Point defects in oxide and nitride compounds, alloys and heterostructures

Vera Prozheeva
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**Abstract**
In this work, positron annihilation spectroscopy was used for investigating defects in transparent semiconducting oxides and III-nitrides. These semiconductor materials are technologically important for next generation optical devices, space-qualified electronic components as well as for high-power and high-frequency applications. We demonstrate that the presence, concentration and nature of point defects are a subject of growth conditions, doping and post-growth processing in all of the materials in question.

In Sb-doped ZnO, the zinc vacancy $V_{Zn}$-associated defects including complexes with oxygen vacancies $V_O$ are detected irrespective of the Sb content. Heavy Sb doping results in compensating zinc vacancies dominating the positron data. The compensating zinc vacancies are likely to lead to the significant decrease in the conduction electron concentration at the highest Sb content in thin-film ZnO. The $V_{Zn} - V_O$ complexes induced by mechanical polishing in ZnO substrates are found to be the dominant defect in bulk material. Removal of parasitic Li and associated polishing-induced damage are most effective under series of high-temperature annealings.

In (In$_{x}$Ga$_{1-x}$)$_2$O$_3$ with graded In/Ga composition, an increase in the indium content leads to suppressed vacancy formation, while Ga-rich regions are characterised with gallium vacancy $V_{Ga}^-$-like defects. This behaviour is in accordance with In$_2$O$_3$ or Ga$_2$O$_3$-like signal dominating the positron data depending on the alloy composition. Doping (In$_{x}$Ga$_{1-x}$)$_2$O$_3$ with Si results in a high concentration of indium vacancy $V_{In}^-$-associated point defects.

Indium vacancies $V_{In}$ and vacancy clusters are observed in He$^+$-implanted In$_{x}$Ga$_{1-x}$N. The changes in the dominant defect type between the In$_{x}$Ga$_{1-x}$N layers and In$_{x}$Ga$_{1-x}$N – Si interface suggest redistribution of metal atoms in indium-rich regions or a closer rearrangement of such regions in the vicinity of the thin film – substrate interface triggered by the high-fluence He$^+$-implantation.

Experimental methods combined with theoretical modeling enabled defect identification in Be-doped GaN and in N-polar GaN/AlGaN/GaN HEMT-like heterostructures. Substituting Be$_{Ga}$ defects are the dominant positron traps in Be-doped GaN. Gallium vacancies $V_{Ga}$ emerging after thermal annealing indicate amphoteric behaviour of Be via the Be$_{Ga} \rightarrow V_{Ga} + Be$ mechanism. In heterostructures, the defect state at the bottom AlGaN/GaN interface is attributed to significant nitrogen deficiency in form of nitrogen vacancies $V_N$. This finding implies that in unoptimised N-polar heterostructures excess holes might be driven to the nitrogen vacancies located at the bottom AlGaN/GaN interface. That leads to the charge compensation effect and subsequent light sensitivity and current collapse of the actual devices. Si doping of N-polar heterostructures with graded Al$_x$Ga$_{1-x}$N layer compensates the trapping to the $V_N$ due to screening of the built-in electric fields.

**Keywords** semiconductor, III-nitride, transparent semiconducting oxide, point defect, positron annihilation spectroscopy

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Preface

This thesis has been prepared based on the work conducted mostly in the Anti-matter and Nuclear Engineering Group at the Department of Applied Physics at Aalto University School of Science during the years 2012 – 2017.

The first piece of the gratitude cake goes to Prof. Filip Tuomisto for his supervision and guidance. It was not only the opportunity to conduct research but also illuminating discussions which were vital for progressing with this thesis. The practical work in the positron lab as I know it would be unimaginable without Dr. Klaus Rytsölä. I would also like to thank Dr. Ilja Makkonen for support with the theoretical calculations. The group has changed the name (once) and location (twice), but the best memories of co-working and atmosphere of discussion and development remain. I am thankful to the past and present group members for that as well as for some of our lunch discussions which are worth a gem stone in an emperor’s crown. I am also grateful to Dr. Mikko Mikkola for his collection of fossil computer parts and never being too busy to help with IT-related issues.

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Attending the courses at the Language Centre of Aalto University brought me the joy of understanding of complex concepts aside from point defects in semiconductors. I would like to express paljon kiitoksia to Ms. Seija Koski and herzliche Anerkennung to Ms. Caren Schröder for guiding me towards the beauty hidden in books in the original language.

Undoubtedly, this work would have been totally different without the support of
my mum and brother. I thank my friends for being present in my life irrespective of time zones and geographical locations. Katariina, there is no better flatmate than you. Simon, thank you.

Lastly, thank you, Reader, for your interest in this work.

Helsinki, March 25, 2020,

Vera Prozheeva
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List of Publications

This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.


VI V. Prozheeva, I. Makkonen, H. Li, S. Keller, U. K. Mishra, and F. Tuomisto. Direct experimental evidence of interfacial N vacancies in GaN/AlGaN/GaN
Author’s Contribution

Publication I: “Cation vacancies and electrical compensation in Sb-doped thin-film SnO\textsubscript{2} and ZnO”

The author performed the positron measurements in ZnO and wrote the corresponding part of the manuscript.

Publication II: “Subsurface damage in polishing–annealing processed ZnO substrates”

The author performed the positron measurements, analysed the data and is the main author of the article.

Publication III: “Amphoteric Be in GaN: Experimental Evidence for Switching between Substitutional and Interstitial Lattice Sites”

The author performed and analysed the Doppler broadening measurements in coincidence mode and participated in writing of the manuscript.

Publication IV: “Radiation-induced alloy rearrangement in In\textsubscript{x}Ga\textsubscript{1−x}N”

The author performed the positron measurements, analysed the data and is the main author of the article.
Author's Contribution

Publication V: “Effects of alloy composition and Si-doping on vacancy defect formation in \((\text{In}_{x}\text{Ga}_{1-x})_2\text{O}_3\) thin films”

The author planned the research, performed the experiments, analysed the data and is the main author of the article.

Publication VI: “Direct experimental evidence of interfacial N vacancies in GaN/AlGaN/GaN heterostructures”

The author performed the experiments, analysed the data and wrote the first draft of the manuscript.
The amount of carry-on devices used each day is overwhelming. The customs of first checking the news on a screen of a mobile phone on the go, then browsing cat videos with a tablet while preparing a meal and finally getting to work nearly at any location all over the globe using a laptop have deeply integrated the world of technology into western society. It took no more than 5 years for traditional light bulbs to disappear completely from the shelves in stores, as the government and individuals try to take more energy-saving and cost-efficient way of living – and switch to using LEDs-based lightning devices. What lies behind these improvements is the research in the field of semiconductor materials. A simple gesture over a touch screen is enabled by the fundamental studies in semiconductor heterostructures started in the 1970s. Most if not all terrestrial infrastructure is dependent on semiconductor technology: semiconductor-based sensors, controllers and data processing systems grant cooperation and functioning of such complex objects as railway networks. The application range of Si, GaAs, GaP, Ge, GaN, SiC, to name a few widely used semiconductors, spans far outside from Earth. A demand for radiation-resistant transistors calls for further development of materials used for space applications which should remain economically profitable for manufacturing.

While GaN and related III-nitrides are used for commercial manufacturing of LEDs operating in blue to UV spectral region enabled by the tunable wide band gap, the hopes for ZnO as for p-type dopable material are gone for good. However, the advances in ZnO growth have produced its effects for ZnO application as a substrate in homo- and heteroepitaxy. The heated interest in Ga$_2$O$_3$, which is claimed as a strong opponent for GaN in field-effect transistors (FETs), see for example Ref. [1], and other sesquioxides and their alloys has significantly increased the number of participants of meetings like International Workshop on Gallium Oxide and Related Materials (IWGO). At the same time, the most frequently asked question at III-nitrides symposia switched to production-oriented availability of 150-mm native substrates. In the meantime, application of GaN-related material systems grown on silicon has been commercially established for electronic devices such as high electron mobility transistors (HEMTs). GaN-based HEMTs optimised for high frequency and
high efficiency switching performance are required for manufacturing of a wide range of products: adapters and quick chargers, air conditioners and washing machines, components for data centers and telephony including such heated sphere as 5G. One of the earliest applications of fast switching GaN HEMTs for audio amplifiers allowed for improved audio quality and miniaturised device size compared to Si-based technology. State-of-the-art commercial GaN HEMTs suffer from high manufacturing price and some performance limitations such as narrow gate-source voltage range. Resolving those issues would result in developed ecosystem for GaN power devices and increased overall product performance.

Irrespective of the material in question, the study subject is the same: structural, optical and electrical properties of a semiconductor. Doping and related lattice imperfections, growth and post-growth treatment, selection and availability of substrates are addressed by various qualification and quantification methods including positron annihilation spectroscopy. This measurement technique provides information on negative and neutral point defects in semiconductors with concentrations ranging from $10^{15}$ to $10^{19}$ cm$^{-3}$ which cannot be efficiently assessed by more wide-spread techniques like electron diffraction or scanning probe microscopy. For microscopy techniques, introduction of defects might occur during sample preparation or measurement process. To compare, doping levels required for operation of semiconductor-based devices start from $10^{14}$ cm$^{-3}$ of impurities.

Point defect identification and assessment allow for resolving electronic structure intricacies, and facilitate control over material properties. The aspects of point defect formation such as growth parameters, formation energies, presence of impurities in the system, availability of native substrates, annealing, implantation or irradiation damage, if any, are necessarily considered when optically active or compensating centers are limiting the performance of semiconductor materials. For positron annihilation spectroscopy, the main focus is often on identification of vacant sites in cation sublattice of binary compounds and their alloys. It is achieved via implanting positrons in a sample and then recording and interpreting the changes in the positron lifetime caused by local variations in electron density or in the annihilation spectra of positron-electron pairs caused by local variations in electron momentum density.

The goal of this thesis is to present findings on defect identification in binary compounds ZnO and GaN, ternaries $\text{In}_x\text{Ga}_{1-x}\text{N}$ and $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ as well as in III-nitrides-based HEMT structures. A brief introduction to basics of defect classification and characterisation is given in Chapter 2. Chapter 3 provides an overview of positron annihilation spectroscopy as the primary measurement technique used in this work. Publications I – III on Sb-doped ZnO, post-growth treated ZnO and Be-doped GaN are covered in Chapter 4. Publication I deals with the effect of Sb doping on MBE-grown ZnO. The findings show that vacancy clusters are formed along with single zinc vacancies $V_{\text{Zn}}$ at low to medium dopant concentrations. At high dopant concentrations $V_{\text{Zn}}$ dominate the positron data
and are responsible for electrical compensation. Publication II shows that in HT-grown ZnO the distribution of Li, which is inevitably present in the material due to the mineralizer used during growth, is altered after high-temperature annealing. Annealing at 1200 °C and higher temperatures leads to most of Li being accumulated in the sub-surface region. Subsequent polishing aimed at Li removal induces $V_{Zn}-V_{O}$ vacancy complexes. The damage is found to decrease below the detection limit after re-annealing at minimum temperature of 800 °C. The amphoteric behaviour of Be in GaN is investigated in Publication III. Similarly to Li in ZnO, Be switches from gallium substitutional sites $Be_{Ga}$ to interstitial $Be_{i}$ lattice positions leading to $V_{Ga}$ formation upon annealing. The identification of $Be_{Ga}$ in semi-insulating GaN is supported by \textit{ab initio} electronic structure calculations. Chapter 5 presents results on defect identification in He$^+\text{-}\text{-implanted In}_{x}\text{Ga}_{1-x}\text{N}$ (Publication IV) and $(\text{In}_{x}\text{Ga}_{1-x})_2\text{O}_3$ with graded indium content (Publication V). It is shown that the increasing complexity of the studied systems inevitably complicates defect identification. In $\text{In}_{x}\text{Ga}_{1-x}\text{N}$, high-dose implantation damage is shown to induce redistribution of In/Ga composition with expanding indium-rich regions close to the film-substrate interface. This effect manifests itself in defects with annihilation characteristics similar to indium vacancies $V_{In}$ in InN. In $(\text{In}_{x}\text{Ga}_{1-x})_2\text{O}_3$, alloy composition follows the trend for cation vacancy-type defects: defect formation is enhanced up to 40 – 60 at. % In, and over 70 at. % In in the thin film leads to defect suppression. Si doping of $(\text{In}_{x}\text{Ga}_{1-x})_2\text{O}_3$ is found to lead to $V_{In}$-like defects with minimal concentration of mid-$10^{18}$ cm$^{-3}$. Origin of interface traps in N-polar (Al,Ga)N HEMTs investigated in Publication VI is discussed in Chapter 6. Experimental results coupled with theoretical calculations suggest that nitrogen vacancies $V_N$ localized at undoped AlGaN/GaN interface trap positrons and might as well lead to current collapse in HEMTs due to hole trapping during their operation. Finally, Chapter 7 summarises the key findings of this work.
2. **Semiconductor characterisation**

A completely pure, or intrinsic, semiconductor is nothing but an idealization: prior to thermal activation of an electron, all electrons are occupying the valence band and all holes are residing in the conduction band. The total number of charge carriers of each sign in intrinsic semiconductor is equal. In this model, there are no free charge carriers at absolute zero temperature \((T = 0 \text{ K})\). At temperatures above absolute zero thermal energy enables electrons to cross the distance between the top of valence band \(E_V\) and the bottom of conduction band \(E_C\). This distance is called the forbidden energy gap or bandgap \(E_G\) and is one of the most significant semiconductor properties. Typically, \(E_G\) is in the range from one tenth to a few eV. At room temperature increase in \(E_G\) manifests itself in decrease in charge carrier density \(n_i\), e.g., Ge with \(E_G = 0.66 \text{ eV}\) has \(n_i = 2 \times 10^{13} \text{ cm}^{-3}\) and Si with \(E_G = 1.12 \text{ eV}\) has \(n_i = 1 \times 10^{10} \text{ cm}^{-3}\).

The nature of real crystalline solids results in relatively low mobility of atoms at low temperatures which in turn limits the regeneration of imperfections (or defects) introduced during growth or post-processing. Even in their purest form, Si and Ge contain approximately \(10^{10} \text{ cm}^{-3}\) of defects. The electrical and optical properties of semiconducting material are changed once new states are, intentionally or not, introduced in the forbidden energy gap when manipulating with crystal’s structural features. Impurity content starting from \(10^{14} \text{ cm}^{-3}\) is typically required for operation of semiconductor-based devices.

Instead of making doomed efforts to eliminate all defects, the effects they cause on material properties should be thoroughly considered. Changes in semiconductor properties caused by impurities at dilute concentrations include bandgap reduction, increase in carrier mobilities, colouration, and ferromagnetic properties, to name a few. At the same time, the unwanted impurities inevitably present in the growth system, such as Li in hydrothermally-grown ZnO, should be minimised either by optimisation of growth methods or via post-growth treatment.

Defect classification as well as some characterisation methods of semiconduc-
Semiconductor characterisation

Defect properties are introduced in this chapter. Positron annihilation spectroscopy, method primarily used for investigation of point defects in this thesis, is discussed in more detail in Chapter 3.

2.1 Subject of characterisation: defects in semiconductors

Defects in semiconductors are introduced during growth or as a result of preparation: via thermal treatment, plastic deformation, ion implantation and irradiation, diffusion and neutron transmutation. Development of, for example, a vacant lattice site in a crystal during these processes affects the immediate neighbouring atoms within several lattice sites. Dimension-wise defects are classified into (i) point defects with spatial extent in the order of a few atomic sites and their agglomerations, and (ii) extended defects. Extended defects include edge and screw dislocations, grain boundaries, stacking faults, precipitates, inclusions and voids. Vacancies, antisites, interstitial and substitutional atoms belong to the family of point defects. The nature of a defect defines its attribution to native or extrinsic group. Thus, a vacancy is considered as a native defect, whereas impurity atoms are entirely extrinsic. In light of that, doping might be considered as process of intentional creation of extrinsic defects in semiconductors which is often accompanied by formation of intrinsic defects. During growth and subsequent cooling, vacancies might diffuse and then migrate to the crystal surface, recombine with interstitials and dislocations, merge into clusters or result in new crystal phase formation. These phenomena complicate defect characterisation due to increased variety of forms and mixing between numerous defect signatures [2].

In thermodynamic equilibrium, if a defect is created in an otherwise perfect lattice, the defect formation energy is the difference in the total energy between the two crystal states, before and after introduction of the defect. Defect formation energy \( E_f \) is the leading factor for estimating defect concentration \( n \) due to exponential dependence

\[
    n \sim e^{-E_f/k_BT}
\]

where \( T \) is the temperature and \( k_B \) is the Boltzmann constant. Defect charge state has an impact on formation energy: negative charge state decreases \( E_f \) and positive charge state increases it by a value of \( qE_F \) where \( q \) is the charge state and \( E_F \) is the Fermi energy. This mechanism might lead to compensation effects when, e.g., donor defects compensate for the acceptor dopants in \( p \)-type material as donor formation is energetically favourable in \( p \)-type material due to low \( E_F \) and resulting reduced formation energy. Defect formation energy is also dependent on chemical potentials, i.e., on the chemical environment of the semiconductor and on the ambient conditions including temperature and pressure. Defects are mobile at high growth temperatures and might remain in a semiconductor after cooling process if energy requirements for the defect migration barrier are met. However, conditions of many growth methods are far from thermodynamical equilibrium. To illustrate, such aspects as surface adatom mobility, lattice mismatch between different
layers and parasitic impurities present in the growth system take the leading role during epitaxy growth. As a result, kinetic processes often dominate defect formation.

The possibility of controlled impurity introduction (doping) made semiconducting technology crucial for the society by providing materials with required electrical and optical properties. Changes in crystal structure associated with introduction of impurities and intrinsic point defects during growth might result in energy levels in the semiconductor band gap. A defect trapping electrons from the valence band acts as an acceptor. Single acceptors exist in a neutral or negatively charged state. Electron exitation to the conduction band might happen from donor states. Single donors are either in positively charged or neutral state. More complex case, when a defect can act both as an acceptor and a donor, is called amphoteric. In this case the position of the Fermi level $E_F$ defines the charge state of the defect. Doping changes the position of the Fermi level in the band gap: $n$-type dopants increase charge carrier concentration making the defects more negative and $p$-type doping moves $E_F$ closer to the valence band leading to defects in positive charge state. In either case, any other defects present in the material might be an obstacle to controlled doping as they limit the conductivity and even overcompensate it [3, 4]. In addition, a defect might manifest itself as colouration of a semiconducting material via creating optically active states in the band gap. This is the case for example for diamond [5], GaP [6, 7] and ZnSe [8].

Previously, the defect states were referred to as shallow or deep based on their proximity to the band edges. This notion suggests that if a donor (acceptor) level is close to the conduction (valence) band minimum (maximum) it is considered as a shallow level. Typical binding energy of a shallow level at room temperature is $\sim 3k_B T$ ($T = 300$ K) and is in order of tens of meV. Deep level defects, in turn, have energy levels far from the band edges. A more recent approach distinguishes between the shallow and deep levels depending on the localization of the charge carrier associated with the defect. A shallow level can be represented by a hydrogenic model, while the wave function of a deep state is spatially localized [3, 4]. In GaN, Mg is found to be a deep acceptor, even though the associated energy level is relatively close to the valence band allowing Mg for being state-of-the-art $p$-type dopant for GaN [9].

2.2 Semiconductor characterisation methods

Detailed characterization of defects in semiconductors involves structural, electrical and optical experimental techniques as well as particle beam methods. Feedback provided through characterization is vital for technological development. Theoretical modelling is often employed to evaluate material properties as well as defect formation energies and transition levels. Most traditional characterisation methods do not allow for direct defect identification. Thus combining
several experimental methods with first-principles calculations increases the
degree of detail on the impact of defects in semiconductors. It is worth noticing that
while a qualitative comparison of results obtained by different characterisation
methods is often employed, a thorough quantitative comparison of, e.g., the total
concentration of ionized acceptors and the concentration of negatively charged
vacancy-type defects is rare [10–12]. Most common measurement techniques
are briefly introduced in this chapter. Some additional details are provided for
the experimental methods applied in this thesis.

Electrical characterization methods reveal such properties as conductivity,
and charge carrier type, mobility and concentration, which are often linked
with the electrically active defects present in the sample. Deep level transient
spectroscopy (DLTS) provides information on concentration of deep majority
and minority (under special experimental conditions) carrier traps and their
position in the band gap. Use of DLTS implies a need in a \( p-n \) junction or a
Schottky contact which might be a limiting factor for some materials. Hall
effect measurements combined with resistivity measurements in four-point
probe van der Pauw geometry [13] are based on recording the voltage drop
across the selected pairs of contacts. The change in the resistance between two
diametrically opposite contacts, due to the presence of magnetic field, yields the
Hall mobility, provided that the thickness of the sample is known. This method
requires good Ohmic contacts which can be tested with current-voltage (IV)
measurements. Single-layer Ohmic contacts are easily achieved by sputtering,
for example Au is used for ZnO, and W or WSi\(_x\) for InN; for Ga\(_2\)O\(_3\) and alloys
thereof presented in Publication V multilayer contacts were applied.

The output of optical techniques for structural characterisation includes but is
not limited to the thickness of the thin film layers required, e.g., for the Hall effect
measurements as stated in the previous paragraph. Thin film interference occurs
between light reflected from the surface and light travelling through the thin
film and reveals the thickness of the studied layer(s). A transmission spectrum is
obtained for a range of wavelengths by measuring the intensities of the incident
monochromated light and the light passing through the sample. Analysis of
multilayer structures and thin films with thickness of several tens of microns
is best performed with ellipsometry systems, where the polarization change
is measured as light is reflected or transmitted through a medium [14, 15].
Ellipsometry has been used to verify (In\(_x\)Ga\(_{1-x}\))\(_2\)O\(_3\) film thickness in Publication
V.

Presence of optically active defects is typically addressed by photoluminescence
(PL), Raman scattering and Fourier transform infrared spectroscopy (FTIR). PL
is emission spectroscopy technique which utilises electron-hole pair generation
by a monochromatic light source for observation of optical transitions between
energy levels. Vibrational modes obtained in Raman scattering measurements
and FTIR are representative of atomic structure of defects and charge carrier
concentration. It should be noted that these optical methods strongly rely on
theoretical modelling for defect identification. To illustrate, the dispute on
the origin of yellow luminescence in GaN has been settled for the benefit of C impurity [16] while defect responsible for green luminescence in GaN keeps trapping electrons without revealing its identity [12].

Defect symmetry and in certain cases chemical identity of a defect are determined with electron paramagnetic resonance (EPR). EPR uses microwave radiation to detect electron spins in a sample placed in a static magnetic field. The method is based on recording of the magnetic interaction between the magnetic momenta of unpaired electrons of a defect and magnetic momenta of the surrounding atoms. Applied magnetic field is rotated with respect to a crystal axis to reveal defect orientations. EPR is applicable to paramagnetic defects in non-highly conductive samples.

Energetic ion beams are used for investigation of thin-film elemental composition and crystallinity (Rutherford backscattering) and impurity concentration (secondary ion mass spectrometry). Secondary ion mass spectrometry (SIMS) is employed to study the dominant impurities and their concentration in semiconductor surfaces and thin films as a function of depth [17]. The detection limit depends on the configuration of the measurement system and studied material and is in the range $10^{13} – 10^{18}$ cm$^{-3}$. A beam of energetic ions (typically $O_2^+$ or $Cs^+$, depending on the required polarity of the secondary ions) with energies between 0.5 and 20 keV is used to bombard the sample, resulting in a sputtering process. During the sputtering a fraction of the emitted particles is ionized forming a secondary ion beam and then accelerated and filtered by energy and mass before hitting a detector. SIMS is a destructive technique, as rastering of the primary beam creates a crater on the sample surface. Determination of intrinsic defect concentration is unattainable for SIMS. In addition, surface roughness might limit the depth resolution of a measurement. There are three operational modes of SIMS. In depth profiling mode, the signal obtained from the secondary ion beam as a function of the time of ion bombardment is converted into concentration of sputtered ions as a function of depth. Mass spectrum mode shows the presence of various isotopes in the studied sample. In ion imaging mode, the distribution of isotopes over the rastered plane is recorded. For the SIMS depth profiling measurements presented in Publication II a beam of 10 keV $O_2^+$ ions was rastered over a surface area of $150 \times 150 \mu m^2$.

X-ray absorption near edge spectroscopy (XANES) is a particle beam method which probes core electron levels and is suitable for identification of atomic structures and their valence states. Measurement results obtained with XANES require comparison to a defect model. XANES simulations (unpublished) were carried for $(In_xGa_{1-x})_2O_3$ in order to assess the evolution of the In/Ga valence states and their local environment as a function of compositional gradient.

The elemental composition of thin films can be obtained by energy-dispersive x-ray spectroscopy (EDX) with high lateral resolution. The method is based on detection of x-ray fluorescence excited in a probed region by a focused electron beam [18]. The qualitative analysis of the collected x-ray spectrum involves identification of the characteristic spectral lines specific of an element. The
Figure 2.1. SEM images obtained in Si-doped (In$_{0.4}$Ga$_{0.6}$)$_2$O$_3$ thin films grown by pulsed-laser deposition in continuous composition spread mode at oxygen background pressure of $8 \times 10^{-3}$ mbar (left) and $8 \times 10^{-2}$ mbar (right). Data were acquired at Semiconductor Physics Group, Leipzig University, Germany.

limitations of the method include poor sensitivity at low concentrations of few at. % and insensitivity to light elements. For the quantitative characterisation, the line intensities are compared to that of the standard samples with known elemental composition and to theoretical models. EDX measurements are usually combined with scanning electron microscopy (SEM), when a scanning electron microscope is equipped with an additional energy dispersive system for photon detection. The corresponding detection limits depend on the measurement conditions and are typically in the order of 0.1 % mass fraction of an element. Spatial maps of In/Ga distribution have been recorded for all samples studied in Publication V using SEM equipped with EDX facility due to the ready accessibility of the tool. SEM images obtained for the studied Si-doped (In$_x$Ga$_{1-x}$)$_2$O$_3$ samples reveal the rough surface of the thin films as shown in Figure 2.1. Typical SEM provides two-dimensional images of objects with spatial resolution of 50 – 100 nm and depends on the system design and the volume of specimen interacting with the electron beam. Imaging of individual atoms is possible with techniques based on transmission electron microscopy (TEM). Diffraction images are obtained by transmitting an electron beam through a thin specimen. As a result, sophisticated requirements for sample preparation limit the use of TEM in studying point defects, and special care has to be taken to identify defects induced during thinning process.

Another technique using x-rays for structural analysis of matter is x-ray diffraction (XRD) [19]. It has been extensively used for material characterisation in Publication V. It is a direct application of Bragg’s law, which describes the interferences of x-rays scattered from crystallographic planes. XRD patterns are invaluable for phase identification and provide information on grain size, strain and lattice parameters. Detection of minority phases depends on the elemental composition and starts from 1 wt. % [20].

The common drawback of the techniques considered in this section is the
incomplete information on defect structure and identification. The presence of open-volume defects as well as their nature, charge state, atomic environment and concentration can be resolved by means of positron annihilation spectroscopy. This family of characterisation methods includes tools for studying both, bulk and thin film samples, and is presented in more details in the following chapter.
Semiconductor characterisation
3. Positron annihilation spectroscopy

The main tool for semiconductor characterisation used within the framework of this thesis is positron annihilation spectroscopy. It is a measurement method for probing local electron density and atomic structure, sensitive to open volume defects in solids. Positrons implanted in a target material will annihilate with the electrons of the sample producing 511 keV $\gamma$-photons. In a defect-free lattice, the positron density is delocalized over the whole crystal, while neutral and negatively charged vacancies act as positron traps due to locally reduced Coulomb repulsion of the positive nuclei. The size of the open volume is reflected via changes in positron lifetime: for a positron trapped in a vacancy the positron lifetime is longer than that of the positron annihilating in a free state in a lattice. Measurements of Doppler broadening of positron-electron annihilation line are based on the momentum conservation of the annihilating pair and provide information on the chemical surrounding of a vacancy. The interpretation of the experimental results requires a comprehensive theory of electron-positron interaction. The *ab initio* electronic structure calculations are often employed to model the positron annihilation parameters in the defect-free lattice and for various defect configurations. Comparison of experimental and computational results provides an insight into the measurement data as has been shown for Be$_{\text{Ga}}$ in GaN in Publication III and $V_N$ at AlGaN/GaN interfaces in Publication VI.

It is important to note that the neutral and negatively charged vacancies are not the only source of positron trapping. Small substitutional elements, such as Li on a Zn site in ZnO [21], and negative ions are able to trap positrons as well. In the former case, the substitutional atom leaves enough space to be seen by the positrons. In the latter case, the trapping occurs to hydrogen-like shallow Rydberg states, and can be outlined in temperature-dependent experiments. The details on the measurement technique and theoretical foundations of positrons in solids can be found in Refs. [22, 23] and references therein.
3.1 Positrons in semiconductors

The most common source of positrons is $\beta^+$ decay of radioactive isotope $^{22}\text{Na}$ due to its optimal price to half-life ratio. The positron emission spectrum is characterised by a wide energy distribution with a maximum at 0.54 MeV. Typically several hundreds micrometers thick samples are investigated with energetic positrons when the $^{22}\text{Na}$ source is placed between two identical sample pieces. For thin films moderated monoenergetic positrons are required. During moderation the energy of emitted positrons is reduced to a few eV thus forming quasi-energetic positron beam [24]. The detection limits vary slightly depending on the charge state of a defect starting from $10^{15}$ cm$^{-3}$ peaking at $\sim 10^{17}$ cm$^{-3}$ and reaching the so-called saturation trapping at $\sim 10^{19}$ cm$^{-3}$.

When a positron enters a solid, it thermalizes within a few picoseconds through ionization, core electron excitation, electron-hole excitation and phonon emission. The dominant process is dependent on the positron binding energy. After thermalization, the positron is in Bloch-like state and diffuses for a few hundred picoseconds in thermal equilibrium with the environment. The characteristic diffusion length $L_+^+$ of 100 – 200 nm at room temperature follows from the diffusion theory and the random-walk theory and is determined by the diffusion coefficient $D_+^+$ and the positron lifetime $\tau$ as

$$L_+^+ = \sqrt{\tau D_+^+}. \quad (3.1)$$

During its thermal motion the positron interacts with vacancy-type point defects, which represent potential wells in positron potential landscape, and might eventually get trapped into a localized state. Mean free path of the positron is typically ten times shorter than the characteristic diffusion length. The effective diffusion length is reduced due to positron trapping into defects before annihilation. The following annihilation with an electron produces two 511 keV $\gamma$-photons emitted into approximately opposite directions. In this process both, energy and momentum, are conserved. When the distribution of defects in the crystal is homogeneous and the positron is diffusing fast, trapping into defects is limited by transition of the positron into the localized state. If the defects are distant from each other and the diffusion to a defect is slow but the following localization occurs fast, the trapping process is diffusion-limited. The positron trapping rate $\kappa_D$ into a defect D correlates with the defect density $c_D$ via

$$\kappa_D = \frac{\mu_D}{N_{\text{at}}} c_D, \quad (3.2)$$

where $N_{\text{at}}$ is the atomic density and $\mu_D$ is the positron-to-defect trapping coefficient. For semiconductors, trapping coefficient for neutral vacancies is temperature-independent. Positively charged vacancies are usually unseen by positrons due to the Coloumb repulsion which leads to low trapping coefficient $\mu_D$. Trapping to a positively charged vacancy would require positron tunneling to the potential well taking longer than the positron lifetime. For
a negatively-charged vacancy, the trapping coefficient has a $T^{-0.5}$ dependence. The positron trapping at Rydberg states induced by isolated negative ions is only observed at low temperatures ($T < 100 \text{ K}$) as a $T^{-0.5}$ dependence as well [25].

The competition between the negative ions and the vacancies can be ruled out as a decrease of average positron lifetime at low temperatures. While the exact determination of the trapping coefficient $\mu_D$ is complicated, comparison with other characterisation techniques has shown that typically used at 300 K value for negatively charged vacancy type defects $\mu_D = 2 - 3 \times 10^{15} \text{ s}^{-1}$ is correct within the factor of 2. Trapping coefficient is a charge-dependent value and for neutral vacancies it is often taken as $\mu_D = 10^{15} \text{ s}^{-1}$ at 300 K.

### 3.2 Positron lifetime spectroscopy

In a conventional "fast-fast coincidence" setup the lifetime of an individual positron is measured as the time difference between detections of 1.27 MeV and 511 keV $\gamma$-photons (Fig. 3.1). The 1.27 MeV $\gamma$-photon is emitted in the $\beta^+$ decay process of $^{22}\text{Na}$ right after the excited $^{22}\text{Ne}$ nucleus goes to its ground state and serves as start signal for a measurement event. The 511 keV $\gamma$-photon signalizes the positron-electron annihilation and the end of the measurement event. Detectors made of plastic scintillators and photomultiplier tubes are often used for registering the measurement signals for further processing either with analogue electronics or with a digital oscilloscope. A so-called "sandwich geometry" when a $^{22}\text{Na}$ source is placed between two pieces of the sample is applied to maximise the positron annihilation in the specimen volume. In this case, the stopping profile of energetic positrons emitted by a radioactive source is exponential

$$P(x) = a \exp(-ax), a = 16 \frac{\rho[\text{g/cm}^3]}{E_{\text{max[MeV]}}} \text{cm}^{-1},$$

where $\rho$ is the density of the solid and $E_{\text{max}}$ is the maximum energy of the continuous radiation spectrum. The broad energy distribution of unmoderated positrons induces long mean implantation depth in order of tens to hundreds micrometers, making this technique solely usable for a few hundreds micrometers thick bulk samples. To limit unwanted false coincidence events, the typical activity of a source produced by depositing $^{22}\text{Na}$ salt on Al or Ni foil should not exceed 1 MBq. However, some false coincidences are still present and contribute to background in the positron lifetime spectrum.

The annihilation rate $\lambda$ is the inverse of the positron lifetime $\tau$ and is proportional to the overlap of the electron and positron densities on the annihilation site [26]. In a vacancy, the electron density is lower than in the defect-free lattice, which leads to a decrease of the annihilation rate of trapped positrons. The positron lifetime spectrum represents the probability histogram of positron
annihilating at a given time $t$

$$- \frac{dn(t)}{dt} = \sum_i I_i \lambda_i e^{-\lambda_i t},$$ (3.4)

where $n(t)$ is the number of positrons in the sample, $i$ corresponds to the positron state and $I_i$ is the intensity of the annihilation rate $\lambda_i$. By carefully fitting exponential components to a spectrum it is possible to deduce the corresponding lifetimes $\tau_i = 1/\lambda_i$. It should be noted that the experimental lifetime spectrum is a convolution of the ideal spectrum with the resolution function of the detectors. Detector resolution function should preferably be of Gaussian form to ensure reliable data analysis. The slope of the resolution function on semilogarithmic scale sets the limit of the lowest measurable lifetime. Additional components arise from positron annihilations in the source material and foil casing.

The center of mass of the lifetime spectrum can be determined with a subpicosecond accuracy, and coincides with the average lifetime $\tau_{ave}$

$$\tau_{ave} = \int_{-\infty}^{\infty} t \left( - \frac{dn(t)}{dt} \right) dt = \sum_i I_i \tau_i.$$ (3.5)

In case one type of defect present and no detrapping occurring the average lifetime is defined as

$$\tau_{ave} = (1 - \eta_D) \tau_B + \eta_D \tau_D,$$ (3.6)

where $\eta_B$ and $\eta_D$ are the positron annihilation fractions in the lattice and in the open-volume defect, respectively, and $\eta_B + \eta_D = 1$ [23].

The increase of the lifetime correlates with increasing open volume of the vacancy-type defect. In binary compound semiconductors GaN and ZnO the cation monovacancy usually produces a lifetime that is 70 – 80 ps longer than in the lattice, but the sensitivity of the measurement decreases somewhat when the positron is trapped in vacancy clusters larger than 4 – 5 missing atoms [11, 27]. If the bulk lifetime is known, it is possible to estimate the vacancy concentration based on Eq. (3.2).
For the work presented in Publication III, the bulk Be-doped GaN samples were mounted on a sample holder in thermal contact with a closed cycle He cryostat. Such assembly together with a lifetime spectrometer allowed positron lifetime measurements in the 35 – 500 K temperature range.

### 3.3 Doppler broadening spectroscopy

The positron lifetime spectroscopy is incapable of characterisation of chemical surroundings of vacancy-type defects due to the weak influence of the latter on the electron density. The chemical surrounding of an annihilation site has a stronger impact on the momentum distribution of the electron-positron pair [22]. The momentum of thermalized positron is negligible compared to that of the bound electrons. Two $\gamma$-photons emitted in an annihilation event obtain the momentum of the annihilating pair (see Fig. 3.1). The Doppler shift of the 511 keV annihilation line is caused mainly by the momentum of the annihilating electrons

$$\Delta E = \frac{1}{2} c p_L,$$

where $p_L$ is the longitudinal momentum component of the electron-positron pair in the direction of the annihilation photon emission. A Doppler shift of 1 keV corresponds to a momentum of $p_L = 0.54$ a. u. (atomic units).

The lineshape of the 511 keV electron-positron annihilation peak is described with one-dimensional momentum distribution of the annihilation radiation. A Doppler broadening spectrum can be thought of as a combination of positron interactions with valence and core electrons. The former ones are loosely bound while the latter ones are confined in space. As a manifestation of the Heisenberg's uncertainty principle, core electrons have wider momentum distribution. The momentum distribution arising from positrons trapped at an open-volume defect is slightly narrower than that of a perfect crystal due to a reduced overlap with ion cores leading to a considerable decrease in annihilation with high-momentum core electrons. Each annihilation state has its own signature lineshape, e.g., $V_{Ga}$ in GaN (see Sect. 4.2), which makes it possible to resolve defects even with similar open volume.

High purity germanium (HPGe) detectors are used for recording the annihilation $\gamma$-photons due to their energy resolution superior to scintillator detectors [28]. The energy resolution of the HPGe detectors is determined by measuring the detector response to a monoenergetic source of radiation and recording the obtained full width at half maximum (FWHM). Typical energy resolution of an HPGe detector is around 1.1 – 1.5 keV at 511 keV annihilation peak. The total width of the annihilation peak is about 2 – 3 keV, thus the experimental lineshape is strongly affected by the detector resolution (Fig. 3.2). In a conventional Doppler measurement the peak-to-background ratio is only about $10^2$. There one or two HPGe detectors are usually used without any limitations to pulse counting. The background in a conventional Doppler mea-
Figure 3.2. Doppler broadening spectrum obtained with a single HPGe detector before and after background correction. The $S$ and $W$ parameter windows are highlighted.

Measurement mainly results from the incomplete charge collection in the HPGe detectors, electronic noise, statistical fluctuation in the number of charge carriers and should be subtracted prior to the lineshape analysis. The Compton continuum and background radiation affect the measured energy spectra, too. The peak-to-background ratio can be significantly improved (up to $10^4$) when using two HPGe detectors in collinear geometry in time coincidence mode [23, 29, 30]. On top of that, energy conservation $E_{\gamma,1} + E_{\gamma,2} \approx 1.022$ MeV condition improves peak-to-background ratio to $10^6$.

The direct comparison of spectra measured in conventional mode is hardly reasonable due to statistical considerations, and lineshape parameters are used instead. Figure 3.2 illustrates the energy ranges for the $S$ and $W$ parameters as well as the Doppler broadening spectra before and after background correction. First, the low electron-momentum parameter $S$, which describes annihilations mainly with valence electrons, is the number of counts in the central part of the 511 keV peak divided by the total amount of the counts in the broadened line. Second characteristic is the $W$ parameter, which is more sensitive to highly localized core electrons, and is calculated as the fraction of the area below the wing region far from the center [22, 23, 31]. In addition to valence electrons, the $S$ parameter region also includes a contribution from core electrons. The $S$ parameter region is chosen to cover approximately 50% of the annihilation peak. At the same time the $W$ parameter regions should be far enough from the peak center to minimize the influence of valence electrons. The integration windows are set symmetrically around the peak, and for the measurements presented in
this thesis were set to about $|E_\gamma - 511\text{ keV}| < 0.76\text{ keV}$ ($p_L < 0.4\text{ a. u.}$) for the $S$ parameter and about $2.92\text{ keV} < |E_\gamma - 511\text{ keV}| < 7.41\text{ keV}$ ($1.5\text{ a. u.} < p_L < 4\text{ a. u.}$) for the $W$ windows.

The measured $S$ and $W$ parameters are superpositions of the various annihilation states seen by the positron. Assuming only one vacancy-type defect present in the sample, the parameters are

$$S = \eta_B S_B + \eta_D S_D,$$
$$W = \eta_B W_B + \eta_D W_D,$$  \hspace{1cm} (3.8)

where $\eta$ is a fraction of annihilating positrons, subscripts $B$ and $D$ refer to annihilations in the bulk and in a defect, respectively, and $\eta_D + \eta_B = 1$. Importantly, if the same defect is present in a set of samples with varying vacancy concentration, the data will follow a straight line in an $(S, W)$ plot. The values of $S$ and $W$ are heavily influenced by detector geometry, resolution, calibration, amplifier gain, etc., and selected integration regions [32]. Thus, when possible, it is advisable to normalize measured data to a reference which is defect-free from positron point of view.

Using the conventional sample-source "sandwich geometry" described in Sec. 3.2 allows a straightforward measurement. To control the implantation energy and the depth distribution of positrons for thin-film experiments monoenergetic positrons are used. In a slow positron beam, fast positrons from a source are moderated by material which has a negative workfunction for positrons, e.g., tungsten. The efficiency of a thin W foil moderator is low, only 0.001 %, as most of the positrons either pass through, annihilate inside the foil or get trapped at the surface states. As a result, sufficiently high activity of a positron source ($\sim 5 \times 10^9\text{ MBq}$) is required to perform the measurements with a slow positron beam.

After moderation, fast positrons are discarded in a velocity selector and monoenergetic positrons are guided with a magnetic field towards the target. Then the positrons forming a focused particle beam are accelerated by a tunable electric field. In a slow positron beam, the positron incident energy can be electrostatically tuned typically in the range from 0.2 to 50 keV. The high activity of the source implies construction of intensive radiation protection and / or sufficient spatial separation between the HPGe detectors and the source end.

For monoenergetic positrons obtained with a low-energy positron beam the stopping profile can be described with a Makhovian function

$$P(x) = -\frac{d}{dx}\exp(-\frac{x}{x_0})^2).$$  \hspace{1cm} (3.9)

The mean positron implantation depth is

$$x_{\text{mean}} = AE^n[\text{keV}],$$  \hspace{1cm} (3.10)

where $A \approx \frac{4}{\rho}\mu\text{g/cm}^2$, $n \approx 1.6$, $\rho$ is the material density, $x_{\text{mean}} = 0.886x_0$. Figure 3.3 shows the positron stopping profiles for implantation energies of 4, 10 and
17 keV in In$_{0.37}$Ga$_{0.63}$N thin films studied in Publication IV of this thesis. The masked regions show the 95.5% probability area neglecting the implantation profile tail above double mean implantation depth. The larger the mean implantation depth is, the deeper the stopping profile extends into the sample. For more details on the stopping profiles refer to Ref. [33]. Depth-dependent defect profiles can be obtained by solving numerically one-dimensional diffusion equation

\[ D \frac{d^2}{dx^2} n(x) - \frac{d}{dx}(\mu_+ E_d(x)n(x)) - (\kappa_D c_D(x) + \lambda_B)n(x) + I(x) = 0, \quad (3.11) \]

where \( n(x) \) is the time averaged positron density, \( \mu_+ \) is the positron mobility, \( E_d(x) \) is the electric field in the sample, \( \lambda_B \) is the bulk annihilation rate and \( I(x) \) is the positron implantation rate. Modelling of the implantation energy-dependent data is implemented in a program package VEPFIT [34], which was used for data analysis in Publications II and VI. The effective positron diffusion length \( L_{\text{eff}}^+ \) decreases along with increase in positron trapping rate at defects [23].

The majority of the experiments presented in this thesis were performed with slow positron beams in conventional Doppler mode. The coincidence Doppler broadening measurements with two HPGe detectors were utilized in Publications III and VI.
3.4 Computational approach

The modelling of the positron-electron annihilation parameters is performed based on extended density functional theory (DFT) model, the two-component DFT [26]. In DFT, energy functionals of electron density describe the ground state properties of the system instead of many-body wavefunctions [35]. The ground state density $n(r)$ is derived for a system consisting of non-interacting electrons with the Kohn-Sham ansatz [36]

$$E_{KS}[n] = T_s[n] + E_H[n] + \int V_{ext}(r)n(r')dr + E_{XC}[n],$$  \hspace{1cm} (3.12)

where $T_s[n]$ is the kinetic energy of the non-interacting electrons with the density $n$, $E_H[n]$ is Hartree interaction energy, $V_{ext}(r)$ is external potential due to Coulomb interaction between electron and nuclei, and $E_{XC}[n]$ is the exchange-correlation correction term. Hartree energy term describes electrostatic repulsion between electrons and interaction of the electron with itself and is in the form

$$E_H[n] = \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} drdr'.$$  \hspace{1cm} (3.13)

The exchange-correlation term $E_{XC}[n]$ is the unknown term of the total energy functional $E_{KS}[n]$. It includes many-body effects and must be approximated. In local density approximation (LDA) approach, the exchange-correlation energy density is expressed as a function of the local density of a uniform gas where electrons are homogeneously distributed at any given point [36].

The corresponding total energy functional for the positron-electron system in an external potential $V_{ext}(r)$ is then defined as

\begin{align*}
E[n_-, n_+] &= T_s[n_-] + E_H[n_-] + E_{XC}[n_-] + T_s[n_+] + E_H[n_+] + E_{XC}[n_+] \\
&\quad - \int \int \frac{n_-(r)n_+(r')}{|r-r'|} drdr' + \int V_{ext}(r)[n_-(r)-n_+(r)]dr + E_{e-p}^{corr}[n_-, n_+] \hspace{1cm} (3.14)
\end{align*}

and depends on both, electron $n_-(r)$ and positron $n_+(r)$ densities. In order to overcome the limitations of two-component DFT related to the electron-positron correlation functional $E_{e-p}^{corr}$ at finite positron densities, the LDA is employed. The electron-electron exchange-correlation energy is approximated with the LDA parametrization [37]. It is assumed that the delocalized positron does not affect the average electron density $n_-(r)$ [26]. Further, the value of the electron-positron pair correlation function at zero distance (the enhancement factor) for the localized positron is evaluated at the zero positron-density limit as if for delocalized positrons. This concept holds when considering the positron localized at a defect and its screening electron cloud as a neutral quasiparticle [26]. Similar to the actual measurements, in calculations it is assumed that there is one positron in the studied structure at any given time. To account for that, terms $E_H[n_+]$ and $E_{XC}[n_+]$ cancel each other, thus positron self-interaction is
Positron annihilation spectroscopy

Ignored. The LDA scheme gives the potential for the positron single particle wave function as a sum of the attractive Hartree potential due to electrons, the external potential due to the nuclei and the zero-positron-density limit of the electron-positron correlation potential

\[ V_+(\mathbf{r}) = -\int \frac{n_-(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - V_{\text{ext}}(\mathbf{r}) + V_{\text{corr}}(\mathbf{r}), \quad (3.15) \]

where

\[ V_{\text{corr}}(\mathbf{r}) = \frac{\delta E_{\text{e-p}} [n_-, n_+]}{\delta n_+(\mathbf{r})}, \quad n_+ \to 0. \quad (3.16) \]

Prior to solving the positron lowest energy single particle wavefunction with \( V_+(\mathbf{r}) \), the electron density is calculated independently. The single particle wavefunctions are solved iteratively starting with selected trial particle density. Once the difference between the electron densities obtained from two subsequent iterations are self-consistent, \( i.e. \), are within pre-defined tolerance limit, the iterations stop, and the ground state particle density is obtained.

After obtaining the electron and positron densities, the positron lifetime and the momentum density of annihilating pairs are calculated. With the so-called state-dependent scheme [38] the short-range screening of the positron by electrons is taken into account as the electron state-dependent and position- and momentum-independent enhancement factor \( \gamma_j \) of states \( j \) and is defined via the ratio of the annihilation rates \( \lambda_j \) as

\[ \gamma_j = \frac{\lambda_j^{(\text{LDA})}}{\lambda_j^{(\text{IPM})}} = \frac{\pi r_e^2 c \int n_+(\mathbf{r}) n_j (\mathbf{r}) \gamma(\mathbf{r}) d\mathbf{r}}{\pi r_e^2 c \int n_+(\mathbf{r}) n_j (\mathbf{r}) d\mathbf{r}}. \quad (3.17) \]

The constants \( r_e \) and \( c \) are the classical electron radius and the speed of light, respectively. The enhancement factor \( \gamma(n_-(\mathbf{r})) \) is evaluated at the zero-positron-density limit [26]. The independent particle model (IPM) neglects effects of the screening of the positron by electrons and approximates \( \gamma(n_-(\mathbf{r})) \equiv 1 \). The positron lifetime is derived from the annihilation rate \( \lambda_j^{(\text{LDA})} \)

\[ \tau = \frac{1}{\lambda} = \left\{ \pi r_e^2 c \int n_+(\mathbf{r}) n_-(\mathbf{r}) \gamma(\mathbf{r}) d\mathbf{r} \right\}^{-1}. \quad (3.18) \]

The momentum distribution of the annihilating electron-positron pairs is given by

\[ \rho(p) = \pi r_e^2 c \sum_j \gamma_j \left| \int d\mathbf{r} e^{-ip \cdot \mathbf{r}} \psi_j(\mathbf{r}) \right|^2, \quad (3.19) \]

where the summation goes over occupied electron states \( \psi_j(\mathbf{r}) \), and \( \psi_+(\mathbf{r}) \) is the positron state obtained based on Eq. (3.15).

The calculation results are helpful for interpreting the experimental data, which is best illustrated in Publications III and VI and in Refs. [21, 39, 40]. Calculated positron lifetimes are consistently underestimated compared to the measured ones owing to the shortcomings of DFT when 3d electrons are involved. However, the difference between the positron lifetime in the lattice and in
other annihilation states is in line with the experiments. The comparison of the Doppler spectra is achieved by first projecting the calculated momentum distribution to a selected spatial direction and then convoluting it with the detector resolution function. Deconvolution of the experimental Doppler spectra and comparing them to theoretically calculated spectra are rarely performed.
Positron annihilation spectroscopy
4. Binary compounds: ZnO and GaN

In order to approach the level of importance of Si, Ge and GaAs, any semiconductor should not only possess appealing characteristics and potential to be implemented within a certain technological area, but also be both n- and p-type dopable. Another significant criterion is availability of large-area native substrates. A long-term research quest for ZnO and GaN, both wurtzite binary compound semiconductors with direct wide bandgap, has proven that neither of them is currently able to replace Si in the market: reliable p-type doping has been achieved for GaN with Mg, but no stable process for ZnO has been reported so far. On the opposite, ZnO native substrates are freely available in the market, while free-standing GaN wafers currently available are mostly 50 mm in diameter.

In wurtzite crystal structure, such as ZnO and GaN, a cation is bound to four anions in tetragonal configuration as demonstrated in Figure 4.1. The stacking of alternating atomic layers along the c-axis induces spontaneous electrical polarization. As a result, growth kinetics, oxygen incorporation, defect formation, electrical and material properties depend on the orientation and, hence, on the polarity of the material [41]. To illustrate, in GaN the growth polarity is known to have a crucial impact on the defect formation, with the N-polar face being more reactive and richer in cation vacancy-type defects than the Ga-polar side [42].

Zn vacancies $V_{Zn}$ in n-type ZnO and Ga vacancy $V_{Ga}$-related defects in both unintentionally and intentionally n-type doped GaN are identified as important acceptor-type (compensating) centers, irrespective of the growth method [11, 31, 44–47]. Yet the current systematic studies of effects of varying doping conditions and post-growth processing are insufficient. Results presented in this chapter and in Publications I – III shed light on the defect formation in Sb-doped thin film ZnO, polishing–annealing processed bulk ZnO substrates and Be-doped GaN, both in its bulk and epitaxial thin-film forms.
4.1 Zinc oxide

Experimental reports on achieving $p$-type ZnO with group V element Sb doping exist [48–50], but their stability and reproducibility appear low [51]. The reported conductivity of doped material is heavily dependent on the concentration and type of compensating point defects and the doping level control. Theoretical calculations predict, on one hand, that $V_{\text{Zn}}$–Sb$_{\text{Zn}}$–$V_{\text{Zn}}$ complexes could act as shallow acceptors [52], and that such defect complexes involving substitutional Sb are rather deep and thus cannot be accounted for as effective acceptors [53, 54]. On the other hand, strong $n$-type doping pushes the Fermi level up and decreases the formation energy of negatively charged cation vacancies [45, 53], suggesting that the cation vacancies could act as important compensating centers in highly $n$-type material.

Doping with group I elements, Li among them, has been proven to be unrealizable due to the amphoteric nature of Li: the formation of self-compensating donors $\text{Li}_i$ becomes more favourable than of acceptors $\text{Li}_{\text{Zn}}$ as the Fermi level shifts towards the valence band maximum [55]. The presence of Li impurities in hydrothermally-grown (HT) bulk ZnO has been shown to be one of the dominating factors controlling the electrical and optical properties of the material [21, 56–58]. Another complication is the surface damage of the as-received substrates which makes them unsuitable for homoepitaxy but can be recovered during high temperature annealing [59, 60]. High temperature annealing has been also shown to lead to Li accumulation in the sub-surface region [61]. Polishing required for Li removal and substrate preparation induces subsurface damage and implies post-polishing heat treatment to be essential for epitaxial growth on ZnO substrates.

Defect identification was carried by Doppler broadening spectroscopy in Sb-doped ZnO thin films grown by plasma-assisted molecular beam epitaxy (PA-
Figure 4.2. The (S,W) plot for the Sb-doped ZnO thin films. The layer-specific values are normalized to those of the reference sample [11]. The tendency for increasing vacancy cluster size is as demonstrated in Ref. [40].

MBE) in Publication I and HT-grown ZnO substrates subjected to thermal annealing and mechanical polishing in Publication II. In the PA-MBE thin-film series grown on sapphire substrates the Sb-doping concentration was varied by adjusting the Sb cell temperature from 430 °C to 550 °C. The carrier concentrations in the samples were determined by room temperature Hall measurements demonstrating that the layers exhibit n-type conductivity with the carrier concentration varying from 10₁⁶ to 10²⁰ cm⁻³ [51]. The as-received HT-grown ZnO substrates were subjected to thermal pre-annealing (1200 °C or 1500 °C) and mechanical polishing processing followed by a post-annealing step (600 °C, 800 °C or 1000 °C). Pre- and post-annealings were performed in air for one hour. The incorporation of Li and other impurities during HT-growth has been examined with SIMS.

4.1.1 Electrical compensation in Sb-doped ZnO

The results of slow positron beam experiments in epitaxially-grown ZnO are presented in Figure 4.2 which depicts the layer-specific S and W parameters normalized to the corresponding values in a bulk ZnO single crystal reference. The point corresponding to the saturation trapping at Zn vacancies as determined in Ref. [11] is marked with \( V_{\text{Zn}} \). The data points for the Sb-doped samples follow a line which does not cross the (S, W) point representative of the ZnO lattice. Such behaviour is indicative of the presence of vacancy clusters involving at least two Zn vacancies decorated with O vacancies \( V_{\text{Zn}}-nV_{\text{O}}, n \geq 2 \) [40]. The proximity of the (S, W) points for samples Z2 – Z4 to the \( V_{\text{Zn}} \) point suggests a competition in positron trapping between \( V_{\text{Zn}} \) and vacancy clusters, with samples Z3 and Z4 being closer to the saturation trapping condition. It should be noted that these
two samples were grown at the highest Sb cell temperature and thus have the highest Sb concentration in the series.

The decrease of the conduction electron concentration despite the increasing Sb cell temperature, and, hence, the Sb concentration in the thin films is attributed to the introduction of compensating $V_{\text{Zn}}$-type defects. The evolution of the $(S, W)$ parameters after rapid thermal annealing (sample pairs Z1 – Z1* and Z2 – Z5*) suggests formation of vacancy clusters during the annealing process. Moreover, the $(S, W)$ parameters of sample Z1 point to the existence of $V_{\text{Zn}}$-$nV_{\text{O}}$ vacancy clusters prior to annealing. Heavy Sb doping via increase of the Sb cell temperature reduces the concentration of vacancy clusters and leads to predomination of $V_{\text{Zn}}$ in the positron signal similar to what has been observed in Ga-doped ZnO [62].

### 4.1.2 Polishing-induced defects in ZnO

In the HT-grown bulk ZnO substrates, Al and Li were found to be the dominant impurities. The SIMS data (Figure 4.3) show that the distribution of Al is uniform ($0.8 - 2 \times 10^{17}$ cm$^{-3}$) for most of the samples except for unpolished set pre-annealed at 1500 °C (1500/U/*). The bulk concentration of Li is significantly reduced after thermal treatments, whilst the as-received sample RT/U/RT possesses a uniform concentration of Li of $\sim 4 \times 10^{17}$ cm$^{-3}$. Nearly the same Li concentration is observed in the near-surface region of the sample 1500/U/RT pre-annealed at 1500 °C without any further processing. Its polished counterpart 1500/P/RT demonstrates a rapid decrease of Li concentration already after the depth of 100 nm. Some of the samples contain Na as contaminant as well.

![Figure 4.3.](image)

Figure 4.3. (a) Al and (b) Li concentrations versus depth profiles for selected HT-grown bulk polished, */P/*, and unpolished, */U/*, ZnO substrates as measured by SIMS. The numbers in the legend indicate the annealing temperatures, RT stands for no annealing. Data were acquired at Micro and Nanotechnology laboratory, University of Oslo, Norway.
Figure 4.4 displays the \((S, W)\) plots for the unpolished and polished subsets of the studied substrates. The data were first analysed fitting the stationary positron diffusion equation (see Eq. 3.11), scaled for different energy calibrations and detector resolutions in accordance with Ref. [32] and then normalized to a defect-free from the positron point of view ZnO reference. The points corresponding to substitutional Li\(_{Zn}\) and saturation trapping at \(V_{Zn}\) estimated from Ref. [11, 21, 46] are shown for reference.

Comparison between the annihilation parameters of the unpolished and polished samples demonstrates the introduction of vacancy complexes involving both \(V_{Zn}\) and \(V_{O}\) induced by polishing. The post-polishing annealing at temperatures of 600 °C and 800 °C leads to oxidation of the samples. ZnO is known to decompose with a preferential loss of oxygen atoms with heating ZnO crystals at temperatures above 1000 °C in air [63]. The introduction of \(V_{O}\) is observed as a rightward shift of the data points in the \((S, W)\) plane [40], as is the case with the post-polishing annealing at 1100 °C.

The positron data are in agreement with the SIMS measurements in Fig. 4.3 and Ref. [61]: the pre-annealing at 1500 °C causes Li redistribution with a notable reduction of Li content in the bulk. Clearly, polishing used to remove the Li-rich layer also induces the sub-surface damage in as-grown and pre-annealed HT-ZnO. The treatment sequence “pre-annealing at 1500 °C – polishing – post-annealing at 800 °C” (sample 1500/P/800) results in the lowest total concentration of detectable point defects. This implies that the post-annealing of HT-ZnO with removed Li layer at high enough temperature reduces the concentration of polishing-induced defects below the detection limit. Some of the unpolished samples are characterised with the \((S, W)\) parameters close to the ZnO lattice values as well. However, the slightly lower \(W\) parameter might indicate the competition for Zn sites between Na and Li as reported in Ref. [64].
4.2 Be-doped gallium nitride

Unintentionally doped GaN is slightly n-type, which favours the use of group-IV dopants (typically Si) in order to achieve controllable n-type conductivity. The situation with p-type doping is far from being ideal: so far the state-of-the-art process involves incorporation of Mg during growth and subsequent high temperature annealing [65], yet the acceptor activation efficiency is low due to high thermal activation energy of Mg in GaN [66, 67]. That as well as self-compensation by native defects [68–71] have promoted the research interest in Be as a potential p-type dopant for GaN. However, the autocompensation mechanisms and low solubility of Be in GaN being the tip of the iceberg of doping complications resulted in decreased work on the subject. Recent findings on yellow luminescence and the semi-insulating properties of Be-doped GaN have revived the investigation of this dopant [72, 73]. The photoluminescence (PL) characterisation and photoluminescence excitation experiments (PLE) on bulk crystals grown by high nitrogen pressure solution (HNPS) demonstrated the efficiency of GaN:Be crystals as converters for blue LEDs [72]. Unveiling the mechanisms behind behaviour of Be in GaN is clearly required for developing energy-efficient high-power electronics.

4.2.1 Identification of Be$_{Ga}$

Defect identification was carried in Be-doped GaN MBE-grown thin films as well as in HNPS bulk crystals (Publication III). The thin-film series included N-polar and pairs of Ga-polar samples grown at 675–770 °C and with Ga flux of 9–16×10$^{-7}$ Torr. One of the samples from each Ga-polar pair was subjected to postgrowth annealing at 900 °C for 2 h in N$_2$ atmosphere [74]. The growth of bulk HNPS crystals with oxygen concentration [O] $\sim$ 10$^{19}$ cm$^{-3}$ at a temperature of 1450 °C and under 1 GPa of nitrogen pressure is described in Ref. [72].

The conventional Doppler measurements were carried out at room temperature showing that the S parameter of most of the as-grown samples is close to that of the p-type GaN reference, while the data for the annealed samples demonstrate presence of vacancy type defects in the studied layers. After averaging the S and W parameters over the region representative of the layer in the thin films and over the high implantation energy region for the bulk crystals, the data are normalized to those of the reference GaN sample and presented in Figure 4.5 (left). The (S, W) point representing isolated V$_{Ga}$ is estimated from earlier experiments [75–77]. The measured data points for all GaN:Be samples are clearly shifted below the line connecting the GaN lattice to the V$_{Ga}$ point indicating presence of a defect with smaller open volume than that of the cation vacancy. Inspired by the results for Li on Zn site in ZnO [21], substitutional Be on Ga site was considered as one of the candidates for a small open volume defect. In order to resolve the positron trapping state, ab initio electronic structure calculations were performed with a 768-atom cell, with results shown
Figure 4.5. (left) The normalized $S$ and $W$ parameters for the studied GaN:Be samples and the theoretically calculated $(S, W)$ parameters for BeGa-related defects and $V_{Ga}$ complexes. (right) Ratio curves obtained from Doppler broadening measurements in coincidence mode in Ga-polar samples and from theoretical calculations.

in Figure 4.5 (left) as square symbols. Comparison between the calculated $(S, W)$ parameters and the data points measured in Be-doped GaN suggests positron trapping in BeGa-like defects. Further support for this observation is obtained from Doppler measurements in coincidence mode. The ratio curves for selected as-grown and annealed Ga-polar thin-film samples, both experimental, and for Be$_{Ga}$, Be$_{Ga}$–H, Be$_{Ga}$–$V_{N}$, Be$_{Ga}$–$O_{N}$, $V_{Ga}$, and $V_{Ga}$–2H, all theoretically calculated, are displayed in Figure 4.5 (right). The lineshape of the ratio curve for the as-grown sample clearly indicates the presence of Be$_{Ga}$, Be$_{Ga}$–H, Be$_{Ga}$–$V_{N}$ or Be$_{Ga}$–$O_{N}$, while the annealed sample contains a detectable amount of $V_{Ga}$ in addition to BeGa-like features. The presence of Be$_{Ga}$–$V_{N}$ in the studied sample series can be excluded as the ratio curve for this defect complex is different from the experimental data in the momentum region $< 2$ a. u. which can be as well seen in Fig. 4.5 (left): the calculated $(S, W)$ point for Be$_{Ga}$–$V_{N}$ is shifted to the right from the measured values.

Positron lifetime measurements were performed in the bulk HNPS-grown Be-doped GaN crystals with [O] $\sim$ $10^{19}$ cm$^{-3}$ providing average lifetime 5 – 10 ps longer than that of the GaN lattice at temperatures below 300 K, see Fig. 4.6. The lifetime characteristic of the GaN lattice was measured in a highly Mg-doped ammonothermally (AT) grown GaN crystal [78]. The theoretical calculations predict a 5 – 15 ps increase in lifetimes for the Be$_{Ga}$-related defects compared to the GaN lattice, demonstrating an agreement with the measured data. Compared to the obtained data, the earlier measurements in GaN with [O] $\sim$ $10^{20}$ cm$^{-3}$ [79] demonstrate the emergence of the second lifetime component $\tau_{2} \approx 230$ ps as shown in Fig. 4.6, top, revealing the presence of Ga vacancy-related defects that become visible at temperatures above 300 K.

Overall, the positron data provide evidence of the presence of the Be$_{Ga}$-related defects at least in the $10^{17}$ cm$^{-3}$ range in the as-grown Ga-polar Be-doped thin films and in the N-polar samples grown at high Ga flux ($16 \times 10^{-7}$ Torr), all
Binary compounds: ZnO and GaN

MBE-grown, and in the Be-doped HNPS GaN bulk crystals with low oxygen concentration (∼10^{19} \text{ cm}^{-3}). The suggested vacancy concentration is consistent with the lowest Be doping (5 \times 10^{19} \text{ cm}^{-3}). The results for the low Ga flux (9 \times 10^{-7} \text{ Torr}) N-polar and the annealed Ga-polar MBE-grown thin films, and the Be-doped HNPS GaN single crystal with [O] ∼ 10^{20} \text{ cm}^{-3} sample point at the presence of V_{Ga}-type defects in addition to the Be_{Ga}-related defects. The observation of the V_{Ga}-related defects in the annealed samples agrees well with the emergence of a photoluminescence band at 3.38 eV in earlier results for the studied MBE-grown Be-doped thin films [74].

4.2.2 Amphoteric nature of Be in GaN

High formation energy of V_{Ga} [80, 81] along with the relatively low-lying Fermi level of semi-insulating Be-doped GaN do not favour the formation of V_{Ga}-type defects in the as-grown thin films. The low Ga flux employed during growth of one of the N-polar samples explains the shift of the associated data point in the (S, W) plot towards the “GaN lattice – V_{Ga}” line. The emergence of V_{Ga}-related defects in the annealed samples could involve a direct switching process between interstitial and substitutional sites of Be. Another option, thermal vacancy formation would also require the excitation of acceptors Be_{Ga} switching to donor Be_{i} positions in the lattice. However, the estimated equilibrium Ga vacancy concentration at the annealing temperature of 900 °C in the latter case (3 \times 10^{16} \text{ cm}^{-3}) is at least an order of magnitude lower than that of Be_{Ga} and thus insufficient. Based on that, it is more likely that the formation of V_{Ga} in the thin film samples is based on the direct switching mechanism Be_{Ga} → V_{Ga} +
Be	extsubscript{i} with the activation energy $E_A$ estimated to be in the range 3–4 eV to have an impact at applied annealing temperature.

The MBE-grown Be-doped thin films are semi-insulating before and after subjection to heat treatment indicating that the process $\text{Be}_{\text{Ga}} \rightarrow V_{\text{Ga}} + \text{Be}_i$ is reversible. The lineshape of the ratio curve for annealed GaN:Be shown in Figure 4.5 (right) implies that only about 10 % of the total Be	extsubscript{i} concentration persist during cooling, and concomitant cation vacancies $V_{\text{Ga}}$ lead to the higher intensity of the positron signal up to 0.7 a. u. and lowered shoulder feature compared to that of the as-grown sample. Manifestation of $V_{\text{Ga}}$ emerging after annealing accounts for the appearance of additional donor-acceptor pair observed in photoluminescence experiments reported in Ref. [74]. In the HNPS-grown GaN, thermal switching of Be from $\text{Be}_{\text{Ga}}$ at low temperatures to Be	extsubscript{i} at high temperatures accompanied with formation of $V_{\text{Ga}}$ is observed for both Be-doped bulk crystals irrespective of the [O] range. The observation of $V_{\text{Ga}}$ only in the [O] $\sim 10^{20}$ cm$^{-3}$ case displayed in Fig. 4.6 is attributed to the formation of $V_{\text{Ga}}$ complexes with O during cooling from the growth temperatures as shown in Ref. [82].
Binary compounds: ZnO and GaN
The art of semiconductor technology lies in band gap engineering by controllable doping during or after growth. Starting from the fabrication of early junction transistors, alloying has been widely employed in semiconductor industry. In the III-nitride field, creating heterostructures based on GaN alloyed with InN and AlN extends the LED emission range from UV to IR and enables the development of a homogeneous platform for various light emitting devices. The major difficulty on this way is the optimisation of the growth conditions [83], as the lattice mismatch between AlN and GaN of about 3.5 % and the mismatch between GaN and InN of about 10 % result in defect formation [84] and subsequent deterioration of electrical properties and decrease in device efficiency. Major research interest in transparent semiconducting oxides (TSOs) so far has been mostly devoted to binaries. Among them, ZnO is so far the most studied semiconducting oxide, while In2O3, Ga2O3 and SnO2 are gaining increased attention even of the nitride community. Similarly to III-nitrides, the scope of TSOs can be significantly extended by alloying Ga2O3 with In2O3 or α-Al2O3. That implies band gap tuning in the wide range from 2.9 eV to 8.8 eV and allows development of photodetectors and heterostructures operating at tuned wavelengths [85, 86]. It should be stressed that despite all expectations of Ga2O3-based alloys to be an alternative to GaN, the actual status of practical application of the ternary TSOs is in its elementary state [87].

Positron annihilation spectroscopy has been previously used to study irradiation damage in GaN and InN [88, 89] and doping effects in Ga2O3 and In2O3 [90, 91]. The effect of He⁺ implantation-induced radiation damage on the defect and alloy structure in InₓGa1−ₓN thin films was studied in Publication IV. The properties of thin-film (InₓGa1−ₓ)2O3 with graded indium or dopant (silicon) content are presented in Publication V.

5.1 Radiation damage in InₓGa1−ₓN alloys

The high heat capacity and resistance to ionizing radiation promotes GaN and its alloys with InN for electronics applications including solar cells for outer...
space [92–94]. Correct estimation of solar cell degradation rate in radiative environment is in the long run vital for space mission planning. In case of In$_x$Ga$_{1-x}$N, defect-related phenomena induced by radiation damage, such as inhomogenous indium distribution, remain a controversial issue [95–97]. An increase in energy conversion efficiency of In$_x$Ga$_{1-x}$N-based solar cells can be achieved by employing In$_x$Ga$_{1-x}$N / Si heterostructures even despite the lattice mismatch with Si and associated cracking and high dislocation density [98–102]. Earlier attempts to elucidate using Doppler broadening measurements [103] whether vacancies or alloy homogeneity effects play the leading role in the In$_x$Ga$_{1-x}$N-based device performance have left questions open for further investigation. To address this issue, irradiation-induced changes in In$_x$Ga$_{1-x}$N will be addressed in this section.

The studied In$_x$Ga$_{1-x}$N, $x = 0.37$ and 0.45, thin film samples were grown by metal-organic chemical vapour deposition (MOCVD) on 10-nm-thick In$_x$Al$_{1-x}$N buffer layers deposited on Si (111) substrates. The samples were doubly implanted at energies of 40 keV and 100 keV with He$^+$ fluences ranging from $10^{12}$ cm$^{-2}$ to $10^{15}$ cm$^{-2}$. Those fluences are chosen as they are expected to produce a homogeneous damage profile over the whole layer thickness with the displacement damage dose $D_d$ in the range $8.0 \times 10^{13} – 2.0 \times 10^{16}$ MeV/g. Parameter $D_d$ is often used for calibration of radiation damage induced by different types of energetic particles [104]. The corresponding implantation-induced damage was estimated with Stopping and Range of Ions in Matter (SRIM) program [105] to be in the range $9 \times 10^{18} – 2 \times 10^{21}$ cm$^{-3}$.

The lineshape parameters for the as-grown and He$^+$-implanted samples are presented in Figure 5.1. The data points selected as representative of the In$_x$Ga$_{1-x}$N epilayer (smaller markers) and the near-interface In$_x$Ga$_{1-x}$N / Si region (larger markers) are normalized with the $(S, W)$ values of the defect-free $p$-type GaN reference sample. The reference points, GaN and InN lattices, gallium vacancy $V_{Ga}$ in GaN, and indium vacancy $V_{In}$ and indium vacancy decorated with several nitrogen vacancies $V_{In} – nV_{N}$, $n \geq 2$, both in InN, are shown for comparison [39, 106, 107]. The regions corresponding to defect-free alloys with $37 \% < x < 50 \%$ indium and the scatter of the Doppler parameters in In$_x$Ga$_{1-x}$N systems containing a metal vacancy are marked [103].

The data from the layer region of the non-implanted samples demonstrate saturation trapping at group III cation vacancies or vacancy-related complexes, indicating cation vacancy concentration of at least $10^{18}$ cm$^{-3}$. The $(S, W)$ values obtained from the In$_x$Ga$_{1-x}$N / Si interface region (larger symbols in Fig. 5.1) are shifted towards higher $S$ parameters. Similar observations were made in MBE-grown In$_x$Ga$_{1-x}$N and in InN for cation vacancy – nitrogen vacancy complexes $V_{III} – nV_{N}$, where $n \geq 2$ [39, 108]. Here the annihilation parameters are in the vicinity of those for $V_{In} – nV_{N}$ calculated for InN indicating an increase in the number of $V_{N}$ associated with a cation vacancy as shown in Ref. [39]. This observation suggests a higher indium content in the near-interface region. However, it does not testify in favour of preferential formation of cation vacancy
Ternary alloys: $\text{In}_x\text{Ga}_{1-x}\text{N}$ and $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$

Figure 5.1. (left) The relative ($S$, $W$) values at the epilayers (smaller markers) and near-interface $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{Si}$ region (larger markers). The highlighted region on the GaN – InN line corresponds to defect-free alloys with 37% – 50% indium. The shaded region of the $\text{V}_{\text{Ga}}$ – $\text{V}_{\text{In}}$ line shows modelled scattering span of the ($S$, $W$) parameters in $\text{In}_x\text{Ga}_{1-x}\text{N}$ systems containing a cation vacancy. Estimated displacement damage dose $D_d$ for He$^+$ implanted samples is specified in the legend. (right) Calculated ($S$, $W$) parameters for systems with varying In/Ga distribution containing a metal vacancy.

defects in the regions of higher indium content in random alloys as the cation vacancy formation energy is higher in InN than in GaN [109–111].

The low-dose implantation does not significantly modify the annihilation parameters in relation to the as-grown samples, with the estimated vacancy concentration being therefore in agreement with the SRIM estimate. An increase in the implantation dose does not affect the data from the $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{Si}$ near-interface where the cation vacancies exhibit $\text{V}_{\text{In}}$ – $n\text{V}_{\text{N}}$-like character for the whole series. A different picture is observed in the epilayers themselves. At higher implantation doses the annihilation parameters converge towards the $\text{V}_{\text{In}}$ point. In InN, He$^+$ implantation under similar conditions was found to produce single cation vacancy type defects [89]. The observed changes can be explained taking into account the fact that the cation shell has the most impact on the positron data. Comparing binaries, GaN and InN, formation of $\text{V}_{\text{Ga}}$ under irradiation has been shown to be much more efficient than formation of $\text{V}_{\text{In}}$ [88]. In addition, irradiation is known to induce more damage in Ga-rich than in In-rich $\text{In}_x\text{Ga}_{1-x}\text{N}$ [92]. It can be thus concluded that the high-fluence implantation leads to an increase of the indium content of the In-rich regions or to a closer rearrangement of In-rich regions via a mechanism mediated by cation vacancies.
Ternary alloys: In$_x$Ga$_{1-x}$N and (In$_x$Ga$_{1-x}$)$_2$O$_3$

5.2 Defects in (In$_x$Ga$_{1-x}$)$_2$O$_3$

Unlike the extensive research on ZnO (for a review see Ref. [23] and references therein) the investigation of vacancy type defects in group-III sesquioxides with positrons is rather limited at the moment. Initial study of binaries In$_2$O$_3$ [91] and Ga$_2$O$_3$ [90] has demonstrated that V$_{In}$ are much less abundant in In$_2$O$_3$ than V$_{Ga}$ in Ga$_2$O$_3$. Compared to that, the formation energy of V$_{Zn}$ in ZnO is much lower than that of V$_{In}$ in In$_2$O$_3$. In highly n-type In$_2$O$_3$ interstitial oxygen is more likely to act as compensating centers rather than V$_{In}$ [91]. In Si-doped Ga$_2$O$_3$, V$_{Ga}$ were determined as main compensating centers for n-type doping [90].

Focus on material properties important for device fabrication facilitated the work on n-type doping of Ga$_2$O$_3$ and In$_2$O$_3$ and solubility limits of their ternary alloys. The investigation of compositional dependence on the properties of ternary alloys has been performed in a number of publications [112–118]. The presence of the monoclinic β-Ga$_2$O$_3$, hexagonal InGaO$_3$ II and bixbyite bcc-In$_2$O$_3$ phases was shown for (In$_x$Ga$_{1-x}$)$_2$O$_3$ in Ref. [119]. The experimentally determined solubility limit of In in Ga$_2$O$_3$ is about 0.43 [87]. The incorporation of In$_2$O$_3$ in Ga$_2$O$_3$ enables reduction of the bandgap down to 4.1 eV for $x \leq 0.4$. On the other side of the alloy composition scale, addition of Ga$_2$O$_3$ into In$_2$O$_3$ results in energy increase up to 3.95 eV for $x \geq 0.5$. The attempts to dope ternary alloy (In$_x$Ga$_{1-x}$)$_2$O$_3$ with Ge and Sn demonstrated that the conductivity was independent of the doping level [120, 121] suggesting the influence of V$_O$ on the electrical properties of thin films. Doping with Si is expected to increase the electrical conductivity of thin film (In$_x$Ga$_{1-x}$)$_2$O$_3$ similarly to what has been shown for Ga$_2$O$_3$ [122].

Among thin film growth methods, pulsed laser deposition (PLD) in continuous composition spread (CCS) mode has the advantage of controlled preparation of multicomponent oxides with laterally distributed chemical composition of the films [123]. The correlation between Si doping and In incorporation demonstrated suppressed formation of cubic bixbyite phase in CCS-PLD (In$_x$Ga$_{1-x}$)$_2$O$_3$ thin films [124]. The performance of ultraviolet photodiodes fabricated of Si-doped (In$_x$Ga$_{1-x}$)$_2$O$_3$ has demonstrated the feasibility of this approach for devices operating in a wide spectral range from 3.22 to 4.83 eV [125]. However, the interplay between defect formation and structural properties which could improve the performance of the (In$_x$Ga$_{1-x}$)$_2$O$_3$-based sensors is still not understood. In the following, results obtained in undoped and Si-doped thin-film sample series grown by CCS-PLD presented in Publication V will be discussed.

The growth conditions and crystallographic properties of the samples as obtained by spatially resolved x-ray diffraction (XRD) are summarised in Table 5.1. An exemplary spatially resolved scan along the compositional gradient for sample S is presented in Figure 5.2. The spatial variation of In in the investigated undoped samples was found to correlate with the oxygen background pressure as predicted by Monte-Carlo simulations [123] similar to results reported for
Ternary alloys: $\text{In}_x\text{Ga}_{1-x}\text{N}$ and $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$

Table 5.1. Growth conditions and crystallographic phases observed in $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ samples. The dopant fraction [Si] refers to the content of the PLD targets used. The regions are referred to as following: 'mcl' stands for monoclinic $\beta$-$\text{Ga}_2\text{O}_3$, 'bcc' and 'hex' are for cubic bixbyite $\text{In}_2\text{O}_3$ and hexagonal $\text{InGaO}_3$ II, respectively. The S-series samples were grown $c$-plane $\alpha$-sapphire. Sample M was grown on (100)-oriented MgO substrate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$p_{O_2}$, mbar</th>
<th>$T$, °C</th>
<th>[Si], at. %</th>
<th>[In], at. %</th>
<th>Crystallographic phase</th>
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<tr>
<td>S-low-$p$</td>
<td>$3\times10^{-4}$</td>
<td>650</td>
<td>&lt; 20</td>
<td>mcl</td>
<td></td>
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<td>20 - 80</td>
<td>mcl, bcc, hex</td>
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<td></td>
<td>&gt; 80</td>
<td>bcc, hex [126]</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>$8\times10^{-2}$</td>
<td>680</td>
<td>&lt; 30</td>
<td>bcc</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30 - 70</td>
<td>hex, bcc</td>
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<td>&gt; 70</td>
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<td></td>
</tr>
<tr>
<td>S-30-Si</td>
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<td>665</td>
<td>0.5</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>hex</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-40-Si</td>
<td>$8\times10^{-2}$</td>
<td>661</td>
<td>0.5</td>
<td>40</td>
<td></td>
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<td></td>
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<td></td>
<td>hex</td>
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<tr>
<td>M</td>
<td>$8\times10^{-2}$</td>
<td>650</td>
<td>&lt; 30</td>
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<td></td>
<td></td>
<td>&gt; 65</td>
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</table>

The dopant fraction [Si] refers to the content of the PLD targets used. The regions are referred to as following: 'mcl' stands for monoclinic $\beta$-$\text{Ga}_2\text{O}_3$, 'bcc' and 'hex' are for cubic bixbyite $\text{In}_2\text{O}_3$ and hexagonal $\text{InGaO}_3$ II, respectively. The S-series samples were grown $c$-plane $\alpha$-sapphire. Sample M was grown on (100)-oriented MgO substrate.

Table 5.1. Growth conditions and crystallographic phases observed in $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ samples. The dopant fraction [Si] refers to the content of the PLD targets used. The regions are referred to as following: 'mcl' stands for monoclinic $\beta$-$\text{Ga}_2\text{O}_3$, 'bcc' and 'hex' are for cubic bixbyite $\text{In}_2\text{O}_3$ and hexagonal $\text{InGaO}_3$ II, respectively. The S-series samples were grown $c$-plane $\alpha$-sapphire. Sample M was grown on (100)-oriented MgO substrate.

For the measurement points corresponding to the bcc-$\text{In}_2\text{O}_3$ phase region of...
Ternary alloys: In$_x$Ga$_{1-x}$N and (In$_x$Ga$_{1-x}$)$_2$O$_3$

Figure 5.2. (left) False colour representation of wide-angle 2θ − ω scans for the undoped (In$_x$Ga$_{1-x}$)$_2$O$_3$ sample S along the In gradient. (right) Individual XRD patterns at selected In content. The substrate-related peaks are marked in grey as (006) and (0012), bcc-In$_2$O$_3$ and hex-InGaO$_3$ II phases are marked with the subscripts 'c' and 'hex', respectively. Data were acquired at Semiconductor Physics Group, Leipzig University, Germany.

For the considered samples, the span $S_{defect} \geq 1.03 \times S_{bulk}$ and $W_{defect} \leq 0.91 \times W_{bulk}$ represents the estimated defect parameters, in agreement with the earlier experimental findings for Mg- and Sn-doped In$_2$O$_3$ and with theoretical calculations for V$_{In}$ in In$_2$O$_3$[40, 91]. Based on that, the data from the Si-doped samples should represent the saturation trapping state suggesting that the V$_{In}$ concentration in both samples S-30-Si and S-40-Si is at least mid-10$^{18}$ cm$^{-3}$ irrespective of the doping level.

These results on (In$_x$Ga$_{1-x}$)$_2$O$_3$ demonstrate behaviour comparable to binaries In$_2$O$_3$ and Ga$_2$O$_3$, depending on the In content of the alloy. On top of that, observed trends are similar to those reported for III-nitrides, such as low concentration of cation vacancies in InN compared to that in GaN.
Ternary alloys: In$_x$Ga$_{1-x}$N and (In$_x$Ga$_{1-x}$)$_2$O$_3$

Figure 5.3. (left column) The ($S, W$) parameter plots for studied samples. Point corresponding to positron annihilations in bulk state of In$_2$O$_3$ is shown for reference. (right column) The $S$ parameter as a function of In gradient. The colour of the legend text and background indicates the crystal structure: green for monoclinic $\beta$-Ga$_2$O$_3$, blue for cubic bixbyite In$_2$O$_3$, black/grey for hexagonal InGaO$_3$ II or mixed phase, and orange stands for amorphous region.
Ternary alloys: $\text{In}_x\text{Ga}_{1-x}\text{N}$ and $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$
6. GaN/AlGaN/GaN heterostructures for HEMTs

High electron mobility transistors (HEMTs) have come a nearly 40-years long way from supercomputers to wireless charger components and are widely employed for tasks requiring high-voltage and high-frequency performance. Power switching applications up to 600 V are best supported by GaN-based transistors: the polarization fields inherent in III-nitrides result in two-dimensional electron gas (2DEG) densities up to $\sim 10^{13}$ cm$^{-2}$ superior to those in Si- or GaAs-based heterostructures [131–133]. The polarization properties of III-nitrides are due to (i) lattice mismatch-induced strain during growth and associated deviation from wurtzite lattice geometry and (ii) strong polar bonding between cation – anion atoms along the [0001] direction. Crystal polarity defines the properties of the 2DEG. For GaN, Ga-polar growth direction is traditionally preferred over N-polar due to higher chemical stability and smoother surface morphology. However, N-polar GaN notably facilitates the electron transport properties and the performance of GaN/AlGaN/GaN HEMTs [132, 134, 135]. The surface polarity also affects oxygen incorporation, typically with higher oxygen concentration on the N-face [136, 137]. In addition, radiation hardness of III-nitrides makes them material of choice for HEMTs in devices subjected to ionizing radiation such as satellites.

6.1 Trap states at AlGaN/GaN interface of N-polar HEMTs

A schematic cross-section of a typical N-polar HEMT is presented in Figure 6.1(a). It consists of a GaN/AlGaN/GaN heterostructure grown on a-sapphire substrate with about 1.5-μm-thick semi-insulating (S.I.) GaN base layer and covered with AlGaN/GaN cap layers, Si$_x$N$_y$ passivation layer and metallisation layers. Growth conditions are reported in detail in Refs. [138, 139]. N-polar HEMTs with Si-doped GaN/AlGaN/GaN heterostructures with fixed Al/Ga ratio were found to be light-sensitive and prone to current collapse. The charge compensation effect was localized at the bottom AlGaN/GaN interface and attributed to states within the device structure, namely donor-like hole traps at approximately 60 meV from the valence band. To keep the Fermi level from the trap level close
to the valence band, graded design of the Al$_x$Ga$_{1-x}$N:Si layer was introduced with heterostructure similar to that shown in Fig. 6.1(c). The graded structure enhanced HEMTs performance but did not account for the identification of the hole traps [132]. In the energy band diagram in Fig. 6.1(b) the proximity of the valence band to the Fermi level in the undoped heterostructure leads to electron-hole recombination at the bottom AlGaN/GaN interface in N-polar heterostructure in agreement with Ref. [132]. High Si doping ([Si] = 9 × 10$^{18}$ cm$^{-3}$) pushes the valence band significantly lower than the Fermi level thus preventing the modulation of donor traps.

Figure 6.1. (a) Schematic cross-section of a typical N-polar HEMT. (b) Schematic energy band diagram of N-polar undoped and highly-doped GaN/AlGaN/GaN heterostructures (after Ref. [132]). (c) Schematics of the undoped and Si-doped GaN/AlGaN/GaN N-polar heterostructures with graded design Al$_x$Ga$_{1-x}$N layer, 0.05 ≤ $x$ ≤ 0.38, [Si] = 5.5 × 10$^{16}$ cm$^{-3}$ / 9 × 10$^{18}$ cm$^{-3}$.

Figure 6.2(a) displays the $S$ parameter as a function of positron implantation energy measured in N-polar graded design GaN/Al$_x$Ga$_{1-x}$N/GaN heterostructures, $x = 0.05 – 0.38$, with varying Si doping levels. The GaN reference parameters obtained from high-quality GaN:Mg where positrons only annihilate in the free state in the lattice are shown for comparison [106]. The bottom AlGaN/GaN interface is probed at mean implantation depths of 50 – 250 nm. The signal is affected by widening implantation profile, especially at higher implantation energies as discussed in Section 3.3. The $S$ ($W$) parameter for the undoped sample is lower (higher) than that of the Si-doped samples, while the two doping levels produce signals practically indistinguishable from each other. Measured annihilation parameters are clearly different from the reference values thus indicating presence of defects. An increase in the $S$ parameter typically indicates increase in vacancy-type defect concentration or increase in vacancy volume [140–142]. However, the shape of the ($S$, $W$) plot for the undoped and highly Si-doped sample ([Si] = 9 × 10$^{18}$ cm$^{-3}$) in Fig. 6.2(b) only reveals the presence of $V$$_{Ga}$-like defects in the top GaN cap layer, while the difference between annihilation parameters of the undoped and Si-doped heterostructures remains unresolved. Prior to measurements in samples with graded Al/Ga composition the GaN cap thickness
Figure 6.2. (a) The $S$ parameter as a function of positron implantation energy and mean implantation depth in graded design GaN/AlGaN/GaN heterostructures. The region of maximal difference between the undoped and doped structures is highlighted. Inset: GaN cap thickness optimization. (b) The $(S, W)$ parameters for undoped and Si-doped GaN/AlGaN/GaN heterostructures. was optimised as shown in the inset in Fig. 6.2 with sample structure shown in Fig. 6.3(b). The most pronounced signal was obtained from the sample with 100 nm GaN cap (referred to as "ungraded" in the following), which determined the cap thickness for graded design heterostructures.

Fitting the stationary positron diffusion equation using the VEPFIT program [34] to the measurement data was employed to obtain effective positron diffusion length $L_{\text{eff}}^+$ in the layers. According to the 3-layer model with simultaneous fitting of the $S$ and $W$ parameters and the positron diffusion length, Si doping results in doubled $L_{\text{eff}}^+$ in the graded AlGaN layer (from $15 \pm 5$ nm to $35 \pm 5$ nm) and over ten-fold increase in $L_{\text{eff}}^+$ for the bottom GaN layer (from $5 \pm 5$ nm to $80 \pm 15$ nm). Thus the increase in the $S$ parameter for the Si-doped heterostructures seen in Fig. 6.2(a) is associated with the increase of the $L_{\text{eff}}^+$ as cation vacancies cannot account for the observed changes. The abrupt decrease in the $S$ parameter around mean implantation depth of 100 nm is associated with the low $L_{\text{eff}}^+$ around the bottom interface in the undoped sample. In the doped samples, the positron back-diffusion results in less steep reduction of the $S$ parameter.

The changes in the $L_{\text{eff}}^+$ indicate the presence of a positron trap at the bottom AlGaN/GaN interface of the undoped heterostructure, with its $S$ parameter lower than that of the $V_{\text{Ga}}$-type defects. This assumption was further verified by comparing the heterostructure with graded composition of the AlGaN layer to Ga- and N-polar heterostructures with Al$_{0.25}$Ga$_{0.75}$N layer and specially designed Ga- and N-polar multi-quantum-well (MQW) samples with 4 periods of Al$_{0.4}$Ga$_{0.6}$N / GaN shown in Figure 6.3(b)–(c). Remarkably, graded design without doping does not notably vary the $S$ parameter compared to the ungraded
structure as seen in Figure 6.3(a). The data for N-polar MQW differ from the undoped heterostructure mostly at high energies ($E > 20$ keV) where larger sample thickness plays a role. Both Ga-polar samples are very different from their N-polar counterparts. There the positron signal reminds that of the reference sample indicating that positrons are attracted to the top AlGaN/GaN interface, and no trapping at the investigated positron trap is observed.

![Figure 6.3](image)

**Figure 6.3.** (a) The $S$ parameter as a function of positron implantation energy and mean implantation depth in constant composition (ungraded) design heterostructures and MQWs. Undoped heterostructure with graded AlGaN layer and GaN reference are shown for comparison. The region of maximal difference between the undoped and doped structures seen in Fig. 6.2 is highlighted. The structures are N-polar unless Ga-polarity is indicated. (b) Schematics of ungraded N- and Ga-polar heterostructures with Al$_{0.25}$Ga$_{0.75}$N layer. (c) Schematics of Ga-/N-polar MQW samples with 4 periods of Al$_{0.4}$Ga$_{0.6}$N/GaN.

### 6.2 Nitrogen vacancies at AlGaN/GaN interface of N-polar HEMTs

To resolve the nature of the positron trap at the bottom AlGaN/GaN interface Doppler broadening measurements in coincidence mode were employed. Normalized ratio curves for the heterostructures with graded Al/Ga content, the N- and Ga-polar MQWs, the AlN lattice as well as for the theoretically calculated $V_{Ga}$ (Ref. [75], Publ. III) are presented in Figure 6.4(a). The ratio curve for the Ga-polar MQW is close to unity in agreement with Fig. 6.3 thus confirming the similarity of Ga-polar samples to the GaN lattice for positrons. The AlN lattice signal has no effect on the positron data for the measured heterostructures.

The shape of the coincidence Doppler spectra for the N-polar samples indicates the presence of open volume defects different from $V_{Ga}$ as the ratio curve for the interface-characteristic MQW structure is missing the characteristic shoulder-like feature at 1 a. u. $< p_L < 1.5$ a. u. and cannot be categorised as a linear combination of unity and $V_{Ga}$-like signal. The ratio curves of the
heterostructures can be modelled as a linear combination of the N-polar MQW and the $V_{Ga}$ spectra as shown in Fig. 6.4(b). The undoped heterostructure with graded AlGaN layer exhibits strong influence of interface MQW signal (80%) and less pronounced $V_{Ga}$-like feature (20%) due to impact of the GaN cap as discussed in Sec. 6.1. On the contrary, the Si-doped heterostructure with graded Al/Ga content can be remotely represented as a combination of 25 – 30% of interface and 70 – 75% of $V_{Ga}$ ratio curves, while the shoulder-like feature and lower intensity at $p_L > 2$ a. u. remain unaccounted.

As the interface signal evidently has no $V_{Ga}$-related component nor does it resemble the perfect AlN/GaN interface theoretically calculated in Ref. [143], AlN/GaN heterostructures with N vacancies $V_N$ placed at the interface were modelled. Figure 6.4(c) shows ratio curves for the MQW sample, representative of the bottom AlGaN/GaN interface, and theoretically calculated AlN/GaN heterostructures containing $V_N$ at the interface. The calculated ratio curve for the perfect AlN/GaN structure coincides with that calculated for the structure with one $V_N$ and is not shown here. When $V_N$ are placed away from the interface, no positron trapping occurs. Positron confinement to the interface region is a prerequisite for the observed changes in the calculated annihilation spectra. In Fig. 6.4, the theoretical curves for $V_N$ show an agreement with the experimental data from the interface-characteristic MQW sample in both, low and high momenta, regions. This implies that the investigated positron trap is an open volume defect involving $V_N$ localized at the bottom AlGaN/GaN interface in the heterostructures with graded AlGaN layer. Neutral $V_N$, which is a likely case in $n$-type GaN [144, 145], will not interfere with electric-field-driven positron confinement at the interface. In Si-doped heterostructure, weakened contribution of the interface signal is in agreement with the $n$-type doping screening the electric fields driving positron trapping.

Similar to the effect of Si doping, the presence of ionized donors would as well lead to changes in the electric fields landscape resulting in restrained positron localization at the bottom AlGaN/GaN interface. The experimental and theoretical positron annihilation spectra for the N-polar GaN/AlGaN/GaN heterostructures demonstrate positron annihilation at the aforementioned interface region which contains neutral $V_N$ in the sheet concentration of approximately $\sim 10^{14}$ cm$^{-2}$, comparable to the sheet carrier concentration at the top interface of HEMTs [134]. Previously N deficiency has been observed indirectly through the increase in the number of $V_N$ in $V_{In} - nV_{N}$ complexes at InN/GaN interfaces [39, 146, 147]. Nitrogen vacancies are deep donors in GaN and AlN and can potentially act as hole traps in their alloys [144, 145]. Based on that, the charge compensation effect leading to light sensitivity and current collapse in unoptimised N-polar HEMTs might result from trapping of excess holes driven to the bottom AlGaN/GaN at the nitrogen vacancies, and Si doping of the AlGaN/GaN layers compensates for the traps.

These findings call for the following observations: (i) positron annihilation spectroscopy is applicable for studying complex layered HEMTs-like structures,
and (ii) careful experimental design united with theoretical calculations allows for identification of anion vacancies in III-nitrides.

**Figure 6.4.** (a) Normalized coincidence Doppler spectra of the studied heterostructures measured at room temperature. The structures are N-polar unless Ga polarity is indicated. (b) Ratio curves and linear combinations of N-polar MQW signal and $V_{\text{Ga}}$ for the undoped and doped graded heterostructures. (c) Normalized coincidence Doppler spectra of the N-polar MQW sample and calculated $V_{\text{N}}$ for different number of N vacancies at the AlN/GaN interface in the supercell. Regions representative of the $(S, W)$ parameters are highlighted.
In this thesis, defect identification in binary compounds ZnO and GaN, ternary alloys \( \text{In}_x\text{Ga}_{1-x}\text{N} \) and \( (\text{In}_x\text{Ga}_{1-x})_2\text{O}_3 \) as well as in III-nitrides based HEMT structures was carried with positron annihilation spectroscopy. Introduction of defects is deeply rooted in semiconductor growth. There would be no semiconductor industry without this phenomenon, as defects are the salt and pepper of material properties. Gradual understanding that \( p \)-type doping is not achievable in ZnO or is of relatively low efficiency in GaN does not eliminate the applicability of these two semiconductor materials since their other features might be exploited. As an example, wide-range tuning of bandgap by alloying GaN with InN grants increased energy conversion efficiencies and exceptional resistance to irradiation damage for solar cells designs. ZnO, in turn, offers advantages as a substrate of choice for epitaxy growth. Clearly, these applications require control over defects present in the semiconductor materials. Experimental positron annihilation methods used for defect characterisation and assisted by modelling of positron-electron interactions with DFT calculations provide valuable means for investigating formation and behaviour of point defects in lattice. This aspect is especially relevant when developing doping techniques or optimizing growth conditions and post-growth treatment.

The results for the Sb-doped MBE-grown thin film ZnO show that cation vacancies \( V_{\text{Zn}} \) compensate the \( n \)-type doping when \([\text{Sb}]\) is in the order of \( 10^{20} \text{ cm}^{-3} \). At lower \([\text{Sb}]\), the defect landscape also includes vacancy clusters competing with \( V_{\text{Zn}} \). Annealing at 600 °C of low \([\text{Sb}]\) samples promotes vacancy clusters to status of main positron trap without significant impact on conductivity. The presence of \( V_{\text{Zn}}-nV_{\text{O}} \) vacancy clusters in HT-grown ZnO is brought in connection with pre- and post-growth treatment involving high-temperature annealing and mechanical polishing. HT growth is always accompanied by presence of Li which was shown to accumulate close to the surface in samples pre-annealed at 1200 – 1500 °C while as-received material is characterised with uniform distribution of Li within 2 μm into the bulk. Concentration of defects induced by removal of the Li-rich layer is found to drop below the detection limit in case of second annealing at 800 °C. High-temperature second annealing does not affect the polishing-induced defects for the samples pre-annealed below the Li
Conclusions

Redistribution temperature threshold.

Conventional and coincidence Doppler broadening measurements coupled with first-principle electronic structure calculations have revealed that substitutional BeGa-related defects are the main positron traps in the Be-doped MBE-grown thin-film GaN. In samples annealed at 900 °C, generation of \( V_{Ga} \) in concentrations similar to those of BeGa is suggested to originate from Be switching from substitutional to interstitial lattice sites. Further observation of a single lifetime component \( (\tau_{bulk} + 5...10) \) ps in Be-doped HNPS bulk GaN crystals below 300 K and \( V_{Ga} \)-related defects above 300 K supports the interpretation suggested for thin film measurement results and is in agreement with earlier photoluminescence measurements for HNPS bulk GaN. The transition of Be from a substitutional to an interstitial position is found to be reversible, similar to that known for Na and Li in ZnO.

In high-In MOCVD \( In_xGa_{1-x}N \), the effect of He\(^+\) implantation at 40 keV and 100 keV was studied. Upon high-fluence implantation, the redistribution of the metal atoms in the lattice and the enhancement of indium-rich regions were revealed. The associated compositional fluctuations are in charge of defect nature changing from those reminding of \( V_{In} \)-\( V_N \) complexes in InN to \( V_{In} \)-characteristic fingerprint.

The connection between alloy composition and vacancy formation in CSS-PLD \( (In_xGa_{1-x})_2O_3 \) with graded In content was investigated. Indium incorporation improves with increasing oxygen background pressure. Formation of hexagonal phase InGaO\(_3\) II at medium In concentrations is followed by bcc-In\(_2\)O\(_3\) phase at the highest indium content. For increasing In concentration, we find enhanced defect formation which is suppressed for \( (In_xGa_{1-x})_2O_3 \) with \( x > 0.7 \) following the structural changes observed with XRD. Graded Si-doping of \( (In_xGa_{1-x})_2O_3 \) results in high free carrier concentration, up to \( 1 \times 10^{20} \) cm\(^{-3}\), but the mobility of charge carriers is low. In Si-doped \( (In_xGa_{1-x})_2O_3 \), the saturation positron trapping in \( V_{In} \)-like defects suggests substantial defect concentration of at least mid-10\(^{18} \) cm\(^{-3}\), irrespective of the doping level.

The hole trapping at the bottom GaN/AlGaN/GaN heterostructure interface in HEMTs was attributed to significant concentration of \( V_N \). As the AlGaN barrier layer is doped with Si, the donor-like hole traps are no longer deterring the device performance due to introduced electric field screening. The observation of neutral \( V_N \)-like defects was possible at the interface region in undoped N-polar III-nitride heterostructure where the built-in electric fields lead to spatial confinement of positron state.

To sum up, this thesis highlights the importance of point defects for mastering material properties. Understanding the defect formation does not only shed the light on properties of semiconductor materials and devices made thereof but also highlights the practical risks for devices designed to operate at extreme conditions. Our results show similarities between binary semiconductors ZnO and GaN as well as alike trends for ternary alloys. Identification of common trends observed in experiments coupled with actively applied theoretical calculations
provides advanced capability for data interpretation. The first-time observation of interfacial $V_N$-like defects in III-nitride heterostructures demonstrates the synergy of experimental and theoretical methods at its best.
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Point defects in oxide and nitride compounds, alloys and heterostructures