Ga₂O₃ from experiment and theory

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Monoclinic gallium sesquioxide (β -Ga₂O₃) belongs to the transparent semiconducting oxides with promising results regarding applications in power electronics and solar-blind photodetectors due to its 4.8 eV ultra-wide bandgap and the large range of *n*-type dopability [1]. For device fabrication, the method of choice is homoepitaxy of device critical layers on β -Ga₂O₃ substrates. Large-area substrate wafers are obtained from single-crystals grown from the melt (mainly by edge-defined film-fed growth or the Czochralski method) at temperatures near 2000°C. At these high temperatures the incorporation of impurities, mainly transition metals (TMs) from Ir crucibles, Ga₂O₃ starting material, and thermal insulation, is unavoidable. Usually, TMs act as acceptors in *n*-type β -Ga₂O₃ and compensate donor dopants. Although counteracting intentional *n*-type doping, the compensation of residual donor impurities is favorable for producing semi-insulating substrate crystals. The latter is presently performed by doping with magnesium or the 3*d*-TM iron. While Mg has its acceptor level about 1 eV above the valence band maximum, the acceptor level of Fe is positioned about 0.7 eV below the conduction band minimum. Since the peak operating temperatures in power devices presumably exceed room temperature considerably, thermal ionization of the mentioned acceptors is to be expected leading to a loss of the insulating state of the substrates. Therefore, it is necessary to search for other acceptor impurities possessing deeper transition levels more close to the middle of the band gap and a reasonably high solubility for intentional doping. In this respect, 3*d*-TMs are promising.

We have investigated the optical, electrical and paramagnetic properties of the 3*d*-TM Co in β -Ga₂O₃ both experimentally and theoretically. The Co doped crystals were grown by the Czochralski method [2]. In Fig. 1 the main features of the electron paramagnetic resonance (EPR) spectroscopy results, which essentially agree with those recently reported in [3], are summarized. The dominant EPR lines are due to cobalt most probably on the octahedral gallium site Co_{GaII}. By more closely inspecting the EPR spectra, we discuss the possibility of Co incorporation on tetrahedral Ga site too. Optical absorption spectroscopy (Fig. 2) combined with photoconductivity measurements reveal the optical charge transfer energies. These are compared with the charge state transition levels of cobalt in β -Ga₂O₃ obtained by density functional theory calculations employing hybrid functionals (Fig. 3). By including the expected Franck-Condon shifts we arrive at the energy level scheme depicted in Fig. 4. Due to the location of the Co acceptor level nearly 2 eV below the conduction band minimum and the high solubility of Co (comparable to Fe and Mg), Co seems to be the better choice for producing insulating β -Ga₂O₃ than Fe or Mg. Finally, we also looked for the expected internal transitions of Co²⁺ in the infrared spectral range.



FIG. 1. EPR spectra of Co doped β -Ga₂O₃ for the static magnetic field along principal crystallographic directions (microwave frequency ~9.4 GHz, T = 20 K). Eight-fold line splitting due to ⁵⁹Co (100%, I = 7/2). Co²⁺ (S = 3/2) corresponds to the acceptor state Co_{Ga}⁻.



FIG. 3. Formation energy of Co substituting for tetrahedrally coordinated Ga_I and for octahedrally coordinated Ga_{II} in dependence on the Fermi level related to the valence band maximum under Ga- or O-rich growth conditions. Density functional theory calculations using hybrid functionals. Energies of the charge state transition levels can be read from the curves' kink positions.



FIG. 2. Optical absorption spectra for two different Co doping levels (T = 10 K). Arrows indicate Co related absorptions.



FIG. 4. Energy level scheme for Co_{GaII}. Interpretation of the observed absorption bands (cf. Fig. 2 and 3; Franck-Condon shift $\Delta_{FC} \sim 0.7 \text{ eV}$ is a theoretical estimate): (Blue arrow) Co⁰_{GaII} \rightarrow Co⁻_{GaII} + h_{vb} $E_{abs, theo} = 2.9 \text{ eV} + \Delta_{FC} = 3.6 \text{ eV}$ $E_{abs, exp} = 3.7 \dots 3.8 \text{ eV}$ (Violet arrow) Co⁰_{GaII} \rightarrow Co⁺_{GaII} + e_{cb} $E_{abs, theo} = (4.8 - 0.7) \text{ eV} + \Delta_{FC} = 4.8 \text{ eV}$ $E_{abs, exp} = 4.4 \dots 4.5 \text{ eV}$

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Identification of Fe-, Ti- and H-related Charge-state Transition Levels in β -Ga₂O₃

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Gallium sesquioxide (β -Ga₂O₃) is an ultra-wide band gap semiconductor ($E_g \approx 4.8 \text{ eV}$) which has attracted considerable attention in recent years for its potential use in power electronics and UV photo-detectors [1]. For β -Ga₂O₃ to live up to its potential, the influence of defects on its electrical and optical properties needs to be better understood. Depending on a defect's charge-state transition level, it can, e.g., act as an efficient recombination center, influence the overall conductivity of the material or pin the Fermi level at the interface of semiconductor– insulator-metal junctions used in power electronics. Intentional and unintentional impurities are particularly relevant defects in β -Ga₂O₃. Fe-doping is used to obtain semi-insulating β -Ga₂O₃ bulk crystals, whereas Ti is used for Ohmic contacts in β-Ga₂O₃-based power electronics, and both are also common unintentional impurities in bulk crystals [1]. H has been shown to be an ubiquitous impurity in as-grown β -Ga₂O₃ bulk crystals [2]. In this contribution, we will present results of deep-level transient spectroscopy (DLTS), steady-state photo-capacitance measurements (SSPC), secondary ion mass spectrometry (SIMS) and Fourier-transform infra-red spectroscopy (FTIR) aimed at identifying charge-state transition levels related to Fe, Ti and H in β -Ga₂O₃. The presented experimental results are supported by hybrid-functional calculations.



Figure 1: (a) DLTS spectra recorded on β -Ga₂O₃ bulk crystals grown by edge-defined film-fed growth (EFG). (b) Comparison of the Ti concentration ([Ti]) measured using SIMS and the concentration of E₃ ([E₃]) measured by DLTS for different β -Ga₂O₃ bulk crystals grown by EFG and the Czochralski method (CZ).

Typically, two charge-state transition levels labeled E_2 ($E_A \approx 0.75 \text{ eV}$) and E_3 ($E_A \approx 0.95 \text{ eV}$) are observed in β -Ga₂O₃ bulk crystals (see Figure 1 (a)), whereas the level labeled E_1 ($E_A \approx 0.57 \text{ eV}$) is more sporadically reported [3]. Previously, E_2 has been shown to be related to Fe_{Ga} [3]. We show that E_2 , indeed, consists of two charge-state transition levels labeled E_{2a} and E_{2b} which we assign to Fe substituting on octahedral and tetrahedral Ga sites, respectively [4]. Moreover, we find that Ti substituting on a octahedral Ga site gives rise to E_3 (see Figure

1 (b)) [4]. Using SSPC, we are also able to identify the optical signatures related to E_{2a} , E_{2b} and E_3 [5].

We further employed hydrogenation of β -Ga₂O₃ bulk crystals and thin-films grown by halidevapor phase epitaxy (HVPE) to study the influence of H on charge-state transition levels in β -Ga₂O₃. We find that E₁ is likely related to H (see Figure 2 (a)), and, tentatively, assign the level to H substituting on a O site or a hydrogenated di-vacancy based on hybrid-functional calculations. Moreover, we show using SSPC in combination with hybrid-functional calculations that hydrogenation leads to the promotion of several other deep-level defects which might be related to different hydrogenated Ga vacancies and di-vacancies.



Figure 2: (a) E_1 concentration obtained from DLTS measurements on hydrogenated EFG-grown β -Ga₂O₃ bulk crystals. The hydrogenation was performed at 900 °C for a duration t_{ann} . The box plots represent the E_1 concentration obtained on various Schottky barrier diodes deposited on bulk crystals subjected to the same annealing condition. (b) DLTS spectra recorded on Schottky barrier diodes comprising HVPE-grown β -Ga₂O₃ thin-films subjected to He- and H-implantation and subsequent heat-treatments with and without reverse bias voltage.

Finally, we utilize He- and H-implantation in conjunction with heat-treatments to further study the interplay of H and intrinsic defects in HVPE-grown β -Ga₂O₃ thin-films [6]. We perform heat-treatments on Schottky barrier diodes (Ni/ β -Ga₂O₃), and hence, we are able to manipulate the Fermi-level position during heat-treatment by applying a reverse bias voltage (see Figure 2 (b)). We find that the formation of the charge-state transition level E₂^{*} ($E_A \approx 0.71$ eV) after He- and/or H-implantation is promoted during heat-treatments with a Fermi-level position further away from the conduction band edge. Conversely, the concentration associated with E₂^{*} is seen to decrease after heat-treatments under *n*-type conditions. Using hybrid-functional calculations, we are able to show that E₂^{*} is likely associated with a specific configuration of a hydrogenated di-vacancy defect [7].

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Abstracts: Pre-recorded presentations

The impact of surface defects created by the high-temperature GaN growth on the InGaN/GaN quantum well efficiency

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A low-indium-content InGaN underlayer (UL) or InGaN/GaN supperlattice (SL) is essential to grow before the InGaN/GaN quantum well (QW) active region in commercial blue lightemitting diodes to achieve high quantum efficiency. Although such an UL is commonly used, the reason for this performance boost is still under debate. Recent studies attributed it to a defect reduction mechanism during growth: the indium reacts with defects standing on the surface during the growth, preventing them to segregate towards the active region to form non-radiative recombination centers [1-3]. Previous results also indicated that these defect might come from the high-temperature-grown GaN buffer underneath the InGaN layer [4]. However, the studies on the origin and the nature of this defect are still scarce. In this work, we use an InGaN/GaN single QW (SQW) as a probe to monitor the density of surface defects (SDs) preexisting in GaN epilayer as their incorporation into the well directly affects the quantum efficiency [5]. By employing time-resolved photoluminescence, we observe that the effective lifetime of a SOW deposited on GaN buffer decreases from several ns to less than 100 ps when the growth temperature of the GaN buffer increases from 870 °C to 1045 °C (Fig. 1). This indicates the creation of intrinsic defects in the high temperature-grown GaN buffer. A theoretical study on the formation energy of native defects in GaN when grown at high temperature (HT), suggests that the most likely defect is a nitrogen vacancy (V_N) (Fig. 2). Finally, we study the SD formation dynamics during the HT GaN growth. The results show that most SDs are generated within a few tens of nanometers. The next step is to investigate the SD generation dependence on other growth parameters, especially the ammonia flow rate. Preliminary results show that compared to the growth temperature, the impact of ammonia flow is less on SD generation.

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Figure 1 (Left) sample structure used for the study on the impact of GaN growth temperature on InGaN/GaN quantum well efficiency. (Right) the 300 K effective lifetime of each sample in the function of GaN buffer growth temperature. Dash line used as guide to eye.



Figure 2 Theoretical concentration of nitrogen vacancy (lines) and experimental SD concentration estimated from PL decay time (red diamonds) as a function of the growth temperature of the GaN buffer layer.

Nitrogen-displacement-related hole traps introduced by electron beam irradiations in MOVPE-grown homoepitaxial p-type GaN

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GaN-based power switching devices have attracted considerable attention. To realize superior device performances, understanding and controlling point defects in GaN is essential. However, most of origins of deep levels are still unclear. Intentional introduction of point defects by electron beam (EB) irradiation is one of the effective methods to investigate the deep levels originated from intrinsic defects. We have reported EB irradiation with the energy of 137 keV to n-type GaN to displace N atoms selectively and observation of two electron traps originated from by V_N and N_I [1]. On the other hand, there are few reports on hole traps for EB-irradiated GaN with such a low energy. In this study, we have investigated hole traps in MOVPE-grown p-type GaN formed by 137 keV EB irradiation, where only N atom displacement occurred.

The samples of GaN p⁻-n⁺ diode (PND) with mesa structure were used. The PNDs comprised a 0.1-µm-thick Mg-doped p⁺-GaN / 3-µm-thick Mg-doped p⁻-GaN / 0.5-µm-thick Si-doped n⁺-GaN structure grown by MOVPE on freestanding HVPE-grown n⁺-type GaN substrate. The vertical mesa structure was formed by ICP-RIE to a depth of 4 µm. The Mg concentration of p⁻-GaN layer of 8×10^{15} cm⁻³ was obtained via SIMS. For Ohmic contacts to p-type GaN, Ni / Au meal were deposited on the frontside and then sintered at 823 K for 5 min. The Ohmic contact formation was performed prior to EB irradiation to avoid annealing out of the EBinduced traps by the high-temperature sintering. The EB irradiation were performed at the energy of 137 keV and the fluence of 5×10^{15} and 2×10^{16} cm⁻². DLTS and ICTS measurements were performed to investigate hole trap levels.

Figure 1 shows the ICTS spectra at 300 K for as-grown sample (black line) and EB-irradiated sample with the fluence of 2×10^{16} cm⁻² (red line). For all of the EB-irradiated samples, a hole trap level EHa (activation energy $E_a = 0.52 \text{ eV}$) was observed, in addition to the hole trap level Hd, originating from carbon impurity in the epilayer. When the fluence increased, the apparent trap concentration of EHa increased and the values for the fluence of 5×10^{15} and 2×10^{16} cm⁻² were 3.8×10^{14} and 2.7×10^{15} cm⁻³, respectively. Furthermore, ICTS spectra was varied by minority carrier injection. After minority carrier injection for 500 s by applying forward bias in the PND, a new hole trap level EHb ($E_a = 0.5$ eV) appeared with decreasing the EHa peak intensity (blue line in Fig. 1). These changes were not due to Joule heating by applying forward bias in PND, which was confirmed by experiments of annealing at 530 K for 2 h. Since the decrease of the EHa and the increase of EHb occurred simultaneously, we speculated that a part of point defects formed EHa was changed to other defects which produce EHb. The origin of EHa is likely to be V_N (3+/+) or N_I (2+/+), since the activation energy of EHa was close to the energy levels (E_V + 0.47 eV for V_N (3+/+) and E_V + 0.54 eV for N_I (2+/+)) predicted by the first-principle calculation [2]. The EHb would be formed by a complex composed of the origin of EHa (V_N or N_I) and other defects.

In conclusion, we observed hole trap level EHa and EHb, and the origin of these trap levels is speculated to be nitrogen displacement related defects. Since the decrease of EHa and the increase of EHb were observed after minority carrier injection, there would be correlation between the origins of EHa and EHb. These results are essential information for controlling defects in p-type GaN.

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Fig. 1. ICTS spectra obtained from p-GaN epilayers; as-grown sample (black line), sample irradiated with 137-keV electron beam (red line), which is the sample before minority carrier injection, and after minority carrier injection for 500 s (blue line). Hd originates from carbon impurity in the epilayer. EHa was observed after EB irradiation. In addition, EHb appeared with decreasing the EHa peak after minority carrier injection. The reason for the small reduction of Hd is unclear now.

Defect structures in (001) zincblende GaN/3C-SiC nucleation layers

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Solving the green gap problem is a key challenge for the development of future LED-based lighting systems. A possible approach to achieve higher LED efficiencies in the green spectral region is the growth of III-nitrides in the cubic zincblende phase (zb). Cubic zb-GaN with (001) orientation is polarisation field free and has a narrower bandgap than its wurtzite structure counterpart, due to which less indium is required in InGaN quantum wells for green light emission [1]. However, given that zb-GaN is metastable under normal growth conditions and has strong similarities with the energetically preferred wurtzite phase, zb-GaN epilayers often exhibit phase mixture and a rich defect structure, which both may negatively influence the optical properties of the material.

In our presentation, we will report on the defect structure in zb-GaN nucleation layers (NLs) grown on (001) 3C-SiC/Si pseudo-substrates, and will discuss mechanisms for the formation of the observed defects more broadly.

High-resolution transmission electron microscopy (TEM) images of individual nucleation islands like in Figure 1 show a characteristic ABCABC stacking of the {111} bi-layers in zb-GaN. This reveals that the GaN islands grow epitaxially in the zb phase and (001) orientation on the 3C-SiC surface, with no observable amorphous layer at the interface.



Figure 1: Cross-sectional HRSTEM image of the nominally 3 nm-thick as-grown zb-GaN NL with characteristic ABCABC stacking shown in the inset.

The absence of a shift between the patterns of Ga atoms in zb-GaN and Si atoms in 3C-SiC at the interface implies that Ga atoms occupy Si-sites and N atoms occupy C-sites in the zb structure, suggesting that zb-GaN is attached to 3C-SiC via Si-N bonds and C-Ga bonds.

Facet angles present in the islands prior to the coalescence were measured by the atomic force microscopy (AFM) and TEM and some corresponded to short {111} facets, which might induce stacking fault (SF) nucleation. Most of the defects present in the NLs were formed close to the GaN/SiC heterointerface and include perfect dislocations, partial dislocations and predominantly intrinsic {111}-type SFs as shown in Figure 2 (a). Perfect dislocations and partial dislocations are identified as 60° mixed-type respectively 30° Shockley partial dislocations, which both act as misfit dislocations to relieve the compressive lattice mismatch strain in GaN. No regular arrangement of these misfit dislocations is found at the zb-GaN/3C-SiC interface of our samples, which is in contrast to reports about zb-GaN layers grown on GaAs [2] and can be explained by the much lower lattice mismatch for 3C-SiC/Si pseudo-substrates compared to GaAs substrates. Intrinsic SFs are mainly bounded at the interface by 30° Shockley partial dislocations and rarely by sessile Lomer-Cottrell partial dislocations. The latter of which are found next to SiC step edges in the GaN/3C-SiC interface (see Fig. 2 (b)) and hence are possibly initiated by these. Based on our findings, we conclude that partial dislocations and intrinsic SFs either originate from the dissociation of perfect dislocations at the interface or that they directly form at the free surface as a partial dislocation half-loop. This highlights the importance of controlling the NL conditions for zb-GaN growth on 3C-SiC, to reduce the defect formation in the NLs, and consequently in the following zb-GaN thin films.



Figure 2: Cross-sectional HRSTEM images of the zb-GaN/3C-SiC (001) interface highlighting the presence of Shockley partial dislocations (SP) and intrinsic stacking faults (i-SF) (a), as well as stair-rod partial dislocation (b).

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Vibrational modes of mono-, di- and tri-carbon defects in GaN:C

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Carbon doped GaN (GaN:C) is used to produce semi-insulating layers or substrates for GaNbased devices. However, the variety of formed carbon defects is not yet enough investigated.[1] Previously, we attributed two infrared (IR) absorption lines 1678 cm⁻¹ and 1718 cm⁻¹ to local vibrational modes (LVMs) of tri-carbon molecule-like complexes, which are formed at carbon concentrations above 5×10^{17} cm⁻³. [2,3,4] In current work, we investigate different carbon defects manifesting as LVMs in GaN:C in IR absorption and Raman scattering spectra. The modes are observed in about 500 µm GaN layers grown on sapphire templates by hydride vapor phase epitaxy (HVPE) with carbon concentration [C] in the range $3.2 \times 10^{17} - 3.5 \times 10^{19}$ cm⁻³ and natural isotope composition (99% ¹²C, 1% ¹³C).[3] The isotope effect is investigated for two samples with middle (50%) and extreme (~99%) isotope ¹³C abundance. Typical spectra of GaN:C with natural isotope composition reveal several non-intrinsic lines: at 765 cm⁻¹ (i), 773 cm^{-1} (ii), 1678 cm^{-1} (iii), 1717 cm^{-1} (iv), and 1978 cm^{-1} (v). We demonstrate that all of them are LVMs of carbon related defects, which significantly change the vibration frequencies (i.e., wavenumber or Raman shift) in the sample with extreme ¹³C abundance. According to the harmonic oscillator model, the isotope effect appears as the frequency shift when the reduced mass of the oscillator changes due to the different isotope masses. Furthermore, this model can unequivocally determine the number of C atoms and some structural properties of the carbon defects such as bond angles from the number, spectral positions, and intensities of the LVMs in the sample with middle ¹³C abundance. The original LVMs in this case split into two (i, ii), four (v), six (iii) and eight (iv) lines and associate to vibrations of defects including one (i, ii), two (v) or three (iii, iv) carbon atoms within the defect structure.

Comparing the intensities of the original LVMs (i - v), relative density of the defects can be estimated as a function of [C]. We also show that under photoexcitation in the range of the strong carbon-related absorption between 370 nm and 500 nm (see [2,4]) all these defects change their respective LVM intensities and hence, their charge states. Furthermore, the intensities of the LVMs observed in Raman spectra strongly depend on the excitation wavelength in the same spectral range, what we ascribe to a resonance Raman effect.

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Supplementary information



Figure 1. Room temperature Raman spectra of GaN:C with different carbon concentration and natural composition of the isotopes $[{}^{12}C]\approx[C]$ (left). The two LVMs at 764 (i) and 773 cm⁻¹ (ii) increase intensity with carbon concentration. In the right figure there are spectra with different isotope composition normalized to the intrinsic line at 735 cm⁻¹. The isotope mass effect leads to shifts of the vibration frequencies in the sample with $[{}^{13}C]\approx[C]$ and to additional splitting in the sample with $[{}^{12}C]\approx[C]/2$. The number of lines corresponds to one carbon atom within the defect structure.



Figure 2. LVMs 12B and 12A captured at 10 K (left(a), at **room** temp. found at 1678 (iii) and 1718 cm⁻¹ (iv)) and their splitting to 6 (left,b) and 8 (left,c) lines, correspondingly. The mode 12B is observable for $E_{\perp c}$ polarization (perpendicular to the wurtzite c-axis) and disappears for polarization $E_{\perp c}$, while the mode 12A can be detect for both polarizations, but for $E_{\perp c}$ in a few times attenuated. Thus, the modes are well-distinguished for different polarizations. From combined analysis of the isotope splitting and the polarization dependence, we attribute the LVMs 12A and 12B to the tri-carbon complex in two crystallographically inequivalent configurations. On the right part of the figure, the original position of the LVM 1978 cm⁻¹(v), its isotope shift (right,a), and the 4-line splitting (right,b) are shown. From the amount of the lines we conclude that the defect originating the mode (v) consists from 2 carbon atoms. The Raman spectrum (right,c) completely reproduce the infrared absorption spectral curve.

Carrier dynamics in and around trench defects in InGaN QWs probed by time resolved cathodoluminescence

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Heteroepitaxial growth of III-nitrides on substrates like Al2O3, Si and SiC typically results in the incorporation of defects. These defects can act as nonradiative recombination centres, reducing the performance of devices. Trench defects are one such defect found in InGaN/GaN quantum wells (QW), InAlGaN QWs and InGaN epilayers [1-3]. They have been shown to consist of an

I1-type basal plane stacking fault located in the active region of the device which is bounded by a vertical stacking mismatch boundary that threads towards the surface and opens as a series of coalescing pits [1]. Trench defects display different and diverse emission properties compared to the material surrounding it [2,3].

Here, we present the use of temperature (10K-300K) and power (25 pA to 60 nA) dependent as well as time-resolved cathodoluminescence (CL) to study the emission and carrier dynamics of trench defects in InGaN/GaN 10 multiple QW structures grown by MOVPE.

Spectra were extracted from hyperspectral maps recorded in CW mode such that the emission properties could be analyzed, while time-traces where recorded with a time correlated single photon counting setup with a time resolution of ~100 ps.



Three different regions of interest were identified on the sample: unperturbed material and defects with a wide (Trench 1 ~50 nm) and narrow (Trench 2 ~30 nm) trench. Power dependent measurements at 300K showed the wide trench defects to be brighter than the surrounding material at low probe currents but to become darker at higher probe current. For these defects, a red-shift was observed under low probe currents compared to the surrounding material. No such shift was observed at high probe currents. Narrow trench defects remain darker than the surrounding material at all probe currents investigated.

For the temperature-dependent time-resolved measurements (see Figure), the surrounding material shows the slowest decay at all temperatures investigated. At temperatures below 100K, the wide trench defects (Trench 1) show the fastest decay with the narrow trenches being intermediate. For temperatures above 100K, the narrow trench defects (Trench 2) now show the fastest decay with the wide trenches being intermediate.

Our CL results demonstrate that the carrier dynamics in the material enclosed within trench defects (in particular those of narrow trenches) is noticeably different from the carrier dynamics of the unperturbed material.

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Gyrotron Microwave Beam Parameter Influence on P-Conductivity in Co-Implanted and Annealed GaN: Optical and Electrical Studies

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The success of future (Al)GaN-based power devices depends partly on the ability to form selectivearea p-type regions, which can be accomplished by ion implantation of the prevailing acceptor dopant, Mg. Ion implantation induces lattice damage and creates undesired single and clustered point defects including vacancies and interstitials in addition to the desired dopant substitutional defects. Removal of point defects, especially donor-like nitrogen vacancies (V_N) in the material can be accomplished through high temperature annealing and may be aided by co-implantation with N [1]. It is speculated that compensation of implant-induced V_N may be enhanced during the annealing process by diffusion of excess N into the N lattice site.

To restore the bulk crystalline quality, lower the concentration of defects, and activate the implanted dopants requires temperatures >1000 °C, which is beyond the thermodynamic equilibrium stability of GaN and can cause decomposition of the surface [2]. Specialized annealing techniques that either heat very rapidly [3] and/or use ultra-high pressure conditions [4] are required to obtain high-conductivity p-type material, and activation of Mg-implanted material remains an area of active study.

In this study, we report on the improvement in electrical and optical properties of Mg/N coimplanted GaN through the study of pulsed gyrotron annealing conditions of temperature and pulse length. Co-implanted MOCVD-grown unintentionally doped (UID) GaN is capped with AlN and annealed using a gyrotron under an N₂ overpressure of 3 MPa. Pulse maximum and minimum temperatures between 1350–1550 °C, minimum temperature between 775–1000 °C, and pulse lengths of 1.5–10 s are explored.

The optical and electrical properties of the resulting films are characterized optically by photoluminescence (PL) and electroluminescence and electrically by C-V and diode I-V. Statistical analysis of spatially resolved low-temperature PL maps of annealed films show highly uniform luminescence at the optimized anneal condition of 5 pulses at 1450 °C maximum temperature, 900 °C minimum temperature, and 8 s pulse length. The average intensity ratio of the Mg_{Ga}-related UVL to the V_N-related GL2 is 6.6 with a standard deviation 4.3 across the material, suggesting high and uniform acceptor activation. Additionally, some regions of the sample contain a previously reported GL2 suppression and a dominant YL in the 2.2–2.5 eV range, which is attributed to unintentionally introduced C_N-O_N complexes in GaN grown by MOCVD [5]. Diode I-V measurements indicate clear p-n diode behavior in ~40% of devices with threshold voltages between 3.1-3.5 V and I_{on}/I_{off} ratio of up to 10^6 .

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Figure: (A) Low-temperature (20 K) PL indicates high average UVL:GL2 intensity ratio of 6.6 at 13 points across the 1 cm x 1 cm sample surface after high-temperature gyrotron annealing (B) Threshold voltages on 40% of vertical diode arrays indicate p-n junction with V_{Th} of 3.1–3.5 V and relatively high I_{ON}/I_{OFF} of up to 10⁶ A/A.

Defect Mediated Color-tunability in Eu-doped GaN-based LEDs

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The emission spectrum from typical white LEDs based on GaN has a substantial blue light component. This has been shown to have a negative effect on human circadian rhythms, which can be a concern in display applications. One method to circumvent this issue is to mix the three primary colors using individual red, green, and blue LEDs, which has been achieved using lateral monolithic integration of blue and green InGaN-based LEDs with a Eu-doped GaN-based red LED.[1] Alternatively, it was found that the relative intensities of the different Eu³⁺ related emission lines in Eu-doped GaN-based LEDs can be electrically tuned, producing red, orange, and yellow light from a **single diode** depending on the pumping conditions.[2] This behavior arises from the strong coupling between the Eu³⁺ ions and local defects, facilitating efficient energy transfer, and is promising for micro-display applications.

The underlying mechanism behind the color-tunability is a redistribution of energy between the various ⁵D_J states of the Eu³⁺ ion and a localized defect (Fig. 1a). We have modeled the energy redistribution using a series of rate equations for a defect complex consisting of a Eu³⁺ ion and another local defect, which utilizes experimentally determined constants such as transfer rates and lifetimes. Different injection current pulse sequences and carrier densities are used to simulate various experimental conditions. This model can then be used to predict the



Fig. 1. (a) Model for defect-mediated energy transfer in Eudoped GaN. Under current injection, (1) injected carriers localize to the defect. (2) Energy is then transferred to the Eu^{3+} ion or back to the defect. (3) the Eu^{3+} ion emits a red, yellow or green photon. (b) Simulation results showing that the population of the ⁵D₀ state changes based on the current injection conditions. (c) LED operating under the simulation conditions in (b).

relative populations of the ${}^{5}D_{0}$ and ${}^{5}D_{1}$ states of the Eu³⁺ ions (Fig. 1b). By mixing the red emission from the ${}^{5}D_{0}$ state with green emission from the ${}^{5}D_{1}$ state, these populations can be used to predict the overall color coordinate for each excitation condition. In this contribution, we will compare the predicted and experimentally observed behaviors (Fig. 1). We will also discuss the potential to enhance the color-space coverage by externally manipulating the radiative rates of the Eu³⁺ states through cavity confinement.[2]

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The Role of Threading Edge Dislocations in the Electronic Properties of AlGaN/GaN Heterostructures: Experimental and First-principles Insights

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Owing to the superior properties such as wide bandgaps, high breakdown fields, high saturation electron drift velocities, and strong polarization, AlGaN/GaN heterostructures have achieved great success in high-frequency and high-power applications.^[1] After decades of development, epitaxy of high quality AlGaN/GaN heterostructures has shown great success on substrates such as silicon, silicon carbide and sapphire. Due to the thermal and lattice mismatch between GaN and its substrates, high density of threading dislocations exists in AlGaN/GaN heterostructures. For AlGaN/GaN heterostructures, the density and thus the effect of threading edge dislocations (DLs) are greater than those of threading screw or mixed dislocations. Therefore, understanding the properties of DLs in AlGaN/GaN heterostructures is highly desired for the application of AlGaN/GaN heterostructures.

In this work, we demonstrate that DLs in AlGaN/GaN heterostructures are spontaneously decorated by acceptors during the epitaxial process. For unintentionally doped AlGaN/GaN heterostructures, group-III vacancies (V_{III}) spontaneously decorate DLs in the AlGaN barrier, which is evidenced by the two-stage Frenkel-Poole (FP) emission for reversely biased AlGaN/GaN heterostructures.^[2] The V_{III}-decoration of threading edge dislocations (V_{III} -DLs) also gives rise to the reduced reverse leakage current of AlGaN/GaN heterostructures after the low-fluence neutron irradiation.^[3] Our work opens a pathway to adopt low-fluence neutron irradiation as a new post-processing treatment to reduce the reverse leakage current of AlGaN/GaN heterostructures.

Fig. 1 (a) shows the relaxed structure and calculated charge density isosurface of occupied deep levels for the dislocation core of 5-7-atom ring core DL investigated in this work. It is featured by the alternating Ga-Ga and N-N dimers in the dislocation core. As shown in Fig. 1 (c), the defect level of the DL above the valance band maximum (VBM) of GaN is fully occupied, the dislocation will interact with acceptors owning partially occupied or unoccupied states by electron transfer. The most common acceptor in undoped GaN is V_{Ga} because of the unintentional *n*-type doping.^[4] Therefore, V_{Ga} would spontaneously decorate DLs in GaN. This is verified by the negative decoration energy of -4.65 eV and localization of electrons near V_{Ga} for V_{Ga}-DLs, as shown in Fig. 1 (b).



Fig. 1 Calculated charge density isosurfaces of occupied deep levels above the VBM of GaN containing (a) the pure 5-7-atom ring core DL and (b) V_{Ga} -decorated DL. (c) Electron transfer and formation of the deep state of the threading dislocation.

The calculated density of states of DL and V_{III} -DL (V_{III} includes V_{Ga} and V_{Al}), as well as their derivation from GaN to $Al_{0.25}Ga_{0.75}N$ is shown in Fig. 2. Combining the defect analysis and calculated density of states, we find there's two distinct unoccupied defect states under the conduction band minimum (CBM) of $Al_{0.25}Ga_{0.75}N$, which may serve as two distinct electron transfer channels for reversely biased AlGaN/GaN heterostructures.



Fig. 2 (a) Physical derivation of electronic properties of DLs and V_{III} -DLs in $Al_{0.25}Ga_{0.75}N$. Electronic states of pure and V_{III} -DLs are denoted by gray and red regions, respectively. (b) Current of AlGaN/GaN SBDs before and after neutron irradiation.

We then fabricate AlGaN/GaN Schottky barrier diodes (SBDs), and check their conduction mechanism of reversely biased AlGaN/GaN SBDs. As shown in Fig. 2 (b), temperature dependent I-V measurements indicate that the FP emission dominants the current leakage of reversed biased AlGaN/GaN SBDs. Interestingly, there exists two FP emission regions for reversely biased AlGaN/GaN SBDs, corresponding to electron transfer via VGa-DLs and pure DLs, respectively.

The evolution of DLs is also investigated by neutron irradiation. We find the low-fluence neutron irradiation significantly reduces the reverse leakage current of SBDs while maintains other electronic properties almost unchanged [Fig. 3 (a)]. It is well accepted that incident neutrons cause scattering and displacement of group-III atoms in AlGaN. The neutron scattered group-III interstitials are mobile and prone to passivate V_{III} -DLs, changing the configuration of DLs to monomorphic pure DLs in AlGaN. This gives rise to the change of two-stage FP emission to monomorphic single FP emission for reversely biased AlGaN/GaN SBDs, as shown in Fig. 3 (b). After the saturation of the passivation, neutron scattered group-III interstitials begin to escape from the system, which gives rise to the reduced reverse leakage current of SBDs, as shown in Fig. 3 (c).



Fig. 3 (a) Current of AlGaN/GaN SBDs before and after neutron irradiation. (b) Current of AlGaN/GaN SBDs before and after neutron irradiation. (c) Schematic band diagram showing the effect of DL-evolution on the electronic properties of AlGaN/GaN heterostructures.

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Cathodoluminescence imaging of non-radiative point defects buried in InGaN/GaN quantum wells

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Crystalline point defects (PDs) with energy levels deep in the bandgap can act as efficient electron-hole recombination centres. This PD recombination often results in unwanted light emission, or even no emission at all, and such *non-radiative* PDs can dramatically decrease the internal quantum efficiency (IQE) of optoelectronic devices such as light emitting diodes (LEDs), laser diodes, and solar cells [1][2]. However, spatially resolving, imaging, and studying these non-radiative PDs remains a serious bottleneck, especially when they are buried in more complex semiconductor heterostructures such as quantum wells (QWs)—this is particularly significant given the widespread use of QWs in the active regions of devices and nanostructures.

The critical role of PDs in QWs is exemplified perfectly by III-nitride semiconductors: recent literature indicates that an intrinsic PD in InGaN/GaN QWs acts as a highly-effective non-radiative recombination centre, killing the IQE of green to near-ultraviolet LEDs [3]–[5]. The density of these defects can be reduced by an indium-containing underlayer grown before the InGaN/GaN QW, since this underlayer traps surface defects and therefore prevents their incorporation into the QW as PDs [5]. Hence varying the thickness of the underlayer allows for precise PD density control in the QW. We chose an In0.17Al0.83N/GaN superlattice as the underlayer and grew five samples, varying the periods in the superlattice from 0 (no underlayer) to 24—these samples are referred to as P0–P24. Each structure was tailored for high-resolution cathodoluminescence (CL), with an ultra-thin (about 0.8 nm) single In0.15Ga0.85N QW only 15 nm below the sample surface, and a 5 nm Al0.05Ga0.95N cap to avoid surface recombination.

Using CL with ~ 80 nm spatial resolution, we image and analyse individual non-radiative PDs in the InGaN/GaN QWs of these samples (Fig. 1). We elucidate the nature of PDs in the QWs, identifying two different types and showing that only one type, linked to a mid-gap deep state, seriously impacts the IQE (Figs. 2a & b). This type of defect is demonstrated to reduce from a density of 10^{16} cm⁻³ down to 10^{14} cm⁻³ as the underlayer thickness is increased (Fig. 2b). We evidence the direct impact of PD density on carrier diffusion lengths in the QW (Fig. 2c), and likewise the impact of carrier density on PD non-radiative recombination. These results reveal the nanoscale origin of many PD effects that could previously only be supposed from macroscale measurements, and serve as a proof-of-concept for buried PD imaging and direct analysis.

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Fig. 1. $\mathbf{a} - \mathbf{e}$ Secondary electron (SE) images for each sample (P0 – P24); underlayer thickness is increased from P0 through to P24. Step-edges are clear as parallel lines and V-shaped pits are visible as dark spots. All are $2 \times 2 \mu m^2$ with a 500 nm scale bar. $\mathbf{f} - \mathbf{j}$ and $\mathbf{k} - \mathbf{o}$ show the InGaN/GaN QW CL integrated intensity images acquired *on the same* $2 \times 2 \mu m^2$ areas at 170 K and 10 K, respectively. Dark regions are a direct consequence of non-radiative recombination at PDs, and clearly decrease in density as the underlayer is made thicker from P0 \rightarrow P24. Each image is plotted on an absolute intensity scale from 0 - 1 (normalised to the highest intensity point in P24). The red squares in \mathbf{i} , \mathbf{j} , \mathbf{n} , and \mathbf{o} indicate examples of two different types of defects: type-I PDs with a strong impact on high-temperature intensity, and type-II PDs with a lesser impact. The 170 K intensity for P0 has been multiplied by three to make the image visible.



Fig. 2. a Temperature-dependent IQEs for all samples, as extracted from time-resolved photoluminescence measurements (not shown here); underlayer thickness is increased from P0 to P24. The IQE of samples with thinner underlayers significantly decreases with temperature, in-line with the higher density of PDs in these samples (see Fig. 1). **b** 3-D type-I and type-II PD densities in the QW for each sample, obtained from a counting analysis on the CL images in Fig. 1. A drastic decrease in type-I PD density occurs with increasing underlayer thickness, while the type-II PD density is near constant. Comparing this to the IQEs, we can conclude type-I PDs are the "killer centres" responsible for the decrease in IQE for samples with thinner underlayers. Dashed lines are guides to the eye. **c** Type-I PD density for each sample compared to carrier diffusion lengths in the QW at 170 K, as calculated from a diffusion analysis procedure on CL images. The shortening of diffusion lengths by high PD concentrations is clearly visible.

Dominating migration barrier for intrinsic defects in gallium oxide at and above room temperature

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Beta gallium oxide (β -Ga₂O₃) is an ultra wide bandgap semiconductor, attracting massive research interest on behalf of its unique physical properties and potentials for device applications [1]. Significant progress in understanding of point defect properties in β -Ga₂O₃ has been achieved by *ab-initio* calculations. For example, the migration barriers for the gallium (V_{Ga}) and oxygen (V_O) vacancies we calculated in the range of 0.5-2.3 and 1.2-4.0 eV, respectively [2]; notably the ranges are wide because of taking into consideration different charge states and migration paths for the defects. On the other hand, direct experimental data to correlate with theory are limited; in practice, even making a reliable estimate of an average or dominating migration barrier could be a step forward, in parallel, doing comparisons with theory.

In the present study, to make such estimate, we monitored the radiation defect dynamics in β -Ga₂O₃ by varying two irradiation parameters, specifically the ion flux (*J*) and the irradiation temperature (*T_i*), i.e. by measuring so-called "dose-rate effect" [3]. In short, the radiation disorder buildup was studied in monoclinic (010) β -Ga₂O₃ single crystals (Tamura Corp.) implanted with 400 keV ⁵⁸Ni⁺ ions in a wide ranges of *J* and *T_i*, while keeping the total accumulated ion dose constant at 6×10^{13} Ni/cm². Notably, the Ni dose was low enough to neglect extrinsic effects. The samples were characterized by the Rutherford backscattering spectrometry in channeling mode (RBS/C) and x-ray diffraction.

The dose-rate effect concept [3] is illustrated by schematics in Fig. 1 where the effective



Fig. 1 Schematics of the dose-rate effect balancing the irradiation temperature and ion flux with t_{ov} and t_s labeling the characteristic time intervals for collision cascade overlapping and defect stabilization within effective individual cascades, respectively.

cascade areas determined by diffusion of defects. the escaped from the thermalized collision cascades, are shown tear-shaped regions. by Increasing the ion flux at the fixed irradiation temperature boosts the probability for the neighboring collision cascade appear within a time to interval when the defects from the first impact are not yet annihilated or stabilized (t_s) . That should lead to the overlapping of the effective collision cascades and. therefore, enhance may accumulation of the defects. The overlapping time (t_{ov}) is inversely proportional to the ion flux, i.e. $t_{ov} \sim J^1$. The outcome of the dose-rate effect depends on the balance between t_{ov} and t_s , exhibiting strongest impact at $t_{ov} \approx t_s$. In its turn, dynamic annealing processes become more efficient with increasing temperature, so that the defect annihilation/stabilization occurs much faster resulting in the decrease of t_s and, therefore, in the less efficient interaction of the defects from different collision cascades. As a result, for prominent dose-rate effect outcomes, the ion flux range shifts up with increasing irradiation temperature. In either way, the activation energy of the dose-rate effect will characterize the dominating migration barrier for intrinsic defects.

The results obtained for β -Ga₂O₃ are in a full agreement with the scenario presented above and Fig. 2 summarizes the data, plotting the maximum relative disorder, as deduced from the RBS/C spectra, as a function of T_i for three different J. The trends in Fig. 2 illustrate the balance between defect generation and annihilation rates, so that the critical transition



Fig. 2 Maximum relative disorder as deduced from the RBS/C spectra in (010) β -Ga₂O₃ implanted with 400 keV Ni ions to 6×10^{13} cm⁻² as a function of T_i for three different J as indicated in the legend. The inset shows the Arrhenius plot used to extract the activation energy of the dose-rate effect in β -Ga₂O₃.

temperature for each *J* can be readily determined [3]. The inset in Fig. 2 shows the Arrhenius plot for the *J* vs this critical transition temperature; the Arrhenius analysis results in the activation energy of E_a $= 0.8\pm0.1$ eV characterizing the dose-rate effect in β - Ga_2O_3 . Importantly, the E_a value from Fig. 2 is within the V_{Ga} migration barrier range, but out of the Vo range [2]. Thus, taking into account the fact that we analyzed the disorder in Ga sublattice, we correlate E_a - the dose-rate effect activation energy - with the migration barrier for V_{Ga} . Notably, Ga interstitials are expected to be much more mobile at the temperatures of our measurements [4]. Thus,

our results provide probably the first reliable experimental estimate of the migration barrier for V_{Ga} in β -Ga₂O₃, as reported in literature.

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Interstitial defects stability at a β-(Al_xGa_{1-x})₂O₃/β-Ga₂O₃ interface

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Alloying ultra-wide band-gap monoclinic β -Ga₂O₃ (E_g = 4.8eV) with monoclinic Al₂O₃ (E_g = 7.24 eV) to form β -(Al_xGa_{1-x})₂O₃/ β -Ga₂O₃ heterostructures opens doors to many horizons for device design with enhanced electronic properties that are useful for many applications such as high-power electronics [1]. The defects that are induced during the growth process of these heterostructures can drastically modify the electronic properties of the device and are now subject to extensive experimental and theoretical studies [2].

In this work, we use High Angle Annular Dark Field - Scanning Transmission Electron Microscopy (HAADF-STEM) combined with Electron Energy Loss Spectroscopy (EELS) and density functional theory (DFT) calculations to uncover the interfacial and electronic structure of β -(Al_{0.2}Ga_{0.8})₂O₃/ β -Ga₂O₃ epitaxial film grown by molecular beam epitaxy technique. This investigation shows presence of multiple point defects along the β -(Al_{0.2}Ga_{0.8})₂O₃/ β -Ga₂O₃ interface such as Al and Ga interstitial atoms whose presence will modify the crystal structure of the material creating vacancy di-interstitial complexes.

Figure 1.a shows a HAADF-STEM image of the β -(Al_{0.2}Ga_{0.8})₂O₃/ β -Ga₂O₃ interface. The insert shows a zoomed-in image of one of interstitial atom that sits in between two tetrahedralcoordinated Ga atoms. DFT calculations have been carried out with the Vienna Ab initio Simulation Package (VASP). Figure 1.b shows a relaxed structure of β -(Al_{0.2}Ga_{0.8})₂O₃ within one Ga interstitial showing that the latter can be stabilized in the β -(Al_{0.2}Ga_{0.8})₂O₃ crystal structure however it disturbs its local environment by pushing nearest Ga atoms out of their initial positions creating di-interstitial-vacancy complexes. Further calculations and EELS experiments showed that these complexes will form deep level states in the band structure of the material and will affect the bandgap and the effective mass of electrons at the interface. These findings provide great insight into the electronic properties of β -(Al_xGa_{1-x})₂O₃/Ga₂O₃ heterostructures for future device design.

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Figure 1. (a) HAADF-STEM image of the β -(Al_{0.2}Ga_{0.8})₂O₃/ β -Ga₂O₃ interface in the [001] projection. Insert: zoom-in image on a Ga interstitial. (b) Crystal structure model of Ga_i in (Al_{0.2}Ga_{0.8})₂O₃ with two Al atoms surrounding the Ga interstitial. The presence of the latter locally disturbs the crystal structure of β -(Al_{0.2}Ga_{0.8})₂O₃.

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Multistability of Ga-O divacancies in β-Ga₂O₃

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Owing to the low symmetry of the monoclinic gallium sesquioxide (β -Ga₂O₃) crystal structure, defects in this material can generally assume several different configurations. For example, in addition to the five simple Ga- and O-site monovacancies, Ga vacancies can occur in three different split-vacancy configurations, as predicted from first-principles calculations [1,2]. For defect complexes, such as the close-associate Ga-O divacancy, the defect configuration space grows even larger, which can make experimental identification challenging.

This work explores the electrical properties and relative stability of 19 configurations of the divacancy in β -Ga₂O₃, including its complexes with H impurities, using hybrid functional calculations [1]. The divacancy is predicted to be an electrically active defect exhibiting a low formation energy under *n*-type conditions (Fig. 1). Our results reveal that key properties of the monovacancies are retained by the divacancy, including polaronic and negative-*U* behavior, where the latter is associated with the formation of a Ga-Ga dimer as the divacancy goes from the – to the 3– charge state (Fig. 2). Interestingly, we can divide the divacancy configurations into three groups based on the positions of the thermodynamic (–/3–) transition, which we rationalize from the three possible Ga-Ga dimerizations resulting from tetrahedral and octahedral Ga sites. The relative formation energy of the different divacancy configurations is found to depend on the Fermi-level position, and the energy barriers for transformation between the configurations are explored from nudged elastic band calculations. The divacancy is proposed as a potential origin of the so-called E_2^* center previously observed by deep-level transient spectroscopy after irradiation, and the behavior is discussed following recent findings on the temperature and Fermi-level dependence of E_2^* [3].

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 $(V_{\text{Ga2}}V_{\text{O2}})^{-} \xrightarrow{+2e^{-}} (V_{\text{Ga2}}V_{\text{O2}})^{3-}$

FIG. 2: Relaxed structures of $V_{Ga2}V_{O2}$, showing the deep defect state (blue isosurface) associated with the large lattice distortion to form a Ga1-Ga1 dimer when going from the – to the 3– charge state.

FIG. 1: Formation energy of the most favorable divacancy configurations under O-rich conditions. The grey bars highlight the Fermi level region with (-/3-) transitions for divacancies with Ga1-Ga1 or Ga1-Ga2 dimerization.

Radiation resistance and Cascade Density Effect in beta-Ga₂O₃

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Beta gallium oxide (β -Ga₂O₃) is an ultra-wide bandgap (~4.85 eV) semiconductor, having the high break-down field value (a theoretical estimation is ~8 MV×cm⁻¹). It is the most attractive material for the next generation power electronics as well as for solar blind UV photodetectors and sensors. However, despite the technological importance of ion implantation for electronic device fabrication, information on radiation-related phenomena in β -Ga₂O₃ is very sparse. In this contribution, we study the structural disorder in β -Ga₂O₃ single crystals irradiated at room temperature with monatomic P⁺ and F⁺ and molecular PF_n⁺ (*n* =2, 4) ions. All the implants were carried out at 7° off the channeling direction to similar doses expressed in displacements per target atom (DPA). Ion energy was kept constant at 1.3 and 3.2 keV/amu, which is equal to 40 and 100 keV for P ions respectively. Implantation-produced disorder was measured by RBS/C spectrometry.



Fig.1. Relative disorder created in β -Ga₂O₃ by different ions as indicated in the legend (symbols) and vacancy distribution simulated by TRIM (line).

Fig. 1 presents typical depth distributions of structural disorder formed in β -Ga₂O₃ after irradiation with different ions to the same dose of 0.44 DPA. At all the energies used, the damage created by monatomic ions is bimodal. It consists of two distinct peaks, one located at the sample surface, and the second formed in the bulk, close to the maximum of the nuclear energy loss. In its turn, molecular ions create only one broad defect peak with the maximum situated near the surface. When solids are bombarded with cluster ions, collision cascades created by individual constituent atoms of the cluster overlap each other near the surface enhancing the probability of formation spacial regions with increased density of

atomic displacements [1]. Higher energy density is deposited in the area of overlapping. Thus, the formation of structural damage in the target may be dramatically enhanced under the impact of molecules as compared to monatomic ions, i.e. increased cascade density causes enhancement in damage formation. Further, irrespective of ion species, the damage does not reach the amorphization level, saturating at ~ 80 - 90%.

Our finding reveals that the β -Ga₂O₃ is more than one order of magnitude less radiation resistant as compared to GaN.

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Defect properties of SiO₂ and Al₂O₃ in the metal oxide semiconductor capacitors of β -Ga₂O₃

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 β -Ga₂O₃ is promising for power electronics and RF electronics. Due to the difficulty in p-type doping, a high barrier height is desired to block the leakage current. The typical Schottky barrier height is 1.0-1.5 eV using metal Schottky contact [1]. When using p-type NiO[2] and oxidized platinum group metal (PtO_x, IrO_x, PdO_x, RuO_x) Schottky contacts[3], the barrier height can be increased up to 2.3 eV. Another approach is using a dielectric layer for MOSFET. Critical factors are dielectric constant, band offset, dielectric defect, and interface defect, as well as thermodynamics and kinetic stabilities. Through a few reports on dielectrics of HfO₂[4, 5], HfAlO[6], (YSc)₂O₃[7], the typical SiO₂ [8-10]and Al₂O₃ [10-13]are still of great interest due to the large conduction band offset.

Here we report the characterization of defect properties in ALD-grown SiO₂ using UV-assisted CV and deep level transient spectroscopy (DLTS). We discuss the defect properties on orientations of (100), (010), and (-201), and with or without O₂ plasma for the ALD SiO₂ layer. We also compare ALD SiO₂ with MOCVD-grown Al₂O₃ and we find an intriguing difference in hysteresis direction and sign of DLTS. We use these comparisons to help understand the MOS structures of β -Ga₂O₃.

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Identification of the M-center in 4H-SiC as a carbon self-interstitial

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The identification of self-interstitials in technological crystalline materials, such as semiconductors, have profound repercussions on a wide range of scientific areas. Examples of benefited fields are mass transport, crystal growth, doping and defect engineering in both mature and emerging technologies. Supported on detailed first-principles modeling and junction spectroscopy experiments, we present unambiguous evidence that the M-center in 4H-SiC [1,2] is the carbon self-interstitial [3]. The M-center is a bistable defect whose Deep Level Transient Spectroscopic (DLTS) signal depends on the bias/thermal history of the sample. Spectrum labeled 'A' comprising traps M₁ ($E_c - 0.42 \text{ eV}$) and M₃ ($\sim E_c - 0.83 \text{ eV}$), is obtained when the sample is cooled from room temperature under reverse bias. On the other hand, when the DLTS scan is preceded by a gentle annealing at T > 140 °C without bias, spectrum 'B' appears, showing up a single emission M₂ ($E_c - 0.63 \text{ eV}$) [1,2]. The carbon self-interstitial is predicted to adopt different sublattice sites depending on the Fermi level location. In n-type material, double negative C_i in the cubic site is the ground state, whereas under intrinsic conditions (reverse biased n-type 4H-SiC) the defect performs an exothermic jump towards the hexagonal site. The model developed incorporates the observed features of M, including charge states, bistability, annealing, reconfiguration kinetics and electronic transition levels. The observation of a new peak by isothermal DLTS (also accounted for by the C_i model) [3], labeled $M_4(E_c - 0.86 \text{ eV})$ and previously postulated as a fourth acceptor transition of the M-center [2], provides an important piece of evidence in the connection between M and the self-interstitial. Our findings represent an important step towards obtaining control over countless solid-state reactions involving self-interstitials in 4H-SiC, including the formation of defects for quantum technologies or the fabrication of more efficient power electronic devices.

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Kramers doublet transition metal point defects in hexagonal silicon carbide

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Transition metal (TM) point defects in silicon carbide (SiC) have attracted special attention recently owing to their highly promising properties with respect to quantum technology applications. Paramagnetic electronic structure of these defects exhibits a rich set of interesting and not yet fully resolved physics. In particular, character of wavefunctions and the corresponding strong electron-phonon coupling may highly influence their interaction with external magnetic fields. Complex interplay between the electronic orbitals, phonons and electron spin determines the effective pseudospin of the system that we demonstrate on vanadium and molybdenum defects in hexagonal silicon carbide (SiC) by means of *ab initio* calculations [1]. Furthermore, we show that this interaction leads to the giant anisotropy in the *g*-tensor of the TM defects with Kramers doublet spin ground state, resulting in reduced and vanishing interaction with the magnetic field in parallel and transverse directions, respectively [1]. The consequences of our finding in the application of these defects for quantum information processing are briefly discussed.

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Laser Interferometry Lithography and Quantum Efficiency Measurements of Nanograting Silicon PN Junctions

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Abstract: A new geometry based doping method called surface Nanograting (NG) has been developed to create a PN junction on the surface of a p-type Si substrate without using external impurities but just by creating periodic nano-size indents using laser interferometry lithography. Quantum efficiency and spectral response measurements have shown that the carrier transport and photon absorption happens in these NG based PN junction and the NG patterns are indeed contributing to the carrier transport. The surface XPS analysis proved no external impurity is present on NG surface and the main electric field is indeed created from the NG pattern. This findings facilitate the fabrication of emerging NG solar cells where the n-type partner is no more required to create a PN junction for carrier collection.

Introduction: Recent developments in nanotechnology have enabled the fabrication of low dimensional periodic nanostructures including the nanograting (NG) patterns (Fig. 1A). The periodic nano size patterns (30-50 nm) have shown to dramatically change the electrical, optical and thermal behaviour of the electronic, thermoelectric, and optoelectronic devices [1]. These unusual but attractive properties are observed when the NG dimensions become comparable to the de Broglie wavelength (λ) of the electrons. NG patterns impose special boundary conditions on the electron's wavefunction and forbid certain quantum states in valence band of the NG layer and reduce the density of the quantum states therein [2]. Some energy levels in the valence band become forbidden, and the rejected electrons have to occupy the energy levels of the conduction band. Thus, the electron concentration increases in the conduction band equivalent to donor doping (Fig. 1B). This novel physical concept could have a revolutionary impact on the structure and performance of electronic and optoelectronic devices especially in PN junction devices including solar cells. This project aims to create a thin NG geometrical pattern on the surface of p-type substrate as a replacement for n-type layer. Here we present our measurements of the quantum efficiency and the spectral response of a Si substrate with nanograting periodical pattern on Si surface where we expect that a PN-junction forms [3]. Our objective to run these measurements is to ensure the quality of photo-absorption in a NG device and to investigate the carrier transport and photogeneration rate in these emerging PN junctions. The XPS surface analysis has also been performed to demonstrate if the surface impurities are involved in PN junction formation at the top or this electrical behaviour is solely emerging from the quantum limitations imposed by the NG patterns on the DOS of the indented region. This will open the possibility to fabricate efficient and reliable solar cells with only nano-size patterns on the surface of the Si substrate and we call it geometry doping (G-doping).

Experimental procedure: We used commercially available p-type Si substrates with resistivity $1-10 \Omega$.cm cut in 10 mm × 10 mm size. A coherent laser with 375 nm wavelength of a laser interference lithography, Lloyd interferometer and Reactive Ion Etching (RIE) was used to pattern the chips with periodic indents of 30 nm depth. For the electrical measurements, Al contact was deposited by thermal evaporation and Ti/Ag on the NG patterns using R.F. magnetron sputtering [4]. The surface composition of NG was scanned by VG Microtech

electron energy analyzer (XPS system). External quantum efficiency measurements were performed using a 100 W tungsten halogen lamp source.



Fig. 1, A) NG device structure, B) energy diagram, C) XPS measurements, C) EQE and D) spectral response.

The surface composition analysis was conducted on NG samples to ensure there is no external impurity or defect complex, which, contributes to PN junction formation or will not impact on device characterization and charge collection efficiency. Fig. 1C shows the range scan for Oxygen analysis on surface. Only Oxygen was detected on surface and no metallic oxide components were formed, thus, there is no probability of Schottky junction formation at this surface and the impurities have no role in PN junction formation. The external quantum efficiency has been plotted for the NG samples in Fig. 1D. EQE is associated with the light transmission and reflection from the NG junction and the photoabsorption within the substrate and the architecture of the junction and is a measure of charge collection efficiency across the junction. The charge collection in a NG based PN-junction is our purpose of this study as we intend to show that the electric field is created by NG on the surface of the Si layer. Fig. 1D shows the spectral response of the Si substrates with and without the NG patterns on surface. A better spectral response for the patterned substrate might be due to increased light trapping on the surface and the internal reflection to the patterned area [5]. The spectral response is the ratio of the current generated by the device to power incident on the device. According to Fig. 1E, the current output of the NG based PN junction was more than its plane counterpart. This also proves that we could extract photocurrent from the NG device without a need to n-type layer. Further research on current extraction from NG devices will results in improved EQE and SR.

In **summary**, Laser interferometry lithography and reactive ion etching has been used to create nanograting patterns on the surface of p-type Si substrate. This believed to create a PN junction without a need to n-type partner and only by nano-size indents on surface which show highly conductive properties. XPS surface analysis has confirmed that the surface oxidation is not related to metallic oxide formation and thus there is no impurity on surface. The EQE and Spectral response measurements have shown that the NG patterns contributed to the photoabsorption in the Si substrate and enhance the photogeneration rate in NG samples. EQE as a measure of charge collection in this NG based PN junctions showed promising efficiency.

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Improving the doping efficiency of AI in 4H-SiC by co-doping group-IVB elements

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Due to the large ionization energy of its *p*-type dopants, the doping efficiency of p-type silicon carbide (SiC) is rather low compared with its *n*-type counterpart. Currently, the most widely used p-type dopant is aluminum (Al), which has the ionization energy of ~ 0.23 eV. When the doping concentration is up to 10^{18} cm⁻³, the ionization rate of Al is no more than ~ 30% at room temperature. A series of troubles are brought by the low *p*-type doping efficiency of SiC, such as low carrier density, low mobility, difficulties fabricating ohmic contacts, and challenges attaining low resistivity, which greatly hinds the development of SiC-based electronic devices.

We propose co-doping group-IVB elements with Al can effectively lower the ionization energy of Al through the Coulomb repulsion formed between the energy levels of group-IVB elements and that of Al. As shown in Figure.1(a), group-IVB elements introduce one fully unoccupied single a_1 state and two fully unoccupied double-degenerated e state near the valance band maximum, which repel the 3/4 occupied e state of Al down to shallow level. Among the group-IVB elements, co-doping Ti has the most prominent effectiveness. It decreases the ionization energy of Al by nearly 50%, leading to a value as low as ~ 0.13 eV. As a result, the ionization rate of Al with Ti co-doping is up to ~ 5 times larger than that without co-doping at room temperature at the doping concentration close to 10^{18} cm⁻³(Fig.1(b)). This work offers us a fundamental and achievable approach to address the low-efficiency *p*-type doping of SiC.



Fig. 1 (a)Single-electron levels of Al, Ti, Zr, Hf, Ti+Al, Zr+Al and Hf+Al in 4H-SiC. All the dopants substitute Si in 4H-SiC. (b)The ionization rate of Al with the co-doping of Ti (solid lines) and without co-doping (dash lines) at different doping concentrations as a function of temperature.

Formation of interstitial boron-substitutional carbon complex and capture radii for interstitial boron in silicon

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Detailed studies of the annealing kinetics of interstitial boron-interstitial oxygen defect (B_iO_i) at temperatures 160-200 °C have been performed. Diodes made of epitaxial and Czochralskigrown silicon differ in boron and carbon concentrations have been used. A preliminary irradiation with 0.9, 4 and 6 MeV electrons and alpha-particles was performed before annealing. Radiation-induced defects were monitored using DLTS and C-V measurements.

It has been found that the annealing results in the formation of several new traps and the additional growth of a DLTS peak related to the interstitial carbon-interstitial oxygen (C_iO_i) complex. One of the traps formed under the annealing has an energy level of E_v +0.28 eV (H028) and was identified according to Ref. 1 as complex of interstitial boron-substitutional carbon (B_iC_s).

Analysis of the annealing features shows that in order to get a consistent interpretation of the obtained experimental data one has to take into account the following defect reactions

$$B_i O_i \Leftrightarrow B_i + O_i, \tag{1}$$

$$B_i + B_s \to B_i B_s, \tag{2}$$

$$B_i + C_s \to B_i C_s, \tag{3}$$

$$B_i + C_s \to B_s + C_i, \tag{4}$$

Reaction (2) describes the main channel of interstitial boron capture in low resistivity epitaxial diodes. The formation of B_iB_s complexes hinders a carrier concentration recovery after B_iO_i disappearance.

An essential component in our considerations is reaction (4) which allows to explain the growth of the C_iO_i concentration during the annealing process and to get the correct dependence of B_iC_s concentration on carbon and boron content. The study of this dependence enabled us to determine the ratio between capture radii of interstitial boron by substitutional boron and carbon.

An ab initio analysis of the formation and stability of the $C_s + B_i$ defect has been performed. It shows that a split B-C configuration is the most stable configuration of the defect.

It is supposed to use the carbon-by-boron replacement reaction in order to activate implanted boron at low temperatures.

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Stacking fault expansion in 4H-SiC due to low energy electron beam irradiation

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Stacking faults (SFs) in 4H-SiC are harmful defects, which can be generated under excess carrier injection and degraded the power device parameters. This stimulates investigations of SF generation and expansion in 4H-SiC. It is widely accepted that SF expansion under mechanical stress or excess carrier injection is driven by recombination-enhanced gliding of partial dislocation with Si core. However, the partial dislocation dynamics under excess carrier injection are not totally understood up to now. In the present paper a SF generation and expansion under low energy electron beam irradiation (LEEBI) has been studied.

The investigations were carried out on 10 µm thick n-type 4H-SiC epitaxial layers with a donor concentration of 5×10^{15} cm⁻³ grown on a highly doped off-axis (0001) substrate with off-cut by 4° toward the [11 $\overline{2}$ 0] direction. Dislocation sources were intentionally introduced by scratching or indenting the sample surface with a diamond scriber at a load of 0.5 N. A SSF expansion was stimulated by LEEBI in a scanning electron microscope with a beam current I_b in the 20-100 nA range and E_b of 25 keV. The SF generation and expansion is monitored by the cathodoluminescence (CL) at wavelength near 425 nm (2.94 eV).

It is shown that the velocity of partial dislocations driving the SF expansion is practically independent of a distance from the indentation that means that the driving force for SF expansion is mainly determined the energy gain due to the electron capture into SSFs (so called "quantum well effect") [1]. As shown in [2], the binding energy of electron in SFs is of 0.213 eV, i.e. at room and lower temperatures the Fermi level in the structures studied is higher than the SSF energy level, therefore, the "quantum well effect" can take place.

The dependence of dislocation velocity on beam current and temperature has been studied. It is shown that under LEEBI SSFs can expand even at 80 K. At all temperatures the partial dislocation velocity is proportional to beam current that well correlates with the assumption about the recombination-enhanced dislocation glide (REDG) mechanism. The activation energy for the glide was estimated as lower than 8 meV, i.e. essentially lower than the activation energy for the dislocation glide under a share stress (~ 1.5 eV). The REDG is usually explained by a redirection of energy released due to excess carrier recombination on some centers in the dislocation core, which assists the formation and migration of kinks. The results obtained show that under LEEBI the barriers for both formation of kinks and their migration along dislocations practically disappear. The other possibility could be that the energy for the kink migration along partial 30° dislocations with Si core is rather low. Such assumption allows also to understand why rather long dislocation moves as a line even under point irradiation because in this case the energy is necessary for the kink formation only.

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Coherent phonon generation of ultrafast exciton trapping at V_{Se}+O₂ defect complex in monolayer MoSe₂

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In recent years, optical electronic excitations and photocarrier dynamics in transition metal dichalcogenides (TMDCs) have been actively investigated in view of understanding photophysics in atomically thin materials and their optical device applications. According to recent studies on pristine TMDCs, acoustic phonons are involved in exciton generation and electron cooling processes [1,2]. In practical situations, TMDC samples usually contain a certain amount of defects and adsorbates, which act as ultrafast photocarrier trapping centers [3,4]. Meanwhile, although the exciton-phonon interaction in pristine TMDC is relatively well studied, defect-related photocarrier trappings remain vague.

Here, we report a spectroscopic evidence of ultrafast exciton trapping by lattice defects in few-layer transition metal dichalcogenides, specifically by $V_{Se}+O_2$ defect complex in monolayer MoSe₂. By combining the ultrafast time-resolved transmission measurement and *ab initio* constraint density functional theory (CDFT) approach, we reveal that $V_{Se}+O_2$ defect complex in monolayer MoSe₂ behaves as a dominant exciton trapping center confirmed in our coherent phonon spectra. The excellent agreement between the experiment and the simulated photoluminescence signal by the exciton trapping of $V_{Se}+O_2$ further verifies our



Figure 1. The trapped exciton at V_{Se}+O₂ defect center in monolayer MoSe₂ calculated by occupancy constraint density functional theory.
(a) The calculated potential energy surface, exciton charge density and the defect phonon.
(b) The experimental and simulated photoluminescence spectra of the trapped exciton at V_{Se}+O₂ defect center.

finding. This work unveils a dominant decay channel of photoexcited carriers in monolayer TMDC, thus would bring a significant insight on existing optoelectronics and nanophotonics.

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Optical and spin properties of shallow implanted nitrogen vacancy centers in diamond

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Optically addressable defect qubits such as nitrogen-vacancy (NV) center in diamond show exceptional potential for implementation of a wide range of quantum technologies. The first step towards scalable realization is to demonstrate on-demand creation of near-surface (≤ 100 nm) identical coherent defects. We create single NVs by targeted ¹⁵N ion-implantation and high-temperature vacuum annealing. Provenance of the NVs is verified by optically detected magnetic resonance spectra. We then perform resonant excitation experiments to characterize NV optical coherence.

First, near lifetime limited optical linewidths (<60 MHz) are observed for majority of the ¹⁵NVs at an implantation depth of 100 nm (85 keV). Long-term temporal stability of the NV spectral emission and charge-state is also demonstrated. Further, measurements on multiple samples with similar implants reveal high degree of reproducibility.

Secondly, NVs with shallower implant depth of 20 nm produced via an angled implant with the same implantation energy (85 keV), exhibit reduced optical coherence. Our results suggest that the surface is a larger source of perturbation than implantation damage for shallow NVs. It is likely that in the future, surface engineering will be required for on-demand defect formation.



(100 nm NV sample, 85 keV ¹⁵N implant) **a.** Pulsed ODMR scheme utilized to identify the N isotope. **b.** Confocal PL map of the implanted region with the measured NV centers indicated by their isotope (green-¹⁵N, red-¹⁴N). **c.** ODMR spectra for the marked NV incorporating implanted ¹⁵N. **d.** ODMR spectra for the marked NV incorporating grown-in ¹⁴N. **e.** Resonant excitation (PLE) scheme utilized for characterizing the optical coherence of the marked NVs. **f.** Time traces of PLE scans measured at 10K for three NVs. Off-resonant re-pump between scans are indicated by green squares in the right column.

Position-controlled quantum emitters with reproducible emission wavelength in hBN

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In the context of photonic quantum information science, hexagonal boron nitride (hBN) has recently emerged as a very promising material. The bidimensional character of hBN renders it attractive for the realisation of heterostructures and integrated photonic devices. Moreover, this wide-gap material has been recently shown to host single photon emitters (SPEs) with appealing optical properties in the red and near infrared regions [1]. However, these deep defects suffer from the wide distribution of their emission wavelength and, in most cases, a random spatial location [2,3]. These limitations hinder the scalability of the system for applications.

Here we demonstrate a new approach towards deterministic positioning of SPEs with similar emission wavelengths, based on irradiation with an electron beam [4]. The SPEs are electronically activated in exfoliated hBN flakes and subsequently characterised using microphotoluminescence (fig. 1). They exhibit narrow linewidth at low temperature (below the $\sim 100 \,\mu\text{eV}$ resolution of the spectrometer) and a drastically reduced ensemble distribution of their emission wavelength ($\Delta\lambda < 1 \,\text{nm}$). Individual emitters display low $g^{(2)}(0)$ as well as high and stable count rates. Moreover, emission is observed up to room temperature.

Our results suggest new avenues towards top-down realisation of integrated quantum optical devices based on indistinguishable single photon sources in hBN.



Fig. 1: hBN flake with eight irradiation sites and corresponding confocal map and spectra, displaying reduced statistical dispersion of the emission wavelength.

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Position-controlled quantum emitters with reproducible emission wavelength in hBN

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Ion Implantation Damage of Hyperdoped Semiconductors Investigated Using Time-resolved Terahertz Spectroscopy

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In many optoelectronic applications, silicon (Si) is still the most viable semiconductor material currently available in the industry. Transparency to the lower energy photons below the bandgap energy, especially in the IR region is the limiting factor of pure silicon being a good candidate for specific applications. Incorporating high concentrations of dopants; hyperdoping, is a method to form an intermediate band and facilitate lower energy photon transitions. The hyperdoping process consist of two steps; introduction of dopant via ion implantation and subsequent nanosecond pulsed laser melting (PLM). Implantation of the dopant atoms amorphizes the host semiconductor material and PLM is performed to rectify the damage. During the PLM process, the molten hyperdoped layer, if deep enough, will resolidify off from the silicon substrate thus making the hyperdoped material crystalline [1,2]. In this work we evaluate the material quality by using time resolved terahertz spectroscopy (TRTS).

The PLM melt depth is crucial for controlling the resolidified material quality as well as the amount of dopants incorporated. The lattice below the amorphous layer, is predicted to be disturbed due to direct collisions, forwards recoil damage and channeled ions. Given that the silicon just below the melt depth serves as a template, the regrown layer can be only as good as the seed and hence the melt depth should be sufficiently deep enough. Nevertheless, to achieve high enough dopant concentration for intermediate band formation, a shallow melt depth is required. The melt depth, which is determined by the pulse energy, affects the resolidifying interface velocity which needs to be faster than dopant's diffusive velocity for dopant incorporation. When the melt depth is deeper, the interface velocity would be slower resulting in a lower dopant concentration.

Considering the fact that the melt depth should be deep enough to ensure recrystallization and also shallow enough to achieve supersaturation, we carried out a systematic study on material quality of PLM Si self-implanted with Si (Si:Si). First, Si wafers were implanted with a dose of 2×10^{15} atoms/cm² Si ions and then melted to various depths. We quantified the lattice damage vs depth by simulating atomic collisions utilizing the Binary Collision Approximation. We then evaluated the material analyzing the lifetime of the charge carriers TRTS. Typically, cross-sectional transmission electron microscopy (XTEM) reveals that the regrown layer was observed to be single crystalline and free of extended defect [1,2]. However, in our work, TRTS shows that charge carrier lifetime could be as short as 10 ps, even when the material is single crystalline.

TRTS is a non-contact photoconductive measurement technique with sub-picosecond time resolution. We used fs-laser pump pulse to excite the charge carriers in the material and probe with a broadband sub-picosecond THz pulse to map the photoconductivity decay dynamics [3]. We studied the charge carrier dynamics corresponding to two different pump wavelengths; 266nm and 400nm. The different penetration depths in the material accessed by different wavelength probes gave us insight to differentiate defects near the surface and deeper in the material. We carried out an investigation to infer defect information above and below melt depth and to deduce an optimal melt depth for a good quality epitaxial regrowth.



Figure 1 – Charge carrier dynamics of Si:Si self-implant series and the damage concentration profile. (a) PLM depth 110nm. Excitation wavelengths are 400 nm (blue) and 266 nm (orange) (b) PLM depth 150 nm and (c) PLM depth 195 nm



Figure 2 – recombination rate estimated from half-life (left) and weighted damage concentration for each pump wavelength (right). As a function of PLM depth, the recombination rates agree qualitatively with calculated weighted damage concentration. The weighted damage concentration assumes the PLM layer is a constant value as the seed.

Our study shows that carrier lifetime in Si:Si samples improved significantly as PLM depth increases, regardless of the pump wavelength (Figure 1). This is consistent with the simulated defect concentration profile, as the amount of defects decreases with the depth and hence the seed for the regrown material gets better, resulting in a better quality material. Also, for PLM melt depth shallower than 150nm, the carrier lifetime is shorter when excited by 266-nm pump revealing damage near the surface of the material. In order to explain this further, we calculated the weighted damage concentration at different photoexcitation wavelengths. (Figure 2b). We extracted the half-life from the decay dynamics and estimated a recombination rate (Figure 2a). Qualitatively, as a function of PLM melt depth, the weighted damaged concentration correlates with carrier recombination rate. Therefore, our work suggests that TRTS is a useful technique to evaluate material quality since charge carrier lifetime is hindered by defects that were not detected by conventional microscopic and spectroscopic techniques.

Furthermore, we plan to characterize these defects using DLTS measurements to support the above observation. Additionally, to mitigate the ion implantation damage and improve the material quality, we studied oven annealing at a lower temperature (350 °C) prior to PLM treatment. The TRTS charge carrier lifetime implies that pre-annealing improves the silicon substrate quality.

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Electron-Hole Recombination and Spin Dynamics for Quantum Defects in Two Dimensions

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When applying first-principles computational techniques to quantum defects in twodimensional systems, care needs to be taken in handling the Coulomb interactions with the reduced dimensionality and stronger many-body interaction. We will discuss our recent development on recombination processes in low-dimensional quantum defects, demonstrating the effect of dimensionality and strain on radiative[1] and phonon-assisted non-radiative lifetimes of defects in hexagonal boron nitride[2]. We will then show our recent work on discovery of new spin defects with large exciton-defect couplings and spin-orbit induced intersystem crossing rates [3].

Lastly, we will briefly show our recently developed methodology for spin dynamics based on real-time density-matrix Lindblad dynamics with electron-electron, electron-phonon, electron-defect couplings and self-consistent spin-orbit coupling fully from first-principles [4,5], which is necessary to predict spin lifetime (relaxation and decoherence) for general systems, critical for quantum-information science, spintronics and valleytronics applications.

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Thermal evolution of point and extended defects in N-implanted ZnO and (ZnO)_{1-x}(GaN)_x thin films: STEM-EELS investigations

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Point and extended defects -as well as their interaction with dopants- directly influence semiconductor properties hence, identifying different defect-types and understanding their evolution is crucial. ZnO is a wide and direct band-gap semiconductor exhibiting potential for a variety of next generation solid-state devices. However, the doping asymmetry -where only n-type conductivity can be accomplished- hinders the realization of ZnO applications. Nitrogen (N), has been considered as one of the most promising candidates for p-type doping in ZnO, however, the results obtained so far are quite contradictory and reliable p-type doping is still challenging. Furthermore, N has also attracted fundamental interest since it exhibits a strikingly different behavior in terms of defect evolution, in comparison to other dopants in ZnO. In particular, an exceptional thermal stability of vacancy-clusters has been reported, as well as nonlinear thermal evolution trends. However, the defect formation mechanism is not yet understood and atomically-resolved investigations are still pending in order to elucidate the role of N in defect evolution in ZnO.

This study provides a thorough comprehensive STEM-EELS investigation on the atomic scale, in order to elucidate the nitrogen behavior as a dopant in ZnO-based structures. In this respect, N-implanted ZnO single crystals were initially studied, to investigate the fundamentals regarding formation and thermal evolution of the N-induced defects [1]. The study continued to novel semiconductor alloys $(ZnO)_{1-x}(GaN)_x$ (ZOGN), that are strong candidates for bandgap engineering, ideal for photovoltaic and solar water-splitting applications [2], [3], [4], [5].

In our study, taking advantage of the possibility to use multiple detectors simultaneously, a direct correlation of the atomic structure to chemical information and bonding-type gave valuable insight into the elemental and bonding distribution on the atomic scale and its correlation to different defect-types. In this respect, (Scanning) Transmission Electron Microscopy ((S)TEM) was employed, combined with Electron Energy-Loss Spectroscopy (EELS) and Energy-Dispersive X-ray spectroscopy (EDX). STEM-imaging was conducted using simultaneously high-angle annular dark field (HAADF), annular dark field (ADF) and annular bright field (ABF) detectors, providing complementary views of the same defected region. Low-loss EELS was employed for band gap measurements of the alloys and for the sample thickness evaluation. Time-resolved electron-beam irradiation was also performed in order to modify in-situ a defected area, while simultaneously recording EELS spectra. Geometric Phase Analysis (GPA) was performed on high resolution (S)TEM images to extract lattice phase maps and for the nanoscale localization of strained regions. All investigations were conducted on an FEI Titan G2 60-300 kV equipped with a CEOS DCOR probe-corrector, monochromator and Super-X EDX detectors.

This study elucidates the behavior of nitrogen into ZnO and ZOGN host matrix and proposes a model describing the evolution of N-related defects. EELS showed direct evidence for the formation of N_2 molecules, supporting previous reports on the low stability of N

substitution on O sites (N₀), thus limiting p-type doping. Vacancy (V_{Zn}) -clusters were found to be stabilized by N₂-trapping, resulting in an exceptional thermal stability compared to the situation with other dopants, and leading to a suppression of V_{zn}-Zn_i recombination. The highly mobile Zn interstitials preferentially condense on the basal planes forming interstitial-type extended defects. The dominant extended defects were the energetically favorable basal stacking faults of I₁-type terminated by stacking mismatched boundaries or Frank-Shockley dislocations, which again provide energetically favorable sites for N₂-trapping as a way to reduce local strain fields. The same trend was observed in ZOGN alloys, where thermallyinduced nano-sized voids (V_{Zn+Ga}) filled with molecular nitrogen (N_2) were formed along grain boundaries. The voids reached an equilibrium shape defined by the energetically favorable facets, mainly on the semi-polar planes and the O-terminated internal polar plane. This study revealed that the N-N bonding is an alternative path for nitrogen after annealing of ZOGN alloys, in addition to the increase in the Ga-N bonds that reduce the total energy of the system. Despite this re-arrangement of N-bonds, no phase separation phenomena were observed (ZnO vs. GaN) indicating that the previously reported bandgap of the system is the result of a homogeneous ZOGN alloy and not an average of a mixture of different phases [6].



High-resolution HAADF-STEM image from the N-implanted ZnO region and monochromated EELS spectrum acquired from V_{Zn} -clusters revealing molecular nitrogen N_2 -trapping.

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Passivation mechanism of harmful defects in Se alloyed CdTe

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Point defects are unavoidable in semiconductor devices and are detrimental to device performance. In photovoltaic materials, defects leading to mid-gap states can act as non-radiative carrier trap centers and can reduce power conversion efficiency severely. Extrinsic doping and/or alloying of the material is a plausible known mechanism of intrinsic defect passivation.

Cadmium telluride (CdTe) solar cells are still at the front end of the few thin film technologies exceeding 22% of efficiency. The latter record was made possible by Se alloying in the CdTe absorber[1]. CdTe has a band-gap value of ~1.5 eV close to the optimum band-gap of 1.34 eV for maximum theoretical solar cell efficiency according to the Shockley–Queisser thermodynamic limit. It has been shown that Se alloying can improve the CdTe solar cell efficiency. A first effect comes from a band-gap grading from 1.46 to 1.36 eV leading to an increase of the wavelengths absorption range. In addition to band-gap grading, Se diffusion inside the CdTe absorber has been recently probed by means of cathodoluminescence experiments coupled with Secondary Ion Mass Spectrometry (SIMS) measurements [2] as a key for the passivation of some critical defects thus explaining the higher luminescence efficiency in Se alloyed solar cell.

In this contribution, using density functional theory (DFT), we will provide the missing microscopic picture for the role of Se in this passivation process. Our study is two folds. We scanned over several Se point defects, identifying the diffusing defect and the corresponding mechanism for Se diffusion. Next, we studied the interaction of Se diffusing defect with harmful known defects, namely Te-antisite and Cd vacancy. This understanding of the underlying diffusion mechanism allow us to derive in an exhaustive way the 9 different possible complexes resulting from such an interaction. Among them, we identify that the most stable configurations have no defect states deep in the band-gap and thus are passivating the two harmful defects.

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Enhancement of Er luminescence from bridge-type photonic crystal nanocavities with Er,O-codoped GaAs

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Er,O-codoped GaAs (GaAs:Er, O) exhibited a sharp luminescence peak at 1.54 µm, which is located in the minimum loss region of silica fiber, with Er-2O luminescent center formed in the GaAs. Since the intra-4f-shell transition of Er^{3+} ions is sheltered by the outer $(5s)^2(5p)^6$ electron orbit, this material shows the insensitivity of the luminescence wavelength to temperature, and hence should have excellent application prospects towards application in fiber optic communication or quantum information systems [1]. However, due to the relatively low optical gain of Er,O-codoped GaAs, laser oscillation from Er,O-codoped GaAs has not yet been realized. To overcome the problem, an optical nanocavity with high Q factor and small modal volume is essential according to the Purcell effect. The photonic crystal (PhC) nanocavity is one of the effective solutions owing to its ultra-high Q factor and extremely-small modal volume. We have so far demonstrated the observation of the enhanced Er luminescence induced by the Purcell effect in L3 PhC nanocavities, which would lead to the realization of laser oscillation [2]. In this contribution, we propose and demonstrate a bridge-type PhC as a nanocavity structure to further improve the Q factor of the device in order to realize the laser oscillation [3, 4]. The numerical simulation of the bridge-type PhC nanocavities with the finitedifference time-domain (FDTD) method is conducted to evaluate the threshold Q factor of the laser oscillation in this material system and investigate the effect of the number of holes on higher-order modes and Q factor. The Er,O-codoped GaAs sample with bridge-type PhC nanocavities is prepared, and their characteristics of the Er-2O luminescent center are evaluated.



Fig. 1. Correlation between threshold gain and Q-factor by FDTD simulations.



Fig. 2. Top-view SEM images of a GaAs:Er,O bridgetype PhC nanocavity.

According to previous several reports, GaAs:Er,O has a gain of 8 cm⁻¹ at 77 K [3]. As shown in Fig. 1, the numerical simulation using the FDTD method shows that the threshold Q factor of the laser oscillation is 2.0×10^4 . The Q factor of designed GaAs:Er,O bridge PhC calculated using reported value is 6.0×10^5 [5]. In addition, numerical simulations of PhC nanocavities with various number of holes is performed to study the effect of the number of holes on high-order modes and Q factor, and the maximum design Q factor of 1.2×10^6 is obtained with 27 holes. Since the high-order mode is suppressed by reducing the number of circular holes, the proposed bridge-type PhC structure is able to satisfy the threshold of the Q factor for laser oscillation while suppressing high-order modes.



Fig. 3. (a) μ-PL spectra of a GaAs:Er,O bridge PhC nanocavity at 77 K (red line) and a GaAs:Er,O bulk sample.(b) Excitation power dependence of cavity (red circle) and bulk (blue circle) peaks of the PhC nanocavity.

In this study, the GaAs:Er,O active layer was grown on an AlGaAs sacrificial layer formed on GaAs substrates by organometallic vapor phase epitaxy (OMVPE), whose detailed growth conditions are described in our previous publications [2]. The bridge-type PhC, as shown in Fig. 2, is fabricated without collapse of the bridge structure even after undergoing electron beam lithography to form patterns, dry etching process to form circular holes, and wet etching process with hydrofluoric acid to remove the sacrificial layer to form a hollow bridge structure. The optical characterization of the GaAs:Er,O bridge PhC nanocavity is performed by using conventional micro photoluminescence (μ -PL) setup with excitation by He-Ne laser. Fig. 3(a) shows the µ-PL spectra at 77 K of both bridge-type PhC nanocavity and bulk samples for comparison. The µ-PL spectrum of the bulk material shows typical luminescence from Er-2O ions in GaAs:Er,O at 1538 nm, while that of the PhC nanocavity shows several sharp intense peaks originating from the modes of the bridge PhC cavity. One of them is exactly coupled to the peak of Er-2O luminescence at 1538 nm, and the peak intensity of the Er-2O luminescence is 8.3-hold enhanced at the pump power of 40 nW. The linewidth of the cavity mode is ~0.128 nm, which is almost corresponding to the resolution limit of the µ-PL setup. Therefore, the experimental Q factor is estimated to be larger than 1.2×10^4 . This value is much larger than our previous report on L3 PhC cavity [2]. Fig. 3(b) shows a logarithmic plot of the peak intensity of the main cavity peak at 1538 nm of the bridge PhC cavity as well as that of the bulk sample. The slope of the curve is superlinear in the range of 5-20 nW having an exponent of greater than 1, while that of the bulk shows sublinear behavior. Then the slope tends to saturate when the pump power is greater than 100 nW, which is due to the saturation of Er-2O luminescence. The observed results are similar to our previous study on the Er-2O luminescence embedded in the microdisk structure, and would be suggestive of the reduction of the lifetime due to the Purcell effect [6]. These results show that the PhC structures are a promising step toward realizing a laser diode based on a rare-earth-doped compound semiconductor.

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Enhancing dielectric constant of pulsed laser deposition grown ZnO via co-doping of acceptor and donor

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Materials having high dielectric constant and low dielectric loss stably constant over a wide range of frequency is ideal gate material in capacitive devices like metal oxide semiconductor field effect transistor (MOSFET) [1] and thin film transistor (TFT) [2]. Moreover, it is also crucial for realizing dielectric battery for the application in high-density energy storage system. It was recently demonstrated colossal dielectric constant CDC and relatively low dielectric loss $(\varepsilon_r \sim 10^4 \text{ and } \tan \delta \sim 0.1 \text{ at the frequency of } 1 \text{ kHz})$ could be achieved in ceramic oxides via codoping of acceptors and donors (for examples, Nd-In co-doped TiO₂ [3] and Li-Al co-doped ZnO [4]). The CDC of these ceramic materials were stable over a wide frequency range up to 10⁶ Hz. Hu et al [3] proposed that the CDC was associated with the hopping of electron localized around an electron pinned defect dipole which was the defect complex comprising of the acceptor and donor according to the external electric field [3]. Huang et al [4] studied in details the dielectric properties and relaxation, clearly revealing relaxation processes associated with correlated barrier hopping CBH between two neighboring defect states in the band gap. The frequency dependent dielectric constant and loss data can be well simulated by a model involving the CBH of these defects using Kirkwood's theory and Kramer-Krönig transformation. The CDC was associated with the CBH between neighboring defect complexes comprising of the acceptor and donor.

In the current study, we attempted to transplant this idea to ZnO film grown by pulsed laser deposition (PLD) to achieve transparent high-k film. which would find application in transparent capacitive devices like transparent With appropriate Cu-Ga doping TFT [2]. compositions, the ZnO film exhibit a dielectric constant of ~200 and relative low dielectric loss of ~0.2 at the frequency of 1 kHz. The dielectric constant was stable up to a frequency of 10^5 Hz (see Figure 1). A sharp dip in the dielectric constant vs frequency spectrum, which is probably related to the resonance of electron oscillation, is outside the scope of the current abstract. The high-k film was optically transparent in the range of visible wavelength having optical transmittance of ~80 %.

Ac conductivity measurement was conducted to understand the relaxation processes, for which the results were shown in Figure 2. The ac conductivity is given by the universal dielectric response law: $\sigma(f) = \sigma_{dc} + \sigma_0 f^s$, where σ_{dc} is the dc conductivity, σ_0 is a constant, f is the frequency of the driving electrical field, and



Figure 1 Dielectric constant vs Frequency



Figure 1 Ac conductivity vs Frequency

0 < s < 1 is the frequency exponent. Linear fitting to the ac conductivity data yielded two

different s values, namely 0.93 and 0.29 respectively in the frequency ranges of 10^2 - 10^5 Hz (P1) and 10^5 - 10^6 Hz (P2). It is known that *s*>0.90 is characteristic for the CBH process and *s*<0.7 is characteristic for the small polaron tunneling (SPT) mechanism [5]. The CBH as found in the current PLD grown transparent ZnO film was also observed in the CDC ZnO ceramic sample, and it was the origin leading to the observed CDC [4]. Concerning the SPT that only observed in the current PLD grown high-k ZnO thin film, electron in a defect site would induce displacement of the nearby positively charged atomic core to form the polaron bound state. If the polarons are localized and not overlapping with the nearly defect states, electron hopping is not likely to occur. However, electron of the polaron state could tunnel to the nearby defect state with phonon assist [5]. With the model involving the CBH and SPT using Kirkwood's theory and Kramer-Krönig transformation, the frequency dependent dielectric constant data can be well fitted in the frequency range up to 10^5 Hz (see the fitting curve in Figure 1). It is thus plausible to associate the high-k phenomenon introduced by Cu-Ga co-doping into the PLD grown ZnO film to CBH and SPT of electrons between the polaron states and defect complex states, for which the corresponding defects comprise of the acceptor and donor dopants.

ACKHOWLEDGEMENT

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Multiple defect-assisted mechanisms determine blinking of I-III-VI quantum dots

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One of the most remarkable feature of semiconductor quantum dots (QDs) is their fluorescence intermittency, so called blinking, observed on the single-particle level even for continuous excitation. The first theoretical model describing the origin of dark state formation in individual quantum dots was proposed by Efros and Rosen in 1997 [1]. It assumes the only pathway for radiative relaxation is assigned for excitons. Dark states are formed due to internal charge disturbances after charge-trapping events e.g. by Auger autoionization process. This model proved to be very useful in the explanation of blinking observed in various binary compounds for which the excitonic channel is dominant. However its direct applicability to the compounds, where main radiative recombination channel is defect-related like ternary I-III-VI semiconductors, seems to be insufficient to fully understand the complexity of excited state relaxation in these materials.

This work address the issue of dark states formation in ternary QDs either by excitonic channel and pure defect-assisted radiative transitions. It is shown experimentally that defect assisted radiative transitions in a single AgInS2 and CuInS2 QDs lead to untypical blinking character that cannot be explained on the base of commonly adopted charged excitons model. Numerical simulations performed in terms of Kinetic Monte Carlo has revealed that dark states formation doesn't have to be limited to mechanisms of charged excitons dynamics and may also be observed for independent defect assisted relaxations. Two additional transition schemes including correlated single/double charge trapping at a single defect center and uncorrelated trapping with radiative relaxation from two different types of defect centers have been proposed. We show that intermittent emission of many characters may be observed even for almost none emission from excitons. Models described here can be applied to a wide range of natively defected compounds i.e. I-III-VI as well as multinary compounds.

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An atomic scale study of isoelectronic dopant pairs in GaAs using X-STM and DFT

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Isoelectronic doping of GaAs with Bi can be used to generate longer wavelength devices on GaAs substrates. The Bi dopants lower the size of the band gap of GaAs by shifting up the valence band maximum (VBM). Due to this shift of the VBM and spin-orbit split-off band (SO), the Auger recombination losses are also suppressed. Incorporating large amounts of Bi dopants in GaAs is difficult, however, due to the low Ga-Bi reactivity and the strong tendency of Bi to segregate. One way of influencing the Bi incorporation in GaAs is co-doping of the material with N. Another reason for co-doping the material with N dopants is the fact that N doping of GaAs lowers the size of the band gap by lowering the conduction band maximum (CBM). This means that in a co-doped region, both the electrons and holes are confined, which enhances recombination.

Here the interaction between Bi and N dopants in GaAs is studied using cross-sectional scanning tunneling microscopy (X-STM) and density functional theory (DFT). Specifically, the occurrence of the various nearest neighbor (NN) pairs are studied in order to better understand the interaction between the dopants. Using DFT, both bulk and growth surface simulations of GaAs doped with Bi and/or N are performed. The bulk calculations predict Bi-Bi and N-N anticlustering and Bi-N clustering. Through dopant pair counting of the observed Bi-Bi pairs found in X-STM measurements of GaAs:BiN it is concluded however that a large amount of first NN Bi-Bi pairs is present in GaAs:Bi. Another observation from these measurements is that a relatively low amount of fourth NN Bi-Bi pairs is present in GaAs:Bi. Simulations of Bi-Bi pairs in the (001) growth surface of GaAs show that these first NN Bi-Bi pairs are likely to be formed during the growth. Since the first and fourth NN Bi-Bi pair visible in our X-STM measurements are both situated on top of the (001) growth surface, the fourth NN Bi-Bi pairs are likely converted into first NN Bi-Bi pairs during the growth of the material.
CaCuP: A Degenerate Wide Band Gap Phosphide for Transparent Conducting Applications

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Transparent conducting materials (TCMs) are a vital component in a vast range of optoelectronic devices, many of which have become integral to modern day life. P-type TCMs have been historically more difficult to synthesise than their n-type counterparts and often display inferior opto-electronic properties. As the demand for transparent electronics grows, with exciting functionalities such as pop up display in automobile windshields and fully transparent touch-display screens, there is an increasing pressure to develop a high performance transparent p-n junction, in turn requiring a high performance p-type TCM.

In 2017, CaCuP (and MCuP where M = Mg, Sr and Ba) was identified as a potential p-type TCM by *Williamson et al* owing to its large valence band dispersion and optical absorption onset of around 2.7 eV [1]. Phase pure powders were synthesised and pressed into pellets which possessed a similar direct absorption onset at 2.7 eV, and displayed p-type conductivity of around 2 x 10⁻³ S cm⁻¹ which was thought to be due to Cu vacancies. This is remarkably good conductivity for pressed powder samples that likely contain a high number of grain boundaries, and prompted an in depth defect study which was the motivation for this work.

The full intrinsic defect chemistry of CaCuP has been studied using VASP, a periodic plane wave DFT code, [3] and defect formation energies have been calculated according to the scheme proposed by Lany and Zunger. [4] It has been found that the Cu vacancy possesses an extremely low formation energy, and is stable into the valence band maximum (VBM), giving rise to degenerate semiconducting behaviour. The charge density of the hole generated by this Cu vacancy is extremely delocalised, indicating high hole mobility as suggested by the highly dispersed valence band.

Phase pure thin films with a varying Cu gradient were grown using PLD, improving the p-type conductivity to 1040 S cm⁻¹. Hall measurements indicate a carrier concentration of around 1.8 x 10^{20} cm⁻³ at room temperature and mobility of around 36 cm² V⁻¹ s⁻¹, supporting the behaviour predicted by the transition level diagram. Work is ongoing to better understand the optical absorption of the thin films, which is not as large as the DFT predictions or the pellet samples.

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Tailoring oxygen-related point defects with a technology to create and irradiate negatively charged oxygen (O⁻) ions to control electrical, optical properties and band gaps of Sn-doped In₂O₃ films

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n-type doped In₂O₃-based films (Fig. 1) have been largely used as electrodes in LCD panels and photovoltaic cells.[1,2] We have demonstrated that the-state-of-the art technology to create and postirradiate negatively charged oxygen (O⁻) ions is very effective for tailoring O-related point defects, as results; electrical resistivity (ρ), carrier concentration (n_e) (Fig. 2: *ho* and *lo* denote highly and lowly oxidized conditions), and optical band gap (E_g) in a wide range for polycrystalline 50-nm-thick Sn-doped In₂O₃ (ITO) films deposited on non-alkali glass substrates at 200 °C by reactive plasma deposition with direct-current arc discharge.[3] Asdeposited ITO films grown on showed n_e of 9.2×10^{20} /cm³ and ρ of $1.5 \times 10^{-4} \Omega$ cm, which were determined by Hall effect measurements, and E_g of 3.50 eV. A sintered mixture of In₂O₃ and SnO₂ (SnO₂ concentration of 5 wt.%, corresponds to [Sn] = 1.4×10^{21} /cm³; 4.6 at.%) was used as a source material. The flow rate of oxygen (O₂) gas (OFR) that was introduced into the deposition chamber during film growth was 12 sccm.



 $n_e^{19} = 10^{20}$ $n_e / \text{ cm}^{-3}$

Figure 2 shows electrical properties determined by Hall effect measurements of as-deposited and O⁻-ions irradiated ITO films: The postirradiation of O⁻ ions for 180 min at 250 °C decreased n_e to 2.4×10^{18} cm⁻³. This resulted in a significant increase in ρ from 1.5×10^{-4} of as-deposited films to 3.5×10^{-1} Ωcm while retaining the crystal structure and the spacial distribution of one of dominant donors, Sn. The postirradiation of O⁻ ions led to the continuous decrease in the E_g ranging from 3.50 of as-deposited films to 3.02 eV that is smaller than that of undoped In₂O₃.



Fig. 3. (a) to (e) correspond to a series of occupied sites of incorporated O atoms during the Irradiation of O⁻ ions. V_O and O_{VSO} denote an oxygen vacancy and an interstitial O atom located at a structural-defect site (Fig. 1)), respectively. (f), (g) and (h) illustrates a change in energy regions of conduction (CB) and valence band (VB) shifted with the Irradiation of O⁻ ions, respectively. E_o , ΔE_{BM} , ΔE_g , and ΔE_{hyb} mean E_g of as-deposited films, Burstein–Moss shift, band-gap shrinkage due to electron-electron and electron-impurity interactions, and upward shift in energy originated in the hybridization of *p* states of interstitial O atoms and *d* states of In atoms in the vicinity of the O sites of top at VB, respectively. K_F and λ_{MFP} are Femi wave number and mean free path of carrier electrons, respectively.

Figure 3 illustrates the effects of the irradiation of O^- ions on O-related point defects such as O vacancy (V₀) and interstitial oxygen atoms occupied at some of the structural vacant sites (O_{VSO}) shown in Fig.1 and energy-band structure of ITO films on the basis of the analysis of theories and experimental-measurement results.

The postirradiation of O⁻ ions enables us to markedly change the electrical and optical properties of polycrystalline ITO films by the insertion of a large number of O_{VSO} interstitials at V_{SO} sites that are inherent to the bixbyite structure. In such films, we found a reduction in n_e in degenerate and non-degenerate semiconductors without the rearrangement of the spatial distributions of In and Sn atoms, i.e., no additional phases such as In₄Sn₃O₁₂ nor precipitation such as SnO₂. On the basis of Ioffe–Regel theory [4] utilizing the product of λ_{MFP} and k_F , we determined critical n_e at which ITO films show a boundary between degenerate and nondegenerate semiconductors.

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Abstracts: Poster presentations

Diverse structural and electronic properties of carbon-substituted silicene nanoribbons

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Abstract:

Diverse structural and electronic properties of carbon-substituted armchair silicene nanoribbons (ASiNRs) are studied using the first-principles calculations. The physical quantities of formation energy, optimal lattice parameter, charge density distribution, band structure and density of states are developed under the first-principles DFT calculations that is sufficient to thoroughly analyze the structural and electronic properties of the substituted systems. The optimal configurations include substitutions of the single C adatom, the double C adatoms under various adatoms distributions of meta-, ortho- and para-types and the 100% C adatoms, in which buckling of the pristine system gets smaller values in the substituted systems that becomes the planar 1D SiC structure under 100% substitution configuration. As a result, the band gap of the pristine system are shrunk under the single and double adatoms configurations, while the 100% adatom configuration opens the band gap of 1.8 eV. The diverse electronic properties of the carbon-substituted ASiNRs will be very potential 1D semiconducting materials for nanoelectronic devices.

Keywords: silicene nanoribbons, substitution, formation energy, charge density distribution, band structure, density of states and nanoelectronic device.

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Telecom-frequency, silicon-based impurities embedded in dielectric Mie resonators towards directional emission

Abstract: Sub-micrometric, dielectric objects featuring high permittivity and reduced absorption losses enable for efficient light management, potentially enhancing and extending the performances of optoelectronic devices [1]. The resonant scattering supported by individual dielectric antennas is generally rather broad [2] (50-100 nm for the fundamental Mie resonances at visible and near-infrared frequency). Common materials for the implementation of these devices are IV-IV-based compounds. As such, light emission in these systems has been elusive so far.

Here we use low-resolution optical lithography and plasma etching joined with solid state dewetting of crystalline, ultra-thin silicon on insulator (c-UT-SOI) to form monocrystalline, atomically-smooth, siliconbased Mie resonators in well controlled large periodic arrays. By using ion implant of carbon followed by high temperature annealing and proton implant, we activate telecom frequency, light emitting G-centers (complex impurities) within the Si-based antennas. We engineer the light emission by tuning carbon dose, beam energy and islands size in order to optimize the coupling between the emitters and the Mie resonances.

These results are relevant for the fabrication of quantum light emitters with high directivity exploiting individual G-centers embedded in sub-micrometric antennas.

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Substitutional boron-doping of silicene nanoribbons when the presence of external field

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The structural and electronic properties of semiconducting silicene nanoribbons (SiNRs) under boron (B) doping are fully explored in the first-principles calculations, in which these feature-rich properties have been determined through the complete first-principles theoretical framework, including the binding energies, optimal lattice parameters, atom-dominated band structures, spatial charge density distributions, and atom- and orbital-projected density of states. The optimal configurations of the B-substituted SiNRs include the single B, the double B, and the 100% configurations, where the double B substitutions can lead to various adatom distributions of ortho-, para, and meta-configurations. The substitution configurations of the single, meta, para, and 100% B adatoms exhibit the metallic behavior with high free hole density, while only the ortho configuration remains the semiconducting behavior with reduced band gap of 0.14eV. Especially, all the B substitution configurations present the 1D flat SiC structure that comes from the surviving of the very strong chemical bonds on the 1D plane. The appearance of an external electric field changes the material's properties, the adsorption energy as well as the electromagnetic properties of the material. The first-principles theoretical framework developed in this study can be fully generalized to other emergent layered materials.

Keywords: Silicene nanoribbons; boron doping; feature-rich properties; substitution configurations.

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Investigation of Electrically Active Defects in GeSiSn/Si Multi Quantum Wells Using Deep Level Transient Spectroscopy Technique

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Ge_{1-x-v}Si_xSn_v Semiconductors are promising for many applications, such as integrated silicon photonics, micro- and nanoelectronics and photovoltaics. However, to realise their full potential, it is important to understand the impact of defects on device performance. In this work, we investigated the electrically active defects in GeSiSn/Si multi quantum wells p-i-n structures grown by Molecular Beam Epitaxy (MBE) technique. The samples have fixed Sn content (10%) and varying compositions of Ge (30-50%) and Si (60-40%) (see Figure 1). Their electrical properties investigated by using current-voltage (I-V), capacitance-voltage (C-V) and Deep Level Transient Spectroscopy (DLTS). From I-V measurements, the most important parameters such as ideality factor, barrier height and series resistance were extracted, e.g. the ideality factor was found to increase with increasing Ge content. C-V measurements indicated that the doping concentrations were similar in all samples. DLTS measurements under a reverse bias of Vr= -1 V, only one deep level trap with activation energy of 0.44 ± 0.09 eV and a concentration of 2.60×10¹⁶ cm⁻³ was detected in the 30% Ge sample. This deep trap has similar signatures to those reported in Ge_{1-x-y}Si_xSn_y grown on Ge substrates [1]. In addition, deep traps were observed in both 40% Ge and 50% Ge samples, with similar activation energies of approximately 0.62 ± 0.02 eV and 0.64 ± 0.02 eV, respectively. Grillot and Ringe [2] reported a defect in pure Germanium with an activation energy of 0.60 eV. The capture cross sections and trap concentrations of all traps were also determined. These findings, which provide a better understanding of the defects present in GeSiSn/Si multi quantum wells p-i-n structures, will further help to improve their performance in device applications.

p ⁺ -Si, 5*10 ¹⁸ cm ⁻³ 300nm, 450°C	p ⁺ -Si, 5*10 ¹⁸ cm ⁻³ 300nm, 450°C	p ⁺ -Si, 5*10 ¹⁸ cm ⁻³ 300nm, 450°C		
i-Si, 150nm, 450°C	i-Si, 150nm, 450°C	i-Si, 150nm, 450°C		
i-Si, 10nm, 450°C	i-Si, 10nm, 450°C	i-Si, 10nm, 450°C		
i-Ge _{0.3} Si _{0.6} Sn _{0.1} , 2nm, 150°C	i-Ge _{0.4} Si _{0.5} Sn _{0.1} , 2nm, 150°C	i-Ge _{0.5} Si _{0.4} Sn _{0.1} , 2nm, 150°C		
i-Si BL, 200nm, 700°C	i-Si BL, 200nm, 700°C	i-Si BL, 200nm, 700°C		
n ⁺ -Si(100) SEA-0.01	n ⁺ -Si(100) SEA-0.01	n ⁺ -Si(100) SEA-0.01		

Figure 1 Schematic diagram of the structure investigated

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Electrical Properties of In_{0.5}Ga_{0.5}P n-i-p solar cells grown by metal organic chemical vapor deposition using I-V, C-V and Deep level Transient Spectroscopy

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In this study, a detailed investigation was carried out on electrically active defects in In_{0.5}Ga_{0.5}P n-i-p solar cells structures (see Fig.1) grown by metal organic chemical vapor deposition (MOCVD) on p⁺⁺ GaAs substrates. Ohmic contacts were formed on the front and back of this structure by metallization process (see Fig.1). The effects of the growth temperature on the electrical properties of In_{0.5}Ga_{0.5}P n-i-p solar cells were investigated by using current -voltage (I-V), capacitance-voltage (C-V) and Deep level Transient Spectroscopy (DLTS) in the temperature range from 20-450 K. All samples showed at room temperature a low reverse current at a reverse bias of -4V, indicating that the devices are well-suited for DLTS and Laplace DLTS (LDLTS) experiments. The ideality factor and barrier height, obtained from I-V characteristics at room temperature, were found to be 1.89 and 0.84eV, and 2 and 0.84eV for samples grown at temperature 560°C and 590°C, respectively. The net free carrier concentration was calculated to be $\approx 9.23 \times 10^{17} cm^{-3}$ and 6.84 $\times 10^{17} cm^{-3}$ for samples grown at 560°C and 590°C, respectively. DLTS measurement showed one (0.11eV) and two (0.09eV and 0.14eV) traps for samples grown at 560°C and 590°C, respectively.



Fig. 1. (a) Schematic diagram of the layer structure of $In_{0.5}Ga_{0.5}P$ n-i-p solar cells grown by MOCVD at different growth temperatures and (b) Photograph of samples mounted on TO5 header.

Ga₂O₃ Schottky Photodiodes: Effects of Holes Trapping on Photosensitivity

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Due to a large bandgap close to 5 eV and the high crystalline quality, films and crystals of stable β-polytype of Ga₂O₃ are very promising for use in high-power electronics and in solarblind photodetectors operable in deep UV spectral range. In the latter case, the attraction is not only due to the high value of bandgap conducive to solar-blind operation, but also owing to the high external quantum efficiency EQE in the UV range often reported to be hundreds and even thousands percent and to high rejection ratio for visible light (see e.g. a recent review [1] quoting multiple original papers). The unusually high EQE observed by many researchers has been variously attributed to impact ionization in high electric field (see e.g. [2] among many other papers), to the contribution of self-trapped holes/polarons causing the modification of electric field of Schottky diodes under illumination [3] or to trapping of holes by deep acceptor states in the bandgap [4, 5]. In our earlier work [5] we have demonstrated that neutron irradiation of lightly doped HVPE Ga₂O₃ films leads to a very strong increase of photocurrent (Fig. 1(a)) and to a large enhancement of charge collection efficiency in electron beam induced current (EBIC) greatly exceeding the values expected based on the estimates of absorbed energy of the electron beam (Fig. 2(a)). We noticed that the enhancement of the photocurrent and of the EBIC collection efficiency could be tied to the increase of the deep acceptors concentration caused by exposure to neutrons. These changes in deep hole traps are reflected in variations of the space charge density under illumination causing changes in effective Schottky barrier height. It has been suggested that similar changes are to be expected for samples subjected to treatment in dense Ar plasma, creating high concentrations of deep hole and electron traps in the near surface region of the samples (~0.1 µm) [5] and in proton irradiated samples known to introduce such states. Indeed, we do observe strong increase in photosensitivity in UV spectral range in Ar plasma treated sample and in proton irradiated sample (Fig. 1(a)) that correlate with the observed changes in the density of deep acceptors determined from C-V profiling measurements with monochromatic illumination (Fig. 1(b)). The results of EBIC collection efficiency changes as a function of beam energy E_b and applied voltage are in agreement with the proposed mechanism. All measurements were performed on several pieces of HVPE samples cut from the same wafer and the data in Fig. 1, 2 are shown for the reference sample before irradiation, the sample treated in dense Ar plasma, the sample irradiated with the fluence of 4×10^{14} cm⁻² fast reactor neutrons and the sample irradiated with 10^{14} cm⁻² of 20 MeV protons. We also observe that the time of the EBIC signal build-up and decay are quite long (Fig. 2(b) shows the data for the Ar plasma treated, neutron irradiated and electron irradiated samples), in agreement with our previous measurements of photocurrent build-up and decay times [5]. These long time constants can be qualitatively explained based on the model discussed in [4] and taking into account electrons and holes trapping via tunneling and hopping via Poole-Frenkel current flow with subsequent recombination. These results seem to be opening a possible avenue of improving the photosensitivity of the Ga_2O_3 solar-blind photodetectors

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Diverse Electronic and Magnetic Properties of Semiconducting Silicene Nanoribbons Under Halogen Adsorption Effect

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Structural, electronic, and magnetic properties of halogen-adsorbed silicene nanoribbons (SiNRs) are investigated under the first-principles calculations. The halogen-diversified structural, electronic, and magnetic properties are fully identified through the developed physical quantities, including the formation energy, optimal lattice parameter, phonon spectrum, atom-dominated band structure, atom- and orbital-projected density of states (DOSs), charge density distribution, magnetic moment and spin density distribution. Halogen adatoms are optimally adsorbed at the top site of SiNRs among the valley, bridge, and hollow sites, regardless of their concentrations and distributions. For single adatom adsorptions, the directgap semiconducting behaviors become the p-type metallic behaviors. The metallicsemiconducting transitions of halogen-adsorbed armchair systems are occurred at the critical adatom concentrations of 50%. The largest band gap of 1.61 eV is found at the 100% adsoption system. The anti-ferromagnetic configuration of pristine zigzag system transforms into the ferromagnetic one in the single adatom-adsorbed zigzag systems. Especially, under the double adatom adsorptions, whether the anti-ferromagnetic configuration becomes ferromagnetic or nonmagnetic ones that strongly depends on the adatom distributions across the zizag edges. The ferromagnetic-nonmagnetic transition of the halogen-adsorbed zagzag systems is found at the critical concentration of 25%. The diverse properties of halogen-adsorbed silicene nanoribbons are very essential for applications in nanoelectronics and spintronics.

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Dislocations in GaN: the activation energy for the glide and dislocation–related luminescence

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Despite the fact that technologies of GaN films and crystals and GaN-based structures growth have reached considerable progress, dislocations in this material still have densities about 10^{6} - 10^{9} cm⁻², and in spite of great practical importance their properties have not been fully studied yet. In this work we present the results of studies the optical properties of both freshly introduced by plastic deformation (indentation and scratching) and grown-in dislocations in GaN, as well as the effects of low-energy electron beam irradiation (LEEBI).

A large set of GaN films and crystals with different conductivity types (HVPE n-GaN thick crystal, ELOG n-GaN film, MOCVD n-GaN and p-GaN thin films) were used in our studies. All investigated structures were grown in the <0001> direction. Deformation was carried out either by using a Vickers-type indenter in the temperature range from room temperature to 873 K or by scratching at room temperature. In both cases, the load was of 1 N. The cathodoluminescence (CL) studies and LEEBI were carried out in a scanning electron microscope JSM-6490 (Jeol) with the MonoCL-3 system in the temperature range from liquid nitrogen to room temperature. The electron beam energy both during irradiation and imaging was 10 keV.

It is known that dislocations in GaN can be introduced by plastic deformation at room temperature, and the emission at photon energy of 3.1 eV appears. In the literature, this line is most often associated either with complete screw dislocations or with dissociated screw dislocations. However, our studies have shown that this luminescence line is most likely associated with point defect complexes generated by gliding dislocations [1].

Since dislocations in GaN can move at room temperature, the question arises about the activation energy for the dislocation glide at low temperatures. Studies of the dislocation rosette size temperature dependence in GaN samples with n- and p-type conductivity in the temperature range from room temperature to 873 K allowed to estimate the activation energy for the dislocation glide for the first time. In n-GaN it is of about 720 \pm 160 meV, while in p-GaN it is about 450 \pm 100 meV [2, 3].

As shown [4], dislocations in GaN under LEEBI, i.e., under excess carrier injection conditions, demonstrate the recombination-enhanced dislocation glide (REDG) effect. A study of temperature dependence of REDG allowed to estimate the activation energy for this process as lower than 0.2 eV.

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Feature-Rich Electronic Properties of Germanene Nanoribbons Under Fluorine Doping Effect: A DFT Study

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The first-principles calculations are carried out to study the structural and electronic properties of fluorine-adsorbed germanene nanoribbons (GeNRs). Specifically, the featurerich properties are determined through the complete theoretical framework developed under the DFT calculations, including the binding energies, optimal lattice parameters, atomprojected band structures, orbital- and atom-projected density of states (DOSs), and charge density distributions. Fluorine (F) adatom favorably adsorbs at the top site of GeNRs, regardless of concentrations, edge structures, and distributions. The F adatom absorbs electron from GeNRs to leave free hole in the system due to its very strong electron affinity that can be regarded as the p-type doping. The F-doped systems belong to chemical adsorptions due to their large binding energies, resulting in very strong chemical bonding in F-Ge. Whether the π bonding is seriously distorted or terminated that directly determines the p-type metallic or semiconducting behaviors. Under the single F adatom adsorption, the pristine GeNRs become the p-type metal with high free hole density. The p-type metallic-semiconducting transition occurs at the critical concentration of 16.6% and the band gap further opens under higher concentrations. The greatest band gap is found at the 100% adatom adsorption. The featurerich electronic properties of GeNRs induced by F adatom doping effect are suitable for various applications in electronic devices.

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Thermal annealing of GaN implanted with Be

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The production of high-quality conductive *p*-type GaN by ion implantation remains a challenge. Currently, the only *p*-type dopant in GaN is Mg. However, relatively high ionization energy (0.22 eV) of the Mg_{Ga} acceptor requires high doping concentrations to achieve *p*-type conductivity suitable for practical applications. Recently, we showed that Be in GaN exhibits a shallow acceptor state at 113±5 meV above the valence band [1]. It is responsible for a photoluminescence (PL) band with a sharp peak at 3.38 eV, followed by a series of LO phonon replicas (labeled UVL_{Be}). The UVL_{Be} band is often observed in GaN layers grown by molecular beam epitaxy (MBE) and doped with Be. However, we are not aware of any work in which the UVL_{Be} band was observed in GaN after implantation with Be. The reason may include the low mobility of Be in GaN and the low fraction of Be substituting for Ga atoms [2,3]. This work demonstrates that activation of the Be_{Ga} acceptors in Be-implanted GaN can be successfully achieved by post-implantation annealing at high temperatures and high nitrogen pressure.

GaN layers grown by hydride vapor phase epitaxy (HVPE) on sapphire substrates and on ammonothermal GaN wafers were implanted with different doses and energies of Be⁺ ions. The samples were annealed at atmospheric nitrogen pressure at temperatures up to 1100 °C and alternatively at ultrahigh nitrogen pressure (1 GPa) and high temperatures (up to 1400 °C. The typical PL spectra for the two types of annealing are shown in Fig. 1. In samples annealed under nitrogen ppurge, the UVL_{Be} band could not be found, in agreement with the literature data. In many samples, the green luminescence band (GL2) with a maximum at 2.35 eV was detected (Fig. 1(a)). The band is attributed to the isolated nitrogen vacancy (V_N).

In contrast, the PL spectrum from samples annealed at ultrahigh nitrogen pressure contains the UVL_{Be} band with a maximum at 3.38 eV (Fig. 1(b)). These samples were implanted with higher Be doses and energy, which may explain the higher concentration of defects resulting in a lower intensity of the near-band-edge (NBE) emission. In addition to the UVL_{Be} band, the PL spectra from these samples contained an Mg-related UVL band (UVL_{Mg}) and a very broad redyellow band. By changing excitation intensity or temperature, a red band and a yellow band could be resolved with the maxima at about 1.8 eV and 2.2 eV, respectively. The shape and position of the yellow band are similar to those of the YL_{Be} band observed in Be-doped GaN grown by MBE [1].

Four samples were co-implanted with Be and N and annealed at ultra-high pressure and various temperatures [2]. The purpose of the implantation with nitrogen ions was to reduce the formation of the V_N . In this sample set, the V_N -related GL2 band was observed after annealing at 1250 and 1300 °C but not at higher temperatures. The UVL_{Be} band was observed in all GaN samples co-implanted with Be and N. The highest intensity of this band was achieved in a sample annealed at 1300 °C.

To the best of our knowledge, this is the first observation of the shallow Be acceptor state in GaN implanted with Be. Previously it was observed only in GaN doped with Be during growth. No electrical measurements have been conducted so far. However, the observation of the GL2 band indicates that the samples are semi-insulating. Further studies will be focused on exploring optimal implantation and annealing conditions to find a route for efficient p-type doping activation.



Fig. 1. PL spectra from GaN implanted with Be. (a) GaN implanted with Be⁺ (E = 40 keV, $\Phi = 10^{14} \text{ cm}^{-2}$) and annealed at 1100 °C in N₂ ambient. (b) GaN implanted with Be⁺ (E = 500 keV, $\Phi = 2 \times 10^{15} \text{ cm}^{-2}$) and annealed at 1400 °C and ultrahigh N₂ pressure.

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Investigation of MOCVD parameters correlation vs A^{III}B^V quality

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Investigation of the metalorganic chemical vapor deposition (MOCVD) parameters during growth process influence on several $A^{III}B^V$ material types quality (e.g. GaN films) is presented. For example nonpolar a-GaN films were grown on a r-sapphire substrate without ex-situ preparation. The process of high temperature nucleation in a combination with a low temperature GaN buffer layer growth was used to achieve a smooth morphology and "mirror" surface.

The macro defects structure was investigated by SEM and AFM. It was confirmed that macro defects were like V-defects. Using the wet etching, the defects internal structure was investigated.



Figure 1. SEM defects image

It was shown that, by analogy with semi-polar films, those defects were formed at the emergence areas inclined dislocations formed as nanotubes. Using X-ray diffractometer and 2θ - ω scanning it was detected, that there was a strong correlation between V-defects density and mixed threading dislocations (TDs) density. This correlation can be interpreted as a confirmation - the V-defects nucleation probability is higher for mixed TDs than for a pure edge dislocation.

According to the results, the mixed TDs density reduction is the main way to reduce a density of these defects. Achieved results show that higher growth temperature provides lower V-defects density. This result is explained by the V-defects formation mechanism kinetic, however, this result is reliable for a r-sapphire substrate without ex-situ preparation.

Segregation mechanism of arsenic dopants at Si grain boundaries

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Arsenic (As) atoms are important *n*-type dopants in silicon (Si) due to their excellent physical properties suitable for Si nano-devices, such as high solubility and low diffusivity. However, they preferentially segregate at defects such as grain boundaries (GBs) rather than distribute homogeneously in grains, and this nature induces a fluctuation in spatial distribution of dopant atoms affecting the reliability and performance of electronic devices with poly-Si, especially in nano-devices. In the last decade, As segregation at GBs is experimentally examined at an atomistic level by using atom probe tomography (APT), scanning transmission electron microscopy (STEM), etc. These experimental data are, however, obtained from the GBs of which the GB character is unknown, in polycrystalline-Si nano-devices that are irradiated with As ions and then annealed at high temperatures. The segregation mechanism is, therefore, still uncertain because the diffusion and interaction of As atoms would depend on the GB structure and defects in the irradiated materials. Even though some mechanisms of As segregation at the typical GBs are theoretically proposed, they are not fully validated.

In this work, we have systematically examined, by correlative analytical methods using APT combined with low-temperature focused ion beam (LT-FIB) and STEM, the segregation ability of four kinds of <1-10> tilt GBs; i.e., $\Sigma3\{111\}$ and $\Sigma9\{221\}$ GBs as the typical GBs free from dangling bonds, and $\Sigma9\{114\}$ and $\Sigma9\{111\}/\{115\}$ GBs with the stretched <1-10> bonds that would contain small amount of dangling bonds. The preferential segregation sites and the segregation mechanism are discussed with an assistance of *ab initio* calculations.

 Σ 3{111} GBs, consisting of only 6-membered rings with small bond distortions, do not exhibit an apparent As segregation, while As atoms segregate at the other GBs (Fig. 1). Ab initio calculations for $\Sigma9{221}$ GBs show preferential As segregation at 5-membered rings in the GBs, via anisotropic bond distortions spontaneously introduced so as to lower the donor level, as Jahn-Teller distortions (Fig. 2). Due to this electronic effects, As atoms inducing compressive strains in Si would segregate at the lattice sites under compressive strains, unlike the GB segregation of neutral impurities, such as oxygen, due to elastic interactions that can reduce local strains [1]. Meanwhile, high segregation abilities for $\Sigma9\{114\}$ and $\Sigma9\{111\}/\{115\}$ GBs are not explained only with the anisotropic bond distortion model. APT combined with LT-FIB, that can suppress the compositional modification by FIB processing [2], for $\Sigma 9$ {114} GBs suggests preferential As segregation around stretched $\langle 1\overline{1}0 \rangle$ bonds (Fig. 3), that are not introduced in Σ 3{111} and Σ 9{221} GBs but are inevitably introduced in the $\langle 1\overline{1}0 \rangle$ tilt GBs with the tilt angle larger than 70.5°. Ab initio calculations suggest that As atoms would form As dimers around the stretched bonds, due to the tendency of As with five valence electrons to form a 3-coordinated configuration attained by As dimers. GB segregation of As dopants is, therefore, determined by electronic interactions depending on the characteristics of valence electrons of As atoms as well as on local bond distortions at GBs, via anisotropic bond distortions and dimerization, and the hypothesis is also consistent with the segregation models calculated for different GBs [3, 4].

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Fig. 1 APT As maps for (a) $\Sigma 3\{111\}$, (b) $\Sigma 9\{221\}$, (c) $\Sigma 9\{114\}$, (d) $\Sigma 9\{111\}/\{115\}$ GBs viewed along the GB plane. The inset in each figure shows the As concentration profile across the GB plane. (e) Number of As atoms at GBs Γ_{As} vs. the GB energy γ_{GB} .



Fig. 2 (a) Supercell for $\Sigma 9\{221\}$ GBs viewed along $\langle 1\overline{1}0 \rangle$ (3.27 × 1.16 × 1.52 nm³). The sites for potential As segregation are marked out with numbers. (b) the segregation energy γ_{seg} vs. the distance from the GB plane. (c) PDOS for As atoms at the sites 6, 8, and 15 around the Fermi energy E_{F} .



Fig. 3 (a) As concentration profiles across a $\Sigma9\{114\}$ GB obtained with APT specimens fabricated by (a) LT-FIB and (b) conventional FIB operated at room temperature, overlaid on the corresponding HAADF-STEM image of the GB.

Mg related charge transitions in Ga₂O₃ as studied by photo-induced electron paramagnetic resonance

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Gallium oxide is a wide bandgap (4.6-4.9 eV) semiconductor that has potential for power electronics. Doping Ga₂O₃ with Mg produces semi-insulating material, which can be an integral part of power devices. For such applications, knowledge of the Mg-related charge transitions is essential. Density functional theory (DFT) calculations predict a Mg acceptor level (Mg^{-/0}) between 1.2 and 1.6 eV above the valence band maximum (VBM) whereas thermal measurements using electron paramagnetic resonance (EPR) place the level ~0.65 eV above VBM [1-3]. To address the disagreement between the reported defect levels, we investigate optical absorption of neutral Mg acceptors (Mg⁰) using photoinduced EPR (photo-EPR). In this work, two Mg-doped β -Ga₂O₃ crystals S1 and S2, which were grown by the Czochralski method at two different institutions, are investigated. The samples contain (2-4) x 10¹⁸ cm⁻³ Mg and 5 x10¹⁷ cm⁻³ unintentional Ir. In addition, the samples contain unintentional impurities such as Fe, Si, and Cr, concentrations of which in S1 (~10¹⁶-10¹⁷ cm⁻³) are higher by an order of magnitude than in S2. The crystals are irradiated with energies between 0.6 and 4.7 eV after Mg⁰ is generated with an LED (4.4±0.2 eV), and the effect on the amount of Mg⁰ is investigated at 130 K.

Figure 1 shows steady-state EPR spectra for Mg⁰ in sample S1 with magnetic field along the a-axis, obtained before any illumination (black), and during illumination at 4.4 eV (red) and 3.6 eV (blue) for 20 min. The steady-state EPR results (Fig. 2) show that the amount of Mg⁰ starts to decrease near 1.5 eV, and the decrease becomes smaller above 3 eV. The 1.5 eV photo-threshold is consistent with theoretically predicted Mg^{-/0} level [1, 2]. Since no other defects such as Fe³⁺ and Ir⁴⁺ have changes that correlate with the Mg⁰ changes, we suggest the decrease in the amount of Mg⁰ occurs as a result of excitation of electrons from the valence band to Mg⁰, thereby changing Mg⁰ to Mg⁻. The decrease in the quenching of Mg⁰ above 3 eV in Figure 2 suggests onset of excitation, which is confirmed by observation of Mg⁰ with photon energy as low as 3 eV as shown in Figure 3. For photoexcitation, hole capture is the only viable process due to polaronic nature of Mg⁰ in Ga₂O₃ [1]. Additional measurements demonstrate that electron excitation to impurities, such as Fe and Ir, does not contribute to creation of the holes. Further, gallium vacancies likely do not participate since their characteristic EPR spectrum is never seen. For these reasons, we speculate that the defects responsible for the hole formation and consequent excitation of the neutral Mg are oxygen vacancies.

In summary, our experimental observations demonstrate that there are two charge transitions related to Mg in the bandgap of Ga₂O₃. One occurs near 1.5 eV for photo-quenching and the other near 3 eV for photoexcitation of Mg⁰. Although the 1.5 eV photo-quenching threshold is in reasonable agreement with the predicted Mg^{-/0} level, incorporation of the relaxation energy into the analysis of the experimentally determined optical cross section spectrum is needed to conclusively determine the defect level. Initial time-dependent photo-EPR data obtained from sample S1 has been analyzed using an approach similar to the one we used earlier to successfully determine the Fe^{2+/3+} level in Ga₂O₃ [4]. Preliminary results for the optical cross

section spectrum for Mg^0 suggest that the $Mg^{-/0}$ defect level lies >1 eV above VBM, consistent with the theoretically predicted values. In the talk, we will discuss the optical cross section spectrum for Mg^0 obtained from multiple data sets and resolve the conflicting values presently available for the $Mg^{-/0}$ defect level.

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Figure 1. Steady-state EPR spectra of Mg^0 in sample S1, taken at 130 K in this order: before any illumination in dark (black), and during illumination at 4.4 eV (red) and 3.6 eV (blue). Magnetic field is along the a-axis.



Figure 2. Steady-state photo-EPR for quenching of Mg^0 in sample S1 (triangles) and S2 (circles). The data plotted at '0 eV' were taken during illumination with the 4.4 eV-LED.



Figure 3. Steady-state photo-EPR for excitation of Mg^0 in sample S1. In this measurement, the sample was not exposed to the 4.4 eV LED prior to illumination at the photon energy shown here.

A Study on the vdW Semiconductor with Ferroelectric Polymer

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The neuromorphic computing has been considered that can overcome the limitation of von Neumann-based computing systems with its characteristics of parallel computing capability. From an energy efficiency point of view at the neuromorphic system, many candidates for synaptic devices have been suggested such as phase-change memory, resistive change memory, conductive bridge memory, and ferroelectric memory. However, it is still challenging to implement low power neuromorphic system with these emerging memories since more switching power reduction should be realized for parallel array application. The ferroelectric device is one of the promising candidates for synaptic devices due to its low power and fast switching characteristics. In this work, we investigated the ferroelectric synaptic device based on ferroelectric field effect transistor (FeFET) structure using polyvinylidenefluoridetrifluoroethylene (P(VDF-TrFE)) copolymer and tungsten diselenide (WSe₂). We fabricated FeFETs with respect to various PVDF weight percents, PVDF / TrFE composition ratio, and thickness of the ferroelectric polymer. Each sample's ferroelectric characteristics e.g. coercive field, remnant polarization, and hysteresis were evaluated. Additionally, the synaptic plasticity characteristics such as long-term potentiation and long-term depression (LTP/LTD), and spiketiming-dependent plasticity (STDP) were thoroughly examined with each FeFETs. With these efforts, we could analyze the relation between ferroelectric switching properties and synaptic plasticity characteristics.

A Study on the Spin Coating Process Optimization

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The spin coating process is the method to make a thin film having a uniform thickness. In the semiconductor industry, the spin coating is mostly conducted for the photo-resist coating to be used as masking film during the photolithography process. It proceeds as a wafer is placed on the rotating chuck and then the photo-resist is deposited on the center area of the wafer and the photo-resist spreads out to the edge side of the wafer and forms a thin film. It is important to understand the impact of each control factor on the thickness and uniformity of the photo-resist to achieve predictable and reproducible photo-resist thickness. In this paper, we investigated the thickness variation phenomenon with respect to the viscosity of the photo-resist on each wafer position using computational fluid dynamics simulation. In addition, we conducted experiments on the real wafers reflecting the simulation results and evaluating the optimum condition to reduce the thickness variation.

Conversion pathways of primary defects by annealing in proton-irradiated *n*-type 4*H*-SiC

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Silicon carbide (SiC) is a technologically important semiconductor, attracting growing interest for different device applications, most notably high-power electronics and quantum technologies (QT). For these applications, targeted control over point defect formation is crucial: deep level defects can act as recombination centers, such as the prominent carbon vacancy (V_C) in 4H-SiC that is known to be a minority lifetime killer defect. Other intrinsic defects such as the silicon vacancy (V_{Si}^{0}) and the divacancy $(V_{Si}V_{C}^{0})$ have been shown to be promising for QT applications because of their single photon emission characteristics [1] and long electron spin coherence times [2]. It was also shown recently that the charge state of the V_{Si} can be controlled by embedding defect populations in the electric field of a Schottky barrier diode, allowing the switching of light emission intensity from V_{si} by applying a voltage [3]. To exploit point defects for QT devices, targeted introduction of defect states into the material is key. This is usually achieved by ion or electron irradiation or implantation, creating a variety of defects independent of their thermodynamic equilibrium formation energies. Thermal posttreatment of irradiated or implanted samples is often employed to alleviate most of the introduced damage. In the present work, we monitor the pathways by which point defects in irradiated 4H-SiC anneal out, or convert into other defects, during such thermal treatments.

In this study [4], we used *n*-type 4*H*-SiC epilayers irradiated with 1.8 MeV protons to explore thermal interconversion pathways in a multi-stage annealing experiment, employing a combination of deep level transient spectroscopy (DLTS) and photoluminescence spectroscopy



Figure 1: DLTS spectra obtained in the pre-diffusion stage from samples irradiated to three fluences. Inset: high-resolution spectra of the EH₄ and EH₅ levels, demonstrating a substructure in the former.

(PL) for defect detection and identification. We used a large range of proton fluences between 1.10¹¹ cm^{-2} and $6 \cdot 10^{13}$ cm^{-2} , enabling measurements on samples with defect concentrations in the dilute regime (*n*-type) as well as heavily compensated (intrinsic) ones. This approach enabled us to map out defect conversion and annealing pathways that are activated or blocked for various positions of the Fermi level. The annealing was carried out in accumulative steps in a tube furnace in N₂ flow at 300 °C ("pre-diffusion"), 400 °C, 600 °C, 800 °C and 1000 °C for 30 minutes. An initial assessment of the defect

An initial assessment of the defect population, i.e. in the pre-diffusion

stage, showed that the four main intrinsic defects that can be directly detected by either method are the V_C, V_{Si}, the carbon antisite-vacancy pair (C_{Si}V_C, or CAV), and the divacancy (V_{Si}V_C, or VV). The known PL emission lines for the CAV, V_{Si} and VV defects (AB, V, and PL4 lines) were used for identification. DLTS defect signatures attributed to V_{Si} and V_C are known (see Figure 1), namely the S₁ and S₂ (for V_{Si} [3]) and the Z_{1/2} and EH_{6/7} levels (for V_C [5]). Furthermore, we have made the tentative, but as we show well-supported, assignment of the frequently found EH₄ and EH₅ levels to the (+/0) charge transition level of the four different configurations of the CAV. Based on these assignments, we have constructed a defect interconversion model (see Figure 2) that takes into account both the annealing temperature and the initial position of the Fermi level.



Figure 2: Illustration of the proposed defect interconversion model. Color gradients encode concentration of the defects produced by the reactions (darker = higher concentration).

At annealing temperatures up to 300 °C, closely spaced pairs of Si and C vacancies and interstitials $(V_C(Si/C)_i)$ and $V_{Si}(Si/C)_i$) either annihilate or electrically form inactive antisite defects [6,7] (C_{Si}, Sic) easily in both *n*-type and compensated material. Increasing the temperature leads to continued recombination of non-nearest neighbor vacancy interstitial pairs in *n*-type but not in compensated material, because long-range interstitial diffusion is severely hampered in the by increasingly latter an

positive charge state of the defects [8]. The next annealing stage is a dissociation of CAV into individual V_C and C_{Si} defects – a process formerly unrecognized as a conversion channel for CAV that is triggered at lower annealing temperatures for compensated samples. At even higher temperatures, conversion of V_{Si} to CAV occurs in the compensated samples while this route is blocked in *n*-type material due to charge state mismatch and high associated defect migration barriers. For the highest annealing temperatures, the formation of VV via the diffusion of V_{Si} and binding to V_C is observed.

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SYNTHESIS AND ELECTRICAL CHARACTERIZATION OF GaN GROWN BY ELECTROCHEMICAL DEPOSITION

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ABSTRACT

The III-Nitride semiconductor materials are wide bandgap materials and can be crystalline as structure of wurtzite and zinc blende types. Wurtzite InN, GaN and AlN have direct band gap 1.9 eV, 3.4 eV and 6.2 eV, respectively [1]. GaN is an extremely promising material for the blue and white light emitting diodes LEDs, leaser and detectors [2].

In this study GaN thin films were deposited on Si (111) substrates at room temperature using an electrochemical technique. The deposition was done by placing the Si substrate in a solution of $Ga(NO_3)_3$ and NH_4NO_3 in deionized water at room temperature and applying a current density of 1 mA/cm². Good quality of Schottky diode were fabricated on the GaN thin films, with *IV* barrier height of 0.68 eV and *CV* barrier heights of 0.97 eV for GaN deposited using 1 mA/cm² current density. Deep-level transient spectroscopy measurements were performed see Fig. 1, and electron traps with activation energy of 0.47 eV and 0.29 eV were observed in GaN thin film grown by the electrochemical deposition technique. More detailed explanation for GaN will be discussed and related with structural and morphological of sample using the X-ray diffraction, scanning electron micorscopy.



Fig. 1 DLTS signal for Au/Ni/GaN/Al Schottky diode at reverse bias -2 V and pulse bias 0 V from 50 K -350 K.

Keywords: GaN, electrochemical deposition, Schottky diodes, DLTS, characterization.

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Edge and screw threading dislocations in heteroepitaxial GaN layers

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A major problem in heteroepitaxial layers is related to the strain relaxation processes mainly induced by the lattice mismatch at the interface between layer and substrate. In the strain engineering context, a quantitative analysis of the emerged structural defects, as well as a deeper understanding of their nature became highly desirable tasks for further development of the devices.

In this study, structural investigations of the mismatched gallium nitride (GaN) layers grown on SiC, Al₂O₃ and Si substrates, were performed using X-ray reciprocal space maps (RSMs) and rocking curves on symmetric and asymmetric reflections. The results are completed by grazing incidence X-ray diffraction investigations which allowed us to obtain the X-ray absorption profiles, that reflect the sample absorption and the presence of dislocations. In Figure 1 are shown symmetric RSMs on (0002), which allowed us to get the lattice mismatch, lateral correlation length, mosaicity, tilt and twist. The resulted threading dislocation density evolved from the lattice mismatch was quantified in two independent ways: firstly, using the mosaic block model[1], which takes into account peak width and, secondly, using the diffuse scattering model[2], which consider only the tails of the rocking curves. Both models indicated the close relationship between the dislocation density and the lattice mismatch, that plays a fundamental role in TDs' generation. It is well-known that the lattice mismatch leads to a considerable elastic energy in layer, which further releases via dislocation formation [3,4]. To gain further insights regarding threading dislocations, grazing incidence x-ray diffraction was employed to obtain the absorption profiles of the x-rays[5], which can provide supplementary information concerning the distribution of threading dislocations along z-axis, as well as about the annihilation mechanisms between adjacent dislocations. Although these profiles encompass the contributions of both sample absorption and dislocations, we decoupled these two effects in the framework of the dynamical theory of diffraction, showing that the existence of dislocations governs different power law dependencies for the experimental absorption profiles. Further, pole figures also indicate a broadening of the spots corresponding to both GaN (0002) and (10-11) GaN. In addition, photoluminescence peaks found at 3.41 eV, 3.39 eV and 3.35 eV correspond to near band-edge (NBE) and ultraviolet donor-acceptor pair (DAP) transition. Significant changes of their intensity ratio, as well as the additional broadening of E2 (high) Raman peak confirm the presence of TDs in the investigated GaN thin films.





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Impact of growth conditions on the optoelectronics applications of CH₃NH₃PbI₃, studied by low-energy μSR

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Perovskite-based solar cells and light-emitting diodes (LEDs) fabricated with simple solution methods have achieved unprecedented breakthroughs with performance skyrocketed to the level of single-crystalline devices within a decade. As of writing, a certified power conversion efficiency of 25.5% and an external quantum efficiency of over 20% have been achieved for perovskite solar cells and LEDs, respectively, [1-5]. However, to fully exploit the potential of metal halide perovskites, several important challenges must be overcome. Given the nature of the materials—relatively soft ionic solids—one of these challenges is the understanding and control of their defect structures. It is shown that the defects formed under different film growth conditions, such as the precursor ratio, annealing temperature, and annealing time impact the properties and operational stability of metal halide perovskite optoelectronic devices. Well-controlled processing can effectively improve the interfaces and reduce harmful internal defects, [6, 7].

The effectiveness of low-energy µSR has been proven in studying the interfaces and defects in semiconductors and thin-film solar cells, [8-11]. It can give the depth distribution of defects in the films. The implanted muons in those materials can capture an electron to form the paramagnetic, hydrogen-like neutral muonium state. When defects exist in the films, the implanted muons prefer to stop at the defect sites, which results in an increase of the diamagnetic fraction, [9]. In this study, µSR measurements of MAPbI₃ films with different precursor ratios were carried out at the low-energy muon beam facility (LEM) at PSI. We found that there is much more muonium formation in the MAPbI₃ film (i.e. less defects) when the precursor ratio of MAI: PbI₂ is 1.05:1, compared to a film with precursor ratio MAI: PbI₂ of 1.0:1. This is because MAI will volatilize during the annealing process and produce Schottky defects (anion and cation vacancies occurring together). The excess MAI in the precursor solution can compensate for this loss. Dae-Yong Son et al. have studied the influence of excess MAI, which shows that 6 mol% excess MAI can suppress non-radiative recombination and improve hole and electron extraction at the grain boundaries, which results in a better power conversion efficiency, [12]. Qi Chen et al. think that excess PbI₂ also plays a positive role in the perovskite film in solar cell devices [13]. To clarify the fundamental defect chemistry in the metal halide perovskites for low-cost and efficient optoelectronic applications, MAPbI₃ films with five precursor ratios of MAI: PbI₂ which are 1.1:1, 1.05:1, 1.0:1, 0.95:1, and 0.9:1 will be studied as a next step by low-energy µSR at PSI. The annealing temperature which determines the mass transfer including Ostwald ripening and MAI vaporization during film growth is another important factor causing non-stoichiometry and defect formation in MAPbI₃ films. Weina Peng et al. point out that the dominant defect states are from bulk trap states within the high growth temperature, which will deteriorate the optoelectronic properties of perovskites, [14]. We plan to carry out three growth temperatures which are 80, 100, and 120 °C with a precursor ratio of MAI: PbI_2 is 1.0:1. At the same time, we will fabricate LED and solar cell devices to find out the defect influence on the optoelectronic performance. In this way, one can correlate the muonium formation probability at various implantation energies with the growth conditions, i.e., the distribution of defects with unprecedented depth resolution, to improve the optoelectronic performance of the perovskite devices.

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Interstitial and substitutional nitrogen in silicon crystal studied by infrared absorption spectroscopy of multiple peaks

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Nitrogen doping is the basic technique to suppress microdefects in bulk silicon crystal. We have found 551 [1] and 726 and 778 cm⁻¹ [2] infrared absorption bands in the electron irradiated nitrogen doped FZ silicon crystal, and 689 cm⁻¹ band [3] after post annealing. The 726 and 778 cm⁻¹ bands accompanied the loss of <u>766 and 963 cm⁻¹ NN (SiN_iSiN_i four member ring)</u> absorption bands [1], and the 689 cm⁻¹ band with the loss of the 726 and 778 cm⁻¹ bands [3], respectively. We assigned the <u>726 and 778 cm⁻¹</u> bands as <u>VNN (N_i-N_i on vacancy)</u> originated [3]. They were observed later by the similar study on electron irradiation of CZ Si and the assignment was supported [4]. The 551 and 689 cm⁻¹ absorption bands have been observed in the ion implanted and laser annealed sample, the latter being after post furnace annealing [5]. The most reliable assignment of them was given by the theoretical analysis to be N_i and VN_s [6]. However, mainly due to that the <u>689 cm⁻¹</u> band appeared with the loss of VNN absorption, we assigned it as <u>VVNN (VNVN, a pair of VN_s facing with each other</u>) [3, 7, 8]. We observed the 551 [3] and 689 cm⁻¹ absorption bands in as-grown crystals also. Here we examined them in detail.

Samples were several groups of as-grown CZ and FZ silicon crystals of 2mm thickness with mirror polished surfaces. Infrared absorption measurement was done at room temperature with wavenumber resolution of 2 cm⁻¹. More than 1000 scans were employed to improve the S/N. The smallest peak absorbance resolvable was about $1x10^{-5}$ which roughly corresponds to the complex concentration of $1x10^{13}$ /cm³. To determine the peak wavenumber and width, fitting of Lorentzian function was employed. Electron irradiation dose was $1x10^{17}$ /cm².

<u>Ni</u>: <u>551cm⁻¹</u> absorption band was observed in all as-grown CZ and FZ crystals. The relation between the peak absorption coefficient of 551 cm⁻¹ band and that of 766 cm⁻¹ band in as-grown FZ silicon is shown in Fig. 1(a). The peak of 551 cm⁻¹ band is about 1/3 and proportional to that of 766 cm⁻¹ band from NN.





between the peak absorption coefficient of 551 and 689 cm⁻¹ band with 766 cm⁻¹ band. (b) Spectra around 551 cm⁻¹ after annealing at various temperatures for several hours. 10 mm thick. (c) Annealing temperature dependence of absorbance of 4 peaks.

<u>Ni-Oi</u>: Fig. 1(b) shows the spectra around 551 cm⁻¹ after the annealing of CZ Si. There is a peak at <u>552 cm⁻¹</u> also and the peak moves between 551 and 552 cm⁻¹ for different annealing temperatures. Moreover, there is another pair of absorption band at <u>556 and 557 cm⁻¹</u>, and more weakly band at <u>544 and 559 cm⁻¹</u>. We took care that the 551 cm⁻¹ band was broad to the higher wavenumber side (for example Fig. 3 in ref. 8). Here, it was revealed to be due to the peak at 552 cm⁻¹. Fig. 1(c) shows the annealing temperature dependence of the peak height. The <u>551</u>, <u>552 cm⁻¹ pair</u> is big under 450 °C and above 800 °C, whereas the 556, 557 cm⁻¹ pair is big between 450 and 800 °C. This is similar to the well-known change between NN and NN-O_{1,2} bands. That is the attach and detach of O_n to NN. Therefore, similar N_i + O_{ni} \rightarrow N_i- (Si-) O_{ni}

may take place. N_i - O_{ni} was theoretically examined to have a deep donor level [9Ewels96]. We attribute the 556 and 557 cm⁻¹ absorption to N_i - O_i here. The relative size of the peak in the pair changes among the samples. The origin of pair bands is unknown yet.

<u>VNs</u>: Fig. 2(a) shows the spectra around 689 cm⁻¹ of as-grown FZ crystals. Absorption band was observed at <u>688 cm⁻¹</u>, not 689 cm⁻¹ that was observed after irradiation and annealing. It was not observed in CZ silicon. Its absorbance was about 1/5 of that of 551 cm⁻¹ band as shown in Fig. 1(a). The 688 cm⁻¹ band accompanies the neighboring bands, like the 551 cm⁻¹ band does, at <u>677</u> cm⁻¹ and more weakly at <u>684 and 695</u> cm⁻¹. Fig. 2(b) shows the spectra after irradiation and annealing, using the as-grown sample as the reference. After the irradiation, no peak was observed, showing that the 688 cm⁻¹ band in as-grown sample did not change by the irradiation. After 200 °C annealing, the absorbance at 688 cm⁻¹ increased a little. After 400 °C annealing the spectrum extended to the higher wavenumber side.

<u>VVNN</u>: To examine in more detail, the Lorentzian function at 688.0 cm⁻¹ (FWHM 5.0 cm⁻¹) was fitted and subtracted. The residual is shown by the broken lines in Fig. 2(b). Small absorption band with the peak at about <u>690 cm⁻¹</u> appeared at 400 °C. It is likely that this band is purely from VVNN, whose calculated peak was 6 cm⁻¹ higher than that of VN_s [6]. We took care that the 689 cm⁻¹ band was wide [8]. Here it was revealed to be due to that the 689 cm⁻¹ band is the mix of 688 and 690 cm⁻¹ bands. This suggests that a part of VNN and NN changed into both VN_s and VVNN. At 600 and 800 °C, small amount of VN_s and VVNN were formed, while most VNN returned to NN as was already

shown [2].

Fig. 2 Differential absorption spectra of (a) as-grown FZ samples, and (b) irradiated and annealed samples (reference: asgrown).





The absorbance of N complexes is summarized in the Table. There are 4 kinds of N complexes in as-grown Si crystal, NN- O_n rings, N_i, NO- O_n rings (shallow thermal donor, STD, in CZ, reported in the separate paper [10]) and VN_s (in FZ). By the annealing of CZ Si, N_i changes to N_i- O_n . By the irradiation of FZ Si, a part of NN forms VNN and N_i changes. By the post annealing, a part of

Tab. Peak absorption coefficient of N complexes in silicon crystal (cm-1). Wavenumber calculation in '90 and '00 is shown. NO ring in CZ Si (STD) [12] is not shown.

		cm−1	cal90	cal00	as-gr	as-irr.	400oC	
NiNi	CZ,FZ	763	769	773	0.184	-0.0104	-0.0150	
VNs	FZ	688	-	663	0.012	+0	+0.0104	
VNN	FZ	778	-	774	0.000	0.0092	0.0023	
VVNN	FZ	690	-	669	0.000	0.0000	0.0023	
Ni	CZ,FZ	551	700	550	0.070	-	-0.0069	
Ni-Oi	CZ	556		-	-	-	0.029	

and N_i changes. By the post annealing, a part of N_i forms VNs, while NN and VNN form VVNN. STD absorption at 855 cm⁻¹ ([11], ONO double ring [12]) has multiple peaks also.

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Defect-annealing in Si⁺-implanted β-Ga₂O₃

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Gallium oxide (Ga₂O₃) has potential applications as a transparent conducting oxide or in UV detectors and high voltage diodes, and has become a material of high technological relevance and scientific importance. Under ambient conditions, β -Ga₂O₃ is the most stable polytype, with a monoclinic crystal structure. The bandgap of β -Ga₂O₃ is approximately 4.7 eV [1]. High quality β -Ga₂O₃ bulk crystals can be fabricated through e.g. edge-defined film-fed growth (EFG) or Czochralski growth. Moreover, several dopant species can act as shallow donors in β -Ga₂O₃, e.g. Si and Sn, of which the former is also a dominant background impurity in β -Ga₂O₃ [2]. Tuning of the β -Ga₂O₃ conductivity over three orders of magnitude by Si-doping has been demonstrated [3]. For device fabrication, implantation of these donors is essential, and has been demonstrated [4]. However, controlling charge carrier concentration profiles by ion implantation remains a major challenge for Ga₂O₃-based devices. This includes both dopant activation in the desired atomic configuration and control of ion-induced damage. Improved knowledge of defect annealing is therefore indispensable for improving β -Ga₂O₃ device fabrication.

An EFG-grown bulk ($\overline{2}01$) β -Ga₂O₃ wafer was laser cut into 5x5 mm samples, and the samples were implanted with 300 keV Si⁺-ions to doses of 1×10^{14} , 1×10^{15} , 1×10^{16} and 2×10^{16} cm⁻² in an NEC Tandem Accelerator. Following implantation, an isochronal (30 minutes) heat-treatment series was applied sequentially to the implanted samples under ambient atmosphere in a Gero tube furnace. The annealing temperatures used were 300, 500, 700, 900 and 1000 °C. The samples were characterized using channeling-mode Rutherford Backscattering Spectroscopy (c-RBS) and X-ray diffraction (XRD) after implantation and after each heat-treatment step.

c-RBS data for all samples after each heat treatment step are shown in Figure 1. The sample with implantation dose 1×10^{14} cm⁻² showed defect levels comparable to the as-grown sample after annealing at 700 °C, with significant reduction of disorder after annealing at 300 °C. The as-implanted damage levels were higher in the sample implanted with dose 1×10^{15} cm⁻². In the near-surface region, defect anneling of this sample began at approximately 500-700 °C, but a high dechanneling level behind the damage peak persisted even after annealing at 1000 °C. The damage levels were even higher in the final two samples (1×10^{16} and 2×10^{16} cm⁻²), with minor or no changes even after annealing at 1000 °C. However, the height of the c-RBS spectra in the implanted region did not reach the random level, indicating that there was no complete amorphization. For the highest implantation doses, a slight increase in damage near the sample surface was seen after annealing at 300 °C, reducing back to as-implanted levels after annealing at 500-700 °C. Due to large mass difference, only damage in the Ga sublattice could be analyzed from the c-RBS data.

XRD diffractograms did not show formation of new phases for any of the implantation doses or heat treatment temperatures. For all implantation doses, the major diffraction peak around 59 degrees 2 θ , the ($\overline{6}03$)-reflex, displayed a secondary peak or shoulder at smaller angles. Generally, this feature was reduced as the annealing temperature was increased. This feature may be due to a local increase in tensile strain from implantation-induced defects. Increased annealing temperature yielded higher diffraction peak intensity and reduced diffraction peak asymmetry. Figure 2 shows diffractograms around 59 degrees 2 θ for the highest and lowest implantation doses.



Figure 1: c-RBS spectra for each implantation dose after each heat-treatment step. (a): 1×10^{14} cm⁻², (b): 1×10^{15} cm⁻², (c): 1×10^{16} cm⁻², (d): 2×10^{16} cm⁻². Ga depth scale given on top.



Figure 2: XRD 2 θ spectra around the ($\overline{6}03$)-diffraction peak for implantation dose 1×10^{14} cm⁻², (**a**), and 2×10^{16} cm⁻², (**b**).

This work shows that required temperatures for defect annealing of Si⁺-implanted Ga₂O₃ is highly dependent on implantation dose. After annealing at 900 °C, the defect concentration observed by RBS returned to values close to those of the as-grown state for the lowest implantation dose, whereas minor or no change was observed for the highest dose even after annealing at 1000 °C. In the presentation, we will also discuss the defect evolution at higher temperatures, and compare with the disorder observed by transmission electron microscopy.

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Deep levels at native defects and impurities in cesium lead bromide

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Lead halide perovskites such as CsPbBr₃ have achieved widespread attention as optoelectronic materials, due in large part to their good performance despite significant defect densities. [1,2] This "defect tolerance" has often been explained by hypothesizing that there is negligible trap-assisted non-radiative recombination in these materials because none of the dominant defects give rise to deep levels in the gap. [3,4] We refer to this as the "shallow defect hypothesis" (SDH). The SDH remains controversial, with mounting experimental [5,6] and theoretical [7,8,9] evidence suggesting deep levels are present in the lead halide perovskites and may contribute to non-radiative recombination.

In this work, [9] we reject the shallow defect hypothesis for CsPbBr₃. Via a thorough firstprinciples inventory of native defects and hydrogen impurities, we show that a number of relevant defects do in fact have deep levels, most notably the bromine interstitial and hydrogen interstitial. This adds to a growing body of evidence against the shallow defect hypothesis, suggesting that the observed defect tolerance may be due instead to relatively low recombination rates at deep levels. Guided by the theoretical identification of these defects, experiments can take steps to mitigate trap-assisted non-radiative recombination, further boosting the efficiency of lead halide perovskite optoelectronics.



In addition to minimizing loss mechanisms, optimizing CsPbBr₃-based optoelectronics requires an understanding of impurity and dopant behavior so that carrier densities can be maximized. We will also discuss our latest results in understanding the role of common impurities and dopants.

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Origin of the external quantum efficiency reduction in InGaP/InAlGaP micro light emitting diodes

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The emergence of new applications in the field of micro-displays, like for instance augmented and virtual reality, automotive or wearable devices, drives the development of micro-light emitting diodes (μ LEDs). Micro-displays built with inorganic LEDs have many merits such as brightness, low power consumption, a short response time, high stability and long life, compared to those using others technologies [1]. InAlGaP lattice matched to GaAs is suited for LEDs operating in the red, orange, yellow, and yellow–green wavelength range [2]. However, the reduction of the pixel size leads to a decrease of the external quantum efficiency (EQE), possibly explained by carrier losses at sidewall defects [3-5].

The epitaxial of InGaP/InAlGaP μ LEDs was grown by metalorganic chemical vapor deposition on lattice matched GaAs substrate. The unintentionally doped active region is formed by five multi-quantum wells (MQWs) of InGaP, which are separated and surrounded by InAlGaP barriers. This active region is sandwiched between n-type and p-type doped bilayers of InAlGaP/GaAs located on the top and the bottom, respectively (Figure 1). The epitaxy is then processed by BCl₃/Ar reactive ion etching to form square-shaped pixels with sides ranging from 400 μ m to 8 μ m (Table 1). Photoluminescence measurements performed with a laser excitation of 514 nm revealed that the MQWs emit at 635 nm.



Side (µm) $A(10^3 \mu m^2)$ P (mm) $A/P(\mu m)$ 400 100 160 1.6 200 40 0.8 50 100 10 0.4 25 16 (20×20) 102.4 25.6 4 8 (100×100) 640 320 2

Figure 1 : InGaP/InAlGaP µLED structure.

Table	1:	Side	length,	area	(A),	perimeter	(P)	and
area/p	erin	ieter r	atio (A/I	P) for j	five p	ixels.		

The measured EQE as a function of the pixel size falls down when the side of the square mesa is lower than 80 μ m. It is expected that this reduction of the LED emission efficiency results from non-radiative recombinations at sidewall defects. Indeed, when the pixel size decreases, the contribution of sidewalls in recombination processes becomes less and less negligible compared to that of the top surface since the area/perimeter ratio reduces (Table 1).

Deep Level Transient Spectroscopy was used to investigate non-radiative recombinations as a function of the pixel size. Spectra of square μ LEDs with sides of 400 μ m, 100 μ m, 16 μ m and

8 µm are reported in figure 2 (T_W is the period width and t_P is the filling time). We observe a common peak to all diodes around 175 K and a broad signal between 350 K and 520 K, which appears only for the smallest pixels (side length < 100 µm). The apparent activation energy extracted from the peak at 175 K depends on the filling time and is in the range of 0.25-0.38 eV. The defect related to this level is assigned to DX center, often observed in Si doped InGaP and InAlGaP materials [6].

In figure 3, we see a strong dependence of the high temperature signal on the reverse bias (V_R) and the filling pulse voltage (V_P) applied to the anode of the smallest µLED. The positive peak, which corresponds to electron emission, has an apparent activation energy between 0.76 eV and 0.86 eV, depending on the applied voltages. This level is consistent with interface traps in InGaP [7] or other reported traps in InGaP or InAlGaP after proton or electron irradiation, all involving a phosphorus vacancy. Consequently, we believe that the plasma etching used to define the size of the pixels is responsible for the appearance of this level. Furthermore, Dekker *et al.* [6] demonstrated that the lifetime extracted from photoluminescence decay transients of a InGaP quantum well is inversely proportional to the concentration of this trap. It is then likely that the trap associated with the positive peak in the temperature range 350 K – 520 K and the reduction of the EQE for small µLEDs are linked.



Figure 2 : DLTS spectra of 4 pixels recorded with Figure 3 : DLTS spectra of the pixel with a side $T_W = 20 \text{ ms}, t_P = 10 \text{ ms}, V_R = -2 \text{ V and } V_P = 0 \text{ V}.$ of 8 µm recorded with $T_W = 20 \text{ ms}$ and $t_P = 50 \text{ ms}.$

Under particular conditions, three hole traps appear in DLTS spectra of the smallest μ LED as negative peaks, like in figure 3 for $V_P = 1$ V. They seem similar to the levels produced in InGaP after electron irradiation [8] and could have been formed during the reactive ion etching step.

Finally, we demonstrated a link between the EQE reduction and electrically active defects mainly located at the sidewalls of the pixels. An appropriate surface cleaning treatment and an efficient passivation are needed to suppress these traps, probably formed during the device fabrication, in order to enhance μ LED luminescence yield.

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Defects in 10-13 GaN: An electron microscopy study

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(10-13) GaN is one of the lesser studied but nevertheless, promising semipolar crystal orientations for the design of optoelectronic devices. While all semipolar structures reduce the piezo and spontaneous polarization fields, only (10-13) offers a negative electric field across an InGaN-GaN quantum well, similar to (0001), which greatly improves hole confinement.

Furthermore, the low angle of 32.04° of the (10-13) to the (0001) plane increases the energy needed to form a basal plane stacking faults (BSF), the dominant defect in semipolar heteroepitaxy. While a functioning blue InGaN/GaN LED structure utilizing (10-13) GaN was demonstrated 15 years ago[1], little further research has been published. Both BSFs, and other defects such as dislocations, can have significant impacts on the optical properties of semipolar heterostructures. In this work, we have utilized electron channeling contrast imaging (ECCI) and cathodoluminescence hyperspectral imaging (CL) to analyze the spatial distribution, the type and the optical properties of defects in (10-13) GaN. The sample was grown on m-plane sapphire using directional AlN sputtering and further overgrowth was done by metal-organic vapor phase epitaxy [3]. ECCI is becoming one of the go-to techniques for the analysis of defects in nitride semiconductors, thanks to it being non-destructive, spatially resolved and able to achieve statistically significant results. CL is the ideal correlative technique for ECCI, providing complementary information about the optical properties of the material at or close to the defects.



The majority of defects were I₁ type basal plane stacking faults and bounded partial dislocations, with perfect threading dislocations and prismatic stacking faults also being present. Low temperature (10K) cathodoluminescence hyperspectral imaging revealed light emission associated with I₁ stacking faults and prismatic stacking faults. The stacking fault density in the (10-13) GaN layer was $(3.5 \pm 1.0)*10^4$ cm⁻¹, and a low threading + partial dislocations density (7 \pm 2)*10⁸ cm⁻² was also observed. These defect densities are one order of magnitude below densities reported for hetero-epitaxial (11-22) or (11-20) GaN [4], which together with the negative polarization field make (10-13) a very attractive semipolar orientation for long wavelength LEDs.

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Size-dependent quantum efficiency of red emission from GaN:Eu micro-structures

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When the dimensions of LEDs decrease, there arise problems due to the smaller feature sizes in terms of the emission efficiency. Especially red micro-LEDs, which are typically based on AlGaInP, strongly suffer from lower efficiencies due to its high surface recombination velocities and large carrier diffusion lengths, and solutions like sidewall passivation show only limited improvements.

We demonstrate that for red-emitting Eu-doped GaN, sidewall related non-radiative recombination is hardly an issue for its emission efficiency [1]. The photoluminescence quantum efficiency (PL QE) of Eu-related emission as a function of the size of square mesa structures ranging from 1 to 100 μ m shows an increasing trend for smaller structures. This can be explained by an improving light extraction efficiency (LEE) due to a larger sidewall-to-surface ratio. With the support of finite-difference time-domain simulations, which also include material losses, we show how the dimensions influence the optical losses and LEE. For structures smaller than ~10 μ m there is an increasing influence of the sidewall-related non-radiative recombination of carriers on the internal quantum efficiency (IQE), however, it is only a minor effect as a result of the limited carrier diffusion length L_D . An analysis of the IQE as function of mesa size reflects the short diffusion length of carriers that was found by ultrafast THz spectroscopy [2].

These beneficial properties, combined with its high internal efficiency of luminescence, indicate the potential of this material for micro-LED applications.

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Fig. 1. SEM image of 1 µm sized mesa.

Fig 2. Relative IQ as function of mesa size. The red line indicates IQE for a carrier diffusion length $L_D = 110$ nm.

The influence of Cd and Hg doping on defect states formation in AgInS₂ quantum dots

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Recent years have brought a revived interest in a broad range of quantum confined multinary nanoparticles [1]. This may be seen as a result of intensive search for new functional nanomaterials devoted for emerging applications. Shifting the scientific focus toward multicomponent or off-stoichiometric nanoparticles seems to be a step in the right direction given ample possibilities of tunability of their physical properties extending the conventional bandgap tunability concept. That covers wide range of properties resulting from deep defects engineering including heterogeneous ions alloying, point defect engineering or intentional off-stoichiometry resulting in metal rich or metal poor materials. Such defect engineering is typically limited for well-known binary compounds.

Special attention should be paid to the $A^{I}-B^{III}-X^{VI}$ system, where $A^{I} = Cu$, Ag, $B^{III} = AI$, Ga, In and $X^{VI} = S$, Se, Te. These compounds may be treated as a direct derivative of the II-VI compounds exhibiting several valuable factors that are not observed for their binary analogues [2]. Probably the best-known feature is related to structural defects ordering leading to unexpected stability of non-stoichiometric phases e.g., A^IB₅^{III}X₈^{VI}, A^IB₃^{III}X₅^{VI}, A₃^IB₅^{III}X₉^{VI}. Further, one may point to self-doping phenomena realized via native point defects or weak electrical activity of deep defects, what results in very good electrical conductivity even for polycrystalline samples [2]. Along with the study of native defect many works have also been devoted to heterogeneous defects resulting from Zn or Mn alloying [3]. It has been already shown that Zn doped samples show improved spectral properties whereas Mn doped AgInS₂ ODs are characterized by dual emission band [4.5] Promising activity of Zn^{2+} ion on surface states minimization has also been reported [6]. In this work we have focused our attention on defects formation in orthorhombic AgInS₂ QDs, that are induced by Zn²⁺ ions and its heavier homologues including cadmium (Cd^{2+}) and mercury (Hg^{2+}). The results are here discussed in terms of experimental and theoretical approach performed within the Density Functional Theory.

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Transport phenomena in copper doped cadmium telluride: calculation from the first principles

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Cadmium telluride possesses unique physical properties necessary for photovoltaic converters of solar energy, namely, a required band gap width and needed absorption coefficient value. The optical and electrical properties of this material (in particular, the absorption coefficient and the transport phenomena) strongly depend on the structure of intrinsic and impurity point defects. Therefore, the study of the defects structure of CdTe is an actual applied problem. In literature there is a wide range of works where the ab initio approach is used to calculate the structure of defects in cadmium telluride. However, a common disadvantage of these works is the absence of connection between the structure of point defects and the kinetic characteristics of CdTe, which determine the electronic properties of the material.

In the proposed study the point defects caused by the introduction of copper impurity are considered, namely: Cu_{Cd} , $V_{Te} - Cu_{Cd}$, $Cu_{Cd} - Te_{Cd}$, $Cu_{Cd} - V_{Cd}$. To calculate the energy spectrum of the defect structure the supercell method was used on the base of the ABINIT code: for Cu_{Cd} – supercell Cd_7Te_8Cu (1×1×2 sphalerite cubic structure); for V_{Te} – Cu_{Cd} – supercell Cd_7Te_7Cu (1×1×2 sphalerite cubic structure); Cu_{Cd} – Te_{Cd} – supercell $Cd_{14}Te_{17}Cu$ (2×1×2 sphalerite cubic structure); Cu_{Cd} – V_{Cd} – supercell $Cd_{14}Te_{16}Cu$ (2×1×2 sphalerite cubic structure). Analogous calculations were performed for the ideal supercell Cd_8Te_8 (1×1×2 sphalerite cubic structure) and $Cd_{16}Te_{16}$ (2×1×2 sphalerite cubic structure).

To establish the temperature dependence of the energy spectrum of an ideal Cd_8Te_8 (or $Cd_{16}Te_{16}$) supercell an empirical formula to determine the temperature dependence of the band gap of CdTe was used: $E_g=1.65 - 5.35 \times 10^4$ T eV[1]. By choosing a certain mixture of the usual exchange-correlation GGA potential and the Hartree-Fock exchange potential (this mixture is determined by the "exchmix" parameter of the ABINIT code), a coincidence of experimental and theoretical values of the band gap for temperatures 0 ($E_g=1.65$, exchmix=0.09 – Cd_8Te_8 , exchmix=0.076 – $Cd_{16}Te_{16}$) and 300 K ($E_g=1.48$, exchmix=0.0182 – Cd_8Te_8 , exchmix=0.00571 – $Cd_{16}Te_{16}$) was achieved. Using these values of the exchmix parameter the energy spectra of defect supercells for 0 and 300 K respectively were obtained. Comparison of the energy spectra of an ideal and defect supercell enables to determine the ionization energies of the acceptor defects ΔE_A at 0 and 300 K. Assuming a linear dependence of the defect ionization energy on temperature the dependences ΔE_A (T) were obtained for the considered types of acceptor defects.

The description of the transport phenomena in p-CdTe was performed on the basis of shortrange heavy hole scattering models [2-4]. The above mentioned scattering models require the calculation of certain scattering constants, which, in turn, require the determination of the valence band wave function and the crystal potential.

The calculation of the wave function and crystal potential was performed for a CdTe unit cell with a sphalerite structure within the frame of the ABINIT code. Similarly to the case of the supercell method, the calculation for the unit cell was performed so that a coincidence of the experimental and theoretical values of the band gap for temperatures 0 and 300 K was achieved. This occurs when the value of the parameter exchmix = 0.397 at 0 K and exchmix = 0.288 at 300 K. The resulting wave function and crystal potential are in accordance with the abovementioned temperatures. It should be noted that this approach allows to calculate the

wave function and crystal potential for any predetermined temperature. It is always provide a coincidence with the experiment, namely with the width of the crystal band gap.

The scattering constants of the short-range models are represented as integrals over the wave function Ψ and the crystal potential U. Since Ψ and U are depend on temperature, the scattering constants also depend on temperature. Assuming a linear dependence, the temperature dependences of the following scattering parameters are calculated: scattering constant on polar optical phonons; scattering constant on piezoacoustic and piezooptic phonons; acoustic deformation potential constant; optical deformation potential constant.

Using three-dimensional B-spline interpolation [5] the effective mass of heavy holes at 0 and 300 K is calculated. Assuming a linear dependence, the temperature dependence of the effective mass of heavy holes is established.

The calculation of p-CdTe kinetic coefficients was performed for the defect with the lowest ionization energy, namely for CuCd - VCd. For crystals with defect concentration $1 \times 10^{14} \div 1 \times 10^{18}$ cm⁻³ the temperature dependences of heavy hole mobility and Hall factor in the range 15 – 850 K are calculated. The influence of different scattering mechanisms on the heavy hole mobility is considered. The theoretical curves obtained in the short-range approach differ qualitatively and quantitatively from those obtained within the long-range models in relaxation time approximation.

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Identification of mechanism of defect formation in plastically relaxed individual semiconductor heteronanowires by transmission electron microscopy

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1. Introduction

Due to high surface to volume ratio the monocrystalline semiconductor core-shell nanowires (NW) are very attractive as building blocks of solar cells, optoelectronic, electronic and environmental sensor devices. They are also perfect model structures for investigations of nanomechanic behavior of defects appearing during strain relaxation. For this purpose ternary semiconductors core-shell NWs were grown by molecular beam epitaxy (MBE) on Si and GaAs substrate using Vapor-Liquid-Solid (VLS) growth mechanism with gold as catalyst. The mismatch of the lattice parameters of basic compounds: ZnTe, CdTe, MgTe, GaAs, InAs constituting core-shell NWs studied by us can exceed 7%. By modification of the growth conditions (temperature, stoichiometry) nonstandard crystal structure of NWs comprising above mentioned compounds can be obtained.

2. Residual strain analysis and mechanisms of relaxation in radial nanowires

We study two semiconductor radial NW heterostructures: the first one based on wurtzite (hexagonal) (In,Ga)As, the second one on cubic (Cd, Zn)Te. The stiffness coefficients as well as defect creation energies are significantly different for these two compounds. The residual strain field and core-shell interface misfit dislocation spatial configurations are studied for individual NWs by Transmission Electron Microscopy (TEM) and scanning TEM (STEM). The Dislocation Individual NWs are investigated in two configurations: (i) plan view – a NW lying on a TEM grid; (ii) cross-sectional view - thin NW slice cut in the direction perpendicular to NW axis. The letter has been achieved using focused ion beam (FIB) technique. The Dislocation Density Tensor mapping was realized using extension of the Geometric Phase Analysis [1] performed on High-Resolution (HR) TEM and HR-STEM images of both specimen types at different zone axes. The NW morphology, core diameter, shell thickness, elemental distribution and concentration are determined by STEM and Energy-dispersive X-ray spectroscopy (EDX) as shown in Fig 1a, c. EDX analysis reveals that indium concentration is about 20at% in the 50 nm thick NW core and the average GaAs shell thickness in the analyzed area is around 10 nm. For this NW the plastic relaxation of the shell occurs by creation of misfit dislocation loops (MDLs) around the core but they arenot regularly spaced in the axial direction. Additional (0002) plane in the GaAs shell emerges, as shown in Fig. 1d. The residual strain field can be easily visualized by Bright Field (BF) TEM contrast (Fig. 1b). GPA can measure the local lattice strain around dislocation from HR-TEM or HR-STEM images. The $\beta_{[0001]}$ (definition in [1]) component of the lattice distortion tensor for single dislocation at the core/shell interface is shown in Fig. 1d.

The CdTe/ZnTe NW are crystalized in the standard zinc blende form. CdTe and ZnTe have much lower elastic constant and lower energy of defect formation than InGaAs/GaAs

heterostructure, however the lattice mismatch for CdTe/ZnTe is significantly higher (-7%), as compared to about 2% for InGaAs/GaAs (with In content applied here). In the case of NWs with CdTe core, the stress relaxation occurs by creation of misfit dislocations network at the core-shell interface which consist of 60° dislocations and dissociated Lomer dislocations. We show that axial and radial spacing between dislocations depends strongly on the local shell thickness and on the core diameter (Fig. 2). These findings are in qualitative agreement with the theoretical predictions [2]. Additionally, we found a fundamental difference in the defect types in the case of the NWs with ZnTe core. The basal plane (or (111) plane) Stacking Faults (SFs) of the core interact with the (-111) plane SFs formed in the Cd rich shell (image not shown) which results in formation of partial dislocations (Cottrell-Lomer Lock and Hirth lock) at the intersection of these two sets of SFs.

We conclude that the difference of the mechanism of strain relaxation depends not only on lattice mismatch, the shell thickness and the core diameter but also on the type of crystal structure (wurtzite or zinc blende) and the energy of defect formation.



Figure 1. (a) STEM image of plastically relaxed InGaAs/GaAs nanowire; (b) visualization of the residual strains of the NW confined to the frame marked at panel (a) using the Bright Field TEM contrast. (c) distribution of In, Ga and As by EDX; (d) HRTEM image and $\beta_{[0001]}$ component of lattice distortion tensor of individual misfit dislocation at core/shell interface of wurtzite segment of the same NW determined by GPA.



Figure 2. GPA analysis of STEM image of the partially relaxed NW with CdTe core and asymmetric ZnTe shell, clearly showing misfit dislocation network at the core/shell interface; GPA phase (a) and amplitude (b); (c) the $\beta_{[0001]}$ component of lattice distortion.

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Terahertz time-domain spectroscopy of GaAs epitaxial layers treated with the use of fast atom bombardment

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Recently, a semiconductor surface treatment, the so-called fast atom bombardment is attracting much attention because it enables wafer bonding between different semiconductors, for example, Si and GaN wafer bonding. It is expected that the fast atom bombardment is applicable to fabricating highly efficient tandem-type solar cells. The advantage of the fast bombardment is featured by the fact that the wafer bonding does not require relatively high temperature, which prevents quality degradation. It is, on the other hand, apparent that the accelerated atom beam, for example, Ar and novel gas beams give damages to surfaces of semiconductors during the bombardment. It is, therefore, meaningful to characterize the semiconductor surfaces after the bombardment. We note that the dynamics of carriers and phonons is more informative than surface shape assessments such as atomic microscopy because the characteristics electronic and/or optoelectronic devices are influenced by the above-mentioned issues. This is because that ultrafast spectroscopy in the time scale of femtoseconds provides the information on carriers and phonons as a time-domain signal.

In the present paper, we explore the fusibility of terahertz time-domain spectroscopy for characterizing semiconductor surfaces after the fast atom bombardment. We observed that the reference sample without the fast atom bombardment treatment emits the terahertz electromagnetic wave composed of the ultrafast current of photogenerated carriers, coherent longitudinal optical (LO) phonon, and the coherent LO-phonon-plasmon coupled (LOPC) mode. In the samples treated with the fast atom bombardment, we found that the terahertz-band intensity arising from ultrafast photocurrent is decreased and that the terahertz band of the LOPC mode disappears. The decay time of the coherent LO phonon becomes longer with an increase in exposure time of the fast atom bombardment. We conclude that the dephasing of the coherent LO phonon is suppressed by the reduction of the photogenerated carrier scattering and, as a result, the decay time of the coherent LO phonon becomes longer.

The present samples, which were grown by metal-organic vaper phase epitaxy, were GaAsbased epitaxial structures consisting of the undoped GaAs top layer with the thickness of 50 nm and the *n*-type bottom GaAs layer with the thickness and doping concentration of 3.0μ m and 3×10^{18} cm⁻³. The substrate was a (001)-oriented semi-insulating GaAs wafer. The fast atom bombardment was performed with the use of Ar gas. The flow rate of the Ar gas was 8.0 sccm. The acceleration voltage and current, which were applied to the generator of the fast atom beam, were 1.5 kV and 20 mA, respectively, and the incidence angle of the beam to the sample and accelerated Ar beam energy were 45° and 1.0 keV, respectively. The terahertz time-domain signals were measured using an optical gating method with the use of a photoconductive dipole antenna formed on a low-temperature-grown GaAs epilayer. The pump and probe light source was a Ti:sapphire laser with pulse duration of 40 fs and a repetition rate of 90 MHz. The photon energy was 1.55 eV. The beam profile was a Gaussian type. The diameter of the spot was about 100 μ m on the sample surface.

Figure 1 shows the time-domain signal of each sample. The bipolar signal, which is located at the time delay of 0 ps, originates from ultrafast photocurrent generated by the pump pulse. The bipolar pulse follows the long-lived oscillation pattern with the period of 114 fs. The period of 114 fs correspond to the LO phonon frequency, meaning that the coherent LO phonon is observed. We note that the decay time of the terahertz wave from the coherent phonon becomes longer as the fast atom bombardment time is longer. We clarified that the decay time of the coherent phonon is dominated by the photogenerated carrier density via the scattering by each other [1]. After the fast atom bombardment, it is reasonable to consider that the photogenerated carrier density is lowered owing to defects at the surface. Consequently, the scattering effect on coherent LO phonon becomes less, leading to the longer decay time of the coherent LO phonons. In order to the time-domain signals in detail, we carried out Fourier transform, of the result which is shown in Fig 2. The terahertz band, which originates from the ultrafast photocurrent, is located at the frequency of 1.5 THz. The intensity of this band is reduced as the fast atom bombardment time is increased; namely, the photogenerated carrier density is decreased. This result coincides with the above discussion on the longer decay time of the coherent LO phonon. The band at 8.8 THz is attributed to the coherent LO phonon. After the fast atom bombardment, the coherent LO phonon band widths become narrow and the peak value of the band is increased. This reflects the decay characteristics of the coherent LO phonon terahertz wave shown in Fig. 1. In the Fourier power spectrum of the reference sample without the fast atom bombardment, the coherent LOPC band of the lower branch clearly appears at 4.8 THz. In contrast, the coherent LOPC band disappears in the sample with the fast atom bombardment. In terahertz time-domain spectroscopy, only the coherent signal is observed in principle. The disappearance of the coherent LOPC mode band indicates that the fast atom bombardment reduces the coherency of the coherent LOPC mode.



Fig. 1: Terahertz waveform of each sample.



Fig. 2: Fourier power spectra of the terahertz waveforms shown in Fig. 2

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Al-Catalyzed Si Nanowire Formations on Thin Si Substrates and Photovoltaic Applications

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Thin silicon (Si) solar cells have been candidates to suppress the Si material consumption and to develop into flexible devices. This advantage has come with a trading-off in solar cell performance. Light absorption loss in a thin Si wafer is an important issue to be overcome for enhancing the efficiency of solar cells. From our previous reports [1-4], several Si nanowire (NW) structures showed their ability of extreme light trapping, suggesting the integration of SiNWs on thin Si substrates is promising to realize high-performance thin solar cells. VLS growth is of particular interest technique from various SiNW synthesis methods owing to its effectiveness in providing single-crystalline SiNWs, compatibility with the process for thin Si substrates, and expandability to large-scale manufacturing. Moreover, using aluminum (Al) as a metal catalyst can create high-density SiNW arrays with automatically p-type doping, resolving the catalyst contamination problem.

Although the Al-catalyzed VLS-SiNWs are in turn highlights for photovoltaic application, the influence of NW surface defects acting as recombination sites and the Al concentration activating as impurity doping in SiNWs has to be considered. In this study, we investigated Al-catalyzed SiNW formations by the VLS mechanism of thermal CVD system on thin Si substrates. The chemical pre-etching and mechanical post-polishing were applied to demonstrate thin Si materials and fabricate thin SiNW-based solar cells. The effective minority carrier lifetime of SiNWs on both thin substrates, NW surface defects, and the Al concentration in SiNWs were evaluated and optimized.

The experiments were carried out using n-Si(111) wafers. The pre-etched Si substrates of approximately 80-µm thick were prepared by dipping into HF/H₂O₂/CH₃COOH solution and the bulk Si wafers were used for post-polished samples. Then, Al-catalyst films were sputtered prior to the VLS process. SiNW formation on both thin Si substrates was performed with a fixed substrate temperature of 700 °C [4]. For solar cell fabrication, the p⁺-Si shell layer was added onto SiNWs at 750 °C with a boron concentration of ~4×10¹⁹ atoms per cm⁻³ [1-4]. The post-polished samples were processed to reduce the thickness as similar to the pre-etched cells using the diamond solution. The back surface field or n⁺-Si layer was applied by spin-coating phosphorus-containing solution and annealing at 850 °C under a pressure of 100 Pa in the N₂ atmosphere. Lastly, sputtering of a 120 nm-thick ITO film followed by a 200 nm-thick Ti/Ag with a micro-grid pattern for the front electrode and a 150 nm-thick Ag back contact was performed.

Figure 1 shows SEM images and optical properties of SiNWs on thin Si wafers provided by pre-etching and post-polishing. The vertical Al-catalyzed SiNWs were better controlled on post-polished Si substrate along [111] direction. The higher NW density and smaller NW diameter were also observed. Improved light absorbance was detected from all SiNW samples. Figure 2 shows the Raman spectra of SiNWs grown on pre-etched and post-polished thin Si substrates. Raman spectrum with a shift of the Si optical phonon peak toward a lower wavenumber and a little broader FWHM from SiNWs on the pre-etched substrate was inspected, indicating more presence of polycrystalline Si components. The asymmetric line shapes could be estimated using the fitting to the Fano equation [5-7] as an active Al doping

concentration inside the SiNWs between 10^{16} - 10^{18} atoms per cm³ in comparison to B-doped Si wafers.

Figure 3 shows J-V characteristics and EQE of Al-catalyzed SiNW solar cells on thin Si wafers fabricated using p^+ -pn-n⁺ structure compared to planar solar cell and Al-catalyzed SiNW solar cell on bulk Si. The maximum efficiency of thin SiNW solar cells was achieved to 6.1% and 6.6% by using pre-etched and post-polished Si substrates, respectively. Although EQE of SiNW cell on thin-Si substrates showed a good carrier generation, the efficiencies were lower than on bulk-Si and planar cell with a poorer fill-factor. These results attributed to the cell and junction leakages owing to thin Si substrates. The parameters of Alcatalyzed SiNW formation, preparation of thin Si substrates, and their solar cell fabrications are being optimized to improve thin solar cell performances. The NW surface passivation will also be performed. The low-cost materials and processes, including high throughput techniques in this study are expected to increase the potential of new alternative Al-catalyzed SiNWs providing for future technologies, involving the devices.

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Fig. 1 SEM images of Al-catalyzed SiNWs formed on (a) pre-etched and (b) post-polished thin Si substrates. (c) Light transmittance, (d) reflectance, and (e) absorbance of with and without SiNWs on thin and bulk Si substrates compared to bulk Si.



Fig. 2 (a) Raman spectra of SiNWs grown on pre-etched and post-polished thin Si substrates and (b) the Fano parameters q and Γ estimated by the fitting of the Si optical phonon peaks.



Fig. 3 (a) J-V characteristics measured under AM1.5G and (b) EQE of planar solar cell, Al-catalyzed SiNW solar cell on bulk Si, and Al-catalyzed SiNW solar cell on thin Si wafer.

Investigation of the effect of gamma radiation on the electrical properties of n-type GaAs_{1-x}Bi_x layers grown by Molecular Beam Epitaxy.

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Recently, dilute bismide alloys grown on GaAs have attracted much attention due to their physical properties and potential applications in photonic devices and long wavelength optoelectronics[1,2]. The incorporation of a few atomic percent of Bi into GaAs (substitution of As atoms with Bi atoms) strongly affects the properties of GaAs. For example, a giant bandgap bowing effect was observed, leading to a strong reduction in the bandgap energy by 88 meV per % Bi. In addition, the increase in the spin–orbit (SO) splitting energy with Bi concentration[3,4] makes GaAsBi-based structures suitable for spintronic device applications[5]. In this work, we present experiment confirmation on the effect of gamma irradiation (γ -) in n-type dilute GaAs1–xBix epilayer structures grown by Molecular Beam Epitaxy (MBE) on n+ (100) GaAs substrate by using Current – Voltage (I-V), Capacitance - Voltage (C-V), deep level defects spectroscopy (DLTS) and Laplace (LDLTS).

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Analyzing the polarization properties of O-H centers in β -Ga₂O₃

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Hydrogen in β -Ga₂O₃ forms O-H centers that can impact electrical properties [1]. IR absorption spectroscopy provides a powerful strategy for investigating this class of defects in the low-symmetry monoclinic structure of β -Ga₂O₃. In this presentation, the use of polarized absorption as an experimental method to determine both the orientation of the principal dielectric axes of the crystal in the near IR and the direction of the vibrational transition moment of O-H centers will be discussed [2].

The ion implantation of H^+ and D^+ into Ga_2O_3 produces several O-H and O-D centers [3]. These defects include the dominant $V_{Ga(1)}$ -2H and $V_{Ga(1)}$ -2D centers studied previously [4] along with additional defects that can be converted into this structure by thermal annealing. We have found that the polarized O-D absorption has a strong angular dependence (Fig. 1, for example) that provides important clues about defect structure. Two types of defects have been found by experiment with different polarization properties and different thermal stabilities [3].

Theory suggests that two classes of O-H centers are formed in Ga₂O₃ that has been implanted with protons (or deuterons) [3]. The first consists of two H atoms trapped at a relaxed configuration of the $V_{Ga(1)}$ center predicted by Kyrtsos *et al.* [Fig 2(a)] [5]. A second consists of two H atoms trapped at a relaxed configuration of $V_{Ga(1)}$ predicted by Varley *et al.* [Fig. 2(b)] [6]. These different core structures can explain the two classes of O-H centers seen by experiment along with their characteristic polarization properties.

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Fig. 1. IR absorption spectra (77 K) of the $V_{Ga(1)}$ -2D center in (010) Ga_2O_3 as a function of the angle of the transmission axis of an analyzing polarizer (measured with respect to the [102] axis).



Fig. 2. Two different configurations of the $V_{Ga(1)}$ -2D center in (010) Ga_2O_3 .

Contrasting character of Cr and Mn solitary dopants in CdTe

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Identifying materials hosting defects with well defined deep state character and localized isolated spins is a key to design new platforms in quantum technologies. An important criterion for a successful defect configuration is the ability to address coherently the spin, both electrically and optically, in a solid-state device. In particular, defects formed by the association of light dopant with native crystal impurities such as N-V, Si-V centers in diamond, or N_C - V_{Si} defect in SiC have been extensively characterized in the recent years. In parallel to these defect complexes, single magnetic atoms embedded in II-VI and III-V semiconductor quantum dots (QDs) have attracted attention in the quantum technology community [1]. The manganese (Mn) was the first and thus the most extensively studied single magnetic dopant in QDs for direct spin readout and manipulation [2].

Among the several other choices of magnetic impurities, chromium (Cr) in semiconductor QDs is of particular interest due to its S=2 spin, zero nuclear spin and non-zero orbital momentum L=2. The latter point opens the way for a coherent mechanical control of the Cr spin through surface acoustic waves for example. Such Cr-doped CdTe/ZnTe QDs were grown by molecular beam epitaxy and allow us to demonstrate optical control of individual Cr spin by excitation of the Cr spin using laser-pumping and read-out through photo-luminescence [3]. However, the number of QDs presenting the correct defect configuration for the Cr atom turn to be much lower in comparison to Mn-doped CdTe/ZnTe QDs grown by the same approach. In order to understand this puzzle, we performed DFT calculations for the two solitary dopants analyzing their electronic structure for different ground state configurations and their interactions with the lattice environment. Based on this contrast, we will propose various factors that could explain the challenge of Cr dopant identification in our optical experiments.

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Dopability of Telluride Diamond-Like Semiconductors and Ordered Vacancy Compounds for Thermoelectric Applications

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Computation-driven search for candidate thermoelectric materials has recently seen several successes, but many of the predicted materials often prove to be difficult to dope in the lab. Here we will review our recent work which has focused on building a combined computational and experimental approach to identify highly dopable semiconductors for use as candidate thermoelectrics. We consider defect chemisty and dopability in a chemicallydiverse set of telluride-based diamond-like semiconductors in the IBIIITe2 space, with I_B=(Cu,Ag), III=(In,Ga) and Cu₂(Zn,Cd,Hg)(Si,Ge,Sn)Te₄. These materials are typically observed to be p-type, but a materials descriptor suggests that they would be more effective as thermoelectrics if they could be doped n-type. By combining first-principles methods and experimental phase boundary mapping, we assess dopabilities and seek extrinsic dopants in this space. Using phase boundary mapping, experimental carrier concentrations are measured and compared to the predicted values. For all compounds, a competition between III, III, and V_I defects governs the achievable range of carrier concentrations. Enabling n-type behavior requires suppressing the IIII antisite and VI vacancy defects while increasing the number of III_I antisites. Using this observation as a design strategy, we are able to screen a large number of compounds and identify candidate diamond like semiconductors and ordered vacancy compounds that are more amenable to n-type doping. The results of this comprehensive search are used to generate a chemically intuitive framework for predicting dopabilities in this family of materials without the need to carry out full-scale first-principles analysis.

Bundle-type columnar Cu₂O photoabsorbers with vertical grainboundaries using instant strike processed metallic seeds and their enhanced photoelectrochemical efficiency

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Controlling and designing grain-boundaries (GBs), which cause recombination losses as planar defects in the absorbing layers are an essential strategy for the development of the highly efficient photoelectrochemical reaction systems. We suggest the method to design progressive bundle-type columnar structure as an alternative of single crystal with the fewest defects, where the GBs were aligned in parallel with charge transport movement and electric field direction. The instant strike bias (10 msec) in the same electrolytes induces the formation of island-shaped metallic Cu nanoparticles in the initial stage as seed crystals for controlling the Cu₂O growth evolution, and results in the dramatically high density Cu₂O nuclei and bundle-type columnar Cu₂O growth with longitudinal GBs, contrary to the typical randomly-crystallized Cu₂O. The metallic Cu seeds with stronger electric field than the exposed ITO region provide the selective crystallization sites for Cu₂O growth along the <111> ionic bonding. Despite ultimately instant strike interval, the *p*-type Cu₂O photoelectrodes retain outstanding photocurrent of 5.2 mA/cm² and on-set potential of 0.7 V at 0 V_{RHE}, owing to highly improved transport and transfer efficiencies inside the Cu₂O by suppressing effectively charge scattering in the GBs. Consequently, it is decisive that designing the bundle-type columnar structure could be a good strategy in developing the photocathodes with enhanced photoelectrochemical reaction.

Achieving bulk-insulating states in Pb(Bi,Sb)₂(Te,Se)₄ topological insulator

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Topological insulators (TIs) are known to exhibit characteristic gapless Dirac surface states. However, the detection of the surface states is generally difficult because, in most of the TIs identified so far, the bulk resistivity is considerably low and the characteristic surface conduction is masked by bulk conduction. Therefore, one of the most important tasks in the field of TIs is to achieve a bulk-insulating state, which is a prerequisite for the study of characteristic surface-transport phenomena.

In PbBi₂Te₄, a member of the Pb-based layered chalcogenides, a single Dirac cone has been observed by angle-resolved photoemission spectroscopy (ARPES) [1,2]. Furthermore, it has been theoretically shown that PbBi₂Te₄ has a more isotropic Dirac cone than related binary TIs such as Bi₂Te₃ [3,4]. Such an isotropic Dirac cone should work for suppressing the scattering of surface electrons. Thus, PbBi₂Te₄ is considered as one of the promising candidates for future spintronics material with a large spin current density. However, experimental studies of its surface transport properties have not yet been reported, owing to a lack of bulk insulating crystals. ARPES studies by Souma et al. [1] have shown that the chemical potential can be tuned by Sb substitution for Bi in PbBi₂Te₄; whereas PbBi₂Te₄ is n-type materials, PbSb₂Te₄ is a p-type one. Following the studies, we achieved bulk insulating states in Pb(Bi,Sb)₂Te₄ topological insulators by tuning compositional ratio of Bi and Sb [5]. N- to p-type transition in bulk conduction occurred at Sb molar ratio with ~0.80. Semiconducting behavior with a negative temperature coefficient of resistivity was observed with resistivity values as high as 180 mΩcm at 2 K around the transition composition.

Recently, it was theoretically predicted that, in $PbBi_2Te_4$, partial substitution of Te by Se and their ordering structure would lead to larger band gap [6], which indicates the possibility of further improvement of bulk-insulation in Pb-based chalcogenides TIs. In fact, our experimental observation by using scanning transmission electron microscopy (STEM) and powder x-ray diffraction revealed that the Se ordering structure is formed in Pb(Bi,Sb)₂(Te,Se)₄ [7].

In the present study, Pb(Bi,Sb)₂(Te,Se)₄ crystals were grown using the Bridgman method. Sb molar ratio x = Sb/(Sb + Bi) was fixed around 0.80, while Se molar ratio y = Se/(Se + Te)was varied from 0.10 to 0.30. Single crystals were retrieved from the ingot by breaking the ingot along the cleavage planes for electrical transport measurements. The sample size was approximately $2 \times 1 \times 0.2$ mm³. Electrical resistivity measurements were conducted by a sixprobe method using a physical property measurement system (PPMS) in the temperature range between 2 and 300 K. Carrier densities were evaluated by measuring the Hall effect at 2 K. As resistivity measurements, some of the samples with (x, y) =result of а (0.80, 0.10), (0.80, 0.20), (0.82, 0.30) exhibited semiconducting behavior, while others exhibited metallic behavior. In addition, Hall effects consistent with n- and p-type carriers were observed in the single crystals retrieved from the same ingot. The results indicate that even in the same ingot, charged defects are nonuniformly distributed and the semiconducting and metallic regions are included. Thus, in order to find out semiconducting regions with higher resistivity, electrical resistivity measurements for microsamples were conducted. Columnar samples approximately 20 μ m² in cross-section area, approximately 12 μ m in length were cut out from the single crystal with (*x*, *y*) = (0.82, 0.30), which exhibited highest electrical resistivity: 47.5 mΩcm at 2 K, by using focused ion beam (FIB). Then, electrical resistivity measurements were conducted using PPMS in the temperature range between 2 and 300 K. The magnetoresistance (MR) was also measured at various temperatures in an out-of-plane magnetic field up to 9 T.

As a result, some of the microsamples exhibited higher resistivity than millimeter-scale samples. The result indicates that semiconducting regions with higher resistivity, in fact, locally distributed. In some semiconducting microsamples, the MR increased in the low magnetic field region and decreased in the higher magnetic field region, which can be explained by three-dimensional (3D) weak antilocalization combined with 3D electron-electron interaction theory.

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Energy structure and luminescence line shapes of point defects in AIN

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Group-III nitrides are promising for creation of various electronic and optoelectronic devices, such as light-emitting diodes and laser diodes of the ultraviolet and visible range, highfrequency transistors, photodetectors, and single-photon sources. To improve the quality of materials, it is necessary to know the atomic and energy structure of native point defects and impurity centers. In recent years, interest in the study of point defects has increased significantly in connection with the possibility of using such centers as the basic elements for quantum computations. Optical methods, such as photoluminescence and absorption spectroscopy are effective instruments for investigation of energy structure of defects. For identification of defect luminescence bands it is necessary to consider theoretically the local electron-phonon coupling determining luminescence line shape and its dependence on the temperature. In experiments, luminescence bands with donor-acceptor nature are often observed. Therefore, calculations of the luminescence line shapes of donor-acceptor transitions taking into account lattice relaxations for deep-level defects is necessary for the luminescence bands identification. In this work we have investigated theoretically the energy structure and electron coupling with local lattice vibrations for deep centers in AlN [1]. Using hybrid functional density functional theory, we have calculated local phonon energies, Huang-Rhys parameters, formation energies, charge state thermodynamic transition energies, and luminescence line shapes for different defects in AlN. The defects for luminescence line shape calculations were selected based on their formation energies considering native defects in AlN, defects and defect complexes containing most common unintentional impurities of carbon, oxygen and silicon. Luminescence line shapes of band to deep center transitions in AlN have been calculated in dependence on temperature for most abundant defects in AlN. Donor-acceptor luminescence line shapes for shallow donor to deep acceptor and deep donor to deep acceptor transitions have been considered theoretically. Configuration diagrams of oxygen and silicon DX-centers have been calculated, and peak energies of optical transitions of an electron from the DX-centers to deep acceptors have been estimated. Possible assignments of the experimental luminescence bands in AlN based on the calculations have been discussed.

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Detection of Interstitial-Defect Levels in Mg-Ion-Implanted GaN Using MOS Diodes

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GaN is one of the promising materials to realize high-efficiency power devices because it has a wide band gap, a high breakdown field, a high electron mobility, and a good thermal conductivity. These excellent properties can be derived fully in a GaN MOSFET. To fabricate an inversion-type MOSFET, ion implantation technology should be developed for selective doping. However, this technology for achieving p-type doping is challenging. To establish this technology, the behavior of defects generated in implanted GaN should be investigated comprehensively. For Mg-ion-implanted GaN, nitrogen-vacancy-related defects or vacancy complex defects are detected in the previous reports [1-3]. Nevertheless, the behavior of the Ga (Ga_i) and N (N_i) interstitial defects generated by ion-implantation should be also investigated for understanding and controlling the defects perfectly.

Here, we focused on the detection of interstitial defects in MOS diodes constructed with implanted GaN. By using MOS diodes, we can investigate even the defects localized in the near-surface region. Furthermore, experimental data on defect levels in n-type GaN have been frequently reported. Therefore, we used n-type MOS diodes consisted of lightly Mg-ion-implanted GaN.

Simulation results of the high-frequency capacitance–voltage (C-V) characteristics of the n-GaN MOS diodes with defects in the near-surface region. In this simulation, the bias voltage is assumed to be swept from the minus side to the plus side so that the electron capture by defect levels is dominant are shown in Fig. 1. In addition, step profiles of Ga_i and N_i distributed within 10 nm from the surface are assumed, while the interface states are ignored. It is also assumed that Ga_i and N_i generate a donor-like defect level at $E_C - 0.8$ eV and an acceptor-like level at $E_C - 0.9$ eV, respectively, according to Ref. [4]. It can be seen that the shallow distribution of defects can affect the C-V characteristics of MOS diodes. It should be noted that the donor-like defect of Ga_i generates a bump in the C-V curve on the negative-bias side of the ideal curve, while the acceptor-like defect of N_i generates a bump on the positive bias side. In this way, we can distinguish the type, *i.e.*, donor or acceptor, of defect levels. Furthermore, for donor-like defect levels, the C-V curve over the bump is identical with the ideal curve when the interface states are ignored. On the other hand, for the acceptor-like defect levels, the C-V characteristics under the bump is identical with the ideal curve. Thus, there is possibility that these defect levels can be detected by the high-frequency capacitance method usually used to detect interface states.

Actually, we detected the interstitial-defect levels experimentally. The sample was prepared as follow. The n-GaN ($n = 5 \times 10^{17}$ cm⁻³) epitaxial layer was grown on a free-standing n⁺-GaN substrate. Mg-ion implantation was carried out with 50-KeV energy and 1.5×10^{11} -cm⁻² dosage ([Mg]_{max} = 2×10^{16} cm⁻³). Thereafter, the sample was annealed at 600 °C for 30 h with using SiN or Al₂O₃ cap layer. After removal of the cap layer, MOS diodes were completed by depositing Al₂O₃ layer, the top electrode, and the bottom ohmic contact. The *C*–*V* characteristics were measured at 1 MHz with the bias sweep of 50 mV/s. The measured *C*–*V* characteristics are shown in Fig. 2. We found that the characteristics are dependent on the cap layer materials used during annealing. For the sample annealed with the SiN cap layer, a bump was observed on the negative bias side of the ideal curve as shown in Fig. 2(a), which was similar to Fig. 1(a).

Moreover, for the sample annealed with Al₂O₃ cap layer, C-V characteristics similar to Fig. 1(b) was measured as shown in Fig. 2(b). The electron trap density distribution was derived as shown in Fig. 3. A discrete level at $E_{\rm C} - 0.8$ eV was detected for the SiN-cap-layer sample, while another discrete level at $E_{\rm C} - 0.9$ eV was detected for the Al₂O₃-cap-layer sample. Considering C-V characteristics, the former is the donor-like level and the latter the acceptor-like level. Therefore, there is possibility that the Ga_i level was detected for the SiN-cap-layer sample, while the N_i level might have been detected for the Al₂O₃-cap-layer sample. SIMS was carried out at the process step after annealing before the removal of the cap layer. The SIMS results indicated that the Ga atoms were diffused into Al₂O₃ cap layer with the extent dependent on the Mg-ion dosage, while they did not diffuse into the SiN cap layer. Consequently, the detection of the Ga_i defect level was confirmed.

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Fig. 1. Simulated C-V curves.



Fig. 2. Measured *C*–*V* curves.

Fig. 3. Detected electron traps.

Computational Design of Quantum Defects in Low-Dimensional Semiconductors

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2D materials are known to host intriguing electronic properties and thus offer a fascinating platform for quantum photonics. In particular, 2D materials have been shown to host single-photon emitters (SPE). It is therefore vital to investigate the influence of defects within different host materials which are much easier to create and control in monolayers compared to bulk systems. Based on the computational 2D materials database (C2DB) [1] we first perform a computational screening for intrinsic point defects of stable theoretically predicted and experimentally known low-dimensional semiconductors. We present a tool within the atomic simulation environment (ASE) [2] and the atomic simulation recipes (ASR) to automatically identify intrinsic point defects for given structures and calculate various physical properties in a high-throughput manner. We thereby pave the way towards creating a publicly available database of defects in 2D semiconductors which will provide useful reference data for both theoreticians and experimentalists.

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Probing the SiO₂/SiC interface with nanometer depth resolution using low-energy muons

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Silicon carbide (SiC) is a wide-bandgap semiconductor with promising applications in highvoltage power devices with low leakage currents. The performance of SiC-based devices relies mainly on surface and interfaces effects, with oxidation-induced defects at the SiO₂/SiC interface playing a crucial role. Thus, further improvement in processing of these devices strongly benefits from the study of such regions with suitable techniques.

Low-energy muon spin spectroscopy (LE- μ SR) is a unique tool that uses positive spin-polarized muons with keV energies to investigate thin-films, near-surface and interface regions with nanometer-scale resolution. Defect regions in semiconductors can be localized by LE- μ SR: in the presence of defects neutral, the formation of muonium (Mu⁰) is suppressed, and the so-called diamagnetic fraction (F_D) increases [1]. LE- μ SR has also been shown to be able to distinguish between carbon and silicon vacancies present in near-surface regions of 4H-SiC [2]. We investigated the oxide interface formed with 4H-SiC during different oxide growth processes – thermal oxidation and plasma-enhanced chemical deposition (PECVD) of silicon dioxide (SiO₂).

Sample Name	Crystal Orientation	N_D (cm ⁻³)	Oxidation Process
SiC-A	(0001)	8 x 10 ¹⁵	Deposited
SiC-B	(0001)	$\sim 1 \times 10^{19}$	Thermal
SiC-C	(0001)	8 x 10 ¹⁵	Therm + dep
SiC-D	(0001)	~1 x 10 ¹⁹	Therm, HF, dep

TT 11	1	111 0.0	1	•
Table	1:	4H-SiC	samples	overview.
			pres	0101110111

Here, we report the analysis of the measured F_D , which can be modelled in order to obtain a depth-resolved profile, using the simulated stopping depth profiles of the low-energy muons [3]. The changes of F_D allow us to determine the depth distribution of oxidation-induced defects with a resolution of a few nanometers. This shows that LE-µSR provides valuable information in the localization of defect regions, not only because of its depth-resolution, but also due its sensitivity to the presence of free charge carriers and disorder.

The results show that Mu^0 formation is strongly suppressed in deposited SiO₂ (SiC-A), as seen by the higher F_D value in the oxide layer compared to less than 20% F_D in thermally grown SiO₂ (SiC-B). This is in accordance with the higher structural order with less defects expected for thermal SiO₂ compared to non-annealed deposited SiO₂. Looking at the interface, represented in Figure 1 by the region between the dotted lines, SiC-A is not affected by the deposited SiO₂ while thermal oxidation leads to a change of the defect concentration close to the oxide/semiconductor interface, evident by the suppression of Mu^0 formation, with and extension of 15 nm in SiO₂ and 30 nm within SiC. Furthermore, F_D depends on the growth orientation: both SiC-B and SiC-C have a thermal SiO₂ layer, but we only observe a larger F_D in the oxide of the first sample. This can be attributed to the faster oxidation on C-face, resulting in a broadened defective region compared to Si-face. In SiC-D, a SiO₂ layer was deposited after HF etching of the thermal oxide and no defective region in oxide layer near the interface is observed. The different doping of the SiC samples is also reflected in the observed diamagnetic fraction, which is about 20% larger for highly doped SiC-B, since the higher concentration of free charge carriers (electrons) causes an increase of F_D.



Figure 1: Top: Diamagnetic fraction F_D measured at T=10 and 260 K with muon implantation energies E=4-20 keV. The colored curves correspond to the fit to the experimental points obtained when a step-like shape of F_D as function of sample depth, represented in the bottom plots, is assumed. Bottom: Depth-models of F_D variation within the SiO2/4H-SiC samples. The width of the colored lines indicates the standard deviation of the fit parameters. The dashed lines represent the interface position uncertainty measured with XRR [4].

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Modeling of the point defect migration across the AIN/GaN interfaces – *ab initio* study

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Increased diffusion of defects near interfaces is a commonly observed phenomenon that is influenced by temperature, pressure, electric fields and defects concentration gradients. Migration of substitutional defects and self-diffusion of atoms usually takes place via vacancy mediated mechanism and such migration is of a primary importance in the materials used in high power, high frequency microelectronic devices, like high-electron-mobility transistors (HEMTs). Recently, the AlGaN/GaN or AlN/GaN high-electron-mobility transistors (HEMTs) with an ultrathin AlN barrier operating at higher frequencies have attracted considerable interest due to possibility of obtaining both high carrier density and excellent high frequency performance [1,2]. However, the AlN/GaN interfacial quality can be affected by a number of factors including a high density of threading dislocations, interface roughness, or cracking of the highly strained AlN layer. A mechanism of defect diffusion at the AlGaN/GaN heterointerface is also not fully identified [3-5], and it requires an intensive research to address high requirements connected with application of these materials as high quality HEMTs.

In the present paper we performed DFT-based modeling of point defects migration through the AlN/GaN heterointerfaces in order to find the preferred directions of such migration and to check possibilities for accumulation of certain defects at the interface area. We studied a motion of single nitrogen, aluminum, and gallium vacancies (V_N , V_{Al} , V_{ga}), in various charge states, as well as of complexes $Ga_{Al}+V_{Al}$, $Al_{Ga}+V_{Ga}$ consisting of substitutional atom and metal vacancy. For this purpose a model of the stoichiometric superlattice with the AlN/GaN interface type adapted to two growth modes of AlN on GaN along hexagonal *c* axis: pseudomorphic and lattice matched ones was used, in analogy to that of paper [6]. We used a 4x4x6 supercell consisting of 384 atoms in both types of AlN/GaN interfaces. In the following, by means of the Nudged Elastic Band (NEB) method we calculated the migration energy barriers of the above defects in bulk wurtzite GaN and AlN crystals. Heights of energy barriers were determined both in *a* and *c* crystallographic directions, and they served as benchmark for the corresponding energy barriers present near the AlN/GaN heterointerface.

We show in particular that the formation energy of V_N in bulk GaN and AlN crystals is smaller than that of metal vacancy, both in N-rich and Ga(Al)-rich growth conditions. The presence of Al_{Ga} decreases formation energy of metal vacancy V_{Ga} in bulk GaN. The energy barrier related with diffusion of single nitrogen vacancy in bulk GaN and AlN crystals is larger than that of metal vacancy. Depending on the migration direction, it is in the energy range 2.78 – 3.5 eV and 3.13 – 4.06 eV for AlN and GaN, respectively. Migration of charged defects in GaN is accompanied by smaller energy barrier than that of neutral defects.

In the case of bulk AlN we observe an increase of energy barrier related with the migration of V_N^{3+} and V_{Al}^{3-} along *a* axis by about 0.2 eV and 0.5 eV, respectively. The presence of internal electric field in bulk AlN and GaN crystals enhances migration of charged metal vacancies V_{Al}^{3-} , V_{Ga}^{3-} along *c* axis, by decreasing their energy barrier by about 0.5 eV. This behavior is

more pronounced for nitrogen vacancy $V_N^{3^+}$ in bulk GaN, where the height of energy barrier is decreased by ~ 1.6 eV. In the case of AlN/GaN heterointerfaces, we have found a preferred migration direction for all investigated defects. In particular, we demonstrate that nitrogen vacancy migrates with a decreasing potential energy barrier, when moving from AlN towards GaN material. The smallest migration energy barrier is related with crossing of the AlN/GaN interface and it amounts 2.81 eV (V_N^0), see Fig. 1, or 2.52 eV ($V_N^{3^+}$). As can be seen, these heights are in general smaller than those in bulk crystals, down to ~1 eV.

Finally, we demonstrate the influence of in-plane strain on the preferable direction of defect motion, the role of built-in electric field and charge dipole effect on the mobility of point defects in the AlN/GaN interface region.



Fig. 1. A model of AlN/GaN heterointerface and the corresponding potential energy barriers related with the migration of V_N^0 along the heterostructure's growth direction (green arrows show preferable motion direction (smaller barrier), while red arrows display the adverse one).

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High-Throughput Search of Point Defects in SiC

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Point defects in wide-band-gap semiconductors are used in many applications such as single photon emitters. Before a point defect can be utilized in these applications, an important step is to identify and understand both the defect type and different configurations. This identification is difficult due to the vast number of possible defects that can be present in a material. A promising way to identify a defect is to compare experimental data with *ab initio* calculations for many different magneto-optical properties, including zero-phonon lines, zero field splitting, and hyperfine coupling parameters. In earlier work, we made a convergence study for divacancy configurations in 4H-SiC.[1]

Based on our understanding of the convergence of these calculations, we made a collection of automatic workflows called ADAQ.[2] Here, each defect is calculated for a large range of different configurations, charges, spins, and possible excitations. Currently, we are running these calculations and producing a database for an array of different defects. So far, we have screened about 8000 intrinsic defects in 4H-SiC. Our preliminary results suggest that with this choice of methodology, useful data are obtained at a feasible computational cost for a large number of defect types and configurations available in SiC.[3]

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Dislocation relaxation in wide band gap heterostructures with trigonal and hexagonal crystal lattices

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In recent years, wide band gap semiconductor materials are increasingly replacing traditional Si semiconductors in power electronics devices including those for the space and nuclear industries, in UV radiation photoelectric converters, in high power radio-frequency devices, etc. [1-3] For example, some of these wide bandgap materials are GaN, AlN and their possible solid solutions, which have been actively studied since the beginning of the 2000s [1]. Recently, one more promising wide band gap semiconductor Ga₂O₃ has been added to these materials [4]. Compared to AlN and GaN, Ga₂O₃ has a wider band gap. This advantage allows one to use Ga₂O₃ in high power devices operating at high voltages.

Production of modern semiconductor devices based on promising wide band gap semiconductor materials is impossible without high-quality device structures. Their physical properties depend not only on their chemical composition, but also on the phase geometry, the presence of internal mechanical stresses and the presence of defects, for example, misfit and threading dislocations (MDs and TDs), cracks, pores, etc. Internal mechanical stresses can be caused both by the difference in the crystal lattice parameters of the heterostructure materials (misfit stresses) and by the difference in the coefficients of thermal expansion of these materials (thermoelastic stresses). The control of mechanical stresses leads to achieve a better crystalline quality of the heterostructure by reducing the defect density and allows one to produce heterostructures of high instrumental quality with predictable physical properties.

Now a days, there are theoretical models that describe the relaxation of coherency stresses via formation of MDs in III-nitride heterostructures on semipolar oriented substrates taking into account the operation of a set of dislocation slip systems [8,9]. The relaxation in heterostructures can be understood in the framework of Matthews-Blakeslee (M-B) energy balance approach that predicts a critical thickness for MD formation [10,11].

Among various crystal modifications of Ga₂O₃ α -phase belongs to the trigonal system [5] and can be described using either rhombohedral or hexagonal unit cell. Therefore, α -Ga₂O₃ has similarity in crystal structure with III-nitrides, which makes it possible to mutually integrate these materials into a single device with improved characteristics [6,7]. In present work, we are exploring the M-B approach to Ga₂O₃/Al₂O₃ heterostructures accounting for trigonal symmetry of the materials. For this we explore the hexagonal geometry of Ga₂O₃/Al₂O₃ heterostructures and use nonzero value of elastic constant C_{14} in our calculations [12].

Figure 1 shows the calculated dependences of M-B critical thickness h_c on inclination angle ϑ (angle between the [0001] crystallographic direction and the direction of heterostructure growth) and schematic for heterostructure. The blue and red curves show the dependences for generation of MDs originating from basal (BSMDs) or prismatic (PSMDs) plane, respectively. Solid curves correspond to Ga₂O₃/Al₂O₃ heterostructure, dashed curves correspond to AlN/GaN heterostructure. We can see from Fig. 1 that there is the critical angle ϑ_c which indicate the changing in relaxation mechanisms. In the case of Ga₂O₃/Al₂O₃ heterostructure, for the angles ϑ lower than $\vartheta_c \sim 60^\circ$, the generation of BSMDs is energetically favorable than PSMDs, and vice versa. In the case of AlN/GaN heterostructure $\vartheta_c \sim 70^\circ$. This means that for some growth orientations of considered heterostructures biaxial relaxation of misfit stresses can be realized.

Finally, we can conclude that similar critical conditions for BSMDs generation in Ga₂O₃/Al₂O₃ and AlN/GaN heterostructures are realized, but relaxation by PSMDs generation in Ga₂O₃/Al₂O₃ heterostructure occurs at smaller inclination angles ϑ than in AlN/GaN heterostructure.



Figure 1. Comparison of Ga₂O₃/Al₂O₃ and AlN/GaN heterostructures. (a) dependences of the critical thickness h_c on the inclination angle ϑ for Ga₂O₃/Al₂O₃ and AlN/GaN heterostructures.

The solid curves describe the Ga₂O₃/Al₂O₃ heterostructure, the dashed curves correspond to AlN/GaN heterostructure. The blue curves describe the case of BSMDs, the red curves correspond to PSMDs. (b) Schematic of layer/substrate heterostructures with hexagonal geometries of the material crystal lattice. ϑ is angle between the [0001] crystallographic direction and the direction of heterostructure growth. *b* is the Burgers vector; DL is used to designate dislocation lines.

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Can muons probe charge carrier kinetics in direct gap semiconductors?

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Muons, as a bulk probe of materials, can be used to study the charge carrier kinetics in semiconductors. The photoexcited muon spin spectroscopy technique ("photo- μ SR") can optically generate excess carriers in semiconductor wafers, while implanted spin-polarized muons can interact with the carriers. This interaction is manifested as an additional relaxation rate in the muon spin asymmetry signal, which can be used as a probe of the excess carrier density. As a result, carrier recombination lifetime spectra can be obtained by changing the delay between the muon and laser pulse.

In semiconductors, an implanted positively charged muon μ^+ captures an electron e⁻ and forms a bound state called muonium Mu [1, 2]. This hydrogen-like atom can be in a neutral or charged state (*e.g.* as a negatively charged Mu with two e⁻ *i.e.* Mu⁻) localized at interstitial sites. If free carriers are present in the system, Mu will interact with them via a few types of microscopic mechanisms [2]. The most relevant one in this study is considered as the carrier exchange interaction. In this process, muon spin depolarization occurs when Mu in the triplet state $|\uparrow\uparrow>$, where the first and second arrow denote the muon and electron spin respectively, is ionized by a free hole h⁺ and subsequently captures a free electron. Because the electron has its spin either in the $|\uparrow>$ or $|\downarrow>$ state, the regenerated Mu is in either the $|\uparrow\uparrow>$ or $|\uparrow\downarrow>$ state with equal probability, where the muon spin in the latter state will precess at the hyperfine frequency (in the order of GHz) and be depolarized. Based on this model, one can expect quite naturally that the induced spin relaxation rate λ will be proportional to the excess carrier density Δn .

The technique was first developed in a system of silicon [3], and then applied to the study of germanium wafers as reported in ICDS-30 [4]. Recently, we have extended the study to measure the carrier lifetime spectrum at multiple depths in a Si wafer by changing the implantation depth of a muon beam [5]. The depth-dependent lifetime spectra enable us to de-convolute and accurately measure the bulk carrier lifetime and surface recombination velocity, which is difficult to achieve with other traditional lifetime spectroscopy techniques. We anticipate a wide range of future applications centered on photovoltaics and power semiconductors.

In this method, however, it is difficult to measure carrier lifetimes shorter than ~1 μ s because Δn is assumed to stay nearly constant during the μ SR time window, where λ is measured [3, 4]. In contrast, there are many modern semiconductor materials with a direct band structure, where carrier lifetimes are typically in the order of ns. With the aim of applying the photo- μ SR technique to these systems, we have demonstrated the measurement of carrier lifetimes in GaAs as a prototype system. It is known that optically generated carriers can interact with Mu⁻ in n-type GaAs via the carrier exchange interaction [6]. The muon spin depolarization takes place during the short period before the excess carriers recombine. For measuring this transient effect in μ SR time spectra, the muon and laser pulse were synchronized to an accuracy limited by the pulse jitter (~1 ns), and the data acquisition system was configured to take μ SR time spectra with and


Figure 1. (light OFF) – (light ON) μ SR time spectra. The laser pulse was incident on the sample at $t = 0.50 \ \mu$ s.

without pump laser light *i.e.* (light OFF) – (light ON). Therefore, the amplitude of the step represents the muon spin asymmetry signal depolarized by the Mucarrier interaction. The transient curves were fitted to an exponential function and gave time constants, 4.4(9) and 20(2) ns for 290 and 21 K, respectively, which may indicate thermally activated impurity sites introducing the faster carrier recombination at RT.

The method, therefore, seems to be capable of measuring the fast carrier kinetics. However, the study requires careful consideration because the time resolution of the measurement is not only limited by the experimental setup, but

also governed by the hyperfine frequency of the Mu centers, which can exist in a few different forms in semiconductors depending on their crystalline site (e.g. tetrahedral interstitial site and bond-centered site). In addition, it is known in the studies of silicon that they can change the state dynamically with the presence of excess carriers in the system, and form a complex network transitioning from one Mu state to another [2, 3]. Hence, the validity of the method should be investigated in this perspective by simulating the time evolution of the muon spin in GaAs and studying what Mu states are involved in the depolarization mechanism. In this presentation, we will focus on illustrating the interaction between Mu and optically generated excess carriers in n-GaAs, and discuss the feasibility in applying the method to different semiconductor systems.

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Effect of pulling speed on oxygen related defects in Czochralski silicon ingots

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The Czochralski process is the most commonly used method for growing monocrystalline silicon ingots for PV applications. In the recent years, the monocrystalline silicon production has increased, creating a need for improving the current productivity. One method is to apply an active cooling technology, which makes it possible to increase the pulling speed, increasing the yield of the process. However, the effect of increasing pulling speed is not fully understood.

In this work, we aimed to investigate the effect of pulling speed on the oxygen related defects formation and their distribution. For this purpose, two ingots produced with different pulling speeds were investigated for their electrical and chemical properties, using a variety of characterization techniques, such as: Fourier Transform Infrared Spectroscopy (FTIR), Four Point Probe (FPP), Lateral Photovoltage Scanning (LPS) and micro Photoconductance Decay (μ -PCD). The ingots were cut to samples of 11 cm x 11 cm, two from each ingot: one from the crown region, which included the seed, and the other from the "body" region. The samples were first characterized under as-cut condition, while later they were submitted to a two-step (4 h at 750 °C and 16 h at 1050 °C) heat treatment to investigate its effect on the oxygen concentration and distribution.

The results indicate that the interstitial oxygen level was slightly lower in the ingot produced with higher pulling speed in the as-cut samples. Moreover, a correlation was found between the oxygen distribution, the lifetime maps, resistivity and the LPS-images: the regions with high oxygen content showed decreased lifetime and reduced resistivity, which again was recognized as a region of low resolution in the LPS-images. In addition, for the heat-treated samples, it was found that while for both crown-samples the interstitial oxygen concentration decreased after heat treatment, the body samples showed different trends. In the ingot pulled with higher pulling speed, the O_i content increased in the region of around 120-180 mm below the seed, while for the ingot produced without active cooling, the interstitial oxygen concentration was reduced after the heat treatment. We suggest that this mechanism is due to the oxygen nuclei formed during the pulling process are smaller when active cooling is applied. This would lead to dissolution during the heat treatment rather than growth.

Diffusion of donor dopants in β–Ga₂O₃ and interplay with gallium vacancies

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Vacancy-assisted impurity diffusion in semiconductors plays a central role in both device processing and fundamental understanding of the defect interplay. This is particularly true for semiconducting oxides, including beta gallium oxide (β -Ga₂O₃), a wide-bandgap semiconductor that displays exceptionally high break-down electrical fields, and that has recently attracted considerable attention as a potential candidate for power electronics and deep-UV optoelectronics.

Controlling the conductivity of β -Ga₂O₃ is important for device applications, where silicon (Si) and tin (Sn) are the most commonly used donor dopants for control of the n-type conductivity. Thus, understanding the diffusion of these elements is therefore of high technological interest. In addition, such studies can also reveal important information about the intrinsic defects in this material and their interaction with the dopant. This is in particular true for vacancies, as vacancy assisted diffusion is often the dominating mechanism for dopants replacing the cat-ion site. For



Figure 1: Depth versus Sn concentration of (a) as grown as well as samples heat treated up to 1250 °C (markers) in oxygen ambient, where the simulated profiles are shown as solid lines, and (b) show the results of the depth distribution from the diffusion simulation of the Ga-vacancies (V_{Ga}), substitutional Sn (Sn_{Ga}), the Sn_{Ga}-V_{Ga} complex, as well as the carrier concentration, *n*.

example, density functional theory (DFT) predicts the formation energy of gallium vacancies (V_{Ga}) to be highly dependent not only on the Fermi level position, but also on the chemical potential or annealing ambient. Hence, control of the intrinsic defects can in turn be utilized to control dopant diffusion in oxides.

To study the diffusion of Sn we utilize high quality films (001) grown by vaporphase epitaxy (HVPE) on Sn-doped bulk (001) substrates ([Sn] ~ 4×10^{18} cm⁻³), purchased from Novel Crystal Technology Inc. In the study, the Sn doped substrate acted as a source and the diffusion into the Sn-free HVPE layer was studied using secondary ion mass spectrometry (SIMS). The samples were heat treated in either an oxygen or nitrogen ambient for a duration of 30 min at temperatures ranging from 900°C to 1250°C.

The depth profiles of Sn in the heat-treated samples under oxygen ambient, with the as-grown profile as a reference, are shown in Fig. 1a. The profiles reveal that Sn starts to migrate from the bulk substrate into the HVPE epi-layer at temperatures above 1000°C. The diffusion profiles exhibit a plateau of Sn and a sharp drop in concentration at the diffusion front. Interestingly, under nitrogen ambient, no diffusion is observed in the same temperature range. Strongly indicating that oxygen ambient promotes Ga-vacancies and nitrogen ambient suppress them. The diffusion profiles can be simulated using a reaction diffusion model, based on a vacancy-assisted diffusion mechanism that has been successfully utilized for ZnO [1]. Fig. 1b. shows the depth distribution of the V_{Ga}, Sn_{Ga}, the Sn_{Ga}-V_{Ga} complex, and *n*.

In this model the high Fermi-level in the Sn doped region is close to the conduction band, resulting in a low formation energy of V_{Ga} , and hence contribute with an increased concentration of Ga-vacancies in the Sn-doped region. At the diffusion front, the drop in the Fermi-level resulting in a substantially lower vacancy concentration which then drastically reduce the migration of the dopants and provides a sharp gradient in the Sn-concentration. The model assumes a triply charged V_{Ga} in the upper part of the band gap, as expected from theoretical considerations [2], resulting in an even stronger Fermi-level dependence than that of the zinc vacancy in Zinc oxide [3].

The vacancy assisted diffusion modelling is further supported by hybrid functional calculations of the formation energies of Sn_{Ga} , V_{Ga} and the $V_{Ga}Sn_{Ga}$ complex. Sn prefers the octahedral Ga2 site over the tetrahedral Ga1 site in β –Ga₂O₃. This is also found for the $V_{Ga}Sn_{Ga}$ complexes, where the lowest energy configuration has Sn occupying the octahedral ic site in an off-site V_{Ga} . The attractive electrostatic interaction between the Sn_{Ga} donor and V_{Ga} acceptor results in a highly stable $V_{Ga}Sn_{Ga}$ complex. As shown in Fig. 2, the calculated binding energy is 1.63 eV under n-type conditions.



Figure 2: Left: Formation energy of Sn_{Ga} , V_{Ga} and the $V_{Ga}Sn_{Ga}$ complex as a function of Fermi-level position under O-rich conditions. Only the lowest-energy configurations are shown for the two latter defects. Right: Binding energy of the $V_{Ga}Sn_{Ga}$ complex, calculated as the difference in formation energy between the complex and the sum of the formation energies of its constituents in their most favorable configuration.

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Machine Learning Assisted Identification of Threading Dislocations

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Electron channelling contrast imaging (ECCI) is a non-destructive scanning electron microscope (SEM) surface imaging technique that is sensitive to distortion of planes in crystal lattices. It detects the diffraction intensity of electrons incident on a sample, where the angles between detector, sample normal, and the SEM electron beam, are carefully chosen so that the orientation of diffracting planes with respect to the incident electron beam is approaching their Bragg angle, creating strong contrast in the image. Local lattice strain induced deviations to the crystallographic orientation or lattice constant will then affect the intensity of the backscattered electrons, and produce a variation in contrast in the resulting surface image that indicates the presence of a defect. These images are over a relatively wide area (~100 μ m²), with a resolution of ~20 nm, and allow us to detect and classify threading dislocations, grain boundaries, and other defects at semiconductor surfaces [1].

Of particular interest is the ability to conduct a quantitative analysis of threading dislocations (TDs) present in a GaN thin film, which manifest in ECCI as spots with a black-white (B-W) contrast. One obstacle to this is the need for the painstaking marking and manual analysis of each individual experimental image by a skilled researcher. Bulk epitaxial GaN thin films often have TD area densities of 10^8 to 10^9 cm⁻² [2], adding to the scale of the problem. This creates a need for a fast, automated, and relatively accurate method of extracting defect data from multiple images.

Supervised machine learning techniques have been proven in recent years to be able to achieve a high degree of success in detecting predetermined features, particularly in the medical imaging field [3]. We have utilised previously documented techniques for quickly identifying TDs on III-Nitrides [1,4] to build a training dataset for a deep fully convolutional network architecture [5,6]. This includes images of defects both with a strong B-W contrast and dislocations at close to the invisibility criteria which are faintly resolved.

The neural network that is trained on this set can then relatively reliably detect the positions of TDs in ECCI of GaN with an accuracy on the order of 90% for independent testing data (i.e. marked images unseen by the network during training), with the main source of errors being false positives and the merger of the binary masks on defects placed very close together. The prediction process for a 2576×1936 px image currently takes around 90 seconds when using a modern 8-core consumer grade CPU. For our current dataset size the network can be trained to convergence in 30 ± 10 minutes when using a single NVIDIA A100 GPU. Fig. 1 shows the marked locations for a cluster of dislocations in GaN. We will also be discussing further work in building a general dataset for training neural networks to perform TD detection and type classification.



Figure 1: Two successful examples of the model with a predictive accuracy of ~95% (left) and ~92% (right).

Top row: Raw ECC images of different dislocation clusters spanning a $\sim 5 \ \mu m^2$ area, taken for a GaN sample grown on a nano-patterned substrate.

Bottom row: Binary mask predictions marking the positions of the dislocations on the original image.

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Fine core structure and spectral luminescence features of freshly introduced dislocations in Fe-doped GaN

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Dislocation-related luminescence (DRL) - the appearance of intrinsic, characteristic spectral bands (lines), is well known phenomenon in many semiconductors with tetrahedral coordination such as silicon, germanium and A_2B_6 , A_3B_5 compounds [1]. In the most materials the dislocations responsible for DRL were found to dissociate into partials bounded by stacking fault ribbons. The dislocations with the perfect core were observed rather seldom and no data about their luminescent property were available until recent report by Albrecht et al. [2] on the TEM observation and on DRL of the perfect a-screw dislocations in semi-insulating Fe-doped GaN plastically deformed by scratching on basal plane (0001). DRL in GaN:Fe possessed a narrow peak at 3.35 eV (called as dislocation bound exciton, DBE, that will be here further used for its designation).

On the other hand, similar type of dislocations freshly-introduced in low-ohmic n-GaN also by scratching or by indentation exhibited the dissociated core structure and the DRL band noticeable redshifted to 3.1-3.2 eV with a fine doublet structure. Besides, the formation of extended nodes at the dislocation intersections in the basal plane was observed, which also exhibited ultraviolet luminescence with a characteristic peak energy at 3.3 eV (called intersection related luminescence or IRL) [3] that is rather close to the DBE peak energy.

In this work we performed a detailed combined investigation of Fe-doped GaN plastically deformed by special type of the indentation to find correspondence between the dislocation type and core structure and their characteristic spectral luminescent features.

Semi-insulating Fe-doped wurzite-type GaN free-standing a-plane wafers produced by Suzhou Nanowin Science and Technology CO Ltd. with density of grown-in dislocations of few 10^5 cm⁻² were used as a starting material. Dislocations were introduced by the microindentation with Vickers tip in the a-plane. Cathodoluminescence (CL) experiments were conducted with Gatan MonoCL 3+ system in a chamber of SEM-Zeiss Supra at 12 K. The structural investigation was performed with TEM Zeiss Libra 200FE at room temperature in scanning mode (STEM). Two cross-section lamellas were cut in the vicinity either parallel, or perpendicular to (0001) plane with Ga focused ion beam system of Zeiss Auriga dual beam station.

Fig.1a represents CL panchromatic microgram near indentation point demonstrating the luminescence intensity enhancement due to the introduced defects. The luminous dislocation rosette consists of two arms stretching in the projection of possible $[1\bar{2}10]$ directions onto basal plane which is consistent with the expected propagating directions of the dislocation with $[1\bar{2}10]$ Burgers vector, which are perpendicular and inclined under 30° to the image surface. Recorded CL spectra revealed a peculiar regularity: in a central bright part of the network there the strongest CL signal corresponds to DRL doublet (fig.1b red graph) while closer to periphery, where bright contrast starts to fade, the main CL peak position is similar to DBE observed by M. Albrecht or (fig.1b blue graph). Such regularity sustained at different stresses and orientation of the pricks.

STEM microgram of lamella cut perpendicularly to the (0001) plane at fig.1c shows dislocation line contrasts (marked with yellow rectangles) with double contrast propagating inside the

sample orthogonally to surface a-plane. They disappear completely when lamella is tilted to the center of $0\overline{1}10$ zone (fig.1d), (former dislocation positions are also marked with same yellow rectangles), confirming, thus, their origin as perfect a-screw dislocations propagating along [$\overline{2}110$]. In the lamella with the surface parallel to (0001) plane beside the perfect core segments (fig.1e yellow rectangle) the dissociated dislocations and the dislocation extended nodes were observed (fig.1 e,f). As it can be seen in fig 1f dissociation width of the dislocations was of about 10 nm, and the extended node sizes were about ~50 nm that are greater than reported in [3] for low-ohmic n-GaN samples (5 nm and 15 nm respectively).

An examination of the CL spectra acquired both in central and peripheral part of the luminous dislocation rosette reveals the presence of an additional CL-band between DRL and DBE bands. Based on the present STEM results and previous studies [3] is presumed to be IRL.



Figure 1. a – polychromatic CL image of an area near indentation prick (black square contrast); b – CL spectra from central part (red) and periphery (blue) of the dislocation network; c,d – STEM images of lamella cut perpendicular to the (0001) plane with yellow rectangles showing perfect dislocations; e,f - STEM images of lamella cut in (0001) plane with yellow rectangle showing perfect dislocation segment, and blue rectangle in «e» marks area shown in «f».

In conclusion, the freshly introduced dislocations in Fe-doped GaN in this work exhibit not only DBE band reported by M. Albrecht et al [3], but also the bands IRL and DRL found in n-GaN [3]. Our STEM study revealed coexistence of the dislocations with dissociated and with perfect core as well as with extended dislocation nodes, thus establishing the correlation between observed previously luminescence bands and fine dislocation core structure.

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Carbon vacancy control in silicon carbide p⁺-n diodes and thick ultra-low doped n-type epi-layers

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Even though many of the bottlenecks with SiC technology have recently been resolved, point defects issues in SiC continue arresting attention of the semiconductor physics and electrical engineering communities. Indeed, one of the remaining roadblocks on the power electronics avenue is the insufficient charge carrier lifetime in SiC bipolar components. In this context, much of the attention is attracted to the carbon vacancy (V_C), known as the prime carrier lifetime killer in SiC [1]. In 4H-SiC, V_C is an electrically active defect exhibiting a double acceptor (V_C(2-/0)) at ~0.7 eV below the conduction band edge (E_C) known in literature as Z_{1/2} level and a single donor (V_C(0/+)) at ~E_C-1.5 eV known as EH_{6,7} level [2]. Typically, the V_C concentration ([V_C]) in the modern 4H-SiC epi-layers remains in the range of ~5x10¹² cm⁻³, hindering charge carrier lifetime in excess of ~5 μ s. Thus, dedicated efforts were undertaken to reduce the [V_C] in 4H-SiC by post-growth processing of the epi-wafers; in particular by injecting highly mobile carbon interstitials (C_i's) from the surface or the near surface region into the "bulk" of the epi-layer to recombine with V_C's [3-5]; targeting [V_C] < 10¹¹ cm⁻³. However, in spite of the spectacular demonstrations of the [V_C] control, there are at least two open questions:

(i) Most of the literature data verifying V_C contents were collected by doing capacitance spectroscopy on Schottky diodes, i.e. not involving high temperature processing steps inevitable in the p⁺-n diodes manufacturing; e.g. ~1800 °C anneals are necessary to activate p-type dopants introduced by ion implantation. This aspect makes the initial mastering of the $[V_C] < 10^{11}$ cm⁻³ in the epi-wafers dedicated for the bipolar device manufacturing not practical; since 1800 °C anneals might be sufficient to re-generate V_C accounting for its formation energy of ~4.8 eV [6,7]. Thus, testing the compatibility of the C_i-injection strategies with the key steps of the bipolar device manufacturing is of great added value to the field.

(ii) The V_C contents and the corresponding evolution of the lifetimes were predominantly measured in relatively thin epi-layers, not always clearly discriminating the surface proximity effects; e.g. for the lifetime measurements, even performed in a cross-sectional geometry, the proximity to the surface severely affects the data. Concurrently, performing C_i -injection experiments in sufficiently thick and lower doped epi-layer enables broader ranges for corresponding modelling not yet explored in literature.



Fig.1. (a) DLTS spectra of the $V_C(2-/0)$ in p⁺-n diodes subjected to different anneals and (b) corresponding [V_C].

In the present contribution, we report the data in line with the directions (i) and (ii). Fig.1 summarizes our the data on the C_i – injection by applying so-called carbon-cap anneals to p⁺-n diodes [8]. The peaks in Fig.1(a) demonstrates the evolution of the [V_C] as a result of anneals in the p⁺-n diode, labelled as sample C (notably, sample A was not used for the p⁺-component manufacturing and the "as-grown" data was measured by fabricating a Schottky diode on as received sample). It is clearly seen that the 1800 °C anneal, i.e. step 1) in Fig.1(a), generates V_C. Nevertheless, we also show that the "equilibrating" carbon-cap anneal at 1500 °C, i.e. step 2) in Fig.1(a), sets the [V_C] below the detection limit. Fig.1(b) summarizes the [V_C] as measured by DLTS after several different annealing steps, demonstrating that V_C is indeed a refractory defect. However, the instructive message of our work is that, the processing recipes might be extended with an additional carbon-cap annealing step at 1500-1600 °C intended to remove the V_C's generated in 4H-SiC by high temperature.

Notably, the data in Fig.1 were obtained on a standard production grade 100 mm diameter 4H-SiC wafer purchased from Cree Inc., with ~10 μ m thick epi-layer exhibiting free carrier (electron) concentration of ~1x10¹⁵ cm⁻³ as determined by the capacitance-voltage (CV) measurements undertaken at room temperature (RT) with a 1 MHz probe frequency. To explore the kinetics of the C_i-injection and to enable corresponding cross-sectional carrier lifetime monitoring, we selected additional thicker and lower doped epi-layers for further investigations. Specifically, ~150 µm thick epi exhibiting ~1x10¹⁴ cm⁻³ free electron concentration at RT, were purchased from ASCATRON. This thicker and lower doped sample was also subjected to V_C generation anneals at 1800 °C, identical in duration, temperature up/down ramps, etc. to that used in Fig.1. Notably, upon this treatment, the 150 µm thick epi was converted to highly compensated state; see Fig.2 showing data measured using Schottky diodes.



As seen from the CV data in Fig.2(a), \sim 50 µm thick region was inaccessible at RT. Less compensated material was revealed at higher temperatures. Due to compensation, the $Z_{1/2}$ level was accessible; not however, the deeper $EH_{6.7}$ level was detectable and

Fig.2. (a) free carrier profiles as measured in 1800 °C annealed 150 μ m thick epis by CV at different temperatures and (b) DLTS profiling of the EH_{6,7} level representing the single donor state (V_C(0/+)) at ~E_C-1.5 eV. Notably, the correlating free carrier profile (measured at 650K) is also shown in panel (b).

Fig.2(b) shows its depth profile, in correlation with the free carrier profile as measured at 650K. Notably, the experiment with 150 μ m thick epis is still in progress and we are presently re-doing the V_C generation anneals at lower temperatures resulting (hopefully) in less compensation and, as such, high flexibility for the DLTS measurements. Nevertheless, even being incomplete, the data in Fig.2 provide interesting insights. Indeed, the EH_{6,7} contribution to the free carrier concentration can explain the temperature dependence in Fig.2(a) and the non-uniform EH_{6,7} profile in Fig.2(b) correlates with the carrier profile in Fig.2(b); however, it is not clear why V_C generation in this 150 μ m epi sample exhibits such a strong inhomogeneity?

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Interplay between intrinsic and extrinsic defects in ZnSnN₂

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Zn-IV-N₂, with IV = Sn, Ge or Si, belong to a novel class of semiconductors, representing an earth-abundant alternative to conventional III-nitrides, currently dominating the optoelectronic market and playing a vital role in a quest for record-high efficient solar cells, specifically in multi-junction architectures. Zn-IV-N₂ semiconductors exhibit close similarities to the III-nitrides in terms of the functional properties, e.g., optical band gap tunability [1-3]. Such close similarities invite for both the knowledge transfer and combinational utilization of the III-nitride and Zn-IV-nitride systems. The main challenge for Zn-IV-N₂ in general, and for ZnSnN₂ in particular, is in controlling intrinsic and extrinsic defects, governing the carrier concentration (*n*). For clarity, in the rest of the text, we focus on ZnSnN₂, but the consideration can be generalized for the rest of the Zn-IV-N₂ systems too.

Typically, for stoichiometric ZnSnN₂, *n* remains in the range of $5 \times 10^{19} - 5 \times 10^{20}$ cm⁻³, i.e. too high for further use of the material. Possible defects causing the degeneracy in ZnSnN₂ have been identified by first-principles calculations, where the three most probable intrinsic point defects to occur are all shallow donors, i.e., the tin-zinc antisite (Sn_{Zn}), the nitrogen vacancy (V_N), and the zinc interstitial (Zn_i) [4,5]. Furthermore, common impurities in nitrides incorporated during growth, such as oxygen substituting for nitrogen (O_N), hydrogen interstitials (H_i) and substitutional hydrogen (H_N), also form donor states in ZnSnN₂ [4,5]. Nonstoichiometric growth, i.e., the fabrication of Zn-rich ZnSnN₂, is the prevailing route for controlling *n*; respectively, reducing and enhancing the formation probability of Sn_{Zn} donors and Zn_{Sn} acceptors [6]. Meanwhile, in most of literature reports, the carrier mobility (μ) remained unacceptably low (< 10 cm²V⁻¹s⁻¹). Possible *p*-type dopants in ZnSnN₂ have also been identified by first-principles calculations, where Na_{Zn} and K_{Zn} are predicted to exhibit deep acceptor levels, while Li_{Zn} is predicted to be a shallow acceptor [7]. However, the corresponding experimental explorations are rare or missing.

Here, we report on ZnSnN₂ thin films grown by high-power impulse magnetron sputtering (HiPIMS) exploring intrinsic and extrinsic defects in this interesting material. Stoichiometric and non-stoichiometric conditions were tested with and without introducing Li doping. Figure 1 shows a summary of the electrical data for stoichiometric, Zn-rich and Li-doped ZnSnN₂ thin films, as measured by Hall effect. Notably, systematic data confirming high structural quality of similar films grown by HiPIMS can be found elsewhere [8]. The results for the undoped samples (grey data points in Fig. 1) show that the increase in the Zn_{Sn}/Sn_{Zn} ratio (induced by changing the Sn target power) effectively reduces *n*; concurrently μ increases to a recordbreaking value of ~100 cm²V⁻¹s⁻¹. As such, these data are consistent with a hypothesis that Sn_{Zn} is a dominant donor-defect in ZnSnN₂. The effective band gap (E_g), estimated by the Tauc method from the optical absorption data, was gradually reduced with increasing Zn-richness, from ~1.78 eV to ~1.28 eV. Such prominent reduction in E_g as a function of *n* suggests the Burstein-Moss to be responsible for the blueshift of the fundamental band gap in the stoichiometric ZnSnN₂, due to the excess of the Sn_{Zn} donors.

Furthermore, our results confirm that Li acts as an acceptor in ZnSnN₂, reducing *n* in the stoichiometric film by an order of magnitude (see Fig.1(a-c)), while keeping μ at a reasonable high value, $\mu \sim 60 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (Fig.1(d-f)). The Li concentration ([Li]) for the stoichiometric



Figure 1. Survey of the Hall effect data for stoichiometric, Zn-rich, and Li-doped $ZnSnN_2$ thin films grown by HiPIMS; (a) the carrier concentration at room temperature as a function of Sn target power, scaling the Zn richness, (b) and (c) the carrier concentration as a function of temperature for two selected samples. (d-f) carrier mobility for the same samples.

film was determined by secondary ion mass spectrometry (SIMS), $[Li] \sim 1 \times 10^{21}$ cm⁻³, uniformly distributed through the film. As predicted by Wang *et al.* [7], Lizn acts as a shallow acceptor in ZnSnN₂; however, in the interstitial configuration (Li_i), Li may act as a donor too. Nevertheless, even both Lizn and Li_i are possible to occur in our samples, the significant reduction in *n* for the stoichiometric film, see Fig.1(a), suggests that the majority of the incorporated Li is in the form of Li_{Zn} acceptors. As mentioned earlier, the increase of the Zn-rich conditions is accompanied with the reduction of *n* too. Importantly, SIMS confirmed even slightly higher [Li] while doping the non-stoichiometric films, $\sim 2 \times 10^{21}$ cm⁻³. Notably, having similar [Li] in all samples was intentional, since only Zn-target was Li contaminated, while the stoichiometry variations were reached by varying the Sn-target power, see Fig.1(a). Thus, assuming the Li_{Zn}/Li_i incorporation ratio in stoichiometric and non-stoichiometric films. However, the data in Fig.1(a) reveal no trivial additive trends, suggesting more complex dependences between the Zn_{Sn}/Sn_{Zn} contents and the Li_{Zn}/Li_i ratios in the non-stoichiometric samples. In other words, we observed an intriguing interplay between intrinsic and extrinsic defects in ZnSN.

In conclusion, there are two interesting strategies to resolve the challenge of reducing n in ZnSnN₂ to meet the application-specific requirements; the non-stoichiometric growth, i.e., increasing the Zn_{Sn}/Sn_{Zn} ratio, and introducing extrinsic Li_{Zn} shallow acceptor states. We applied these two strategies in combination and observed that the interplay between the intrinsic and extrinsic defects is not simply additive in ZnSnN₂; calling for further studies to understand the physics and to master the corresponding synthesis conditions.

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Steady-state Photo-capacitance Spectroscopy of Intrinsic Defects in Electron-Irradiated β -Ga₂O₃

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Monoclinic gallium oxide (β -Ga₂O₃) is an ultrawide-band gap semiconductor receiving considerable research interest as a promising material for high-power electronics applications [1]. Realization of β -Ga₂O₃ devices requires a mature understanding of both the types of point defects in the material and how to control them. In particular, intrinsic defects, such as vacancies and interstitials, are expected to be electrically active and may influence the performance of a device. From density functional theory (DFT) calculations, gallium vacancies (V_{Ga}) are predicted to act as deep acceptors, the gallium interstitial (Ga_i) is associated with a donor state, the oxygen vacancies (V_O) give rise to deep donor states, and the oxygen interstitial (O_i) can be both a donor or acceptor depending on its configuration [2, 3]. However, the experimental verification of the intrinsic defect transition levels remains elusive.

In this study, intrinsic point defects in β -Ga₂O₃ were introduced by electron irradiation of varying energy and fluence. Electrically-active defects across the entire band gap of β -Ga₂O₃ were studied



Figure 1: Derivative SSPC spectra of electron irradiated HVPE β -Ga₂O₃. (a) The spectra are recorded on two samples irradiated by 400 keV electrons with two different fluences, 1×10^{16} cm⁻² and 5×10^{16} cm⁻². The recorded spectrum of an as-grown sample is also shown. (b) Two spectra from samples irradiated with the same fluence of 1×10^{16} cm⁻² and two different electron irradiation energies of 400 keV and 1.5 MeV.

using space-charge spectroscopy techniques including deep-level transient spectroscopy (DLTS) and steady-state photo-capacitance (SSPC) spectroscopy. The study draws motivation from similar studies conducted on zinc oxide [4, 5], where variable energy electron irradiation was used to create point defects selectively on the different sublattices.

The samples studied here are halide vapor-phase epitaxy (HVPE) grown, (001)-oriented β -Ga₂O₃ thin-films with a carrier concentration (N_d) of ~ 2 × 10¹⁶ cm⁻³ purchased from Novel Crystal Technology Inc. The samples were irradiated at room temperature by electrons with energies of either 400 keV or 1.5 MeV and with fluences of either 1 × 10¹⁶ cm⁻² or 5 × 10¹⁶ cm⁻² at the SIRIUS irradiation facility [6]. Schottky barrier diodes (SBDs) were formed on the samples using a stack of Ti (10 nm) and Al (120 nm) as back side ohmic contacts and Ni (150 nm) deposited through a shadow mask as front side Schottky contacts. The SSPC measurements were conducted at 80 K, with the SBDs kept in reverse bias throughout the measurement and illuminated with a near-monochromatic light at a certain energy for 300 s before measuring the steady-state capacitance.

Derivative SSPC spectra for the photon energy range 2.0 to 3.5 eV are shown in Fig. 1. The SSPC signal for the samples irradiated with 400 keV electrons for two different fluences, as well as from an unirradiated reference sample are given in Fig. 1a. The 400 keV electron irradiation gives rise to at least two features that are not present in the unirradiated reference sample. The increase in the height of the SSPC features with increased fluence leads us to tentatively assign them to intrinsic defects, which is consistent with previous studies [7]. Spectra recorded on samples irradiated with equal fluence and different energies are shown in Fig. 1b. The appearance of the two spectra in this figure are quite similar. However, there appears to be a slight shift in the highest intensity peak towards higher photon energies for the 1.5 MeV irradiated sample. Interestingly, this shift can possibly be attributed to the creation of additional intrinsic defects or defect complexes, due to the increased formation of V_{Ga} in samples irradiated with 1.5 MeV electrons compared to 400 keV electrons. These results will be discussed in relation to theoretical estimations from DFT calculations and modeling of the SSPC spectra.

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Study of Ti contacts to corundum α -Ga₂O₃ – ohmic behavior and interfacial reactions

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Gallium Oxide (Ga₂O₃) is an emerging wide bandgap semiconductor with applications in solarblind ultraviolet (UV) sensing, and high-power electronics [1]. This material exists under several phases (α , β , γ , δ , ε , κ), with the monoclinic β -phase attracting most attention owing to its thermodynamic stability. In comparison, the rhombohedral α -phase is metastable but displays several advantages compared to the other phases of Ga₂O₃: for example it (i) exhibits the largest bandgap (5.3 eV) amongst all phases, (ii) is isostructural with several other semiconducting group-III or transition metal sesquioxides (*e.g.* In₂O₃, Ti₂O₃) and (iii) is isostructural with the cheap and widely available sapphire (α -Al₂O₃) substrate.

Metallic contacts play a central role in the working principle and overall properties of semiconductor devices. In β -Ga₂O₃, Ti is routinely used as the metal of choice in order to produce ohmic contacts [1]. However, in this phase the metallic layer has been reported to react with the semiconductor to form a thin TiO_x interlayer upon annealing [2]. In α -Ga₂O₃, the properties (ohmic/rectifying) and chemical stability of metallic contacts are, at the moment, unexplored. It is however important to conduct a phase-specific investigation of contacts as the band alignment and perhaps more importantly the thermodynamic stability of Ga₂O₃ are inherently different for the β and α phases. In this study, we investigate the properties of Ti contacts on α -Ga₂O₃ films grown by atomic layer deposition.

Films of non-intentionally doped α -Ga₂O₃ (thickness 250 nm) were produced by atomic layer deposition, and Ti/Au (20/80 nm) contacts were evaporated and subsequently annealed under N₂ ambient for 2 min at temperatures of 350-600°C. The films were characterized by atomic force microscopy (AFM), X-ray diffraction (XRD), UV light-assisted I-V measurements and high-resolution scanning transmission electron microscopy (HR-STEM) with energy dispersive X-ray spectroscopy (EDX).

Topographical and structural analysis from AFM and XRD reveal no observable changes in α -Ga₂O₃ film structure and morphology upon annealing. Figure 1(a) shows the AFM and XRD data of the sample after growth – which remained unchanged upon contact deposition and annealing treatment.

Electrical characterization of the samples in the dark and under 240 nm and 350 nm light confirm that the structures can be used for solar-blind photodetection. Because the films are undoped and highly resistive, the ohmic or rectifying behavior was assessed under 240 nm illumination [3]. All the contact structures displayed ohmic behavior, irrespective of the annealing temperature. We note however strong variation in contact performance with annealing temperature. The maximal (photo)conductivity was obtained for the structure annealed at 450°C, while the device electrical properties degrading rapidly for higher annealing temperatures.

To understand the impact of annealing on the contact structure, HR-STEM and EDX were conducted on the as-deposited device and the sample annealed at 600°C. In the as-deposited sample, the semiconductor and metallic layers can be clearly distinguished (Figure 1(b)). Voids at the Ga_2O_3/Ti interface can be observed in places, which may help explain why the electrical properties can be improved using gentle annealing.

On the other hand, the sample annealed at 600°C exhibits a distinguishably different structure (Figure 1(c)). The Ga₂O₃ film contains several voids, and the Ti film has transformed almost entirely into a TiO_x film. This is a clear evidence of reduction of Ga₂O₃ by Ti, where the grain boundaries and amorphous inclusions in the film provide fast diffusion pathways for this reaction, leaving the α -Ga₂O₃ crystallites relatively unaffected. It is interesting to note that the obtained structure is different from that observed in β -Ga₂O₃ [2], which underlines the necessity for a phase- and method-specific study of contacts in Ga₂O₃ devices.



Figure 1 – (a) XRD and AFM (inset) scans of the as-deposited sample demonstrating α -phase Ga₂O₃ films were obtained. STEM and EDX maps of the (b) as-deposited sample, and (c) sample annealed at 600°C.

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Electrically Active Extended Defects in Ferromagnetic Structures based on Ga(Mn)InAs compounds

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Heterostructures with a small lattice mismatch on the base of epitaxially grown compound semiconductor layers are of a wide usage in modern micro- and nanoelecronics. However, a formation of a specific surface morphology known as cross-hatch pattern (CHP) [1] may essentially affect the homogeneity of active layers and result in a dispersion of their electrical, magnetic and optical properties that, in turn, could influence the device performance and stability. Most of current explanations of CHP nature relate the surface CHP with the network of misfit dislocations (MDs) at the lattice-mismatched interfaces between internal layers of heterostructure. For instance, in (Ga,Mn)As/(In,Ga)As/GaAs ferromagnetic structures considered in this work, the geometry of characteristic CHP features (valleys and ridges) on surface is correlated with MDs network on the (In,Ga)As/GaAs interface. However, the phenomenon of CHP formation is not understood completely, and a few contradicting models are regarded [1,2]. Therefore, the study of the defects formed in InGaAs and GaMnAs layers during a growth and a lattice relaxation looks as useful and promising approach for further understanding of the phenomenon. Recently, the specific electrically active extended defects were detected in the InGaAs buffer layers of (Ga,Mn)As/(In,Ga)As/GaAs structures by electron beam induced current (EBIC) [3,4]. It was shown that these defects were located in the vicinity of GaAs/(In,Ga)As interface and in the InGaAs layer. The orientation of these defects was found to be the same as that of CHP on the surface of heterostructures. Presumably, these defects are formed in the dislocation slip planes under strain relaxation of growing epilayers and may participate in CHP formation.

The heterostructures studied were fabricated on n⁺-GaAs substrate and consisted of GaAs and InGaAs buffer layers, grown by vapor phase epitaxy at 650°C and capped by upper p⁺-GaMnAs layer formed by laser sputtering technique at 330°C. Epitaxial buffer layers (InGaAs and GaAs) were doped by n- or p-type dopants in different samples that allows to analyze the electrically active defects in various areas of the structure. The electrically active defects in GaAs and (In,Ga)As buffer layers were studied by the deep level (DL) transient spectroscopy (DLTS) and capacitance-voltage (CV) profiling. Only one DL, the well known EL2 center, was found in n-type GaAs/(In,Ga)As buffer layers. By the study of carrier capture kinetics, it is shown that one of them, the DL E_V +0.65 eV, can be identified as an extended defect. The depth distribution of the defects demonstrates descending dependence on the distance from the GaAs/InGaAs interface; nevertheless, the defects are detectable in the whole width of the InGaAs epitaxial layer. The origin of the revealed DL defects, their possible relation to the extended defects observed by EBIC [4] and to the process of CHP-formation are discussed.

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Highlights of 15R crystal phase in au-catalyzed ZnS nanowires

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Unique growth mechanisms involved in semiconductor nanowires (NWs) pave the way to the achievement of new crystallographic phases and remarkable material properties, and hence, studying polytypism in semiconductor NWs arouses a strong interest for the next generation of electronic and photonic applications. Interestingly, in the case of 1D nanostructures, polytypism can arise due to the particular growth mode below a catalyst droplet, that may induce different stacking sequences along the length of the nanowire. In semiconducting NWs, a high density of randomly distributed twin defects and stacking faults has commonly been observed[1]. However, the stacking faults can be correlated and form ordered arrays, until giving rise to new phases (polytypes) with distinct properties[2,3]. Hence, 4H, 6H, 8H, and 10H (so-called high order polytypes) have been observed in nanowires[4].

ZnS is an important II-VI semiconductor which has a wide range of optoelectronic applications including luminescent devices, infrared windows, and UV-photodetectors [5]. Bulk ZnS compound exhibits numerous unstable polytypes at high temperatures, but their stable occurrence is highly anticipated in a nanowire due to its special quasi-dimensional shape and growth modes. In this work, Au-assisted ZnS nanowires were grown by metalorganic chemical vapor deposition (MOCVD), directly on GaAs (111B) substrate, and on ZnS (buffer)/GaAs (111B). This latter case is illustrated in Figure 1. The idea is to provide a change in the growth mechanism *via* the physical state of catalyst droplet (liquid or solid) and hence, study the induced structural modifications in ZnS nanowires.



Fig. 1. The schematic diagram of ZnS nanowires growth on ZnS buffer/GaAs (111)B

Using GaAs, Ga from the substrate diffuses into the Au droplet which results in the formation of an alloyed nanoparticle, liquid at NW growth temperature (550° C). Thus, the NW growth mode in such case is called VLS (vapour-liquid-solid). On the other hand, by depositing a buffer layer of ZnS on GaAs (111)B, the gold droplet is prevented from diffusion of Ga from the substrate. The catalyst droplet remains solid and therefore the growth may proceed as a VSS (vapour-solid-solid). ZnS nanowires with length up to 1.4 µm and diameter in the range 10–34 nm was successfully achieved. Their structural characterization using TEM is shown in Fig 2(a-b) and allowed to compare the two growth modes. Nanowires grown directly on GaAs (VLS mode) shows the 15R crystal structure⁶. This structure is highlighted for first time in ZnS nanowires. Interestingly, regarding nanowires grown on ZnS buffer (VSS mode, solid catalyst), a different crystal structure made of pure ZB and WZ phases was observed.

The cathodoluminescence studies were performed on both type of nanowires. No significant luminescence was observed due to non-radiative surface recombination. To tackle

this issue, a 15-20 nm ZnMgS shell was deposited around the ZnS nanowires to passivate the surface. The cathodoluminescence spectrum of ZnS/ZnMgS core/shell structure grown on GaAs is given in figure 3, and confirms the significant luminescence coming from the core at 326, 390 and 480 nm, as well as from the shell at 316 nm.



Fig. 2. HRTEM image of ZnS nanowires (a) VLS process: 15R crystal structure, (b) VSS process: WZ/ZB pure phases.



Fig. 3. Cathodoluminescence spectra of ZnS/ZnMgS core/shell nanowires

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Electron Irradiation-Induced Defects In Carbon doped n-GaN

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Gallium nitride (GaN) is a promising material for applications in devices designed to work in the aerospace and thus knowledge on radiation induced defects is of high importance. To fabricate devices for high performance and high reliability applications they have to have excellent structural quality but primarily, devices with low number of defects present in the crystal structure is the key issue. Otherwise, one can expect efficiency decrease and fast device degradation.

Moreover, there are very limited papers dealing with irradiation in GaN and the origin of the radiation-induced defects is still not clear and speculative only.

In this paper, we present our initial results on deep traps in n-GaN layers created in the process of electron irradiation with energy of 9-MeV. Two types of the samples have been analyzed and discussed: i) medium (C~1x10¹⁷ cm⁻³) and low carbon doped (C<1x10¹⁶ cm⁻³) n-GaN diodes grown by the MOCVD technique, respectively. We observed a new peak in DLTS spectra after electron irradiation with a dose of $1x10^{14}$ cm⁻³. New signal appears at low temperatures (T~100K) and the activation energy related to radiation-induced electron trap is close to 145 meV.

Our results have been analyzed mostly with the use of Deep Level Transient Spectroscopy (DLTS) [1] and High Resolution Laplace DLTS [2] technique (LDLTS). We also verified the radiation impact on optical properties and thus the samples were studied by Photoluminescence (PL) and Cathodoluminescence (CL).

The samples studied in this paper were n-GaN Schottky diodes grown on 2-inches sapphire substrate as well as on 1.5 inch native GaN substrate. Both sample sets were grown by MOCVD (*Metal-Organic Chemical Vapor Deposition*) technique where 0.7-1 µm thick n-GaN layer (Si:1-3x10¹⁶ cm⁻³) was deposited on highly doped (Si:2x10¹⁸ cm⁻³) sapphire template or n-type Ammono-GaN substrate [3]. The metal contacts were fabricated using standard photolithography technology with commonly used metal stack consisting of Ti/Al/Ni/Au for ohmic contacts deposition followed by annealing in nitrogen atmosphere at 850 °C for contact formation. Circular Schottky diodes with standard Ni/Au (200/1000 Å) contact metallization were fabricated. The diodes were then exposed to 9-MeV electron irradiation with an expose dose of $1x10^{14}$ cm⁻³ at 300K.

The diodes were then tested @300K with Hg-probe C-V (*Capacitance-Voltage*) and I-V (*Current-Voltage*) measurements. The net donor concentration profile (N_D-N_A) obtained from C-V was uniform and estimated to 2×10^{16} cm⁻³ and 2.8×10^{16} cm⁻³ for samples on sapphire and GaN substrate, respectively. The net donor concentration has slightly changed after irradiation what is shown in figure 1. Finally, n-GaN:C SBDs have been studied by the DLTS and Laplace DLTS techniques in temperature range from 80K to 500K.

Typical DLTS spectra measured for irradiated (black curve) and non-irradiated (red curve) n-GaN:C diodes on sapphire are presented in figure 2. Besides commonly observed in n-GaN

electron traps: Ec-0.25-eV, Ec-0.45-eV and Ec-0.7-eV, a trap with an activation energy of 0.145-eV is present in irradiated sample as well. Similar DLTS signal was observed by others however reported activation energies are slightly different: Ec-0.18-eV [4] and Ec-0.12-eV [5]. This discrepancy can be somehow related to lower radiation energies used by Fang (1-MeV) and Duc (2-MeV) in respect to 9-MeV used in this study. Moreover, Duc [5] studied n-GaN samples grown by HVPE technique. Additionally, one can see that 9-MeV irradiation resulted in a slight shift of 400K peak to lower temperature suggesting formation of a new defect after irradiation. In general, the concentration of radiation-induced defects is around 10¹³ cm⁻³.

Finally, PL and CL analysis performed at 300K and 77K did not reveal any new features in the measured spectra. However, we expect that low temperature luminescence (4K) could give more information related to donor-bound exciton transition as shown by Look [6] and these experiments are planned to be carried out soon.



Figure 1. The net donor concentration profile (Nd-Na) taken at 300K for irradiated and non-irradiated sample.



Figure 2. Typical DLTS spectra for 9-MeV irradiated and non-irradiated n-GaN:C sample grown on Al2O3.

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Robust spin coherence with optical access for the Zink-Vacancy in ZnSe

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Despite long history of defect centers in ZnSe, knowlegde of spin coherence times, in particular of Zn and Se vacancy centers, is litte. This study presents time resolved pump probe resolved measurments TRPP. Spin beatings are used to unambigious characterization of defect center type and coherence time characterization. Temperature, magnetic field pertupations as well as several host crystals, isotopically purified, natural composed as well as ex situ created defects by ion implantation or intrinsic defect of imperfect MBE growing were used to identify the most important decoherence mechanisms.

In case of isotopically purified host crystal the dominant hyperfine interaction is sufficiently switched off and a robust coherence time of 100 (-400) ns in room (cryogenic) temperature was found. The anisotropic exchange interaction (Dzyaloshinskii-Moriya interaction) was indentified as next main limitation. In its essence it describes the next neighbor spin interaction. Such as a control of defect density may lead to further improvements in coherence time.



Fig. 1: **a** PL of ZnSe epilayer with ex situ (A) and intrinsic (B) Zn vacancy centers. **b** zoom into bandgap region of ZnSe. Pronounced exciton features are observed resonant to excitation energies for TRPP measurments . **c** TRPP signal with characteristic spin beatings.

Evolution of hydrogen-related defects in float zone-grown silicon wafers under dark annealing: resistivity change vs. FT-IR

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Hydrogen plays a crucial role in conventional silicon-based solar cells because it passivates the electrical activity of a wide range of point defects and impurities [1]. Recently, however, the presence of hydrogen was connected with detrimental light-induced degradation (LID) mechanisms, such as the light and elevated temperature-induced degradation (LeTID). The defect (or defects) responsible for LeTID has not been identified and is related to the difficulty in directly detecting hydrogen-related defects. In silicon, electrically inactive dimeric forms of hydrogen are energetically preferable over those containing a single hydrogen. Furthermore, hydrogen-related species typically occur in low concentrations (<10¹⁵ cm⁻³) in commercial wafers that are below the detection limit of most conventional techniques. A method to indirectly quantify hydrogen in silicon wafers was recently proposed and is based on measuring the resistivity change after dark annealing at ~160 °C for over 200 hours [2]. The method assumes a constant hydrogen concentration between two species (H₂ and HB) and that prolonged annealing converts H₂ into HB. Despite its simplicity, the resistivity change technique cannot distinguish between different hydrogen-related species and imposes restrictions on the. Fourier Transform-Infrared (FT-IR) spectroscopy is a powerful technique that can distinguish between various hydrogen-containing impurities in a material by their localized vibrational modes (LVMs), but its use has been limited by the need for large bulk pieces with long path lengths.

Recently, we presented a method for preparing thin (~180 μ m thick) commercial silicon wafers for low temperature FT-IR by mechanically polishing a stack of silicon wafers to optical quality [3]. Here, we use this method to compare the evolution of hydrogen-related species in commercial *p*-type (B-doped) float zone-grown silicon wafers during prolonged dark annealing at 160 °C between the resistivity change and FT-IR techniques.



annealing for 0, 16, 64, and 233 hours.

Figure 1 shows IR absorbance spectra of the LVMs of HB (1904 cm⁻¹) and the isolated H₂ molecule (3618.4 cm⁻¹) measured in wafers halted after annealing for 0, 16, 64, and 233 hours. No other H-related LVMs were detected in the samples. With prolonged annealing the HB and H₂ LVMs increase and decrease, respectively. After annealing for 233 h, the H2 LVM is below the detection limit of our measurements.

The resistivity change method assumes that all of the hydrogen is present as a dimeric species, in this case H₂. However, the data in Figure 1 show that HB is present in the initial (t=0) state, which likely depends on how rapidly the wafers are cooled to room temperature after the firing process.



Figure 2. Comparison of the H_2 and HB concentrations during isothermal dark annealing at 160 °C for increasing annealing time determined by low temperature FT-IR (solid points) and from the resistivity change (solid curves). The total H concentration, 2[H₂]+[HB], is given by the unfilled squares (FT-IR) and the dashed line (resistivity change). The red and grey shaded regions indicate the uncertainty about the solid curves.

Figure 2 compares the temporal evolution of the H₂ and HB concentrations determined by the two different techniques. We find good agreement on both aspects between the two techniques within the experimental uncertainties. Interestingly, the total H concentration determined by FT-IR does not appear to be constant, but rather increases with annealing time. Low temperature FT-IR measurements (not shown) of nonhydrogenated wafers after 233 h of dark annealing show an increase in the HB concentration in the order of 10¹⁴ cm⁻³, whereas the H₂ LVM is not detected at any stage of annealing. These observations suggest that another hydrogen-related species "hidden" from our measurements also dissociates during dark annealing at 160 °C, which supports recent suggestions in the literature [4].

Resistivity change measurements are easy to implement, simple, and require no additional sample preparation outside of the normal processing scheme. In contrast, low temperature FT-IR measurements require an

advanced instrument and specialized equipment such as a cryostat. In addition, measurements of hydrogen-related vibrational lines can require several hours of measurements depending on the desired signal-to-noise ratio. The time requirement also limits the number of samples that can be analysed by FT-IR. However, the key advantage of FT-IR is the direct identification of hydrogen-related species and their quantification. Direct measurements by FT-IR can provide invaluable insights into the relevant species and their concentrations as a starting point for more complex models.

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Generation rates of electron-hole pairs due to a passage of protons and Si ions: investigation by the methods of time-dependent density functional theory and electron force field

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We have carried out a direct simulation of the passage of protons and silicon ions through silicon by the methods of electron force field implemented in molecular dynamics approach and time-dependent functional theory (TDDFT). In the first approach, we calculated a stopping power for moving protons and Si ions and determine energy spectrum for excited electrons and also their spatial distribution with respect to the track of the initial ion. We have found that the results of this calculation are strongly dependent on the correctness of description of an ion charge at a fixed energy [1]. In the second one (TDDFT), we also have calculated stopping power of protons and Si ions in silicon. We have found a good agreement between the methods we used at the energies of passed particles where the degree of ionization of passing silicon ion does not exceed the number of electrons described by the plane-waves basis instead of the frozen solution into the pseudopotential. Usage of average energy required for electron-hole pair production (3.62 eV)[2] allows us to estimate the generation rates of such paires in both aprroaches we used.

Also, we concluded that the collision of a single ion with a lonely target atom can be described by the TDDFT approach at an incident ion energy limited by 100 keV/nucleon.

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Electronic structure of neutral group-IV Vacancy colour centres in diamond

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Impurities in diamond is of interest due to their broad range of applicability. Various point defects embedded in diamond and realized as a solid-state quantum bit, bioimaging agent, or ultrasensitive electric or magnetic field sensor. The negative SiV was demonstrated to be indistinguishable single photon source in diamond with addressable electron spin. However it has a short spin coherence time even at cryogenic temperatures. Recently it has been found that the neutral SiV as a S=1 system has a long coherence time and is verv promising for quantum communication applications [1]. However, the electronic structure of SiV⁰ is not yet completely understood. In our work [2], we employ plane-wave supercell calculations on SiV⁰, GeV⁰, SnV⁰ and PbV⁰ with density functional theory methods and beyond then compare the results with the experimental data.

Initially the 1.31 eV ZPL was erroneously assigned [3] to a ${}^{3}A_{2g} \leftrightarrow {}^{3}A_{1u}$ transition. Recent uniaxial stress measurements revealed [4] that the ZPL itself is a



Figure 1 - (a) Potential energy surface of triplet states of SiV^0 . We show the optical zero phonon line (ZPL) with a black solid arrow. We label the electron-phonon coupled solutions by tilde in the excited state with energy gap of 6.7 meV. (b) Triplet states of SiV^{0} . (c) Geometry of the undistorted SiV^0 defect with D_{3d} symmetry. We also depict the X and Y distortion paths of the E_g phonon mode that are quasi-localized on the six carbon atoms.

 ${}^{3}A_{2e} \leftrightarrow {}^{3}E_{u}$ transition and there is an optically inactive 3A2u state below the 3Eu excited state by 6.7 meV. Our present model model agrees well with this result and provides a physical background for these findings. We propose that the excited state of SiV⁰ is a $(e_g \otimes e_u) \otimes E_g$ type product Jahn-Teller (JT) system [5] as depicted in Figs. 1 and 2. According to our results there is one hole on eu and a second one on eg one-electron orbital in the excited state of SiV⁰, see Fig 3. for details. These two holes cooperatively create an even greater geometric distortion (see Eg phonon mode in Fig. 1c) known as JT effect that was observed in SiV⁻, or other XV⁻ defects already [6]. In summary we provide a model for SiV⁰ center and predict the properties of GeV⁰, SnV⁰, PbV⁰ centres that might be also interesting qubit candidates if successfully embedded in diamond.

This work is described in Ref. [2].



Figure 2 – (a) Ab initio adiabatic potential energy surface (APES) as obtained from Kohn-Sham DFT for the optically excited states of SiV(0), where m_c refers to reduced mass of the vibration. The four layers of the APES are corresponding to the four electronic excited states depicted in Fig. 3(a). The X=0 point refers to undistorted geometry exhibiting D_{3d} symmetry. The global minimum in APES is obtained upon releasing all symmetry constraints that yields $E_{JT}^{(1)}$ energy. We determined the $E_{JT}^{(2)}$ energy by fitting quadratic polynomials on the data points. (b) The convergent polaronic (strongly electron-phonon coupled) eigenstates and expectation value of the distortion (R) from the D_{3d} symmetry in dimensionless unit. We label the lowest two vibronic solutions and their δ energy gap between them ($|^3A_{2u}\rangle$ and $|^3E_u\rangle$) that can be associated with the optical signals of SiV(0).



Figure 3 – (a) Kohn-Sham levels of the SiV(0) defect in its $|{}^{3}A_{2g}\rangle$ ground state and its four excited state single determinants, as obtained from ab initio DFT calculations. The Kohn-Sham orbitals in the spin-up (spin-down) channel are represented by triangles pointing upwards (downwards). The filled (empty) triangles depict occupied (empty) orbitals. The e_{ux}, e_{uy} orbitals in the spin-down channel fall into the valence band (VB) and are smeared, so their position is very schematic. However, the e_{ux}, e_{uy} orbitals in the spin-up channel form resonant and localized states above the VB edge far from the conduction band (CB). We show the optical excitation path of the $|{}^{3}A_{2g}\rangle$ ground state by an inclined arrow pointing upwards. (b) Visualization of single particle Kohn-Sham wavefunctions.

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Tailoring quantum defect properties for quantum transduction with trapped ions

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Neutral shallow donors (D^0) in zinc oxide (ZnO), such as indium, gallium, or aluminum substituting for zinc (In_{Zn}, Ga_{Zn}, or Al_{Zn}, respectively) are promising solid-state spin qubits for quantum communication applications. We have demonstrated that ensembles of Ga_{Zn} donors in hydro-thermally grown ZnO have spin relaxation times of up to 500 ms and spin-echo times of 50 µs [1]. In the direct bandgap semiconductor ZnO, D⁰ couple optically to the neutral donorbound excitons D^0X with high radiative efficiency, which proves useful in achieving communication involving disparate photon-based quantum systems. One such example is a trapped ytterbium ion Yb⁺ whose ${}^2P_{1/2}$ to ${}^2S_{1/2}$ transition with wavelength near 369 nm, similar to the D⁰X to D⁰ transition of the In_{Zn} donors.

In this contribution we will be discussing the potential quantum transduction applications involving ZnO donor qubits and Yb⁺ via optical channels. This study is motivated by the lack of a qubit system that out-performs its competitors in all computation-related tasks. Hybrid quantum systems will assign tasks that are optimally designed for each quantum system. However, one must modify/engineer the quantum systems so they can efficiently communicate with each other. Here, we explore two potential methods to use the ZnO donors and Yb⁺ platforms; a) the photon-heralded entanglement of a single donor with a single trapped ion [2], and b) the storage of a single photon emitted by a trapped ion in an ensemble of ZnO donors that acts as an optical quantum memory.

To achieve photon-heralded entanglement between the two systems, the emitted photons must originate from disparate single photon sources with indistinguishable emission characteristics. There is little research on single donor isolation on ZnO. Two potential solutions are the use of ZnO nanowires which will result in a small donor concentration, or indium diffusion into the surface of an indium-free ZnO crystal. Compared to, the Yb⁺ $^{2}P_{1/2}$ to $^{2}S_{1/2}$ transition, the D⁰X to D⁰ transition of the In_{Zn} is detuned by approximately 0.36 THz and has a 6 times shorter lifetime (see Figure 1(a) and Figure 1(b) for the energy diagrams). Contrary to the Yb⁺, the defect system has high potential for tunability; a feature we aim to exploit. For example, the frequency mismatch can be bridged via the dc Stark effect. Using the dc Stark effect requires the application of electrodes on the surface of the sample. As we propose in [2], using a detuned cavity-assisted Raman scheme and weak excitation with shaped laser pulses, it is possible to generate photons with 99 % temporal overlap. Methods that are currently investigated for optimal cavity design are ZnO nanowires and cavities fabricated on bulk samples via focused ion beam milling. Utilizing cavities will also allow for frequency tuning in case the Stark-shift cannot achieve shifts as high as 0.36 THz.

For optical quantum memory schemes, frequency matching and large optical depths (OD) are required. Using transmission and reflection spectroscopy on a 300 μ m thick ZnO bulk crystal, we measured the OD of D⁰X ensembles to be approximately 10. This OD is large enough to

enable optical quantum memory schemes like the controlled reversible inhomogeneous broadening (CRIB), atomic frequency combs, or DLCZ, as summarized in [3]. These potential protocols require different levels of engineering (e.g., the use of electrodes for CRIB). Such schemes will enable ZnO donor ensembles to be used in quantum repeaters for efficient photon-heralded state transfer of Yb⁺, or turning Yb⁺ to an on-demand single photon source.

In conclusion, our work will encourage the use of engineered hybrid systems for various quantum computing and communication applications.



Figure 1 Partial energy level diagrams of the ZnO donor (a) and ¹⁷¹Yb⁺ (b). Energies are not to scale, except for the $|e\rangle \rightarrow |1\rangle$ transitions. The qubit system in ZnO is composed of the two electron spins $|0\rangle$ and $|1\rangle$ with excited level $|e\rangle$ of the neutral donor D⁰. This state is optically coupled to the donor-bound-exciton state D⁰X consisting of the donor, two-electron spin singlet, and hole. The ¹⁷¹Yb⁺ qubit is formed by the $|F = 0, m_F = 0\rangle$ and $|F = 1, m_F = -1\rangle$ hyperfine levels in the ²S_{1/2} ground state.

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Comparison of β-Ga₂O₃ photoluminescence upon anneals in vacuum, oxygen- and gallium-rich atmospheres

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Monoclinic gallium oxide (β -Ga₂O₃) is a modern ultra-wide bandgap semiconductor, characterized by a bandgap of ~4.9 eV, and attracting much of attention because of its potentials in power electronics and UV optoelectronics [1]. Meanwhile, the light emission properties of β -Ga₂O₃, e.g. in form of the photoluminescence (PL), are remarkable in terms of its undermined near-band-edge (NBE) emission. Instead, the PL spectrum of β -Ga₂O₃ consists of several bands, abbreviated as UV luminescence (UVL), blue luminescence (BL), green luminescence (GL), and red luminescence (RL) bands in literature. The UVL band is related to the recombination of free electrons and self-trapped holes [2] and is taken out of the consideration in the rest of the abstract, while the prime focus is on the BL and GL bands.

Indeed, in literature, the BL and GL bands have been attributed to transitions involving deep donors and acceptors. Assuming intrinsic material, possible donors under consideration are oxygen vacancies (V_O) and Ga interstitial (Ga_i); while possible acceptors are Ga vacancies (V_{Ga}) or V_O - V_{Ga} complexes. [3, 4]. Considering the theoretical stabilities of the intrinsic defects and connecting it to the experimental observations, the BL components at 3.0 and 2.8 eV were correlated with V_O - V_{Ga} and V_{Ga} on tetrahedral site, respectively; while the GL and RL components at 2.4 eV and 1.8 eV were assigned to the neutral Oi and V_{Ga} acceptor on tetrahedral site, respectively [5]. However, even though this identification is currently accepted in literature, the complexity is certainly very high and searching for reliable experimental arguments is of great value.

Notably, tuning intrinsic defects balance in oxides by anneals metal/oxygen atmospheres has shown to be useful in optical defect identification previously [6]. In present work, we applied this approach to β -Ga₂O₃, comparing PL data after anneals in vacuum, gallium-rich, and oxygen-rich atmospheres. Our benchmark is that, in accordance with the theoretical calculations V_{Ga} and V_O-V_{Ga} exhibit lower formation energies under oxygen-rich conditions, while Ga_i and V_O have lower formation energies under gallium-rich conditions [5]. Further, we assume that, vaccum anneals are assisted with the increase in the V_O-V_{Ga} content.

Bulk (-201) β -Ga₂O₃ crystals used in the present work were purchased from Novel Crystal Technology. The samples were nominally undoped, exhibiting free (electron) carrier concentration of 2.4 x 10¹⁷ cm⁻³ as measured by the Hall effect at room temperature (RT). The samples were cut into 5x5 mm and subsequently sealed in quartz ampoules (synthetic – to avoid alkali impurities) for vacuum and gallium-rich atmospheric anneals. Oxygen-rich anneals were performed in a tube furnace with an oxygen flow of 1 sccm. PL properties of the samples were investigated at 10 K employing a 246-nm-wavelength laser with an output power of 11 mW as an excitation source.

Figure 1 shows an example of the 10K PL spectra of β -Ga₂O₃ annealed under three different atmospheric conditions at 600 °C and 900 °C for 1h in comparison with the virgin sample. Firstly, shape of the spectra are common for β -Ga₂O₃, demonstrating a dominating peak at ~3.06



Fig.1: 10K PL spectra of β -Ga₂O₃ annealed under (a) Ga-rich atmosphere, (b) O-rich atmosphere and (c) vacuum. The dashed line is for eye-guidance, marking the dominant peak position.

eV, even though different bands can be deconvoluted. Secondly, it is evident that while vacuum and gallium-rich anneals prominently affect the PL intensity, the oxygen-rich anneals induced much less dramatic changes; consistently with the initial hypothesis of variable defect stabilities. It must be noted, this work is in progress; similarly to the approach in Ref.6, we are presently doing converse O/Ga-rich anneals on the samples from Fig.1 (a) and (b), respectively; to cross-check whether the PL intensities will be re-established. Corresponding electrical data, in combination with Rutherford backscattering (RBS), UV-Vis spectroscopy and X-ray diffraction (XRD) are used to support our conclusions.

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Polytypism in Zinc Sulphide thin films during RF Magnetron Sputtering

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Polytypism widely exists in IV-IV, III-V, and II-VI semiconductors due to their freedom in the atomic stacking of layers consisting of cations and anions or simply characterized as stacking faults, a planar type defect. An excellent example is SiC compound, which has more than 200 polytypes [1]. Interestingly, both experimental and theoretical studies have shown that the zincblende ZB (3C) and the wurtzite WZ (2H) phases are the most common polytypes of II-VI and III-V compounds; having a bilayer stacking of ABCABC in the ZB-[111] direction, and ABABAB in the WZ-[0001] direction, see Fig. 1. The WZ and ZB crystal structures share many similarities in terms of atomic arrangements, where each atom has four nearest-neighbor bonds, and it is only the third-nearest-neighbor geometry, which distinguish the crystal structures [2]. The difference in total energies between two phases are also small, hence, both of them can be prepared experimentally. Controlled polytypism has been documented in nanostructures, for example, in the III-V InAs & InSb nanowires [3] and II-VI CdSe [4] & CdTe [5] nanocrystals.

diffraction X-rav (XRD) and transmission electron microscopy (TEM) were used to an accurate determination of the lattice parameters of ZB, WZ, and 4H polytypes and the analysis shows that the occurrence of hexagonal bilayers tend to stretch the distances of atomic layers parallel to the c axis and to reduce the in-plane distances compared to those in ZB phase. Moreover, the lattice parameters scale linearly with the hexagonality of the polytype (i.e., the fraction of bilayers with hexagonal character - 2H, 4H, 6H, etc.).



Fig. 1: Primitive unit cells for hexagonal xH polytypes (6H, 4H and 2H-wurtzite), and cubic (3C-zincblende) symmetry of ZnS polytypes. The stacking sequence of the cationanion bilayers are indicated by the symbols A, B, or C.

Zinc sulfide (ZnS), an important wide band gap semiconductor of the IIB-VI groups, mostly found in one of two structural forms cubic ZB (sphalerite) or hexagonal WZ, which have wide bandgaps of 3.58 eV and 3.80 eV, respectively at room temperature (RT) [6]. Further development of the optoelectronic and photoelectric devices requires an achievement of controllable band-gap engineering (BGE), which can be achieved by isoelectronic replacement of host anions or cations, for example, with wurtzite ZnO (3.3 eV at RT) leading to formation of $ZnO_{1-x}S_x$ alloys with bandgap in the range of 2.7 to 3.62 eV [7]. Various growth methods been utilized for preparing ZnS thin films, among them RF magnetron sputtering has the ability to control the deposition parameters more easily. To date, most of the studies focus on

deposition parameters like temperature, sputtering powder and sputtering atmosphere (Ar, Ar/H₂S, Ar/H₂, etc.). Importantly, careful examination by XRD suggests predominant stabilization of wurtzite structure over zincblende structure [8].

In the present work, influence of chamber pressure (1.6 - 11.6 mTorr) on the formation of different types of ZnS polytypes along with other process parameters; temperature (RT - 600

°C), substrate (c-Al₂O₃, r-Al₂O₃, fused silica, Si (100), Si (111), and Si (110)), and sputtering power (50W - 125W) was investigated. Studies show that low process pressure stabilizes cubic ZB structure, while increasing the process pressure stabilizes 2H and then 4H polytype, respectively. Another factor is the deposition rate, which influences the stabilization of different polytypes. Similar observations has been made in gallium nitride (GaN), where the metastable ZB phase was formed at low process pressure and thermodynamically stable WZ phase at high process pressure [9]. This study shows that RF magnetron sputtering could potentially utilized to deposit different polytypes of II-VI, III-V compounds by controlling the extent of stacking fault formation for specific applications.



Fig. 2: XRD spectra of ZnS thin films deposited by RF Magnetron sputtering with 90W sputtering power at different process pressure. The dashed lines represent the characteristic XRD peaks of ZB, WZ and 4H polytypes of ZnS.

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Muonium in β-Ga2O3

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As a transparent conducting oxide (TCO), β -Ga2O3 has a band gap of nearly 5 eV and nearly 10^{18} cm⁻³ free carrier concentration, making it both conductive and transparent well into the ultraviolet [1]. In addition to a melting point of nearly 2000 K, β -Ga2O3 is a suitable candidate for high-temperature gas sensors [2]. The source of some properties (e.g. conductivity) in TCOs are still being investigated, though current work suggests hydrogen and related impurities may form shallow donor states contributing to the conductivity. Shallow donor behavior of hydrogen as a contributing source in a number of oxides has been verified by Muon Spin Research (MuSR) experiments (e.g. see [3]). Direct study of the isolated hydrogen impurities in semiconductors is not generally possible due to hydrogen's high reactivity or solubility limitations within the host; however, muonium (Mu⁰= μ^+e^-) is an experimentally accessible analog to isolated hydrogen, which allows for an investigation into the stability and dynamics of these impurity centers (e.g. see [4]).

Previous Muon Spin Research (MuSR) work on β -Ga2O3 identified a shallow donor as well as two static states below 400 K that convert to a dynamic state above 400 K [5]. Our previous work included a series of measurements that provided some options for the likely configurations: (1) relaxed bond-centered O–Mu–Ga; (2) antibonding with an O atom in an (O–Mu)⁻ configuration; or (3) bridge bond where the Mu is shared between nearby O. Ultimately our β -Ga2O3 project was put on hold as other materials took priority. Due to the recent spike in interest in β -Ga2O3, we revisited these old data and completed a new experiment utilizing the quadrupolar level-crossing resonance (QLCR) technique on the EMU spectrometer at the Science and Technology Facility Council *ISIS Neutron and Muon Source* (STFC-ISIS; Didcot, UK) in order to gain insight into the specific bonding configurations and try to better characterize associated Mu dynamics. Since Ga is spin 3/2, QLCR measurements [4] provide detail on the proximity to a nearby Ga and hence clarify the Mu (H) bonding configurations.

We report on the behavior and characteristics of neutral and charged muonium ($Mu^{0;+;-}$; c.f. $H^{0;+;-}$) in β -Ga2O3. Through a combination of new muon quadrupolar level-crossing resonance data and our collaboration's previous work we have been able to develop a better model of the Mu states in this system.

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Quantum-well features of Shockley stacking faults in 4H-SiC

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Silicon carbide is a popular wide bandgap semiconductor with broad range of industrial applications and an emerging interest in quantum technology. More than 200 polytypes with competing energies are reported for unique stacking arrangements of Si-C unit layer. As a result, SiC is prone to stacking faults introduced by local slippage in stacking sequence. On the other hand, stacking faults in 4H-SiC polytype have recently attracted attention for hosting color centers that can function as room temperature qubits [1]. Motivated by this recent finding, we investigate Shockley stacking faults in 4H-SiC both in experiment and first principles simulations. In the latter, we investigate the energetics and electronic structure of Shockley stacking faults using large-scale supercell calculations and different levels of theoretical approximations. We report that the stacking faults introduce quantum well-like states below the conduction edge and exhibit luminescence distinct from bulk 4H-SiC, in agreement with experiments. By comparing the unique electronic structures of the stacking faults with photoluminescence spectra, we identify various Shockley stacking faults in our sample. Our results could assist in improvement of quantum emitters in 4H-SiC.

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Influence of annealing on the electrical properties of ITO deposited under different ambient atmospheres

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Indium-tin oxide (ITO) is a transparent conducting oxide (TCO) that is widely used in device applications such as flat-panel displays, flexible electronics, thin film photovoltaics, smart glass windows, etc., and often device fabrication involves thermal and chemical treatments. General requirements for TCOs are low electrical resistivity and high transparency in visible spectral region. Although ITO films show high transparency and electrical conductivity at room temperature, the electrical property often degrades, when ITO films are exposed to oxidizing atmospheres (Air or oxygen-O₂) at temperatures higher than 300 °C. The increase in resistivity was attributed to the decrease of oxygen vacancies or compensating oxygen interstitials in the ITO film. Nevertheless, annealing in inert nitrogen (N₂) atmospheres improve the electrical conductivity due to formation of donor-like oxygen vacancies. Importantly, in ITO enriched with oxygen vacancies, the conduction band is pinned to the Fermi level affecting the work function [1].

ITO films can be fabricated by DC and RF magnetron sputtering, electron beam evaporation, thermal evaporation, spray pyrolysis, chemical solution deposition, and sol-gel method. Among the various methods, magnetron sputtering often used by industry to fabricate commercial optoelectronic devices. Magnetron sputtering enables control of the electrical and optical properties of the films through different process parameters such as sputtering pressure, sputtering power, substrate temperature, discharge voltage and ambient gases. Among these parameters, the ambient gases are important parameters that determine the electrical and optical properties of the ITO films, but have only precursory evaluation in the literature. Sputtering has been reported with singular ambient gases including inert argon (Ar), oxygen (O₂), hydrogen (H_2) and nitrogen (N_2) to enhance the electrical and optical performances of the ITO films. The oxygen vacancies (V₀) are believed to be responsible for the lowering resistivity and decreasing optical transmittance in the ITO films. Normally, ITO films sputtered with Ar+O₂ ambient to suppress V₀ in the ITO films and post-annealed in H2 atmosphere to improve the electrical the optical properties. The enhancement of oxygen concentrations in ITO films is a challenging process for the researchers and only a few reports were available for the preparation of ITO films sputtered with different ambient combinations (e.g. Ar with two reactive gases). For example, initial reports provided a preliminary investigation into the use of an Ar+O₂+H₂ ambient mixture, which was suitable for producing high quality (lowest sheet resistance and high optical transmittance) ITO films [2]. To build on this promising preliminary work and develop deeper insight into the effect of ambient atmospheres on ITO film growth, this study provides a more detailed investigation of the effects of ambient combinations of Ar, O₂, H₂ on sputtered ITO films. Magnetron sputtered ITO films are deposited under the Ar, Ar with O₂, Ar with O₂ and N₂, Ar with O₂ and H₂ and Ar with O₂, N₂ and H₂ ambient combinations and characterized for structural, electrical and optical properties.
In this study, five different ITO films were prepared with different ambient atmospheres: (1) Ar only, (2) Ar+ O_2 , (3) $Ar+O_2+N_2$, (4) $Ar+O_2+H_2$, and (3) $Ar+O_2+N_2+H_2$. For all the cases, the flow of Ar was maintained constant at 18 sccm and for the respective cases the O₂, N₂ and H₂ was fixed at 1 sccm; in addition to Ar flow. ITO films were deposited on Corning glass substrates by DC magnetron sputtering at room temperature by keeping all other process parameters constant. The experiments were repeated three times reproducibility to ensure the of sputtered film properties. Figure 1 shows the sheet resistivity of the asdeposited ITO films under different



Fig. 1: Four-probe sheet resistivity of as-deposited and post-annealed ITO films prepared under different ambient sputtering atmospheres.

ambient combinations and post-annealed in air atmosphere for 1 hour. A correlation is performed between the electrical and optical properties of ITO films followed by post-annealing, which were presented and discussed in detail to gain an understanding of the material growth and how the optoelectronic properties influenced by different ambient combinations.

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Elastic constants of pseudo-graphenes

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Graphene is a very promising two-dimensional material for various applications [1]. Due to its high mechanical and outstanding electronic properties, graphene is in the center of active theoretical and experimental studies for almost two decades.

Defects in the crystal lattice of graphene, among which wedge disclinations are often encountered, significantly affect its physical and mechanical properties [2]. Highly density networks of disclinations of alternating signs in graphene lead to the formation of new 2D carbon allotropes called pseudo-graphenes (PG) [2].

Pseudo-graphenes demonstrate a strong difference in properties compared to graphene. For example, some of PGs change their electronic band structure from semi-metallic to semiconducting [3] or metallic [4] ones.

In this work, we present the results of computer simulation of the elastic constants of pseudographenes with low excess energy compared to graphene. The calculations were performed using the molecular dynamics (MD) method and density functional theory (DFT). MD method was implemented within the LAMMPS software package. Different potentials of interatomic interaction, such as REAX, AIREBO, Tersoff and LCBOP were used. When modeling with the DFT we used the "Quantum Espresso" package. The exchange-correlation potential was treated in the framework of the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE).

The values of elastic constants for several low excess energy pseudo-graphenes (see Fig. 1) found in simulations are presented in Table 1. A comparison of the results obtained by aforementioned methods as well as a comparison of the interatomic interaction potentials used in simulations are presented and the applicability of these potentials for calculations by the MD technique are discussed.



(phagraphene)

Fig. 1. Graphene and two low excess energy pseudo-graphenes: 5-7A and 5-7B.

Material		DFT	Tersoff (MD)	AIREBO (MD)
Graphene	E, GPa	960	1160	847
	ν	0.180	-0.159	0.299
PG 5-7 A	E1, GPa	890	850	840
	E2, GPa	931	853	860
	v ₂₁	0.208	0.015	0.282
	v ₁₂	0.194	0.058	0.231
PG 5-7 B	E1, GPa	857	579	940
	E2, GPa	916	635	941
	V21	0.214	0.399	0.074
	v ₁₂	0.205	0.292	0.109

Table 1. Young's modulus and Poisson ratio of graphene and low excess energy pseudographenes

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Near-Surface SiV Charge Behavior After Cold Hydrogen Treatment

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Optically-active, solid-state spins coupled to integrated photonic circuits are among the most promising platforms for scalable generation of cluster states. Unfortunately, the most studied defects in diamond, the negatively charged nitrogen-vacancy (NV⁻) and silicon-vacancy (SiV⁻) center lack the appropriate combination of optical stability, and long spin coherence times needed for robust quantum experiments. Recent work[1] suggests that the neutral charge state, SiV⁰, may possess both a lifetime limited linewidth, and ms long coherence times yet a full understanding of this charge state is lacking. Currently, photoluminescence (PL) from SiV⁰ has only directly been observed in highly p-doped diamond, and only one group has observed single SiV⁰ confocally. We investigate the PL of shallow, co-implanted SiV and NV after hydrogen termination to quantify the magnitude of band bending, and the relative charge behavior of both. We describe the development of a reversible, cold hydrogen plasma treatment that hydrogen-terminates the surface of our diamond while minimizing etching and ion implantation into the diamond[2]. We also discuss measurements to directly measure the photoluminescence from SiV⁰.



Fig. 1: Wetting contact angles before and after hydrogen termination for samples with NV/SiV implanted 60 nm and 15 nm deep in sample are shown on left. Confocal scans of implanted squares, showing slightly reduced PL at 60 nm, and complete disappearance of PL at 15 nm are shown on right. The PL returns for the 15 nm sample after an acid clean, demonstrating the reversibility of the process.

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Positively Charged Muonium in Cadmium Oxide

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Cadmium oxide is a transparent conducting oxide (TCO) that has many applications in optoelectronic devices, such as solar cells, photo transistors and diodes. CdO is a naturally n-type TCO [1, 2] with hydrogen acting as a shallow donor [2]. Muon Spin Research (MuSR) [3] utilizes positive muons to study hydrogen-like defects in semiconductors since the muon is the same charge and spin as the proton, but 1/9 the mass. Muonium ($Mu=\mu^+e^-$) is treated as a short lived, light isotope of hydrogen that can show the early time history of isolated hydrogen defects.

MuSR zero field measurements were collected, from 20 K to 800 K, to investigate the diffusion properties of positive Mu defects (c.f. H^+) in CdO powder sample. The Mu⁰ shallow donor signal is seen up to 200 K when it ionizes, as was also seen by Cox, et. al. [4]. There are two Mu⁺ sites seen, Mu₁ and Mu₂. At 425 K, Mu₂ becomes mobile and transitions to the Mu₁ site. By 550 K, only the Mu₁ site is occupied. Details relating to the transitions between sites, barrier energies, rates for capture processes, and muonium diffusion in CdO will be discussed in this presentation.

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Electronic states and radiative transitions in germanium doped with shallow donors: effect of short-range potential

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The energies of electronic states of group-V donors in germanium are well known from experimental data [1, 2] and can be classified in accordance with the states of the hydrogen atom: orbitally degenerate excited states (2p and higher) are in quantitative agreement with the theoretical calculations of Faulkner [3] within the framework of the effective mass method, while the ground 1s state splits into a $1s(A_1)$ singlet and $1s(T_2)$ triplet [4] due to the valley-orbit interaction [5] caused by the "central cell" potential (the short-range part of the impurity potential) [6]. While the experimental data are a fairly reliable source of information on the energy spectra of donors, the analysis of the rates of intracenter radiative and nonradiative transitions and the quantitative prediction of an external influence on donors that can increase the quantum efficiency of THz photon generation requires the calculation of the wave functions of localized carriers.

In our previous work [7], using the envelope function approximation and the Ritz variational method, we calculated the envelope functions of low-lying $1s(A_1)$, 2s, $2p_0$, $2p_{\pm}$, $3p_0$ states of shallow donor centers P, As, Sb in germanium, taking into account the short-range impurity potential. Each impurity was characterized by its own field

$$U_{sh-r}(\mathbf{r}) = -\frac{Ge_0^2}{|\mathbf{r} - \mathbf{R}_0|} \left(B \exp\left(-\eta |\mathbf{r} - \mathbf{R}_0|\right) + \left(1 - B - \frac{1}{\varepsilon_s}\right) \exp\left(-\kappa |\mathbf{r} - \mathbf{R}_0|\right) \right), \tag{1}$$

where G, B, η and κ are phenomenological parameters, which are fitted individually for each impurity. The parameter G plays the role of effective charge of ion core, while B, η and κ describe decay of the short-range potential with the distance from impurity.

Donor	В	$\eta (a_0^{-1})$	$\kappa(a_0^{-1})$	G
Ge:P	0.47	0.42	0.41	1
Ge:As	0.47	0.40	0.41	1
Ge:Sb	0.47	0.49	0.48	1

Table 1. Phenomenological characteristics of impurity potential for each donor in germanium. They differ from parameters presented in [7] due to advance in calculations.

The proposed approach [7] made it possible to distinguish the wave functions for each impurity and to obtain the dependence of the energies of excited states on the type of impurity. However, the constructed model was limited to the single-valley approximation, which has a high accuracy for excited states [3], but does not allow us to introduce the triplet level $1s(T_2)$ into consideration, and also to describe the valley-orbit splitting of the 1s state [6]. In a current work, the previously proposed method was developed taking into account the

multivalley nature of the conduction band of germanium; in particular, the wave functions of the singlet and triplet, consistent with excited hydrogen-like states, were calculated for substitutional donors P, As, Sb.

We solve the Shrödinger equation in a multi-valley approximation. The problem with the onevalley anisotropic Hamiltonian and the short-range potential is solved using the Ritz method, while valley-orbit interaction is treated as a perturbation. The wave functions $\Psi(\mathbf{r})$ of localized states are calculated as a sum over Bloch states $\varphi_i(\mathbf{r})$ of four *L* valleys:

$$\Psi(\mathbf{r}) = \sum_{j} \alpha_{j} F_{j}(\mathbf{r}) \varphi_{j}(\mathbf{r}), \qquad (2)$$

where $F_i(\mathbf{r})$ are envelopes in coordinate representation, and α_i satisfy the condition

$$\sum_{j} \left| \alpha_{j} \right|^{2} = 1.$$
(3)

We search for envelopes in the following 4-parametric form:

$$F_{j}(\mathbf{r}) = N_{0} \left(\exp\left(-\sqrt{x^{2} + y^{2} + (\beta/\gamma)z^{2}}/R_{1}\right) + C_{0} \exp\left(-\sqrt{x^{2} + y^{2} + (\beta/\gamma)z^{2}}/R_{2}\right) \right), \quad (4)$$

where $\gamma = m_{\perp}/m_{\parallel}$ is the anisotropy parameter of the effective Hamiltonian in the singlevalley limit, R_1 and R_2 have the meaning of two effective radii of the envelope function (R_1 has a magnitude of the effective Bohr radius, while R_2 reflects influence of the short-range potential), C_0 is the dimensionless "weight" factor determining the "mixture" of these contributions, N_0 is the normalization factor, and β characterizes the anisotropy of the envelope function. In order to characterize the intervalley mixing in some universal manner we introduce the parameter Q that can be considered as amplitude of the valley-orbit mixing for each donor center. The results of calculations are presented in Table 2.

Table 2. Energies and parameters of the envelope functions of the unperturbed state (without valley-orbital interaction). $Ry^* = \frac{m_\perp e_0^4}{2\hbar^2 \varepsilon^2} \approx 4.33 \text{ meV}, a_B = \hbar^2 \varepsilon_s / m_\perp e_0^2 \approx 10.39 \text{ nm}.$

Donor	$E^{(0)} (Ry^*)$	$R_1(a_B)$	$R_2(a_B)$	C_0	β	$Q, Ry^* \cdot a_B^3$
Ge:P	-2.48	0.51	0.044	1.19	0.48	0.0034
Ge:As	-2.54	0.50	0.045	1.27	0.48	0.0035
Ge:Sb	-2.33	0.55	0.040	0.91	0.46	0.0046

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Illumination-Induced Defectivity in β-Ga₂O₃ Epilayers

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We have shown that high-temperature annealing of β -Ga₂O₃ under above-bandgap illumination drastically alters defect kinetics and distribution compared to annealing without illumination. Traditionally, diffusion of defects in β -Ga₂O₃ and other semiconductors is assumed to be controlled by thermodynamic processes, with kinetics only coming into play as a rate-limiting factor. However, in wide-bandgap semiconductors the electron-hole recombination energy often exceeds the defect formation energy, meaning that excess carrier recombination can generate and annihilate defects without any thermodynamic input. The easiest way to generate such carriers is through shining above-bandgap light on a sample. To investigate the alteration of defects by this carrier generation/recombination, we annealed β-Ga₂O₃ epilayers in air at high temperatures (≥1000 °C) while shining above-bandgap light on the samples, then subsequently guenched rapidly to room temperature to lock in the generated defects. Electrical JV, CV, and DLTS characterization revealed an entirely new slate of never-before-seen defects in the illuminated samples compared to control samples annealed under the same conditions but with no light. These defects drastically altered and degraded the electrical properties of the epilayers, and were generated both near the surface as well as deeper within the epilayer. The illuminated and non-illuminated annealed samples show no overlap in DLTS signatures; both contain numerous distinct defects. Control samples at room temperature showed that these effects only occur when annealed at elevated temperatures. We investigate the multiple methods by which the light-sample interaction at high temperature could alter the slate of defects and reproduce our observations. Direct generation of electron-hole pairs within the sample from the above-bandgap light followed by recombination imparting energy to the lattice is the most likely possibility. It is also possible that the light excites the oxygen in the air or converts it to ozone, altering the boundary conditions of the diffusion problem. This work shows the promise of using such non-thermodynamic factors to alter defect diffusion and kinetics, opening up an entirely new class of methods to fine-tune the electrical properties of not only β -Ga₂O₃ but wide-bandgap semiconductors in general.

A Framework for Calculating Defect Concentrations Including Under Generalized Quenching Implemented in MATLAB

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The framework for calculation of the equilibrium concentrations of point defects in a charge-neutral, infinite material at a given temperature is in principle well-established (with allowances for uncertainties of chemical potentials and formation energies as functions of temperature), as is the case for quenching all defects from a high growth or processing temperature. Both of these limiting cases provide extremely-useful limiting cases for defect concentrations exhibited by real-world samples at room or cryogenic temperatures where measurements are carried out and devices operated. However, neither limit will ever be strictly obeyed because kinetic processes such as mass transport via diffusion and reactions between defects are required to establish equilibrium. We introduce the concept of generalized quenching to predict defect concentrations for a system of defects each of which has a different freezing-in temperature based on its diffusion rate.

In real-world samples of finite dimensions and having boundaries that can act as sources or sinks for defects, different defects' concentrations freeze-in at different temperatures during growth and processing by virtue of the various diffusion mechanisms required to bring them towards equilibrium. The observed concentrations and freezing-in temperatures depend at least on the sample geometry (characteristic dimensions), assuming no thermal gradients. A concrete example might be the temperatures at which vacancy concentrations are frozen into bulk-grown boules of 1 mm diameter compared to 100 mm diameter; in the later case the center of the boule will tend to see vacancy aggregation at higher temperatures where vacancies can still escape to the surface of the smaller boule. Modern ab-initio calculations have progressed to the point where the diffusion barriers for various defects' diffusion and the reactions between defects can be predicted with reasonable accuracy.

In this work we developed a calculation framework and implement it in MATLAB for prediction of defect concentrations under conditions of equilibrium governed by chemical potentials, under full quenching from high to low temperature, and under conditions of generalized quenching. The inputs to the calculations are the standard information for each defect's charge states including sublattice density, formation enthalpy (e.g. from DFT), the influences of chemical potentials and Fermi level.

The case of generalized quenching allows the user to specify separate freeze-in temperatures for each type of defect and a list of temperatures at which the defects' charge states' concentrations should be computed (at minimum, a max and min temperature). The calculation then proceeds by equilibrating the defects at the max temperature, then sequentially freezing in the total concentration of each defect type as each freeze-in temperature is crossed. The unfrozen defects at each temperature are equilibrated according to their Fermi level and chemical potentials while the frozen defects' total numbers are fixed (from some higher temperature) while their fractions of charge states allowed to vary with Fermi energy. Charge balance is enforced on the collection of frozen and un-frozen defects in order to determine the Fermi level and concentrations. At the next temperature, the new set of frozen and un-frozen defects are identified and the procedure repeated until the desired lowest temperature is reached. While generalized quenching obviously reduces the generality of calculations (in fact the freezing temperatures should be assigned for each defect according to the sample dimension squared, its diffusion barrier, and an estimated attempt prefactor), this approach can be powerful for estimating concentrations in real-world samples especially in cases of high contrast in diffusion rates – for example when both interstitials and vacancies are present. Examples are given using the system of native defects in β -Ga₂O₃. The goal is to make these MATLAB tools for defect concentration calculations under non-standard conditions available to the semiconductor defects community at <u>https://scarpulla.eng.utah.edu</u> by the time of the conference.



Figure 1 – Schematic of diffusion lengths for three hypothetical defects compared to the characteristic dimension of a real-world sample at different temperatures. Starting from the maximum temperature, Defect 1 is the first to freeze-in. For all lower temperatures, its total concentration is fixed but the fraction of its various charge states can vary. At a temperature above T_o , Defect 3 freezes in while Defect 2 (a very fast diffuser) can still equilibrate according to the chemical potentials on the sample boundary.

Spin-dependent transport in silicon carbide devices

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We report on the development of a compact room temperature low field electrically detected magnetic resonance (EDMR) spectrometer recently established at the University of Melbourne. The system is being used to investigate atomic-scale paramagnetic defects involved in the spin-dependent recombination (SDR) process in various silicon carbide (SiC) devices. Deep level defects in SiC have recently drawn significant interest as promising candidates for quantum applications as it has been shown that some defects have coherence times comparable to the nitrogen-vacancy centers (NV) in diamond [1,2]. In addition to being a material more amenable to electrical device fabrication than diamond, CMOS-compatible SiC has a range of polytypes available which allow the properties of a particular defect to be tuned.

At low magnetic fields where the internal magnetic field due to the presence of nuclear spin starts to dominates, hyperfine-induced spin-mixing is observed [3], similar to giant magnetoresistance-related effects previously reported in organic electronic devices [4]. Magnetometry based on this effect is explored in a junction diode device and experimentally optimized to achieve a sensitivity of approximately 30 nT/ \sqrt{Hz} . The all-electrical self-calibrating magnetometer is applicable to a wide range of applications where cost, compactness, and power consumption requirements are critical [5]. This hyperfine-induced spin-mixing effect is also observed in a commercial SiC power transistor, where it was found to have a unique and strong dependence on electric field and temperature. These results may provide new insights on the underlying physics of the hyperfine-induced spin-mixing effect, but also demonstrates that commercial SiC power transistors are readily available device platforms suitable for studying spin-dependent transport.

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Electronic properties and the dominant levels in ZnON

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Zinc Oxynitride (ZnON) is a novel material system that has received a significant increase in research publications over the last few years, due to its potential as a high mobility thin film transistor. However, ZnON also has potential as an n-type top cell absorber in tandem solar cells. The band gap is tunable in the vicinity of 1.7 eV [1], [2], [3] by varying the O:N ratio. Sputter deposited films have been demonstrated with electron mobilities up to $120 \text{cm}^2/\text{Vs}$ [4] and carrier concentrations between $10^{17} - 10^{18} \text{ cm}^{-3}$ [5], [6]. Furthermore, it is often reported as either an amorphous or nanocrystalline semiconductor [7], [8]. ZnON films can be achieved with magnetron sputtering, utilizing cheap, abundant and non-toxic target materials.

We have deposited ZnON films by both RF and DC magnetron sputtering at room temperature, utilizing 150W and 100W respectively. The flow of N₂ and O₂ were varied between samples, but the sum $O_2 + N_2$ was kept constant at 20sccm. Samples were deposited on fused silica substrates and on 7.5 Ω cm B doped Cz-Si to create pn-junctions and. Film thickness range from 950 to 1240 nm. Room temperature Hall, X-ray diffraction (XRD) and UV-VIS-NIR has been utilized to characterize films grown on fused silica. Mesa diodes were created by e-beam evaporating 300nm Al top contacts, a subsequent 1M HCl etch of the surrounding film. Silver paste were used as the back contact. Current voltage (IV) and Thermal admittance spectroscopy (TAS) were used to characterize these diodes.

As illustrated in Fig. 1, Hall mobility decrease with increasing O-content for the RF-series, from 88 to $24\text{cm}^2/\text{Vs}$. This trend is also observed for carrier concentrations, where deposition with 0.9 sccm O₂ result in a carrier concentration of $1.5e16 \text{ cm}^{-3}$. UV-VIS-NIR reveal a light absorption onset in the vicinity of 1.9 eV for both the DC and RF sample at 0.9sccm. Reducing the oxygen flow below 0.9sccm result in a clear shift of absorption onset, down to $\sim 1.1eV$ for 0.4sccm. From X-ray diffraction we observe the presence of stressed ZnO and Zn₃N₂ phases in samples grown with respectively $\geq 0.9 \text{ sccm}$ and $\leq 0.6 \text{ sccm O}_2$, respectively.

IV investigations (Fig. 2) on mesa diodes from the DC sputtered film reveal a rectification of 10^4 between -1 and 1V and an ideality factor of 1.1. RF-sputtered films show ideality factors above 1.3 and rectifications of 30-300 between -1 and 1V. TAS consistently reveal a shallow state located at 30K in Fig. 3, which is believed to be freeze out of majority carriers in the Si-substrate. Furthermore, a second state is observed at higher temperatures in most samples. Activation energy for this second state increase with increasing oxygen flow for the RF series, up to 0.19 eV for the 0.9sccm sample. Due to the strong dependence of deposition parameters, this second state is likely to originate in the ZnON films.



Figure 1: Room temperature Hall measurements.



Figure 2: JV of ZnON:p-Si MESA diodes on both RF and DC sputtered thin films as a function of oxygen flow during deposition.



Figure 3: Thermal admittance spectroscopy at performed at -1V, illustrated by the 1MHz G/w signal

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Quantum emitters in silicon: identification attempt in the context of recent literature data

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Quantum emitters or, more specifically, light sources emitting single photons on-demand are at the heart of quantum technologies; such as quantum computers, quantum networks, and quantum communications [1]. During the last two decades, single-photon generation has been demonstrated in a variety of systems. Nevertheless, for practical applications, the ideal singlephoton source must exhibit high efficiency, room temperature functionality, compatibility with the present-day integrated circuits manufacturing, and, preferably, telecom wavelength operation. Very prominent results have been achieved using quantum dots (QDs) [2]; however, best performing QDs are typically based on III-IV semiconductors making their integration with silicon-based circuits non-trivial. Meanwhile, alternative approaches to use point defect as single photon emitters, e.g., in silicon carbide (SiC) [3] and, more recently, in silicon (Si) [4] have shown promising results too. However, significant advances in defect formation, identification, charge-state control, emission tuning, etc. are still necessary to integrate optically-active point defects within silicon-based quantum photonics and nanophotonics platforms.

In the present study, n- and p-type CZ and FZ Si wafers were irradiated with 1.8 MeV protons in a range of fluencies from 5E10 to 5E16 cm⁻². The low-temperature (4K) photoluminescence (PL) spectroscopy was employed for identification of the irradiation-induced defects and for monitoring their evolution during the post-annealing treatments. The PL probing depth was optimized to match the projected range of ions by using 405 nm wavelength cw-laser as an excitation source. The structural evolution of the irradiation-induced damage and corresponding electrically active defects were monitored by high-resolution X-ray diffraction and deep level transient spectroscopy, respectively.

Figure 1 illustrates spectral developments of the proton irradiated Si as a function of fluence. As can be seen from Fig. 1(a), the apparent irradiation effects are in gradual suppression of the excitonic features along with the build-up of a broad background emission stretching throughout the entire spectral range. Importantly, also numerous isolated emission lines emerge with several narrow peaks considered as potential candidates for single-photon emitters. Figs. 1 (b, c, d) show proton fluence dependencies of the spectral features representing the developments of crystallinity, irradiation-induced and intrinsic defects and their complexes (integrated PL, W- and C-line, respectively). Figure 1 (e) exemplifies the emission lines emerging upon irradiation at 5E16 proton/cm² in the context of recently reported single-photon emitters in Si with the peak position labelled as SD1-SD6 [5]. The target of present study is identification of the SD1-SD6 by varying impurity background and the irradiation parameters. Moreover, the autocorrelation measurements of the candidate single-photon emitters are also projected before the time of the conference.



Fig.1. (a) PL spectra obtained at 4K of 1.8 MeV proton irradiated n-Si as a function of ion fluence. Vertical markers indicate expected positions of the relevant emission lines according to the literature. Proton fluence dependencies of the integrated PL intensity (b), irradiation-induced W-line (c), and characteristic C-line (d) obtained for n- and p-type Si, respectively. (e) Enlarged region of PL spectrum with baseline subtracted for 5E16 cm⁻² CZ n-Si sample revealing multiplicity of emission lines. The single-photon emitters established in Ref. [5] as SD1-SD6 are listed alongside our data to provide literature context for further investigations.

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Deep Levels in 4H-SiC Implanted with Amphoteric Species

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Despite being a candidate for dilute magnetic semiconductors [1], Mn can be used for semiinsulating (SI) SiC. Like V, Mn substitutes at a Si-site and it is an amphoteric impurity, with an acceptor and a donor level at 0.68-0.70 eV and 1.38-1.47 eV below the conduction band edge (E_C), respectively [1]. Even if Mn is more abundant and cheaper than V, little is known on the electronic properties of Mn in SiC. For this reason, we performed an electrical characterization study of Mn implanted SiC in order to answer the following questions: is Mn viable for SI-SiC? Are there any Mn-related electrically active defects?

15 µm thick N-doped (10^{16} cm⁻³) 4H-SiC epilayers were implanted with multiple energies (total dose of 1.5×10^{12} cm⁻²) in order to create a 0.2 µm deep box profile ($\sim 10^{17}$ cm⁻³). Other samples were implanted with 350 keV Mn (10^{11} cm⁻²) so to simulate the implant tail region of the box-shaped profile. Box-profile implanted samples were characterized by I-V, while the others were characterized by C-V and DLTS. All samples were annealed in the 1000-1800°C temperature range.

In fig.1, we show the I-V characteristics of the box-profile implanted samples for the asimplanted, 1200°C and 1600°C annealed samples. In the as-implanted sample, the resistivity (ρ) is 20 k Ω cm for and becomes 2.5 k Ω cm after 30 min at 1200°C. After annealing 30 min at 1600°C, ρ decreases to 2 k Ω cm and does not change after annealing at 1700°C or 1800°C.

Fig. 2 shows the thermal behavior of the net donor concentration (N_d) of the implanted samples, as well as the SRIM simulation of the 350 keV implanted Mn. After implantation, N_d is compensated up to a depth of 0.8 μ m from the surface. However, annealing at 1200°C is enough to reactivate N_d close to the implantation profile. After 1600°C, N_d is fully reactivated also in the implanted region.

Fig. 3 shows the DLTS spectra after implantation and annealing. After implantation (fig.3(a)), we observe a level at $E_{\rm C}$ -0.4 eV (6.6x10¹³ cm⁻³), labelled MN1. Its broad DLTS peak might conceal minor contributions, like the Z_{1/2} one. After 30min at 1200°C (fig.3(b)), different levels are detected: MN2 ($E_{\rm C}$ -0.38 eV, 1.4x10¹⁴ cm⁻³), the Z_{1/2} (1.7x10¹⁴ cm⁻³), MN3 ($E_{\rm C}$ -0.78 eV, 1.6x10¹⁴ cm⁻³), MN4 ($E_{\rm C}$ -0.92 eV, 1.4x10¹⁴ cm⁻³), MN5 ($E_{\rm C}$ -1.0 eV, 2x10¹⁴ cm⁻³) and MN6 ($E_{\rm C}$ -1.4 eV, 2x10¹⁵ cm⁻³). Annealing at 1600°C (fig.3(c)), results in the annealing of MN2, MN3 and MN5. However, subsequent heat treatments at 1800°C (fig.3(d)) gives rise to other new levels, like the MN6 ($E_{\rm C}$ -0.3 eV, 8.6x10¹² cm⁻³), MN7 ($E_{\rm C}$ -0.58 eV, 1.3x10¹³ cm⁻³) and MN8 ($E_{\rm C}$ -1.68 eV, 2x10¹⁴ cm⁻³). In addition, the EH_{6/7} level, which was probably hidden under the broad MN6 DLTS signal, can also be detected.

The MN8 level position (detected when the N_d is reactivated in the implanted area) is close to the predicted position of the Mn donor level [1]. Depth profiling measurement of MN8 (fig. 4(a)), with constant pulse voltage height (2 V), shows that MN8 is rather shallow, located in the implanted region and follows the simulated Mn profile. This is a strong hint that MN8 could be identified as the Mn donor level. In addition, Poole-Frenkel measurements (fig.4(b)) show an electric field dependence of the emission time. Two models were employed and, as the figure shows, the best fit is obtained for a square-well potential (with unitary charge) rather than Coulombic potential.

Coming to the question of Mn viability for SI-SiC, the p values are lower than those obtained

after V-implantation [3]. The highly resistive region, up to 0.8 μ m (fig. 2), does not survive annealing at moderate temperatures (1200°C). This suggests that while Mn cannot be employed for SI-SiC, it can be used to obtain moderately resistive SiC layers, e.g., $10 < \rho < 10^4$ kΩcm. The poor efficiency of Mn might be due to the low solubility limit of Mn in SiC, which cannot exceed 10^{17} cm⁻³ [3]. Regarding the question of the presence of Mn-related defects, the MN8 level can be identified as the donor level of Mn, as predicted in Ref. [1].

Our investigation is currently focusing on the detection of the acceptor level of Mn. This is carried out by considering that, since the Mn acceptor has an energy level position very close to that of $Z_{1/2}[1]$, it can be possible that its DLTS signal might be hidden under that of $Z_{1/2}$. Furthermore, minority carrier transient spectroscopy (MCTS) measurements are in progress, to shed light on the presence of electrically active levels in the lower part of 4H-SiC band gap.

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Fig.1. I-V measurement of the box-profile-implanted samples, before and after annealing.



Fig.2. SRIM simulation of the Mn, vacancies profile together to the N_d of the single energy implanted and annealed samples. N_d after 1600°C annealing is increased two times for better visualization.





Fig.3. DLTS spectra of the (a) as-implanted, (b) 1200° C, (c) 1600° C and (d) 1800° C single energy implanted samples. The reverse bias was set to -10 V, to cover the whole Mn implantation profile. Pulse voltage was 10 V and period width 0.2 s.

Fig.4. Depth profile (lambda effect included) and (b) Poole-Frenkel measurement of the MN8 level.

Approaches to Kinetics of Point Defect Formation and Evolution in Gallium Oxide

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 β -gallium oxide (Ga₂O₃) is a promising material for applications in power electronics and as a transparent conducting oxide due to its wide bandgap of 4.8 eV and high breakdown electric field estimated at 8 MV/cm. Fundamental properties such as doping, mobility, optical absorption, luminescence, and charge trapping are determined by the device's ensemble of defects. Thermodynamic calculations for defect concentrations model the limiting case where the system has reached equilibrium; however, all real systems are limited by both kinetics and thermodynamics during device processing and operation.

Herein, we have adapted a coupled reaction-diffusion-Poisson solver [1,2] to study timedependent defect concentrations in β -Ga₂O₃ in 0D and 1D, using DFT-computed formation enthalpies but going beyond the thermodynamic equilibrium predictions for time-independent defect concentrations. We assume typical attempt frequencies for each reaction or diffusion process, and utilize migration barriers computed from DFT also. This approach is flexible and allows the simulation of many different aspects of transient defect formation reactions in bulk and at surfaces followed by the spatio-temporal evolution of populations. Calculations can be carried out for assumed fixed chemical potentials for scenarios ranging from growth specified by temperature vs time to in-operando conditions specified by temperature, applied bias, and time. Thus the evolution of defects can be simulated from cradle to grave.

We first study the introduction of Ga vacancies into Ga₂O₃ under O-rich annealing conditions. Two primary pathways exist: bulk formation of Ga vacancy-interstitial pairs followed by outdiffusion of interstitials which are converted to Ga₂O₃ upon reacting with O₂ at the surface, and formation of vacancies at the surface (presumably with lower formation enthalpy than in the bulk) followed by their in-diffusion. For the first mechanism, we further study the detailed reaction mechanism in terms of the formation of charge-neutral combinations of Ga vacancy, Ga interstitial and either a hole or electron. Interestingly, we find that the formation such Schottky defect pairs has the lowest formation enthalpy when the vacancy and interstitial are not equal but opposite in charge. Using this lowest-enthalpy mechanism, we then study the time evolution starting from a perfect crystal (Figure 1). The implicit time stepping scheme (unconditionally stable) enables the study of an extraordinary range of time scales, from femtoseconds to years, unlocking possibilities to simulate device lifetime reliability in addition to device processing. Additionally, carrier-defect reactions such as capture, emission, and recombination are captured as elementary quasichemical processes; thus in principle the same solver can be utilized to simulation various experiments such as IV, CV, DLTS, and even PL.

We will also present results on the 2nd mechanism of vacancy introduction during annealing, as well as the evolution of both mechanisms in 1D. We will also present results from a more full



Figure 1 – Evolution at 1000 K and O-rich conditions of doubly- and triply- charged V_{Ga} and Ga_i from fs to 1 day timescales in a homogeneous Ga_2O_3 volume (termed 0D because of no spatial dependencies). (Left) Intrinsic Ga2O3. (Right) N-type extrinsically doped.

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Using Illumination to Modify Defects in β-Ga₂O₃ at 1000 °C

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In most considerations, point defect formation in semiconductors during growth or processing is considered to take place under conditions of thermal equilibrium. This is a useful and powerful approximation and its predictive capability is remarkable given the purposeful simplification of neglecting kinetics. However it is possible to intentionally break away from equilibrium conditions, in fact this is done in every crystal growth process to a greater or lesser extent. Electronic excitation in semiconductors such as above-gap light is an accessible form of far-from-equilibrium conditions and opens the door to non-equilibrium defect ensembles that simply cannot be achieved via variation of temperature and chemical potentials vs. time.

In this work we demonstrate that the point defects present in the near-surface region of β -Ga₂O₃ can be modified under above-bandgap illumination even during annealing at >1000 °C. We used ~10¹⁶ /cm³ n-type layers grown on (010) substrates using OMVPE and thus having high crystalline perfection and better surface quality than wafers for these experiments. Illumination with above-gap light alters the defect kinetics and spatial distributions compared to annealing without illumination. After quenching in the defects present in samples with and without light, electrical JV, CV, and DLTS characterization revealed an entirely new slate of never-before-reported defects (of unknown identities). Both the defects present and their concentration distributions differ, especially near the surface. In fact the illuminated and non-illuminated annealed samples show no overlap in DLTS signatures; both contain numerous distinct defects. As-received control samples illuminated at room temperature showed that these effects only occur when annealed at elevated temperatures. We will discuss the wide range of physical effects on defect populations that are possible as a result of illumination, and attempt to narrow the possibilities dominating these results.

This work demonstrates the dramatic changes in defect chemistry that can be accessed via processing with light sources that differ from an isothermal blackbody. Whether or not such illuminated processing can be harnessed for desired technological benefits in various materials remains to be determined; however the existence proof of non-trivial differences at least makes it probable that in some materials and processes, the use of this orthogonal thermodynamic "knob" may help overcome current limitations. It also implies that light-driven heating processes such as RTA and laser annealing, as well as growth and processing in which illumination is an uncontrolled variable may be fundamentally distinct from their common conceptualization simply in terms of temperature and time. Excess carriers should be considered in processing at least in terms of their chemical potentials in the same manner applied to chemical species. We hope that demonstrations such as these experiments can shed light on puzzling old results, as well as serving as a beacon for future directions of inquiry.

Theory and experiment of Si – cation vacancy interactions in nitride semiconductors

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Semiconducting nitrides such as GaN and AlGaN are essential for the development of optoand power electronics and deep ultraviolet (UV) light sources. In common, these semiconductors appear to suffer from limited electrical conductivity due to compensation of charge carriers despite the use of p- or n-type doping. There are two typical reasons for compensation of n-type conductivity in nitrides: (a) cation vacancy defects or (b) acceptor impurities. These cation vacancy defects, where one or metal atoms are missing from a lattice site, are often present in rather high concentrations in compound semiconductors due to their relatively low formation enthalpies combined with relatively high stabilities [1 - 3].

Si doping is routinely used to enhance *n*-type conductivity in GaN and AlGaN thin films. However, it has been recently found that highly Si-doped GaN crystals may exhibit low *n*-type conductivity even if acceptor-type defects are present in relatively low concentrations [4, 5]. Al-rich $Al_xGa_{1-x}N$ films generally exhibit severe compensation issues that limit the conductivity even at high Si levels [6]. The conductivity in these materials can be limited not only by an increasing ionization energy but potentially also by the formation of cation vacancy defects that are known to act as compensating acceptors in *n*-type GaN and AlN. Another specific feature of these alloys is the transition of Si donor into negative DX configuration, which becomes energetically favorable after a certain level of Si doping [7].

In order to support our experimental findings we are performing calculations based on densityfunctional theory (DFT) utilizing advanced hybrid functionals. Our first goal is to obtain data on Si-Si interactions in GaN, which is expected to give valuable insights on the possible selfpassivation of Si donors. Our second aim is to study local vs. global phenomena related to electrical levels of Si in AlGaN semiconducting alloys by investigating the effects of local environment and alloy disorder on Si-DX behaviour.

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The effect of deep levels on the efficiency of InGaAs quantum wire intermediate-band solar cells based nanostructures grown by molecular beam epitaxy

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Recently, there has been an increasing interest in developing new technologies and novel concepts of producing high efficiency solar cells. For example a great research effort has been devoted to investigate the intermediate band solar cells (IBSC) as an innovative way to enhance the efficiency of solar cells. Usually, a system consisting of zero-dimensional quantum dots (QDs) is used to form an intermediate band in the space-charge region of a single junction solar cell. As a result, photocurrent enhancement could be achieved due to the absorption of photons with energies less than the band gap of the bulk junction material. However, the open circuit voltage decreases resulting in the degradation of the performance of the solar cell. To prevent the drop of the open circuit voltage it was found necessary to dope the intermediate band [1]. In addition, it was observed that doping creates additional carriers in the QDs that enhance the infrared (IR) absorption and the photocurrent.

In order to understand the possible mechanisms of the efficiency loss, it is worthwhile to investigate the electrically active defects present in these structures. In this work, we present detailed studies of InGaAs quantum wire (QWr) intermediate-band solar cell based nanostructures grown by molecular beam epitaxy [2]. Current–voltage (I–V) and capacitance–voltage (C-V) techniques are used to study the electrical and interface properties of these solar cell devices. These measurements were found to change with temperature over a wide range of 20–340 K. Deep-level transient spectroscopy (DLTS) was used to investigate the present of the electron and hole traps in these devices. The traps detected by the DLTS in the QWr-doped devices are directly or indirectly related to the insertion of the Si δ -layer used to dope the wires. Moreover, the detected traps with activation energies of 0.0037, 0.0053, and 0.041 eV could be correlated to the reduction of the solar conversion efficiencies at low temperatures and the associated reduction of the integrated external quantum efficiency through InGaAs.

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