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Revealing the Origin of electrically-active Defects in \( \beta\text{-Ga}_2\text{O}_3 \) and \( \text{r-TiO}_2 \)

Thesis submitted for the degree of Philosophiae Doctor

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Christian Zimmermann
Oslo, May 2020
List of Papers

Paper I

Ti- and Fe-related charge transition levels in $\beta$-$\text{Ga}_2\text{O}_3$

My contribution: Sample preparation, conducting of conventional deep-level transient spectroscopy measurements, analysis of conventional deep-level transient spectroscopy measurements, writing manuscript with input from co-authors, discussion, manuscript revision

Paper II

C. Zimmermann, V. Rønning, Y. K. Frodason, J. B. Varley, V. Bobal, L. Vines
Primary intrinsic defects and their charge transition levels in $\beta$-$\text{Ga}_2\text{O}_3$

My contribution: Sample preparation, development of steady-state photo-capacitance setup, conducting of steady-state photo-capacitance measurements, analysis of steady-state photo-capacitance measurements, discussions, writing of manuscript with input from co-authors, manuscript revisions

Paper III

C. Zimmermann, Y. K. Frodason, V. Rønning, J. B. Varley, L. Vines
Combining Steady-state Photo-capacitance Spectra with First-principles Calculations: The Case of Fe and Ti in $\beta$-$\text{Ga}_2\text{O}_3$

My contribution: Sample preparation, development of steady-state photo-capacitance setup, conducting of steady-state photo-capacitance measurements, analysis of steady-state photo-capacitance measurements, development of the simulation of steady-state photo-capacitance spectra, discussions, writing of manuscript with input from co-authors
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Paper IV

C. Zimmermann, E. F. Verhoeven, Y. K. Frodason, J. B. Varley, P. M. Weiser, L. Vines
*Formation and control of the $E_{2}^{\ast}$ center in implanted $\beta$-Ga$_{2}$O$_{3}$ by reverse-bias and zero-bias annealing*

My contribution: Sample preparation, conducting of capacitance-voltage and deep-level transient spectroscopy measurements, analysis of capacitance-voltage and deep-level transient spectroscopy measurements, discussions, writing of manuscript with input from co-authors

Paper V

*Fabrication and characterization of Schottky barrier diodes on rutile TiO$_{2}$*
*Materials Research Express* (submitted).

My contribution: Sample preparation, conducting of electrical measurements, analysis of electrical measurements, proof-reading of manuscript

Paper VI

*Influence of annealing atmosphere on formation of electrically-active defects in rutile TiO$_{2}$*

My contribution: Sample preparation, conducting of electrical measurements, analysis of electrical measurements, writing manuscript with input from co-authors, discussion, manuscript revision

Paper VII

P. M. Weiser, C. Zimmermann, J. Bonkerud, L. Vines, E. V. Monakhov
*Donors and polaronic absorption in rutile TiO$_{2}$ single crystals*

My contribution: Sample preparation, conducting of conductivity measurements and UV/VIS transmittance measurements, analysis of conductivity measurements, discussions, proof-reading of manuscript
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Related work by the author, not presented in this thesis

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Chapter 1

Introduction

In 2015, the United Nations adopted seventeen goals for sustainable development in order to serve as a guide for global politics in the next decade(s) [1]. One of the goals calls for access to affordable and clean energy for everybody [1]. Technological advancements can play a key role in achieving this goal. Material science is paramount for developing materials and devices for energy-harvesting and -storage which promise clean and affordable electricity. Today, semiconductors already play a significant role in producing clean energy, for example, in the form of silicon-based photo-voltaic power-generation [2]. However, novel solutions are needed especially for storing and converting electricity [2]. Semiconducting oxides are a class of semiconducting materials which have shown potential for a host of applications in energy-harvesting and -storage as well as electricity conversion. In this thesis, the semiconducting oxides titanium dioxide and gallium sesquioxide were studied. Titanium dioxide has shown promise as a photo-catalyst, and can be used to facilitate hydrogen production from water and sun light [3, 4], while gallium sesquioxide is a promising material for power electronics, and hence can be used in efficient electricity conversion [5, 6].

For many applications of semiconductors, material defects are of paramount importance. Material defects are structural imperfections in materials, and are associated with a local breaking of symmetry. The macroscopic features of a material are an emergent property of its constituent elements and their structural arrangement [7]. Hence, defects do not only alter the local structural characteristics of semiconductors, but also their macroscopic properties, such as their optical and electrical properties. The material’s optical and electrical characteristics have a huge influence on the efficiency of devices for energy-harvesting and -storage as well as electricity conversion.

Point defects are imperfections on the scale of an atom, and are often of particular interest. Importantly, small amounts of point defects in a material can already have a pronounced influence on the macroscopic properties of a material. Studying point defects and their impact on material properties is often akin to finding the needle in the haystack and characterizing the needle’s properties at the same time. Interestingly, this analogy cuts two ways [8]. On the one hand, it illustrates that it is generally challenging to study small amounts of microscopic entities dispersed in a large volume. On the other hand, the needle or defect is distinct from the hay or the surrounding material, and hence it might be easy to pick it out, even if there are only very small amounts of it.

For this thesis, the second interpretation of the needle-in-the-haystack analogy is more fitting. Many defects have properties that distinguish them from the surrounding material, and can be seen as defect-specific fingerprints. Charge state transition levels are such a defect-specific property [9]. Charge state
transition levels are energy levels related to the interaction between electrons and charged defects. Charge state transitions of defects can be triggered thermally (thermodynamic) or by photons (optical). One of the main objectives of this thesis was the assignment of charge state transition levels to specific (electrically-active) defects in the semiconducting oxides titanium dioxide and gallium sesquioxide. This work is akin to matching a fingerprint to the specific person it belongs to. Once the fingerprints are assigned, they can be used in further studies to unambiguously identify the perpetrator (or defect). Notably, the assignment of fingerprints to defects can be done in fairly simple model systems, and it is often possible to use the gained knowledge also in less simple, potentially more application-relevant, situations. Generally, one needs to use a combination of (characterization) techniques to match charge state transition levels to specific defects. Besides techniques used for characterizing the properties of materials or defects, one also employs tools to controllably introduce defects into materials. Often, a particular study design will be suitable for identifying a particular class of defects. Defect identification is often done by identifying correlations between results from several techniques or correlations between sample-treatments and results from characterization techniques. In this thesis, defect-related charge state transition levels in semiconductors were probed with a class of characterization methods called space-charge spectroscopy [9]. These methods are sensitive to very small amounts of defects. However, it is necessary to use electrical junctions as the probe, hence suitable junctions involving the material of interest need to be fabricated. First-principles computations have seen significant advancements in the last years due to, for example, the introduction of hybrid-functionals, and particularly the prediction of charge state transition levels in semiconductors has been improved [10–12]. Thus, it has become common to use first-principles calculations to corroborate or falsify experimental findings [10, 11]. However, it can be challenging to compare calculated defect signatures to experimental results. Hence, it is important to find ways to generate expected experimental signatures, for example, for a specific defect from its calculated properties. Indeed, one often needs to combine computations, theory and experiment in order to identify defects. For semiconducting oxides, such as titanium dioxide and gallium sesquioxide, to live up to their promise for applications, defects in the materials need to be understood better. Particularly, the charge state transition levels of defects play an important role in the material properties relevant for their respective applications. In titanium dioxide, defects can significantly improve its photo-catalytic behavior by extending the optical absorption of the material spectrally as well as by improving the charge transfer at the surface essential for its functioning as a catalyst. For gallium sesquioxide, defects are important in controlling its electrical conductivity by acting as donors or acceptors in the material. Furthermore, defects can govern the characteristics of electrical junctions comprising gallium sesquioxide used in, for example, power electronics. In this thesis, a wide range of characterization techniques were employed to identify defects in the semiconducting oxides titanium dioxide and gallium
sesquioxide. For most studies, techniques designed for detecting charge state transition levels were combined with techniques that probe the presence of structural defects or residual impurities. If correlations were found, computational results were used to corroborate the results if possible. In order to identify defects in novel materials, it is often necessary to extend the limits of existing characterization tools. In this thesis, a new setup for identifying optical charge state transition levels was developed utilizing steady-state photo-capacitance measurements. Specifically, a setup was developed which allows for unique studies involving the controlled generation of intrinsic defects combined with the detection of their corresponding optical charge state transition levels. The developed setup can be useful in studying defects in any kind of semiconducting material.

This thesis is split into nine parts, including this introduction. In Sec. 2, the basic principles of semiconductors will be introduced. The focus of the description will be on the properties of defects, and specifically their charge state transition levels. For the most part, charge state transition levels of defects in semiconducting oxides were identified by space-charge spectroscopy techniques which utilize electrical junctions as probes, and hence junctions will be introduced in Sec. 3. In Sec. 4, the semiconducting oxides studied here will be introduced, with a focus on their potential applications and what was previously known about (point) defects in the materials. The experimental and computational methods used in this thesis will be presented in Sec. 5, including an introduction to the newly-developed setup for steady-state photo-capacitance measurements. A summary of the results obtained during this PhD project is given in Sec. 6, and the thesis is concluded with an overall summary in Sec. 7. The papers included in this thesis are appended at the end of the thesis. Additional information relevant for the thesis can be found in the Appendix.

Paper I - IV deal with gallium sesquioxide, while Paper V - VII are about titanium dioxide. In Paper I, the charge state transition levels of Ti- and Fe-related defects in monoclinic gallium sesquioxide were identified. Paper II presents results concerning primary intrinsic defects and their optical charge state transition levels in monoclinic gallium sesquioxide. Paper III illustrates how optical charge state transition levels obtained from first-principles calculations and measurements of defect-related optical charge state transitions can be properly compared using Ti- and Fe-related defects in monoclinic gallium sesquioxide as an example. In Paper IV, it was shown how the formation of defect complexes in monoclinic gallium sesquioxide upon ion implantation can be influenced via altering the fermi-level position in the semiconductor by applying an external bias voltage to a Schottky barrier diode. In Paper V, it was presented how rectifying junctions comprising rutile titanium dioxide can be fabricated which allow for space-charge spectroscopy, and hence the detection of charge state transition levels present in rutile titanium dioxide using space-charge spectroscopy. In Paper VI, the influence of heat-treatments on the defects present in rutile titanium dioxide was studied using space-charge spectroscopy. In Paper VII, the optical absorption of titanium dioxide related to defects was studied and related to the presence of polarons as well as different donors in the material.
Chapter 2

Semiconductors

In the following chapter, semiconductors will be introduced. The description will focus on the electrical and optical properties of semiconductors, and particularly, on the influence defects have on these properties. A particular focus of this thesis lay on the interaction of charge carriers and defects which will be introduced in a separate section. More information about semiconductors and their electrical as well as optical properties can be found in the Ref [7, 9, 13].

2.1 Electrical and Optical Properties

Materials consist of a large number of individual atoms ($\approx 1 \times 10^{23} \text{cm}^{-3}$), and are characterized by their chemical composition and structure. Material properties, such as electrical and optical properties, emerge from the structure and composition of materials. Crystalline materials are of special interest for this thesis. Crystalline materials are characterized by symmetries, specifically, translational and rotational symmetries as well as inversion symmetry, and can be described by defining an unit cell, which encompasses all the rotational and inversion symmetries of the material. The unit cell is repeated in all directions of space to form the macroscopic solid.

In individual atoms, (valence) electrons reside at specific energy levels. Joining together a large number of atoms to form a material will lead to a broadening of the discrete energy levels into energy bands as shown in Fig. 2.1 (a). The energy bands can be separated by energy gaps void of electronic states. The energetically highest-lying energy band which is occupied with electrons is called valence band, while the energetically lowest-lying energy band void of electrons is called conduction band. The top of the valence band (valence band edge) is often labeled as $E_V$, while the bottom of the conduction band (conduction band edge) is denoted as $E_C$. The energy gap separating $E_C$ and $E_V$ is called the band gap ($E_g$). The spatial dependence of the energy bands is represented in a so-called band diagram (see Fig. 2.1 (b)). Unoccupied electronic states in the valence band (missing electrons) are called holes. Holes are quasi-particles which can be used to effectively describe the properties of the ensemble of electrons in the valence band.

The band structure refers to the representation of the energy bands in dependence on the momentum $k$ of the electrons or holes (see Fig. 2.1 (c)). From the band structure the effective mass of electrons ($m_{n,\text{eff}}$) and holes ($m_{p,\text{eff}}$) can be deduced. $m_{n,\text{eff}}$ and $m_{p,\text{eff}}$ represent an effective value for the electron or hole mass in a material due to the interaction of the charge carriers with the
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Figure 2.1: **Band diagram and band structure:** (a) Schematic illustration how the discrete electronic states found in atoms broaden into energy bands when materials are formed. (b) Schematic illustration of the band diagram of a typical semiconductor. (c) Schematic illustration of the band structure of a typical semiconductor. The origo in such diagram is often denoted with the Greek letter $\Gamma$. The curvature of the valence and conduction band is also called dispersion and is often approximated around the conduction and valence band edge with parabola (parabolic approximation).

Materials are classified as either metals, semiconductors or insulators depending on their electrical properties. Often, the classification is performed with respect to their band gap $E_g$ and whether the material’s electrical properties can be controlled by doping which will be discussed in Sec. 2.2.1. Materials can conduct electrical current, if either their conduction or valence band is only partially filled with electrons. The fermi-level $E_F$ represents the chemical potential of electrons in the material. The relative position of $E_F$ to $E_C$ or $E_V$ describes the fraction to which the energy bands are filled with electrons. The distribution of electrons across the energy levels $E$ in a material is described by the Fermi-Dirac function $f(E)$:

$$f(E) = \frac{1}{1 + \exp \left( \frac{E - E_F}{k_B T} \right)}.$$  \hfill (2.3)
Here, \( k_B \) is Boltzmann’s constant, while \( T \) is the temperature of the semiconductor. Often, \(|E - E_F| \gg k_B T\) is valid, and hence the Boltzmann distribution

\[
f (E) \sim \exp \left( -\frac{E - E_F}{k_B T} \right)
\]  
(2.4)

can be used as an approximation of Eq. 2.3. \( f (E) \) expresses the fraction of electronic states at an energy \( E \) which will be occupied with electrons. \( N (E) \) is used to describe the density of available electronic states at the energy \( E \). The density of states related to the conduction band (\( N_{CB} (E) \)) and the valence band (\( N_{VB} (E) \)) can be expressed as:

\[
N_{CB} (E) = \frac{g}{2\pi^2} \left( \frac{2m_{n,\text{eff}}}{\hbar^2} \right)^{3/2} \sqrt{E - E_C}
\]  
(2.5)

and

\[
N_{VB} (E) = \frac{g}{2\pi^2} \left( \frac{2m_{p,\text{eff}}}{\hbar^2} \right)^{3/2} \sqrt{E_V - E}.
\]  
(2.6)

\( g \) is the so-called degeneracy taking into account how many equivalent conduction or valence bands exist. Often, one treats the conduction and valence band as an effective electronic state with density \( N_C \) and \( N_V \) located at \( E_C \) and \( E_V \), respectively (see Fig. 2.3 (c)), whereby \( N_C \) and \( N_V \) can be calculated via

\[
N_C = 2g \left( \frac{2\pi m_{n,\text{eff}} k_B T}{\hbar^2} \right)^{3/2}
\]  
(2.7)

and

\[
N_V = 2g \left( \frac{2\pi m_{p,\text{eff}} k_B T}{\hbar^2} \right)^{3/2}.
\]  
(2.8)

When applying an electrical field \( \mathcal{E} \) to a material, electrons or holes are transported through the material. The current density \( j \) describes the amount of charge passing through an area \( A \) of the material per time \( t \). \( j \) can be expressed as

\[
j = \sigma \mathcal{E}.
\]  
(2.9)

\( \sigma \) denotes the electrical conductivity of a material, and can be described by:

\[
\sigma = e (\mu_n n + \mu_p p).
\]  
(2.10)

Here, \( e \) denotes the elementary charge, \( \mu_i \) is the mobility of electrons (\( i = n \)) or holes (\( i = p \)), respectively. \( n \) and \( p \) are the densities of electrons or holes in the conduction or valence band, respectively, while \( \mu_i \) can be calculated by:

\[
\mu_i = \frac{e \tau_i}{m_{i,\text{eff}}} \quad (i = n, p).
\]  
(2.11)

Here, \( \tau_i \) denotes the relaxation time of electrons (\( i = n \)) or holes (\( i = p \)), describing the average time between scattering events. In ideal semiconductors, scattering
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can involve phonons or other charge carriers. $m_{i, \text{eff}}$ is the effective mass of electrons ($i = n$) or holes ($i = p$). For free charge carriers, $m_{n, \text{eff}}$ is determined by Eq. 2.1 while $m_{p, \text{eff}}$ is calculated according to Eq. 2.2. In ideal semiconductors, electrons are thermally-excited from the valence to the conduction band at a material-specific temperature related to $E_g$, increasing $n$ as well as $p$. Thus, semiconductors will become more conductive at such temperatures. Material defects have a pronounced influence on $\sigma$. Indeed, one of the main objectives of this thesis was to probe the influence of defects on properties determining $\sigma$. Thus, the influence of defects on $\sigma$ will be further discussed in Sec. 2.2.1.

The interaction between matter and light is generally described by the complex refractive index $\tilde{n}$ of a material which can be expressed as [13]:

$$\tilde{n} = n + i\kappa. \quad (2.12)$$

$n$ is the real part of the refractive index, and is connected to the refraction of light entering a material. $\kappa$ is the imaginary part of the refractive index, and is related to the attenuation of light propagating through a material. More information regarding the interaction of light and a material described by $\tilde{n}$ can be found in Sec. A of the Appendix.

The attenuation of light inside a material can occur by scattering or absorption. Often scattering is neglected, and the absorption coefficient $\alpha$ is used to describe the attenuation of light inside a material. $\alpha$ and $\kappa$ are connected via:

$$\alpha = \frac{4\pi}{\lambda} \kappa. \quad (2.13)$$

$\lambda$ denotes the wavelength of the light. $\lambda$ and the photon energy $E_{\text{Ph}}$ are related by:

$$E_{\text{Ph}} = \frac{hc}{\lambda}. \quad (2.14)$$

Here, $c$ denotes the speed of light in vacuum.

In semiconductors, the excitation of electrons from the valence to the conduction band can be triggered by photons, and will contribute to optical absorption (band-to-band absorption). Photons can also couple with vibrations of the constituent atoms of a material, and absorbed photons are transformed into phonons, representing the collective motion of the host atoms (lattice absorption). In conductive semiconductors, photons can excite electrons inside the conduction band and/or holes in the valence band (intra-band transitions) which is usually denoted as free charge carrier absorption. Moreover, there are several processes related to defects in semiconductors which will contribute to optical absorption. Such processes were extensively studied in this thesis, and hence will be discussed in more detail in Sec. 2.2.2.

2.2 Defects

A defect is a structural imperfection in a material. Defects are accompanied by the local breaking of the symmetry of the pristine material. In crystalline
Defects in materials, one can distinguish defects according to their dimensionality: three- (for example, particle inclusions), two- (for example, grain boundaries), one- (for example, dislocations) or zero-dimensional defects (for example, impurities, vacancies, self-interstitials) as illustrated in Fig. 2.2.

For this thesis, zero-dimensional or point defects are of particular interest. Point defects can be subdivided into two different categories: Intrinsic and extrinsic defects. Intrinsic defects are imperfections related to atoms which are part of the host material, for example, missing atoms in the lattice (vacancies) or atoms displaced from their actual lattice position residing in a space between lattice sites (self-interstitials). In compounds, i.e., materials consisting of two or more chemical elements, so-called antisite defects can also form. In metal oxides, a metal atom substituting on an oxygen site or an oxygen atom substituting on a metal site are examples of antisite defects. Extrinsic defects involve impurities, i.e., atoms, which are not part of the pristine material. In this thesis, the following notation will be used to denote point defects [14–16]:

$$X^q_{S}.$$ 

Hereby, $X$ denotes the defect species. $V$ represents vacancies, while specific atoms are presented by their element symbol. $S$ denotes the site where the defect resides. For example, $i$ represents an interstitial position, while actual lattice positions are described by the host element that occupies the respective site in the pristine material (see Fig. 2.3 (a)). Notably, crystallographically-inequivalent sites need to be distinguished. $q$ represents the charge of the defect. Here, the charge will be represented as absolute charge [16]. Point defects can also form complexes consisting of two or more point defects in close vicinity. Defect complexes possess properties which are not merely a sum of its constituents. For
defect complexes consisting of two defects $X_S$ and $Y_T$ the following notation will be used in this thesis:

$$(X_S - Y_T)^q.$$ 

A specific defect can exhibit different charge states $q$. A change of charge state is connected to a charge state transition from a charge state $q_1$ to a charge state $q_2$. Charge state transitions are connected to the emission or capture of charge carriers by a defect. The emission and capture of charge carriers from and by defects in semiconductors was used extensively in this thesis to study the properties of defects in semiconductors. Both processes will be thoroughly discussed in Sec. 2.3.1. This thesis focuses on electrical and optical properties of semiconductors, and hence the influence of defects on these properties will be discussed in the following sections.

### 2.2.1 Influence of Defects on the Electrical Properties of Semiconductors

Defects can influence the charge carrier concentration ($n$ and $p$) as well as the mobility of charge carriers ($\mu_n$ and $\mu_p$) in semiconductors, and hence may determine the electrical conductivity of a semiconductor (see Eq. 2.10). Defects can be intentionally introduced into a semiconductor to control $n$ and $p$ which is typically called doping. Semiconductors with an excess of electrons ($n > p$) are called $n$-type, while semiconductors with an excess of holes ($p < n$) are denoted as $p$-type. Conversely, semiconductors with $n = p$ (for example, pristine semiconductors) are called intrinsic semiconductors. Often, $n \gg p$ is valid for $n$-type semiconductors, while $p \gg n$ is valid for $p$-type semiconductors.

One common way to dope a semiconductor is to introduce impurities on substitutional sites (see Fig. 2.2) which have a different valency than the atom they substitute for. If the foreign atom has a higher valency, it may act as a donor, potentially contributing an electron to the semiconductor, and hence increase $n$. If the foreign atom has a lower valency, it can act as an acceptor, potentially contributing a hole to the semiconductor, and hence increase $p$. Notably, intrinsic as well as extrinsic defects introduced on any site in the lattice can act as acceptors or donors. Whether a defect acts as an acceptor or donor depends on the possible charge states the defect can display. For example, a defect which can exhibit more negative charge states than its neutral charge state can act as an acceptor. In principle, the same defect can exhibit acceptor as well as donor behavior [17].

The process of contributing an electron (donor) or hole (acceptor) to the semiconductor is accompanied by the ionization of the dopant, and an energy $E_i$ is needed to ionize the corresponding dopant. Only ionized dopants will contribute to $n$ or $p$. The values of $n$ and $p$ due to ionized dopant atoms can be described by:

$$\begin{align*}
n \quad p \quad &= \quad N_j \exp \left( - \frac{E_i}{k_B T} \right).
\end{align*}$$

(2.15)
Here, $N_j$ is the total concentration of dopant atoms, and $j = D$ will be used to denote donors while $j = A$ will be used to denote acceptors. Shallow dopants have an $E_i$ which is in the order of $k_BT$, and their $E_i$ is often described within the framework of effective mass theory. The process of ionization of a dopant is described as a charge state transition, which is represented by a charge state transition level. In this work, the charge state transition of a defect $D$ from a charge state $q_1$ to a charge state $q_2$ is denoted as $D^{q_1/q_2}$ [10]. Thus, the ionization of an acceptor $A$ is related to the charge state transition $A^{q-1/q}$, while the ionization of a donor $D$ is associated with $D^{q/q+1}$. Deep donors will have charge state transition levels $E_t$ which are more than $k_BT$ below $E_C$, while deep acceptors will possess $E_t$ further above $E_V$ than $k_BT$.

Electrons or holes created due to thermal ionization of dopant atoms will occupy electronic states within the conduction or valence band, respectively. As mentioned before, the occupation of the conduction and valence band with electrons and holes is described by $E_F$ (see Eq. 2.3 and 2.4). Often, one assumes $n = N_D$ for $n$-type semiconductors and $p = N_A$ for $p$-type semiconductors. In these cases, $E_F$ can be calculated by:

$$E_F = \begin{cases} 
E_C - k_BT \ln \left( \frac{N_C}{N_D} \right), \text{ for a } n \text{-type semiconductor} \\
E_V + k_BT \ln \left( \frac{N_N}{N_A} \right), \text{ for a } p \text{-type semiconductor} 
\end{cases} \tag{2.16}$$

Here, $N_C$ and $N_V$ are defined according to Eq. 2.7 and 2.8, respectively.

Often, there will be several defect species present in a semiconductor. For example, if acceptor defects are present in nominally donor-doped material, they

![Defect-related electronic states](image-url)
2. Semiconductors

will decrease \( n \), maintaining overall charge neutrality. One often uses effective dopant concentrations, i.e., the difference in concentration between acceptors and donors as \( |N_D - N_A| \) to describe the doping level of a semiconductor. Indeed, the effective dopant concentration should be used in Eq. 2.16. Generally, the distribution of electrons across electronic states at \( E \) will be described by Eq. 2.3 even in the presence of defect-related electronic states. Charge state transition levels of defects are defect-related electronic states. In band structures, defects introduce dispersion-less states as shown in Fig. 2.3 (b). The density of states connected to point defects is usually assumed to be represented by a peak-like function, such as a delta-, gaussian, lorentzian or double-sigmoidal function [18, 19]. Fig. 2.3 (c) displays schematically the density of states in a semiconductor and the filling of the respective states with electrons if one approximates the valence and conduction band with a single effective electronic state at \( E_V \) and \( E_C \), respectively.

In Sec. 2.1, it was stated that the mobility of charge carriers in a semiconductor is inversely proportional to \( \tau_i \) (\( i = n, p \)), describing the average time between scattering events. Scattering can also occur between charge carriers and ionized defects (for example, with ionized dopant atoms). Defects can also influence the charge carrier transport by trapping of electrons or holes, described by charge state transitions of the corresponding defects. Trapping of electrons and holes is usually described as electron or hole capture. Conversely, the de-trapping of electrons or holes from defects is described as electron or hole emission. The interaction between charge carriers and defects was studied extensively in this thesis, and the concepts of electron as well as hole capture and emission will be introduced in more detail in Sec. 2.3.1. Notably, electrons and holes can also become self-trapped. Self-trapped electrons or holes are often denoted as polarons. Polarons are a special kind of defect, consisting of a charge carrier trapped in a lattice distortion of the host atoms. More information concerning polarons can be found in Sec. B in the Appendix.

2.2.2 Influence of Defects on the Optical Properties of Semiconductors

Fig. 2.4 shows the optical absorption spectrum of a typical semiconductor, illustrating some processes giving rise to optical absorption in semiconductors. There are several processes contributing to optical absorption which are related to defects. Often, there will be a so-called Urbach tail visible as an extension of the band-to-band absorption. This Urbach tail is related to tail states of the conduction and/or valence band, for example, caused by high defect densities. Defects can also give rise to charge state transition levels inside the band gap of a semiconductor. Charge state transitions can be triggered by photons. The optical absorption related to charge state transitions of defects was used extensively in this thesis to identify and study defects, and will be discussed more thoroughly in Sec. 2.3.3. Photons can also couple with vibrations of defects present in the lattice, and hence with phonons. If photons couple with the vibration of defects, the vibrations are associated with localized vibrational modes (LVM) [20].
Interaction between charge carriers and defects

Figure 2.4: **Optical absorption in semiconductors:** Typical optical absorption spectrum of a semiconductor with a band gap of around 2 eV. The insets illustrate the physical origins behind the various features: (I) Optical excitation of electrons from the valence to the conduction band. (II) Optical excitation of electrons involving the tail states of the conduction as well as the valence band (Urbach tail). (III) Defects can give rise to charge state transition levels inside the band gap of a semiconductor. Such charge transitions can also be triggered by the absorption of photons (see Sec. 2.3.3). (IV) Photons can couple with defects in the lattice directly. The absorbed photon will be transformed into a localized vibration. (V) In conductive semiconductors, the conduction or valence band is partially filled with charge carriers. Electrons or holes can be excited by photons inside these bands (intra-band transitions). (V) Photons can also couple with the host lattice itself. Absorbed photons are transformed into phonons, and hence a collective motion of the host atoms.

The photon energy related to the LVM will depend on the reduced mass of the defect [20]. It is common to study impurity-related defects using optical absorption related to LVM. Generally, impurities lighter than the host lattice will exhibit LVMs which are associated with photon energies above the optical absorption due to vibrations of the host lattice. Furthermore, the LVM are only observed in measurements of optical absorption if they are connected to a dipole moment which changes during the vibration [20]. From the energetic position of the LVM as well as the dependence of their intensity on temperature and polarization of the incident light, the structure and charge of the involved defect can be gauged [20]. In this thesis, H-related defects were studied by observing optical absorption due to their LVM.

2.3 Interaction between charge carriers and defects

2.3.1 General Remarks

In this section, the interaction between charge carriers and defects will be introduced more thoroughly. Particularly, the emission and capture of charge...
carriers from and by defects in semiconductors will be discussed. On the one hand, the interaction between charge carriers and defects has a pronounced impact on the electrical and optical properties of a material, and thus can be decisive for the performance of (opto-)electronic devices. On the other hand, the interaction between charge carriers and defects can be used to study defects in semiconductors. The latter was used extensively in this thesis.

Fig. 2.5 (a) displays a semiconductor containing a defect D with a charge state transition $D^{q/q-1}$ exhibiting a charge state transition level $E_t$ inside the semiconductor’s band gap. The trap can either capture electrons ($e^-$) from the conduction band or holes ($h^+$) from the valence band. Such processes can be described by:

$$
D^q + e^- \rightarrow D^{q-1}, \quad D^{q-1} + h^+ \rightarrow D^q.
$$

The corresponding rates for capture are defined as $C_n$ and $C_p$ for electrons and holes, respectively. Electrons or holes can also be emitted from the trap level to...
the conduction or valence band, respectively. Such processes can be described by

\[
\begin{align*}
D^q &\rightarrow D^q - e^- \\
D^q &\rightarrow D^{q-1} + h^+
\end{align*}
\]

(2.18)
The corresponding rates for emission are denoted as \(E_n\) and \(E_p\) for electrons and holes, respectively. \(C_n (E)\) denotes the capture rate for electrons residing at an energy \(E\) by a trap, while \(E_n (E)\) represents the emission rate of electrons from a trap to an energy level at \(E\). The corresponding rates can be calculated by [21]:

\[
C_n = [1 - f (E_t)] \times \frac{N_t}{N(E)} \times f(E) \times \langle c_n \rangle
\]

(2.19)

and

\[
E_n = f (E_t) \times \frac{N_t}{N(E)} \times [1 - f (E)] \times \langle e_n \rangle \times \langle e_n \rangle
\]

(2.20)

Similar expressions can be found for the capture and emission rates for holes denoted as \(C_p (E)\) and \(E_p (E)\), respectively. The occupancy of the trap and states at \(E\) is described by the Fermi-Dirac distribution \(f\) (see Eq. 2.3).

In this thesis, electron processes are considered to be processes that involve electronic states \(E\) in the conduction band, while hole processes are processes that involve electronic states \(E\) in the valence band. To obtain the total rate of capture and emission denoted as \(C_{n,\text{tot}}\) and \(E_{n,\text{tot}}\), respectively, one needs to integrate Eq. 2.19 and 2.20 for all energies \(E\) inside the conduction band. Thus, one obtain

\[
C_{n,\text{tot}} = (1 - f_t) N_t \langle c_n \rangle
\]

(2.21)

and

\[
E_{n,\text{tot}} = f_t N_t (N_C - n) \langle e_n \rangle
\]

(2.22)

if the conduction band is approximated by an effective energy level with an effective density of states \(N_C\) (see Fig. 2.3 (c)) [21]. \(f_t\) is a short-hand notation for \(f (E_t)\), and \(\langle c_n \rangle\) as well as \(\langle e_n \rangle\) are appropriate averages of \(c_n (E)\) and \(e_n (E)\), respectively. Similar expressions can be found for \(C_{p,\text{tot}}\) and \(E_{p,\text{tot}}\) [21]:

\[
C_{p,\text{tot}} = f_t N_t \langle c_p \rangle
\]

(2.23)

and

\[
E_{p,\text{tot}} = (1 - f_t) N_t (N_V - p) \langle e_p \rangle.
\]

(2.24)

It is useful to introduce the short-hand notation \(n_t\) for the number of traps filled with electrons as:

\[
n_t = f_t N_t.
\]

(2.25)
Often, it is relevant to compute the time-dependent (transient) behavior of the capture and emission of charge carriers by and from traps, respectively. The time-evolution of $n_t$ can be described by the following differential equation:

$$\frac{\partial n_t}{\partial t} = C_{n,\text{tot}} + E_{p,\text{tot}} - E_{n,\text{tot}} - C_{p,\text{tot}}. \quad (2.26)$$

Emission and capture processes can involve phonons as well as photons. Processes involving only phonons are thermal and will be denoted with a superscript $\text{th}$ for thermal (see Sec. 2.3.2), while processes involving also photons will be denoted with the superscript $\sigma$ for optical (see Sec. 2.3.3).

Capture and emission processes can be further understood by consulting configuration coordinate diagrams (see Fig. 2.5 (b)) [10, 11, 22]. In a configuration coordinate diagram, the energy of a certain defect configuration is displayed depending on the configuration coordinate $Q$. $Q$ represents the distortion of the lattice around the defect and is usually expressed in momentum space. Stable configurations can be found at the minima of the energy curves which can be approximated with parabola for small distortions. For a charge localized at the defect $D$ ($D^q-1$ in Fig. 2.5 (b)), the stable structure of the defect and the surrounding lattice will be different compared to the stable structure associated with a delocalized electron and the defect ($D^q + e_{\text{CBM}}$ and $D^q + e_{\text{VBM}}$ in Fig. 2.5 (b)). Configuration coordinate diagrams can also be used to describe free as well as bound polarons (see Sec. B) [23]. For example, the excitation of a self-trapped electron (free polaron) to the conduction band can be viewed as a charge state transition of a polaron defect even though no actual lattice defect is present.

### 2.3.2 Thermal Processes

The capture of electrons or holes by a defect is a thermal process usually involving multiple phonons [9–11, 22, 24, 25]. The probability $\langle c_i^{\text{th}} \rangle$ for a trap to capture charge carriers is described by

$$\langle c_i^{\text{th}} \rangle = v_{\text{th},i} \sigma_i^{\text{th}}. \quad (2.27)$$

Here, $v_{\text{th},i}$ denotes the thermal velocity of electrons ($i = n$) or holes ($i = p$). The thermal velocity of charge carriers is calculated via:

$$v_{\text{th},i} = \sqrt{\frac{3k_BT}{m_{i,\text{eff}}}}. \quad (2.28)$$

$m_{i,\text{eff}}$ represents the effective mass for electrons ($i = n$) or holes ($i = p$). Notably, $m_{i,\text{eff}}$ is the effective mass relevant for the transport of the charge carrier species, i.e., for polarons one needs to use the polaron mass (see Sec. B). $\sigma_i^{\text{th}}$ represents the capture cross section describing the propensity of a trap to capture a certain kind of charge carrier. The capture process can be understood by consulting configuration coordinate diagrams (see Fig. 2.5 (b)). For an electron or hole to be
captured, it is necessary to overcome the capture barrier \( E_b \) or \( E_b^* \), respectively, and hence the capture cross section \( \sigma_{i}^{\text{th}} \) can be expressed by [10, 22]:

\[
\sigma_{i}^{\text{th}} = \begin{cases} 
\sigma_{n,\infty}^{\text{th}} \exp \left( -\frac{E_b}{k_B T} \right), & \text{for electrons} \\
\sigma_{p,\infty}^{\text{th}} \exp \left( -\frac{E_b^*}{k_B T} \right), & \text{for holes}
\end{cases}
\] (2.29)

\( \sigma_{i,\infty}^{\text{th}} \) is a pre-factor which also contains a term representing the entropy change accompanying the capture process [22]. For low temperatures, \( \sigma_{i,\infty}^{\text{th}} \) is independent of temperature, while for higher temperatures \( \sigma_{i,\infty}^{\text{th}} \) exhibits a temperature dependence of the form \( 1/\sqrt{T} \) [24, 25].

In thermal equilibrium, \( C_{n,\text{tot}} \) will be equal to \( E_{n,\text{tot}} \), and \( C_{p,\text{tot}} \) will be equal to \( E_{p,\text{tot}} \) (see Eq. 2.21 - 2.24). This reasoning is often called detailed balance [21]. Detailed balance leads to a relation between \( \langle c_{\text{th}}^{\text{i}} \rangle \) and \( \langle e_{\text{th}}^{\text{i}} \rangle \) (i = n, p), and the emission probabilities \( \langle c_{\text{th}}^{\text{i}} \rangle \) can be expressed as

\[
\langle e_{\text{th}}^{\text{n}} \rangle = \langle c_{\text{th}}^{\text{n}} \rangle \exp \left( -\frac{E_C - E_{\text{th}}^{\text{n}}}{k_B T} \right), \quad \text{for electrons}
\]

\[
\langle e_{\text{th}}^{\text{p}} \rangle = \langle c_{\text{th}}^{\text{p}} \rangle \exp \left( -\frac{E_C - E_{\text{th}}^{\text{p}}}{k_B T} \right), \quad \text{for holes}
\] (2.30)

Here, it is assumed that the conduction and valence band can be represented by an effective energy level at \( E_C \) and \( E_V \), respectively. Combining Eq. 2.30 with 2.27 and Eq. 2.29, one obtains:

\[
\langle e_{\text{th}}^{\text{n}} \rangle = v_{\text{th},n}^{\text{th}} \sigma_{n,\infty}^{\text{th}} \exp \left( -\frac{E_b}{k_B T} \right) \exp \left( -\frac{E_C - E_{\text{th}}^{\text{n}}}{k_B T} \right), \quad \text{for electrons}
\]

\[
\langle e_{\text{th}}^{\text{p}} \rangle = v_{\text{th},p}^{\text{th}} \sigma_{p,\infty}^{\text{th}} \exp \left( -\frac{E_b^*}{k_B T} \right) \exp \left( -\frac{E_C - E_{\text{th}}^{\text{p}}}{k_B T} \right), \quad \text{for holes}
\] (2.31)

Often, the following short-hand notations are used:

\[
e_{\text{th}}^{\text{n}} = N_C \langle e_{\text{th}}^{\text{n}} \rangle, \quad \text{(2.32)}
\]

\[
e_{\text{th}}^{\text{p}} = N_V \langle e_{\text{th}}^{\text{p}} \rangle, \quad \text{(2.33)}
\]

\[
c_{\text{th}}^{\text{n}} = \langle c_{\text{th}}^{\text{n}} \rangle \quad \text{(2.34)}
\]

and

\[
c_{\text{th}}^{\text{p}} = \langle c_{\text{th}}^{\text{p}} \rangle. \quad \text{(2.35)}
\]

### 2.3.3 Optical Processes

Defect-related charge state transitions can also be triggered by photons with sufficient energy [9, 11, 26]. The probability of the optically-induced emission of electrons \( \langle e_{\text{th}}^{\text{o}} \rangle \) and holes \( \langle e_{\text{th}}^{\text{o}} \rangle \) can be expressed by [26]:

\[
\langle e_{\text{th}}^{\text{o}} \rangle = \Phi \sigma_{i}^{\text{o}}.
\] (2.36)

Here, \( \Phi \) denotes the photon flux and \( \sigma_{i}^{\text{o}} \) represents the cross-section for optically-induced emission of electrons (i = n) or holes (i = p). \( \sigma_{i}^{\text{o}} \) is often also called
photo-ionization cross section or absorption cross section. Typically, the following short-hand notations are used:

\[ e_n^o = N_C \langle e_n^o \rangle \]  \hspace{1cm} (2.37)

and

\[ e_p^o = N_V \langle e_p^o \rangle. \]  \hspace{1cm} (2.38)

In configuration coordinate diagrams, optically-induced electron and hole emission are represented by vertical transitions: \( E_v^t \) for electron emission and \( E_v^{\ast t} \) for hole emission (see Fig. 2.5 (b)). The difference between \( E_v^t \) and \( E_t \) on the one hand and \( E_v^{\ast t} \) and \( E_t^{\ast} \) on the other hand is called the Franck-Condon shift \( d_{FC} \) or \( d_{FC}^{\ast} \), respectively\[11\]:

\[ E_t = E_v^t - d_{FC} \]  \hspace{1cm} (2.39)

and

\[ E_t^{\ast} = E_v^{\ast t} - d_{FC}^{\ast}. \]  \hspace{1cm} (2.40)

When a defect changes charge state, the lattice configuration will change. Photons carry, however, a negligible amount of momentum and hence the necessary momentum contribution needs to be provided by the excess energy \( d_{FC} \) or \( d_{FC}^{\ast} \) which is transferred to phonons.

There are several approaches to calculate \( \sigma_i^o \), for example, methods presented in Ref. [11, 27–29]. Furthermore, there are approaches specifically developed for polarons (see Sec. B) [30–35]. In this thesis, the approach developed by Kopylov et al. [29] as outlined by Alkauskas et al. [11] was used. Hereby, \( \sigma_i^o \) is calculated via [11]:

\[ \sigma_i^o \sim \frac{\sqrt{\hbar \omega - E_{abs}}}{(\hbar \omega)^3} \quad (i = n, p) \]  \hspace{1cm} (2.41)

when neglecting phonon contributions associated with the excitation of the electron or hole. Here, \( \hbar \omega \) equals the energy of the photon, while \( E_{abs} \) is equal to \( E_v^t \) for \( i = n \), and equal to \( E_v^{\ast t} \) for \( i = p \) as defined in Fig. 2.5 (b). Taking phonon contributions to the optical absorption process into account, one obtains [11]:

\[ \sigma_i^o \sim \int_0^\infty \frac{\exp \left( -\frac{E + E_{abs} - \hbar \omega}{\hbar \omega} \right) \sqrt{E}}{\hbar \omega (E + E_{abs})^2} dE \quad (i = n, p). \]  \hspace{1cm} (2.42)

\( \Gamma \) is a broadening parameter, and is defined as [11]:

\[ \Gamma = \frac{\omega_g}{\omega_0} \sqrt{2d_{FC} \hbar \omega_g}. \]  \hspace{1cm} (2.43)

Here, \( \omega_g \) and \( \omega_0 \) are the vibrational frequencies of the ground and excited state, respectively. The temperature dependence of \( \Gamma \) is described by:

\[ \Gamma = \sqrt{2d_{FC} \hbar \omega_0 \coth \left( \frac{\hbar \omega_0}{k_B T} \right)} \]  \hspace{1cm} (2.44)

when assuming \( \omega_g = \omega_e = \omega_0 \) [11].
Chapter 3

Junctions

Junctions are systems consisting of two or more pieces of material which display different electrical properties, and are the building block of most semiconductor devices. Junctions are often formed by materials with different fermi-level positions relative to the vacuum level, and can either comprise different materials (hetero-junctions) or the same material exhibiting different doping types and/or dopant concentrations (homo-junctions). A special case of a hetero-junction is a junction formed by a semiconductor and a metal, called a Schottky junction. Generally, junctions with Ohmic or rectifying behavior can be distinguished. In this chapter, an overview over the electrical characteristics of junctions will be given. Thus, concepts like the junction current and junction capacitance are introduced. Defects have a pronounced influence on the junction characteristics, and their impact will also be discussed. More information about junctions can be found in Ref. [9, 36–38]. Importantly, rectifying junctions were utilized in this thesis to probe the properties of defects present in semiconductors.

3.1 The Band Diagram

3.1.1 Thermal Equilibrium

To explain the formation of a junction, one can consider a situation where two regions of a material exhibiting different fermi-level positions are brought together, resulting in the diffusion of charge carriers from one region to the other until a constant $E_F$ across the junction is established. Consequently, the charge carriers will leave behind charged defects, i.e., the main dopants, and a space-charge region will be formed. This is accompanied by the formation of an energy barrier inside the space-charge region, represented by the built-in voltage $V_{bi}$ of the junction. Usually, there will be different defects, i.e., not only the main dopants, present in the space-charge region, and their influence on junctions will be discussed in Sec. 3.4.

For a junction consisting of a $n$- and $p$-type semiconductor, $V_{bi}$ can ideally be calculated as

$$V_{bi} = \frac{E_{F,p} - E_{F,n}}{e}.$$  \hspace{1cm} (3.1)

Here, $E_{F,i}$ denote the fermi-level positions relative to the vacuum level in the $n$-type ($i = n$) and $p$-type ($i = p$) semiconductor being joined. In the case of a homo-junction, Eq. 3.1 solely depends on the dopant concentrations in the two material regions (see Eq. 2.16).

Schottky junctions are a special case of a hetero-junction consisting of a metal and a semiconductor, displaying rectifying behavior. The fermi-level position of the metal relative to the vacuum level is equal to the metal work function $\Phi_M$, ...
3. Junctions

and hence

\[ V_{\text{bi}} = \frac{\Phi_M - E_{F,n}}{e} \] (3.2)

is valid for a junction between a metal and a \( n \)-type semiconductor, while

\[ V_{\text{bi}} = \frac{E_{F,p} - \Phi_M}{e} \] (3.3)

applies for a junction consisting of a metal and a \( p \)-type semiconductor. If \( V_{\text{bi}} \) is positive, a rectifying junction is formed. In contrast, an Ohmic contact is established between the metal and the semiconductor for negative \( V_{\text{bi}} \). Often, the so-called barrier height \( \Phi_B \) is also defined for Schottky junctions as

\[ \Phi_B = \Phi_M - E_C \] (3.4)

for a junction between a metal and a \( n \)-type semiconductor, while

\[ \Phi_B = E_g + E_C - \Phi_M \] (3.5)

applies for a junction consisting of a metal and a \( p \)-type semiconductor. The position of \( E_C \) relative to the vacuum level is often denoted as electron affinity. Junctions are often represented by the band diagram across the junction, and hence a representation of the electro-chemical potential \( \Psi \) across the junction.

To compute band diagrams, one starts at Poisson’s equation:

\[ \nabla^2 \Phi = -\frac{\rho}{\epsilon_s \epsilon_0} \] (3.6)

which connects the electrical potential \( \Phi \) and the charge density \( \rho \). \( \Psi \) can be calculated from \( \Phi \). Generally, Eq. 3.6 can be solved iteratively and numerically, starting with an initial guess for \( \Phi \) and \( \rho \). Eq. 3.6 can, however, be solved analytically within the so-called Schottky approximation (see Sec. C). In the Schottky approximation, it is assumed that the charge density \( \rho \) across a \( p-n \) homo-junction can be described by:

\[ \rho = \begin{cases} 
-eN_A, & \text{for } -W_p \leq x \leq 0 \text{ for the } p \text{-type part} \\
+eN_D, & \text{for } 0 < x \leq W_n \text{ for the } n \text{-type part} 
\end{cases} \] (3.7)

and 0 everywhere else. Here, \( W_p \) and \( W_n \) denote the width of the space-charge region on the \( p \)-type and \( n \)-type side of the junction, respectively. Thus, the Schottky approximation assumes sharp boundaries for the space-charge region. The charge density \( \rho \) needs to satisfy overall charge neutrality, and the width \( W = W_n + W_p \) of the space-charge region can be calculated via

\[ W_n = \sqrt{\frac{2\epsilon_0 \epsilon_s N_A}{eN_D} \frac{1}{N_D + N_A} V_{\text{bi}}} \] (3.8)

and

\[ W_p = \sqrt{\frac{2\epsilon_0 \epsilon_s N_D}{eN_A} \frac{1}{N_D + N_A} V_{\text{bi}}} \] (3.9)
Figure 3.1: **Band diagram, electrical field and charge concentration profile of rectifying junctions**: Graphical representation of the band diagram, electrical field and charge concentration profile within the Schottky approximation for (right) a $p$-$n$ homo-junction as well as (left) a Schottky junction between a metal and a $n$-type semiconductor. For the Schottky junction, results are also shown for numerically solving Poisson’s equation (see Eq. 3.6) [40], denoted as exact solution.

Combining Eq. 3.7 with Eq. 3.6, one can compute $\Phi$ as well as the electrical field $E$ across the junction (see Sec. C). For Schottky junctions, the same approach can be used, when either $N_A \to \infty$ (junction between a metal and a $n$-type semiconductor) or $N_D \to \infty$ (junction between a metal and a $p$-type semiconductor) is used in Eq. 3.7. The space-charge region will only extend into the semiconductor to a depth $W$ described by:

$$W = \sqrt{\frac{2\epsilon_0\epsilon_s V_{bi}}{e N_j}}.$$  \hfill (3.10)

Here, $j = D$ needs to be used for a junction between a metal and a $n$-type semiconductor, while $j = A$ is inserted for a junction between a metal and a $p$-type semiconductor.

Fig. 3.1 displays the charge density profile, the electrical field profile as well as the band diagram for a $p$-$n$ homo-junction and a Schottky junction assuming the Schottky approximation to be valid. For the Schottky junction, numerical solutions of Eq. 3.6 are also shown [40].
3.1.2 Junction under an Applied External Voltage

![Graphical representation of the band diagram, the electrical field profile and the charge concentration profile of (left) a \( p-n \) homo-junction and (right) a Schottky junction between a metal and a \( n \)-type semiconductor under an applied external voltage \( V_{\text{ext}} \). The cases of forward bias \( V_{\text{ext}} > 0 \text{ V} \) as well as reverse bias \( V_{\text{ext}} < 0 \text{ V} \) are displayed. The Schottky approximation was assumed to be valid.]

It is often of interest to describe the behavior of rectifying junctions under non-equilibrium conditions, i.e., during illumination or when applying an external bias voltage \( V_{\text{ext}} \). When applying \( V_{\text{ext}} \) to a rectifying junction, one distinguishes the cases of reverse bias \( (V_{\text{ext}} < 0 \text{ V}) \) and forward bias \( (V_{\text{ext}} > 0 \text{ V}) \). \( V_{\text{ext}} \) will alter the internal bias \( V_{\text{int}} \) across the junction:

\[ V_{\text{int}} = V_{\text{bi}} - V_{\text{ext}}. \]  \hspace{1cm} (3.11)

By exchanging \( V_{\text{bi}} \) in the relevant equations with \( V_{\text{int}} \), one obtains the corresponding quantities for the case of an applied external voltage. Fig. 3.2 shows graphical representations of \( \rho \), \( \mathcal{E} \) and the band diagram of a \( p-n \) homo-junction as well as a Schottky junction consisting of a metal and a \( n \)-type semiconductor with and without \( V_{\text{ext}} \). Notably, the size of the space-charge region will change with \( V_{\text{ext}} \).
3.2 Junction Current

In thermal equilibrium (see Sec. 3.1.1), no net current of charge carriers will flow across the junction. In contrast, a net current will flow through the junction when $V_{\text{ext}}$ is applied across the junction. Here, the net current will be described as current density $j$, i.e., the current $I$ divided by the junction area $A$.

For Ohmic junctions, Ohm’s law applies, and

$$j = \frac{V_{\text{ext}}}{R}$$

is valid, with $R$ being the specific resistance of the junction in $\Omega m^2$.

For an ideal rectifying junction, $j$ will be described by:

$$j = j_S \left[ \exp \left( \frac{eV_{\text{ext}}}{k_B T} \right) - 1 \right].$$

Here, $j_S$ is the saturation current density. The expression for calculating $j_S$ depends on the kind of junction and how electrons or holes are transported across the junction. An important difference between Schottky junctions and $p$-$n$ junctions is that for Schottky junctions the current is uni-polar, while in $p$-$n$ junctions the current is ambi-polar, i.e., electron as well as hole transport matters. Generally, $j_S$ will exhibit a temperature-dependence approximately described by:

$$j_S \sim \exp \left( - \frac{\Phi_{\text{eff}}}{k_B T} \right).$$

Here, $\Phi_{\text{eff}}$ represents an effective barrier value describing the energy barrier inside the space-charge region. For ideal $p$-$n$ or Schottky junctions, $\Phi_{\text{eff}}$ will be equal to $V_{\text{bi}}$ (see Eq. 3.1). Tunneling-assisted transport processes will cause $\Phi_{\text{eff}}$ to be smaller than $V_{\text{bi}}$.

In Schottky junctions, $j_S$ is often described within the framework of thermionic emission, and thus:

$$j_S = A^* T^2 \exp \left( - \frac{\Phi_{\text{eff}}}{k_B T} \right).$$

Here, $A^*$ denotes Richardson’s constant which depends on material properties such as the effective mass $m_{i,\text{eff}}$ of the majority charge carrier relevant for transport.

3.3 Junction Capacitance

The space-charge region of rectifying $p$-$n$ or Schottky junctions consists of regions with opposite charge which are spatially separated, and hence the junctions will be associated with a capacitance $C$. In the case of Schottky junctions, the charge in the semiconductor is compensated by the redistribution of mobile charges at the interface with the metal. Ideal Ohmic junctions do not have a space-charge
region, and hence do not exhibit a capacitance. Generally, the capacitance $C$ is defined as

$$C = \frac{dQ}{dV_{\text{int}}}$$  \hspace{1cm} (3.16)

The total charge $Q$ inside a rectifying junction can be expressed by

$$Q = e (N_D W_n + N_A W_p) A,$$  \hspace{1cm} (3.17)

assuming the Schottky approximation to be valid. $W_n$ and $W_p$ are defined in Eq. 3.8 and 3.9 when replacing $V_{\text{bi}}$ according to Eq. 3.11, and hence:

$$C = \sqrt{\frac{A^2 \varepsilon_0 \varepsilon_s e}{2} \frac{N_A N_D}{N_A + N_D} \frac{1}{V_{\text{bi}} - V_{\text{ext}}}}.$$  \hspace{1cm} (3.18)

For a Schottky junction, this equation becomes:

$$C = \sqrt{\frac{A^2 \varepsilon_0 \varepsilon_s e}{2} \frac{N_j}{V_{\text{bi}} - V_{\text{ext}}}}.$$  \hspace{1cm} (3.19)

Here, $N_j$ will be equal to the donor concentration for a Schottky junction consisting of a metal and a $n$-type semiconductor, and $N_j$ will be equal to the acceptor concentration for a Schottky junction consisting of a metal and a $p$-type semiconductor. Additionally, the junction capacitance $C$ will also fulfill the usual relation known for a plate capacitor:

$$C = \frac{\varepsilon_0 \varepsilon_s A}{W_n + W_p}.$$  \hspace{1cm} (3.20)

For a Schottky junction, either $W_n$ or $W_p$ is zero. Often, one simply uses the variable $W$ instead of $W_n$ or $W_p$ in case of a Schottky junction.

### 3.4 Non-ideal Junctions and the Influence of Defects

In this section, non-ideal junctions and, particularly, the influence of deep-level defects will be discussed. Deep-level defects have a pronounced influence on the characteristics of junctions, and alter the measured junction current as well as the junction capacitance. In fact, the influence of defects on the junction capacitance can be used to probe their electrical properties. The corresponding characterization techniques are often referred to as space-charge spectroscopy. Techniques based on space-charge spectroscopy were used extensively in this thesis to study defects in semiconductors. Especially in hetero-junctions, defects, like dangling bonds, are likely to be present at the interface between the two materials. As discussed in Sec. 2.2, defects can introduce charge state transitions levels. When large concentrations of defects are present, they can pin $E_F$ at the interface at the position of the charge
state transition level and change the effective position of the semiconductor’s fermi-level by a value $\Phi_D$, and thus $V_{bi}$ will be changed by $\Phi_D/e$.

For Schottky junctions, an important deviation from the Schottky approximation needs to be taken into account. A charge carrier approaching the interface between the semiconductor and the metal will cause a redistribution of the free electrons in the metal. This effect can effectively be described by an image charge with opposite charge forming inside the metal. The image charge will lower the energetic barrier seen by the charge carrier.

### 3.4.1 Junction Current

There are several physical processes which will cause deviations from Eq. 3.13, and a more general form for $j$ is:

$$j = j_S \left[ \exp \left( \frac{e (V_{ext} - jR_S)}{nk_BT} \right) - 1 \right] + \frac{V_{ext} - jR_S}{R_{Sh}}. \quad (3.21)$$

Here, $R_S$ is the series resistance and $R_{Sh}$ is the shunt resistance, and both are expressed in units of $\Omega m^2$. The ideality factor $n$ captures non-idealities concerning the charge transport through the space-charge region. For example, laterally inhomogeneous junctions [41, 42], the image charge effect in Schottky junctions [36], an interfacial layer [43, 44] or defect-assisted recombination inside the space-charge region [45, 46] are represented by $n$. $n$ will be larger than one for non-ideal junctions and essentially one for the case of a (near-)ideal junction. The series resistance $R_S$ includes contributions from the contact resistances and the resistivity of the material(s) outside of the space-charge region. Notably, defects have a pronounced influence on the resistivity of semiconducting materials (see Sec. 2.2.1). The shunt resistance $R_{Sh}$ describes processes that will lead to a current flow which bypasses the energy barrier inside the space-charge region. Shunts can be caused by current flows along defects (grain boundaries, edges, ...) or when charge carriers tunnel through the space-charge region. Tunneling processes can also be assisted by defects.

### 3.4.2 Junction Capacitance

Defects have a pronounced influence on the capacitance of a rectifying junction (see Fig. 3.3). If we assume, a Schottky junction between a metal and a $n$-type semiconductor, the capacitance will be described by

$$C = \begin{cases} \sqrt{\frac{A^2 \epsilon_0 \epsilon_r e^2 \cdot N_D}{2V_{bi-V_{ext}}}}, & \text{for } e (V_{bi} - V_{ext}) < E_F - E_t \\ \sqrt{\frac{A^2 \epsilon_0 \epsilon_r e^2 N_D + N_u e^2}{2V_{bi-V_{ext}}}}, & \text{for } e (V_{bi} - V_{ext}) \geq E_F - E_t \end{cases}, \quad (3.22)$$

if a trap level with a charge state transition level at $E_t$ below $E_C$ and a concentration of $N_t$ is present inside the space-charge region (see Fig. 3.3 (a)). $u$ will determine whether the trap level is able to follow the frequency $f_{probe}$. 

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**Non-ideal Junctions and the Influence of Defects**
3. Junctions

Figure 3.3: Influence of deep-level defects on the junction capacitance:
(a) Band diagram of a Schottky junction consisting of a metal and a n-type semiconductor under different $V_{\text{ext}}$. A deep-level defect is present inside the space-charge region with a charge state transition level at $E_t$ below $E_C$ and a concentration of $N_t$. The donor concentration is $N_D$. $x_1 = W - \lambda$ is the depth where $E_t$ crosses $E_F$ (see Eq. 3.25). Traps are ionized in between 0 and $x_1$. For $e(V_{\text{bi}} - V_{\text{ext}}) < E_F - E_t$, $E_t$ will not cross $E_F$ inside the space-charge region, and hence $x_1$ is set to zero. (b) Graphical representation of Eq. 3.22 as $1/C^2$ vs. $V_{\text{ext}}$ for two different $f_{\text{probe}}$. In this representation, either $N_D + N_t$ or $N_D$ can be deduced from the slope. The large circles mark the values of $V_{\text{ext}}$ displayed in (a). $1/C^2$ will fall on the red line if only the donors ($N_D$) determine the capacitance, while the blue line is seen if the capacitance is determined by $N_D + N_t$.

used for measuring $C$ (see Sec. 5.2.3), i.e., $u$ will be 0 for $e_n^{\text{th}} \ll f_{\text{probe}}$ and 1 for $e_n^{\text{th}} \gg f_{\text{probe}}$. Here, $e_n^{\text{th}}$ is defined according to Eq. 2.32, and represents the emission rate of electrons from the trap level located at $E_t$. Fig. 3.3 (b) illustrates Eq. 3.22. Eq. 3.20 also needs to be modified if traps are present inside
the space-charge region, and becomes:

$$C = C'_\infty + \left(1 + \left(\frac{2\pi f_{\text{probe}}}{\omega_{\text{trap}}}\right)^2\right)^{-1} \Delta C'. \quad (3.23)$$

$C'_\infty$ is defined as $C$ measured at high $f_{\text{probe}}$, and hence can be calculated by Eq. 3.20, while $\Delta C'$ is equal to:

$$\Delta C' = C'_\infty \frac{N_t}{N_D} \frac{1 - x_1 W}{1 + x_1 \frac{N_t}{W N_D}}. \quad (3.24)$$

$x_1$ is defined in Fig. 3.3 (a), and can be calculated by:

$$x_1 = W - \lambda = W - \sqrt{\frac{2\varepsilon_0 \varepsilon_s}{e^2 N_D} (E_F - E_t)}. \quad (3.25)$$

$x_1$ describes the depth, where $E_t$ crosses $E_F$ inside the junction. For $e (V_{\text{bi}} - V_{\text{ext}})$ smaller than $E_F - E_t$, $x_1$ will be set to zero. $\omega_{\text{trap}}$ is the characteristic frequency associated with a trap level, and can be calculated by:

$$\omega_{\text{trap}} = 4\pi e^\text{th}_n \left(1 + x_1 \frac{N_t}{W N_D}\right). \quad (3.26)$$

Often, one assumes $N_t \ll N_D$, and hence

$$\omega_{\text{trap}} = 4\pi e^\text{th}_n. \quad (3.27)$$

Fig. 3.3 illustrates the situation which leads to using Eq. 3.22. A deep-level defect is present inside the space-charge region with a concentration $N_t$ and a charge state transition level at $E_t$ below $E_C$. For $e (V_{\text{bi}} - V_{\text{ext}})$ larger than $E_F - E_t$, the trap level will be partially above the fermi-level $E_F$ inside the semiconductor, and hence the trap will be ionized between a depth of 0 to $x_1$. If the trap can follow the signal used to probe $C$ (for example, if $e^\text{th}_n \gg f_{\text{probe}}$), the ionized traps at $x_1$ as well as the ionized donors at $W$ will respond and contribute to the recorded $C$. If the applied voltage is such that $e (V_{\text{bi}} - V_{\text{ext}})$ is smaller than $E_F - E_t$, $x_1$ will be 0, and hence only ionized donors will be present inside the space-charge region and contribute to $C$. If the traps cannot follow the probing signal, only ionized donors will contribute to $C$ regardless of $V_{\text{ext}}$.

### 3.4.2.1 Transient Capacitance

Often, it is of interest to measure $C$ under non-equilibrium conditions, and, particularly, to record the capacitance transient $C(t)$. $C(t)$ can be used to deduce information about the defects being present in the space-charge region of a rectifying junction. In this thesis, space-charge spectroscopy techniques utilizing capacitance transients, such as deep-level transient spectroscopy or steady-state photo-capacitance measurements, were employed to study capture
3. Junctions

Figure 3.4: Capacitance transients: (a) Illustration of Schottky junctions comprising a n-type semiconductor under non-equilibrium conditions. (left) The Schottky junction is in non-equilibrium at \( t = 0 \) s due to a defect level being occupied with electrons inside the space-charge region where \( E_t \) lies above \( E_F \). The junction will return to equilibrium for \( t \to \infty \) s due to electrons being emitted from the trap with a rate \( e_{th}^n \) for an individual occupied trap. (right) The Schottky junction is in equilibrium at \( t = 0 \) s. Due to illumination of the junction with monochromatic light whose corresponding photon energy is energetically lower than the band gap energy, electrons and holes are emitted from the trap with rates \( e_{on} \) and \( e_{op} \), respectively. For \( t \to \infty \) s, a steady-state is established, with a steady-state occupation of traps. The steady-state capacitance will depend on the relative magnitude of \( e_{on} \) and \( e_{op} \), and will be between \( C_0 \) and \( C_{\infty,\text{max}} \). (b) Graphical representation of \( C(t) \), \( C_0 \) and \( C_{\infty} \) for the situations shown in (a), and hence according to Eq. 3.34, 3.40 and 3.41.
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and emission of charge carriers by/from defects in semiconductors. The capacitance at \( t = 0 \) s will be denoted as \( C_0 \), while the capacitance for \( t \to \infty \) s is represented by \( C_\infty \). Here, we assume that \( C (t) \) is determined by the emission and capture of charge carriers from/traps present in the space-charge region (see Sec. 2.3.1 and Fig. 3.3 (a)). For small perturbations, the following equation holds, if \( V_{\text{ext}} \) is kept constant:

\[
\frac{1}{C} \frac{\partial C}{\partial t} = -\frac{1}{2} \frac{V_{\text{probe}}}{N_D} \frac{n_t}{\partial t}.
\]

(3.28)

\( \frac{\partial n_t}{\partial t} \) is given by Eq. 2.26, and describes the trap-related capture and emission of charge carriers in the semiconductor. \( V_{\text{probe}} \) takes into account that the non-equilibrium condition might only affect traps in part of the space-charge region, and hence in a so-called probing volume. Eq. 3.28 can be approximated by:

\[
\frac{C_\infty - C (t)}{C_\infty} = -\frac{1}{2} \frac{V_{\text{probe}}}{N_D} [n_{t,\infty} - n_t(t)],
\]

(3.29)

if \( C_\infty = C_{\text{equilibrium}} \), or

\[
\frac{C_0 - C (t)}{C_0} = -\frac{1}{2} \frac{V_{\text{probe}}}{N_D} [n_{t,0} - n_t(t)],
\]

(3.30)

if \( C_0 = C_{\text{equilibrium}} \). Here, \( n_t \) is the number of traps occupied with electrons (see Eq. 2.25), and hence \( n_{t,\infty} \) is the number of traps occupied with electrons for \( t \to \infty \) s, while \( n_{t,0} \) is the number of occupied traps at \( t = 0 \) s. \( \frac{\partial n_t}{\partial t} \) and \( V_{\text{probe}} \) depend on the specific non-equilibrium situation of interest, and have to be calculated for the specific perturbation the junction is subjected to. Fig. 3.4 illustrates two cases relevant for this thesis which will be discussed in the following. We assume that the rectifying junction is a Schottky junction comprising a \( n \)-type semiconductor.

A first example is the case of a non-equilibrium occupation of traps inside the space-charge region (see Sec. 5.2.3.4 and left hand side of Fig. 3.4 (a)). Here, it is assumed that at a time \( t = 0 \) s, traps between the depths \( x_2 \) and \( x_1 \) are occupied with electrons. The junction is out of equilibrium because \( E_t \) is located above \( E_F \) inside the corresponding volume for \( t = 0 \) s. The junction will return to equilibrium for \( t \to \infty \) s (see Eq. 3.29). We expect electron emission to occur inside the part of the space-charge region, where a non-equilibrium occupation of defects with electrons can be found, and hence

\[
V_{\text{probe}} = \frac{x_1^2 - x_2^2}{W^2}
\]

(3.31)

represents the correction factor taking the probing volume into account. Notably, hole emission will not play a role. Furthermore, no free electrons or holes are present in the space-charge region, and hence no electrons or holes will be captured by traps inside the probing volume. Thus, \( \frac{\partial n_t}{\partial t} \) will become:

\[
\frac{\partial n_t}{\partial t} = -E_{n,\text{tot}} = -n_t e^{\text{th}}.
\]

(3.32)
Solving for $n_t$ yields:

$$n_t = N_t \exp \left( -e_n^{\text{th}} t \right), \tag{3.33}$$

with $n_{t,\infty} = 0$ and $n_{t,0} = N_t$. Thus, Eq. 3.29 becomes:

$$C(t) = C_{\text{equilibrium}} \left[ 1 - \frac{1}{2} \frac{x_2^2 - x_2^2}{W^2} \frac{N_t}{N_D} \exp \left( -e_n^{\text{th}} t \right) \right]. \tag{3.34}$$

using $C_{\infty} = C_{\text{equilibrium}}$ (see left hand side of Fig. 3.4 (b)). The situation described above is, for example, relevant for deep-level transient spectroscopy (see Sec. 5.2.3.4).

A second example is the case of a junction under illumination with monochromatic light comprised of photons with a photon energy below the semiconductor’s band gap (see Sec. 5.3 and right hand side of Fig. 3.4 (a)) [26]. In this case, the junction will be in equilibrium at $t = 0 \text{s}$, and will exhibit a constant capacitance $C_{\infty}$ once a steady-state is established for $t \to \infty \text{s}$. Thus, we assume $n_{t,0} = N_t$. Generally, the illumination will lead to the emission of electrons as well as holes. It is assumed that the electrons as well as holes created in the valence and conduction band are swept out of the space-charge region by the electrical field, and hence electron or hole capture are not relevant for the whole space-charge region. However, right at the edge of the space-charge region, free electrons will penetrate into the space-charge region, where they can be re-captured (see Fig. 3.1). This is expressed by the assumption that within the volume defined by $W$ and $W_o$ the occupation of traps is not changed due to illumination, because emitted electrons are recaptured. The corresponding width is described by:

$$W - W_o = \lambda_o \leq L_D \sqrt{2 \ln \left( \frac{N_D c_{n}^{\text{th}}}{e_{n}^{\text{op}}} \right)}. \tag{3.35}$$

Here, $c_{n}^{\text{th}}$ and $e_{n}^{\text{op}}$ are defined according to Eq. 2.34 and 2.37, respectively. $V_{\text{probe}}$ becomes

$$V_{\text{probe}} = \frac{W_o^2 - x_2^2}{W^2}, \tag{3.36}$$

if optically-induced hole emission is neglected, and it is assumed that the junction is in thermal equilibrium at $t = 0 \text{s}$. The situation is more complicated if optically-induced electron and hole emission are relevant. Neglecting electron and hole capture, $\frac{\partial n_t}{\partial t}$ will become

$$\frac{\partial n_t}{\partial t} = E_{p,\text{tot}} - E_{n,\text{tot}} = (N_t - n_t) e_{p} - n_t e_{n}^{\text{op}}. \tag{3.37}$$

Here, $e_{i}^{\text{op}}$ are defined according to Eq. 2.37 and 2.38, and will depend on the photon flux. An expression for $n_t$ can be found, if one assumes $e_{n}^{\text{op}} \gg e_{p}^{\text{op}}$ at the photo energy of interest:

$$n_t = N_t \exp \left( - e_{n}^{\text{op}} t \right). \tag{3.38}$$

Often, it is only relevant to calculate $n_t$ for $t \to \infty \text{s}$, and hence when steady-state ($\frac{\partial n_t}{\partial t} = 0$) is reached, and one obtains

$$n_{t,\infty} = N_t \frac{e_{p}^{\text{op}}}{e_{p}^{\text{op}} + e_{n}^{\text{op}}}. \tag{3.39}$$
Thus, Eq. 3.30 approximately becomes:

$$C_\infty = C_{equilibrium} \left[1 + \frac{1}{2} V_{probe} \frac{N_t}{N_D} \frac{e_n^o}{e_p^o + e_n^o}\right] \quad (3.40)$$

when evaluating for $t \to \infty$ s. For the case of $e_n^o \gg e_p^o$, an explicit form of $C(t)$ can be found:

$$C(t) = C_{equilibrium} \left[1 + \frac{1}{2} \frac{W_0^2}{W^2} \frac{N_t}{N_D} \left\{1 - \exp \left(-e_n^ot\right)\right\}\right]. \quad (3.41)$$

The right hand side of Fig. 3.4 (b) illustrates the corresponding $C(t)$ and $C_\infty$. The situation described above is, for example, relevant for steady-state photo-capacitance measurements (see Sec. 5.3).
Chapter 4

Semiconducting Oxides

Semiconducting oxides exhibit band gaps equivalent to wavelengths ranging from the infrared to the ultra-violet part of the electromagnetic spectrum, and are promising candidates for (opto-)electronic devices, including applications in energy-storage and -harvesting as well as electricity conversion. In this thesis, monoclinic gallium sesquioxide ($\beta$-$\text{Ga}_2\text{O}_3$) and rutile titanium dioxide ($\text{r-TiO}_2$) were investigated. In the following chapter, an overview over the characteristics of those two materials will be given, focusing on the relevant material aspects for the investigations in this thesis. Specifically, the role of defects in the materials will be presented.

4.1 Monoclinic Gallium Sesquioxide

There are six different polymorphs of gallium sesquioxide ($\text{Ga}_2\text{O}_3$) which are denoted by the greek letters $\alpha$, $\beta$, $\gamma$, $\epsilon$, $\kappa$ and $\delta$ [47, 48]. Recently, $\epsilon$-$\text{Ga}_2\text{O}_3$ has been identified as $\kappa$-$\text{Ga}_2\text{O}_3$ exhibiting pronounced disorder [49]. $\beta$-$\text{Ga}_2\text{O}_3$ is the most stable phase [48], and was the focus of this thesis. $\beta$-$\text{Ga}_2\text{O}_3$ has a monoclinic crystal structure and its space group is C2/m [50, 51]. Its unit cell comprises three crystallographically-inequivalent oxygen atoms and two crystallographically-inequivalent gallium atoms (see inset in Fig. 4.1) [51]. The notation for the different lattice sites has been suggested in Ref. [52], where O$_I$ and O$_{II}$ have a three-fold symmetry, while O$_{III}$ exhibits a four-fold symmetry, Ga$_I$ is tetrahedrally coordinated, and Ga$_{II}$ exhibits octahedral coordination. The conduction band (minimum) is made up of Ga-$4s$ states, while the valence band (maximum) is predominantly derived from O-like states [53]. The band gap of $\beta$-$\text{Ga}_2\text{O}_3$ is indirect and was measured to be around 4.7 eV - 4.9 eV [50, 54, 55], whereby the direct band gap is only slightly higher in energy than the lowest band-to-band transition which is of indirect nature [54, 55]. One can expect a pronounced direction-dependence for the band gap of $\beta$-$\text{Ga}_2\text{O}_3$ due to its low-symmetry unit cell [56]. Particularly, this is related to a complicated valence band structure [53, 56]. The static dielectric constant of $\beta$-$\text{Ga}_2\text{O}_3$ depends on the direction and lies in between 9.9 - 12.7 [57, 58]. The effective mass of the electrons is nearly isotropic, and has a value of around $0.22m_e$ - $0.30m_e$ as measured [50, 55] and predicted by first-principles calculations [53, 59]. The effective mass of holes is substantially higher and anisotropic [55]. Notably, holes are very likely to form self-trapped holes (hole polarons), and hence low hole mobilities are expected [60, 61]. The localization of holes has especially a pronounced impact on the luminescence from the material [62–64].

Large $\beta$-$\text{Ga}_2\text{O}_3$ single crystals can be grown by a variety of methods, such as by edge-defined film-fed growth (EFG) [65, 66], the Czochralski method...
4. Semiconducting Oxides

Figure 4.1: Architecture used for MOSFET devices based on β-Ga$_2$O$_3$ [6]: Usually single-crystalline β-Ga$_2$O$_3$ substrates and thin-films are used in devices. The crystal structure of β-Ga$_2$O$_3$ is shown in the inset, including the labeling of the different O and Ga sites. Impurities are incorporated into β-Ga$_2$O$_3$ to control the conductivity of the different layers. (I) illustrates how defects can diffuse into the active layer of MOSFET devices during fabrication or operation: (A) The Ohmic contact is a potential source for Ti, (C) while the semi-insulating β-Ga$_2$O$_3$ substrate is a potential source for Fe. (B) Intrinsic defects might diffuse into the active layer from the region where Si-implantation was used to obtain $n^+$-type β-Ga$_2$O$_3$. (II) Deep-level defects have a pronounced influence on the device characteristics, especially if they are present inside the active layer of the device. For example, deep-level defects will influence the barrier characteristics of MOS structures (see Sec. 3) due to, for example, fermi-level pinning. Moreover, defects can influence the charge transport across the active layer by trapping or scattering.
Monoclinic Gallium Sesquioxide

(CZ) [67, 68] or float-zone growth (FZ) [69]. Importantly, the availability of substrates grown from the melt is an advantage of $\beta$-Ga$_2$O$_3$ compared to several other wide band gap semiconductors, such as GaN or SiC [70]. $\beta$-Ga$_2$O$_3$ thin-films have been successfully deposited using, e.g., molecular-beam epitaxy (MBE) [71, 72], halide vapor-phase epitaxy (HVPE) [73] or metal-organic chemical vapor deposition (MOCVD) [74, 75]. Control of $n$-type doping has been achieved with charge carrier concentrations of up to $1 \times 10^{19}$ cm$^{-3}$ [65–68], and conductive $\beta$-Ga$_2$O$_3$ usually exhibits strong optical absorption related to free charge carriers [56, 76]. $P$-type conductivity, however, can not be reliably obtained [77, 78]. So far, a record electron mobility of 176 cm$^2$ V$^{-1}$ s$^{-1}$ has been achieved at room temperature in a MOCVD-grown $\beta$-Ga$_2$O$_3$ thin-film [74]. This value is very close to the expected theoretical limit of the room temperature electron mobility in $\beta$-Ga$_2$O$_3$ of 290 cm$^2$ V$^{-1}$ s$^{-1}$ - 380 cm$^2$ V$^{-1}$ s$^{-1}$ due to optical phonon scattering [79].

$\beta$-Ga$_2$O$_3$ is a potential candidate for a host of applications, such as gas sensors [80], opto-electronics in the ultra-violet part of the electromagnetic spectrum [81–84] or power electronics [5, 6, 71, 73, 85]. Specifically, its large band gap [54, 55, 59], high break-down electrical fields [85–87] and reliable $n$-type conductivity [65–68] are setting $\beta$-Ga$_2$O$_3$ apart from other semiconducting oxides. Recent focus has predominantly been on opto-electronic and power electronics devices [5, 6, 71, 73, 81–85]. For power electronics, $\beta$-Ga$_2$O$_3$ shows promise for applications involving high voltages as well as high frequencies when comparing the appropriate figures of merit [88, 89] for $\beta$-Ga$_2$O$_3$ with other relevant materials such as GaN or SiC [71, 85, 90–92].

As mentioned before, only $n$-type doping can be reliably achieved. Thus, hetero-junctions [81, 82] and uni-polar devices [71] are of interest for $\beta$-Ga$_2$O$_3$-based power electronics and opto-electronics. Successful UV photo-detectors using hetero-junctions involving GaN or SiC, have been demonstrated [81, 82]. For power electronics, functional devices have been reported using structures, such as Schottky barrier diodes [71, 93–96], metal-oxide-semiconductor field-effect transistors (MOSFET) [6, 87, 97] or metal–semiconductor field-effect transistors (MESFET) [91]. Fig. 4.1 shows an illustration of a MOSFET device using $n$-type $\beta$-Ga$_2$O$_3$ as semiconductor and Al$_2$O$_3$ as insulating oxide layer [6].

It is paramount to control the conductivity of $\beta$-Ga$_2$O$_3$ in devices by incorporating suitable donor or acceptor impurities [91]. Importantly, deep-level defects can alter the operation of devices if present in the active region of the devices [98]. The active region usually comprises $n$-type $\beta$-Ga$_2$O$_3$, and thus, defects with charge state transition levels far away from $E_C$ are considered to be deep-level defects. Deep-level defects can either be present in as-grown $\beta$-Ga$_2$O$_3$ [91, 98–100], are created during fabrication [101] or diffuse in from adjacent layers during fabrication as well as operation [98, 102–104] (see Fig. 4.1). Deep-level defects will influence the operation of devices for power electronics by changing the gate-to-source characteristics due to fermi-level pinning [73, 98, 105, 106], by increasing the on-resistance [107] and by lowering of the break-down voltage [107]. In opto-electronic devices, deep-level defects can act as recombination centers which, for example, may lower the efficiency for photo-
4. Semiconducting Oxides

detection[83]. In both applications, defects will generally alter charge carrier transport by acting as traps or scattering centers[9]. Some effects of defects on the operation of devices for power electronics are illustrated in Fig. 4.1. A further challenge for β-Ga$_2$O$_3$-based devices, especially if they operate at high voltages or high frequencies, is the comparatively poor thermal conductivity of β-Ga$_2$O$_3$[108]. This will require advanced thermal management solutions to be implemented in β-Ga$_2$O$_3$-based devices[109, 110].

4.1.1 Defects in Monoclinic Gallium Sesquioxide

Defects in β-Ga$_2$O$_3$ have attracted considerable interest in recent years, and significant discoveries were made concerning the role of intrinsic as well as extrinsic defects present in the material. For example, several groups have found V$_\text{Ga}$ to be present in as-grown n-type β-Ga$_2$O$_3$[61, 111, 112]. It was found by computations and experiments, however, that V$_\text{Ga}$ in β-Ga$_2$O$_3$ prefers a significantly relaxed structure which is rather represented by an interstitial gallium next to two gallium half-vacancies[113, 114]. A number of residual impurities are commonly found in as-grown β-Ga$_2$O$_3$, whereby Si[64, 66], H[76], Al[64], Fe[64, 99], Mg[64], Ca[64], Co[64] and Ir[115] are the ones most commonly reported. Furthermore, β-Ga$_2$O$_3$ can be doped intentionally with a range of other impurities[76]. Complexes between defects are also thought to play a role in β-Ga$_2$O$_3$[52, 116]. Particularly, the role of H in forming complexes with other extrinsic or intrinsic defects has attracted some attention. It has been shown computationally as well as experimentally that the hydrogenation of V$_\text{Ga}$ with hydrogen is likely to occur[114, 117]. Moreover, H has been shown to form a complex with Mg[115]. A number of other hydrogen-related defects have been found, but not assigned to a chemical or structural origin[118]. The migration of defects is also important, as the defects may enter the active layer of devices during operation or fabrication (see Fig. 4.1). However, defect migration has not been studied to a large extent so far. Notably, the migration of intrinsic defects has been studied computationally[52, 114, 119, 120], where V$_\text{O}$ is expected to be fairly immobile below 800 K with migration barriers of 1.2 eV to 4.0 eV[120]. V$_\text{Ga}$ can easily transform into a relaxed structure which is less mobile than what is expected for the more ideal structures for V$_\text{Ga}$[114, 120]. There is also reports on the expected migration barriers for the interstitial defects: O$_i$ is suggested to be very mobile with a migration barrier of only 0.12 eV[52], while Ga$_i$ is less mobile with a migration barrier of 0.74 eV - 0.94 eV[52]. There was, however, an earlier report predicting a migration barrier of only 0.10 eV for Ga$_i$[119]. Moreover, there are a few experimental studies indicating that H is mobile at temperatures of around 400 °C[117, 118]. Notably, the migration barriers of defects in β-Ga$_2$O$_3$ strongly depend on their charge state[120].
4.1.1.1 Influence of Defects on the Electrical Properties

Historically, the $n$-type conductivity found in as-grown $\beta$-$\text{Ga}_2\text{O}_3$ has been explained by the presence of $V_O$ acting as a shallow donor [121]. However, it has been firmly established that residual Si is most often responsible for the $n$-type conductivity in a wide range of as-grown $\beta$-$\text{Ga}_2\text{O}_3$ [66, 100] exhibiting an ionization energy of around 36 meV [100]. There are, however, various reports on how the $n$-type conductivity of $\beta$-$\text{Ga}_2\text{O}_3$ can be changed by post-growth heat-treatments [66, 67, 76, 118]. Notably, heat-treatments in $H_2$ gas increase the dopant concentration [118], while heat-treatments in $O_2$ decreased the donor concentration [76]. Both findings have been linked to $H_i$ or $H_O$ acting as shallow donors [122, 123], which enter the crystal when annealing in $H_2$ gas, and leave the sample when heat-treatments are performed in $O_2$ gas [76, 118]. Experimentally, it has been show that at least $H_i$ is, indeed, a shallow donor with an ionization energy of around 10 meV to 30 meV [124]. Kuramata et al. showed that annealing in $O_2$ gas leads to a donor concentration independent of the Si concentration, while the donor concentration is correlated with the Si concentration without such heat-treatments [66]. Irmischer et al. reported on the presence of two different shallow donors in $\beta$-$\text{Ga}_2\text{O}_3$ crystals annealed in $O_2$ compared to untreated samples which display only one shallow donor level associated with Si [100]. Notably, the slight differences in the influence of heat-treatments might have parallels to the controversy about the donors in r-$\text{TiO}_2$, where residual contamination of annealing atmospheres with H lead to a wide range of different and seemingly contradictory results [125] (see Sec. 4.2.1). Generally, shallow donor levels in the range of 15 meV - 50 meV are reported with various techniques obtained on various different $\beta$-$\text{Ga}_2\text{O}_3$ samples [96, 100, 124, 126–129]. Some discrepancies in reported donor ionization energies might be related to the dependence of the donor ionization energy on the charge carrier concentration [100, 129, 130]. Several deeper donor levels have been reported in the range between 90 meV to 210 meV [107, 126, 131–133]. Such donor levels would only be partially-ionized at room temperature, and hence could affect the operation of $\beta$-$\text{Ga}_2\text{O}_3$-based devices [107]. Intentional $n$-type doping of $\beta$-$\text{Ga}_2\text{O}_3$ has been demonstrated using, e.g., Si [75, 134], Sn [75, 86, 91, 135, 136] and Ge [137, 138].

There is only a few reports that claim to have produced $p$-type $\beta$-$\text{Ga}_2\text{O}_3$ [139, 140]. However, it is generally thought that significant $p$-type conductivity can not be achieved reliably in $\beta$-$\text{Ga}_2\text{O}_3$, due to i) no shallow acceptor dopants being available [77, 78], ii) the likely formation of self-trapped holes [60, 61] and iii) self-compensation [77]. There is, however, a number of deep acceptors, such as Fe [5, 71, 141], Mn [142], Mg [67, 76, 91, 143], Al [76], Co [76], Ni [76] and N [143] which are used to produce semi-insulating $\beta$-$\text{Ga}_2\text{O}_3$ needed, for example, as a base for $\beta$-$\text{Ga}_2\text{O}_3$-based power electronics (see Fig. 4.1).

The influence of defects on the electrical properties of a material is to a large extent determined by their thermodynamic charge state transition levels [9]. There are a number of reports concerning thermodynamic charge state transition levels within the band gap of $\beta$-$\text{Ga}_2\text{O}_3$. Often, DLTS or related techniques
are used to study these levels in $\beta$-Ga$_2$O$_3$, and an activation energy $E_A$ which is related to the position of the charge state transition level referenced to $E_C$ is determined using these techniques (see Sec. 5.2.3.4). Across many different $\beta$-Ga$_2$O$_3$ samples, the defect levels commonly labeled $E_1$ ($E_A = 0.56 \text{ eV}$) [99, 100, 131, 144–147], $E_2$ ($E_A = 0.78 \text{ eV}$) [98–100, 106, 126, 131, 132, 144–148], $E_3$ ($E_A = 1.01 \text{ eV}$) [99, 100, 126, 131, 137, 144–147] and $E_4$ ($E_A = 1.48 \text{ eV}$) [99, 144, 145] are seen. Assignments of these defect levels to specific defects are, however, rare. One notable exception is $E_2$, which has been identified to be related to Fe$_{\text{Ga}}$ [99, 149]. It was, however, unclear whether both configurations of Fe$_{\text{Ga}}$ [150, 151] contribute to $E_2$ [99]. In terms of $E_1$, $E_3$ and $E_4$, proton irradiation studies have been performed to gauge whether or not the corresponding defects might be related to intrinsic defects [99, 144, 146]. However, there are reports claiming a response of the levels to irradiation [144] as well as reports seeing no response to irradiation [99]. Co has been proposed as a possible candidate for $E_1$ as well as $E_3$ [100]. There are a number of levels which are reported less often with $E_A$ in the range from 0.18 eV to 0.51 eV [131, 137].

Using optical DLTS or photo-induced current spectroscopy, it is possible to study thermodynamic charge state transition levels close to $E_V$. Similarly to DLTS, an activation energy is determined which is related to the distance of the thermodynamic charge state transition level to $E_V$. Defect levels at 0.2 eV - 0.4 eV, 0.32 eV, 1.06 eV, 1.20 eV and 1.35 eV above $E_V$ have been reported [126, 144–146, 148]. Self-trapped holes have been proposed as origin of the level at 0.2 eV - 0.4 eV [145, 146], while Mg is a tentative candidate for the level at 1.06 eV [148].

Several groups have employed irradiation with protons, electrons, neutrons or heavier ions to study defect levels in $\beta$-Ga$_2$O$_3$ related to intrinsic defects [5, 52, 144, 152–156]. Generally, it is found that irradiation reduces the number of charge carriers [52, 152–155], and hence one can assume that compensating acceptors are formed upon irradiation. Heat-treatments at around 500°C need to be employed to recover the charge carriers [52, 153, 156], and it has been suggested that H might be involved in the recovery [52]. Irradiation induces a number of new defect levels which have been studied by DLTS, and are commonly labeled as $E_2^*$ ($E_A = 0.75 \text{ eV}$) [52, 99, 146], $E_4^*$ ($E_A = 1.40 \text{ eV}$) [52, 146] and $E_5^*$ ($E_A = 1.35 \text{ eV}$) [144, 148]. Another irradiation-induced level with an $E_A$ of 0.28 eV is reported [144], but less commonly observed. Notably, $E_2^*$ has also been observed in as-grown $\beta$-Ga$_2$O$_3$ thin-films deposited by MBE, and was found to significantly impact the performance of MESFETs comprising these thin-films [98, 106].

Recently, it has been reported that a number of defects are created in $\beta$-Ga$_2$O$_3$ at elevated temperatures when an electrical field is present inside the material [104]. This finding has great implications for $\beta$-Ga$_2$O$_3$-based devices and their long-term operation.

There is a host of first-principles computations predicting thermodynamic charge state transition levels related to defects in $\beta$-Ga$_2$O$_3$ [52, 77, 78, 114, 120, 123, 157–160], where most reports focus on intrinsic defects. It is often reported that Ga$_i$ is a shallow donor, V$_{\text{Ga}}$ gives rise to deep acceptor states, V$_{\text{O}}$ are thought
to be deep donors and $O_i$ can be a deep donor or acceptor depending on its configuration [52].

### 4.1.1.2 Influence of Defects on the Optical Properties

Defect-related optical absorption in $\beta$-Ga$_2$O$_3$ has been studied with, e.g., optical transmittance measurements [76, 115, 161], space-charge spectroscopy under illumination [113, 126, 137, 144–148, 152, 162], surface photo-voltage spectroscopy [163] or steady-state photo-electron paramagnetic resonance [151, 164]. Assignments of optical absorption to several extrinsic defects, such as Ir [115], Cr [76], Ni [76], Co [76] and Fe [151] exist. For example, the optical absorption related to Fe is located at about 1 eV, and is linked to FeGa [151]. When performing space-charge spectroscopy under illumination, like steady-state photo-capacitance measurements or deep-level optical spectroscopy, one can derive the optical charge state transition levels related to defects in the material under study [26]. Numerous levels are reported in between 0.8 eV to 4.5 eV below $E_C$ [113, 126, 137, 144–148, 152, 162]. However, no clear identification of any of these levels exists yet, showing that more efforts to assign defect signatures to specific defects are needed in $\beta$-Ga$_2$O$_3$. Several levels are reported to respond to irradiation, such as features at 1.3 eV [137, 144, 145, 152], 2.0 - 2.2 eV [137, 147, 152] and 3.2 eV [137, 144]. Only a few reports on optically-induced hole emission from traps exist so far [162, 163].

First-principles calculations have focused on determining formation energies and thermodynamic charge state transition levels of defects in $\beta$-Ga$_2$O$_3$. Deák et al. report on computational results concerning the optical absorption related to intrinsic defects, and state the following values for optical charge state transition levels: 4.33 eV ($O_i$), 4.58 eV ($V_{GaI}$), 4.75 eV ($V_{GaII}$), 3.34 eV ($V_{OI}$), 3.95 eV ($V_{OII}$), 3.15 eV ($V_{OIII}$) [157]. It is, however, better to compare the defect-related absorption cross section spectra with experimental signatures instead of only comparing onset energies [11, 151].

### 4.2 Rutile Titanium Dioxide

Titanium dioxide (TiO$_2$) exhibits three stable phases: rutile, anatase and brookite [165, 166]. In this thesis, investigations were conducted on rutile TiO$_2$ (r-TiO$_2$). The space group of r-TiO$_2$ is $P4_2/mnm$ [165, 166], and the unit cell consists of crystallographically-equivalent O and Ti atoms [166, 167]. The conduction band (minimum) is mainly made up of Ti-$3d$ orbitals, while the valence band (maximum) consists predominantly of O-$2p$ orbitals [168]. r-TiO$_2$ exhibits an indirect band gap [169–171] of around 3.0 eV - 3.2 eV [169–172]. Single crystals of r-TiO$_2$ can be obtained by Verneuil’s method [173] or by float-zone growth [174]. N-type or semi-insulating r-TiO$_2$ is most commonly the result of the growth process and is also relevant for technological applications [4, 172, 175], while $p$-type conductivity has only been achieved in r-TiO$_2$ at very high temperatures and under O-rich conditions [4, 172, 176, 177]. In $n$-type r-TiO$_2$, fairly high effective masses ranging from $1m_e$ to $25m_e$ are found for
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Figure 4.2: Illustration of the systems Pt/TiO$_2$ or Pd/TiO$_2$ for photo-catalysis: Usually, TiO$_2$ powders or nano-crystals are used to maximize the reactive surface, while Pd or Pt are used as co-catalyst. The unit cell of r-TiO$_2$ is shown in the inset. For photo-catalytic water-splitting the following steps are important: (I) Photons are absorbed in TiO$_2$ and generate electron-hole pairs (see Eq. 4.1). The absorption can be mediated by defects. (II) Electrons and holes travel through the material to reach a reaction site at the Pd/TiO$_2$ or Pt/TiO$_2$ interface. Defects have a pronounced influence on the charge transport, acting as traps, recombination or scattering centers. (III) At the Pd/TiO$_2$ or Pt/TiO$_2$ interface, water molecules are adsorbed. Holes from TiO$_2$ and electrons from the metal trigger partial reactions which will contribute to the water-splitting reaction. Defects at the surface can assist the charge transfer, and enhance the chemical reactions (see Eq. 4.3 and 4.2).

electrons in transport measurements[171, 178–182]. This is in accordance with the observation of polarons in the material[167, 183, 184] (see Sec. B). Consequently, the static dielectric constant $\epsilon_s$ is reported to be between 90 - 170 at room temperature[185, 186] with a pronounced dependence on temperature[186] and sample treatment[187].

TiO$_2$ is used in applications such as solar cells[188, 189], photo-catalysis[3, 4, 190–195] and hydrogen sensors[196–199], but also in other types of industries such as for pigments in paints[200]. In most applications, TiO$_2$ is being used in poly-crystalline form, for example, as nano-crystals or powders[188, 192, 200]. For applications in photo-catalysis and solar cells, rutile as well as anatase TiO$_2$ are of interest[188, 192]. Moreover, for these two applications defects are of particular importance[4, 188, 192, 201, 202].

The studies performed in this thesis are particularly relevant for r-TiO$_2$ for photo-catalytic applications, and hence some more aspects of this application will be discussed in the following. Fig. 4.2 illustrates the relevant steps for a photo-catalytic reaction, and particularly shows the influence of defects on the
photo-catalysis. Often, $n$-type TiO$_2$ is used in photo-catalysis together with a co-catalyst, like Pt or Pd [201, 203–207]. TiO$_2$/Pd or TiO$_2$/Pt systems are relevant for a host of photo-catalytic reactions, like water-splitting or water purification [4, 193, 194]. Photo-catalytic water-splitting is a promising pathway to store solar energy in the form of hydrogen. The overall (chemical) reactions relevant for photo-catalytic water-splitting are [208]:

\[
2\gamma \rightarrow 2e^- + 2h^+ \quad (4.1)
\]

\[
\text{H}_2\text{O} + 2h^+ \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2 \quad (4.2)
\]

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad (4.3)
\]

Eq. 4.1 describes the generation of electron-hole pairs inside TiO$_2$ by absorbing photons ($\gamma$), while Eq. 4.2 and 4.3 represent the chemical reaction for splitting water assisted by the photo-generated charge carriers provided by TiO$_2$.

From a material science point of view, the following physical processes are relevant for photo-catalysis in Pd/TiO$_2$ or Pt/TiO$_2$ systems (see Fig. 4.2):

I. Incident photons are absorbed in TiO$_2$, and electrons as well as holes are created (see Eq. 4.1). Due to its band gap of around 3.0 eV - 3.2 eV [169–172], pristine TiO$_2$ only absorbs light in the ultra-violet part of the electromagnetic spectrum, and hence only about 5 % of the solar spectrum [209] are absorbed by pristine TiO$_2$, and are used for generating electron-hole pairs. Several approaches have been explored to extend the optical absorption of TiO$_2$ further into the visible and infrared part of the electromagnetic spectrum [201, 210, 211], e.g., doping with impurities [212–216], reducing heat-treatments [201, 210, 211, 217, 218] or hydrogenation [219–221]. Particularly, reducing and/or hydrogenation of TiO$_2$ have attracted considerable attention. It is, however, an ongoing debate whether point defects [201, 210, 211, 218, 220–222] play a role in the extended optical absorption, or if the changes seen are rather related to structural changes and disorder [217, 219]. Notably, some authors emphasize the role of defect bands being formed due to a large number of point defects being introduced [201, 215].

II. Electrons and holes are transported through TiO$_2$, and can reach the surface where molecular species, such as H$_2$O, are adsorbed. Defects influence the transport of electrons and holes by acting as scattering centers as well as traps (see Sec. 2.3.1) [9].

III. Holes are transferred between TiO$_2$ and adsorbed H$_2$O, while electrons are transferred between the metal co-catalyst and H$^+$. The charge transfer triggers chemical reactions (see Eq. 4.2 and 4.2). Defects at or close to the interface can aid the charge transfer significantly, and lower the enthalpy which needs to be overcome for the chemical reactions stated in Eq. 4.2 and 4.3 to happen [4].
Thus, defects might play an important part in all described stages relevant for photo-catalytic water-splitting. The stages for photo-catalytic water purification are similar [4], and hence the same reasoning applies. Experiments performed on single-crystalline TiO$_2$ and junctions between single-crystalline TiO$_2$ and Pd or Pt can help to properly assess the role of defects for the physical processes relevant for photo-catalysis [167]. In the following sections, the role of defects in r-TiO$_2$ and junctions between r-TiO$_2$ and various metals, focusing on Pd and Pt, will be further introduced. TiO$_2$ is often used as powder or nano-crystals in applications, one can therefore expect a large concentration of intrinsic defects to be relevant for the material’s properties.

4.2.1 Defects in Rutile Titanium Dioxide

In general, intrinsic defects like oxygen interstitials (O$_i$), titanium interstitials (Ti$_i$), titanium vacancies (V$_{Ti}$) as well as oxygen vacancies (V$_O$) can all be present in r-TiO$_2$ [4, 172]. O$_i$ are not expected to form in significant concentrations [223], except under very O-rich conditions, which are usually not relevant for r-TiO$_2$ [4]. For moderately O-rich conditions, V$_{Ti}$ was found to be the dominant intrinsic defect [4, 172, 176, 177]. Conversely, under reducing conditions, one expects V$_O$ and Ti$_i$ to have the lowest formation energies [224, 225]. Electron paramagnetic resonance spectroscopy (EPR) studies report on the presence of V$_O$ [167, 226–228] as well as Ti$_i$ [229, 230]. However, the assignment of a certain EPR signature to Ti$_i$ has been disputed [231], and hence it is still under debate if Ti$_i$ is present in typical r-TiO$_2$ samples. Experimentally, it was found that V$_O$ determines the conductivity of r-TiO$_2$ at high temperatures and under reducing conditions [4, 172, 176, 177]. From first-principles studies, it was deduced that the formation of defect-complexes involving several intrinsic defects is also likely [224].

Besides intrinsic defects, extrinsic defects are also present in r-TiO$_2$. The most commonly observed residual impurities are Si, Cr, Fe, Al, Mg, Ni, Ga and H [167, 232, 233]. Technologically-relevant impurities for doping include, for example, Nb or Li [178, 181]. H has been studied extensively in r-TiO$_2$ [167, 231, 232, 234–240], where the incorporation as interstitial defect (H$_i$) is most favourable [224]. Using fourier-transform infra-red spectroscopy as well as EPR, it was found that the O-H$_i$ bond is perpendicular to the c axis (see Fig. 4.2) [224, 231, 237]. Moreover, H is also likely to form complexes with various other defects [232]. Notably, H has a large diffusion coefficient in r-TiO$_2$ [241], and it has been shown that H can in-diffuse into r-TiO$_2$ during heat-treatments even if H is only present as a residual impurity in the annealing atmosphere [125].

A common feature of many defects in r-TiO$_2$ is the localization of the excess charge. Excess electrons are usually not found to be localized at the defect itself, but rather at a neighboring Ti atom, distorting the lattice and forming a bound polaron [167, 226, 227, 231, 236, 242–245]. Likewise, a self-trapped electron or free polaron can form easily [167, 184]. Notably, it has been observed that defect configurations exist that only differ in the distance between the lattice defect and the specific Ti atom the excess electron is localized at [238].

A host of first-principles investigations have been performed with respect to the
formation of defects in r-TiO$_2$ [224, 235, 242, 243, 246–249]. However, r-TiO$_2$ is a challenging material for first-principles calculations as can, for example, be seen in the pronounced influence computational parameters have on the prediction of defect parameters [223, 224, 244, 250]. Furthermore, r-TiO$_2$ exhibits strong polaronic effects, and hence thermodynamic charge state transition levels (see Sec. 4.2.1.1) and optical charge state transition levels (see Sec. 4.2.1.2) related to defects can differ substantially [10, 251]. This has made defect identification in r-TiO$_2$ a challenging task.

4.2.1.1 Influence of Defects on the Electrical Properties

There are several methods to reliably achieve $n$-type doping in r-TiO$_2$. For example, doping with Nb [181, 252, 253], Li [178, 254], reduction in vacuum [255] or hydrogenation [181, 185, 256] have been shown to lead to conductive $n$-type r-TiO$_2$. It has been proposed that either H$_i$ or V$_O$ act as donors in reduced and/or hydrogenated r-TiO$_2$ [125, 228, 231, 257]. There is, however, some controversy surrounding the nature of dopants in hydrogenated and reduced r-TiO$_2$ [125, 258, 259]. Ohlsen et al. showed that heat-treating r-TiO$_2$ in vacuum with low levels of contamination from oils did not lead to conductive r-TiO$_2$ [125], suggesting that indeed H$_i$ or some other residual impurity are the dominant donor in reduced r-TiO$_2$ [125, 260].

Donor ionization energies ($E_i$) are reported for a few donors in r-TiO$_2$: Nb ($E_i = 20$ meV [181]), Li ($E_i = 30$ meV [178]), H$_i$ ($E_i = 4.4$ [181] - 10 meV [237, 240, 261]) and V$_O$ ($E_i = 2.8$ meV [228]). Notably, H$_i$ and V$_O$ are reported to be shallow donors. However, first-principles calculations show considerable disagreement in terms of whether or not particular defects give rise to shallow or deep electronic states [224, 225, 235, 247, 248, 251, 262–264]. For example, H$_i$ [235, 247] as well as V$_O$ [225, 247, 248, 251, 262–264] have been reported to give rise to shallow donor states as well as deep donor states. There is generally less information about acceptor defects in r-TiO$_2$ due to the difficulty to obtain $p$-type doping. However, it has been shown that impurities, such as Fe, Al, Y, Ga, In or Cr compensate $n$-type conductivity [175, 182, 265, 266].

There are a number of reports on experimental findings concerning deep thermodynamic charge state transition levels in r-TiO$_2$ [178, 253, 267–269]. Kobayashi et al. reported two electron traps at 0.24 eV and 0.37 eV below $E_C$ [253]. Duckworth et al. also reported on an electron trap at 0.37 eV below $E_C$ [267]. Hillhouse investigated doped and undoped r-TiO$_2$ and found a variety of electron traps at 0.14 eV, 0.18 eV, 0.22 eV, 0.32 eV, 0.41 eV, 0.50 eV, 0.77 eV and 1.04 eV below $E_C$ [268]. An electron trap at 0.50 eV has been tentatively assigned to 2Al$_{Ti}$-V$_O$ [178, 269]. No further assignments exist so far for any of the other electron traps.

4.2.1.2 Influence of Defects on the Optical Properties

Conductive $n$-type r-TiO$_2$ usually exhibits a bluish color, regardless of the method used for $n$-type doping [254]. The bluish color is associated with a broad
absorption band in the photon energy region from around 0.3 eV to 2.0 eV, and hence in the visible/near infrared part of the electromagnetic spectrum [185, 232, 254, 257, 270–272]. It is also possible to induce optical absorption in r-TiO$_2$ in the same region using neutron irradiation [273]. The temperature- as well as polarization-dependence of the absorption band suggests the presence of several overlapping signatures [254, 270]. Additionally, impurities, such as Fe, Co, Cr and Mn, were shown to give rise to an absorption band close to the band edge of r-TiO$_2$ or in the visible part of the electromagnetic spectrum [232, 268]. Using deep-level optical spectroscopy, Nakano et al. also detected optical absorption related to electrically-active defects in between 1.0 eV and 2.1 eV [274, 275].

Especially, the absorption band in the visible/near-infrared part of the electromagnetic spectrum has been studied extensively. Bogomolov et al. showed that the strength of the corresponding absorption band exhibits a linear relationship with the conductivity of the sample, and a common slope of around 530 $\Omega$ is found which is independent of the method used for doping [254]. This observation implies a dopant-independent origin for the absorption band, and lead Bogomolov et al. as well as other authors to assign the absorption band to free polarons [232, 254, 260], i.e., to the optical transition from Ti$^{+3}$ to Ti$^{+4}$, whereby Ti$^{+3}$ is equivalent to Ti$^{+4}$ and an electron polaron. This assignment is supported by ultraviolet photo-electron spectroscopy [276, 277]. Further experimental support for the association of the absorption band with polarons originates from so-called pump-probe experiments. Here, it could be shown that absorption in the visible/infrared part of the electromagnetic spectrum can also be induced by illuminating semi-insulating r-TiO$_2$ with above band gap light [234, 278]. It can be considered an open question whether the corresponding transition is related to an excitation of the electron to the conduction band or rather to an optically-induced transfer from the electron between two Ti atoms [23]. The role of bound polarons, i.e., polarons in the vicinity of a defect, is also unclear.

Other authors suggest different origins of the ubiquitous absorption band in n-type r-TiO$_2$. Khomenko et al. suggest Ti$_i$ to give rise to the absorption band which is supported by the detection of Ti$_i$ in their samples by EPR [270]. However, the original assignment of the corresponding EPR signature to Ti$_i$ [229, 230] has been in doubt with Brant et al. assigning it to H$_i$ instead [231]. V$_O$ has also been suggested to be associated with the observed absorption band [257, 273, 279, 280]. It has proven to be challenging to assign optical absorption in n-type r-TiO$_2$ to intrinsic defects, due to the fact that such assignments are often made based on the method of doping, e.g., the specific heat-treatments used [257]. It has, however, been shown that impurities, such as H, can easily in-diffuse [125, 260], and hence might be responsible for the observed absorption band.

First-principles calculations have been reported on r-TiO$_2$ in order to predict the absorption related to defects in the material. The corresponding reports suggest that Nb$_{Ti}$, H$_i$, Ti$_i$ and V$_O$ all give rise to optical absorption in the range between 0.6 eV and 2.0 eV [224, 243, 251, 281–283]. The similarities seen for a wide range of different defects is usually ascribed to the formation of polarons [251, 283].
4.2.2 Junctions between Rutile Titanium Dioxide and various Metals

Schottky junctions involving r-TiO$_2$ can be achieved when using Ni, Au, Pd or Pt as metal contact on n-type r-TiO$_2$ [197–199, 253, 256, 267, 284–289] (see Sec. 3). However, the rectifying characteristics of such junctions depend on preparation conditions, e.g., the defect chemistry of the involved r-TiO$_2$ [290] or the surface preparation prior to contact deposition [256, 291]. Generally, ideality factors ranging from 1.5 to 4.0 have been found for Schottky junctions involving r-TiO$_2$ [256, 285, 289, 292, 293]. A barrier height of around 1.2 eV - 1.3 eV has been reported for Pt/TiO$_2$ junctions [287]. Ohmic contacts to n-type r-TiO$_2$ have been formed using, for example, eutectic In-Ga alloys [256]. At the interface between Au and hydrogenated r-TiO$_2$, an insulating hydroxil layer was found which influences the electrical characteristics but could be removed by specific surface treatments [256]. For Schottky junctions between Pd and hydrogenated r-TiO$_2$, it was observed that the barrier height of the junction shifted when H$_2$ was introduced in the surrounding atmosphere, suggesting that H changes the Pd/r-TiO$_2$ interface [197, 198, 284]. The changes in barrier height strongly depend on the surface orientation of r-TiO$_2$ [284]. Notably, Pd/TiO$_2$ as well as Pt/TiO$_2$ systems are used as hydrogen sensors [196–199]. The diffusion of charged species is altered by the electrical field present in the Schottky junction [294], and hence out- or in-diffusion of H into r-TiO$_2$ might be different for the space-charge region as compared to the bulk [259]. Importantly, it was demonstrated that the surface reaction occurring at the Pd/r-TiO$_2$ interface depends on the fermi-level position in r-TiO$_2$ [295].
Chapter 5

Methods

In this chapter, the methods used in this thesis will be introduced. This includes methods for sample treatment/preparation, electrical characterization, steady-state photo-capacitance (SSPC) measurements, optical characterization, compositional characterization and computational methods. SSPC measurements were of particular interest for this thesis and will be introduced in Sec. 5.3 together with a description of a new experimental setup for performing such measurements which was developed during this PhD project in collaboration with the master student Vegard Rønning [296].

5.1 Sample Treatment and Preparation

In this section, methods for sample treatment and preparation will be introduced. Methods for sample treatment and preparation served two purposes: i) introducing defects in a controlled way, and ii) enabling measurements involving semiconducting materials. Heat-treatments in different atmospheres as well as ion beams were used to introduce defects into the materials studied here. For example, heat-treatments were utilized for diffusing H into samples (hydrogenation). Ions beams were used to generate intrinsic defects in semiconductors, and ion implantation as well as irradiation will be described in more detail in Sec. 5.1.1. Space-charge spectroscopy was one of the work horses in this thesis, and rectifying junctions are needed to perform the corresponding measurements. For β-Ga$_2$O$_3$ and r-TiO$_2$, Schottky junctions are suitable rectifying junctions for performing space-charge spectroscopy, and hence the fabrication of such junctions will be outlined in Sec. 5.1.2. Notably, when performing heat-treatments on Schottky junctions, it is possible to manipulate the fermi-level position inside the space-charge region during the heat-treatment by applying an external bias voltage [297, 298]. Such heat-treatments can be used to gauge the dependence of defect formation on the fermi-level position (see Sec. 5.6).

5.1.1 Proton Irradiation and Ion Implantation

In this thesis, proton irradiation and H as well as He implantation were utilized [299–301]. He is often used for implantation because it will not act as an electrically-active center inside a material [302]. Here, irradiation is distinguished from implantation by the penetration depth for the species the irradiation or implantation is performed with relative to the region of interest. When performing irradiation, the penetration depth is deeper inside the material than the region of interest, while for implantation the penetration depth is comparable to the region of interest. For example, when performing space-charge
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Figure 5.1: Ion implantation/proton irradiation and metal contact deposition: (a) Results based on SRIM simulations [299] of ion implantation (H as well as He) into a Ni/β-Ga2O3 system. The upper panel shows the expected depth profile for the generation of V_O in the material upon implantation with H using various kinetic energies. The lower panel displays the projected range R_p for the generation of V_O when using H as well as He implantation. (b) Images illustrating how semi-transparent Schottky contacts were fabricated by a two-step process using e-beam evaporation with two shadow masks which align. The bottom panel shows a microscope image of the resulting contact layout. The figure was taken from Ref. [296] and modified.
ions can be found. Alternatively, one can also define $R_p$ for the generated defects. $R_p$ can be used to gauge if a certain implantation experiment can be considered as irradiation or implantation with respect to the region of interest. The simulated defect generation is often used to calculate the introduction rate ($IR$) which describes the amount of defects created per implanted ion, and can be compared to experimental results. Importantly, only a fraction of the generated Frenkel-pairs survives after irradiation/implantation due to the so-called dynamic annealing [301, 303]. Further, diffusion of defects may occur and change the defect chemistry, e.g., by formation of defect complexes or annihilation of Frenkel-pairs. This can be exploited in order to change the defect chemistry after irradiation or ion implantation by heat-treating samples. Furthermore, it can be useful to perform irradiation or ion implantation at cryogenic temperatures in order to suppress the diffusion of defects [304, 305].

5.1.2 Fabrication of Schottky Junctions

The majority of the characterization techniques used for this thesis were based on measuring the junction current (see Sec. 3.2) or the junction capacitance (see Sec. 3.3) of Schottky junctions. For this purpose, Schottky junctions needed to be fabricated. The typical steps for the fabrication of Schottky junctions are [100, 133, 306]:

1. Cleaning of the semiconductor in aceton, isopropanol and de-ionized water inside an ultra-sonic bath for several minutes each. The cleaning step prepares the surfaces for the deposition of metals.

2. Deposition of an Ohmic (back) contact using e-beam evaporation. In e-beam evaporation, the metal to be deposited is placed inside a crucible and the evaporation of the metal is achieved by a focused e-beam. The e-beam evaporation is conducted inside a vacuum ($\approx 1 \times 10^{-6}$ Torr). For $\beta$-Ga$_2$O$_3$ as well as r-TiO$_2$, a stack consisting of Ti/Al or eutectic InGa were used as Ohmic (back) contact. Typically, a thickness of 10 nm was used for Ti, while 150 nm of Al were deposited.

3. Repetition of the afore-mentioned cleaning step.

4. Deposition of a Schottky (front) contact using e-beam evaporation in combination with a shadow mask. Using a shadow mask, one can deposit contacts with well-defined circular shape and diameters. For $\beta$-Ga$_2$O$_3$, Ni or Pt were used as Schottky contact [100, 133], while for r-TiO$_2$ either Pd, Pt or Ni were employed as Schottky (front) contacts. Typically, thicknesses of around 150 nm were used.

In order to electrically connect the front contacts of the samples, one can either use wire-bonding or simply place a probe on top of the contact. The Ohmic back contact was an area contact, and hence was simply placed on top of a conductive substrate, i.e., a conductive sample stage or the conductive gold part of a chip for wire-bonding.
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For some measurements (see Sec. 5.3), semi-transparent Schottky front contacts were needed in order to enable light to penetrate into the Schottky junction. For this purpose, the Schottky contact deposition was performed in two subsequent steps [296]:

1. Semi-transparent Schottky contacts with a thickness of 10 nm - 20 nm were deposited by e-beam evaporation using a shadow mask with contact diameters of 300 µm, 600 µm and 900 µm.

2. To ensure mechanical stability of the contacts for wire-bonding, a second metal deposition (thickness = 150 nm) was performed using a shadow mask (with only circular openings displaying a diameter of 300 µm) which aligned with the semi-transparent contacts.

The procedure used for the deposition of semi-transparent front contacts is illustrated in Fig. 5.1 (b).

5.2 Electrical Characterization

In this section, electrical characterization methods will be introduced. In this thesis, space-charge spectroscopy was utilized to a large extent for studying defects in semiconductors, and hence a focus of this introduction will be on such techniques.

5.2.1 Conductivity Measurements

There is a variety of methods which can be used to measure the electrical conductivity (σ) of a semiconductor, for example, Hall [9, 307] or four-point probe measurements [9, 308]. It is, however, challenging to perform Hall measurements on semiconductor crystals displaying low charge carrier mobilities [309, 310], for example, due to polaron formation (see Sec. B). In four-point probe measurements, it is necessary to place four probes on the surface of the semiconductor under investigation. The resulting junctions should ideally display Ohmic behavior. Van der Pauw and Horkstra developed the theory behind measuring σ using four-point probe measurements [308, 311]. They proposed the following formula [312]:

\[
\exp (-\pi R_{AB,CD}h\sigma) + \exp (-\pi R_{BC,DA}h\sigma) = 1
\]

which can be solved numerically for σ. h is the thickness of the semiconductor, while \( R_{ij,kl} \) are defined according to Ohm’s law as:

\[
R_{ij,kl} = \frac{V_{ij}}{I_{kl}}.
\]

i, j, k and l describe the four contacts used in a four-point probe measurement. \( V_{ij} \) is applied between contact i and j, while \( I_{kl} \) is measured between the contacts k and l. The geometrical arrangement of the four contacts is irrelevant for the determination of σ when using Eq. 5.1 [9, 308, 311].
5.2.2 Current-Voltage Measurements

Current-Voltage (IV) measurements are particularly important when investigating the electrical properties of rectifying junctions (see Sec. 3) [9]. In principle, IV measurements are performed in two-probe configurations, i.e., $V_{\text{ext}}$ will be applied between the same contacts between which $I$ will be measured. Usually, $I$ is recorded while scanning $V_{\text{ext}}$ across a range of values while the temperature $T$ is kept constant. Generally, Eq. 3.21 can be used to model the recorded data for a rectifying junction. However, more complex equivalent circuits might be necessary to describe a particular junction, and further modifications might have to be added [43, 313]. Fig. 5.2 displays IV curves simulated based on Eq. 3.21 in order to illustrate how the ideality factor $n$, the series resistance $R_S$, the shunt resistance $R_{\text{Sh}}$, and the temperature $T$ influence IV curves recorded on a Schottky junction. The temperature-dependence is determined by the temperature-dependence of the saturation current density $j_S$ as stated in Eq. 3.15.

For analysing recorded IV curves, several approaches were deployed in this

![Figure 5.2: IV curves: Simulated IV curves according to Eq. 3.21. Results are presented for different values of (a) the ideality factor $n$, (b) the series resistance $R_S$, (c) the shunt resistance $R_{\text{Sh}}$ and (d) the temperature $T$. The temperature-dependence is determined by Eq. 3.15.](image)

thesis. Firstly, measured IV curves can be fitted with Eq. 3.21. Secondly, approximations of Eq. 3.21 can be used which enable the determination of relevant device parameters [9, 314, 315]. From temperature-dependent IV measurements, an effective value of the barrier height (see Eq. 3.15) can be extracted when obtaining values for $j_S$ at each temperature. Thirdly, one can solely extract phenomenological parameters from IV curves, like the rectification, i.e., the difference between $I(-V_{\text{ext}})$ and $I(V_{\text{ext}})$ stated in orders of magnitude.

5.2.3 Capacitance-based Measurements

Capacitance-based measurements are powerful techniques when rectifying junctions, such as Schottky or $p$-$n$ junctions (see Sec. 3.3), are available. There is a variety of capacitance-based techniques which can be used to probe the
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electrical properties of defects in semiconductors. In this thesis, Impedance spectroscopy [316–318], Capacitance-Voltage measurements [9, 319, 320], thermal admittance spectroscopy (TAS) [9, 321, 322] and deep-level transient spectroscopy (DLTS) [9, 323] were performed. Additionally, SSPC measurements are also based on capacitance measurements, and will be introduced in Sec. 5.3. All these techniques are similar in terms of how the measurements are performed, but differ in the experimental conditions and with respect to data collection. TAS, DLTS and SSPC measurements are considered space-charge spectroscopy techniques. In capacitance measurements, the rectifying junction is kept at a fixed bias $V_{\text{ext}}$ during the measurement. Capacitance measurements are performed by applying an alternate-current signal $V_S$ with a probing frequency $f_{\text{probe}}$ to the junction under investigation:

$$V_S = V_0 \exp (-i 2\pi f_{\text{probe}} t). \quad (5.3)$$

$V_0$ should be small compared to $V_{\text{ext}}$ [9]. The AC signal will lead to an additional junction current $I_S$ described by:

$$I_S = I_0 \exp (-i 2\pi f_{\text{probe}} t + i\phi). \quad (5.4)$$

The impedance $Z$ (the complex resistance) of the junction can be calculated from the ratio $V_0/I_0$ and the phase shift $\phi$. $Z$ is generally described by:

$$Z = Z_{\text{real}} + i Z_{\text{im}} = |Z| \exp (-i\phi). \quad (5.5)$$

In order to extract the capacitance ($C$) of a junction from $Z$, it is necessary to assume a specific equivalent circuit describing the junction [316–318, 324].

5.2.3.1 Impedance Spectroscopy

In impedance spectroscopy (IS), the impedance of a junction is measured using different $f_{\text{probe}}$ at a fixed $V_{\text{ext}}$. Such measurements can, for example, be used to investigate which equivalent circuit is suitable for describing the investigated junction [316–318, 324]. It is common in IS to represent $Z$ in different plots: Nyquist plot ($Z_{\text{real}}$ vs. $-Z_{\text{im}}$), Phase plot ($\phi$ vs. $f_{\text{probe}}$) and displaying $|Z|$ vs. $f_{\text{probe}}$. Furthermore, it has been shown that defining the quantity $\alpha_Z$ as

$$\alpha_Z = -\frac{d \log (Z_{\text{im}})}{d \log (f_{\text{probe}})} \quad (5.6)$$

can be helpful in determining appropriate equivalent circuits [324–326]. Fig. 5.3 shows examples for all aforementioned plots for a variety of equivalent circuits. Modelling $Z$ by using the aforementioned plots is usually used to determine the equivalent circuit and the corresponding parameters describing the elements of the circuit [316–318, 324, 327–329]. The individual impedances of electrical
Electrical Characterization

Figure 5.3: Impedance of different equivalent circuits: Simulations of $Z$ for four different equivalent circuits shown in (a). Four different representations of the data sets are shown: (a) Nyquist plot, (b) Phase plot, (c) $|Z|$ vs. $f_{\text{probe}}$ and (d) $\alpha_Z$ vs. $f_{\text{probe}}$ (see Eq. 5.6). (b), (c) and (d) are usually presented as semi-logarithmic plots, and (d) is often also presented as double-logarithmic plot.

Circuit elements are described by the following equations [317, 318, 330]:

$$Z_i = \begin{cases} 
  R & \text{, for Resistances (} i = R \text{)} \\
  \frac{1}{i2\pi f_{\text{probe}}C} & \text{, for Capacitances (} i = C \text{)} \\
  i2\pi f_{\text{probe}}L & \text{, for Inductances (} i = L \text{)} \\
  \frac{1}{(i2\pi f_{\text{probe}})^nQ} & \text{, for Constant – Phase Elements (} i = \text{CPE} \text{)}
\end{cases} \quad \text{(5.7)}$$

Constant-phase elements (CPE) are empirical circuit elements [330] which have been used to model a distribution of $RC$-elements in electrical circuits, for example, due to a distribution of trap states [331] or grain boundaries [332]. Using the known rules for how to calculate the overall $Z$ of a circuit from its constituent elemental impedances, one can find an expression for $Z$ which can be compared to recorded data [330]. It is necessary to model at least two of the representations shown in Fig. 5.3 simultaneously in order to account for all aspects of the measured $Z$ [330]. However, different equivalent circuits will not necessarily yield unique $Z$ [324]. On the other hand, it is often possible to determine the number of individual $RC$-circuits present [324] and the influence of the series resistance. In Fig. 5.3, simulations of $Z$ for four different equivalent circuits are displayed. The corresponding circuits consist of a number of $RC$-elements, and can be distinguished by the number of corresponding features in
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the representations shown. In Nyquist plots, different $RC$-circuits are represented by one semi-circle each, while the series resistance shifts the curve to the right. In Phase plots, when plotting $|Z|$ vs. $f_{\text{probe}}$ or $\alpha_Z$ vs. $f_{\text{probe}}$, different $RC$-circuits are seen as steps or dips, while the series resistance changes the behavior of the curve for high $f_{\text{probe}}$. It is often instructive to verify the validity of data recorded for $Z$ by testing their compliance with the Kramers-Kronig relations which connect $Z_{\text{real}}$ and $Z_{\text{im}}$.[330, 333, 334].

IS is paramount in identifying rectifying junctions suitable for space-charge spectroscopy. In this thesis, IS was used to ensure suitable device characteristics, particularly with respect to the presence of several $RC$-circuits, potentially distorting results obtained by space-charge spectroscopy measurements[335].

5.2.3.2 Capacitance-Voltage Profiling

In Capacitance-Voltage (CV) profiling or measurements, the capacitance $C$ of a rectifying junction is measured with a fixed $f_{\text{probe}}$ while varying the applied bias $V_{\text{ext}}$ (see Sec. 3.3). In order to obtain $C$ from the measured $Z$, one needs to assume a particular equivalent circuit for the junction. Commonly, simple circuits consisting of a capacitor and a resistance are used. One can either use a parallel circuit consisting of a capacitor $C_p$ and a parallel resistance $R_p$ or a series circuit between a capacitor $C_s$ and a series resistance $R_s$. It is useful to perform IS measurements in order to verify that the assumed circuit is close to the actual equivalent circuit.

If the extracted $C$ is related to a rectifying junction with a small amount of traps, Eq. 3.18 or 3.19 will hold. For a Schottky junction, one can rewrite Eq. 3.19 as:

$$\frac{1}{C^2} = \frac{2}{A^2 \varepsilon \varepsilon_0 \varepsilon_s} N_j (V_{\text{bi}} - V_{\text{ext}}).$$  \hspace{1cm} (5.8)

The effective dopant concentration $N_j$ ($j = A$ for a $p$-type semiconductor and $j = D$ for a $n$-type semiconductor) can be extracted from the slope $m$, while the built-in voltage $V_{\text{bi}}$ can be extracted from the intersect $y$ and $m$. If $N_j$ is inhomogeneous, it is instructive to extract the dopant profile by using the derivative of Eq. 5.8:

$$N_j (W) = -\frac{2}{A^2 \varepsilon \varepsilon_0 \varepsilon_s} \left( \frac{\partial \left( \frac{1}{C^2} \right)}{\partial V_{\text{ext}}} \right)^{-1}. \hspace{1cm} (5.9)$$

$W$ is the depth of the depletion layer and can be calculated from Eq. 3.20.

In case, a large number of traps is present in the junction volume, Eq. 3.18, 3.19 and 3.20 do not hold anymore, except for sufficiently high probing frequencies $f_{\text{probe}}$ (see Eq. 3.23 as well as Sec. 5.2.3.3). It is, however, still possible to obtain $V_{\text{bi}}$ from Eq. 5.8 as long as one uses a linear fit to $1/C^2$ at moderate forward bias voltages $V_{\text{ext}}$ (see Fig. 3.3 (b))[9].
5.2.3.3 Thermal Admittance Spectroscopy

In Sec. 3.3, it was shown that traps inside the space-charge region will modify the capacitance related to the space-charge region. While this is a challenge for CV measurements when extracting parameters such as the dopant concentration or the built-in voltage, one can make use of this aspect in order to investigate the traps themselves. One such approach is called thermal admittance spectroscopy (TAS) [9, 321, 322]. Here, the junction capacitance $C$ is measured at several different $f_{\text{probe}}$ while scanning the sample temperature $T$. The temperature dependence of $C (C (T))$ can be described by using Eq. 3.23 and 3.27:

$$C (T) = C'_\infty + \left(1 + \left[\frac{f_{\text{probe}}}{2\varepsilon_{i}^{\text{th}}}\right]^2\right)^{-1} \Delta C'$$ \hspace{1cm} (5.10)

if one assumes $N_t \ll N_D$ to be valid. Here, $\varepsilon_{i}^{\text{th}}$ is defined according to Eq. 2.32 and 2.33. $i = n$ is relevant for a Schottky junction between a metal and an $n$-type semiconductor, while $i = p$ applies to a Schottky junction between a metal and a $p$-type semiconductor. From $\Delta C'$ the concentration of the corresponding dopant can be calculated [9].

A plot of $C (T)$ vs. $T$ displays a step in $C (T)$ at a temperature $T_{\text{probe}}$ depending on $\varepsilon_{i}^{\text{th}}$ and $f_{\text{probe}}$. Alternatively, the derivative $\partial C (T)/\partial T$ or the conductance $G$ of the junction can be investigated, and peaks can be seen at $T_{\text{probe}}$ [9, 336]. At $T_{\text{probe}}$, $2\varepsilon_{i}^{\text{th}}$ will be equal to $f_{\text{probe}}$ if $N_t \ll N_D$ is valid, and hence [9]

$$f_{\text{probe}} \sim N_C \varepsilon_{n}^{\text{th}} \sigma_{n, \infty}^{\text{th}} \exp \left(-\frac{E_b}{k_b T_{\text{probe}}}\right) \exp \left(-\frac{E_C - E_t}{k_b T_{\text{probe}}}\right)$$ \hspace{1cm} (5.11)

is found for an $n$-type semiconductor being part of a Schottky junction when combining Eq. 2.32 with Eq. 2.31. An equivalent expression can be found for a $p$-type semiconductor being part of a Schottky junction. When using Eq. 2.7 and 2.28, Eq. 5.11 can be rewritten as

$$\ln \left(\frac{f_{\text{probe}}}{T_{\text{probe}}^2}\right) = K - \frac{E_b}{k_b T_{\text{probe}}} - \frac{E_C - E_t}{k_b T_{\text{probe}}}$$ \hspace{1cm} (5.12)

which represents a so-called Arrhenius relation. $K$ is independent of temperature. Notably, from such Arrhenius plots the activation energy of a trap can be derived:

$$E_A = E_b + (E_C - E_t).$$ \hspace{1cm} (5.13)

At a certain temperature, the main dopant will have a low emission rate $\varepsilon_{i}^{\text{th}}$ and will no longer respond to the probing signal used for measuring $C$. This is usually called freeze-out. Close to the freeze-out temperature, a modified expression of Eq. 5.12 needs to be used [322].

Generally, TAS can also be used to determine the properties and concentrations of traps if $N_t \ll N_D$ is not valid. However, Eq. 5.11 will need to be modified (see Sec. 3.4.2) [9].
Figure 5.4: **Principle and analysis of DLTS**: (a) Illustration of the measurement principle of DLTS. The upper panel shows the applied voltage during the measurement. The lower panel displays the recorded capacitance $C$. $C$ displayed in black are quiescent values. After the voltage pulse, the junction will return to equilibrium as described by Eq. 5.14. The DLTS signal $S_j$ (see (b)) is constructed by analysing different parts of the transient expressed by the window length $t_{\text{window}}$ (see Eq. 5.17). (b) The lower panel shows an illustration what the DLTS signal would look like for the situation depicted in (a). A lockin-filter (GS2) was used as $w(t)$ in Eq. 5.17 to obtain $S_j$. $S_j$ is shown for two different rate windows $j = 1$ and $j = 2$ which correspond to $t_{\text{window}}$ and $2t_{\text{window}}$, respectively. The corresponding emission rates $e_n^{\text{th}}$ are stated in the plot. Both $S_j$ will exhibit a maximum at a certain temperature $T_{j_{\text{max}}}$. The pairs of $T_{j_{\text{max}}}$ and $e_n^{\text{th}}$ can be used to construct the Arrhenius plot displayed in the upper panel (see Eq. 5.20). From the slope of the Arrhenius plot, $E_A/k_B$ can be determined (see Eq. 5.13). (c) Comparison of the influence of different $w(t)$ on $S$. The filter functions are defined in Ref. [337, 338]. Here, it was assumed that three different traps are present whose emission is determined by the same capture cross section $\sigma_{n,\infty}^{\text{th}}$, but different $E_A$ equaling 0.37 eV, 0.40 eV and 0.43 eV, respectively. The $e_n^{\text{th}}$ were chosen to be similar for all $w(t)$, and are stated in the plot.
5.2.3.4 Deep-level transient spectroscopy

Deep-level transient spectroscopy (DLTS) is a powerful tool for studying electron or hole traps in semiconductors [9, 323]. In the following, DLTS will be described for the case of a Schottky junction between a metal and a \( n \)-type semiconductor. In DLTS, the Schottky junction is kept at a reverse bias \( V_{\text{ext}} \). At \( V_{\text{ext}} \), the junction will display the capacitance \( C_0 \) described by Eq. 3.19. At a time \( t_0 \) a voltage pulse \( V_{\text{pulse}} \) is applied lasting for a duration \( t_{\text{pulse}} \), resulting in a capacitance \( C_{\text{pulse}} \). After the voltage pulse, traps above \( E_F \) will be filled with electrons, and hence a non-equilibrium situation exists (see Fig. 3.4 (a)). At this time, one will measure the capacitance \( C^* \). Subsequently, electrons will be emitted from the traps located above \( E_F \), and the capacitance will return to the value \( C_0 \) (see Fig. 3.4 (b)). In DLTS, the capacitance transient \( C(t) \) is recorded after the voltage pulse has ended. In practice, the capacitance transient is recorded for a certain time \( t_{\text{transient}} \) after the pulse ended plus an additional delay time \( t_{\text{delay}} \). If the trap concentration is much smaller than the dopant concentration (small perturbation), the recorded \( C(t) \) will be described by Eq. 3.34, and hence:

\[
C(t) = C_0 \left[ 1 - \frac{1}{2} x_1^2 - x_2^2 \right] \frac{N_t}{N_D} \exp \left( -\varepsilon_{\text{th},t} t \right). \quad (5.14)
\]

All symbols are defined in Sec. 3.3, and specifically in Fig. 3.4 (a). Eq. 2.32 describes \( \varepsilon_{\text{th},t} \). The factor \( \left( x_1^2 - x_2^2 \right) / W^2 \) is often referred to as \( \lambda \)-correction [9]. If several traps \( i \) are present, Eq. 5.14 is written as a superposition of individual transients assuming the emission of individual traps is independent of each other:

\[
C(t) = C_0 \sum_i \left[ 1 - \frac{1}{2} x_{1,i}^2 - x_{2,i}^2 \right] \frac{N_{t,i}}{N_D} \exp \left( -\varepsilon_{\text{th},i} t \right). \quad (5.15)
\]

In DLTS, \( C(t) \) is measured at different temperatures \( T \). In order to study the properties of traps, it is necessary to extract \( N_{t,i} \) as well as \( \varepsilon_{\text{th},i} \) for each \( T \). Conventional DLTS analysis is based on the original concept proposed by Lang [323]. However, alternative approaches exist as well. For example, one can use the fact that Eq. 5.15 essentially represents a Laplace transformation of \( C(t) \) [339]. In Laplace DLTS, an inverse Laplace transformation of the measured \( C(t) \) is performed in order to extract \( N_{t,i} \) as well as \( \varepsilon_{\text{th},i} \) for individual traps [339]. Lang and several other authors developed a method to represent all capacitance transients in one intuitive graph and extract trap parameters by defining the DLTS signal \( S \) as [323, 337, 340]:

\[
S(T) = \frac{1}{t_{\text{transient}}} \int_{t_{\text{delay}}}^{t_{\text{delay}} + t_{\text{transient}}} \int_{t_{\text{delay}}}^t C(t) w(t) \, dt, \quad (5.16)
\]

where \( w(t) \) is the so-called weighting function. In the following, analyzing DLTS measurements using this method will be denoted as conventional DLTS. There are several expressions for \( w(t) \) which can be used. Most commonly, a lock-in
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function (in this thesis, labeled as GS2) is utilized [337, 340]. In this thesis, more complex \( w(t) \), like GS4, are also employed [337]. \( w(t) \) represent the application of an approximate inverse Laplace transformation [337, 340] which was developed by Gaver [341] and Stehfest [342].

Experimentally, \( C(t) \) will not be measured continuously, and hence the integral in Eq. 5.16 needs to be rewritten as a discrete sum:

\[
S_j(T) = \frac{1}{j+1} \sum_{k=0}^{j} C\left(t_{\text{delay}} + \frac{t_{\text{window}}}{4} + k\frac{t_{\text{window}}}{2}\right) \times \left(w\left(t_{\text{delay}} + \frac{t_{\text{window}}}{4} + k\frac{t_{\text{window}}}{2}\right)\right).
\]

(5.17)

Here, the subscript \( j \) was introduced to signify the so-called rate window. In practice, rate windows are linked to analyzing different sections of \( C(t) \) (see Fig. 5.4 (a) and (b)), and hence \( t_{\text{window}} \leq t_{\text{transient}} \) needs to be fulfilled. Different rate windows are sensitive to different values of \( e_{\text{th},n} \), and hence can be regarded as frequency filters. Often, \( C\left(t_{\text{delay}} + \frac{t_{\text{window}}}{4} + k\frac{t_{\text{window}}}{2}\right) \) is found by averaging the measured \( C(t) \) in an appropriate time interval. The DLTS signals \( S_j(T) \) will be a function of \( T \), exhibiting a peak at \( T_{\text{max}}^j \) (see Fig. 5.4 (b)). The peak position can be found from

\[
\frac{dS_j}{dT}_{T=T_{\text{max}}^j} = \frac{dS_j}{dT}_{T=T_{\text{max}}^j} = 0
\]

(5.18)

assuming the presence of a single trap with an emission rate \( e_{\text{th},n} \). Eq. 5.18 will be solved for a specific \( e_{\text{th},n} \) depending on the parameters used for calculating \( S_j(T) \) such as \( t_{\text{delay}}, t_{\text{window}} \) and \( w(t) \). Values for \( N_t \) can be found from the maximum of \( S_j(T) \) \( \left(S_{\text{max}}^j\right) \) according to:

\[
N_t = 2\frac{\Delta C}{C_0} N_D = 2\frac{g_j S_{\text{max}}}{C_0} N_D.
\]

(5.19)

\( \Delta C \) is the amplitude of the capacitance transient. \( g_j \) is a correction factor which needs to be applied to calculate \( \Delta C \) from \( S_{\text{max}}^j \). \( g_j \) will depend on \( t_{\text{delay}}, t_{\text{window}} \) and \( w(t) \), and an overview of calculated values for \( g_j \) can be found in Ref. [338]. From Laplace as well as conventional DLTS measurements, pairs of \( T \) and \( e_{\text{th},n} \) are extracted. Using the expression for \( e_{\text{th},n}(T) \) given in Eq. 2.31 and 2.32, an Arrhenius plot can be constructed:

\[
\ln\left(\frac{e_{\text{th},n}}{T^2}\right) = \beta \sigma_{\text{th},n,\infty} - \frac{E_A}{k_BT}.
\]

(5.20)

\( E_A \) is defined according to Eq. 5.13, while \( \beta \) is a material constant, and can be calculated by:

\[
\beta = 2\sqrt{3} \left(\frac{2\pi}{\hbar^2}\right)^{3/2} k_B m_{n,\text{eff}}.
\]

(5.21)
Notably, the electrical field present inside the junction will have an influence on the determined value for $E_A$ if the corresponding trap is a donor defect [9, 343]. According to Eq. 5.13, $E_A$ comprises the charge state transition level of a defect expressed by $E_C - E_A$ as well as the capture barrier $E_b$. In DLTS, it is possible to measure $E_b$ independently by performing DLTS measurements depending on $t_{\text{pulse}}$.

For conventional DLTS, traps which have similar emission rates $e_{n,i}^{\text{th}}$ pose a challenge since it may not be possible to simply determine $T_{j,\text{max}}$ for each trap individually. This problem can be somewhat mitigated by using more complex $w(t)$, which may increase the energy resolution [337, 340]. The improved resolution usually comes at the expense of a reduced signal-to-noise ratio. Further challenges arise from the determination of the correction factor $g_j$ which is strictly only possible if a single trap is measured in the given temperature interval [338]. Here, simulations of conventional DLTS spectra can be useful. In this thesis, DLTS spectra were also simulated using Eq. 5.17 in conjunction with Eq. 5.15 for a given $w(t)$.

Further challenges for the interpretation of DLTS measurements are caused by large trap concentrations, especially if $N_i > 0.2N_D$ [9] or if the junction under investigation exhibits non-ideal properties, such as high series resistance [9, 344, 345] or the presence of several $RC$-circuits [335].

### 5.3 Steady-State Photo-Capacitance Measurements

SSPC measurements [26, 137, 147, 346–350] were instrumental in this thesis to probe defect levels in $\beta$-Ga$_2$O$_3$. Indeed, one of the main objectives of this PhD project was the development of an experimental setup for performing SSPC measurements [296]. In SSPC measurements, a rectifying junction is used to detect the optical ionization of traps inside a semiconductor. An advantage of this detection method is its sensitivity for small concentrations of traps as well as the fact that such measurements can easily be calibrated, and hence absolute trap concentrations can be obtained. Electrical characterization techniques, such as DLTS (see Sec. 5.2.3.4), make use of this self-calibration also. However, in DLTS, thermally-activated electron emission from traps is used to probe trap properties, potentially rendering a large part of the band inaccessibile. For example, using a $\beta$-Ga$_2$O$_3$-based Schottky junction, it is typically possible to probe trap levels which are up to 1.4 eV below $E_C$ [52]. Using light instead of temperature to trigger electron emission from traps, one can access a larger part of the band gap, i.e., one can access the middle or lower part of the band gap [26].

#### 5.3.1 Principle of Steady-State Photo-capacitance Measurements

Here, we assume that a Schottky junction comprising a $n$-type semiconductor is used for SSPC measurements. In SSPC measurements, the capacitance of a rectifying junction is recorded in dark ($C_{\text{dark}}$) and after illumination with near-monochromatic (sub-band gap) light ($C_{\text{illumination}}$). Ideally, the illumination
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![Figure 5.5: SSPC spectra and resolution of the experimental setup developed for SSPC measurements:](image)

(a) Graphical representation of Eq. 5.23 as (upper panel) derivative SSPC spectrum \(dS(E)/dE\) and (lower panel) SSPC spectrum \(S(E)\). The presence of four traps was assumed for the calculation. The trap concentration can be determined from the height of the individual steps in the SSPC spectrum or from the area under the peaks seen in the derivative SSPC spectrum. The feature at around 3.2 eV consists of two signatures. This is more clearly visible in the derivative SSPC spectrum. (b) Plots illustrating the spectral resolution of the optical excitation used for SSPC measurements. The upper panel shows the spectrally-resolved optical output when the monochromator is set to a wavelength of 500 nm. There is a slight offset in the set position of the monochromator and the spectral position of the optical output. The recorded data were fitted with gaussian line shapes. In the lower panel, the full-width at half maximum of the spectrally-resolved optical output is displayed, showing a dependence on the slit width of the monochromator’s exit slit. Data are shown for two different gratings used in this thesis as well as different nominal wavelength positions (\(\lambda_{\text{spec}}\)) of the monochromator. The figure is reprinted from Paper II with permission from APS Publishing.

should be performed for a sufficiently long duration to establish steady-state conditions. The junction is kept at a fixed reverse bias during illumination and when recording the capacitance. A SSPC spectrum \(S(E)\) is recorded by repeating the measurement at a variety of photon energies. \(S(E)\) is usually presented as:

\[
S(E) = 2N_D \frac{C_{\text{illumination}} - C_{\text{dark}}}{C_{\text{dark}}} = 2N_D \frac{\Delta C_{\text{illumination}}}{C_{\text{dark}}}. \tag{5.22}
\]

The underlying physical process and the capacitance to be expected are described in Sec. 3.3.

There is a variety of practical implementations of SSPC measurements. One approach is to perform SSPC measurements by resetting the junctions to 0 V conditions between every photon energy step used for recording the SSPC spectrum [137, 147, 346]. It is also common to perform measurements by
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constantly illuminating the junction with above band gap light in addition to the (sub-band gap) light used for SSPC measurements (two-beam measurements) [26, 351]. Another approach is to perform SSPC measurements in a differential mode by scanning the photon energy continuously while measuring [351]. Regardless how SSPC measurements are performed, \( S(E) \) exhibits an increasing or a decreasing capacitance signal with photon energy, where a step indicates the presence of an optically- and electrically-active trap in the space-charge region. Thus, \( S(E) \) can be de-convoluted with an empirically-motivated model described by:

\[
S(E) = 2N_D \sum_i \frac{\Delta C_{\text{illumination},i}}{C_{\text{dark}}} \frac{1}{1 + \exp \left( -\frac{E_i - E}{\gamma_i} \right)}. \tag{5.23}
\]

Here, the presence of multiple traps \( i \) is assumed. \( \Delta C_{\text{illumination},i} \) is the height of a certain step in \( S(E) \). Features with \( \Delta C_{\text{illumination},i}/C_{\text{dark}} > 0 \) (optically-induced electron emission) as well as \( \Delta C_{\text{illumination},i}/C_{\text{dark}} < 0 \) (optically-induced hole emission) can occur [9, 26, 137, 147, 152]. \( E_i \) and \( \gamma_i \) are parameters describing the position and steepness of the corresponding capacitance step. SSPC spectra can also be displayed as \( dS(E)/dE \), and are called derivative SSPC spectra. In \( dS(E)/dE \), steps in SSPC spectra at \( E_i \) are transformed into peaks at \( E_i \) (see Fig. 5.5 (a)). Derivative SSPC spectra can aid the de-convolution of spectra into its components \( i \).

It follows from Eq. 3.40 that the concentration of an individual trap \( N_{t,i} \) can be calculated via [9]

\[
N_{t,i} = 2N_D \frac{W^2}{W_0^2 - x_i^2} \frac{\Delta C_{\text{illumination},i}}{C_{\text{dark}}} \tag{5.24}
\]

for the case of a Schottky junction consisting of a metal and a \( n \)-type semiconductor and if optically-induced hole emission from the corresponding trap is neglected.

At low temperatures and high photon fluxes, \( W_0 \) can be assumed to be approximately equal to \( W \) (see Eq. 3.35). Hence, it is crucial to perform SSPC measurements at low temperatures. Notably, Eq. 5.24 is only valid if the overall trap concentration \( N_t \) is much smaller than \( N_D \) (see Sec. 6.3.1) [9].

5.3.2 Specifications of Setup used for Steady-State Photo-capacitance Measurements

One of the main activities in this PhD project was the development and implementation of an experimental setup capable of performing SSPC measurements at the beam line of a MeV ion implanter (on-line). The development and build-up was performed in close collaboration with the master student Vegard Rønning [296]. A schematic overview of the setup is shown in Fig. 5.6. For illumination, the laser-driven plasma light source EQ-77 from Energetiq is used [352]. The light source covers the spectral range from 190 nm to 2500 nm. Its main advantage is its comparatively high brightness and long life time. The white light
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Figure 5.6: **Experimental setup for SSPC measurements**: A monochromator (MC) utilizing diffraction gratings (RG) is used to spectrally disperse a white light source (LS) in order to obtain optical excitation at variable wavelength. The near-monochromatic light is steered towards the sample (SH) using parabolic mirrors (M1 and M2). Long-pass filters (FW) are used to suppress artifacts due to second order diffraction. The sample (SH) is placed inside a cryostat which is directly connected to the beamline of a MeV ion implanter (I), and hence SSPC measurements can be performed on-line as well as at low temperatures. The inset shows the contact layout: Semi-transparent contacts are electrically connected by wire-bonding to minimize shadowing for light and ions (see Fig. 5.1 (b)).

is spectrally dispersed using a diffraction grating monochromator (*Shamrock 500i* from *ANDOR*) [353]. It is possible to choose between a variety of gratings. Typically, a grating with a blaze at 400 nm and 1200 lines/mm was used for SSPC measurements. In some cases, a grating with a blaze at 1250 nm and 150 lines/mm was utilized. The combination of the grating used and the width of the exit slit of the monochromator determines the spectral resolution of the optical excitation (see Fig. 5.5 (b)). Typical measurements were performed with fully opened entrance and exit slits at 2.5 mm, resulting in a resolution of around 5 meV - 30 meV depending on the output wavelength. The near-monochromatic light is delivered to the sample using two off-axis parabolic mirrors from *Thorlabs* [354]. Parabolic mirrors have the advantage of very low spectral dispersion as compared to lenses [13]. It is possible to insert filters into the beam path before the near-monochromatic light reaches the sample. Appropriate low-pass filters are inserted in order to suppress second order diffraction being sent out from the monochromator [296]. The low-pass-filters had to be chosen according
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to the spectral range used for the measurement. The filters are placed inside a filter wheel from Thorlabs [355], which allows for the automated change of filters during SSPC measurements. Low-pass filters were purchased from Thorlabs [356] and Semrock [357]. The sample itself is placed inside a closed-cycle He cryostat directly connected to the beam line of a MeV ion implanter. This enables SSPC measurements at low temperatures as well as performing irradiation and implantation with ions at cryogenic temperatures (see Sec. 5.1.1). The light enters the cryostat through a sapphire window enabling even deep-ultraviolet light to pass through the window with minimal losses. Notably, the beam path is purged with N₂. A custom-made LabView [358] program is used to perform SSPC measurements.

The sample itself needs to be a rectifying junction in order to perform SSPC measurements. In case of a Schottky junction, semi-transparent metal contacts are needed, and their fabrication has been outlined in Sec. 5.1.2 and Fig. 5.1 (b) [296]. For SSPC measurements, the sample needs to be electrically connected to the measurement equipment, such as a capacitance meter. This was done by wire-bonding in order to minimize shadowing for light and ions.

An important characteristic of the system used for optical excitation is its power spectrum (see Fig. 5.7). The power output of the system for optical excitation was measured with a calibrated thermal power-meter placed at the sample position. The power spectrum is displayed as photon flux \( \Phi \), which can be calculated from the measured optical power \( P \) by:

\[
\Phi = \frac{P}{AE_{\text{Ph}}}. \tag{5.25}
\]

Here, \( A \) is the area of the power-meter. The influence of \( \Phi \) on SSPC spectra will be discussed in Sec. 6.3.2.

Figure 5.7: Measured spectral distribution of the optical output of the system for optical excitation used for SSPC measurements: The optical output is shown as photon flux \( \Phi \). Data are shown for the two different gratings usually used in this thesis. Measurements were performed with different low-pass filters inserted in the beam path, and their filter edges are stated in the legend.
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5.4 Optical Characterization

In this thesis, the optical absorption of semiconductors was determined from the measured optical transmittance. Two different methods for measuring optical transmittance were employed: UV/VIS spectroscopy (see Sec. 5.4.1) and Fourier-transform (infrared) spectroscopy (see Sec. 5.4.2).

The optical absorption of a material is described by the absorption coefficient $\alpha$ (see Sec. 2.1). The measured intensity $I_T$ of light transmitted through a sample with thickness $d$ is approximately related to $\alpha$ by

$$\alpha = -\frac{1}{d} \ln \left( \frac{I_T}{I_0 [1 - R]^2} \right)$$  \hspace{1cm} (5.26)

when taking multiple internal reflections into account (see Sec. A) [359, 360]. $I_0$ is the intensity of the incident light, and $R$ is the reflection coefficient. It is often of interest to obtain the spectral dependence of $\alpha$, i.e., the dependence of $\alpha$ on the photon energy of the incoming light. $I_0$ comprises the spectral characteristics of the light source and the optical response of the system for light delivery (lenses and/or mirrors) as well as the detection system.

The main focus of this thesis was the investigation of optical absorption due to localized vibrational modes associated with H-related defects [20] and optical absorption due to charge state transitions of defects [11, 27–29] as well as polarons [30–35]. For these investigations, it is particularly interesting to study how the optical absorption is influenced by temperature as well as the polarization of the incoming light. The sample temperature can be controlled by placing the samples inside a cryostat, while the polarization of the incident light is controlled by a polarization filter.

5.4.1 UV/VIS Spectroscopy

In UV/VIS spectroscopy, gratings are used to disperse a white light source into its spectral components. The near-monochromatic light is then directed towards the sample by means of mirrors and/or lenses. A measurement of $\alpha$ will be performed at each wavelength separately. $I_T$ is measured by placing the sample in the beam path, while $I_0$ is recorded without a sample in the beam path. Usually, an integrating sphere is used for collection of all transmitted light. Often, UV/VIS spectroscopy is performed in the electromagnetic spectrum covering the near-infrared up to the ultra-violet, and hence different gratings and/or photo-detectors need to be used during one scan.

5.4.2 Fourier-transform (Infrared) Spectroscopy

Fourier-transform (infrared) spectroscopy (FTIR) is often used to investigate optical absorption in the infrared part of the electromagnetic spectrum, and specifically optical absorption associated with localized vibrational modes and free charge carriers [20]. However, FTIR can also be used in the visible and
ultra-violet part of the electromagnetic spectrum. FTIR uses a measurement configuration resembling a Michelson interferometer. The white light source is not spectrally dispersed, but divided into two sub beams by a beam splitter. The two light beams travel along two different paths, exhibiting a path difference \( \Delta x \). The beams are reunited, and the resulting beam is steered towards the sample by mirrors. When the beams reunite, interference will occur. Subsequently, \( I_T \) is measured with a photo-detector. Measuring \( I_0 \) is done similarly, but without a sample inside the beam path. During the measurement \( \Delta x \) is changed, and a so-called interferogram (\( I_T \) vs. \( \Delta x \) or \( I_0 \) vs. \( \Delta x \)) is recorded. By performing an inverse Fourier-transform, the spectral representation of \( I_T \) and \( I_0 \) can be calculated, and hence the name Fourier-transform (infrared) spectroscopy. Notably, the resolution of a FTIR measurement will depend on the maximum \( \Delta x \) used for the measurement. In contrast to UV/VIS spectroscopy, the sample is illuminated with the full spectrum of the white light source at all times.

5.5 Compositional Characterization

Secondary ion mass spectrometry (SIMS) was conducted in order to analyze the composition of semiconducting oxides\[361, 362\]. Particularly, SIMS was used to determine the concentration of residual impurities. Depending on the element, SIMS can detect concentrations as low as parts-per-million to parts-per-billion. In SIMS, an ion beam is directed towards the sample surface typically exhibiting a kinetic energy in the order of a few keV. Often, either \( \text{O}_2^+ \) or \( \text{Cs}^+ \) ions are used. The incident ions will sputter atoms from the sample surface and ionize a fraction of them. The sputtered ions which become ionized are accelerated towards a mass spectrometer. A mass-filtering is applied using electrical and magnetic fields to select only ions with a specific mass-to-charge ratio. Subsequently, the selected ions are counted by a detector. The count of detected ions is proportional to their concentration in the sample. It is possible to obtain absolute concentrations for residual impurities in the investigated samples by performing a calibration. The material which is being investigated for its residual impurity content can be implanted (see Sec. 5.1.1) with a known amount of the impurity of interest to serve as a calibration standard. Furthermore, SIMS can be used to obtain the spatial distribution of residual impurities in materials. Here, depth profiles for residual impurities were of particular interest. For this purpose, the number of detected impurities is continuously recorded while the ion beam sputters into the sample. After the measurement, the depth of the resulting sputter crater can be measured to translate sputtering time into depth, and one can obtain a depth profile of the measured impurity concentration.

5.6 Computational Methods

First-principles calculations based on density-functional theory (DFT) are routinely used to predict material properties, including the properties of defects in semiconductors\[10, 363–365\]. In DFT, electron densities are used to describe
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electronic systems\[366\]. Using some approximations, this approach can be used to
generally describe the ground-state energy of materials using the so-called
Kohn-Sham equations\[367\]. To solve the Kohn-Sham equations, one needs
to approximate the exchange-correlation potential\[367\]. For calculations used
in this thesis, the PBEsol functional\[368\] as well as Heyd-Scuseria-Ernzerhof
screened hybrid-functional (HSE)\[12\] as implemented in the VASP code\[369\]
were used to approximate the exchange-correlation potential.

First-principles calculations based on DFT can be used to obtain the formation
energy $E_{f}^{q}$ of a charged defect $X_{S}^{q}$ in a material by computing\[370–372\]:

$$E_{f}^{q} = E_{\text{tot}}[X_{S}^{q}] - E_{\text{tot}}[\text{bulk}] - \sum_{i} n_{i}\mu_{i} + qE_{F} + E_{\text{corr}}.$$ \hspace{1cm} (5.27)

$E_{\text{tot}}[\text{bulk}]$ is the ground state energy of the pristine material, while $E_{\text{tot}}[X_{S}^{q}]$ is
the ground state energy of the material with $X_{S}^{q}$ being present. $E_{\text{tot}}[X_{S}^{q}]$ can be
obtained from calculations using a so-called super cell including one defect in
a pristine lattice consisting of many host atoms. $\sum_{i} n_{i}\mu_{i}$ expresses the energy
contribution when adding or removing atoms to or from the lattice when forming
the defect, whereby $n_{i}$ is the number of atoms of species $i$ which have been added
or removed and $\mu_{i}$ is the corresponding chemical potential of the reservoir. Thus,
defect calculations will depend on the conditions assumed during formation of
defects. For semiconducting oxides, it is relevant for defect formation whether a
material experiences, for example, O-rich or O-poor conditions. The term $qE_{F}$ is
related to the availability of electrons for the formation of charged defects. $E_{\text{corr}}$
is a correction term. For example, corrections need to be performed because finite
super cells are used for the calculation of $E_{\text{tot}}[X_{S}^{q}]$\[373–375\]. From Eq. 5.27, it
is possible to obtain thermodynamic charge state transition levels\[370\] as
well as vertical transition levels associated with optical absorption\[10, 375\] (see
Sec. 2.3.1). Furthermore, effective one-dimensional configuration coordinate
diagrams (see Fig. 2.5 (b)) can be computed\[11, 374\] which can be used to
obtain, for example, defect-related optical absorption spectra\[11\].

In this thesis, first-principles calculations based on DFT were also used to
calculate migration barriers associated with defects. Starting from Eq. 5.27, this
can be achieved by, for example, using the climbing nudged elastic band method
(cNEB)\[376\].
Chapter 6
Results and Discussion

In this chapter, the results obtained during this PhD project are summarized and discussed, whereby the focus of the investigations lay on studying defects in the two semiconducting oxides $\beta$-Ga$_2$O$_3$ and r-TiO$_2$. Both materials are wide bandgap semiconductors relevant for a host of applications, including applications in energy-conversion, -storage and -harvesting. Defects influence the electrical and optical properties of $\beta$-Ga$_2$O$_3$ as well as r-TiO$_2$ in a significant way, and need to be understood to improve the materials for their respective applications. To a large extent, defects were studied in these materials by probing defect-related charge state transition levels.

The results concerning $\beta$-Ga$_2$O$_3$ (see Sec. 6.1) and r-TiO$_2$ (see Sec. 6.2) will be presented in separate sections. Additionally, results obtained concerning SSPC measurements as a technique, and specifically its analysis will be presented in Sec. 6.3, whereby $\beta$-Ga$_2$O$_3$ served as a test case.

6.1 Results on Monoclinic Gallium Sesquioxide

One of the main objectives of studying defects in $\beta$-Ga$_2$O$_3$ was the assignment of structural and chemical origins to defect-related charge state transition levels. Techniques, such as DLTS and SSPC measurements were extensively used to identify charge state transition levels in $\beta$-Ga$_2$O$_3$. Typically, results from DLTS or SSPC measurements were correlated with first-principles calculations or other experimental results to propose origins for the charge state transition levels detected by DLTS or SSPC measurements. Rectifying junctions are needed to perform DLTS as well as SSPC measurements, and it is paramount to ensure that the junction characteristics are suitable for performing space-charge spectroscopy (see Sec. 5.2.3.1). Hence, in Sec. 6.1.1, the suitability of Ni/$\beta$-Ga$_2$O$_3$ and Pt/$\beta$-Ga$_2$O$_3$ Schottky junctions [133] for DLTS and SSPC measurements will be discussed. Using (suitable) $\beta$-Ga$_2$O$_3$-based Schottky junctions, impurity-related (see Sec. 6.1.2.1) as well as intrinsic (see Sec. 6.1.2.2) defects in $\beta$-Ga$_2$O$_3$ were studied.

6.1.1 Rectifying Junctions involving Monoclinic Gallium Sesquioxide

For this PhD project, electrical junctions between Ni or Pt, $\beta$-Ga$_2$O$_3$ and Ti/Al or InGa were used to study defects in $\beta$-Ga$_2$O$_3$. Ni and Pt form a Schottky junction with $\beta$-Ga$_2$O$_3$ [100, 133, 377], while Ti/Al and InGa are believed to form an Ohmic contact with $\beta$-Ga$_2$O$_3$ [5, 71, 100, 102, 103]. Generally, Ni/$\beta$-Ga$_2$O$_3$ or Pt/$\beta$-Ga$_2$O$_3$ junctions comprising either HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films with
6. Results and Discussion

![Figure 6.1](image)

**Figure 6.1: Results of IV and IS measurements on Ni/β-Ga$_2$O$_3$/Ti/Al Schottky junctions:** (a) IV curves recorded at room temperature on Ni/β-Ga$_2$O$_3$/Ti/Al Schottky junctions comprising EFG-grown and HVPE-grown β-Ga$_2$O$_3$. The corresponding surface orientation is stated in the plot. The recorded data were modeled according to Eq. 3.21, and the models are shown with solid lines. (b) IV curves measured at different temperatures for a Ni/β-Ga$_2$O$_3$/Ti/Al Schottky junction comprising an EFG-grown β-Ga$_2$O$_3$ crystal with a (010) surface orientation. The solid lines are simulated IV curves based on Eq. 3.21. (c) and (d) Results of IS recorded on the same junction and for the same temperatures as shown in (b). The results are displayed as (c) Nyquist and (d) phase plot (see Sec. 5.2.3.1). The measured data were compared to simulations based on the equivalent circuit shown in the inset of (c). The simulated curves are shown as solid lines.

A surface orientation of (001) grown on bulk β-Ga$_2$O$_3$, EFG-grown β-Ga$_2$O$_3$ crystals with a (-201) surface orientation or CZ-grown β-Ga$_2$O$_3$ crystals with a (100) surface orientation, all display good IV (see Fig. 6.1 (a)) as well as impedance characteristics (not shown) regardless of the Ohmic (back) contact used [100, 133]. Notably, for junctions with HVPE-grown β-Ga$_2$O$_3$ thin-films, the Ti/Al contact is deposited onto the substrate. In contrast, Schottky junctions comprising EFG-grown β-Ga$_2$O$_3$ crystals with a (010) surface orientation usually display high series resistance as measured by IV (see Fig. 6.1 (a)). IV curves recorded at different temperatures unveil a pronounced temperature-dependence of the series resistance (see Fig. 6.1 (b)). Indeed, temperature-dependent measurements of the corresponding impedance spectra shown in Fig. 6.1 (c) and (d) unveil that the series resistance seen in IV measurements is connected to the presence of two RC-circuits in the equivalent circuit of Ni/β-Ga$_2$O$_3$ Schottky junctions comprising EFG-grown β-Ga$_2$O$_3$ crystals with a (010) surface orientation. Indeed, one of the RC-circuits displays a similar resistance value.
Results on Monoclinic Gallium Sesquioxide

as determined from IV curves for the overall series resistance of the junction. Tentatively, the two RC-circuits can be assigned to the front and back contact, both displaying rectifying behavior [102, 103, 313]. For forward bias conditions, the back contact is blocking the current, and hence the overall current flow is determined by the corresponding resistance of the RC-circuit representing the back contact.

Thus, it appears that the formation of Ohmic contacts on β-Ga₂O₃ displaying (010) surfaces is more challenging compared to β-Ga₂O₃ displaying (001), (100) or (-201) surfaces. It has been proposed that heat-treatments of Ti/β-Ga₂O₃ junctions can improve their Ohmic behavior [71, 102, 103]. However, such heat-treatments have not been investigated in this thesis. The non-ideal behavior of Ni/β-Ga₂O₃ junctions when using particular surface orientations of β-Ga₂O₃ underlines the necessity to verify the suitability of rectifying junctions for space-charge spectroscopy.

In Paper I, Ni/β-Ga₂O₃ and Pt/β-Ga₂O₃ Schottky junctions comprising either HVPE-grown β-Ga₂O₃ thin-films with a (001) surface, EFG-grown β-Ga₂O₃ with a (-201) surface or CZ-grown β-Ga₂O₃ with a (100) surface were utilized. InGa and Ti/Al were used as Ohmic back contacts. In Paper II and III, semi-transparent Ni contacts were used to form Schottky contacts on HVPE-grown β-Ga₂O₃ thin-films with a surface orientation of (001) or EFG-grown β-Ga₂O₃ crystals with a surface orientation of (-201) which enable light to penetrate into the space-charge region. The corresponding semi-transparent contacts also display sufficiently good IV and impedance characteristics for space-charge spectroscopy (not shown). In Paper IV, Ni/β-Ga₂O₃ Schottky junctions comprising HVPE-grown β-Ga₂O₃ thin-films with a (001) surface were utilized.

6.1.2 Defects in Monoclinic Gallium Sesquioxide and their Charge State Transition Levels

6.1.2.1 Impurity-related Defects

A variety of charge state transition levels have been observed in β-Ga₂O₃ using DLTS and related techniques (see Sec. 4.1). Three defect levels labeled E₁, E₂ and E₃ are commonly observed in EFG- or CZ-grown β-Ga₂O₃ single crystals [99, 100]. Fig. 6.2 shows DLTS spectra recorded on two EFG-grown β-Ga₂O₃ crystals, displaying the DLTS signatures for E₁, E₂ and E₃. Interestingly, none of these signatures responds to irradiation [99], and hence impurities are likely to be involved. Indeed, E₂ was previously shown to be related to FeGa [99]. In Paper I, this previous assignment was further supported by demonstrating that E₂, indeed, consists of at least two defect signatures labeled E₂a (Eₐ = 0.66 eV, \( \sigma_{th,n,\infty} = 4 \times 10^{-16} \text{ cm}^2 \)) and E₂b (Eₐ = 0.73 eV, \( \sigma_{th,n,\infty} = 1 \times 10^{-15} \text{ cm}^2 \)). The concentrations of E₂b as well as E₂a correlate with the Fe concentration determined by SIMS for the investigated samples. Taking previous results from first-principles calculations into account [99], E₂a is tentatively assigned to Fe²⁺/⁰ (FeGa is Fe substituting Ga on a tetrahedral Ga site), while E₂b is proposed
6. Results and Discussion

a) Filter: GS4

\[ \text{en}_{\text{max}} (\text{s}^{-1}): \]

- 5.27
- 20.28
- 70.67

Data

Model

E_{2a}

E_{2b}

E_{3}

b)EFG (-201)

E_{3}

E_{2b}

E_{2a}

E_{1}

\times 50

EFG (-201)

Figure 6.2: Deep-level defects in as-grown $\beta$-Ga$_2$O$_3$ bulk crystals: DLTS spectra recorded on two different as-grown pieces of EFG-grown $\beta$-Ga$_2$O$_3$ single crystals. The pieces originate from two different wafers. Both $\beta$-Ga$_2$O$_3$ crystals contained defects giving rise to the defect levels $E_{2a}$, $E_{2b}$ and $E_{3}$, while the sample for which data are shown in (b) also contained $E_{1}$. The DLTS spectra were constructed with a GS4 filter, and a model curve (solid lines) was simulated to obtain parameters characterizing the defect levels. (a) is reprinted from Paper I with permission from AIP Publishing.

to be related to $\text{Fe}^{0/0}_{\text{GaII}}$ ($\text{Fe}_{\text{GaII}}$ is Fe substituting Ga on an octahedral Ga site). Fig. 6.3 (a) shows $[E_{2a}]$ plotted against $[E_{2b}]$ (Here, square brackets denote concentration). A correlation is found, whereby $[E_{2a}] = 0.2 [E_{2b}]$ is a good fit to the data. This finding further corroborates our assignment of $E_{2b}$ and $E_{2a}$ to $\text{Fe}_{\text{GaII}}$ and $\text{Fe}_{\text{Gal}}$, respectively, because a ratio of 1:5 for $[E_{2a}]:[E_{2b}]$ is expected from predicted formation energies for $\text{Fe}_{\text{Gal}}$ and $\text{Fe}_{\text{GaII}}$ [99]. Notably, a ratio of 1:5 for $[\text{Fe}_{\text{Gal}}]:[\text{Fe}_{\text{GaII}}]$ has also been found by an electron paramagnetic resonance study on melt-grown $\beta$-Ga$_2$O$_3$ [150].

No specific defect has previously been assigned to $E_{3}$ ($E_A = 0.95 \text{eV}$, $\sigma^{\text{th}}_{n,\infty} = 4 \times 10^{-14} \text{cm}^2$). In Paper I, we utilize calibrated SIMS measurements in conjunction with DLTS measurements, and find that the concentration of $E_{3}$ (determined from simulated conventional DLTS spectra by taking the $\lambda$-correction into account) correlates with the Ti concentration in the investigated samples (see Fig. 6.3 (b)). Notably, the relationship $[E_{3}] = [\text{Ti}]$ holds, implying that the defect giving rise to $E_{3}$ consists of one Ti atom and is the dominant Ti-related defect in melt-grown $\beta$-Ga$_2$O$_3$. First-principles calculations based on hybrid-functional indicate that $E_{3}$ can be assigned to $\text{Ti}^{0+/+}_{\text{GalII}}$ since the expected charge state transition level for $\text{Ti}^{0+/+}_{\text{GalII}}$ is close to the $E_A$ determined for $E_{3}$. Moreover, $\text{Ti}_{\text{GalII}}$ is found to have the lowest formation energy of a variety of simple Ti-related defects, including $\text{Ti}_{\text{Gal}}$. This finding is confirmed by previous electron paramagnetic resonance studies which found $\text{Ti}_{\text{GalII}}$ to be the dominant Ti-related defect in $\beta$-Ga$_2$O$_3$ [378–380]. Notably, HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films were also studied, and $E_{3}$ was not detected. Consequently, the detected Ti concentration in such samples can be regarded as the detection limit for Ti using SIMS.

The observation of charge state transition levels related to Ti and Fe within the band gap of $\beta$-Ga$_2$O$_3$ is of great relevance for applications. Both elements are already used in technological application of $\beta$-Ga$_2$O$_3$: Ti is used for Ohmic contacts [5, 71, 73, 102, 103, 133], while Fe is used to achieve semi-insulating
Figure 6.3: Impurity-related defects in $\beta$-$\text{Ga}_2\text{O}_3$: (a) Plot of $[E_{2a}]$ vs. $[E_{2b}]$ as determined from DLTS taking the $\lambda$-correction into account. Areas are shown, if the uncertainties for $[E_{2a}]$ and $[E_{2b}]$ are larger than the data points displayed. A linear relationship between $[E_{2a}]$ and $[E_{2b}]$ can be seen. As a guide, a line corresponding to $[E_{2a}] = 0.2[E_{2b}]$ is shown. The color code follows the legend shown in (b). (b) Relation between the titanium concentration obtained from calibrated SIMS measurements and the trap concentration related to $E_3$ determined by simulating conventional DLTS spectra and taking the $\lambda$-correction into account. Areas are shown, if the uncertainties for $[E_3]$ are larger than the data points displayed. The detection limit for [Ti] as measured by SIMS is estimated to be around $1 \times 10^{15}$ cm$^{-3}$. As a guide, a line corresponding to $[E_3] = [\text{Ti}]$ is shown. (b) is reprinted from Paper I with permission from AIP Publishing.

$\beta$-$\text{Ga}_2\text{O}_3$ needed for power electronic devices [5, 71]. Hence, both elements might diffuse into the active layer of devices during fabrication or operation, and their associated charge state transition levels might alter the device performance [98, 102, 103]. Indeed, this has been reported for the case of Fe$_{\text{Ga}II}$ [98].

6.1.2.2 Intrinsic Defects

In Sec. 5.3.2, an experimental setup for SSPC measurements connected to the beamline of a MeV ion implanter was presented. In Paper II, this setup was utilized to study primary intrinsic defects in HVPE-grown $\beta$-$\text{Ga}_2\text{O}_3$ thin-films by conducting He implantation at 120 K and subsequent characterization using SSPC measurements. The SSPC measurements were performed at 120 K. At 120 K, all primary intrinsic defects except for O$_i$ are expected to be immobile [52, 120], and it should be possible to detect their corresponding optical charge state transition levels using SSPC measurements.

Several defect-related optical charge state transition levels are already observed in as-received HVPE-grown $\beta$-$\text{Ga}_2\text{O}_3$ thin-films, and are labeled $T_2$ ($E_{\text{on}} = 1.7$ eV), $T_3$ ($E_{\text{on}} = 2.6$ eV), $T_5$ ($E_{\text{on}} = 3.7$ eV) and $T_6$ ($E_{\text{on}} = 4.2$ eV). $E_{\text{on}}$ is defined as the photon energy where a step in SSPC spectra can be seen, and hence $E_{\text{on}}$ is related to the optical charge state transition level of the corresponding defect. After He implantation at 120 K, two new levels appear: $T_1$ ($E_{\text{on}} = 1.3$ eV) and $T_3$ ($E_{\text{on}} = 1.9$ eV). In addition, $T_3$ and $T_6$ also respond to the He implantation. Derivative SSPC spectra reveal that $T_1$ and $T_6$ most likely consist of several defect levels. The typically detected defect concentration is in the range of
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![Graph](image)

**Figure 6.4:** Primary intrinsic defects in $\beta$-Ga$_2$O$_3$: (a) Results of SSPC measurements recorded on a HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film before and after subsequent implantations with He ions at 120 K. The SSPC measurements were also performed at 120 K. The results are displayed as derivative SSPC spectra (upper panel) and as conventional SSPC spectra (lower panel). The legend states the accumulated implantation fluence $\Phi_{\text{tot}}$ for the corresponding data set. The vertical bars indicate where computations based on hybrid-functionals predict the onset of optical absorption of the primary intrinsic defects to occur. (b) Plot of the effective trap concentration $N_{\text{eff},t}$ derived for the features labeled $T_3$, $T_4$ and $T_6$ in dependence of the accumulated He fluence $\Phi_{\text{tot}}$. $N_{\text{eff},t}$ was calculated for the case of $\Delta C_{\text{ill}/C_{\text{dark}}} \ll 0.5$ (see Sec. 5.3) and $\Delta C_{\text{ill}/C_{\text{dark}}} \approx 0.5$ (see Sec. 6.3.1). For $\Delta C_{\text{ill}/C_{\text{dark}}} \ll 0.5$, the corresponding data points cover values computed for the case of neglecting the $\lambda$-correction as well as for assuming a Franck-Condon shift $d_{\text{FC}}$ of 1 eV. The introduction rates $I_R$ were derived from a linear fit and are displayed in the plot. The figure is reprinted from Paper II with permission from APS Publishing.

$1 \times 10^{14}$ cm$^{-3}$ to $1 \times 10^{17}$ cm$^{-3}$. SSPC spectra before and after He implantation at 120 K are displayed in Fig. 6.4 (a). Notably, previous SSPC studies also reported on defect-related optical charge state transition levels with onsets at 2.2 eV, 3.2 eV and 4.4 eV in $\beta$-Ga$_2$O$_3$ [137, 147, 152]. $T_1$ is created upon He implantation, but was only detected in some samples subjected to He implantation. Furthermore, $T_1$ is only introduced in fairly low concentrations, and hence a defect complex, potentially involving an impurity, is proposed to be the defect giving rise to $T_1$. $T_2$ was only detected in some samples, and combined with a lack of response to irradiation/implantation, it is also tentatively assigned to an impurity. $T_5$ does not seem to respond to He implantation, and hence might be related to a residual impurity as well. $T_3$, $T_4$ as well as $T_6$ respond to He implantation at cryogenic temperatures.
Introduction rates (IR) were determined for these three levels using subsequent He implantations at 120K (see Fig. 6.4 (b)). The trap concentrations were calculated using the formulas discussed in Sec. 5.3 as well as an equation more suitable for large trap concentrations (see Sec. 6.3.1). The determined average IR are $3.3 \times 10^4 \text{cm}^{-1} - 6.3 \times 10^4 \text{cm}^{-1}$ ($T_3$), $7.5 \times 10^4 \text{cm}^{-1} - 1.2 \times 10^5 \text{cm}^{-1}$ ($T_4$) and $1.3 \times 10^5 \text{cm}^{-1} - 1.4 \times 10^5 \text{cm}^{-1}$ ($T_0$). From SRIM simulations (see Sec. 5.1.1), the expected IR for vacancy defects was determined to be around $1 \times 10^6 \text{cm}^{-1}$, and hence $T_3$, $T_4$ as well as $T_0$ display IR indicative for the generation of primary intrinsic defects.

Optical absorption cross sections for the primary intrinsic defects were calculated using configuration coordinate diagrams and the approach outlined in Ref. [11, 29] using first-principles calculations based on hybrid-functionals (see Sec. 2.3.3). From the calculated absorption cross sections, an interval was determined for the expected onset of defect-related optical absorption. This interval can be compared to the onsets seen in SSPC spectra (see Sec. 6.3.2 for a further development of this methodology). It was found that Ga$_i^{+/2}$ and/or V$_{\text{Ga}}^{-3/-2}$ are good candidates for the level $T_3$, while the different configurations of V$_O^{0/+}$ as well as V$_{\text{GaI}}^{-3/-2}$ are good candidates for $T_4$. Additionally, several further charge state transition levels associated with V$_{\text{Gal}}$ and V$_{\text{GaII}}$ may contribute to $T_3$. $T_0$ is likely to be related to defect complexes or charge state transitions of the primary intrinsic defects with higher optical transition energies.

The setup used for SSPC measurements allows also to study heat-treatments up to room temperature of samples implanted with He at cryogenic temperatures. These measurements reveal that the defect levels $T_3$ as well as $T_4$ decrease in concentration if samples are exposed to room temperature after He implantation at 120K, while $T_0$ increases in concentration for the same experimental conditions. These findings corroborate the earlier defect assignments. As shown in Paper II by calculating the migration barriers of intrinsic defects in $\beta$-Ga$_2$O$_3$, Ga$_i$ is not expected to be mobile at 120K, but should be mobile at or below room temperature, and hence annihilation reactions between the different configurations of V$_{\text{Ga}}$ and Ga$_i$ are likely to occur. Such reactions could explain the decrease in the concentrations associated with $T_3$ and $T_4$. However, several parallel processes can be expected to play a role, for example, the transformation of V$_{\text{GaI}}$ and V$_{\text{GaII}}$ into structurally different, but more favourable, V$_{\text{Ga}}$ configurations [114] as well as the formation of V$_{\text{Ga}}$-V$_O$ complexes [52].

DLTS measurements on as-received HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films usually reveal the presence of the defect level labeled as $E_2$. After He implantation at 120K, several new defect levels are observed in DLTS measurements: $E_{\text{He,1}}^*$ ($E_A = 200 \text{meV}$, $\sigma_{n,\infty}^{n}= 1 \times 10^{-18} \text{cm}^2$), $E_{\text{He,2}}^*$ ($E_A = 400 \text{meV}$, $\sigma_{n,\infty}^{n}= 1 \times 10^{-15} \text{cm}^2$), $E_{\text{He,3}}^*$ ($E_A = 550 \text{meV}$, $\sigma_{n,\infty}^{n}= 1 \times 10^{-14} \text{cm}^2$) and $E_{\text{He,4}}^*$ ($E_A = 600 \text{meV}$, $\sigma_{n,\infty}^{n}= 5 \times 10^{-14} \text{cm}^2$) (see Fig. 6.5 (a)). Notably, the trap concentrations for all levels detected in DLTS measurements are significantly lower than the trap concentrations detected in SSPC measurements for the implantation-induced levels. Hence, defect complexes are likely to be involved in the defects giving rise to $E_{\text{He,1}}^*$ - $E_{\text{He,4}}^*$. After exposing the sample to room temperature, all
Figure 6.5: Dynamics of implantation-induced defects in $\beta$-Ga$_2$O$_3$: (a) DLTS spectra recorded on a HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film before and after He implantation at 120 K as well as after subsequent exposure to room temperature. The DLTS spectra were constructed using a lock-in filter. Several defect levels appear after He implantation, and are labeled. (b) DLTS spectrum recorded on the same sample as shown in (a) after the sample was subsequently exposed to 700 K. The DLTS spectrum was constructed using a lock-in filter. The observed defect levels are labeled.

levels except for $E_{\text{He,1}}^*$ decrease significantly in concentration (see Fig. 6.5 (a)). Hence, passivation and/or migration of the defects being associated with $E_{\text{He,2}}^*$ - $E_{\text{He,4}}^*$ already occurs at very low temperatures. After exposing the same sample to 700 K under applied reverse bias, additional DLTS measurements in a broader temperature range were performed (see Fig. 6.5 (b)). Here, defect levels commonly observed after irradiation and labeled $E_2^*$ as well as $E_4^*$ are observed [52, 99]. Notably, $E_2^*$ was not present prior to the heat-treatment at 700 K [52]. Additionally, a number of defect levels labeled collectively as $E_{\text{He,5}}^*$ are observed after exposure to 700 K which have not been reported in proton-irradiated HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films previously [52]. Thus, larger complexes could be the origin of these levels. Notably, the defect level $E_{\text{He,1}}^*$ is not detected after exposing the sample to 700 K.

In Paper IV, the formation of $E_2^*$ ($E_A = 0.74$ eV, $\sigma_{n,\infty}^{\text{th}} = 1 \times 10^{-16}$ cm$^2$) was investigated in more detail. For this, HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films were subjected to He, H and He+H implantations at room temperature. Importantly, the studies were performed on Schottky junctions involving HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films. After ion implantation, subsequent heat-treatments with and without applied reverse bias were performed. By applying a reverse bias voltage to a Schottky junction, it is possible to change the fermi-level position in the space-charge region. The results obtained for HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films implanted with He are shown in Fig. 6.6.

After ion implantation, $E_{2}^*$ is either not present or present in fairly low concentrations. Heat-treating the implanted HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films under applied reverse bias voltage leads to a significant increase in the concentration of $E_{2}^*$. When implanted HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films are
Results on Monoclinic Gallium Sesquioxide

exposed to elevated temperatures without applying a reverse bias voltage, the concentration related to $E_2^*$ is decreased or not increased. Subsequent heat-treatments under reverse bias voltage can be used to increase the concentration associated with $E_2^*$. Thus, heat-treatments with and without applying a reverse bias voltage can be used to control the formation of $E_2^*$. Notably, no changes in $E_2^*$ are seen if the samples are exposed to temperatures below 500 K regardless if a reverse bias voltage is applied or not. When performing heat-treatments without an applied reverse bias voltage, the decrease in the concentration associated with $E_2^*$ is more pronounced in the presence of H, i.e., for H or H+He implantation. Moreover, it was found that $E_2^*$ is only introduced during heat-treatments under applied reverse bias voltage within the corresponding space-charge region. Furthermore, larger bias voltages applied in reverse bias direction are associated with a higher concentration of introduced $E_2^*$. Using He+H implanted HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films, it was possible to deduce an activation energy between 1.0 eV and 1.3 eV for the thermally-activated introduction of $E_2^*$ when heat-treating samples under an applied reverse bias voltage.

Tentatively, our observations can be explained by $E_2^*$ being related to a defect complex which exhibits different configurations [297, 298]. Applying a bias voltage to a Schottky junction will lead to an altered fermi-level position in the space-charge region, and thus the formation energy of defects will be changed. It is proposed that the defect configuration giving rise to $E_2^*$ is more favorable at lower fermi-level positions, i.e., when $E_F$ is further away from $E_C$. At fermi-level positions closer to $E_C$ found when performing heat-treatments without an applied reverse bias voltage, a defect configuration is most stable which does not exhibit a charge state transition level accessible by the DLTS measurements performed here. H is proposed to form a complex with the defect configuration most stable at fermi-level positions close to $E_C$ which is energetically more favorable, and thus leads to a more pronounced suppression of the defect associated with $E_2^*$. Di-vacancy complexes ($V_{\text{Ga}}$-$V_O$) are proposed to be possible candidates for explaining the observations with respect to the formation of $E_2^*$. Indeed, first-principles calculations exploring the formation energies of all possible configurations for $V_{\text{Ga}}$-$V_O$ can be used to corroborate or falsify this hypothesis.

The results of DLTS and SSPC measurements presented here clearly show that defects related to intrinsic defects give rise to a number of charge state transition levels inside the band gap of $\beta$-Ga$_2$O$_3$. Notably, the primary intrinsic defects are associated with deep levels in $\beta$-Ga$_2$O$_3$. Migration of intrinsic defects as well as the formation of complexes involving intrinsic defects can easily occur already at fairly low temperatures in $\beta$-Ga$_2$O$_3$, and hence such processes may be important for technological applications of $\beta$-Ga$_2$O$_3$. Indeed, it is common to use Si implantation to locally form highly-conductive $\beta$-Ga$_2$O$_3$ to facilitate contact formation with Ti [71, 97, 101]. Upon Si implantation, one can expect the generation of intrinsic defects which may subsequently diffuse into the active layer of devices, and possibly form complexes with defects present in this layer. Moreover, it was shown that the fermi-level position can be decisive in the formation of defect complexes involving intrinsic defects, and particularly that the competition between different defect configurations is of importance.
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Figure 6.6: Formation of \( E^*_2 \) in \( \beta\text{-Ga}_2\text{O}_3 \): DLTS spectra recorded on a HVPE-grown \( \beta\text{-Ga}_2\text{O}_3 \) thin-film after He-implantation at room temperature using an energy of 500 keV and a He fluence of \( 2.5 \times 10^{10} \text{ cm}^{-2} \). Results are shown for two different Schottky barrier diodes located on the same HVPE-grown \( \beta\text{-Ga}_2\text{O}_3 \) thin-film. The diodes were subjected to a different order of heat-treatments as stated in (a) and (b), where roman letters indicate the order of the heat-treatments. Simulated DLTS spectra are shown with solid lines. The figure is reprinted from Paper IV with permission from IOP Publishing.

This finding is particularly important because the fermi-level position found in devices for power electronics will differ from the equilibrium fermi-level position due to band-bending. Specifically, the formation of \( E^*_2 \) was found to strongly depend on the fermi-level position. Interestingly, \( E^*_2 \) has been shown to influence the performance of \( \beta\text{-Ga}_2\text{O}_3 \)-based devices [98]. The presence of H was shown to suppress the formation of \( E^*_2 \), and could be of technological interest for passivating \( E^*_2 \) as well as other detrimental defects in \( \beta\text{-Ga}_2\text{O}_3 \).

6.2 Results on Rutile Titanium Dioxide

Defects play a significant role in applications r-TiO\(_2\) is relevant for. For example, r-TiO\(_2\) has shown promise for photo-catalytic applications, and defects have the potential to spectrally extend the optical absorption of the material as well as improve the properties of r-TiO\(_2\) as a catalyst by enhancing the charge transfer at the surface of r-TiO\(_2\). Here, the optical absorption related to defects as well as their charge state transition levels were investigated. In the investigation of defect-related charge state transition levels, space-charge spectroscopy was utilized. Thus, the fabrication of Schottky junctions comprising r-TiO\(_2\) suitable for space-charge spectroscopy needed to be achieved. First, the findings regarding electrical junctions between Pd, Pt, Ni or Al and r-TiO\(_2\) will be presented. Second, the results concerning defects in r-TiO\(_2\) will be discussed.
Results on Rutile Titanium Dioxide

Figure 6.7: Results of IS on two different Pd/r-TiO$_2$/Ti/Al junctions: The corresponding r-TiO$_2$ crystals were both heat-treated in H$_2$ gas prior to junction fabrication. (a) and (b) show Nyquist plots, while (c) and (d) display phase plots (see Sec. 5.2.3.1). In (a), only the part of the plot corresponding to high $f_{\text{probe}}$ is shown for clarity. Results are displayed for four different $V_{\text{ext}}$ as stated in (a). Data are shown as points, while models are shown as solid lines. The models were simulated using the equivalent circuits shown as insets in the plots, whereby the capacitive elements are constant-phase elements.

6.2.1 Electrical Junctions between Rutile Titanium Dioxide and Pd, Pt, Ni as well as Al

In Paper V, electrical junctions between r-TiO$_2$ and Pd, Pt, Ni as well as Al were investigated. Conductive $n$-type r-TiO$_2$ crystals were employed using r-TiO$_2$:Nb and heat-treated r-TiO$_2$ (see Sec. 6.2.2.1 for further details regarding the doping through heat-treatments). It was shown that Al forms an Ohmic contact with r-TiO$_2$, while Ni, Pd and Pt form Schottky contacts with r-TiO$_2$. The best obtained rectification was eight orders of magnitude when comparing the current at $-4$ V and $4$ V. However, different Schottky barrier diodes fabricated on the same r-TiO$_2$ sample displayed very different electrical characteristics, i.e., rectifications. This observation was generally made for all investigated r-TiO$_2$ crystals regardless of the heat-treatment or dopant species. This suggests a common origin for the observed spread in electrical characteristics. It has been shown in the past that a hydroxil layer can readily form at the r-TiO$_2$ surface, which might influence the electrical characteristics of r-TiO$_2$-based Schottky diodes [256]. However, etching r-TiO$_2$ crystals in HF or H$_2$O$_2$ prior to metal deposition had no influence on the observed results. From CV measurements, the built-in voltage of Pd/r-TiO$_2$ Schottky barrier diodes was estimated to be in the range of 1.2 V to 1.9 V, i.e., similar to what has been observed for Pt/r-TiO$_2$.
junctions previously [287]. The rectification of Pd/r-TiO₂ degrades over time, usually over the course of a few weeks. The degradation is mainly caused by an increase in reverse bias current, while the series resistance does not change significantly, suggesting no change in, for example, the donor concentration (see Sec. 6.2.2.1). Notably, it was shown that the rectification of Pd/r-TiO₂ Schottky barrier diodes can be somewhat restored when polishing-off and redepositing the Pd pads. This observation implies that a surface reaction is involved in the observed degradation. It has been reported previously that a reaction between H and Pd does change the electrical characteristics of Pd/r-TiO₂ Schottky barrier diodes [197, 198, 284]. However, the degradation of Pd/-TiO₂ Schottky barrier diodes was not affected by surface treatments with HF and/or H₂O₂ prior to metal deposition.

Schottky junctions between Pd and r-TiO₂ with either Ti/Al or InGa as Ohmic (back) contacts were used in Paper VI to study electrically-active defects in r-TiO₂ using space-charge spectroscopy, such as DLTS and TAS (see Sec. 6.2.2). However, it proved difficult to reproducibly fabricate Schottky junctions between Pd and r-TiO₂ with sufficiently good electrical characteristic for space-charge spectroscopy. Hence, it was necessary to investigate the circuit properties prior to performing space-charge spectroscopy. For this, impedance spectroscopy was used (see Sec. 5.2.3.1). Fig. 6.7 displays Nyquist and phase plots recorded on a Schottky barrier diode suitable (Sample B), and unsuitable (Sample A) for space-charge spectroscopy. Both junctions displayed a rectification of several orders of magnitude in IV measurements (not shown). The impedance of both samples was modeled using circuits consisting of resistances (R) and constant-phase elements (CPE). The impedance of Sample B could be modeled sufficiently well with a circuit comprising a series resistance and one RCPE-element. Sample A could not be modeled with such a circuit, but a second RCPE-element had to be included for an adequate fit to the experimental data. Notably, for sample A, both RCPE-elements influence the impedance measured at high fₚrobe, and hence will affect DLTS and TAS measurements.

6.2.2 Defects in Rutile Titanium Dioxide and their Charge State Transition Levels

In this thesis, the properties of donors, deep-level defects as well as the optical absorption related to defects in n-type r-TiO₂ were studied. Particularly, the influence of heat-treatments in different atmospheres was investigated. Such investigations can be used to gauge, for example, the influence of H on the defect formation.

6.2.2.1 Donor Defects

It is possible to obtain conductive n-type r-TiO₂ by performing heat-treatments in H₂ gas (H), forming gas (mixture of H₂ gas and N₂ gas) flow (FG) or N₂ gas flow (N) using semi-insulating r-TiO₂ single crystals. All heat-treatments can be regarded as reducing. Additionally, one can expect the incorporation of H
Results on Rutile Titanium Dioxide

when heat-treatments are performed in H-containing atmospheres (FG and H). However, there has been a long-standing debate if nominally H-free atmospheres are indeed H-free [125]. In Paper V, it was found that conductive $n$-type r-TiO$_2$ crystals are particularly suitable for the formation of Schottky junctions with Pd (see Sec. 6.2.1). The conductivity of the heat-treated crystals is around $1 \times 10^{-1} \Omega^{-1} \text{m}^{-1} - 10 \Omega^{-1} \text{m}^{-1}$ as determined in Paper VII. In Paper V and VI, typical $N_D$ of around $1 \times 10^{16} \text{cm}^{-3}$ to $1 \times 10^{18} \text{cm}^{-3}$ were determined by CV measurements.

In Paper VII, it was found that the conductivity of hydrogenated r-TiO$_2$ is proportional to the concentration of $\text{H}_{i}$, and thus $\text{H}_{i}$ is likely to be the main donor in hydrogenated r-TiO$_2$. This finding is corroborated by previous studies identifying $\text{H}_{i}$ as a shallow donor in r-TiO$_2$ [237, 240, 261].

In Paper VI, (shallow) donor levels introduced by the heat-treatments were studied further. TAS measurements were performed which reveal an incomplete carrier freeze-out, even at temperatures as low as 28 K, regardless of the specific heat-treatment performed. This indicates that the main donor(s) responsible for the conductivity in the heat-treated r-TiO$_2$ single crystals are very shallow, and their ionization energy can be estimated to be lower than 25 meV. This is also supported by measurements of optical absorption performed in Paper VII, indicating the presence of polarons at temperatures as low as 5 K.

There are several other slightly deeper donors present in heat-treated r-TiO$_2$ with activation energies between 35 meV to 320 meV below $E_C$ as observed by TAS (see Fig. 6.8 (a)). The donor levels are summarized in Paper VI. Some of these donor levels may be connected to residual impurities. Using SIMS, Fe, Cr, Al, Si and Li have been identified as residual impurities, among which Li has been suggested to give rise to a shallow donor with an ionization energy of 30 meV [178], while 2Al$_{\text{Tl}}$-V$_{\text{O}}$ has been linked to a donor state at 50 meV below $E_C$ [178, 269]. Li as well as 2Al$_{\text{Tl}}$-V$_{\text{O}}$ may be good candidates for some of the observed donor states. Several of the intrinsic defects are also predicted to exhibit relatively shallow donor levels, especially V$_{\text{O}}$ and Ti$_{i}$ [251, 381].

It is challenging to confirm if some of the donor levels seen in samples subjected to different heat-treatments have, indeed, the same origin. Some of the observed levels exhibit similar energy level positions, for example, $D_{2,N}$, $D_{2,\text{FG}}$ and $D_{1,\text{H}}$ as well as $D_{3,N}$ and $D_{3,\text{FG}}$, indicating a common origin. The labeling is according to Paper VI (see Fig. 6.8 (a)). Furthermore, a deep donor at around 200 meV - 320 meV below $E_C$ labeled $D_{4,\text{FG}}$ is observed only sporadically in r-TiO$_2$ heat-treated in forming gas flux. A similar donor state at around 170 meV - 190 meV labeled $D_{4,N}$ is sporadically detected in r-TiO$_2$ heat-treated in N$_2$ flux (see Fig. 6.8 (a)). $D_{4,\text{FG}}$ and $D_{4,N}$ might also have a common origin. The sporadic presence of a defect level is usually seen as indication that the corresponding level is related to a residual impurity. However, the formation of intrinsic defects is generally also very dependent on the presence of residual impurities [4, 172].

The observation that $\text{H}_{i}$ is the main donor in hydrogenated r-TiO$_2$ sheds some light on the long-standing debate regarding the main donors in r-TiO$_2$. Moreover, it was shown that the ionization energy of the main donors in heat-
6. Results and Discussion

Figure 6.8: Shallow and deep defect levels in reduced and hydrogenated r-\(\text{TiO}_2\): Results of (a) TAS and (b) DLTS measurements performed on r-\(\text{TiO}_2\) heat-treated in forming gas and \(\text{N}_2\) flux. Steps in TAS spectra are indicative of the presence of a donor state. The detected donor states are marked with dots and labeled. The DLTS spectra were constructed with a lock-in filter. Peaks in DLTS spectra are indicative for the presence of a deep level. The defect levels detected are marked with dots and labeled. The figure is reprinted from Paper VI with permission from AIP Publishing.

Treated r-\(\text{TiO}_2\) are below 25 meV. The observation of multiple donors with substantial concentrations being present in r-\(\text{TiO}_2\) subjected to reducing and/or hydrogenating heat-treatments indicates the importance of shallow defect levels in such material. Notably, Nitta et al. found that the performance of \(n\)-type \(\text{TiO}_2\) as photo-catalyst is correlated with the energy distribution of shallow levels in the material [192, 382]. However, further research is required to unambiguously identify the defects responsible for the shallow levels.

6.2.2.2 Deep-Level Defects

In Paper VI, using DLTS, electron traps were also studied. Generally, defect levels with activation energies of around 50 meV to 630 meV were observed (see Fig. 6.8 (b)). Some defect levels are commonly observed in samples subjected to similar heat-treatments while other defect levels are only sporadically observed.
It is likely that some of the levels seen for different heat-treatments have indeed common origins: $E_{2,N}$ and $E_{2,FG}/E_{3,N}$, $E_{3,FG}$ and $E_{3,H}/E_{4,N}$, $E_{4,FG}$ and $E_{4,FG}/E_{7,FG}$ and $E_{5,H}$. The labeling is according to Paper VI. Notably, some levels, for example, $E_{2,FG}$, $E_{5,FG}$, $E_{6,FG}$ and $E_{6,N}$, are only detected in samples which were subjected to heat-treatments for long duration or comparatively high temperatures. This observation indicates a relation to intrinsic defects or impurities which diffuse into the $r$-TiO$_2$ crystals during annealing. The defect levels $E_{7,FG}$ and $E_{5,H}$ have been of particular interest in this work. It is suggested that both features have a common origin. The defect levels were not observed in samples heat-treated in N$_2$ flux as presented in Paper VI. However, in later heat-treatments in N$_2$ flux at similar temperatures, a similar defect level was indeed observed. Hence, $E_{7,FG}/E_{5,H}$ is most likely associated with an impurity displaying varying concentration across the $r$-TiO$_2$ crystals studied.

Our results show that there are several deep level defects present in reduced/hydrogenated $r$-TiO$_2$ crystals which can influence the charge carrier transport in $r$-TiO$_2$ as well as play a role in the charge transfer for catalysis. Importantly, space-charge spectroscopy has proven to be useful for studying the presence of deep-level defects, and thus can pave the way for identifying the chemical and structural origin of the observed defect levels.

Figure 6.9: Defect-related optical absorption in Nb-doped and heat-treated $r$-TiO$_2$: (a) Absorption spectra recorded on $r$-TiO$_2$ crystals subjected to different heat-treatments (see Sec. 6.2.2.1 and Nb-doped $r$-TiO$_2$ crystals. The absorption band in the near-infrared/visible part of the electromagnetic spectrum is shown. The absorption band consists of two features labeled as $\omega_1$ and $\omega_2$. (b) Temperature-dependence of the intensity related to $\omega_1$ and $\omega_2$. The data are represented as Arrhenius plots for a $r$-TiO$_2$ crystal heat-treated in H$_2$ gas and a Nb-doped $r$-TiO$_2$ crystal. The figure is reprinted from Paper VII with permission from APS Publishing.
6. Results and Discussion

6.2.2.3 Defect-related Optical Absorption

In Paper VII, the optical absorption of r-TiO$_2$ crystals was studied. Regardless of the doping procedure, conductive $n$-type r-TiO$_2$ crystals are typically of bluish color, exhibiting an absorption band in the visible and near-infrared region of the electromagnetic spectrum. The corresponding absorption band was found to consist of at least two features labeled $\omega_1$ and $\omega_2$ with peak positions at around 3100 cm$^{-1}$ and 6500 cm$^{-1}$, respectively, in heat-treated r-TiO$_2$ crystals (see Fig. 6.9 (a)). For Nb-doped r-TiO$_2$ crystals, the same overall spectral shape for the absorption band was unveiled, while $\omega_1$ and $\omega_2$ were found to be located closer to 3700 cm$^{-1}$ and 7500 cm$^{-1}$, respectively. The intensities related to $\omega_1$ and $\omega_2$ correlate with the electrical conductivity of the heat-treated r-TiO$_2$ crystals, suggesting a relation to polarons [254, 383]. Moreover, the intensities associated with $\omega_1$ and $\omega_2$ exhibit a thermally-activated behavior in all investigated samples (see Fig. 6.9 (a)). Notably, the corresponding activation energy and onset temperature for thermal activation depend on the main donor (see Fig. 6.9 (b)). Higher activation energies as well as onset temperatures for the thermal activation are found for Nb-doped r-TiO$_2$ crystals compared to heat-treated r-TiO$_2$ crystals. Evidence was found that the thermal activation of $\omega_1$ and $\omega_2$ is related to the re-distribution of polarons in the lattice [238]. This suggests that the dynamics of electrons in r-TiO$_2$ is influenced by the dopant species.

Generally, it is found that conductive $n$-type r-TiO$_2$ performs better in photocatalysis which is often explained by its more pronounced optical absorption in the near-infrared and visible part of the electromagnetic spectrum compared to pristine r-TiO$_2$ [201, 210, 211]. However, without knowledge about the origin of the absorption band, it is challenging to gauge its role for photo-catalysis. Our results show that the overall shape of the absorption band is independent of the specific donor, indicating that different doping strategies will lead to an extended optical absorption with similar characteristics. However, we find clear indications that the dynamics of electrons in r-TiO$_2$ strongly depend on the donor, suggesting that the nature of the dopant will influence charge carrier transport significantly.

6.3 Analysis of Steady-State Photo-Capacitance measurements

During this PhD project, an experimental setup for performing SSPC measurements was build (see Sec. 5.3) [296]. In order to utilize SSPC measurements for studying wide bad gap semiconductors, such as $\beta$-Ga$_2$O$_3$ and r-TiO$_2$, conceptual challenges needed to be overcome. In the following, work will be presented regarding the extraction of trap concentrations from SSPC spectra in the case of large overall trap concentrations (see Sec. 6.3.1) as well as a methodology developed for comparing recorded SSPC spectra to results from first-principles calculations (see Sec. 6.3.2).
6.3.1 Extracting Trap Concentrations from Steady-State Photo-Capacitance Measurements

In Sec. 5.3, a formula was presented which can be used to calculate the concentration of traps from their corresponding step in SSPC spectra (see Eq. 5.24) [9]. Eq. 5.24 only applies for low overall trap concentrations \( N_t \), and specifically if \( N_t \ll N_D \) is valid [9]. For large trap concentrations expressed by, for example, \( N_t \approx N_D \), a different approach has to be used to calculate the individual trap concentrations \( N_{t,i} \) from steps in SSPC spectra. Assuming the validity of the Schottky approximation, a scheme was developed in the Supplementary Materials of Paper II which can be used to calculate \( N_{t,i} \). Essentially, the capacitance of a junction under illumination is explicitly solved for the number of ionized donors and photo-ionized traps without utilization of a linear approximation. The main difference to Eq. 5.24 is that for \( N_t \approx N_D \) the overall photo-capacitance is not a linear function of the sum of individual trap concentrations \( N_{t,i} \).

6.3.2 Comparing Steady-State Photo-Capacitance Spectra to Results from First-principles Computations

![Figure 6.10: Comparing recorded SSPC spectra to simulated SSPC spectra:](image)

(a) Derivative SSPC spectra recorded accumulatively on a EFG-grown \( \beta\)-Ga\(_2\)O\(_3\) crystal using different \( t_{\text{illum}} \). The spectra were modeled with Eq. 6.1, and the models are shown in solid lines. A feature related to the spectral shape of \( \Phi \) is marked in grey. (b) Derivative SSPC spectra recorded accumulatively on a HVPE-grown \( \beta\)-Ga\(_2\)O\(_3\) thin-film with \( t_{\text{illum}} = 300 \) s. SSPC spectra were recorded before and after He-implantation at 120 K. Signatures seen in SSPC spectra are marked with arrows. For the SSPC spectra recorded after He-implantation at 120 K a model based on Eq. 6.1 is shown in solid lines assuming the presence of various primary intrinsic defects. The grey area marks the photon energy region where distortions of the spectra due to a change of low-pass filters can be seen. The figure is reprinted from Paper III with permission from IOP Publishing.

In Paper III, a methodology was developed to perform comparisons between recorded SSPC spectra \( S(E, t_{\text{illum}}) \) and results from first-principles calculations.
Equations were developed to simulate SSPC spectra taking the experimental conditions into account (see Sec. 5.3). Particularly, SSPC measurements can be performed accumulatively or non-accumulatively. The following expression was found for simulating accumulatively-recorded SSPC spectra:

\[
S_{\text{acc}}(E^k, t_{\text{illum}}) = S(E^{k-1}, t_{\text{illum}}) + \left[ N_{\text{tr}, \text{eff}}^{ss} \times \left( S(E^{k-1}, t_{\text{illum}}) \right) \right] \times \left[ 1 - \exp \left( -\Sigma_n \sigma_n \sigma_{n, \text{norm}}(E^k) \Phi(E^k) t_{\text{illum}} \right) \right].
\]

(6.1)

Here, \(E^k\) are the photon energies at which SSPC measurement are performed, and the SSPC measurements were performed in ascending order of \(E^k\). \(N_{\text{tr}, \text{eff}}^{ss}\) is the trap concentration measured under steady-state conditions, while \(\Phi(E)\) is the spectral photon flux determined for the optical excitation of the setup (see Sec. 5.3.2). \(\Sigma_n\) is the absolute value of the defect-related absorption cross-section, while \(\sigma_{n, \text{norm}}\) is the normalized defect-related absorption cross section. If several traps \(i\) contribute to \(S_{\text{acc}}(E^k, t_{\text{illum}})\), the overall \(S_{\text{acc}}(E^k, t_{\text{illum}})\) will be a superposition of individual contributions \(S_{\text{acc}, i}(E^k, t_{\text{illum}})\) from each trap \(i\). For the simulations, normalized optical absorption cross sections \(\sigma_{n, \text{norm}}\) for specific defects need to be known which can be obtained by first-principles calculation based on hybrid-functional[11]. Notably, the developed simulation is only valid when optically-induced hole emission can be neglected in the relevant photon energy range. \(\Sigma_n\) and \(N_{\text{tr}, \text{eff}}^{ss}\) are free parameters of the simulation. \(\Sigma_n\) determines the position and width of the specific contribution, while \(N_{\text{tr}, \text{eff}}^{ss}\) scales the corresponding curve.

EFG-grown \(\beta\)-Ga\(_2\)O\(_3\) crystals were studied to corroborate the validity of the developed methodology. Charge state transition levels related to Fe\(^{−0}/+0\)\(_\text{GaI}\), Fe\(^{−0}/+0\)\(_\text{GaII}\) and Ti\(^{0/+}\)\(_\text{GaII}\) in \(\beta\)-Ga\(_2\)O\(_3\) have been identified in this work (see Sec. 6.1.2.1) as well as other studies[99, 149]. Using DLTS, the concentrations of Fe\(_\text{GaI}\), Fe\(_\text{GaII}\) and Ti\(_\text{GaII}\) in a specific EFG-grown \(\beta\)-Ga\(_2\)O\(_3\) crystal were determined, and used to identify a SSPC signature which is likely to be related to the optical charge state transition levels associated with Fe\(^{−0}/+0\)\(_\text{GaI}\), Fe\(^{−0}/+0\)\(_\text{GaII}\) and Ti\(^{0/+}\)\(_\text{GaII}\). The signature labeled \(T^\text{EFG}_{1}\) was identified as a potential candidate, and its association with Fe\(^{−0}/+0\)\(_\text{GaI}\), Fe\(^{−0}/+0\)\(_\text{GaII}\) and Ti\(^{0/+}\)\(_\text{GaII}\) was verified by simulating derivative SSPC spectra using Eq. 6.1. The corresponding comparison between accumulatively-recorded derivative SSPC spectra and simulated derivative SSPC spectra is shown in Fig. 6.10 (a). Notably, the simulations capture the recorded data for varying \(t_{\text{illum}}\) using a common parameter set.

To demonstrate the versatility of the method developed for comparing SSPC measurements to first-principles calculations, we also revisited the case of HVPE-grown \(\beta\)-Ga\(_2\)O\(_3\) thin-films subjected to He-implantation at 120 K (see Sec. 6.1.2.2). Fig. 6.10 (b) shows SSPC spectra recorded accumulatively on a HVPE-grown \(\beta\)-Ga\(_2\)O\(_3\) thin-film before and after He-implantation at 120 K and simulations based on Eq. 6.1. Previously, \(T^\text{HVPE}_3\) has been assigned to Ga\(_{\text{I}}^{+2/+3}\) and \(V^\text{-3/2}_{\text{GaI}}\), while \(T^\text{HVPE}_3\) was proposed to be related to \(V^\text{-3/2}_{\text{GaII}}\), \(V^0/\pm\text{OK} (\text{K} = \text{I}, \text{II}, \text{III})\) as well as other transitions related to \(V_{\text{GaJ}} (\text{J} = \text{I}, \text{II})\) based on first-principles
calculations of the corresponding absorption cross sections. Due to its large mobility at 120 K, no O$_i$-related defect levels were expected to be present after He-implantation at 120 K. Here, we only used the energetically-lowest optical charge state transition levels for the primary intrinsic defects for performing the simulations. For each transition level displayed in Fig. 6.10 (b), there were two free parameters $N_{ss, tr, eff}$ and $\Sigma_n$ which were used for the model. Importantly, $T_{3}^{HVPE}$ and $T_{4}^{HVPE}$ cannot be modeled with only one defect signature. Thus, the simulations further emphasize the presence of several overlapping defect signatures. $T_{3}^{HVPE}$ consists of at least two defect signatures, while $T_{4}^{HVPE}$ contains more than two defect signatures. Importantly, the assignment of $T_{3}^{HVPE}$ to Ga$_i^{+}$ and V$_{Ga}$ is supported by the simulation. The main deviation between data and model can be seen in the region around 2.6 eV. However, the investigated as-prepared HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film already exhibits a defect signature in this region which is most likely still present after He implantation.

The developed methodology paves the way for an in-depth comparison between results of first-principles calculations and SSPC measurements. Particularly, it will help to corroborate defect assignments and to determine the presence of several overlapping defect signatures.
Chapter 7

Conclusions and Outlook

The main objective of this PhD project was to study defects in semiconducting oxides by using their charge state transition levels as fingerprints. Charge state transition levels of defects can be used to distinguish defects from the rest of the semiconductor, and hence they can be used to find the needle (the defect) in the haystack (the material). Furthermore, the charge state transition levels of defects are in themselves important because they will influence the performance of devices. Depending on its charge state transition level a defect may, e.g., act as an efficient recombination center, pin the fermi-level in electrical junctions or act as scattering center for charge carriers. Here, space-charge spectroscopy was used as a workhorse method for identifying charge state transition levels present in a semiconductor. However, other techniques were used in order to probe complementary material properties. Moreover, results from first-principles calculations were utilized to corroborate experimental findings.

The wide band gap semiconductors $\beta$-Ga$_2$O$_3$ and r-TiO$_2$ were studied in this thesis. Both materials are promising for applications in energy-conversion, storage or -harvesting, and hence studying the influence of defects on their optical as well as electrical properties is of utmost importance. For $\beta$-Ga$_2$O$_3$ and r-TiO$_2$, defect-related charge state transition levels proved to be a promising angle for studying and potentially identifying defects in these materials. Moreover, during this PhD project, an unique experimental setup was developed to perform steady-state photo-capacitance measurements which are particularly suited for studying defect-related charge state transition levels in wide band gap semiconductors. In $\beta$-Ga$_2$O$_3$, the origin of the commonly-observed $E_3$ level was found to be TiGaII. This result has great technological importance due to the fact that Ti serves as Ohmic contact for $\beta$-Ga$_2$O$_3$-based power electronics. Using the unique setup developed for SSPC measurements, it was also possible to assign optical charge state transition levels to various primary intrinsic defects. Hence, primary intrinsic defects can be studied further using these fingerprints. Our results also suggest that especially Ga$_i$ is very mobile below room temperature, and that defect complex formation involving the primary intrinsic defects is likely to occur already at room temperature. Furthermore, we found that defect complex formation can be sensitive to the fermi-level position as well as the presence of H in $\beta$-Ga$_2$O$_3$. Particularly, we observed that the defect level $E_2^*$ commonly thought to be related to a defect complex involving intrinsic defects only forms when the fermi-level is far away from $E_C$ and at temperatures of around 600 K after ion implantation. In contrast, at fermi-level positions close to $E_C$, $E_2^*$ is removed during heat-treatments, especially when H is present. For $\beta$-Ga$_2$O$_3$-based devices, ion implantation is used for contact formation, and hence large concentrations of intrinsic defects might be formed. Our results suggest that
diffusion of these intrinsic defects can readily occur at room temperature, and thus defect complex formation is likely to occur. Moreover, our results indicate that complex formation with H plays an important role in β-Ga₂O₃. With respect to r-TiO₂, shallow donors, deep-level defects and defect-related optical absorption were studied. It was possible to show that reducing or hydrogenating heat-treatments can be utilized to obtain conductive n-type r-TiO₂ suitable for forming Schottky barrier diodes with Pd or Pt which can be used for conducting space-charge spectroscopy. Particularly, H₁ was identified as main donor in hydrogenated r-TiO₂, shedding light on a decade-old debate concerning the main donor in hydrogenated r-TiO₂. Several more donor levels as well as defect-related deep levels were unveiled in r-TiO₂. Our observations suggest the relation of some of these levels to residual impurities. Furthermore, some of the detected deep levels are only present in comparatively conductive r-TiO₂. When studying the optical absorption of conductive n-type r-TiO₂ crystals, a defect-related absorption band was unveiled to be present regardless of the nature of the dopant. Its origin is suggested to be connected to polarons, and we found that the movement of transport of polarons through the material is influenced by the donor species. Generally, our results pave the way for further defect studies in r-TiO₂ using space-charge spectroscopy as well as by measuring the optical absorption of the material. Importantly, further knowledge can be obtained on the origin of the ubiquitous absorption band in n-type r-TiO₂.

A successful strategy used in this PhD project was to utilize first-principles calculations in conjunction with experiments in order to identify defect-related charge state transition levels. In order to enable better comparisons between SSPC measurements and first-principles calculations, we developed a new methodology to simulate SSPC spectra from results of first-principles calculations by taking the experimental conditions into account. Our methodology can be helpful in assigning a chemical or structural origin to defect levels detected in SSPC measurements.

### 7.1 Suggestions for Further Work

There are several directions of research which are interesting to pursue for β-Ga₂O₃ as well as r-TiO₂. For β-Ga₂O₃, the commonly-observed defect levels E₂ and E₃ have now been identified. However, the origin of E₁ which is also commonly observed in β-Ga₂O₃ crystals is still unclear. The role of H in β-Ga₂O₃ is also a research topic that should attract more attention. Specifically, its role in suppressing defect formation or passivating defects should be explored more. In this respect, using H implantation at cryogenic temperatures in conjunction with the newly-developed SSPC setup might be used to shed light on the formation of H-related defects, and the kinetics of H in β-Ga₂O₃. Furthermore, SSPC measurements in conjunction with hydrogenating heat-treatments could help to identify the charge state transition levels of V_Ga-2H which has been shown to form during hydrogenating heat-treatments. Additionally, further effort should be invested
Suggestions for Further Work

in investigating the role of reverse bias annealing on defect formation. Further research on r-TiO$_2$ should focus on utilizing Pd/r-TiO$_2$ Schottky barrier diodes for defect studies by conducting space-charge spectroscopy. Here, the newly-built setup for SSPC measurements can also be utilized for r-TiO$_2$. Moreover, combining irradiation and implantation with space-charge spectroscopy can be used to study intrinsic defects in r-TiO$_2$. The optical absorption measurements are also an interesting venue for further exploration. In this regard, it is of particular interest to study the differences between different dopants further, especially including other dopants such as Li. Furthermore, it could be of interest to study different heat-treatments, like annealing in vacuum in addition to the heat-treatments used in this thesis. Combined studies using SSPC measurements and measurements of optical absorption could also be of interest, specifically to identify the mechanism behind the observed absorption band. Additionally, further experiments involving so-called pump-probe experiments can prove to be interesting. One could utilize sub-band gap illumination as pump instead of above-band gap illumination. Particularly, sub-band gap illumination in the range of the observed sub-band gap absorption could be of interest. Last but not least, it is encouraged to conduct more fundamental work regarding how to properly compare first-principles calculations and experimental results. First attempts have been conducted in this thesis and other works. It seems that simulating experimental signatures from first-principles calculations by taking the experimental conditions into account is a promising direction. Proper comparisons between experiments and first-principles calculations could improve current efforts to identify the origins of defect-related charge state transition levels.
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Papers
Paper I

Ti- and Fe-related charge transition levels in $\beta$-Ga$_2$O$_3$

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Paper II

Primary intrinsic defects and their charge transition levels in $\beta$-Ga$_2$O$_3$

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Primary intrinsic defects and their charge transition levels in $\beta$-Ga$_2$O$_3$

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A steady-state photocapacitance (SSPC) setup directly connected to the beam line of a MeV ion implanter is utilized to study primary intrinsic defects in $\beta$-Ga$_2$O$_3$ generated by He implantation at cryogenic temperatures (120 K). At low temperatures, the migration of defects is suppressed, and hence the generation of primary intrinsic defects is expected to prevail. SSPC measurements reveal defect-related optical transitions in HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films with onset energies at 1.3 ($T_1$), 1.7 ($T_2$), 1.9 ($T_3$), 2.6 ($T_4$), 3.7 ($T_5$) and 4.2 eV ($T_6$). $T_1$, $T_2$, $T_5$ and $T_6$ were observed in as-received HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films, whereby $T_3$ is only sporadically observed. The introduction rates for $T_1$, $T_2$ as well as $T_6$ indicate an origin related to primary intrinsic defects. Notably, $T_1$ and $T_2$ are only observed after He implantation at cryogenic temperatures. Hybrid-functional calculations were performed to estimate the optical absorption cross section spectra for the gallium (Ga) and oxygen (O) interstitials as well as the corresponding vacancies (V$_{Ga}$ and V$_O$, respectively), and compared with the measured onsets for optical absorption found by SSPC measurements. Indeed, we propose $T_3$ to be associated with Ga$_{4}^{1+}/2^+$ and/or V$_{Ga}^{1+}/2^+$, while $T_4$ is suggested to be related to V$_{OK}^{0/1}$ ($K$ = I, II, III) and/or V$_{Ga}^{1+}/2^+$. Additionally, several further charge state transition levels associated with V$_{Ga}$ and V$_{O}$ may contribute to $T_5$ and $T_6$. We further studied the kinetics of the defects created with He implantation by exposing the sample to room temperature. The kinetics observed for $T_1$ and $T_2$ further support the proposed assignments of the corresponding defect signatures.

I. INTRODUCTION

Beta gallium oxide (Ga$_2$O$_3$) is a wide band gap semiconductor exhibiting exceptionally high break-down electrical fields, and hence has attracted considerable attention in recent years as a potential candidate for applications in UV sensors and power electronics, respectively. Intrinsic as well as extrinsic defects have a profound influence on the optical and electrical properties of the material. For example, defects can act as recombination centers limiting the efficiency of UV sensors, or act as traps for charge carriers and affect the performance of devices for power electronics. Thus, understanding prominent defects in Ga$_2$O$_3$ is of utmost importance in enabling the material to live up to its potential.

First-principles defect calculations predict several electronic states within the band gap of Ga$_2$O$_3$ associated with the primary intrinsic defects. Gallium vacancies (V$_{Ga}$) are expected to be deep acceptors, the gallium interstitial (Ga$_{I}$) is associated with donor states, and oxygen vacancies (V$_O$) give rise to deep donor states and the oxygen interstitial (O$_{I}$) can be both a donor or acceptor depending on its configuration. Notably, V$_O$ and V$_{Ga}$ can occur in different configurations.

Experimentally, a multitude of electronic states within the band gap of Ga$_2$O$_3$ have so far been unveiled using deep-level transient spectroscopy (DLTS), deep-level optical spectroscopy (DLOS), steady-state photocapacitance (SSPC) measurements, and as well as a variety of other methods. For example, SSPC studies performed by Farzana et al. as well as Zhang et al. on Ga$_2$O$_3$ reveal electronic states inside the Ga$_2$O$_3$ band gap at around 2.2, 3.2 and 4.4 eV below the conduction band edge ($E_C$), while at least six defect levels have been identified in the upper part of the band gap by DLTS. Identifying the microscopic origin of the observed defect signatures, however, remains challenging, and hence only a few assignments have been made so far. One notable exception is the case of Fe$_{Ga}$, which was shown to introduce an electronic state at around 0.78 eV below $E_C$ and identified by DLTS. The electronic levels associated with intrinsic defects and their complexes, however, have so far escaped experimental identification. One approach to study intrinsic defects in semiconductors is by intentionally introducing such defects via irradiation or implantation using neutrons, protons, $\alpha$-particles, electrons or heavier ions. Ga$_2$O$_3$ and O$_2$ are, however, expected to be very mobile at, or even below, room temperature. Furthermore, one can expect impurities, like hydrogen, to have a low migration barrier, and hence they are likely to passivate or form complexes with (intrinsic) defects. Notably, it has been implied by simulations as well as experimental studies that, for example, hydrogen and V$_{Ga}$ can form complexes.

At sufficiently low temperatures, however, primary intrinsic defects as well as impurities are immobile, and hence the formation of primary intrinsic defects should prevail during low temperature irradiation or implantation. This can be utilized by combining low temperature irradiation or implantation with characterization at the beamline of an accelerator (on-line), i.e., irradiation at cryogenic temperatures and subsequent characterization without heating up the sample. Moreover, subsequent exposure of the sample to higher temperatures can shed light on the defect kinetics in the corresponding temperature range, potentially revealing defect complex formation or passivation of defects.
In this work, we present results from on-line SSPC measurements on Ga$_2$O$_3$ thin-films grown by halide vapor-phase epitaxy implanted with He at 120 K. Our measurements reveal several new defect signatures which we propose to be associated with primary intrinsic defects. In particular, Ga$_i$ and/or V$_{Ga}$ formed on a tetrahedral Ga site (V$_{Ga}$) are potential candidates for a level with an onset for optical absorption at around 1.9 eV. We further propose that V$_O$- and other V$_{Ga}$-related defects show optical absorption in the region of 2.5 eV to 3.7 eV. These results are further corroborated by hybrid-functional calculations estimating the optical absorption expected for Ga$_i$ and V$_{Ga}$ and V$_O$. Additionally, our results indicate that passivation and/or migration of such defects indeed occurs already at temperatures below room temperature.

II. METHODOLOGY

A. Experimental Details

The Ga$_2$O$_3$ thin-films studied here were grown by halide vapor-phase epitaxy (HVPE) on conductive Ga$_2$O$_3$ substrates and obtained from Novel Crystal Technology Inc. The thin-films are unintentionally doped with Si and exhibit nominal charge carrier concentrations in the range of $5 \times 10^{16}$ cm$^{-3}$ to $3 \times 10^{17}$ cm$^{-3}$. The thickness of the thin-films is around 10 µm, while their surface corresponds to the (001)-plane. Using a laser cutter, the as-obtained wafers were cut into pieces measuring approximately $5 \times 5$ mm$^2$. The sample pieces were subsequently cleaned with acetone, isopropanol and de-ionized water for 5 min each inside an ultrasonic bath. Afterwards, Ohmic backside contacts consisting of Ti (thickness = 10 nm) and Al (thickness = 150 nm) were deposited by e-beam evaporation. After a subsequent cleaning step, semi-transparent Ni (thickness = 20 nm) Schottky contacts were deposited by e-beam evaporation using a shadow mask with contact diameters of 300, 600 and 900 µm. To ensure mechanical stability of the Ni contacts for wire-bonding, a second deposition of Ni (thickness = 150 nm) was performed using a shadow mask (with only circular openings displaying a diameter of 300 µm) which aligned with the semi-transparent Ni contacts. The contact layout is shown in the inset of Fig. 1. All results shown here were obtained on semi-transparent contacts with a diameter of 600 µm. Wire-bonding on the thick part of the Ni contact was used for connecting the sample to electrical measurement instruments.

He ions were implanted at 120 K with an energy of 180 keV and fluences $\Phi$ ranging from $1.25 \times 10^{13}$ cm$^{-2}$ to $5 \times 10^{14}$ cm$^{-2}$. Negligible heating of the sample during He implantation is expected due to the utilization of low ion currents as well as low ion fluences. The defect generation was simulated utilizing Monte-Carlo simulations implemented within the The Stopping and Range of Ions in Matter (SRIM) package using displacement energies for Ga and O of 25 and 28 eV, respectively. Simulations were run for Ni thicknesses of 20 nm (semi-transparent region) and 170 nm (thick Ni region used for wire-bonding), resulting in projected ranges $R_p$ of 400 nm for a Ni thickness of 170 nm and 610 nm for a Ni thickness of 20 nm, respectively. Notably, during He implantation primary intrinsic defects are generated regardless of their formation energy in thermal equilibrium. After generation, these primary intrinsic defects may form energetically more favorable configurations if they are mobile enough at the sample temperature to relax into the corresponding configurations.

Current-voltage (IV) and Capacitance-Voltage (CV) measurements were carried out under dark conditions at room temperature as well as at 120 K using a Keithley 6487 pico-meter/voltage source and a Boonton 7200 capacitance meter, respectively. CV measurements were performed at a probing frequency $\nu_{probe}$ of 1 MHz. A relative static dielectric constant $\varepsilon_r$ of 10.2 was assumed for Ga$_2$O$_3$. CV and IV measurements were performed inside a closed-cycle He cryostat connected to the beamline of an MeV ion implanter. From the forward bias region of IV curves, we extracted the ideality factor of the investigated Schottky junctions in order to verify the suitability of the junctions for SSPC measurements. SSPC measurements were conducted utilizing the same closed-cycle He cryostat connected to the beamline of an MeV ion implanter (on-line) as was used for IV and CV measurements. Fig. 1 shows the layout of the experimental setup used for on-line SSPC measurements. For studying defect kinetics, subsequent heat-treatments up to room temperature were performed inside the same cryostat without transferring the sample. During SSPC measurements, the capacitance of the junction is recorded after illuminating the junction at a certain wavelength $\lambda$ or photon energy $E$ for a given time. A constant angle of incidence was used for illumination. Here, the photocapacitance was recorded after 5 min using a Boonton 7200 capacitance meter ($\nu_{probe}$ = 1 MHz) while the junction was kept at a fixed external bias (typically between $-8$ V and $-1$ V). A laser-driven light source (EQ-77 from Energgetiq) was used as white light source, covering the spectral range from 190 to 2500 nm. The unpolarized light was dispersed with a grating-based monochromator (Shamrock 500i from ANDOR). Utilizing a grating with 1200 lines/mm (blaze at 400 nm) as well as fully opened exit and entrance slits at 2.5 nm, a typical spectral resolution of ca. 20 meV was obtained. Long-pass filters were used to ensure that no light from second order diffraction reaches the sample. Typical photon fluxes of $1 \times 10^{17}$ m$^{-2}$s$^{-1}$ in the UV and $1 \times 10^{19}$ m$^{-2}$s$^{-1}$ in the visible part of the spectrum were estimated using a calibrated thermal power meter placed at the sample position inside the cryostat. The near-monochromatic light was delivered to the sample using parabolic mirrors. The sample was illuminated starting at the long wavelength end (usually at around 1600 nm), proceeding to shorter wavelengths in steps of 20 or 40 meV. In contrast to other studies, no filling pulse or above-band gap illumination were utilized during SSPC measurements (see, for example, Refs. 28, 44). Samples were, however, pre-illuminated for 30 min at the longest wavelength used for a specific measurement range. This ensures that at the beginning of the measurement, traps responding to longer wavelengths than the ones used for the SSPC measurement are being ionized, and hence the sample is in or close to a steady-state for illumination at such wavelengths.
The resulting photocapacitance signal is accumulative and represents the persistent charge created within the depletion region of the Schottky diode upon illumination at a certain photon energy. SSPC spectra recorded using different measurement ranges usually displayed slight offsets compared to each other. Offsets caused by switching between different measurement ranges were corrected assuming them to be independent of photon energy and using the measurement range for the lowest photon energies as reference.

SSPC spectra $S(E)$ are usually presented as $S(E) = 2N_D \sum_i \frac{\Delta C_{\text{illumination},i}}{C_{\text{dark}}} \frac{1}{1 + \exp \left( \frac{E - E_i}{\gamma} \right)}$, where the individual contributions $i$ are described by sigmoidal functions. $\Delta C_{\text{illumination},i}/C_{\text{dark}}$ represents the relative change in capacitance due to illumination for an individual contribution and is independent of $E$. For a specific contribution $i$, $E_i$ describes the position of the onset of the SSPC signal and $\gamma$ represents the steepness of the corresponding step. Features with $\Delta C_{\text{illumination},i}/C_{\text{dark}} > 0$ (optically-induced electron emission) as well as $\Delta C_{\text{illumination},i}/C_{\text{dark}} < 0$ (optically-induced hole emission) can occur.

SSPC spectra can also be represented as derivatives with respect to photon energy, where step-like features are transformed into peak-like features. Such a representation can greatly improve the interpretation of the technique, and aid deconvolution.

The height $2N_D \Delta C_{\text{illumination},i}/C_{\text{dark}}$ of each step is related to the effective trap concentration $N_{\text{eff},i}$ and serves as a lower bound for the actual concentration $N_{t,i}$. For small total trap concentrations $N_t$ or $\Delta C_{\text{illumination}}/C_{\text{dark}} \ll 0.5$, a linear rela-
FIG. 2. (a) CC diagram for the (+/+2) charge state transition of Ga$_i$. The vertical transition energy connected to optical absorption is marked as $E_{\text{abs}}$, while the thermodynamic transition level is marked as $E_{\text{ZPL}}$. The minima of the parabola signify the (meta-)stable configurations of Ga$_i^+$ and Ga$_i^{+2}$, respectively. The corresponding difference in the configuration coordinate $\Delta Q$ is also marked in the plot. The values for $E_{\text{abs}}$, $E_{\text{ZPL}}$ and $\Delta Q$ for Ga$_i$ (+/+2) as well as various other primary intrinsic defects and some defect complexes involving intrinsic defects are summarized in Tab. I. (b) Absorption cross section spectra calculated for charge state transitions of various primary intrinsic defects. The bars represent the transition energies ($E_{\text{max}}$) as defined in (a) and $E(\alpha_{\text{max}}/1000)$ for the corresponding transition. The position of $E(\alpha_{\text{max}}/1000)$ marks the photon energy at which the absorption cross section decreased by three orders of magnitude as compared to $\alpha_{\text{max}}$, whereas $E(\alpha_{\text{max}}/100)$ marks the photon energy at which the absorption cross section decreased by two orders of magnitude as compared to $\alpha_{\text{max}}$.

B. Computational Details

First-principles calculations were performed using the projector augmented wave method (PAW)\textsuperscript{51,52}, and the Heyd-Scuseria-Ernzerhof screened hybrid functional (HSE)\textsuperscript{53}, as implemented in the VASP code\textsuperscript{54}. The fraction of screened Hartree-Fock exchange was adjusted to $\alpha = 0.32$, which accurately describes both the experimental band gap ($E_g = 4.9$ eV) and structural parameters as reported elsewhere\textsuperscript{21,55,56}. The experimentally determined band gap value can be expected to exhibit an uncertainty of around $\pm 0.1$ eV\textsuperscript{55}. The Ga - 3$d$ and Ti - 3$p$, - 3$d$ as well as - 4$s$ electrons were included as valence states. For defect calculations, we used 160-atom supercells, a plane wave energy cutoff of 400 eV, and a single special $k$-point at (1/4, 1/4, 1/4). Defect formation energies and thermodynamic charge-state transition levels were calculated by following the well established formalism\textsuperscript{57}. For charged defects, we adopted the anisotropic\textsuperscript{58} Freysoldt, Neugebauer and Van de Walle scheme to correct formation energies\textsuperscript{59}, and the method recently proposed by Gake \textit{et al.} to correct vertical transition energies\textsuperscript{60}. Optical absorption energies of defects were estimated by using the effective one-dimensional configuration coordinate (CC) model with parameters obtained from the HSE calculations\textsuperscript{49,59}. However, the absorption onset will be lower than the classical absorption energy $E_{\text{abs}}$ obtained from CC diagrams due to vibrational broadening. Absorption cross sections which include vibrational broadening can be simulated based on CC diagrams by following the scheme outlined in Refs.\textsuperscript{49,61}. Following Ref.\textsuperscript{8}49,61, defect-related optical absorption is mod-
eled as an electronic transition between a ground state (Defect in charge state $q$ and charge carrier localized at or close to the defect) and an excited state (Defect in charge state $q \pm 1$ and delocalized charge carrier in the conduction or valence band) triggered by a photon. Despite the complex optical selection rules in Ga$_2$O$_3$ owing to the crystal symmetry and orbital character of the conduction and valence bands, the corresponding optical transitions are assumed to be allowed. Notably, defect-related optical transitions can be expected to be allowed if the transition is accompanied by strong lattice relaxation which has been reported for various defects in Ga$_2$O$_3$. Moreover, the defect potential is assumed to be represented by a $\delta$-function, in accordance with what is typically assumed for deep-level defects. The excited state is a continuum of states in the conduction or valence band, whereby the bands are assumed to be parabolic. We note that we focus on transitions to the conduction band around $E_C$, which is a highly dispersive state that is predominantly parabolic and exhibits a simpler orbital character than the upper valence band. For the determination of the onset of defect-related optical absorption, the parabolic approximation is not believed to introduce a large error. Furthermore, the transition matrix element relevant for the electronic transition is assumed to be constant, i.e., to be independent of energy or momentum. The model proposed by Alkauskas et al. and Kopylov et al. takes phonon contributions into account: (i) phonons are emitted during the absorption process, and (ii) ground and excited state posses vibrational sub-states which will be occupied at higher temperatures and contribute to the optical absorption. It is assumed that the phonon contributions can be modeled by using an effective frequency for the phonons relevant for the ground and excited state, respectively. Notably, both (i) and (ii) will contribute to a broadening of the defect-related optical absorption cross section spectra and a corresponding shift of the absorption onset. Phonon emission (i) will contribute to the broadening already at 0 K, whereas the contribution of additional vibrational sub-states (ii) will become more pronounced with increasing temperature. The calculations presented in this work were performed at 0 K. For a selection of defects, optical absorption cross section spectra were also calculated assuming 120 K, and we found only minor differences. More information regarding the model used for calculating defect-related optical absorption cross section spectra and their temperature dependence can be found in the Supplementary Material.

Migration barriers were evaluated using the climbing nudged elastic band method (cNEB) using at least five images and requiring the resulting force to be $\leq 0.03$ eV Å$^{-1}$. Owing to their large computational cost, barriers were evaluated using the same supercell geometries and the PBEsol functional and PAW potentials that treated the Ga - 3d electrons in the core. The lowest barriers were evaluated with HSE using the same approach to assess the differences.

### III. RESULTS

#### A. Computational Results

Hybrid-functional calculations were performed to predict optical signatures originating from various primary intrinsic defects in Ga$_2$O$_3$. Specifically, we computed CC diagrams to obtain optical absorption spectra related to charge state transitions associated with the primary intrinsic defects. For each defect, we focused on the charge state transition with the energetically-lowest transition energy associated with optical absorption. However, it can be expected that some primary intrinsic defects will exhibit more than one charge state transition level inside the band gap of Ga$_2$O$_3$. Moreover, we only considered charge state transitions involving the defects and the conduction band (optically-induced electron emission). Due to the likely formation of self-trapped holes in Ga$_2$O$_3$, we assume transitions between the defects and the valence band to not significantly contribute to the measured SSPC spectra (see Supplementary Materials). Calculations were performed for Ga$_2$O$_3$, O$_i$ and Ga$_3$O$_5$ (K = I, II, III) and Ga$_{3+}$ and Ga$_{3-}$, which has been reported for various defects in Ga$_2$O$_3$. Moreover, we considered charge state transitions involving the defects and the conduction band (optically-induced electron emission). Due to the likely formation of self-trapped holes in Ga$_2$O$_3$, we assume transitions between the defects and the valence band to not significantly contribute to the measured SSPC spectra (see Supplementary Materials). Calculations were performed for Ga$_2$O$_3$, O$_i$ and Ga$_3$O$_5$ (K = I, II, III) and Ga$_{3+}$ and Ga$_{3-}$, which has been reported for various defects in Ga$_2$O$_3$. More computational results regarding optical absorption spectra related to primary intrinsic defects can be found in the Supplementary Material.
Defect Charge $\Delta Q$ $E_{ZPL}$, $E_{abs}$ $E (\alpha_{\text{max}}/100)$ $E (\alpha_{\text{max}})$
State \((\sqrt{\text{amuÅ)}}\) (eV) (eV) (eV) (eV)
Transition
Ga$_i$ (+$/-$) 2.22 0.89 2.43 2.04 1.90
O$_i$ (-$/-$) 4.33 1.45 3.16 2.55 2.34
V$_{Oh}$ (0$+$) 3.85 1.68 3.20 2.79 2.63
V$_{Oll}$ (0$+$) 3.26 2.46 3.82 3.38 3.20
V$_{Olll}$ (0$+$) 3.30 1.67 3.00 2.60 2.45
V$_{Gal}$ (-3$/-$) 2.38 1.80 2.63 1.96 1.73
V$_{Gall}$ (-3$/-$) 3.12 2.35 3.21 2.62 2.40
V$_{Ga}^2$ (-3$/-$) 2.24 2.16 3.06 2.42 2.19
V$_{Ga}^3$ (-3$/-$) 2.35 2.02 2.99 2.33 2.10
V$_{Ga}^4$ (-3$/-$) 2.37 2.65 3.48 2.82 2.59
V$_{Ga}^5$ - V$_{Oh}$ (-1$/-$) 2.40 3.04 4.16 3.62 3.42
V$_{Ga}^6$ - V$_{Oh}$ (-1$/-$) 2.32 2.41 3.61 3.06 2.85
V$_{Ga}^7$ - V$_{Oh}$ (-3$/-$) 3.10 1.60 2.55 1.93 1.71

TABLE I. Summary of parameters for various primary intrinsic defects and some di-vacancy complexes obtained from hybrid-functional calculations. Calculations were performed for the charge state transition associated with the energetically-lowest transition energy associated with optical absorption. Hereby, only charge state transitions involving the defects and the conduction band were considered. The parameters $E_{ZPL}$, $E_{abs}$ and $\Delta Q$ are obtained from CC diagrams and defined in Fig. 2 (a). $E (\alpha_{\text{max}}/100)$ is defined as the photon energy at which the absorption cross section decreased by three orders of magnitude as compared to $\alpha_{\text{max}}$, whereas $E (\alpha_{\text{max}}/100)$ denotes the photon energy at which the absorption cross section decreased by two orders of magnitude as compared to $\alpha_{\text{max}}$.

Computed normalized absorption cross section spectra ($\alpha$) are shown in Fig. 2 (b) for various primary intrinsic defects. An interval was extracted from these spectra covering all photon energies from $E_{abs}$ (as defined in Fig. 2 (a)) to $E (\alpha_{\text{max}}/100)$, while the position of $E (\alpha_{\text{max}}/100)$ is also indicated. Hereby, $\alpha_{\text{max}}$ denotes the maximum value of the absorption cross section spectra. $E (\alpha_{\text{max}}/100)$ is defined as the photon energy where $\alpha$ decreased by three orders of magnitude as compared to $\alpha_{\text{max}}$, whereas $E (\alpha_{\text{max}}/100)$ is defined as the photon energy where $\alpha$ decreased by two orders of magnitude as compared to $\alpha_{\text{max}}$. These intervals are used for comparison between computational results and measured SSPC spectra.

To gauge the kinetics of primary intrinsic defects, migration barriers $E_m$ were calculated for Ga$_i$, while results for $E_m$ are already available for O$_i$, V$_O$ and V$_{Gal}$ in the literature $14,15,38$. For O$_i$, a value of 0.12 eV was calculated for $E_m$ $15$. For V$_O$, values from 1.2 to 4 eV were found, while for V$_{Gal}$ barriers between 0.5 and 2.3 eV were computed $14$. Notably, the migration of V$_{Gal}$ ($J = I, II$) is associated with the formation of the configurations V$_{Ga}^M$ (M = a, c, b) $19$. However, the barrier for the V$_{Ga}^M$ (M = a, c, b) configurations to migrate or transform back into V$_{Gal}$ ($J = I, II$) are significantly higher $19$. For Ga$_i$, we find that the lower bound for $E_m$ is strongly dependent on the charge state of Ga$_i$. We find a $E_m$ of 0.65 eV for Ga$_i^-$, and compute a barrier of 0.48 eV for Ga$_i^{+}$ $19$. It is found that Ga$_i^{+}$ is meta-stable and will transform immediately into Ga$_i^{0}$, meaning Ga$_i$ exhibits so-called negative-U behavior $48$. Larger migration barriers were obtained when performing the calculations using the HSE functional, and hence the migration barriers stated above can be seen as lower bounds. More information regarding these calculations can be found in the Supplementary Material $66$.

Following the approach of Kyrtsos et al., a lower temperature can be estimated at which migration of defects will occur $14$. For V$_O$, Kyrtsos et al. estimate that such defects will not be mobile at or below room temperature, while for V$_{Ga}$ some migration might occur already just below room temperature $14$. Notably, this migration is connected to the transformation of V$_{Gal}$ ($J = I, II$) into V$_{Ga}$ (M = a,c,b) $19$. However, the V$_{Ga}$ (M = a, c, b) configurations are less mobile than V$_{Gal}$ ($J = I, II$) and are not expected to migrate at or below room temperature $19$. For Ga$_i$, we can estimate that Ga$_i^+$ will be mobile at around 190 K, while Ga$_i^0$ will be mobile at around 250 K. O$_i$ is expected to be mobile already at around 50 K given its low migration barrier of 0.12 eV $13$. Note also, that electrical fields as they are present within a space-charge region may enhance the diffusion of charged defect species $14,71$.

B. Experimental Results

Fig. 3 (a) shows IV curves recorded on a Ni/Ga$_2$O$_3$/Ti/Al junction comprising a HVPE-grown Ga$_2$O$_3$ thin-film. The junction displays a high rectification of around eight orders of magnitude. The investigated junctions generally display rectifications ranging from three to nine orders of magnitude. The series resistances range from several $\Omega$ to a few hundred $\Omega$ depending on the specific junction. The ideality factor at room temperature is typically around 1 - 1.5, but increases to values of around 3 - 4 for measurements at 120 K. After He implantation, all diodes exhibit an increase in series resistance, while usually no significant change in the reverse bias region is observed.

In Fig. 3 (b), the results of typical CV measurements are displayed for one particular junction (same junction as depicted in Fig. 3 (a)). The donor concentration $N_D$ for all diodes investigated is in the range of $2 \times 10^{16} - 2 \times 10^{17}$ cm$^{-3}$, whereby the donor profiles generally show a slight decrease in donor concentration towards the surface. We estimate the uncertainty for $N_D$ to be around 10 % due to uncertainties in contact area and value of $\varepsilon$ $33,72$. The typical probing depth is in the range of 300 - 700 nm, i.e., the main part of the region where implantation-induced defects are to be expected is within the probing volume. The conductance does not exceed 20 mS. After He implantation, $N_D$ decreases, resulting in a probing depth of approximately 450 - 700 nm.
In the following, we will describe the results obtained from SSPC measurements performed at 120 K. Fig. 4 displays a SSPC spectrum recorded on an as-received HVPE-grown Ga$_2$O$_3$ thin-film. Steps in the SSPC spectrum can be seen with onset energies at 1.7, 2.6, 3.7, 4.2 and 4.8 eV. The corresponding defect signatures are labeled as $T_3$ (1.7 eV), $T_4$ (2.6 eV), $T_5$ (3.7 eV), $T_6$ (4.2 eV), while the signature at 4.8 eV is associated with the band gap and is labeled as $E_g$ in Fig. 4. $T_5$ is also associated with a decreasing SSPC signal starting at a photon energy of around 3.9 eV. The trap concentrations $N_{\text{eff}}$ are estimated to be in the range of $1 \times 10^{14}$ cm$^{-3}$ - $1 \times 10^{16}$ cm$^{-3}$ using Eq. 3. The low defect concentrations confirm that all defect-related photo-excitation processes can be regarded as independent of each other. The detection limit for the sample shown in Fig. 4 is estimated to be around $1 \times 10^{13}$ cm$^{-3}$. Notably, SSPC spectra recorded on various other as-received HVPE-grown Ga$_2$O$_3$ thin-films exhibit the same features with the exception of $T_5$, which is only sporadically observed. Fig. 4 also displays a comparison between SSPC spectra recorded at 120 K before and after He implantation performed at 120 K with a fluence $\Phi$ of $1.25 \times 10^{14}$ cm$^{-2}$. Two new signatures with onset energies at around 1.3 and 1.9 eV appear after He implantation. The corresponding signatures were labeled $T_{1a}$ and $T_{3a}$, respectively. $T_1$ does not appear in all samples subjected to He implantation, while $T_3$ is detected in all samples after He implantation conducted at 120 K. The features labeled $T_{4a}$ and $T_{6a}$ exhibit an apparent shift of their onset position after He implantation (marked with horizontal red arrows in Fig. 4). Furthermore, $T_6$ shows an increase in amplitude, while the apparent amplitude of $T_6$ decreases. There seems to be no significant impact of the He implantation on $T_5$. Finally, the influence of He implantation on the signature labeled $T_2$ is challenging to determine due to its low concentration and sporadic presence.

In Fig. 5 (a), SSPC spectra are shown which were recorded on a HVPE-grown Ga$_2$O$_3$ thin-film. SSPC spectra are displayed for the as-received thin-film as well as for the thin-film after implantation with He ions with different fluences at 120 K. The sample was subjected to two subsequent He implantations, and hence two different accumulated fluences $\Phi_{\text{tot}}$. Derivative SSPC spectra are displayed for comparison in the top panel of Fig. 5 (a). The derivative SSPC spectra suggest the presence of several overlapping defect signatures contributing to $T_4$ and $T_6$ which is supported by modeling the spectra (see Supplementary Materials 50). Notably, the comparison of the derivative SSPC spectra recorded before and after He implantation at 120 K indicates that the sub-features being part of $T_4$ and $T_6$ respond slightly different to He implantation. Vertical bars are displayed in Fig. 5 (a) to indicate the energetic positions of the optical absorption associated with various primary intrinsic defects as predicted by computations based on hybrid-functionals (see Fig. 2 (b)). Indeed, the prediction for the optical absorption related to Ga$_3$ (+$+/2$) and $V_{\text{Ga}}$ overlapped with $T_3$, while the optical absorption related to O$_{\text{I}}$ (+2)$+/0$ (K = I, II, III) and $V_{\text{GaI}}$ overlapped with $T_2$. Note, however, that the onset of optical absorption will depend on the absolute value of the absorption cross section, the light intensity as well as the competition between electron and hole processes 45,73.

From the data shown in Fig. 5 (a), a plot can be constructed displaying the effective trap concentration $N_{\text{eff}}$ of the individual defect levels and their dependence on $\Phi_{\text{tot}}$. The corresponding results are shown in Fig. 5 (b). A linear relationship between $\Phi_{\text{tot}}$ and $N_{\text{eff}}$ is seen for the signatures $T_4$, $T_5$ and $T_6$. However, for $T_6$, a linear relationship is only seen if one assumes $\Delta C_{\text{illumination}}/C_{\text{dark}} \approx 0.5$. This is generally a
better assumption than assuming $\Delta C_{\text{illumination}}/C_{\text{dark}} \ll 0.5$ for the junctions studied here. $T_1$ was not present in this sample. The fact that optically-induced emission of electrons as well as holes is relevant for $T_3$ makes the determination of $N_{\text{eff}}^{\text{Ga}}$ ambiguous, and hence the corresponding results are not shown here.

The introduction rates $IR$ were derived from a linear fit to $N_{\text{eff}}^{\text{Ga}}$ vs. $\Phi_{\text{opt}}$. The following introduction rates were determined for $\Delta C_{\text{illumination}}/C_{\text{dark}} \ll 0.5$ (average for the cases of neglecting the $\lambda$-correction as well as assuming a Franck-Condon shift of up to 1 eV): 6.3 $\times$ 10^4 cm$^{-1}$ ($T_3$), 1.2 $\times$ 10^5 cm$^{-1}$ ($T_4$) and 1.5 $\times$ 10^5 cm$^{-1}$ ($T_5$). For $\Delta C_{\text{illumination}}/C_{\text{dark}} \approx 0.5$ the following introduction rates $IR$ were computed: 3.3 $\times$ 10^4 cm$^{-1}$ ($T_3$), 7.5 $\times$ 10^4 cm$^{-1}$ ($T_4$) and 1.3 $\times$ 10^5 cm$^{-1}$ ($T_5$). Notably, the derived $IR$ do not differ significantly whether we assume $\Delta C_{\text{illumination}}/C_{\text{dark}} \ll 0.5$ or $\Delta C_{\text{illumination}}/C_{\text{dark}} \approx 0.5$. It should be noted that these introduction rates represent a lower bound for the actual introduction rates, due to the fact that $N_{\text{eff}}^{\text{Ga}}$ is always a lower bound for the actual trap concentration $N_{i,1}^{\text{Ga}}$.

The so-called survival rate can be computed when comparing experimental $IR$ to the expected $IR$ for $V_{\text{Ga}}$ and $V_{\text{O}}$ which was estimated to be $1 \times 10^6$ cm$^{-1}$ using SRIM. Using this value, we obtain the following survival rates: 0.03 - 0.06 ($T_3$), 0.08 - 0.12 ($T_4$) and 0.13 - 0.15 ($T_5$) defects per vacancy created.

On-line SSPC measurements combined with He implantation at cryogenic temperatures (120 K) offer a unique possibility to study the electronic states associated with optically- and electrically-active primary intrinsic defects, since the diffusion of defects is suppressed. In addition, the migration and/or passivation of defect species mobile at or below room temperature can be studied by subsequent heat-treatments, potentially revealing further information about the observed defects. Moreover, we explicitly calculated optical absorption spectra related to the primary intrinsic defects in order to relate signatures seen in SSPC spectra to specific intrinsic defects.

SSPC spectra display several features in as-received HVPE-grown Ga$_2$O$_3$ thin-films as well as features that are only visible after He implantation at 120 K. The features labeled $T_1$, $T_3$, $T_5$ and $T_6$ are step-like, and hence indicate optically-induced emission of electrons from trap levels inside the band gap to the conduction band. The feature labeled $T_3$ on the other hand, is peak-like, and hence clearly displays characteristics of processes related to the optical emission of electrons and holes from a trap level to the conduction band and valence band, respectively.44,45 However, the electron and hole emission related to $T_3$ do not have to originate from the same trap. Our results are in accordance with previously reported results, where defect signatures with an onset for optical absorption at around 2.2, 3.2 and 4.4 eV have been measured by SSPC or related techniques.23,24,26,27

Starting with $T_1$, it is only generated in relatively low concentrations upon He implantation compared to the introduction of the other levels responding to He implantation. In addition, not all samples in the present study display the introduction of $T_1$ (see Fig. 5 (a)). Interestingly, Farzana et al. also observed the introduction of a new defect signature with an onset at around 1.3 eV in SSPC measurements after neutron irradiation.28 Furthermore, Polyakov et al. revealed a
level with approximately the same onset energy as T₁ that responded to proton irradiation using CV measurements under illumination. The onsets for optical absorption estimated from hybrid-functional calculations corroborate that no primary intrinsic defect exhibits an onset for optical absorption as low as the one observed for T₁. Hence, we propose that T₁ does not arise from a primary intrinsic defect, but rather from a defect complex or an impurity. Further, T₁ is not affected by exposure of the sample to 300 K after He implantation at 120 K, suggesting that T₁ is related to a defect which is not mobile at or below room temperature.

T₃ does not seem to exhibit a pronounced response to He implantation. The same applies to the signature labeled T₄. The onsets for optical absorption estimated for Vₒ and V₃Ga in Ga₂O₃ are close to those expected for primary intrinsic defects obtained from the hybrid-functional calculations. Importantly, the optical absorption of the primary intrinsic defects to occur (see Fig. 2). I,II and III denote the different configurations found for V₃Ga (J = I, II) and Vₒ (K = I, II, III) will be present, while V₃Ga (M = a,c,b) is also not expected to occur at 120 K. Even if some defect migration or transformation occurs at 120 K, one can at least expect complex formation to be substantially suppressed. Comparing the onset of T₃ with the optical absorption of the primary intrinsic defects obtained from the hybrid-functional calculations, it is evident that the expected onsets for optical absorption computed for Ga₃⁺ and V₃Ga⁺ are close to the position of T₃. Importantly, the optical absorption expected for V₃Ga (K = I, II, III) and O₃ is located at higher photon energies. The optical signatures related to V₃Ga⁺,
FIG. 6. SSPC spectra recorded on a HVPE-grown Ga$_2$O$_3$ thin-film before and after He implantation at 120 K with a fluence of 1.25 × 10$^{11}$ cm$^{-2}$ as well as after a subsequent annealing at 300 K for 5 min. The results are displayed as derivative SSPC spectra (upper panel) and as conventional SSPC spectra (lower panel). The same signatures as seen in Fig. 4 were present in the corresponding Ga$_2$O$_3$ thin-film before He implantation, with the exception of T$_5$. After He implantation, new features labeled T$_4$ and T$_6$ are observed, while the signatures T$_3$ and T$_6$ changed in amplitude. Upon annealing, T$_3$ and T$_6$ decrease in amplitude, while T$_4$ increases in signal. T$_1$ seems not to be affected by the heat-treatment. A panel is also shown with bars representing the computational prediction of optical signatures related to the absorption associated with various primary intrinsic defects as well as di-vacancy complexes. Results are also shown for the relaxed configurations of V$_{Ga}$.

V$_{Ga}$($^{0+/+}$) (K = I, II, III) and O$_{K/2}$ are, however, close to T$_3$. Thus, Ga$_{i}$ and V$_{Ga}$ are potential candidates for T$_3$, whereas V$_{Ga}$ and V$_{O}$ (K = I, II, III) are proposed as candidates for T$_4$.

However, some of the primary intrinsic defects exhibit several optical charge state transition levels in the band gap of Ga$_2$O$_3$ (see Supplementary Material). Particularly, optical transitions related to V$_{Ga}$($^{-2/-1}$) and V$_{Ga}$($^{-1/0}$) (J = I, II) may also contribute to T$_5$. However, the concentration of the defects associated with T$_4$ is significantly higher than the defect concentration related to T$_3$, and hence some defects contributing to T$_4$ are not likely to contribute to T$_3$.

The exposure of samples implanted with He at cryogenic temperatures to room temperature can further aid the assignment of defect signatures seen in SSPC measurements to specific intrinsic defects. The observed decrease in concentration for T$_3$ and T$_4$ upon room temperature exposure may be explained by annihilation reactions of Ga$_{i}$ and V$_{Ga}$ defects. Such annihilation reactions lead to a decrease in Ga$_{i}$ as well as V$_{Ga}$ (J = I, II), and hence to a decrease of T$_3$ and T$_4$. A transformation of V$_{Ga}$ (J = I, II) into V$_{Ga}$($M =$ a,c,b) should, in contrast, lead to a decrease in the concentration associated with T$_3$, and an increase in the concentration associated with T$_4$, taking into account that the transitions related to V$_{Ga}$($M =$ a,c,b) are predicted to be close to T$_6$. However, it is not possible to rule out that both processes, annihilation of Ga$_{i}$ with V$_{Ga}$ as well as transformation of V$_{Ga}$, may contribute to the observed changes in photo-capacitance.

Finally, T$_6$ exhibits an increase in concentration with increasing fluence of He implanted at 120 K, in addition to a distinct increase in concentration after exposure of the samples to room temperature. As mentioned above, several of the intrinsic defects also exhibit charge states in the lower part of the band gap (see Supplementary Material), and might contribute to T$_6$. However, the increase in T$_6$, while T$_3$ and T$_4$ decrease, suggests different origins for T$_6$ compared to T$_3$ as well as T$_4$. Hence, it is tempting to propose that T$_6$ involves a defect complex, rather than a primary intrinsic defect, and di-vacancies may also be potential candidates for T$_6$, although the calculated absorption spectra do not result in an adequate fit to the measured position of T$_6$. Thus, further investigations are required to shed light on the origin of the T$_6$ level.

V. SUMMARY AND CONCLUSION

Using on-line SSPC measurements, we were able to observe optical transitions related to defects in HVPE-grown Ga$_2$O$_3$ thin-films with onset energies at 1.3, 1.7, 1.9, 2.6, 3.7 and 4.2 eV. The levels were labeled T$_1$ - T$_6$ in ascending order of onset energy. T$_3$, T$_4$, T$_5$ and T$_6$ are observed in all as-received HVPE-grown Ga$_2$O$_3$ thin-films, whereby T$_2$ is only observed sporadically. T$_1$ and T$_3$ are only detected after He implantation at 120 K. T$_4$ and T$_6$ also respond to He implantation. The introduction rates for T$_3$, T$_4$ as well as T$_6$ indicate their relation to primary intrinsic defects. We also calculated migration barriers for Ga$_{i}$ as well as use reported migration barriers for the vacancy defects and O$_{i}$, which are not expected to be mobile below 120 K, and hence not present in our samples after He implantation at 120 K. V$_{Ga}$ (K = I, II, III) are expected to be mobile below room temperature, while Ga$_{i}$ should be immobile at 120 K, but mobile at or below room temperature. V$_{Ga}$ (J = I, II) might be mobile just below room temperature, and is predicted to transform into relaxed configurations which are stable at room temperature.

We performed hybrid-functional calculations in order to predict the optical absorption cross section spectra for various primary intrinsic defects. Thus, we tentatively propose T$_3$ to be associated with Ga$_{i}$($^{+/-+}$) and/or V$_{Ga}$($^{-3/-2}$), whereas T$_4$ is suggested to be related to V$_{O}$ (K = I, II, III) and/or V$_{Ga}$($^{-3/-2}$), although an overlap with other charge state transitions, such as V$_{Ga}$($^{-2/-1}$) and V$_{Ga}$($^{-1/0}$) (J = I, II), cannot be excluded.

Further insights were gained by studying the kinetics of the defects created upon He implantation at 120 K. We found that T$_3$, T$_4$ and T$_6$ change in concentration upon exposing samples to room temperature after He implantation at 120 K. T$_3$ and T$_4$
decrease in concentration upon such annealing, while $T_0$ increases in concentration. The kinetics observed for $T_1$ and $T_2$ further support the proposed assignments of the corresponding defect signatures to Ga$_{x}$ and V$_{Ga}$ due to Ga$_{x}$ being mobile already at or below room temperature, and hence annihilation of Ga$_{x}$ and V$_{Ga}$ to be a likely mechanism. For $T_0$, complex formation or passivation involving other defects are proposed to be involved.

VI. ACKNOWLEDGMENTS

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Supplementary Materials: Extraction of trap concentrations from Steady-State Photocapacitance Measurements

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A. Extraction of trap concentrations from Steady-State Photocapacitance measurements

It is generally possible to extract values for the concentration of an electrically- and optically active trap from steady-state photocapacitance (SSPC) measurements. The trap concentration is extracted from the measured value of 2NDΔC_{illumination,i}/C_{dark} (see Eq. 26). The specific way to perform this extraction depends on what assumptions are made regarding the junction under investigation. In the following, two different cases will be discussed and the corresponding formulas to convert photocapacitance changes to trap concentrations will be presented:

- **Low concentration of traps:** ΔC_{illumination}/C_{dark} ≪ 0.5
- **Large concentration of traps:** ΔC_{illumination}/C_{dark} ≈ 0.5

Here, ΔC_{illumination} denotes the overall change of capacitance due to illumination and C_{dark} is the capacitance in the dark. We assume that thermal equilibrium is reached prior to the measurement. Fig. 1 shows a Schottky junction under illumination illustrating aspects relevant for SSPC measurements.

1. Low concentration of traps: ΔC_{illumination}/C_{dark} ≪ 0.5

If the overall concentration of electrically- and optically-active traps is much smaller than the donor concentration N_D, we can assume ΔC_{illumination}/C_{dark} ≪ 0.5 to be valid. With this, we obtain the following relation for the effective trap concentration N_{eff,i,probed} inside the probing volume (see Fig. 1) 1,2:

\[
N_{\text{eff,i,probed}} = 2ND \frac{\Delta C_{\text{illumination},i}}{C_{\text{dark}}}. \tag{1}
\]

Here, ΔC_{illumination,i} denotes the change in capacitance due to illumination when steady-state is reached for a certain trap level i. If N_D inside the junction is inhomogeneous, N_D at the depletion layer depth W corresponding to the applied reverse bias V_{bias} should be used. Eq.1 represents a linear relationship between ΔC_{illumination,i} and N_{eff,i,probed}. N_{eff,i,probed} will generally represent the concentration of traps inside the probing volume in between x_i and W − \lambda_i^{th} as defined in Fig. 1. The following relation can be used to calculate the effective trap concentration N_{eff,i} inside the depletion layer under applied reverse bias V_{bias} 1:

\[
N_{\text{eff,i}} = 2ND \frac{\Delta C_{\text{illumination},i}}{C_{\text{dark}}} \frac{W^2}{(W - \lambda_i^{th})^2 - x_i^2}. \tag{2}
\]

x_i is the depth at which the trap level E_{i,1} crosses the fermi-level E_F and can be computed with the following formula 1:

\[
x_i = W - \sqrt{\frac{2\epsilon_0\epsilon_s}{e^2N_D}} (E_F - E_{i,1}). \tag{3}
\]

Here, \epsilon_0 denotes the vacuum permittivity, \epsilon_s is the relative dielectric constant of the semiconductor and e is the elementary charge. E_F denotes the fermi-level position relative to the conduction band edge, while E_{i,1} is the thermodynamic charge transition level relative to conduction band edge for the corresponding trap level i. E_F can be calculated from the donor concentration determined under dark conditions. E_{i,1} is related to the photon energy E_{i,1}^{th} at which the onset of a photocapacitance step is observed in the SSPC spectra 1,3,4. One can assume that the following relation will hold 3,5:

\[
E_{i,1}^{th} \leq E_{i,1} < E_{i,1}^{th} + d_{FC}. \tag{4}
\]

d_{FC} denotes the so-called Franck-Condon shift 5. \lambda_i^{th} is connected to the re-filling of traps which have been emptied by optical excitation. Its value depends on the ratio between the rate c_i^{th} for electron capture by a certain trap i and the rate of optically-induced electron emission c_i^{th} for the same trap. The Superscript th describes thermal processes, while the Superscript o denotes optical processes. The following expression can be used for calculating \lambda_i^{th} 1:

\[
\lambda_i^{th} = LD\sqrt{2\ln\left(\frac{c_i^{th}}{c_i^{th}}\right)}. \tag{5}
\]

L_D denotes the Debye screening length and can be expressed as 1:

\[
L_D = \sqrt{\frac{\epsilon_0\epsilon_s k_B T}{e^2N_D}}. \tag{6}
\]

Here, k_B denotes Boltzmann’s constant.

The rate c_i^{th} for electrons being captured by a trap can be expressed as 1:

\[
c_i^{th} = n_0v_B\sigma_i^{th}. \tag{7}
\]
$n_0$ is the density of electrons that diffused into the depletion layer from outside the depletion layer. $N_D$ can be regarded as an upper bound for $n_0$. $v_{th}$ is the thermal velocity of electrons and can be calculated by $^1$:

$$v_{th} = \sqrt{\frac{3k_B T}{m_{eff}}}.$$  
(8)

Here, $m_{eff}$ denotes the effective mass of electrons.

The capture cross section $\sigma_{th}$ is specific for a trap. Often, a
energetic barrier $E_{B,i}$ needs to be overcome by the electrons to be captured, and hence the temperature-dependence of $\sigma_{i}^{th}$ can be expressed as $^{3,6}$:

$$\sigma_{i}^{th} \sim \exp \left( - \frac{E_{B,i}}{k_{B}T} \right). \quad (9)$$

The rate $e_{i}^{0}$ of optically-induced electron emission from traps can be expressed as $^{1,2}$:

$$e_{i}^{0} = \Phi \sigma_{i}^{0}. \quad (10)$$

Here, $\Phi$ denotes the photon flux at a certain photon energy and $\sigma_{i}^{0}$ is the cross section for photo-ionization or cross section for optical absorption associated with a specific trap $i$. At low temperatures and by using high photon fluxes, $\lambda_{i}^{0}$ should become comparatively small and can thus be neglected. Hence, the average trap concentration $N_{i}^{eff}$ can be calculated as $^{1}$:

$$N_{i}^{eff} = 2N_{D} \frac{\Delta C_{illumination,1}}{C_{dark}} \frac{W^{2}}{W^{2} - x_{i}^{2}}. \quad (11)$$

Often, one refers to the factor $W^{2}/(W^{2} - x_{i}^{2})$ as $\lambda$-correction $^{1}$. So far, it has been neglected that optically-induced emission of electrons from the valence band to empty trap levels can also occur. Such processes cause that only effective trap concentrations $N_{i}^{eff}$ are determined using SSPC measurements. The relation between the actual trap concentration $N_{i}$ and $N_{i}^{eff}$ is determined by the ratio between the rates of the optical emission processes:

$$N_{i}^{eff} = N_{i,1} \frac{e_{i}^{o,n}}{e_{i}^{o,n} + e_{i}^{o,p}}. \quad (12)$$

$e_{i}^{o,n}$ is the emission rate for the optically-induced emission of electrons from the trap level to the conduction band, while $e_{i}^{o,p}$ is the rate for optically-induced emission of electrons from the valence band to the trap level. $N_{i}^{eff}$ will always be lower than $N_{i,1}$. Generally, Eq. 12 needs to be modified to take into account that the carriers created in the conduction or valence band due to optically-induced electron emission need to be mobile enough to leave the depletion layer in order to contribute to the SSPC signal, and hence:

$$N_{i,1} = N_{i,1,i} \frac{e_{i}^{o,n} s_{p}}{e_{i}^{o,n} s_{n} + e_{i}^{o,p} s_{p}}. \quad (13)$$

Here, $s_{n}$ denotes the probability for an electron in the conduction band to leave the depletion layer while $s_{p}$ is the corresponding probability for a hole in the valence band to leave the depletion layer. In Ga$_2$O$_3$, holes are expected to form small polarons with very low mobilities $^{7}$, and hence one can expect $s_{p} \ll 1$ at low temperatures. If thermal equilibrium is not reached, traps can be filled with electrons at depth lower than the corresponding value for $x_{i}$. In such cases, Eq. 2 is an upper bound for the effective trap concentration, while Eq. 1 can still be seen as a lower bound for the effective trap concentration.

2. Large concentration of traps: $\frac{\Delta C_{illumination}}{C_{dark}} \approx 0.5$

If the overall concentration of electrically- and optically-active traps $N_{i}$ becomes large, i.e., when it becomes comparable to the donor concentration $N_{D}$, Eq. 1 does not hold anymore. The situation shown in Fig. 1 does still hold in principle, but because the overall trap concentration is large, the depletion layer width $W$ will change during illumination. Hence, the linear approximation used in Eq. 1 is not valid any longer $^{1}$. The case for large overall trap concentrations can be treated by explicitly solving the Schottky approximation for the steady-state due to illumination. If one assumes the Schottky approximation to be valid, the charge density $\rho$ for the situation depicted in Fig. 1 can be expressed as:

In the dark:

$$\rho = eN_{D}. \quad (14)$$

After steady-state is reached due to illumination with photons with a photon energy of $E_{1,1}^{o}$:

$$\rho = eN_{D} + eN_{i,1}^{eff}. \quad (15)$$

After steady-state is reached due to illumination with photons with a photon energy of $E_{1,2}^{o}$:

$$\rho = eN_{D} + eN_{i,1}^{eff} + eN_{i,2}^{eff}. \quad (16)$$

$N_{i,1}^{eff}$ represents the average of the effective trap concentration inside the probing volume, while $N_{D}$ represents the average donor concentration inside the probed volume. The following capacitance $C$ is measured at the applied reverse bias $V_{bias}$ in steady-state:

In the dark:

$$C_{dark} = \frac{A^{2}e_{0}e_{s}N_{D}}{2(V_{bias} - V_{th})}. \quad (17)$$

After steady-state is reached due to illumination with photons with a photon energy of $E_{1,1}^{o}$:

$$C_{illumination,1} = \sqrt{\frac{A^{2}e_{0}e_{s}N_{D}^{eff}}{2(V_{bias} - V_{th})}}. \quad (18)$$

After steady-state is reached due to illumination with photons with a photon energy of $E_{1,2}^{o}$:

$$C_{illumination,1+2} = \sqrt{\frac{A^{2}e_{0}e_{s}N_{D}^{eff} + N_{i,1}^{eff} + N_{i,2}^{eff}}{2(V_{bias} - V_{th})}}. \quad (19)$$

Here, $A$ is the area of the Schottky junction and $V_{th}$ denotes the built-in voltage. $C_{illumination,1+2}$ is described by:

$$C_{illumination,1+2} = C_{illumination,1} + C_{illumination,2}. \quad (20)$$

It is assumed, that the built-in voltage $V_{th}$ does not change due to illumination, and hence ionization of traps. This assumption is reasonable if
FIG. 2. (a) Illustration of Eq. 26 as conventional SSPC spectrum plotted as $\Delta C_{\text{illumination}}/C_{\text{dark}}$ over $E$ (lower panel) and as derivative SSPC spectra plotted as $d(\Delta C_{\text{illumination}}/C_{\text{dark}})/dE$ over $E$ (upper panel). Conventional SSPC spectra consist of peaks located at the step position seen in conventional SSPC spectra. Two optically- and electrically-active traps are assumed to be present with onset positions $E_{t,1}$ at 2.0 eV and $E_{t,2}$ at 3.5 eV. The individual step heights $\Delta C_{\text{illumination}}/C_{\text{dark}}$ can be either read from the conventional SSPC spectrum or found by integrating the peaks representing traps in the derivative SSPC spectrum. (b) Results for extracting the relative effective trap concentration $N_{\text{eff}}^{1,2}/N_D$ from $\Delta C_{\text{illumination}}/C_{\text{dark}}$ either by assuming $\Delta C_{\text{illumination}}/C_{\text{dark}} \approx 0.5$ (Eq. 11) or $\Delta C_{\text{illumination}}/C_{\text{dark}} \approx 0.5$ (Eq. 23). For $\Delta C_{\text{illumination}}/C_{\text{dark}} \approx 0.5$, $\Delta C_{\text{illumination}}$ has no influence on $N_{\text{eff}}^{1,2}/N_D$, while for $\Delta C_{\text{illumination}}/C_{\text{dark}} \approx 0.5$, a pronounced influence can be seen. $\Delta C_{\text{illumination}}/C_{\text{dark}} \approx 0.5$ and $\Delta C_{\text{illumination}}/C_{\text{dark}} \approx 0.5$ deviate from each other especially for larger $\Delta C_{\text{illumination}}/C_{\text{dark}}$. Here, the $\lambda$-correction (see Eq. 2) was not taken into account for the case of $\Delta C_{\text{illumination}}/C_{\text{dark}} \approx 0.5$.

- The trap concentration close to the surface of the semiconductor is not very large. If intrinsic defects are generated by implantation, one generally expects higher trap concentrations at a certain distance away from the semiconductor surface.

- The trap occupancy close to the surface is not changed by illumination as is the case if the applied reverse bias $V_{\text{bias}}$ is substantially larger than $E_{\text{g}}/e - V_{\text{bi}}$, because inversion is achieved at the surface.

Eq. 18 and 19 can be rewritten as

$$0 = \frac{\Delta C_{\text{illumination},1}}{C_{\text{dark}}} - \sqrt{1 + n_{t,1}} + 1. \quad (21)$$

and

$$0 = \frac{\Delta C_{\text{illumination},1+2}}{C_{\text{dark}}} - \sqrt{1 + n_{t,2}} + 1 \quad (22)$$

or

$$0 = \frac{\Delta C_{\text{illumination},1}}{C_{\text{dark}}} + \frac{\Delta C_{\text{illumination},2}}{C_{\text{dark}}} - \sqrt{1 + n_{t,2}} + 1. \quad (23)$$

$n_{t,1}$ stands for

$$n_{t,1} = \frac{N_{\text{eff}}^{1}}{N_D} \quad (24)$$

and

$$n_{t,2} = \frac{N_{\text{eff}}^{1} + N_{\text{eff}}^{2}}{N_D}. \quad (25)$$

Eq. 21 and 23 can be solved numerically for $n_{t,1}$ and $n_{t,2}$, respectively. $N_{\text{eff}}^{1}$ can be obtained from $n_{t,1}$ by inserting $N_D$, while $N_{\text{eff}}^{2}$ is obtained from $n_{t,1}$ by inserting $N_{\text{eff}}^{1}$ as well as $N_D$. If more than two traps are present, a similar scheme can be used to obtain all effective trap concentrations $N_{\text{eff}}^{1,2}$. Notably, in order to calculate the effective trap concentration $N_{\text{eff}}^{1,2}$, one needs to have obtained all effective trap concentrations $N_{\text{eff}}^{1,2}$ for traps with lower thresholds for optical ionization. This is an important difference to the case discussed in Sec. A 1 where individual trap concentrations can be obtained separately from each step $\Delta C_{\text{illumination}}/C_{\text{dark}}$ seen in the SSPC spectra.

Eq. 17, 18 and 19 imply that the depletion layer width will be different in the dark and for the two different photon energies the junction is illuminated with, especially if the effective trap concentrations $N_{\text{eff}}^{1,2}$ are comparable to $N_D$. Thus, the probing volume will change during the SSPC measurement itself.

The reasoning related to optical emission of electrons from the valence band to the trap levels captured in Eq. 13 also applies here.

Fig. 2 illustrates the differences related to determining the trap concentration using the approaches presented in Sec. A 1 and A 2.
B. Deconvolution of Steady-State Photocapitance Spectra

SSPC spectra as well as derivative SSPC spectra can be deconvoluted using the following empirically-motivated model:

\[
S(E) = 2N_0 \sum_i \frac{\Delta C_{\text{illumination}i}}{C_{\text{dark}}} \frac{1}{1 + \exp\left(-\frac{E - E_i}{\gamma}\right)},
\]

(26)

where the individual contributions \(i\) are described by sigmoidal functions. \(\Delta C_{\text{illumination}i}/C_{\text{dark}}\) represents the relative change in capacitance due to illumination for an individual contributions and is independent of \(E\). For a specific contribution \(i\), \(E_i\) describes the position of the onset of the SSPC signal and \(\gamma\) represents the steepness of the corresponding step. Fig. 3 illustrates how SSPC spectra as well as derivative SSPC spectra can be deconvoluted into contributions attributed to different trap levels. From the corresponding individual fitting contributions \(i\), parameters such as \(\Delta C_{\text{illumination}i}/C_{\text{dark}}\) can be derived (see also Fig. 2 (a)). These parameters can be used to calculate the trap concentration associated with the corresponding contribution \(i\).

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Supplementary Materials: First-principles calculations of structures, optical charge state transition levels and migration barriers of primary intrinsic defects in $\beta$-Ga$_2$O$_3$

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I. STRUCTURES OF PRIMARY INTRINSIC DEFECTS IN $\beta$-Ga$_2$O$_3$

Fig. 1 displays the relaxed structures calculated for Ga$_i$, O$_j$, V$_{O\text{K}}$ (K = I, II, III), V$_{Ga}$ (J = I, II) and V$_{Ga}^M$ (M = a, c, b)$^{1,2}$. Structures are displayed for the charge states most stable under the fermi-level position commonly found for HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films (typical donor concentration: $N_D = 6 \times 10^{16}$ cm$^{-3}$).

II. OPTICAL CHARGE STATE TRANSITION LEVELS OF PRIMARY INTRINSIC DEFECTS IN $\beta$-Ga$_2$O$_3$

The optical absorption related to a charge state transition of a defect is modeled as an electronic transition involving a ground state (Defect in charge state $q$ and charge carrier localized at or close to the defect) and an excited state (Defect in charge state $q \pm 1$ and delocalized charge carrier in the conduction or valence band) triggered by a photon with a photon energy $E$$^{3,7}$. The optical transition can either be allowed or forbidden. Whether an optical transition is allowed or forbidden will generally depend on the symmetry of the ground and excited state. However, if the optical transition is accompanied by pronounced lattice relaxation, the corresponding transition can be allowed regardless of the symmetry of the ground and excited state$^5$. In $\beta$-Ga$_2$O$_3$, many defect-related optical transitions are accompanied by large lattice relaxation as evidenced by the large values computed for $\Delta Q$ (see Tab. I)$^5$. The defect potential is assumed to be a $\delta$-function (short-range potential) for deep-level defects, whereas the potential associated with shallow defects is often approximated by a Coulomb potential (long-range potential)$^{3,7}$. The excited state is a continuum of states in the conduction or valence band, whereby the bands are typically assumed to be parabolic. The transition matrix element ($M$) connecting the ground and excited state is often considered to be constant$^{3,7}$. However, models for calculating defect-related optical absorption also exist, for example, for assuming $M$ to be proportional to the momentum of the electron in the excited state ($k$)$^4$.

Whereas some models only take electronic contributions into account$^5$, it has generally been shown that phonon contributions are important for the accurate determination of the line shape and onset of defect-related optical absorption cross section spectra$^{3,4}$. Phonons contribute in the following ways to optical absorption: (i) phonons are emitted during the absorption process, and (ii) ground and excited state posses vibrational sub-states which can be occupied at higher temperatures and contribute to the optical absorption. Notably, both (i) and (ii) will contribute to a broadening of the defect-related optical absorption cross section spectra and a corresponding shift of the absorption onset. Phonon emission (i) will contribute to the broadening already at 0 K, whereas the contribution of additional vibrational sub-states (ii) will become more pronounced with increasing temperature. For defect-related transitions accompanied by strong lattice relaxation, the phonons taking part in the optical absorption process are assumed to exhibit a single effective frequency for the ground state ($\omega_g$) and excited state ($\omega_e$), respectively (effective one-dimensional configuration coordinate model). Defect-related transitions associated with strong lattice relaxation suggest strong electron-phonon coupling, and are associated with large Huang-Rhys factors ($S$)$^3$. $S$ represents the number of phonons emitted during optical absorption$^3$.

Generally, defect-related optical absorption cross section spectra ($\alpha(E)$) can be estimated using$^{3,4,6,7}$:

$$\alpha(E) \sim \int_0^\infty B(E',E,E_{abs}) \frac{E^b}{(E+E_{abs})^d} dE'.$$ (1)

Here, it is assumed that $M$ is constant, and the bands are parabolic. The parameter $a$ is 1/2 for allowed optical transitions, and it is 3/2 for forbidden optical transitions, whereas the parameter $b$ is 2 for assuming a $\delta$-function for the defect potential, and it is 4 for using a Coulomb potential for the defect potential. $E_{abs}$ is the energy related to the vertical transition between the ground state and the excited state which can be obtained from configuration coordinate diagrams$^{3,10}$. $B(E',E,E_{abs})$ comprises phonon contributions, and can be calculated via$^{3,4,7}$:

$$B(E',E,E_{abs}) = \exp \left[ \frac{(E' + E_{abs} - E)^2}{\Gamma^2} \right].$$ (2)

Here, $\Gamma$ is a temperature-dependent factor, which is expressed by$^3$:

$$\Gamma = \Gamma_0 \sqrt{\coth \left( \frac{h \omega_g}{k_B T} \right)}.$$ (3)
Here, \( \hbar \) is Planck’s constant (\( h \)) divided by 2\( \pi \) and \( k_B \) is Boltzmann’s constant. \( \Gamma_0 \) is described by \(^3\):

\[
\Gamma_0 = \frac{\hbar}{2k_B} \sqrt{2d_{FC}\hbar \omega_0}.
\]

(4)

Here, \( d_{FC} \) is the Franck-Condon shift which can be calculated by \(^3\):

\[
d_{FC} = E_{abs} - E_{ZPL}.
\]

(5)

Kopylov \textit{et al.} also state a similar relation to Eq. 1 when assuming \( M \sim k \) and a defect potential represented by a \( \delta \)-function \(^4\):

\[
\alpha(E) \sim \int_0^\infty B(E', E, E_{abs}) \frac{E'^{3/2}}{E(E' + E_{abs})^2}dE',
\]

(6)

Fig. 2 displays graphical representations of Eq. 1 and 6 calculated for \( \text{Ga}_{i+}^{+2} \) in \( \beta\)-Ga\(_3\)O\(_2\) (optical transition involving \( \text{Ga}_i \) and the conduction band). Fig. 2 (a) shows a comparison of absorption cross section spectra calculated for 0 K when assuming different defect potentials and dependencies of \( M \) for allowed and forbidden optical transitions. Intervals are extracted that represent the spectral position of the absorption onset, and the extraction of these intervals is outlined in the main article, and specifically in Fig. 2 (a). The absorption cross section spectra expressed by Eq. 1 and 6 exhibit significantly different spectral shapes depending on the assumptions used for the calculations. All models include vibrational broadening, and exhibit significant absorption below \( E_{abs} \). Importantly, for our work, it is only relevant in what way the extracted onsets for optical absorption differ. The optical transition related to \( \text{Ga}_{i+}^{+2} \) can be expected to be allowed because the transition is accompanied by considerable lattice relaxation \(^8\). Moreover, all defect levels considered in this work, including \( \text{Ga}_{i+}^{+2} \), are deep-level defects \(^7\), and hence the defect potential should be represented well by a \( \delta \)-function \(^4\).\(^5\). As can be seen from Fig. 2 (a), the intervals extracted for the onset of optical absorption do not differ much whether one assumes \( M = \text{const.} \) or \( M \sim k \).

Fig. 2 (b) displays absorption cross section spectra calculated for \( \text{Ga}_{i+}^{+2} \) (optical transition involving \( \text{Ga}_i \) and the conduction band) at different temperatures assuming an allowed transition, a defect potential expressed by a \( \delta \)-function and \( M = \text{const.} \) which is the set of assumptions used in the main article. Notably, the optical absorption spectrum calculated at 0 K already shows a pronounced broadening, and considerable absorption below \( E_{abs} \), in contrast to what is expected when only the electronic contribution is taken into account (no vibrational broadening) \(^3\).\(^5\). Spectra calculated for 0 K and 120 K do not differ, and hence the interval for the absorption onsets are the same. Absorption cross section spectra calculated for 300 K show more broadening as compared to spectra computed at 0 K and 120 K. The main difference can, indeed, be seen in the spectral region where the onset of optical absorption occurs. The optical absorption cross section spectra calculated for \( \text{Ga}_{i+}^{+2} \) do not exhibit a strong temperature dependence in-between 0 K and 120 K because they effective phonon frequencies are 38 meV and 51 meV for the ground and excited state, respectively, and hence only a negligible fraction of excited vibrational sub-states will be occupied at 0 K (\( E_{\text{thermal}} = 0 \text{ meV} \)) and 120 K (\( E_{\text{thermal}} = 11 \text{ meV} \)). The weak temperature dependence of defect-related optical absorption cross section spectra can be expected to be a general feature in \( \beta\)-Ga\(_3\)O\(_2\) due to the large vibrational frequencies found for defects in \( \beta\)-Ga\(_3\)O\(_2\). In the main article, results for the optical absorption cross section spectra related to the primary intrinsic defects in \( \beta\)-Ga\(_3\)O\(_2\) were presented. Results were only shown for the energetically lowest optical charge state transition level for a specific primary intrinsic defect. The corresponding absorption is equivalent to the absorption onset expected for a specific defect. Moreover, results were only shown for processes associated with optically-induced electron emission, due to the low mobility expected for holes in \( \beta\)-Ga\(_3\)O\(_2\). All absorption cross section spectra shown in the following assumed allowed optical transitions, a defect potential represented by a \( \delta \)-potential and \( M = \text{const.} \). Moreover, only optical transitions involving defects and the conduction band are considered.

In Tab. I, the configuration coordinate (CC) diagram parameters calculated for all charge state transition levels of the primary intrinsic defects inside the band gap of \( \beta\)-Ga\(_3\)O\(_2\) are displayed. Parameters are also shown for a split-interstitial configuration for \( O \) (\( O^\text{split}_i \)) which is not as energetically favourable as \( O_i^2 \). Notably, both \( \text{Ga}_i^{+} \) and \( V_{\text{OK}}^0 \) (\( K = \text{I, II, III} \)) display negative-U behavior \(^10\) and the optical absorption related to \( \text{Ga}_{i+2}^{+2/3} \) and \( V_{\text{OK}}^{+2/3} \) (\( K = \text{I, II, III} \)) will be at lower energies compared to the optical absorption related to \( \text{Ga}_{i+}^{+2} \) and \( V_{\text{OK}}^{+2} \) (\( K = \text{I, II, III} \)), respectively. Thus, in SSPC measurements, no distinct signature can be expected for \( \text{Ga}_{i+2}^{+2/3} \) and \( V_{\text{OK}}^{+2/3} \) (\( K = \text{I, II, III} \)), but only for \( \text{Ga}_{i+}^{+2} \) and \( V_{\text{OK}}^{+2} \) (\( K = \text{I, II, III} \)). However, the signature related to \( \text{Ga}_{i+}^{+} \) and \( V_{\text{OK}}^{+} \) (\( K = \text{I, II, III} \)) is then associated with the optically-induced emission of two electrons.

Fig. 3 - 9 show graphical representations for all calculated absorption spectra associated with the primary intrinsic defects. Moreover, versions of Fig. 5 (a) and 6 in the main article are shown for comparisons between recorded SSPC spectra and results from first-principles calculations for all charge state transition levels associated with primary intrinsic defects which display sub-band gap absorption. The extraction of the intervals used for predicting the onset of defect-related optical absorption is outlined in the main article, and specifically in Fig. 2 (a).

After He implantation of HVPE-grown \( \beta\)-Ga\(_3\)O\(_2\) thin-films at 120 K, we expect the presence of \( \text{Ga}_i \), \( V_{\text{Gal}}^J \) (\( J = \text{I, II} \)) and \( V_{\text{OK}}^0 \) (\( K = \text{I, II, III} \)) based on the calculated migration barriers in our main article as well as in the literature \(^2\).\(^9\).\(^11\). Considering all charge state transition levels of the primary intrinsic defects in \( \beta\)-Ga\(_3\)O\(_2\), it is evident that only \( \text{Ga}_{i+2}^{+2} \) and \( V_{\text{Gal}}^{+2} \) are viable candidates for the SSPC signature labeled as \( Z_3 \). With respect to \( T_0 \), \( V_{\text{Gal}}^{3/2} \) and \( V_{\text{OK}}^{3/2} \) (\( K = \text{I, II, III} \)) are suitable candidates. Moreover, the calculated signatures of \( V_{\text{Gal}}^{2/2} \) and \( V_{\text{Gal}}^{0/0} \) (\( J = \text{I, II} \)) are within the photon energy region where \( T_0 \)
is expected, while several charge state transition levels related to primary intrinsic defects may contribute to $T_6$.

After exposing He implanted HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films to room temperature, changes in the SSPC spectra are seen, and particularly the annihilation of $V_{GaJ} (J = I, II)$ and $Ga_i$ as well as the formation of $V_{GaM} (M = a, b, c)$ can be expected. Charge state transitions related to $V_{GaM} (M = a, b, c)$ may contribute to $T_4$ and $T_6$.

III. MIGRATION BARRIERS OF PRIMARY INTRINSIC DEFECTS IN $\beta$-Ga$_2$O$_3$

In the main article, we presented computational results for the migration barriers of primary intrinsic defects in $\beta$-Ga$_2$O$_3$ which were calculated using the PBEsol functional. The corresponding barriers were evaluated utilizing the HSE functional to assess the differences. Here, we present more information regarding those computational results. Fig. 10 shows the results obtained for the transformation/migration of a selection of $V_{GaJ}$ defects ($V_{GaJ} (J = I, II)$ and $V_{GaM} (M = a, c, b)$), while Fig. 11 displays the corresponding results for $Ga_i$ and $O_i$. For some migration paths, results obtained using the HSE and PBEsol functionals are shown to illustrate the differences expected when using the different functionals in first-principles calculations. Generally, calculations based using the PBEsol functional yield lower migration barriers compared to HSE-based computations. Thus, migration barriers obtained using the PBEsol functional can be seen as lower bounds.

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6 christian.zimmermann@fys.uio.no
8 J. L. Lyons, A. Alkauskas, A. Janotti, and C. G. Van de Walle, physica status solidi (b) 252, 900 (2015).
FIG. 1: Relaxed structures of various primary intrinsic defects in $\beta$-Ga$_2$O$_3$. Results are shown for the charge states most stable under the fermi-level position commonly found for HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films.

FIG. 2: Absorption cross section spectra calculated for Ga$^{+/+2}$ using Eq. 1 and 6. The corresponding value for $E_{\text{abs}}$ is stated in Tab. I. The bars represent the interval defined by $E_{\text{abs}}$ and $E (\alpha_{\text{max}}/1000)$. The position of $E (\alpha_{\text{max}}/1000)$ is also indicated. $\alpha_{\text{max}}$ denotes the maximum value of the absorption cross section. $E (\alpha_{\text{max}}/1000)$ is defined as the photon energy where the absorption cross section decreased by three orders of magnitude as compared to $\alpha_{\text{max}}$, whereas $E (\alpha_{\text{max}}/100)$ denotes the photon energy where the absorption cross section decreased by two orders of magnitude as compared to $\alpha_{\text{max}}$. (a) The absorption cross section spectra were calculated for 0 K for allowed (upper panel) and forbidden optical transitions (lower panel) using different assumptions regarding the defect potential and $M$. All spectra are presented on a logarithmic scale. (b) The absorption cross section spectra were calculated for different temperatures for allowed optical transitions assuming a defect potential represented by a $\delta$-function and $M = \text{constant}$. The spectra shown on the upper panel are presented on a linear scale, whereas the spectra on the lower panel are displayed on a logarithmic scale.
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TABLE I: Summary of the CC diagram parameters for various primary intrinsic defects obtained from hybrid-functional calculations. Calculations were performed for all charge state transitions with charge state transition levels within the band gap of $\beta$-Ga$_2$O$_3$. Only charge state transitions involving the defects and the conduction band were considered. Notably, both Ga$_i$ and V$_{OK}$ ($K = I, II, III$) display negative-U behavior. The parameters $E_{ZPL}$, $E_{abs}$, and $\Delta Q$ are defined in Fig. 2 (a) of the main article. $\alpha_{max}$ denotes the maximum value of the absorption cross section. $E(\alpha_{max}/1000)$ is defined as the photon energy where the absorption cross section decreased by three orders of magnitude as compared to $\alpha_{max}$, whereas $E(\alpha_{max}/1000)$ denotes the photon energy where the absorption cross section decreased by two orders of magnitude as compared to $\alpha_{max}$.
FIG. 3: (a) Absorption cross section spectra calculated for charge state transitions related to Ga\textsuperscript{i}, O\textsuperscript{i} and O\textsuperscript{split}\textsuperscript{i}. The bars represent the interval defined by $E_{\text{abs}}$ and $E\left(\alpha_{\text{max}}/1000\right)$ for the corresponding transition. The position of $E\left(\alpha_{\text{max}}/100\right)$ is also indicated. $\alpha_{\text{max}}$ denotes the maximum value of the absorption cross section. $E\left(\alpha_{\text{max}}/100\right)$ is defined as the photon energy where the absorption cross section decreased by three orders of magnitude as compared to $\alpha_{\text{max}}$, whereas $E\left(\alpha_{\text{max}}/10\right)$ denotes the photon energy where the absorption cross section decreased by two orders of magnitude as compared to $\alpha_{\text{max}}$. (b) Results of SSPC measurements recorded on a HVPE-grown $\beta$-Ga\textsubscript{2}O\textsubscript{3} thin-film before and after subsequent implantations with He ions at 120 K. The results are displayed as derivative SSPC spectra (upper panel) and as conventional SSPC spectra (lower panel). The legend states the accumulated implantation fluence $\Phi_{\text{tot}}$ for the corresponding data set. The onset positions observed in the SSPC spectra are marked with black vertical arrows. The vertical bars indicate where computations based on hybrid-functionals predict the optical absorption associated with Ga\textsuperscript{i}, O\textsuperscript{i} and O\textsuperscript{split}\textsuperscript{i} to occur.
FIG. 4: (a) Absorption cross section spectra calculated for charge state transitions related to V$_{GaI}$. The bars represent the interval defined by $E_{\text{abs}}$ and $E (\alpha_{\text{max}}/1000)$ for the corresponding transition. The position of $E (\alpha_{\text{max}}/1000)$ is also indicated. $\alpha_{\text{max}}$ denotes the maximum value of the absorption cross section. $E (\alpha_{\text{max}}/1000)$ is defined as the photon energy where the absorption cross section decreased by three orders of magnitude as compared to $\alpha_{\text{max}}$, whereas $E (\alpha_{\text{max}}/100)$ denotes the photon energy where the absorption cross section decreased by two orders of magnitude as compared to $\alpha_{\text{max}}$. (b) Results of SSPC measurements recorded on a HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film before and after subsequent implantations with He ions at 120 K. The results are displayed as derivative SSPC spectra (upper panel) and as conventional SSPC spectra (lower panel). The legend states the accumulated implantation fluence $\Phi_{\text{tot}}$ for the corresponding data set. The onset positions observed in the SSPC spectra are marked with black vertical arrows. The vertical bars indicate where computations based on hybrid-functionals predict the optical absorption associated with V$_{GaI}$ to occur.
FIG. 5: (a) Absorption cross section spectra calculated for charge state transitions related to V_{GaII}. The bars represent the interval defined by $E_{\text{abs}}$ and $E (\alpha_{\text{max}} / 1000)$ for the corresponding transition. The position of $E (\alpha_{\text{max}} / 100)$ is also indicated. $\alpha_{\text{max}}$ denotes the maximum value of the absorption cross section. $E (\alpha_{\text{max}} / 1000)$ is defined as the photon energy where the absorption cross section decreased by three orders of magnitude as compared to $\alpha_{\text{max}}$, whereas $E (\alpha_{\text{max}} / 100)$ denotes the photon energy where the absorption cross section decreased by two orders of magnitude as compared to $\alpha_{\text{max}}$. (b) Results of SSPC measurements recorded on a HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film before and after subsequent implantations with He ions at 120 K. The results are displayed as derivative SSPC spectra (upper panel) and as conventional SSPC spectra (lower panel). The legend states the accumulated implantation fluence $\Phi_{\text{tot}}$ for the corresponding data set. The onset positions observed in the SSPC spectra are marked with black vertical arrows. The vertical bars indicate where computations based on hybrid-functionals predict the optical absorption associated with V_{GaII} to occur.
FIG. 6: (a) Absorption cross section spectra calculated for charge state transitions related to $V_{OK}(K = I, II, III)$. $V_{OK}(K = I, II, III)$ are defects exhibiting negative-U behavior, and the charge state transitions levels related to $V_{OK}^{+/2}(K = I, II, III)$ are not expected to be seen in SSPC measurements. The bars represent the interval defined by $E_{\text{abs}}$ and $E\left(\alpha_{\text{max}}/100\right)$ for the corresponding transition. The position of $E\left(\alpha_{\text{max}}/1000\right)$ is also indicated. $\alpha_{\text{max}}$ denotes the maximum value of the absorption cross section. $E\left(\alpha_{\text{max}}/1000\right)$ is defined as the photon energy where the absorption cross section decreased by three orders of magnitude as compared to $\alpha_{\text{max}}$, whereas $E\left(\alpha_{\text{max}}/100\right)$ denotes the photon energy where the absorption cross section decreased by two orders of magnitude as compared to $\alpha_{\text{max}}$. (b) Results of SSPC measurements recorded on a HVPE-grown $\beta$-$Ga_2O_3$ thin-film before and after subsequent implantations with He ions at 120 K. The results are displayed as derivative SSPC spectra (upper panel) and as conventional SSPC spectra (lower panel). The legend states the accumulated implantation fluence $\Phi_{\text{tot}}$ for the corresponding data set. The onset positions observed in the SSPC spectra are marked with black vertical arrows. The vertical bars indicate where computations based on hybrid-functionals predict the optical absorption associated with $V_{OK}(K = I, II, III)$ to occur.
FIG. 7: (a) Absorption cross section spectra calculated for charge state transitions related to \( V_{Ga}^{\alpha} \). The bars represent the interval defined by \( E_{abs} \) and \( E (\alpha_{max}/1000) \) for the corresponding transition. The position of \( E (\alpha_{max}/1000) \) is also indicated. \( \alpha_{max} \) denotes the maximum value of the absorption cross section. \( E (\alpha_{max}/1000) \) is defined as the photon energy where the absorption cross section decreased by three orders of magnitude as compared to \( \alpha_{max} \), whereas \( E (\alpha_{max}/100) \) denotes the photon energy where the absorption cross section decreased by two orders of magnitude as compared to \( \alpha_{max} \). (b) SSPC spectra recorded on a HVPE-grown \( \beta\)-Ga_2O_3 thin-film before and after He implantation at 120 K with a fluence of \( 1.25 \times 10^{11} \) cm\(^{-2}\) as well as after a subsequent annealing at 300 K for ca. 5 min. The results are displayed as derivative SSPC spectra (upper panel) and as conventional SSPC spectra (lower panel). A panel is shown with bars representing the computational prediction of optical signatures related to the absorption associated with \( V_{Ga}^{\alpha} \).
FIG. 8: (a) Absorption cross section spectra calculated for charge state transitions related to $V_{Ga}^{ib}$. The bars represent the interval defined by $E_{abs}$ and $E (\alpha_{max}/1000)$ for the corresponding transition. The position of $E (\alpha_{max}/100)$ is also indicated. $\alpha_{max}$ denotes the maximum value of the absorption cross section. $E (\alpha_{max}/1000)$ is defined as the photon energy where the absorption cross section decreased by three orders of magnitude as compared to $\alpha_{max}$, whereas $E (\alpha_{max}/100)$ denotes the photon energy where the absorption cross section decreased by two orders of magnitude as compared to $\alpha_{max}$. (b) SSPC spectra recorded on a HVPE-grown $\beta$-$Ga_2O_3$ thin-film before and after He implantation at 120 K with a fluence of $1.25 \times 10^{11}$ cm$^{-2}$ as well as after a subsequent annealing at 300 K for ca. 5 min. The results are displayed as derivative SSPC spectra (upper panel) and as conventional SSPC spectra (lower panel). A panel is shown with bars representing the computational prediction of optical signatures related to the absorption associated with $V_{Ga}^{ib}$. 
FIG. 9: (a) Absorption cross section spectra calculated for charge state transitions related to $V_{Ga}^{\text{ic}}$. The bars represent the interval defined by $E_{\text{abs}}$ and $E\left(\alpha_{\text{max}}/100\right)$ for the corresponding transition. The position of $E\left(\alpha_{\text{max}}/100\right)$ is also indicated. $\alpha_{\text{max}}$ denotes the maximum value of the absorption cross section. $E\left(\alpha_{\text{max}}/100\right)$ is defined as the photon energy where the absorption cross section decreased by three orders of magnitude as compared to $\alpha_{\text{max}}$, whereas $E\left(\alpha_{\text{max}}/100\right)$ denotes the photon energy where the absorption cross section decreased by two orders of magnitude as compared to $\alpha_{\text{max}}$. (b) SSPC spectra recorded on a HVPE-grown $\beta$-$Ga_2O_3$ thin-film before and after He implantation at 120 K with a fluence of $1.25 \times 10^{11}$ cm$^{-2}$ as well as after a subsequent annealing at 300 K for ca. 5 min. The results are displayed as derivative SSPC spectra (upper panel) and as conventional SSPC spectra (lower panel). A panel is shown with bars representing the computational prediction of optical signatures related to the absorption associated with $V_{Ga}^{\text{ic}}$.

FIG. 10: Paths computed for the transformation/migration of a selection of $V_{Ga}$ defects ($V_{GaJ}^I (J = I, II)$ and $V_{GaM}^M (M = a, c, b)$) in $\beta$-$Ga_2O_3$. Results are shown using the PBEsol as well as HSE functional.
FIG. 11: Migration paths computed for (a), (b) Ga\textsubscript{i} and (c) O\textsubscript{i} in β-Ga\textsubscript{2}O\textsubscript{3}. In (a), results are shown using the PBEsol as well as HSE functional, while in (b) and (c) the migration paths are only shown for PBEsol-based computations.
Combining Steady-state Photo-capacitance Spectra with First-principles Calculations: The Case of Fe and Ti in $\beta$-Ga$_2$O$_3$

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Combining Steady-state Photo-capacitance Spectra with First-principles Calculations: The Case of Fe and Ti in $\beta$-Ga$_2$O$_3$

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Abstract. In this study, we demonstrate an approach to identify defects in wide band gap semiconductors by comparing accumulatively-recorded derivative steady-state photo-capacitance (SSPC) spectra to simulations using results from first-principles calculations. Specifically, we present a method to simulate SSPC spectra which adopts inputs both from first-principles calculations and the experimental conditions. The applicability of the developed method is demonstrated using the cases of substitutional Fe (Fe$_{Ga}$) and Ti (Ti$_{Ga}$) defects in $\beta$-Ga$_2$O$_3$. Using deep-level transient spectroscopy, we identify defect levels associated with Fe$_{Ga}^{0/-}$ ($E_A = 0.66$ eV), Fe$_{Ga}^{0/-}$ ($E_A = 0.79$ eV) and Ti$_{Ga}^{+/-0}$ ($E_A = 1.03$ eV) in the $\beta$-Ga$_2$O$_3$ samples studied here. Accumulatively-recorded SSPC spectra reveal several defect levels labeled $T_{1,6}^{EPG}$ with onsets for optical absorption between 1.5 eV and 4.3 eV. The signature $T_{1,6}^{EPG}$ consists of several overlapping defect signatures, and is identified as being related to Fe$_{Ga}^{0/-}$, Fe$_{Ga}^{0/-}$ and Ti$_{Ga}^{+/-0}$ by comparing measured and simulated accumulatively-recorded derivative SSPC spectra.

1. Introduction

Defects have a pronounced influence on the electrical and optical properties of semiconductors, and are fundamentally important in determining the expected performance of a given semiconductor device. Often, defects are studied by using their charge state transition levels (defect levels) as fingerprints, while their unambiguous identification requires the simultaneous utilization of a number of techniques [1, 2]. In recent years, many wide band gap semiconductors, such as monocrystalline gallium sesquioxide ($\beta$-Ga$_2$O$_3$), have attracted considerable research interest due to promising properties for applications ranging from photo-detectors to power electronics [3, 4, 5, 6]. It is, however, a particular challenge to study the electronic properties of defect levels in wide band gap semiconductors.

A widely-used technique to study defect levels in semiconductors is deep-level transient spectroscopy (DLTS) [1, 7], but the accessible part of the band gap is typically limited by the temperature range used for the measurement because DLTS probes defect levels by measuring the thermally-induced emission of charge carriers from defects (traps). For example, in the case of $\beta$-Ga$_2$O$_3$, defect levels up to 1.4 eV below the conduction band edge can typically be observed using DLTS [8, 9]. Steady-state photo-capacitance (SSPC) measurements and related techniques [1, 10] measure the optically-induced emission of charge carriers from traps, and are complimentary to DLTS measurements. Using suitable optical excitation, SSPC measurements can detect defect levels throughout the whole band gap of wide band gap semiconductors. Indeed, SSPC measurements and their transient counter-part deep-level optical spectroscopy have been used to reveal several deep level defects in $\beta$-Ga$_2$O$_3$ [11, 12, 13, 14, 15, 16, 17, 18]. SSPC measurements, as well as DLTS measurements, also provide the concentration of the traps associated with the observed defect levels. This enables a wide range of study designs suitable for identifying extrinsic as well as intrinsic defects.

First-principles calculations for defect levels in semiconductors have seen significant advancements in recent years, for example, by the introduction of hybrid-functionalities, such as the Heyd-Scuseria-Ernzerhof (HSE) functionals [19] which yield an improved description of the atomic and electronic structure of semiconductors, as well as the degree of charge localization at defects [20]. These advances have bridged the gap between calculated defect levels and defect levels observed by techniques like DLTS [21, 22]. For $\beta$-Ga$_2$O$_3$, specific defect levels observed by DLTS have been identified and assigned to Fe$_{\text{GaI}}$ (substitutional Fe on a tetrahedral site), Fe$_{\text{GaII}}$ (substitutional Fe on an octahedral Ga site) and Ti$_{\text{GaII}}$ (substitutional Ti on an octahedral Ga site) by correlating computational and experimental results [8, 23]. Results from first-principles calculations can also be used to correlate signatures seen in SSPC measurements to specific defects present in a material. Specifically, the optical absorption associated with a defect level can be predicted [22, 24]. However, a clear and corroborated methodology to perform such comparisons is still missing. Particularly, the effect of experimental parameters on the spectral position of signatures seen in SSPC measurements should be taken into account.

Here, we report on a methodology to simulate SSPC spectra from results of first-principles calculations, enabling a comparison between first-principles calculations and SSPC measurements. Fe- and Ti-related charge state transition levels which have recently been identified by DLTS in $\beta$-Ga$_2$O$_3$ [8, 23] are used to verify the validity of our method, and thereby, we also identify the corresponding SSPC signatures related to Fe$_{\text{GaI}}$, Fe$_{\text{GaII}}$ and Ti$_{\text{GaII}}$ in $\beta$-Ga$_2$O$_3$.

2. Experimental Details

Bulk $\beta$-Ga$_2$O$_3$ crystals grown by edge-defined film-fed growth (EFG) [25, 26] with a surface orientation of (-201) were obtained from Tamura Corporation. Samples measuring approximately ($5 \times 5$) mm$^2$ were cut with a laser cutter. All samples were prepared for DLTS and SSPC measurements by depositing metal contacts using e-beam evaporation. The samples were cleaned inside an ultrasonic bath using acetone, isopropanol and de-ionized water prior to the metal deposition. Stacks of Ti and Al with a thickness of 10 nm and 120 nm, respectively, were deposited on the back side and used as Ohmic contacts, while front-side Ni contacts were used as semi-transparent Schottky contacts [27, 28]. First, Ni contacts with a thickness of 10 nm were deposited using a shadow mask with diameters of 300 µm, 600 µm and 900 µm. Subsequently, another layer of Ni with a thickness of 150 nm was deposited using a shadow mask with circular openings (diameter = 300 µm) which aligns with the first depo-
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sition such that the thick Ni pads are on top of the semi-transparent Ni pads. The thick Ni parts enable mechanical stability for wire-bonding. Additionally, Pd pads were deposited on top of the thick Ni part to further improve the wire-bonding.

Capacitance-Voltage (CV) and Current-Voltage (IV) measurements were performed using a Keithley 6487 picoammeter/voltage source and either a HP4280 A or Boonton 7200 capacitance meter, respectively. CV measurements were performed at a probing frequency of 1 MHz. CV and IV measurements were performed to ensure device characteristics suitable for DLTS and SSPC measurements as well as to determine the donor concentration \( N_D \) of the \( \beta'-Ga_2O_3 \) samples [1]. For analyzing CV measurements, a relative static dielectric constant \( (\epsilon_r) \) of 10.2 was assumed for \( \beta'-Ga_2O_3 \) [29].

DLTS measurements were performed using a setup described in detail in [23, 30]. The setup allows for DLTS measurements in the temperature range from 150 K to 680 K. DLTS spectra were constructed using a GS4 filter [31]. In order to obtain parameters describing traps, such as trap concentration \( (N_t) \), activation energy \( (E_A) \) and apparent capture cross section \( (\sigma_{na}) \), DLTS spectra were simulated using a python-based script, where the \( \lambda \)-correction was employed to obtain \( N_t \) [32, 1]. \( E_A \) is the sum of the classical activation energy for carrier capture \( (E_b) \) and the thermodynamic charge-state transition level \[1, 21\]. \( \sigma_{na} \) depends both on \( E_b \) and a prefactor \( (\sigma_0) \) which is, for example, dependent on the charge state of the trap \[21, 33, 34, 35, 36, 37\]. For the samples studied here, larger values for \( \sigma_0 \) can be expected for positively-charged traps as compared to neutral traps, whereas neutral traps are expected to exhibit larger values of \( \sigma_0 \) than negatively-charged traps \[34, 37\]. More information regarding the simulation of DLTS spectra and the \( \lambda \)-correction can be found in the Appendix.

SSPC measurements were performed with a setup described in detail in [28]. The photo-capacitance \( (C_{illum}) \) of the samples is recorded after illuminating the junction at a photon energy \( E \) for a time \( t_{illum} \), whereby \( t_{illum} \) between 30 s and 1200 s were employed for this study. \( C_{illum} \) is referenced to the capacitance of the junction in dark \( (C_{dark}) \). All capacitance values were measured at a fixed external bias \( (V_{ext}) \) of \(-8 \) V. SSPC spectra \( S(E, t_{illum}) \) were recorded by subsequently measuring \( C_{illum}(E, t_{illum}) \) at different \( E \) after \( t_{illum} \). Measurements were performed using steps \( (\Delta E) \) of 20 meV in between subsequent \( E \). The spectral distribution of the optical excitation represented by the photon flux \( (\Phi (E)) \) was determined using a calibrated thermal power meter placed at the sample position, and is shown in figure 1. Typical photon fluxes of \( 1 \times 10^{17} \text{m}^{-2}\text{s}^{-1} \) in the UV and \( 1 \times 10^{19} \text{m}^{-2}\text{s}^{-1} \) in the visible part of the spectrum were found. SSPC spectra were recorded at 120 K.

SSPC measurements can be performed accumulatively [28] or non-accumulatively [1, 13]. For the accumulative SSPC measurements conducted here, \( S(E, t_{illum}) \) was recorded at subsequent \( E \) without changing \( V_{ext} \), and the measurements were exclusively performed in ascending order of \( E \). In contrast, in non-accumulative SSPC measurements, \( V_{ext} \) is set to 0 V in between measurements at subsequent \( E \).

3. Methodology

3.1. First-principles Calculations based on Hybrid-Functionals

A detailed description of the first-principles methodology and computational details can be found in [23], thus only a brief summary is given here. All calculations were performed using the Heyd-Scuseria-Ernzerhof [19] range-separated hybrid functional, as implemented in the vasp code [38], with the fraction of screened Hartree-Fock exchange set to \( \alpha = 0.33 \). Defect calculations were performed with 160-atom supercells, a plane-wave energy cutoff of 500 eV and a single \( k \)-point at \((1/4, 1/4, 1/4)\). To remedy the spurious supercell-size dependence of thermodynamic and vertical charge state transition energies, we used the correction schemes of Freysoldt, Neugebauer and van de Walle [39, 40], and Gake, Kumagai, Freysoldt and Oba [41], respectively.

The optical properties of \( \text{FeGaI}_2 \), \( \text{FeGaII}_2 \) and \( \text{TiGaII}_2 \) were investigated within the framework of the one-dimensional configuration coordinate (CC) model [20, 22, 42, 43]. CC diagrams were constructed using model parameters from the hybrid-functional calculations, namely the change in configuration coordinate \( \Delta Q \), the zero-phonon line (ZPL) energy \( E_{ZPL} \), and the effective vibrational frequencies \( \Omega_g \) and \( \Omega_e \) in the ground \((g)\) and excited \((e)\) state, respectively. In the Franck-Condon (FC) approximation, optical transitions are vertical with no change in configuration coordinate. Classical emission and absorption energies can then be defined as \( E_{em} = E_{ZPL} - \beta_k \) and
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\[ E_{\text{abs}} = E_{\text{ZPL}} + d_{\text{FC}}^e, \]

respectively, where \( d_{\text{FC}}^e \) and \( d_{\text{FC}}^o \) are the so-called FC shifts. The normalized absorption cross-section \( \sigma_{\text{norm}}^e(E) \), including temperature-dependent vibrational broadening, can be simulated using the effective vibrational frequencies, as outlined in [22, 24].

\( \sigma_{\text{norm}}^e(E) \) is related to the optically-induced emission of electrons from a defect, while \( \sigma_{\text{p,norm}}^o(E) \) is related to the optically-induced emission of holes. Thus, \( \sigma_{\text{norm}}^e(E) \) is related to processes involving electrons and the conduction band edge, and \( \sigma_{\text{p,norm}}^o(E) \) is associated with processes involving electrons and the valence band edge.

### 3.2. Simulation of Steady-State Photo-capacitance Spectra

The SPC signal \( S(E, t_{\text{illum}}) \) is usually presented as [1, 10]:

\[
S(E, t_{\text{illum}}) = 2 \frac{C_{\text{illum}}(E, t_{\text{illum}}) - C_{\text{dark}}}{C_{\text{dark}}} N_D
\]

\[ = 2 \frac{\Delta C_{\text{illum}}(E, t_{\text{illum}})}{C_{\text{dark}}} N_D = N_{\text{tr eff}}^*(E, t_{\text{illum}}). \quad (1) \]

Here, \( \Delta C_{\text{illum}}(E, t_{\text{illum}}) \) denotes the change in (photo-)capacitance during illumination for \( t_{\text{illum}} \) at \( E \), and \( C_{\text{dark}} \) represents the capacitance of the junction measured in dark. \( N_{\text{tr eff}}^*(E, t_{\text{illum}}) \) is the change in the concentration of ionized traps inside the probing volume due to illumination. However the probing volume will usually not be equal to the volume of the space-charge region [1, 28]. Moreover, equation 1 assumes \( N_D \ll N_{\text{tr eff}}^* \) to be valid.

\( S(E, t_{\text{illum}}) \) can be expressed with the following empirically-motivated formula [28]:

\[
S(E, t_{\text{illum}}) = 2N_D \sum_i \frac{\Delta C_{\text{illum},i}}{C_{\text{dark}}} \frac{1}{1 + \exp \left( \frac{E - E_i}{\gamma_i} \right)} \quad (2)
\]

where \( E_i \) denotes the onset of optical absorption related to trap i, and \( \gamma_i \) describes the steepness of the corresponding step in \( S(E, t_{\text{illum}}) \). \( \Delta C_{\text{illum},i} \) is the (photo-)capacitance change related to photo-excitation of trap i. \( \Delta C_{\text{illum},i} \) are larger than zero for optically-induced electron emission, and are smaller than zero for optically-induced hole emission. Results of SPC measurements can also be presented as derivative SPC spectra \( dS(E, t_{\text{illum}})/dE \) [10, 28, 44]. Peaks at \( E_i \) in \( dS(E, t_{\text{illum}})/dE \) will represent trap i [28].

Notably, the optically-induced emission of a charge carrier only contributes to the recorded \( S(E, t_{\text{illum}}) \) if the charge carrier is swept out of the space-charge region by the electrical field present in the space-charge region. For many semiconducting oxides, self-trapped holes or electrons can form which may not be sufficiently mobile to leave the space-charge region [45]. In \( \beta-\text{Ga}_2\text{O}_3 \), self-trapped holes are expected to form with very low mobility below room temperature [45, 46].

In steady-state, i.e., for sufficiently long \( t_{\text{illum}} \), \( S(E, t_{\text{illum}}) \) will be constant, and equal to \( N_{\text{tr eff}}^s \), representing the steady-state concentration of ionized traps inside the probing volume. \( N_{\text{tr eff}}^s \) is a sum of all \( N_{\text{tr eff},i}^s \), representing the concentration of ionized traps i in steady-state. If optically-induced hole emission can be neglected, \( N_{\text{tr i}} \) can be computed from \( N_{\text{tr eff},i}^s \) via [1]:

\[
N_{\text{tr i}} = N_{\text{tr eff},i}^s \frac{W^2}{x_i^2 - W_{o,i}^2} = cN_{\text{tr eff},i}^s. \quad (3)
\]

\( N_{\text{tr i}} \) is the actual concentration of trap i. \( W \) is the depth of the depletion layer at \( V_{\text{ext}} \), \( x_i \) is the depth where the thermodynamic charge state transition level of trap i \( (E_i^{(b)}) \) crosses the Fermi level \( E_F \), and \( W_{o,i} \) represent the fact that electrons from outside the space-charge region can penetrate into the space-charge region and refill photo-ionized traps. The correction factor \( c \) represents that during SPC measurements traps are only photo-ionized in part of the volume of the space-charge region, and will always be larger than 1. Notably, \( W_{o,i} \) will be smaller for a trap for which electron capture is more likely [1]. Here, \( W_{o,i} \) can be expected to be reduced for donor defects as compared to acceptor defects [34, 37]. Smaller values for \( W_{o,i} \) suggest that traps are photo-ionized in a smaller volume inside the space-charge region, and hence the correction factor \( c \) will be larger. If hole emission cannot be neglected, an additional factor representing the relative magnitude of optically-induced electron emission as compared to optically-induced hole emission needs to be added to the right hand side of equation 3 [10]. For non-ideal junctions, further corrections in addition to equation 3 are necessary due to leakage currents inside the space-charge region [47]. If leakage currents are present, corrections based on equation 3 will underestimate the actual trap concentration. Generally, traps with larger capture cross-section for electrons will capture more electrons from the leakage current, and hence a larger deviation from equation 3 can be expected [47].

In order to obtain computational results which can be compared to measured \( S(E, t_{\text{illum}}) \), one needs to compute \( N_{\text{tr eff}}^s \) (see equation 1). The time-evolution of \( N_{\text{tr eff}}^s \) is described by the following differential equation [1, 10]:

\[
\frac{dN_{\text{tr eff}}^s}{dt} = \sigma_p^o \Phi N_{\text{tr eff}}^s - \sigma_p^o \Phi N_{\text{tr eff}}^s. \quad (4)
\]

Here, \( N_{\text{tr eff}}^s \) denotes the concentration of traps occupied with electrons. \( \sigma_p^o \) are the absorption cross-sections related to the optically-induced emission of electrons \( (i = n) \) or holes \( (i = p) \) from a trap [22]. Often,
optically-induced hole emission can be neglected, and one obtains:
\[
\frac{dN^*_{\text{tr,eff}}}{dt} = \sigma_o^p \Phi N_{\text{tr,eff}}.
\] (5)

Here, \(N_{\text{tr,eff}}\) is equal to \(N_{\text{accum}} - N^*_{\text{tr,eff}}\). Equation 5 can be solved for the experimental conditions encountered in accumulative or non-accumulative SSPC measurements. In the following, \(E^k\) denotes a specific photon energy used for illumination during a SSPC measurement. The \(E^k\) are ordered in ascending order, and hence \(E^k > E^{k-1}\) is valid. For accumulative SSPC measurements, one obtains the following expression for equation 1 when solving equation 5:
\[
S_{\text{acc}} (E^k, t_{\text{illum}}) = S (E^{k-1}, t_{\text{illum}}) + \left[ N_{\text{tr,eff}} - S (E^{k-1}, t_{\text{illum}}) \right] \\
\times \left[ 1 - \exp \left( -\sigma_o^p \Phi (E^k) t_{\text{illum}} \right) \right],
\] if one specific trap is assumed to be present in the space-charge region. Notably, \(k\) starts at 1, and \(S (E^0, t_{\text{illum}})\) is set to zero.

For non-accumulative SSPC measurements, the corresponding expression is:
\[
S_{\text{non-acc}} (E^k, t_{\text{illum}}) = N_{\text{tr,eff}} \\
\times \left[ 1 - \exp \left( -\sigma_o^p \Phi (E^k) t_{\text{illum}} \right) \right],
\] if one specific trap is assumed to be present in the space-charge region. To solve equation 6 and 7, one needs to know \(\sigma_o^p (E^k)\) and \(\Phi (E^k)\). \(\sigma_o^p (E^k)\) can be defined as:
\[
\sigma_o^p (E^k) = \Sigma_n \sigma_o^{n,\text{norm}} (E^k).
\] (8)

\(\sigma_o^{n,\text{norm}}\) can be obtained from first-principles calculations for a specific defect. The absolute value \(\Sigma_n\), however, is challenging to extract from first-principles calculations, and is considered a free parameter of the simulation. \(\Phi (E^k)\) was measured for the optical excitation of the setup used for SSPC measurements (see figure 1). If several traps i are present, \(S_{\text{acc}} (E^k, t_{\text{illum}})\) and \(S_{\text{non-acc}} (E^k, t_{\text{illum}})\) are superpositions of contributions \(S_{\text{acc, i}} (E^k, t_{\text{illum}})\) and \(S_{\text{non-acc, i}} (E^k, t_{\text{illum}})\) from the individual traps i, assuming no interaction between traps, which is a viable assumption in the dilute regime.

The main difference between accumulative and non-accumulative SSPC measurements is the starting point for SSPC measurements performed at subsequent \(E^k\). Accumulative SSPC measurements will exhibit a steeper rise of \(S_{\text{acc}} (E^k, t_{\text{illum}})\) in the vicinity of defect-related optical absorption. Thus, accumulative SSPC measurements are more suitable for reaching steady-state conditions for a given trap. In the Appendix, a detailed derivation of equation 6 and 7 as well as comparisons between the theoretical expressions of \(S_{\text{acc}} (E^k, t_{\text{illum}})\) (see equation 6) and \(S_{\text{non-acc}} (E^k, t_{\text{illum}})\) (see equation 7) are shown.

![Figure 2. Absorption cross-sections \(\sigma_o^{n,\text{norm}}\) and \(\sigma_o^{p,\text{norm}}\) related to \(\text{FeGaI}^{0/-}\), \(\text{FeGaII}^{0/-}\) and \(\text{TiGaII}^{+/0}\). For \(\sigma_o^{n,\text{norm}}\), results are shown with and without taking vibrational broadening into account, while for \(\sigma_o^{p,\text{norm}}\), results are only shown with vibrational broadening. A temperature of 120 K was assumed.](image)

4. Results and Discussion

The CC diagrams for the charge state transitions \(\text{FeGaI}^{0/-}\), \(\text{FeGaII}^{0/-}\) and \(\text{TiGaII}^{+/0}\) were calculated using hybrid-functionals, and the parameters describing \(\text{FeGaI}^{0/-}\), \(\text{FeGaII}^{0/-}\) and \(\text{TiGaII}^{+/0}\) are summarized in table 1 [8, 23]. The computed values are in accordance with other recent studies regarding \(\text{FeGaI}^{0/-}\) and \(\text{FeGaII}^{0/-}\) [48] as well as \(\text{TiGaII}^{+/0}\) [49]. Figure 2 displays results for \(\sigma_o^{n,\text{norm}}\) and \(\sigma_o^{p,\text{norm}}\) related to \(\text{FeGaI}\), \(\text{FeGaII}\) and \(\text{TiGaII}\) in \(\beta\)-Ga\(_2\)O\(_3\). A temperature of 120 K was assumed for the computations. For \(\sigma_o^{n,\text{norm}}\), calculated absorption cross-section spectra are shown with and without taking vibrational broadening into account, while only results including vibrational broadening are shown for \(\sigma_o^{p,\text{norm}}\). Calculated absorption cross-section spectra without vibrational broadening exhibit sharp onsets of absorption, and particularly, exhibit no absorption.

<table>
<thead>
<tr>
<th>Defect</th>
<th>(E_{\text{ZPL}}) (eV)</th>
<th>(\Delta q) (eV)</th>
<th>(\Omega_{\text{g/e}}) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{FeGaI}^{0/-})</td>
<td>0.62</td>
<td>1.01/1.02</td>
<td>1.63</td>
</tr>
<tr>
<td>(\text{FeGaII}^{0/-})</td>
<td>0.72</td>
<td>1.04/0.93</td>
<td>1.22</td>
</tr>
<tr>
<td>(\text{TiGaII}^{+/0})</td>
<td>1.13</td>
<td>1.01/1.14</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Table 1. Summary of parameters describing the CC diagrams for \(\text{FeGaI}^{0/-}\), \(\text{FeGaII}^{0/-}\) and \(\text{TiGaII}^{+/0}\). [8, 23].
below the classical absorption energy $E_{ab}$ [22], in contrast to what is expected in experiments. Hence, absorption cross-sections with vibrational broadening are used in the following. The calculated $\sigma_o^{\text{n,norm}}$ and $\sigma_p^{\text{n,norm}}$ are broad which is in accordance with previous computational results for $\sigma_o^{\text{n,norm}}$ related to primary intrinsic defects in $\beta$-Ga$_2$O$_3$ [28]. Note that the $\sigma_o^{\text{n,norm}}$ related to Fe$^{0/-}$ and Fe$^{0/-}$ show a significant overlap, while $\sigma_p^{\text{n,norm}}$ related to Ti$^{+/0}$ occurs at higher photon energies. Our computational results for $\sigma_o^{\text{n,norm}}$ of Fe$^{0/-}$ and Fe$^{0/-}$ are in accordance with experimental photo-electron paramagnetic resonance studies performed by Bhandari et al. [48, 50]. For Fe$^{0/-}$, Fe$^{0/-}$, and Ti$^{+/0}$, optically-induced hole emission is only observed for photon energies close to $E_0$, i.e., optically-induced hole emission does not occur in the photon energy range where the onset of optically-induced electron emission is observed for these charge-state transitions. Thus, optically-induced hole emission related to Fe$^{0/-}$, Fe$^{0/-}$ and Ti$^{+/0}$ can be neglected when modeling SSPC spectra for photon energies lower than 4.0 eV.

Figure 3 shows DLTS spectra recorded on a EFG-grown $\beta$-Ga$_2$O$_3$ crystal. Three defect signatures labeled as $E_{2a}$ ($E_A = 0.66$ eV, $\sigma_{na} = 4 \times 10^{-16}$ cm$^2$), $E_{2b}$ ($E_A = 0.79$ eV, $\sigma_{na} = 3 \times 10^{-15}$ cm$^2$) and $E_3$ ($E_A = 1.03$ eV, $\sigma_{na} = 1 \times 10^{-13}$ cm$^2$) are found to be present, in accordance with previous studies on EFG-grown $\beta$-Ga$_2$O$_3$ crystals [8, 23]. No other defect levels with smaller activation energies than 1.2 eV were present in concentrations exceeding $1 \times 10^{15}$ cm$^{-3}$ in this sample. $E_{2a}$ and $E_{2b}$ have been assigned to Fe$^{0/-}$ and Fe$^{0/-}$, respectively [8, 23, 51], while $E_3$ is proposed to be related to Ti$^{+/0}$ [23]. This identification is consistent with a recent DLTS study that associated $E_{2a}/E_{2b}$ with a deep acceptor and $E_3$ with a deep donor [52]. Taking the $\Lambda$-correction [1, 32] into account, the concentrations of the corresponding traps were determined to be $2.54 \times 10^{15}$ cm$^{-3}$ (Fe$^{0/-}$), $2.32 \times 10^{16}$ cm$^{-3}$ (Fe$^{0/-}$ or Fe$^{0/-}$) and $5.45 \times 10^{15}$ cm$^{-3}$ ($E_3$ or Ti$^{+/0}$), respectively (see table 2). Thus, using DLTS measurements, we are able to establish the presence and concentration of Fe$^{0/-}$, Fe$^{0/-}$ and Ti$^{+/0}$ in the sample.

Accumulative SSPC measurements were performed on the same EFG-grown $\beta$-Ga$_2$O$_3$ sample for which DLTS spectra are shown in figure 3. Figure 4 (a) displays the recorded SSPC spectrum represented as conventional SSPC spectrum ($S_{\text{acc}}(E)$) and as derivative SSPC spectrum ($dS_{\text{acc}}(E)/dE$). Optically-induced emission of electrons is observed with onsets at 2.2 - 2.3 eV ($T_{\text{EFG}1}$), 2.8 - 2.9 eV ($T_{\text{EFG}2}$), 3.7 - 3.8 eV ($T_{\text{EFG}3}$), 3.8 - 4.0 eV ($T_{\text{EFG}4}$), 4.0 - 4.2 eV ($T_{\text{EFG}5}$) and 4.2 - 4.3 eV ($T_{\text{EFG}6}$). Furthermore, a signature originating from the band gap ($E_G$) of $\beta$-Ga$_2$O$_3$ can be seen. The features $T_{\text{EFG}2}$ and $T_{\text{EFG}3}$ are broad and partially overlap, and hence it is difficult to establish the respective onset position accurately. Interestingly, $T_{\text{EFG}2}$ and $T_{\text{EFG}3}$ can be properly distinguished in $dS_{\text{acc}}(E)/dE$ (see upper panel in figure 4 (a)) which demonstrates the applicability of derivative SSPC spectra [28]. Figure 4 (b) displays a comparison between derivative SSPC spectra recorded accumulatively as well as non-accumulatively on the same EFG-grown $\beta$-Ga$_2$O$_3$ crystal. The spectra were recorded using two different $t_{\text{illum}}$. Data are only shown for the photon energy range where $T_{\text{EFG}1}$ and $T_{\text{EFG}2}$ can be seen. Features in $dS_{\text{acc}}(E)/dE$ are narrower than the corresponding features seen in $dS_{\text{non-acc}}(E)/dE$.

Indeed, it is not possible to distinguish $T_{\text{EFG}1}$ and $T_{\text{EFG}2}$ in $dS_{\text{non-acc}}(E)/dE$. With increasing $t_{\text{illum}}$, the signatures associated with $T_{\text{EFG}1}$ and $T_{\text{EFG}2}$ become significantly more narrow and shift to lower photon energies in $dS_{\text{acc}}(E)/dE$, while only minor changes are seen in $dS_{\text{non-acc}}(E)/dE$. Thus, using accumulative SSPC measurements with long $t_{\text{illum}}$, the spectral

<table>
<thead>
<tr>
<th>Defect</th>
<th>$\Sigma_o^{\text{n}}$</th>
<th>$N_{\text{tr,eff}}^{\text{n}}$</th>
<th>$N_{\text{tr}}^{\text{n}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{0/-}$</td>
<td>0.3</td>
<td>1.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Fe$^{0/-}$</td>
<td>0.3</td>
<td>9.5</td>
<td>23.2</td>
</tr>
<tr>
<td>Ti$^{+/0}$</td>
<td>9.6</td>
<td>1.1</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Table 2. Summary of the parameters used for the model displayed in Fig. 5. The values for $N_{\text{tr,eff}}^{\text{n}}$ were determined from modeling accumulative SSPC spectra (see figure 5), while the values for $N_{\text{tr}}^{\text{n}}$ were obtained from DLTS measurements (see figure 3).
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resolution can be significantly improved. The spectral shape seen for \(T_1^{\text{EFG}}\) and \(T_2^{\text{EFG}}\) in \(\text{d}S_{\text{acc}}/\text{d}E\) recorded with \(t_{\text{illum}} = 1200\) s clearly suggests the presence of several overlapping defect signatures.

As mentioned before, DLTS measurements confirm the presence of Fe\(_{\text{G}}\)\(^0/-\), Fe\(_{\text{Gal}}\)\(^0/-\) and Ti\(_{\text{Gal}}\)\(^+/-\) in this EFG-grown \(\beta\)-Ga\(_2\)O\(_3\) sample, and are thus expected to appear in SSPC spectra as well. It is possible to estimate the onset of defect-related optical absorption by adding the Franck-Condon shift for a specific charge-state transition of a defect to the corresponding activation energy determined by DLTS [21, 22].

Assuming typical Franck-Condon shifts of 0.4 eV to 1.2 eV as reported in \(\beta\)-Ga\(_2\)O\(_3\) previously [11, 12, 28], one expects the optical absorption related to Fe\(_{\text{G}}\)\(^0/-\), Fe\(_{\text{Gal}}\)\(^0/-\) and Ti\(_{\text{Gal}}\)\(^+/-\) to occur at around 1.1 eV to 2.2 eV. Thus, Fe\(_{\text{G}}\)\(^0/-\), Fe\(_{\text{Gal}}\)\(^0/-\) and Ti\(_{\text{Gal}}\)\(^+/-\) are all plausible candidates for \(T_1^{\text{EFG}}\). Further, the amplitude of \(T_2^{\text{EFG}}\) suggests an associated trap concentration in the range of \(1 \times 10^{16}\) cm\(^{-3}\), corroborating the relation to Fe\(_{\text{G}}\)\(^0/-\), Fe\(_{\text{Gal}}\)\(^0/-\) and Ti\(_{\text{Gal}}\)\(^+/-\). Notably, we observed no other defect signatures in DLTS measurements with concentrations above \(1 \times 10^{15}\) cm\(^{-3}\) that are likely candidates for contributing to \(T_2^{\text{EFG}}\).

In order to assign \(T_1^{\text{EFG}}\) to Fe\(_{\text{G}}\)\(^0/-\), Fe\(_{\text{Gal}}\)\(^0/-\) and Ti\(_{\text{Gal}}\)\(^+/-\), however, it is necessary to compare the calculated results for \(\sigma_{\text{n,norm}}\) (see figure 2) to the recorded SSPC spectra. Particularly, it is necessary to take experimental parameters such as \(t_{\text{illum}}\) into account (see figure 4 (b)). One approach is the method presented above, by comparing the experimental data with SSPC spectra simulated by utilizing the absorption cross sections obtained from first-principles calculations. In figure 5, SSPC spectra recorded accumulatively on the same EFG-grown \(\beta\)-Ga\(_2\)O\(_3\) crystal for which results are shown in figure 3 are compared to simulations based on equation 6. Importantly, the overall trap concentration is found to be lower than 20% of \(N_D\). The simulations were performed assuming only the presence of Fe\(_{\text{G}}\)\(^0/-\), Fe\(_{\text{Gal}}\)\(^0/-\) and Ti\(_{\text{Gal}}\)\(^+/-\). The simulation has two free parameters for each defect signature: One pair of \(\Sigma_n\) and \(N_{\text{tr,eff}}\) for Fe\(_{\text{G}}\)\(^0/-\), Fe\(_{\text{Gal}}\)\(^0/-\) and Ti\(_{\text{Gal}}\)\(^+/-\), respectively. Increasing \(\Sigma_n\) will lead to a narrowing of the simulated defect signature and shift it to lower photon energies (see Appendix). Changing \(N_{\text{tr,eff}}\) will scale the simulated...
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6. Acknowledgments

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Appendix A. Simulation of Deep-Level Transient and Steady-State Photo-Capacitance Spectra

Appendix A.1. Simulation of Deep-Level Transient Spectra

In deep-level transient spectroscopy (DLTS) [1, 7], a rectifying junction is kept a reverse-bias voltage ($V_{rev} < 0$ V) and subjected to a voltage pulse ($V_{pulse} > 0$ V) at a time $t_0$ which lasts for a duration $t_{pulse}$. In
the following, it is assumed that DLTS measurements are performed on a Schottky junction comprising a $n$-type semiconductor. Moreover, we assume that a trap exhibiting a concentration of $N_{tr}$ and a single thermodynamic charge-state transition level ($E_t$) is present in the semiconductor. Prior to applying the voltage pulse, the trap will be empty of electrons in-between the surface of the semiconductor and a depth $x_1$. $x_1$ is the depth where the Fermi level ($E_F$) crosses $E_t$, and its value will depend on $V_{rev}$. During the voltage pulse, an additional amount of traps will be filled with electrons, i.e., traps in-between $x_1$ and a depth $x_2$ will also be filled with electrons. $x_2$ is the depth where $E_F$ crosses $E_t$ when the applied bias voltage is equal to $V_{rev} + V_{pulse}$. After the end of the voltage pulse at $t_0 + t_{pulse}$, the charge-state transition level of traps in-between $x_2$ and $x_1$ will be above $E_F$, and thus electron emission will occur until all traps in-between $x_2$ and $x_1$ are void of electrons.

The corresponding electron emission is a thermally-activated process, and its rate $e_n^{th}$ can be expressed by [1, 7]:

$$e_n^{th} = \beta \sigma_{na} T^2 \exp \left( - \frac{E_A}{k_B T} \right). \quad (A.1)$$

Here, $T$ is the sample temperature, $E_A$ is the activation energy for thermally-induced electron emission from the trap, $\sigma_{na}$ is the apparent capture cross section, $k_B$ is Boltzmann’s constant and $\beta$ is a material-specific constant. $E_A$ is the sum of $E_t$ and the corresponding energetic barrier for electron capture ($E_b$) [1, 21]. Assuming parabolic bands, $\beta$ can be computed by [1]:

$$\beta = 2\sqrt{3} \left( \frac{2\pi}{h^2} \right)^{\frac{3}{2}} k_B^2 m_{n,eff}. \quad (A.2)$$

Here, $h$ is Planck’s constant and $m_{n,eff}$ is the effective mass of electrons in the conduction band. For $\beta$-Ga$_2$O$_3$, a value of 0.28$m_e$ was used for $m_{n,eff}$ [53, 54], whereby $m_e$ is the electron mass.

In DLTS, the thermally-induced electron emission is probed by recording the capacitance of the rectifying junction. Particularly, the capacitance transient ($C(t)$) is recorded after the end of the voltage pulse, and is described by [1]

$$C(t) = C_0 \left[ 1 - \frac{N_{tr,probe}}{2N_D} \exp \left( -e_n^{th} t \right) \right], \quad (A.3)$$

assuming $N_{tr} \ll N_D$ to be valid. Here, $C_0$ is the capacitance of the rectifying junction measured prior to the voltage pulse, i.e., the capacitance of the rectifying junction when $V_{rev}$ is applied. $N_D$ is the donor concentration and $N_{tr,probe}$ is the effective trap concentration in the probing volume, i.e., the effective concentration of traps in-between $x_2$ and $x_1$. Following the approach outlined by Lang, the DLTS spectra $S_j(T)$ can be constructed, and $S_j(T)$ is defined as [1, 7, 31]:

$$S_j(T) = \frac{1}{t_j} \int_{t_j}^{t_{delay}+t_j} C(t) w(t) \, dt. \quad (A.4)$$

Here, $t_{delay}$ is the time at which the recording of $C(t)$ starts after the end of the voltage pulse, whereas $t_j$ is the duration for which $C(t)$ is recorded/analyzed. $w(t)$ is the weighting function, e.g., a lock-in function [1] or a GS4 filter function [31]. To analyze DLTS measurements, one needs to use more than one specific $t_j$. Often, $C(t)$ is recorded for a duration $t_{transient}$, and different parts of the transient, represented by $t_j$, are analyzed in order to obtain different $S_j(T)$.

Different $S_j(T)$ essentially correspond to analyzing the recorded $C(t)$ for different values of $e_n^{th}$ (see figure 3 in the manuscript). The recorded $S_j(T)$ can be compared to simulations when combining equations A.4 with equations A.1 and A.3. The free parameters of the simulation are the quantities $N_{tr,probe}$, $E_A$ and $\sigma_{na}$ which describe the concentration and properties of the trap. Often, one represents DLTS spectra as $2N_D \Delta C/C_0$, whereby $\Delta C = C_0 - C(t = 0)$. $S_j(T)$ can be calculated from $S_j(T)$ as outlined in [1, 55].

As mentioned above, $N_{tr,probe}$ represents the effective trap concentration in-between $x_2$ and $x_1$. The actual trap concentration $N_{tr}$ can be determined by using [1]:

$$N_{tr} = \frac{W^2}{x_1 - x_2} N_{tr,probe}. \quad (A.5)$$

Here, $W$ is the width of the space-charge region when applying $V_{rev}$. The correction performed in equation A.5 is often referred to as $\lambda$-correction [1, 32].

### Appendix A.2. Simulation of Steady-State Photo-Capacitance Spectra from First-Principles Calculations

Steady-state photo-capacitance (SSPC) measurements are performed by measuring the photo-capacitance of a rectifying junction after illumination at the photon energy $E^k$ for a duration $t_{illum}$. In the following, it is assumed that SSPC measurements are performed on a Schottky junction comprising a $n$-type semiconductor. Moreover, we assume that a trap exhibiting a concentration of $N_{tr}$ and a single thermodynamic charge-state transition level ($E_t$) is present in the semiconductor.

SSPC spectra $(S(E^k,t_{illum}))$ are constructed by recording the photo-capacitance ($C_{illum}(E^k,t_{illum})$) of the junction at subsequent $E^k$. $S(E^k,t_{illum})$ is usually expressed as [1, 10]:

$$S(E^k,t_{illum}) = 2 \frac{C_{illum}(E^k,t_{illum}) - C_{dark}}{C_{dark}} N_D$$
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Here, \( \Delta C_{\mathrm{illum}}(E^k, t_{\mathrm{illum}}) \) denotes the change in (photo-)capacitance during illumination for \( t_{\mathrm{illum}} \) at \( E^k \), and \( C_{\mathrm{dark}} \) represents the capacitance of the junction measured in the dark. \( N_{\mathrm{tr}}(E^k, t_{\mathrm{illum}}) \) is the change in the concentration of ionized traps inside the probing volume due to illumination. Notably, the probing volume will usually not be equal to the volume of the space-charge region \([1, 28]\). Moreover, equation A.6 assumes \( N_D \ll N_{\mathrm{tr}} \) to be valid.

\[ N_{\mathrm{tr}}^*(E^k, t_{\mathrm{illum}}) = S(E^k, t_{\mathrm{illum}}) \] is described by the following differential equation \([10]\):

\[
\frac{dN_{\mathrm{tr}}^*}{dt} = \sigma_o^* \Phi N_{\mathrm{tr}}^*.
\]

when assuming that the photo-ionization process only involves the defect and the conduction band (optically-induced electron emission), i.e., optically-induced hole emission (photo-ionization processes involving the defect and the valence band) can be neglected. Optically-induced hole emission can be neglected if (i) holes are not sufficiently mobile to leave the space-charge region, or (ii) optically-induced hole emission does not occur in the spectral region of interest \([10, 28]\). In equation A.7, \( \sigma_o^* \) represents the absorption cross-section related to the optically-induced electron emission from the defect, whereas \( \Phi \) denotes the spectral photon flux used for illumination. \( \sigma_o^* \) and \( \Phi \) will be functions of \( E^k \). \( N_{\mathrm{tr}}^* \) is the concentration of defects inside the probing volume which are not ionized, and hence \( N_{\mathrm{tr}}^* = N_{\mathrm{tr}}^* - N_{\mathrm{tr}}^* \). \( N_{\mathrm{tr}}^* \) is the effective concentration of the defect inside the probing volume. Using this, equation A.7 becomes:

\[
\frac{dN_{\mathrm{tr}}^*}{dt} = \sigma_o^* \Phi N_{\mathrm{tr}}^*.
\]

Equation A.8 describes a first-order, non-homogeneous differential equation. The associated homogeneous differential equation is:

\[
\frac{dN_{\mathrm{tr}}^*}{dt} = -\sigma_o^* \Phi N_{\mathrm{tr}}^*.
\]

This differential equation is solved by:

\[ N_{\mathrm{tr}}^* = -A \exp(-\sigma_o^* \Phi t). \]

Here, \( A \) is a constant which needs to be chosen according to the boundary condition. A particular solution for equation A.8 is

\[ N_{\mathrm{tr}}^* = N_{\mathrm{tr}}^*. \]

The overall solution to equation A.8 is obtained by adding equation A.10 and A.11 together, and hence:

\[ N_{\mathrm{tr}}^* = N_{\mathrm{tr}}^* + A \exp(-\sigma_o^* \Phi t). \]

As mentioned above, \( A \) needs to be determined from the boundary condition which will depend on the way SSPC measurements are performed. In non-accumulative SSPC measurements, the defect is re-filled with electrons prior to illumination at \( E^k \), and hence the concentration of (photo-)ionized defects prior to illumination at \( E^k \) inside the probing volume \( (N_{\mathrm{tr}}^*(E^k, t = 0 s)) \) will be expressed by:

\[ N_{\mathrm{tr}}^*(E^k, t = 0 s) = 0. \]

Thus, \( A \) will be equal to \(-N_{\mathrm{tr}}^*\), and hence:

\[ S_{\text{non-acc}}(E^k, t_{\text{illum}}) = N_{\mathrm{tr}}^*(E^k, t_{\text{illum}}) \]

Notably, for \( t_{\text{illum}} \) approaching \( \infty \), \( S_{\text{non-acc}}(E^k, t_{\text{illum}}) \) approaches \( N_{\mathrm{tr}}^* \) and \( t_{\text{illum}} \to \infty \) is equivalent to reaching steady-state conditions, and hence the superscript \( ss \) was used for denoting \( N_{\mathrm{tr}}^* \).

In accumulative SSPC measurements, the rectifying junction under illumination is kept at a fixed reverse-bias voltage while illuminating the junction at different \( E^k \). Importantly, measurements are performed in ascending order of \( E^k \), i.e., \( E^k < E^{k+1} \) is valid. For the first measurement performed at \( E^0 \), the boundary condition stated in equation A.13 holds, and thus

\[ S_{\text{acc}}(E^0, t_{\text{illum}}) = N_{\text{tr}}^*[1 - \exp(-\sigma_o^* \Phi t_{\text{illum}})]. \]

For illumination at subsequent \( E^k \), the following boundary condition holds:

\[ N_{\text{tr}}^*(E^k, t = 0 s) = S_{\text{acc}}(E^{k-1}, t_{\text{illum}}), \]

reflecting that when illumination starts, a certain concentration of defects is already photo-ionized due to illumination at \( E^{k-1} \). Thus \( A \) is equal to

\[ S_{\text{acc}}(E^{k-1}, t_{\text{illum}}) = -N_{\text{tr}}^* \]

\[ S_{\text{acc}}(E^{k-1}, t_{\text{illum}}) = N_{\text{tr}}^* \exp(-\sigma_o^* \Phi t_{\text{illum}}) \]

is valid for \( E^k \neq E^0 \). Adding 0 = \( S_{\text{acc}}(E^{k-1}, t_{\text{illum}}) - S_{\text{acc}}(E^{k-1}, t_{\text{illum}}) \) on the right hand side, equation A.17 can be re-written as:

\[ S_{\text{acc}}(E^k, t_{\text{illum}}) = N_{\text{tr}}^* \exp(-\sigma_o^* \Phi t_{\text{illum}}) \]

This equation is valid for all \( E^k \) if \( S_{\text{acc}}(E^{k-1}, t_{\text{illum}}) \) is set to 0.
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duration $t_{\text{illum}}$ at all photon energies $E^k$ for which $j < k$ is valid. $S_{\text{acc}}(E^k, t_{\text{illum}}, t)$ can be expressed as:

$$S_{\text{acc}}(E^k, t_{\text{illum}}, t) = S(E^{k-1}, t_{\text{illum}}, t_{\text{illum}}) + \left[ N_{\text{tr,eff}}^n - S(E^{k-1}, t_{\text{illum}}, t_{\text{illum}}) \right] \times \left[ 1 - \exp \left( -\sigma^o_k \Phi t \right) \right], \quad \text{(A.19)}$$

while $S_{\text{non-acc}}(E^k, t_{\text{illum}}, t)$ can be calculated by:

$$S_{\text{non-acc}}(E^k, t_{\text{illum}}, t) = N_{\text{tr,eff}}^n \left[ 1 - \exp \left( -\sigma^o_k \Phi t \right) \right]. \quad \text{(A.20)}$$

$\sigma^o_n$ is defined by:

$$\sigma^o_n = \sum_{k} \sigma^o_{k,norm}. \quad \text{(A.21)}$$

Here, $\sigma^o_{k,norm}$ can be obtained from first-principles calculations for a specific trap, while $\sum_{k}$ is a free parameter of the simulation.

In the following, graphical representations of equations A.14, A.18, A.19 and A.20 will be shown. Hereby, the calculated $\sigma^o_{k,norm}$ of $V_{T}^{0/\text{Geff}}$ was used. In table A1, the standard values for the simulation parameters are stated. $\Phi$ is assumed to be constant for all photon energies, and $\Delta E$ is the energy step between two subsequent $E^k$, i.e., $\Delta E = E^{k+1} - E^k$ is valid.

Figure A1 displays graphical representations of equation A.19 and A.20. Figure A1 (a) shows the dependence on $t$, while Figure A1 (b) and (c) show the corresponding dependence on $E^k$. Notably, for the same experimental conditions, non-accumulative SSC measurements will reach steady-state conditions for longer $t_{\text{illum}}$ compared to accumulative SSC measurements. Generally, longer $t_{\text{illum}}$ are associated with steps in SSC spectra shifting to lower photon energies and becoming steeper.

In figure A2 - A5, the influence of a particular parameter on equations A.14 and A.18 is shown. For longer $t_{\text{illum}}$ and higher $\Phi$, steps in $S_{\text{acc}}$ as well as $S_{\text{non-acc}}$ will shift to lower photon energies and become steeper. The corresponding changes are more notable for accumulative SSC spectra under the same experimental conditions. Only $S_{\text{acc}}$ exhibits a change depending on $\Delta E$. For $S_{\text{acc}}$ as well as $S_{\text{non-acc}}$, $N_{\text{tr,eff}}$ is a scaling factor.

**Table A1.** Overview over standard parameters used for the simulation of SSC spectra presented here.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
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<tr>
<td>$\Sigma^o_n$</td>
<td>$\text{m}^2$</td>
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<tr>
<td>$\Phi$</td>
<td>$\text{m}^{-2}\text{s}^{-1}$</td>
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<td>$t_{\text{illum}}$</td>
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<td>$\Delta E$</td>
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<tr>
<td>$2 \times 10^{-20}$</td>
<td>$10^{18}$</td>
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<tr>
<td>$10/300$</td>
<td>$20$</td>
</tr>
<tr>
<td>$10^{16}$</td>
<td>$\text{cm}^{-3}$</td>
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[16] AY Polyakov, NB Smirnov, IV Shchemerov, SJ Pearton, Fan Ren, AV Chernykh, and AI Kochkova. Electrical
Figure A1. Graphical representation of equation A.19 and A.20. Results are shown in dependence of (a) $t_{\text{illum}}$ and (b), (c) $E_k$. In (b) conventional SSPC spectra are shown, while in (c) derivative SSPC spectra are displayed. Here, the $\sigma_{n,\text{norm}}$ calculated for Ti$_3$Ga$_{17}$ was used. The simulations were performed using different $t_{\text{illum}}$ of 1200 s, 300 s and 30 s. Moreover, the following parameters were used: $\Delta E = 0.2\text{eV}$, $\Sigma_{n} = 2 \times 10^{-20}\text{m}^2$, $\Phi = 1 \times 10^{18}\text{m}^{-2}\text{s}$ and $N_{\text{eff}} = 1 \times 10^{16}\text{cm}^{-3}$.

Combining Steady-state Photo-capacitance Spectra with First-principles Calculations

Figure A2. Graphical representation of equation A.14 and A.18 for different photon fluxes \( \Phi \). Results are shown for (a) conventional and (b) derivative SSPC spectra. Here, the \( \sigma_{o, norm} \) calculated for Ti\(_0\)/Ga\(_II\) was used. Moreover, the following parameters were used: \( \Delta E = 20 \text{ meV} \), \( \sum^\infty_{o} = 2 \times 10^{-20} \text{ m}^2 \), \( t_{\text{illum}} = 10 \text{ s} \) and \( N^{q=0}_{\text{tr, eff}} = 1 \times 10^{16} \text{ cm}^{-3} \).


[31] AA Istratov. New correlation procedure for the improve-
Combining Steady-state Photo-capacitance Spectra with First-principles Calculations

Figure A3. Graphical representation of equation A.14 and A.18 for various $t_{\text{illum}}$. Results are shown for (a) conventional and (b) derivative SSPC spectra. Here, the $\sigma_{\text{norm}}$ calculated for $T_{\text{Ga}}^{(0/2)}$ was used. Moreover, the following parameters were used: $\Delta E = 20 \text{ meV}$, $\Sigma_{\text{norm}} = 2 \times 10^{-20} \text{ m}^2$, $\Phi = 1 \times 10^{18} \text{ m}^{-2} \text{ s}$ and $N_{\text{eff}}^{\text{tr}} = 1 \times 10^{16} \text{ cm}^{-3}$.


Combining Steady-state Photo-capacitance Spectra with First-principles Calculations

Figure A4. Graphical representation of equation A.14 and A.18 for various $\Delta E$. Results are shown for (a) conventional and (b) derivative SSPC spectra. Here, the $\sigma^o_n$ calculated for $T_{\text{Ga}_2\text{O}_3}^{0/3}$ was used. Moreover, the following parameters were used: $t_{\text{illum}} = 300$ s, $\Sigma^o_n = 2 \times 10^{20}$ m$^{-2}$, $\Phi = 1 \times 10^{18}$ m$^{-2}$ s and $N_{\text{tr}, \text{eff}} = 1 \times 10^{16}$ cm$^{-3}$.
Figure A5. Graphical representation of equation A.14 and A.18 for various $N_{\text{tr, eff}}^{\text{ss}}$. Results are shown for (a) conventional and (b) derivative SSPC spectra. Here, the $\sigma_{\text{norm}}^2$ calculated for $T_{\text{GaAs}}^{0/20}$ was used. Moreover, the following parameters were used: $t_{\text{illum}} = 300$ s, $\Sigma_{\text{on}} = 2 \times 10^{-20}$ m$^2$, $\Phi = 1 \times 10^{18}$ m$^{-2}$ s and $\Delta E = 20$ meV.
Formation and control of the $E^*_2$ center in implanted $\beta$-Ga$_2$O$_3$ by reverse-bias and zero-bias annealing

Christian Zimmermann, Espen Førdestrøm Verhoeven, Ymir Kalmann Frodason, Joel Basile Varley, Philip Michael Weiser, Lasse Vines

Formation and control of the $E^*_2$ center in implanted $\beta$-Ga$_2$O$_3$ by reverse-bias and zero-bias annealing

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Abstract. Deep-level transient spectroscopy measurements are conducted on $\beta$-Ga$_2$O$_3$ thin-films implanted with helium and hydrogen (H) to study the formation of the defect level $E^*_2$ ($E_A = 0.71$ eV) during heat treatments under an applied reverse-bias voltage (reverse-bias annealing). The formation of $E^*_2$ during reverse-bias annealing is a thermally-activated process exhibiting an activation energy of around $1.0\text{ eV}$ to $1.3\text{ eV}$, and applying larger reverse-bias voltages during the heat treatment results in a larger concentration of $E^*_2$. In contrast, heat treatments without an applied reverse-bias voltage (zero-bias annealing) can be used to decrease the $E^*_2$ concentration. The removal of $E^*_2$ is more pronounced if zero-bias anneals are performed in the presence of H. A scenario for the formation of $E^*_2$ is proposed, where the main effect of reverse-bias annealing is an effective change in the Fermi-level position within the space-charge region, and where $E^*_2$ is related to a defect complex involving intrinsic defects that exhibits several different configurations whose relative formation energies depend on the Fermi-level position. One of these configurations gives rise to $E^*_2$, and is more likely to form if the Fermi-level position is further away from the conduction band edge. The defect complex related to $E^*_2$ can become hydrogenated, and the corresponding hydrogenated complex is likely to form when the Fermi level is close to the conduction band edge. Di-vacancy defects formed by oxygen and gallium vacancies ($V_{O}-V_{Ga}$) fulfill several of these requirements, and are proposed as potential candidates for $E^*_2$.

Keywords: $\beta$-Ga$_2$O$_3$, deep-level transient spectroscopy, defects, hydrogen, irradiation, implantation, reverse-bias annealing, heat treatments, intrinsic defects, thin-films, defect control


1. Introduction

Monoclinic gallium sesquioxide ($\beta$-Ga$_2$O$_3$) has emerged in recent years as a promising material for applications in power electronics and UV photo-detectors due to its wide band gap and exceptionally high break-down electrical field [1, 2, 3, 4, 5, 6]. There has
been significant progress in improving the quality of $\beta$-Ga$_2$O$_3$ bulk crystals and thin-films [7, 8, 9, 10, 4, 11, 12, 13]. However, point defects are still a limiting factor for device performance, and influence the operation of devices for power electronics due to, for example, Fermi-level pinning [14, 15, 16] or an increase in the on-resistance [17]. Indeed, McGlone et al. recently showed that a defect level commonly labeled as $E^*_2$ is limiting the device performance of metal-semiconductor field-effect transistors (MESFETs) based on $\beta$-Ga$_2$O$_3$ [14].

$E^*_2$ is associated with a defect level at around 0.75 eV below the conduction band edge ($E_C$) as determined by deep-level transient spectroscopy (DLTS) [14, 15, 18, 19, 20]. The defect level has been observed in as-grown $\beta$-Ga$_2$O$_3$ thin-films deposited by plasma-assisted molecular beam epitaxy [14, 15], and is suggested to be associated with intrinsic defects due to its formation in $\beta$-Ga$_2$O$_3$ bulk crystals and thin-films upon proton irradiation [18, 19, 20]. Furthermore, the concentration of $E^*_2$ in proton-irradiated $\beta$-Ga$_2$O$_3$ bulk crystals and thin-films increases upon heat treatments in the range of 650 K, indicating the formation of $E^*_2$ through a thermally-activated process [19]. However, no structural origin has so far been attributed to $E^*_2$.

The position of the Fermi level can have a pronounced influence on defect formation processes via the contribution of the electron chemical potential to defect formation energies [21, 22, 23]. Particularly, it has been shown that several defect signatures are introduced in the space-charge region of $\beta$-Ga$_2$O$_3$ Schottky barrier diodes (SBDs) when the diodes are exposed to elevated temperatures in conjunction with an applied bias voltage, causing a change in the Fermi-level position within the space-charge region [24]. Moreover, hydrogen (H) can play an important role in defect formation because H is expected to be mobile at or slightly above room temperature in $\beta$-Ga$_2$O$_3$, and has been shown to form complexes with various acceptor defects [23, 25, 26, 27].

Here, we report on the formation of the defect level $E^*_2$ in $\beta$-Ga$_2$O$_3$ thin-films subjected to helium- (He-) and H-implantation using DLTS. We observe that the introduction of $E^*_2$ is promoted by annealing samples subjected to H- or He-implantation under an applied reverse-bias voltage. Annealing the corresponding samples without an applied reverse-bias voltage leads to a decrease in the $E^*_2$ concentration. Thus, annealing implanted $\beta$-Ga$_2$O$_3$ thin-films with and without an applied reverse-bias voltage can be used to control the concentration of $E^*_2$. Notably, a more pronounced decrease in the $E^*_2$ concentration is seen for heat treatments without an applied reverse-bias voltage in the presence of H. We propose that $E^*_2$ is associated with a defect complex forming more preferably when the Fermi level is further away from $E_C$. Importantly, at Fermi-level positions closer to $E_C$, a different defect complex or configuration is more likely to form that does not give rise to a charge-state transition level accessible for our DLTS measurements. Moreover, for Fermi-level positions close to $E_C$, H is proposed to form a hydrogenated defect complex that competes with the defect giving rise to $E^*_2$. Finally, based on a discussion of the present results in light of first-principles defect calculations available in the literature, di-vacancy complexes formed by oxygen vacancies ($V_O$) and gallium vacancies ($V_{Ga}$) are proposed as a promising class of candidates for $E^*_2$.
2. Experimental

β-Ga₂O₃ thin-films grown by halide vapor-phase epitaxy (HVPE) [4] on conductive β-Ga₂O₃ substrates were obtained from Novel Crystal Technology, Inc. [28]. Samples measuring (5 × 5) mm² were cut with a laser cutter, and cleaned inside an ultrasonic bath using acetone, isopropanol and de-ionized water prior to fabricating SBDs by depositing suitable metals. The metals were deposited using e-beam evaporation, with Ti/Al (thickness = 10 nm/120 nm) serving as Ohmic contact, whereas circular Ni pads (thickness = 150 nm) with diameters of 480 µm or 830 µm, respectively, were used as Schottky contacts [29].

Capacitance-Voltage (CV), Current-Voltage (IV) and DLTS measurements were performed using a setup described in detail in the references [30, 31]. CV and IV measurements were performed in the dark and at room temperature. Generally, all investigated SBDs exhibited a rectification of several orders of magnitude when comparing the current at reverse and forward bias as well as very low conductance values. The depth distribution of the charge-carrier concentration (n) was computed from CV measurements [32] and is denoted as n-profile. A relative static dielectric constant (εs) of 10.2 was assumed for β-Ga₂O₃ [33].

DLTS measurements were performed in the temperature range from 290 K to 450 K during heating of the sample with 2 K min⁻¹. DLTS spectra were constructed using a lock-in (GS2) filter [32, 34]. All DLTS measurements were performed at a reverse-bias voltage of −8 V or −4 V and utilized pulse voltages of 8 V or 4 V. Parameters describing the traps present in the space-charge region, such as the trap concentration (Nt), the activation energy (EA) and the apparent capture cross section (σna) were extracted by simulating the recorded DLTS spectra with a python-based script. From results obtained on various SBDs comprising HVPE-grown β-Ga₂O₃ thin-films, the uncertainty in EA is estimated to be around 0.10 eV, whereas the uncertainty in σna can be expected to be in the order of +/- an order of magnitude. The setup utilized for DLTS measurements was also used for heat treatments of SBDs up to 680 K with and without an applied bias voltage, whereby the samples were inside the setup during the heat-up and cool-down sequence. Typically, heating and cooling ramps of approximately 6 K min⁻¹ were used. Heat treatments with an applied reverse-bias voltage are denoted as reverse-bias anneals, whereas heat treatments without an applied bias voltage are referred to as zero-bias anneals. Unless stated otherwise, reverse-bias anneals were performed using an applied reverse-bias voltage of −8 V.

All H- and He-implantations were performed at room temperature through the Ni contacts, using kinetic energies (E) of 180 keV to 220 keV for H and 500 keV for He. The projected range (Rp) for defect generation due to the ion implantation was computed utilizing Monte-Carlo simulations as implemented within the The Stopping and Range of Ions in Matter package [35] using default displacement energies for Ga and O of 25 eV and 28 eV, respectively. For H implantation, RpH is between 850 nm and 1050 nm, whereas for He implantation, RpHe is around 1150 nm. Typical ion fluences
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Figure 1. (a), (b) $n$-profiles and (c), (d) DLTS spectra recorded on a HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film after He implantation ($E = 500$ keV, $\Phi = 2.5 \times 10^{10}$ cm$^{-2}$). Data (filled circles and triangles) are shown for two different SBDs located on the same HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film. The SBDs were subjected to a different order of heat treatments after He implantation as listed in (a) and (b), where the order is indicated by roman letters. DLTS spectra were recorded using a reverse-bias voltage of $-8$ V and a pulse voltage of 8 V. $R^\text{He}_{\text{p}}$ and the probing depth $W$ expected in DLTS measurements are marked in (a) and (b). In (c) and (d) simulated DLTS spectra are shown as solid lines and the positions of the defect levels $E^*_2$ and $E_2$ are indicated.

for implantation ($\Phi$) were in the range of $5 \times 10^{12}$ cm$^{-2}$ - $1 \times 10^{13}$ cm$^{-2}$ for H and $1 \times 10^{10}$ cm$^{-2}$ - $1 \times 10^{11}$ cm$^{-2}$ for He.

3. Results and Discussion

Figure 1 (a) and (b) display $n$-profiles recorded on a HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film after He implantation, and subsequent reverse-bias and zero-bias anneals at 650 K. In figure 1 (a), results are shown for a SBD immediately after He implantation, and after reverse-bias and zero-bias anneals. After He implantation, the region around $R^\text{He}_{\text{p}}$ is partly compensated, as evidenced by a reduction in the charge-carrier concentration. The first heat treatment leads to a restoration of the charge-carrier concentration, whereas subsequent heat treatments result only in minor changes in the $n$-profile, in accordance with previous reports [19, 36, 37]. In figure 1 (b), $n$-profiles for a second SBD on the same HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film are shown. Here, results are displayed after...
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an initial zero-bias anneal, and for subsequent reverse-bias and zero-bias anneals. The $n$-profiles do not change significantly after the heat treatments, which indicates that the probing depth expected for DLTS measurements ($W$) does not change significantly during subsequent DLTS measurements.

Figure 1 (c) and (d) show DLTS spectra recorded on the same SBDs whose $n$-profiles are shown in panels (a) and (b), respectively. Immediately after He implantation (see figure 1 (c)), a defect signature commonly labeled as $E_2$ ($E_A = 0.74$ eV, $\sigma_{na} = 1 \times 10^{-16}$ cm$^2$) can be seen which has previously been identified as Fe$_{0/-}$Ga$_{II}$ (charge-state transition from neutral Fe$^{3+}$ to an Fe$^{2+}$ acceptor state substituting on an octahedral Ga site) [18, 31]. $E_2$ was also present in as-received HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films (not shown), and no change is observed during the subsequent heat treatments, in accordance with previous reports [19]. Additionally, in figure 1 (c), a shoulder can be seen on the low temperature side of $E_2$, indicating the presence of another defect level where one would expect $E^*_2$ to occur [18, 19]. After a subsequent reverse-bias anneal at 650 K, $E^*_2$ ($E_A = 0.71$ eV, $\sigma_{na} = 1 \times 10^{-19}$ cm$^2$) is introduced with a significantly higher concentration, in accordance with the observations reported in [19]. Notably, the simulations performed to extract $E_A$, $\sigma_{na}$ and $N_t$ do not capture the corresponding signature entirely, indicating the presence of several overlapping defect signatures. The $E^*_2$ concentration decreases after a subsequent zero-bias anneal at 650 K.

Importantly, reversing the order of the heat treatment sequence by starting with a zero-bias anneal at 650 K (see figure 1 (d)) results in a limited introduction of $E^*_2$ upon the initial heat treatment. The effect of reverse-bias annealing is further demonstrated by the subsequent reverse-bias anneal at 650 K, where a considerable increase in the $E^*_2$ concentration can be observed. Interestingly, the concentration of $E^*_2$ does not increase further when the sample is subjected to an additional reverse-bias anneal at 650 K (not shown). Moreover, the concentration associated with $E^*_2$ can be altered by additional heat treatments: subsequent zero-bias and reverse-bias anneals at 650 K cause the concentration to decrease and increase, respectively. However, the $E^*_2$ concentration after the second reverse-bias anneal is lower than what was observed after the first reverse-bias anneal, suggesting that the formation and removal of $E^*_2$ is not entirely reversible. Importantly, it is not possible to decrease the $E^*_2$ concentration by zero-bias annealing to the value which had been observed prior to the first reverse-bias anneal.

Next, we investigated the impact of H on the formation of $E^*_2$. Figure 2 shows DLTS spectra recorded on two different SBDs located on a HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film subjected to H implantation and subsequent heat treatments. Figure 2 (a) shows DLTS spectra for one of the SBDs after H implantation and subsequent heat treatments in the order: reverse-bias, zero-bias, and reverse-bias anneal. After the first reverse-bias anneal, $E^*_2$ is seen in pronounced concentration. Subsequently, the SBD was subjected to a zero-bias anneal, and the concentration related to $E^*_2$ is significantly lowered. Finally, the SBD was subjected to a reverse-bias anneal, and the concentration associated with $E^*_2$ increases yet again. Interestingly, the $E^*_2$ concentration after the second reverse-bias anneal is not as large as after the first one, and hence it seems like
the introduction and removal of $E^*_2$ is not entirely reversible regardless whether H is present or not (see figure 1). Notably, the response of $E^*_2$ to reverse-bias and zero-bias anneals is similar for He- and H-implantation, i.e., the $E^*_2$ concentration increases upon reverse-bias annealing, whereas it decreases due to zero-bias annealing. However, the decrease of the $E^*_2$ concentration upon zero-bias anneals is more pronounced for the case of H implantation (see figure 2) compared to the case of He implantation (see figure 1). In contrast to what has been observed for He implantation (see figure 1), anneals affect the $E_2$ concentration for H-implanted HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films. Particularly, the $E_2$ concentration decreases due to zero-bias anneals, and increases during subsequent reverse-bias anneals. This behavior could be related to the formation and dissociation of complexes involving Fe and H [38].

Figure 2 (b) shows DLTS spectra for the H-implanted sample recorded on a second SBD subjected to a reversed order of heat treatments: zero-bias, reverse-bias, and zero-bias anneal. $E^*_2$ is not observed when the first heat treatment is performed without an applied reverse-bias voltage. Subsequent reverse- and zero-bias anneals at 650 K cause the concentration associated with $E^*_2$ to increase and decrease, respectively.

Further investigations were conducted by He- and subsequent H-implantation to further study the role of H, and the corresponding results are displayed in figure 3. Figure 3 (a) shows DLTS spectra recorded on a HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film subjected to He- and H-implantation, and subsequent heat treatments at temperatures between 625 K and 680 K. Although $E^*_2$ was not observed after the ion implantations or the subsequent zero-bias anneal, its concentration can be enhanced considerably by reverse-bias annealing at 625 K. Subsequent reverse-bias and zero-bias anneals for the He- and H-implanted
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Figure 3. (a) DLTS spectra recorded on a HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film after He- ($E = 500$ keV, $\Phi = 1.25 \times 10^{10}$ cm$^{-2}$) and H-implantation ($E = 220$ keV, $\Phi = 5 \times 10^{12}$ cm$^{-2}$). Data (filled circles) are shown for a SBD subjected to different heat treatments after the ion implantations, and their order is indicated by roman letters. Notably, the annealing duration stated for step III is the accumulated annealing duration, i.e., no zero-bias anneal was performed in-between step II and III. Simulated DLTS spectra are shown as solid lines and the positions of the defect levels $E^*_2$ and $E_2$ are indicated. DLTS spectra were recorded using a reverse-bias voltage of $-8$ V and a pulse voltage of 8 V. The probing depth expected for the DLTS measurements did not change significantly for the different heat treatments. (b) Arrhenius plot constructed using the steady-state concentrations related to $E^*_2$ ($[E^*_2]_{ss}$) obtained by heat-treating a HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film subjected to He- and H-implantation at different temperatures $T_{ann}$ under an applied reverse-bias voltage of $-8$ V. From linear fits to the data (solid lines), the corresponding activation energy is estimated to be around 1.0 eV to 1.3 eV.

Reverse-bias anneals similar to the ones shown in figure 3 (a) were performed for annealing temperatures ($T_{ann}$) of 580 K, 600 K and 625 K using an applied reverse-bias voltage of $-8$ V. The reverse-bias anneals were conducted using different accumulated annealing durations ($t_{ann}$) without performing zero-bias anneals in-between the reverse-bias anneals performed at the same $T_{ann}$. However, zero-bias anneals were performed when switching to a different $T_{ann}$, i.e., the initial $E^*_2$ concentration is nearly the same for each $T_{ann}$. The corresponding results were used to study the thermally-activated
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Figure 4. DLTS spectra recorded on a HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film after He implantation ($E = 500$ keV, $\Phi = 1.25 \times 10^{10}$ cm$^{-2}$) and H implantation ($E = 220$ keV, $\Phi = 5 \times 10^{12}$ cm$^{-2}$) and subsequent reverse-bias anneals at 600 K for 90 min. The reverse-bias anneals were performed at $-4$ V (filled blue circles) and $-8$ V (filled black circles). Different parts of the space-charge region were probed by performing DLTS measurements using different combinations of reverse bias ($V_{bias}$) and pulse voltages ($V_{pulse}$). The respective pairs of $V_{bias}$ and $V_{pulse}$ are stated in the subplots. Simulated DLTS spectra are shown as solid lines and the positions of the defect levels $E^*_2$ and $E_2$ are indicated.

introduction of $E^*_2$ assuming first order kinetics: $[E^*_2] = [E^*_2]_{ss}[1 - \exp(-kt_{ann})]$, where $[E^*_2]_{ss}$ denotes the $E^*_2$ concentration ($[E^*_2]$) in steady-state and $k$ denotes the introduction rate. Interestingly, $k$ was found to be similar for all $T_{ann}$ and exhibited values of around $1/3000$ s$^{-1}$. The resulting Arrhenius plot for $[E^*_2]_{ss}$ is shown in figure 3 (b), and an activation energy of 1.0 eV to 1.3 eV was derived from linear fits to the data for the introduction of $E^*_2$ under an applied reverse-bias voltage of $-8$ V. No change in the $E^*_2$ concentration was observed for heat treatments below 500 K regardless of the kind of ion implantation or whether an external bias voltage was applied or not.

Further experiments were conducted to investigate the influence of the magnitude of the reverse-bias voltage applied during reverse-bias anneals. Figure 4 shows DLTS spectra recorded on a HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film after implantation with He and H, and subsequent reverse-bias anneals at 600 K for 90 min using an applied reverse-bias voltage of either $-4$ V or $-8$ V. The reverse-bias anneal at $-4$ V was performed prior to the one at $-8$ V, and the SBD was subjected to a zero-bias anneal before performing the reverse-bias anneal at $-8$ V. Thus, the concentration associated with $E^*_2$ was low prior to both reverse-bias anneals. When performing the heat treatment under a reverse-bias voltage of $-8$ V, the Fermi level is shifted further away from $E_C$ inside the corresponding space-charge region, and hence in-between the surface of the HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film and $W$ ($-8$ V). Consequently, the Fermi level is affected up to a depth of $W$ ($-4$ V) for a heat treatment under an applied reverse-bias voltage of $-4$ V. In figure 4 (a), DLTS measurements were performed that probe mainly the region from $W$ ($-8$ V) to $W$ ($-4$ V), and $E^*_2$ is only detected in significantly increased concentration for the heat treatment performed under an applied reverse-bias voltage of
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$-8$ V. This suggests that $E^*_2$ is only introduced inside the space-charge region established during the heat treatment. Figure 4 (b) shows DLTS spectra recorded for a probing depth between $W$ ($-4$ V) and the surface of the HVPE-grown $\beta$-Ga$_2$O$_3$ thin-film. An increased concentration of $E^*_2$ can be seen for the reverse-bias anneals performed at $-8$ V and $-4$ V. Importantly, the concentration related to $E^*_2$ is significantly higher for the reverse-bias anneal performed at $-8$ V. In figure 4 (c), DLTS spectra are shown for a probing depth of $W$ ($-8$ V) to the surface. Although both reverse-bias anneals increase the concentration of $E^*_2$, the reverse-bias anneal at $-8$ V produces a larger concentration than the anneal at $-4$ V. The results presented in figure 4 show that $E^*_2$ is introduced inside the space-charge region of SBDs subjected to reverse-bias anneals, and that applying a larger reverse-bias voltage during the heat treatments leads to the introduction of a larger amount of $E^*_2$, suggesting that the defect associated with $E^*_2$ forms more preferably the further away the Fermi-level position is from $E_C$. The $E_2$ concentration is not influenced by the reverse-bias anneals. Its concentration depends, however, on the probing depth of the DLTS measurement which is most likely related to the $\lambda$-correction [32] and/or a slightly inhomogeneous depth distribution of Fe.

To summarize our findings, the formation of $E^*_2$ after ion implantation due to a thermally-activated process suggests a relation of $E^*_2$ to a defect complex comprising at least one intrinsic defect. This is in accordance with a previous study on proton-irradiated $\beta$-Ga$_2$O$_3$ single crystals and thin-films [19]. The formation of $E^*_2$ is considerably enhanced by reverse-bias anneals at temperatures of around 600 K, and its formation is seen to occur inside the space-charge region of SBDs. Notably, $E^*_2$ is introduced to a larger extent when applying larger reverse-bias voltages during reverse-bias anneals. Zero-bias anneals can be used to decrease the concentration of $E^*_2$. The presence of H does not significantly affect the observed introduction of $E^*_2$, but seems to aid the removal of $E^*_2$ when performing zero-bias anneals.

The formation and removal behavior of $E^*_2$ upon reverse-bias and zero-bias anneals can be explained by at least two scenarios: i) the defect complex giving rise to $E^*_2$ consists of constituent defects, which have a barrier for migration that depends strongly on their charge states, and hence the Fermi-level position, or ii) the defect complex associated with $E^*_2$ has several configurations, where only one (or a few) have a charge-state transition level giving rise to $E^*_2$. The configuration associated with $E^*_2$ is more likely to form when the Fermi level is far away from $E_C$, whereas configurations that do not exhibit a charge-state transition level accessible for our DLTS measurements are more favorable for Fermi-level positions close to $E_C$.

Scenario i) is supported by computational studies reporting a strong dependence of the migration barrier of intrinsic defects in $\beta$-Ga$_2$O$_3$ on their respective charge state [19, 39, 40]. For example, $V_O$ exhibits a lower migration barrier in the +2 charge state compared to the one found for the neutral charge state [40]. However, the observation of a reversible formation and removal of the defect giving rise to $E^*_2$ is challenging to reconcile with scenario i). Rather, one would expect that the mobile defect either leaves or enters the space-charge region during the heat treatment, and
thus either the removal or formation of a defect will be observed within the space-charge region. Additionally, the dependence of the introduction of $E^*_2$ on the magnitude of the applied reverse-bias voltage is inconsistent with scenario i). For example, for the situation displayed in figure 4 (b), one would expect a similar $E^*_2$ concentration to be introduced regardless of the reverse-bias voltage applied during the reverse-bias anneal. In contrast, we observed a dependence of the introduced concentration of $E^*_2$ on the magnitude of the applied reverse-bias voltage.

Scenario ii), however, seems to be in better agreement with the experimental observations. Within scenario ii), it is expected that the formation and removal of $E^*_2$ will be reversible. The degree of reversibility will, however, be influenced by other factors, e.g., the presence of other defects and the transformation dynamics between different defect configurations. The observation of a thermally-activated steady-state concentration of $E^*_2$ also agrees with scenario ii) where the formation and removal of $E^*_2$ is related to a Fermi-level-dependent difference in formation energy, i.e., the equilibrium concentration of $E^*_2$ will depend on the Fermi-level position. Thus, we also expect the formation of $E^*_2$ to gradually depend on the magnitude of the applied reverse-bias voltage, in accordance with our observations. We derived an activation energy on the order of around 1.0 eV - 1.3 eV for the thermally-activated formation of $E^*_2$ (see figure 3 (b)). Within scenario ii), this activation energy can be interpreted as the difference in relative formation energy between the defect configuration giving rise to $E^*_2$ and competing defect configurations without a charge-state transition level accessible for our DLTS measurements.

The introduction of $E^*_2$ does not seem to be influenced by the presence of H. In contrast, the removal of $E^*_2$ due to zero-bias anneals is promoted in the presence of H. Within scenario ii), H is proposed to form a hydrogenated version of the defect complex being connected to $E^*_2$, and this hydrogenated defect complex is more likely to form than the non-hydrogenated version for Fermi-level positions close to $E_C$. Thus, H promotes the removal of $E^*_2$ during zero-bias annealing. For Fermi-level positions further away from $E_C$, the hydrogenated defect complex is not as likely to form, and thus plays only a minor or no role in the actual formation of $E^*_2$. Notably, for scenario ii) to be able to explain the experimental results, the transformation between different defect configurations needs to be possible at the temperatures used for the heat treatments, whereby the kinetics of transformation may depend on the charge states of the involved defects.

Further work is necessary to identify the specific defect(s) giving rise to $E^*_2$. However, the formation and removal behavior of $E^*_2$ after ion implantation and proton irradiation and the similarity in behavior seen for a wide range of different $\beta$-Ga$_2$O$_3$ samples implies the association with a defect complex either involving only intrinsic defects or comprising an intrinsic defect and an ubiquitous impurity [19]. Based on these observations, one may speculate about the origin of $E^*_2$. For example, di-vacancy complexes formed by $V_{Ga}$ and $V_{O}$ ($V_{Ga}$-$V_{O}$) possess many of the proposed features; they are intrinsic defect complexes that are expected to exhibit one or more charge-state transition levels in the
Formation and control of the $E^*_2$ center

proposed energy range, and they have a multitude of different configurations [19, 23]. Notably, the formation energies of various $V_{Ga}-V_{O}$ complexes have been found to be comparatively low in $\beta$-Ga$_2$O$_3$, and can be expected to strongly depend on the Fermi-level position [19]. Moreover, $V_{Ga}-V_{O}$ complexes display acceptor behavior for Fermi-level positions close to $E_C$ [19], and thus hydrogenation is likely [23]. Importantly, the migration barriers computed for isolated $V_{Ga}$ and $V_{O}$ suggest that defect transformation involving vacancies will be possible at temperatures around 600 K [23, 40]. However, first-principles calculations are only reported for a few $V_{Ga}-V_{O}$ configurations so far, and are not sufficient to explain the experimental observations entirely [19], which warrants further investigations.

4. Summary and Conclusion

The formation and removal of $E^*_2$ ($E_A = 0.71$ eV, $\sigma_{na} = 1 \times 10^{-19}$ cm$^2$) in HVPE-grown $\beta$-Ga$_2$O$_3$ thin-films subjected to ion implantation and subsequent heat treatments was studied using DLTS. The introduction of $E^*_2$ is promoted by reverse-bias anneals at temperatures in the range of 600 K within the space-charge region of SBDs comprising the $\beta$-Ga$_2$O$_3$ thin-films subjected to He- and/or H-implantation. Subsequent zero-bias anneals at temperatures in the range of 600 K cause the concentration of $E^*_2$ to decrease, whereby the removal of $E^*_2$ is more pronounced if H is present in the space-charge region of the SBD. The formation of $E^*_2$ by reverse-bias annealing is a thermally-activated process with an activation energy of 1.0 eV - 1.3 eV. In summary, our results show how reverse-bias and zero-bias anneals can be used to control the concentration of $E^*_2$ in SBDs comprising He- and/or H-implanted $\beta$-Ga$_2$O$_3$ thin-films. Importantly, it is shown that H can aid the removal of $E^*_2$. The results presented here strongly suggest that $E^*_2$ is likely to form in the space-charge region of $\beta$-Ga$_2$O$_3$-based devices for power electronics if the constituent defects of $E^*_2$ are present. Moreover, it can be expected that the $E^*_2$ concentration will change during device operation. Both points are particularly relevant taking into account that $E^*_2$ has been shown to influence the performance of $\beta$-Ga$_2$O$_3$-based MESFETs [15, 14].

The observed formation behavior of $E^*_2$ is explained by a change in the Fermi-level position inside the space-charge region when applying a reverse-bias voltage. Thus, we propose that $E^*_2$ is related to a defect complex involving intrinsic defects that exhibits different configurations whose relative formation energies depend strongly on the Fermi-level position. Configurations giving rise to $E^*_2$ are more likely to form for Fermi-level positions further away from $E_C$ (reverse-bias annealing), whereas configurations that are preferred for Fermi-level positions close to $E_C$ (zero-bias annealing) do not exhibit defect levels accessible for our DLTS measurements. Furthermore, $E^*_2$ can be passivated by H, and the hydrogenated defect complex is proposed to be more likely to form for Fermi-level positions close to $E_C$. Di-vacancy complexes of the form $V_{Ga}-V_{O}$ are proposed as potential candidates for $E^*_2$, but further investigations are required for an unambiguous identification of the defect level.
5. Acknowledgements

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6. References


Formation and control of the $E_2^*$ center


Paper V

Fabrication and characterization of Schottky barrier diodes on rutile TiO$_2$

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Schottky barrier diodes (SBDs) were fabricated by depositing Pd, Pt or Ni on single crystal, conductive n-type rutile TiO₂ using e-beam evaporation. As-grown and nominally undoped rutile TiO₂ single crystals are semi-insulating, and were heat-treated in forming gas flow, N₂ flow or H₂ gas to obtain conductive n-type crystals displaying electrical conductivities in the range of \((0.5 - 8) \times 10^{-2} \ \Omega^{-1} \ cm^{-1}\). Additionally, SBDs were deposited on Nb-doped conductive n-type rutile TiO₂ with a conductivity of around \(0.25 \Omega^{-1} \ cm^{-1}\). Generally, SBDs displaying a rectification of up to eight orders of magnitude were obtained, when comparing the current under reverse and forward bias. The extracted ideality factors were in the range of \(1.1 - 4.0\). From Capacitance-Voltage measurements, the built-in voltage was derived to be around \(1.2 \ V - 1.9 \ V\), depending on the doping concentration of the specific TiO₂ single crystal. Series resistances as low as \(19 \ \Omega\) were achieved. A considerable variation in the electrical characteristics of different SBDs deposited on the same crystal was found, regardless of the metal or doping strategy used. Moreover, the SBD characteristics change over time, particularly seen as a degradation in rectification, mainly related to an increase in the current under reverse bias. Additional surface treatments such as boiling in H₂O₂ and etching in HF do not have a significant effect on the quality of the SBDs. Clear indications for poor adhesion between TiO₂ and Pd are shown. In conclusion, we demonstrate the fabrication of SBDs which are suitable for studying the fundamental properties of metal/TiO₂ junctions and the characteristics of electrically-active defects in TiO₂ using space-charge spectroscopy.

Keywords: Schottky barrier diodes, TiO₂, degradation

I. INTRODUCTION

Rutile titanium dioxide (TiO₂) is a wide-bandgap semiconductor \((E_g = 3.2 \ eV [1–4])\) well-known for its photo-catalytic properties [5, 6], rendering TiO₂ a promising material for photo-catalytic water-splitting as well as photo-catalytic water purification [6–10]. Conductive n-type TiO₂ is of particular interest for such applications due to its lower resistivity and more pronounced optical absorption in the visible and infrared part of the electromagnetic spectrum compared to pristine TiO₂ [11–14]. It is possible to achieve n-type doping in TiO₂ by incorporating Nb [13, 15–17] or by heat-treating TiO₂ in hydrogenating or reducing atmospheres [11, 14, 15, 18–20]. Hydrogenated as well as reduced TiO₂ have been used in photo-catalytic applications [11, 12, 14, 21]. However, there is still no agreement on the nature of the main donors in hydrogenated or reduced TiO₂ [22–24]. Defects are also believed to play a role in the optical absorption in the visible and infrared part of the electromagnetic spectrum displayed by conductive n-type TiO₂ [14, 25–28]. Thus, understanding the properties of defects in TiO₂ is important to improve photo-catalytic applications involving TiO₂.

In applications for photo-catalysis, systems consisting of TiO₂ and noble metals, such as Pd, Pt, Au or Ag, display a better performance compared to just TiO₂ [29–33]. This is believed to be due to an improved charge transfer at the interface between the metal and TiO₂ due to the formation of a rectifying junction [34]. Besides photo-catalytic applications, rectifying metal/TiO₂ junctions are also of interest for UV photo-detectors [35], hydrogen sensors [36] and switching devices [37–39].

In order to improve metal/TiO₂ junctions for all applications mentioned above, the charge transfer across the interface needs to be understood better. This requires knowledge regarding the electrical characteristics of rectifying metal/TiO₂ junctions, where simplified model systems are often a superior starting point for such investigations. Besides studying the properties of the metal/TiO₂ junctions themselves, the junctions can also be used to probe the properties of defects in TiO₂ using space-charge spectroscopy [16, 40, 41]. Thus, the fabrication of Schottky barrier diodes (SBDs) involving conductive TiO₂ single crystals obtained by employing different doping strategies paves the way for systematic defect studies in such material as well as enables investigations of the fundamental properties of the corresponding metal/TiO₂ junctions.

SBDs have been achieved on TiO₂ using Pt [42–44], Pd [45–47], Ni [48] and Au [19, 49–51]. The characteristics of these SBDs show a varying degree of non-ideal behaviour. Although there is a considerable amount of literature on SBDs
involving TiO$_2$, only a few reports exist comparing SBDs on differently doped TiO$_2$ crystals fabricated in the same laboratory. Additionally, there is a general concern about the long-term stability of metal/TiO$_2$ junctions[42, 46, 52], but the change in electrical characteristics over time has not been addressed in depth. In hydrogenated TiO$_2$, the incorporated H might affect the SBDs. It has been shown that the current in junctions formed between different metals and n-type-type single crystalline TiO$_2$ is sensitive to hydrogen in the ambient [49], and a reaction between H and Pd may cause SBDs to degrade [46, 47, 49].

In the present work, we have systematically studied the electrical behaviour of junctions formed between Pd, Pt, Ni as well as Al and n-type TiO$_2$ single crystals doped with Nb or doped by heat-treatments in hydrogenating or reducing atmospheres. The concentration of interstitial hydrogen (H$_i$) in the different types of TiO$_2$ crystals was measured. The variation in SBD characteristics for diodes deposited on the same TiO$_2$ crystal was investigated. First, SBD characteristics using different metals are compared. SBDs were obtained for Pd/TiO$_2$, Pt/TiO$_2$ and Ni/TiO$_2$ with up to eight orders of magnitude in rectification. Following this, a comparison of Pd/TiO$_2$ SBDs using TiO$_2$ with different dopants and different H$_i$ concentration is presented. The diode characteristics showed a pronounced change over time, related to a decrease in overall rectification. Detailed measurements concerning the degradation are presented. The fabricated Pd/TiO$_2$ junctions are found to exhibit suitable electrical characteristics for studying fundamental junction properties and the characteristics of electrically-active defects in TiO$_2$ using space-charge spectroscopy.

II. EXPERIMENTAL

Rutile TiO$_2$ single crystals with a thickness of 0.5 mm exhibiting different surface orientations grown by the float-zone (FZ) method or the Verneuil (V) method were purchased from MTI Corporation and Shinkosha, respectively. In the following, a TiO$_2$ crystal with surface orientation (X) is denoted as TiO$_2$(X). Nominally undoped FZ- and V-grown single crystals were obtained, while V-grown single crystals doped with 0.05wt% of Nb were also acquired. Nominally undoped TiO$_2$ single crystals were transparent and semi-insulating with a conductivity of $\sigma < 10^{-7}\Omega^{-1}\cdot\text{cm}^{-1}$. The as-received wafers were cut into pieces measuring approximately $5 \times 5 \text{mm}^2$ using a laser cutter. After cutting, all crystals were cleaned in an ultrasonic bath with acetone, isopropanol and de-ionized water for 5 min each (standard cleaning procedure).

Afterwards, the undoped samples were exposed to one of the following heat treatments (annealings):

1. Annealing in forming gas (FG) flow (N$_2$ + H$_2$ with $[\text{H}_2]/[\text{N}_2] \approx 1/9$) at temperatures between 500°C and 600°C. The annealing duration was 35 – 90 min. After annealing, the samples were cooled-down rapidly in the gas flux.

2. Annealing in closed ampoules filled with approximately 0.5 bar of H$_2$ gas. The ampoules were evacuated before filling with H$_2$. These crystals were annealed at temperatures between 400°C and 600°C for 10 – 90 min. After annealing, the crystals stayed in the ampoules during cool-down.

3. Annealing in N$_2$ flow at temperatures between 980°C and 1200°C. The typical annealing duration was in the order of hours (1.25 - 25 h). After annealing, the samples were taken out of the furnace and the cool-down occurred in N$_2$ flow.

A tube furnace was used for annealing. All TiO$_2$ crystals were put into the furnace after the desired annealing temperature was reached. In the following, TiO$_2$ crystals which have been annealed in FG flow, H$_2$ gas or N$_2$ gas are denoted as FG-TiO$_2$, H$_2$-TiO$_2$ and N$_2$-TiO$_2$, respectively. Nb-doped crystals are denoted as Nb-TiO$_2$. Ni, Pd, Pt and Al were deposited onto TiO$_2$ single crystals subjected to the heat-treatments described above, and Pd was deposited onto Nb-TiO$_2$ crystals (thickness ~ 150 nm). Circular metal contacts displaying areas of $(0.67 - 6.36) \times 10^{-3} \text{ cm}^2$ were obtained using a shadow mask. Either eutectic InGa was applied to or a stack of Ti/Al was deposited onto the back side of these crystals as Ohmic contacts. All metal depositions were performed using e-beam evaporation. In between depositing or applying metals, the crystals were cleaned using the standard cleaning procedure described above. Typically, between 15 to 20 SBDs are obtained on a piece of TiO$_2$ crystal (see Fig. 1 for an overview of the resulting sample layout). Some crystals were subjected to surface treatments prior to the deposition of the circular Ni, Pd, Pt or Al contacts. These crystals were exposed to boiling H$_2$O$_2$ for 1 – 3 min, and some of them were additionally exposed to HF for 5 min. Crystals that were exposed to HF in addition to H$_2$O$_2$ will be denoted as TiO$_2$(X)-HF in the following.

Fourier-Transform infrared spectroscopy (FT-IR) was used to determine the concentration of H$_i$ denoted as [H$_i$] in TiO$_2$ single crystals. The investigated TiO$_2$ single crystals had a surface orientation of (001). Infrared (IR) transmittance spectra were measured using an evacuated Bruker IFS 125HR spectrometer equipped with a globar light source, a KBr beamsplitter, and a liquid-nitrogen-cooled InSb detector. The IR beam was kept at normal incidence ($\pm 3^\circ$) with respect to the (001) surface of the TiO$_2$ single crystals. Measurements were performed at room temperature using a
spectral resolution of 1 cm\(^{-1}\). [H\(_1\)] was determined from the integrated area of the optical absorption associated with a local vibrational mode of H\(_1\) [55] using a calibration factor determined by Johnson \textit{et al.} [56].

The electrical conductivity, \(\sigma\), and resistivity, \(\rho\), of TiO\(_2\) single crystals was determined using a four-point probe measurement according to the van-der-Pauw method [57, 58]. The measurement utilized a Keithley 7001 switching system, a Keithley 2182A nano-volt-meter and a Keithley 6221 current source. Eutectic InGa pads were used as Ohmic contacts in the corners of the TiO\(_2\) single crystals.

A sample for Scanning Transmission Electron Microscopy (STEM) was prepared by focused ion beam (FIB) using a Ga-ion JEOL JIB-4500. Before milling, a 700 nm W film was deposited in order to protect the underlying sample against Ga damage.

Current-Voltage (IV) measurements were carried out on the metal/TiO\(_2\) junctions under dark conditions at variable temperatures in the range between 25 K and 330 K using a Keithley 6487 unit. Measurements below room temperature were performed in vacuum and within a closed-cycle He cryostat. Capacitance-Voltage (CV) measurements were carried out under dark conditions using an Agilent 4284A LCR meter at six different probing frequencies \(f_{\text{meas}}\) between 1 kHz and 1 MHz. According to the Mott-Schottky theory of metal-semiconductor junctions, the barrier height, \(\Phi_B\), depends on the metal work function, \(\Phi_m\), and the semiconductor electron affinity, \(\chi_s\): \(\Phi_B = \Phi_m - \chi_s\) [59]. Rectifying junctions are formed for \(\Phi_B > 0\), while Ohmic contacts are obtained for \(\Phi_B < 0\). The expected barrier height \(\Phi_B\) for SBDs between TiO\(_2\) and Pd, Pt, Ni as well as Al are summarized in Tab. I. Here, an electron affinity of \(\chi_s = 4.33\) eV for TiO\(_2\) was assumed [60]. From IV measurements, the series resistance, \(R_s\), shunt resistance, \(R_{sh}\), ideality factor, \(\eta\), and average rectification was deduced. \(\eta\) incorporates all the effects that make the device non-ideal [61]. Here, \(R_s\) represents the transport of charge carriers through the bulk (on-state resistance) and through the Ohmic contact. \(\rho_{\text{IV}}\) was calculated from \(R_s\), extracted from IV measurements on SBDs, and sample dimensions; \(\rho_{\text{IV}} = \frac{R_s A}{l}\). \(l = 500\) \(\mu\)m is the crystal thickness, and \(A\) is the area of the different SBDs. \(R_{sh}\) determines the amount of reverse leakage current. The average rectification of the diodes was calculated by computing the ratio between the average current under reverse and forwards bias. For averaging, the voltage ranges between \(\pm 2\) V and \(\pm 4\) V for \(V\) was chosen. Diodes that showed a rectification lower than one order of magnitude after contact deposition were disregarded. From CV measurements, the donor concentration, \(N_d\), and the built-in voltage, \(V_0\), were deduced, using the depletion approximation [59]. In order to calculate \(N_d\), knowledge of the static relative dielectric constant for TiO\(_2\), \(\epsilon_{\text{TiO}_2}\), is required. Here, a value of \(\epsilon_{\text{TiO}_2} = 160\) at room temperature was assumed [62, 63].

III. RESULTS AND DISCUSSION

A. TiO\(_2\) single crystals

N-type TiO\(_2\) single crystals with a bluish color and conductivities in the range from \((0.5 - 8) \times 10^{-2} \ \Omega^{-1} \ \text{cm}^{-1}\) were obtained by heat-treating as-received nominally-undoped TiO\(_2\) single crystals in forming gas flow, N\(_2\) flow or H\(_2\) gas. Similarly, the Nb-doped TiO\(_2\) single crystals exhibited also n-type conductivity (\(\sigma = 0.25 \ \Omega^{-1} \ \text{cm}^{-1}\)) and a dark bluish color. It is generally observed that conductive n-type TiO\(_2\) single crystals display a bluish color [18, 25, 26, 64-67]. The relation between the electrical conductivity and optical absorption of the heat-treated TiO\(_2\) single crystals is investigated further in Ref. [68].

Fig. 2 displays infrared absorption spectra recorded on as-received TiO\(_2\) single crystals (nominally undoped as well...
as Nb-doped) and heat-treated TiO$_2$ single crystals. Data are shown for the wavenumber region where optical absorption associated with a local vibrational mode of H$_i$ can be estimated \[55\]. From the integrated area of this line, [H$_i$] in the samples can be estimated \[56\]. Typically, nominally-undoped TiO$_2$ single crystals display [H$_i$] in the range of \(10^{17}\text{ cm}^{-3}\), while Nb-doped crystals show [H$_i$] below the detection limit of the measurement which is estimated to be below \(1 \times 10^{15}\text{ cm}^{-3}\). [H$_i$] of TiO$_2$ single crystals heat-treated in FG flux or H$_2$ gas increases, while TiO$_2$ single crystals annealed in N$_2$ display a decreased [H$_i$] concentration compared to nominally-undoped TiO$_2$ crystals. H$_i$ is reported to be a shallow donor in TiO$_2$ \[55, 69, 70\], and is likely to be responsible for the conductivity observed in samples heat-treated in FG flow or H$_2$ gas \[68\]. Notably, no change in the [H$_i$] of the samples was observed over the course of a few months when storing the crystals at around \(-20^\circ\text{C}\) \[68\]. $\sigma$, however, decreased slightly with time. $\sigma$ was measured on FG-TiO$_2$ crystals after annealing, and remeasured 40 days later. These measurements showed a reduction of $\sim 5\%$ in $\sigma$ after 40 days of storage, which was larger than the relative standard deviation of the measurements ($\sim 1\%$).

### B. Metal/TiO$_2$ Junctions

#### 1. Influence of the choice of metal

Fig. 3 shows IV curves recorded on junctions between FZ-grown FG-TiO$_2$(001) and various metals. Rectifying junctions are formed for Pd/TiO$_2$, Pt/TiO$_2$ and Ni/TiO$_2$, while Ohmic contacts are obtained for Al/TiO$_2$, as anticipated from the expected barrier heights stated in Tab. I. The highest rectification observed was eight orders of magnitude and was observed for Pd/TiO$_2$ junctions. Usually, independent of the exact annealing condition, rectifications be-

<table>
<thead>
<tr>
<th>Metal</th>
<th>Metal work function[71]</th>
<th>Expected barrier height $\Phi_B$ (eV)</th>
</tr>
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<tbody>
<tr>
<td>Pd</td>
<td>5.12</td>
<td>0.8</td>
</tr>
<tr>
<td>Pt</td>
<td>5.65</td>
<td>1.3</td>
</tr>
<tr>
<td>Ni</td>
<td>5.15</td>
<td>0.8</td>
</tr>
<tr>
<td>Al</td>
<td>4.28</td>
<td>$-$</td>
</tr>
</tbody>
</table>

Table I. Metal work functions and expected barrier heights $\Phi_B$ for metal/TiO$_2$ junctions, assuming $\chi_{\text{TiO}_2} = 4.33\text{eV}$ \[60\]. Rectifying junctions are expected for Pd, Pt and Ni, while for Al, Ohmic contacts are expected.
tween $2 - 5$ order of magnitude are achieved for Pd, Pt as well as Ni contacts on TiO$_2$. Series resistances in the order of $100\Omega$ to $1\, \text{M}\Omega$ were obtained. Typically, ideality factors between 1.1 and 4.0 are found. $\eta$ larger than 2 can, for example, be related to the presence of a highly-compensated interfacial layer or to recombination in the depletion region [19, 59, 72].

2. Influence of surface orientation and treatment

In Fig. 3, one can observe a significant spread in electrical characteristics of the SBDs deposited on the same TiO$_2$ single crystal (see Fig. 1). There is a wide spread in the values for the current under reverse as well as forward bias. The differences in electrical characteristics seen for SBDs deposited on the same TiO$_2$ crystal originate from a spread in values of $R_s$, $R_{sh}$ and $\eta$, suggesting lateral inhomogeneities over distances of around 1 mm (see Fig. 1). Particularly, the differences seen for $\eta$ suggest significant surface inhomogeneities, e.g., due to lateral inhomogeneities in the density of interface states or the thickness of a highly-compensated interfacial layer [57, 72, 73]. The spread observed for $R_s$ and $R_{sh}$ could also be related to surface inhomogeneities. $R_s$ will here mainly comprise of contributions from the bulk resistivity and the contact resistance of the Ohmic contact, and especially the resistance of the Ohmic contact could be influenced by surface inhomogeneities [57]. $R_{sh}$ is related to leakage currents whose magnitude might, for example, be sensitive to the density of defects within the space-charge region [74]. In Fig. 4, the average rectification determined for
Figure 4. Average rectification determined for metal/TiO$_2$ junctions. For each data point, the rectifications of 15 − 20 SBDs fabricated using the same TiO$_2$ crystal were averaged (see Fig. 1). The displayed uncertainty is the standard deviation of the corresponding average.

Figure 5. $\rho_{IV}$, extracted from IV measurements, as a function of $\rho$ for a series of FZ-grown H$_2$-TiO$_2$ crystals annealed at temperatures from 400 °C to 600 °C for 10 − 90 min. The resistivity of each crystal was measured before Pd contacts were deposited. Each data point corresponds to a measurement on a single SBD.
3. Comparison between resistivity and SBD series resistance

Values for $\rho$ of FZ-grown $\text{H}_2\text{-TiO}_2$ crystals annealed at different temperatures between 400 °C and 600 °C for durations of 10 – 90 min were measured prior to metal contact deposition. In Fig. 5, the resistivity estimated from IV measurements, $\rho_{IV}$, for several SBDs on each $\text{H}_2\text{-TiO}_2$ crystal, is plotted as a function of resistivity, $\rho$. As shown in the figure, the least resistive crystals have values for $\rho_{IV}$ very close to $\rho$. For more resistive crystals, $\rho_{IV}$ are larger than $\rho$. This result indicates that for conductive crystals, the bulk resistivity is limiting the series resistance, but for more resistive crystals, contact resistance becomes important. Moreover, this result suggests that the contact resistance is dependent on the doping concentration of the crystal. The relative deviation in $\rho_{IV}$ between different diodes is similar for all crystals, as shown in the inset of Fig. 5.

4. Influence of doping

Doping levels suitable for electrical measurements were achieved by annealing in forming gas at 600 °C for ~ 1 h, in $\text{H}_2$ at 450 °C for 30 – 60 min, or in $\text{N}_2$ at 1100 °C for ~ 90 min. Fig. 6 shows IV curves recorded on Pd/TiO$_2$ junctions comprising FZ-grown $\text{H}_2\text{-TiO}_2$(001), V-grown FG-TiO$_2$(001), V-grown N$_2$-TiO$_2$(001) and V-grown Nb-TiO$_2$(001). Rectifying junctions are obtained regardless of the doping procedure used. The resulting junctions exhibit ideality factors from 1.1 to 4, and values for the series resistance in the order of 10 $\Omega$ to 100 $\text{M}\Omega$. A large spread in electrical
characteristics is also seen for Pd/TiO$_2$ junctions comprising TiO$_2$ crystals doped using different strategies, both between the differently treated crystals, and between SBDs on the same crystal (see Fig. 1). In Fig. 6, one can observe a significant spread in the values of $R_s$, $R_b$, and $\eta$ of the SBDs deposited on the same TiO$_2$ single crystal, resulting in a wide range of values for the current under reverse as well as forward bias, similar to what is seen in Fig. 3. Notably, Nb-doped TiO$_2$ displays the same spread in electrical characteristics. Thus, one can conclude that the inhomogeneity causing the large spread in electrical characteristics is not caused by heat-treating the samples in reducing or hydrogenating atmospheres. Moreover, H is not likely to play a role in the observed inhomogeneity taking into account that the Nb-doped TiO$_2$ crystals were shown to contain significantly less H than the hydrogenated or reduced TiO$_2$ crystals (see Fig. 2).

5. Schottky barrier height and Built-in voltage

The determination of barrier heights from IV characteristics is only reliable if the current is determined by thermionic emission [75]. For the SBDs studied here, this is not the case, since $\eta$ is larger than 1.1 at room temperature [75]. The SBDs that exhibited the lowest values of $\eta$ were measured also at lower temperatures $T$. IV-$T$ curves from a Pd/H$_2$-TiO$_2$ junction are plotted in Fig. 7 (a). $\eta(T)$ displays an abnormal decrease with increasing $T$, as shown in the inset. Such a temperature-dependence leads to a non-linear shape of the Richardson plot $\ln(I_0/T^2)$ versus $1/T$, where $I_0$ is the reverse saturation current [75], and the value for the effective Richardson constant $A^*$ could not be extracted. A similar temperature dependence of $\eta$ was found regardless of the crystal growth method, choice of metal or the doping procedure used. These measurements are in line with previously reported temperature-dependent IV data measured on Schottky junctions involving TiO$_2$ [44, 48, 76]. Recently, $\Phi_B$ has been deduced from IV-$T$ data measured on junctions involving TiO$_2$ that display similar non-ideal behaviour [48, 76]. In Ref. [76] and [48], $\Phi_B$ was extracted assuming barrier height inhomogeneities (BHI) and using a model proposed by Werner and Gütter [77]. For the junctions studied here, however, which were measured at lower temperatures, this model can only explain the non-ideal behaviour of IV measurements recorded at $T$ larger than $\sim 100$ K. For $T < 100$ K, the requirement of a linear relationship between $\eta$ and $\Phi_B$, which confirms the existence of BHI [78], is not fulfilled. In addition, the modified Richardson plot provides reasonable values for $A^*$ and $\Phi_B$, but only in the temperature range above 100 K. Therefore, it is possible that BHI affect the current transport, but at low temperatures, other mechanisms are also important.

The built-in voltage for Pd/TiO$_2$ junctions was determined from CV measurements. Fig. 7 (b) shows results of CV measurements recorded on Pd/TiO$_2$ junctions comprising FG-TiO$_2$(001), V-grown Nb-TiO$_2$(001) and V-grown Nb-TiO$_2$(001) crystals. The representation of CV measurements as $1/C^2$ vs. $V$ are straight lines, suggesting a homogeneous donor concentration in the depletion region. Notably, CV measurements at different $f_{meas}$ display a

![Figure 7](image-url)
slight dispersion. \( V_0 \) was determined to be 1.2 V – 1.3 V for Pd/FG-TiO\(_2\)(001), 1.4 V – 1.6 V for Pd/Nb-TiO\(_2\)(001) and 1.8 V – 1.9 V for Pd/Nb-TiO\(_2\)(001) junctions, depending on \( f_{\text{meas}} \). Notably, a \( N_d \) of 1.4 \( \times \) 10\(^{19}\) cm\(^{-3}\) was determined for the Nb-TiO\(_2\)(001) crystal, being close to the Nb concentration of 1.38 \( \times \) 10\(^{19}\) cm\(^{-3}\) expected in these crystals according to the wt% of Nb specified by the supplier [54]. Thus, the determination of \( N_d \) from CV measurements is corroborated. The \( V_0 \) deduced is larger than expected, considering the theoretically calculated SBD heights given in Tab. I.

The results shown in Fig. 7(b) show that the fabricated Pd/TiO\(_2\) junctions are suitable for space-charge spectroscopy techniques, such as deep-level transient spectroscopy [79] or thermal admittance spectroscopy [80], and hence the junctions can be used to study electrically-active defects in TiO\(_2\) [41]. It is, however, important to verify the suitability of a specific junction for space-charge spectroscopy, i.e., junctions suitable for space-charge spectroscopy should display low series resistance as well as ideality factors close to 1 [57].

6. Time-evolution of electrical characteristics

Pd/TiO\(_2\) junctions were stored at \(-20^\circ\text{C}\) for several months, and IV curves were recorded every few days. Most Pd/TiO\(_2\) junctions exhibit a decrease in rectification over the course of a few weeks regardless of the doping used for the TiO\(_2\) crystal. It has been reported previously that the electrical characteristics of rectifying metal/TiO\(_2\) junctions change over time, and a reaction between H and Pd has been suggested to be the cause of the degradation [46, 47, 49]. Fig. 8 (a) displays IV curves from a Pd/TiO\(_2\) junction recorded at different times after initial contact deposition. The junction comprises a FZ-grown FG-TiO\(_2\)(001) crystal. The series resistance and ideality factor of the Pd/TiO\(_2\) junction do not change significantly over the course of several weeks, while the current under reverse bias notably increases, and thus the overall rectification decreases. Such a degradation was typically observed for the SBDs comprising FG-TiO\(_2\)(001) crystals. Pd/TiO\(_2\) junctions comprising TiO\(_2\) crystals doped using heat-treatments in H\(_2\) or N\(_2\) also display a similar degradation behaviour. Thus, the observed degradation is related to a decrease in shunt resistance of the Pd/TiO\(_2\) junctions. Fig. 8 (b) shows the current under reverse bias as a function of time. Initially, there is very little change in the magnitude of the reverse current. After a few weeks, a pronounced increase in the current under reverse bias can be seen. We fitted this increase with a first-order kinetics expression: \( I(t) = I_0 - c_1 \cdot \exp(-t/\tau) \), where \( t \) is time, \( I_0 \) and \( c_1 \) are constants that vary with applied voltage and \( \tau \) is the characteristic time constant. At room temperature, the best fit was obtained for \( I_0 = 2.3 \) µA, \( c_1 = 4.8 \) µA for \(-2\) V and \( I_0 = 7.2 \) µA, \( c_1 = 14.7 \) µA for \(-4\) V; and \( \tau = 21 \) days for both \(-2\) V and \(-4\) V.

In FG-TiO\(_2\), H\(_2\) is expected to be the main donor, and thus the observation regarding the series resistance is in accordance with the observation that [H\(_2\)] does not change in similarly treated samples. Interestingly, this is contrary to expectations taking the large diffusion constant for H\(_2\) in TiO\(_2\) (\( D \sim 0.2 \) µm\(^2\)/hour at room temperature) into account [81].

![Graph](image-url)
In order to study the observed degradation further, IV curves of the Pd/TiO$_2$ junctions comprising a FZ-grown H$_2$-TiO$_2$(001) crystal were recorded every few days until the Pd contacts were removed after 42 days. During contact removal, some of the surface was polished off, leaving a rougher surface compared to as-received crystals. Fresh Pd contacts were deposited on the same crystal piece. The average rectification after first contact deposition was initially 5.2. Just before the contacts were removed, the average rectification had dropped to 1.8. Finally, after re-deposition of contacts, the average value increased to 3.0. This experiment demonstrates that a new annealing procedure is not required to improve the quality of the SBDs, and that the degradation is related to the interface. Interestingly, only $R_{th}$ changes over time, suggesting that the change at the Pd/TiO$_2$ interface related to the observed degradation does not affect the barrier itself. This observation may indicate that the degradation is caused by enhanced tunnelling of charge carriers through the space-charge region. The origin of such an enhanced tunnelling is, however, unclear. Studying the defects present at the Pd/TiO$_2$ interface using space-charge spectroscopy could help shedding light on the role of defects in TiO$_2$ regarding the observed leakage current [41].

![STEM micrograph](image)

Figure 9. STEM high-angle annular dark field cross-sectional image of a Pd/TiO$_2$ junction.

### C. Adhesion of Pd on TiO$_2$

In an attempt to study the interface between Pd and TiO$_2$, STEM was performed on a FIB sample fabricated from the edge of a Pd/TiO$_2$ junction, covering both the junction and plain TiO$_2$. Fig. 9 displays a STEM micrograph recorded on a Pd/TiO$_2$ junction after preparing a lamella using FIB. A gap between the Pd contact and TiO$_2$ crystal is clearly visible. A 100 nm thick Pd layer was confirmed present by energy-dispersive X-ray spectroscopy and high-angle annular dark-field imaging. However, it was found that the adhesion of Pd on TiO$_2$ crystals is poor. During FIB milling, local stress relaxation or heating induced by the beam at the Pd-TiO$_2$ interface may have caused the Pd-film to detach. Poor Pd-adhesion was also found during fabrication of the samples: Some Pd contacts detached from the TiO$_2$ during cleaning in acetone and isopropanol in an ultrasonic bath.

### IV. CONCLUSION

We have studied the formation of metal/TiO$_2$ junctions comprising Pd, Pt, Ni and Al. For this purpose, different strategies for obtaining conductive $n$-type TiO$_2$ single crystals were employed. Conductive $n$-type TiO$_2$ with conductivities ranging from $(0.5 - 8) \times 10^{-2} \ \Omega^{-1} \ cm^{-1}$ was obtained by heat-treatments in hydrogenating or reducing atmospheres. For comparison, Nb-doped TiO$_2$ ($\sigma = 0.25 \ \Omega^{-1} \ cm^{-1}$) was also utilized to form metal/TiO$_2$ junctions. Rectifying junctions are obtained for Pd/TiO$_2$, Pt/TiO$_2$ and Ni/TiO$_2$ regardless of the doping procedure or the surface orientation of the TiO$_2$ crystals, while Al forms an Ohmic contact with TiO$_2$. From CV measurements, the built-in voltage was deduced to be around $1.2 \ V - 1.9 \ V$, depending on the doping concentration of the specific TiO$_2$ single crystal. A large spread in electrical characteristics is found for SBDs fabricated on the same TiO$_2$ crystal regardless of the doping strategy or the surface orientation. Ideality factors extracted from IV measurements were in the range of $1.1 - 4.0$ at room temperature, whereas values for the series resistance range from $\sim 10 \ \Omega - 100 \ M\Omega$. Most Pd/TiO$_2$ junctions exhibit a degradation over time. The degradation is related to an increase in the current under reverse bias voltage, whereas the series resistance and ideality factor stay approximately constant. The degradation can be described by first-order kinetics with a time constant of 21 days at room temperature. Adhesion between Pd and TiO$_2$ appears to be poor, which could be one of the reasons for the large spread in electrical characteristics of SBDs. Importantly, we demonstrated the fabrication of Pd/TiO$_2$ junctions which can be used to study fundamental properties of metal/TiO$_2$ junctions and electrically-active defects in TiO$_2$ using space-charge spectroscopy.
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Paper VI

Influence of annealing atmosphere on formation of electrically-active defects in rutile TiO$_2$

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Influence of annealing atmosphere on formation of electrically-active defects in rutile TiO₂

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Electronic states in the upper part of the bandgap of reduced and/or hydrogenated n-type rutile TiO₂ single crystals have been studied by means of thermal admittance and deep-level transient spectroscopy measurements. The studies were performed at sample temperatures between 28 and 300 K. The results reveal limited charge carrier freeze-out even at 28 K and evidence the existence of dominant shallow donors with ionization energies below 25 meV. Interstitial atomic hydrogen is considered to be a major contributor to these shallow donors, substantiated by infrared absorption measurements. Three defect energy levels with positions of about 70 meV, 95 meV, and 120 meV below the conduction band edge occur in all the studied samples, irrespective of the sample production batch and the post-growth heat treatment used. The origin of these levels is discussed in terms of electron polarons, intrinsic point defects, and/or common residual impurities, where especially interstitial titanium atoms, oxygen vacancies, and complexes involving Al atoms appear as likely candidates. In contrast, no common deep-level defect, exhibiting a charge state transition in the 200–700 meV range below the conduction band edge, is found in different samples. This may possibly indicate a strong influence on deep-level defects by the post-growth heat treatments employed. Published by AIP Publishing. https://doi.org/10.1063/1.5011136

I. INTRODUCTION

Titanium dioxide (TiO₂) in its rutile form has gained considerable attention for its photocatalytic properties1–3 or as part of solar cells. 4,5 However, the bandgap of rutile TiO₂ is approximately 3.2 eV,6 which is too wide for utilizing the solar spectrum efficiently.6 Recently, reduced and/or hydrogenated TiO₂ has received increasing interest because it exhibits stronger absorption in the visible/infrared wavelength regime than virgin rutile TiO₂.7,8 However, the understanding of intrinsic and impurity-related defects in this material is not fully developed to date, but it is of key importance in virtually all of its applications.

Reduced and/or hydrogenated rutile TiO₂ exhibits n-type conductivity,9–13 but the nature of the main donor(s) is still under debate even after decades of research. The oxygen vacancy (V₀), titanium interstitial (Tiₐ), and hydrogen on an interstitial site (Hₐ) are considered to be potential sources of n-type doping.10,11,14–19 However, the properties of these donors remain elusive and controversial. The question which of these defects are dominant might furthermore strongly depend on the actual sample treatment.19 Importantly, hydrogen could be present in significant concentrations also in samples which were not intentionally hydrogenated.18

The identification of defects in rutile TiO₂ is particularly challenging as the energy scheme of the defect levels may be influenced by polaronic effects.19–23 First, this makes the theoretical description of defects in rutile TiO₂ exceptionally challenging.19,24 Second, polaronic effects can also lead to different defects having similar experimental signatures as electrons are trapped at similar Ti sites no matter which defect they actually originate from.19 Another consequence of the polaronic effects is that techniques which probe thermal or optical transition energies will yield significantly different values for the same defect. Hence, they cannot directly be used complementarily in identifying defects.19,20,23,24

This can, for example, be observed in the case of Hₐ: Conductivity, transport, electron paramagnetic resonance, and infrared absorption measurements report on a shallow donor level with thermal transition energies of several meV,10,11,25,30–32 while absorption data indicate optical transition energies of around 1–2 eV.8,28,32,33

Another prominent example is V₀. Some experiments indicate that V₀ is a shallow donor in rutile TiO₂, responsible for the n-type conductivity observed in samples annealed at low oxygen partial pressure,13,14,34 while other studies report V₀-related deep states.35,36 This controversy concerning V₀ is further complicated by the results of ab-initio calculations, as different studies strongly disagree on whether V₀ induces shallow effective mass-like states or deep donor levels.27,37–40

Space-charge spectroscopic techniques such as thermal admittance spectroscopy (TAS),41,42 deep-level transient spectroscopy (DLTS),43 and thermally stimulated current spectroscopy (TSC)44 probe thermal transition energies of electrically active defects. So far, only very few studies have been reported in the literature, where TAS,36 DLTS,35 and TSC45,46 are applied to gain insights into defect properties of rutile TiO₂. Various defect levels between 130 meV and 870 meV below the conduction band edge have been reported; however, the identity of the associated defects remains unknown.
The scarcity of reports on space-charge spectroscopy performed on rutile TiO$_2$ is partially related to the difficulty in forming rectifying junctions.\textsuperscript{35,41} However, recent progress, see e.g., Ref. 48, shows promising results for Schottky contacts of sufficient quality to pursue TAS and DLTS studies on rutile TiO$_2$.

In this work, we report on electrically active defects observed by TAS and DLTS measurements on rutile TiO$_2$ single crystals subjected to different reducing and/or hydrogenating heat-treatments. Our results show that techniques such as TAS and DLTS are highly applicable for systematic studies of electrically active defects in non-stoichiometric rutile TiO$_2$.

II. EXPERIMENTAL

The samples used in the present study were (001)-oriented rutile TiO$_2$ single crystals grown by the float zone method and were purchased from MTI Corporation. The samples were cut into 5 mm$^2$-sized samples. After cutting into 5 mm$^2$-sized samples, the crystals were cleaned in an ultrasonic bath with acetone, isopropanol, and deionized water for 5 min each. Afterwards, the samples were subjected to one of the three following heat treatments (annealings) using a tube furnace:

1. Annealing in forming gas flow (N$_2$ + H$_2$ with [H$_2$]/[N$_2$] $\approx$ 1/9, where the square brackets denote the concentration) at temperatures between 500°C and 600°C for 35–75 min. (forming gas annealing)
2. Annealing in closed ampules filled with H$_2$ gas (0.5 bar at room temperature) for 20 min or 40 min. The ampules were evacuated with a roughing pump before filling with H$_2$. (H$_2$ gas annealing)
3. Annealing in N$_2$ flow at temperatures between 980°C and 1250°C for 1.25–25 h. (N$_2$ gas annealing)

The samples were always put into the furnace when the desired annealing temperature $T_{\text{anneal}}$ was reached. After the heat treatment, the samples were cooled-down without force in the cold furnace zone while maintaining the gas flow. Subsequently, the annealed crystals were cleaned again using the afore-mentioned procedure and further boiled in H$_2$O$_2$ (40%) for 1–3 min. This treatment is commonly used for the preparation of Schottky diodes on ZnO and has proven to lead to highly rectifying diodes.\textsuperscript{49}

Between 10 and 15 Pd contacts with a thickness in the range of $\approx$150–200 nm were deposited onto the samples via electron beam evaporation, using a Si shadow mask with pad areas of $0.7 \times 10^{-10}$ to $4.2 \times 10^{-13}$ cm$^2$. Eutectic InGa was used as Ohmic back contact.

Secondary ion mass spectrometry (SIMS) measurements were performed using a Cameca IMS 7f instrument with a primary beam of 10keV O$_2$ ions. Rutile TiO$_2$ samples implanted with Cr, Al, or Si were used as references to obtain absolute concentration values. For other residual elements, relative concentrations were determined. A constant erosion rate was assumed for depth-calibration, where the crater depths were measured using a surface Stylus Profilometer.

Fourier transform infrared (FTIR) absorbance spectra were recorded with a Bruker IFS125 HR spectrometer equipped with a globar or tungsten light source, a KBr or CaF$_2$ beam splitter, and an InSb detector. Measurements were performed with a spectral resolution of 0.5 cm$^{-1}$ and at a sample temperature of 27 K. Unpolarized light was used with the wave vector, $\vec{k}$, directed perpendicular to the $c$-axis of the samples.

The current-voltage (IV) and capacitance-voltage (CV) measurements were carried out under dark conditions at room temperature using a Keithley 6487 unit and an Agilent 4284A LCR meter, respectively.

DLTS was conducted using a refined version of the setup described elsewhere.\textsuperscript{50} In short, the setup utilizes a Boonton 7200 capacitance meter and a closed-cycle He cryostat. During measurements, reverse bias voltages between –4 V and –3 V were applied. Filling pulses with an amplitude of 2 V to 4 V and a duration of 50 ms were employed. The DLTS signal was extracted from the acquired capacitance-versus-time transients using a lock-in weighting function\textsuperscript{51} with six different rate windows in the range of (20 ms)$^{-1}$ to (640 ms)$^{-1}$. A delay time of 5 ms and a temperature resolution of 1 K were used. Measurements were performed both during heat-up and cool-down.

TAS measurements were conducted with a temperature resolution of 1 K during heat-up and cool-down using an Agilent 4284A LCR meter at probe frequencies $f_{\text{meas}}$ between 10 kHz and 1 MHz. Further details about the setup used can be found in Ref. 52.

III. RESULTS

SIMS measurements were performed in order to monitor selected relevant impurities in the heat-treated samples. Cr and Li, Al, and Si are present in significant concentrations, where the relative concentrations vary by at least an order of magnitude from different samples for Cr ($10^{15}$–$10^{17}$ cm$^{-3}$), Al ($10^{16}$–$10^{17}$ cm$^{-3}$), and Li ($10^{15}$–$10^{17}$ cm$^{-3}$), whilst lower variations are found for Si ($10^{17}$ cm$^{-3}$).

FTIR measurements were undertaken to determine the concentration of interstitial hydrogen (H$_i$) from its O–H vibrational mode at $\approx$3290 cm$^{-1}$.\textsuperscript{50,53} The as-received TiO$_2$ samples reveal a H$_i$ concentration in the range of $1\times10^{16}$ cm$^{-3}$. The heat treatments result in an increase of [H$_i$]. For the N$_2$ gas annealed samples, [H$_i$] increases to about 5 $\times 10^{16}$ cm$^{-3}$. Substantially, more H$_i$ is observed in the case of annealing in H$_2$ gas or forming gas. In both cases, precise quantitative measurements are prevented because of the high [H$_i$], leading to saturation of the O–H vibrational mode in the FTIR absorbance spectra.

Generally, different Pd/TiO$_2$/InGa junctions on the same TiO$_2$ sample display different IV characteristics, especially in terms of rectification. This indicates an inhomogeneity of the as-received samples unveiled by the applied annealing procedure. For some diodes, rectifications of up to six orders of magnitude in current can be found when the applied voltage $V$ is varied between –4 V and 4 V. In Fig. 1, examples of
such IV curves are shown for H₂ gas annealed samples. In general, similar results are obtained independently of the annealing procedure used.

In Fig. 2, the results of CV measurements using different probe frequencies (4 kHz–1 MHz) are shown for two Pd/TiO₂/InGa junctions by depicting 1/C² versus V. Two equivalent circuits consisting of only one resistance and capacitance were assumed to deduce the capacitance of the junctions (see also the inset of Fig. 2): (i) Capacitance C_P parallel to a resistance R_P (solid lines and left inset) and (ii) Capacitance C_S and a resistance R_S in series (dashed lines and right inset).

According to the depletion approximation, the depletion layer capacitance C_d of a Schottky junction on an n-type semiconductor is given by

\[ C_d = \frac{A^2 \epsilon_0 \epsilon \text{e} N_D}{\sqrt{2(V_{bi} + V_{bias})}} \]  

(1)

Here, A denotes the junction area, \( \epsilon_0 \) the vacuum permittivity, \( \epsilon \) the static dielectric constant, \( e \) the elementary charge, \( N_D \) the donor concentration, \( V_{bi} \) the built-in voltage, and \( V_{bias} \), the applied bias voltage. A static dielectric constant \( \epsilon \) of 100 was assumed. For a uniform donor concentration, one expects a straight line for 1/C² versus \( V_{bias} \), which holds reasonably well for the highly doped sample in Fig. 2(a). From the slope of the curves, we obtain a donor concentration \( N_D \) of about 3 × 10¹⁸ cm⁻³. For high reverse bias voltages and the highest probe frequency employed (1 MHz), a linear behavior is also observed for the low-doped sample [see Fig. 2(b)]. From the corresponding slope, a donor concentration \( N_D \) of about 1 × 10¹⁷ cm⁻³ is obtained. For low reverse bias voltages and especially low probe frequencies, pronounced deviations from a linear dependence occur as will be commented on in the discussion Sec. IV A.

A. Thermal admittance spectroscopy

In TAS, the capacitance C and conductance G of a rectifying junction are determined as a function of sample temperature T and probe frequency \( f_{meas} \) by assuming an appropriate equivalent circuit for the junction. Here, a series circuit was assumed and the measured capacitance is denoted as \( C_S \) for series capacitance [see also the right inset of Fig. 2(a)].

When crossed by the Fermi level, shallow defect levels being present in the junction give rise to inflection points \( T_{inf} \) in the C–T spectra and can be used to determine the activation energy (enthalpy) \( E_A = E_C - E_D \) (\( E_C \) = conduction band edge and \( E_D \) = defect level position) of shallow states using

\[ \frac{2\pi f_{meas}}{T_{inf}} \sim \exp \left( -\frac{E_A}{k_B T_{inf}} \right) \]  

(2)

where \( k_B \) denotes the Boltzmann constant.

Figure 3 shows representative TAS spectra obtained on four different Pd/TiO₂/InGa junctions. The corresponding TiO₂ samples were forming gas annealed (a) and (b), H₂ gas annealed (c), and N₂ gas annealed (d). Several inflection points in the \( C_S^{-T} \) plots are revealed, which correspond to electron states being present in TiO₂. The values of \( T_{inf} \) to be used in Eq. (2) were extracted from the local maxima positions of the derivative spectra \( dC_S/dT \) [see the example in the inset of Fig. 3(b)].

All the investigated forming gas annealed samples [see Figs. 3(a) and 3(b)] show the electron levels labeled \( D_{2,FG} \) and \( D_{4,FG} \) is only present in some samples in sufficient concentrations to be detected by TAS. The levels labeled \( D_{1,1H}, D_{2,1H}, \) and \( D_{1,1H} \) are seen for all the investigated samples annealed in H₂ gas [see Fig. 3(c)]. For all the investigated samples annealed in N₂ gas, the levels \( D_{2,N} \) and \( D_{3,N} \) are observed, while \( D_{4,N} \) is only detected in a few samples. \( D_{1,1H}, D_{1,1H} \) and \( D_{1,1N} \) can only be resolved at very low temperatures.
By comparing the value pairs \((T_{\text{inf}}, f_{\text{meas}})\) for the electron levels observed in samples subjected to different heat-treatments, it is found that \(D_{2,\text{FG}}\) and \(D_{2,\text{N}}\), as well as \(D_{3,\text{FG}}\) and \(D_{3,\text{N}}\), respectively, can arise from the same electron levels.

Figure 4 displays Arrhenius plots obtained from the TAS spectra shown in Fig. 3 according to Eq. (2). Linear least-squares fits, represented by solid lines in Fig. 4, have been used to determine \(E_A\). In Table I, the obtained activation energy values of the observed electron levels are summarized.

**B. Deep-level transient spectroscopy**

DLTS was used to probe deep electron traps in heat-treated TiO\(_2\) samples. The trap concentration \(N_T\) was deduced assuming a uniform and sufficiently low \((\lesssim 0.1 N_D)\) defect distribution, where\(^{31,54}\)

\[
N_T = 2 \frac{\Delta C}{C_{\text{rb}}} N_D.
\]  

Here, \(\Delta C\) is determined from the measured capacitance transients,\(^{31,54}\) while \(C_{\text{rb}}\) is the capacitance measured at the

<table>
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<th>N(_2) gas annealed</th>
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**FIG. 3.** \(C_S-T\) plots for four different Pd/TiO\(_2\)/InGa junctions. The inset in (b) shows \(dC_S/dT\) over \(T\), which was used to determine \(T_{\text{inf}}\) [see Eq. (2)].

**FIG. 4.** Arrhenius plots derived from the \(C_S-T\) curves shown in Fig. 3 using Eq. (2).
quiescent reverse bias voltage. $N_D$ is derived from CV measurements.\(^{54}\)

For each DLTS rate window, the peak in $\Delta C$ occurs at a different $T_{\text{max}}$. Using the following relation for the electron emission rate $e_n$ at the DLTS peak maximum\(^{54}\)

$$\frac{e_n}{T_{\text{max}}} = \beta \sigma_a \exp\left(-\frac{E_A}{k_B T_{\text{max}}}\right),$$

the apparent capture cross-section $\sigma_a$ and the thermal activation energy $E_A$ for the deep-level defect can be determined. $\beta$ is a material-specific constant and is given by\(^{43,54}\)

$$\beta = 2\sqrt{\frac{2\pi}{m_e^*}} \frac{3^{3/2}}{k_B^2}.$$\(^{5}\)

Here, $m_e^*$ denotes the effective electron mass in TiO$_2$, while $h$ is the Planck constant. There is quite a spread in values reported for $m_e^*$.\(^{11,34,39-64}\) In this study, a value of ten-times the free electron mass $m_e$ is assumed.

Figure 5 displays exemplary DLTS spectra measured on Pd/TiO$_2$/InGa junctions. Figures 5(a) and 5(b) show the results for forming gas annealed samples, where seven different defect levels are observed. The levels labeled $E_{1,\text{FG}}$ and $E_{4,\text{FG}}$ are present in all samples irrespective of the annealing conditions used (duration or temperature) and the specific production batch from which the TiO$_2$ single crystals originated. $E_{1,\text{FG}}$ appears at very low temperatures and was not resolved for all the measurements shown here. The levels $E_{2,\text{FG}}$, $E_{5,\text{FG}}$, $E_{6,\text{FG}}$, and $E_{7,\text{FG}}$ occur occasionally and were not observed in all the investigated samples.

In Fig. 5(c), a DLTS spectrum of a H$_2$ gas annealed sample is shown. Different annealing durations and/or temperatures lead to qualitatively similar DLTS spectra with similar levels being present and $E_{5,\text{H}_2}$ as the dominant one. All the investigated samples originated from the same production batch.

Figures 5(d) and 5(e) show DLTS results for the N$_2$ gas annealed samples. The samples originated from the same production batch but were subjected to different annealing durations and temperatures. The levels $E_{2,\text{N}}$, $E_{3,\text{N}}$, $E_{4,\text{N}}$, and $E_{5,\text{N}}$ are observed in all the samples, whereas $E_{6,\text{N}}$ is only present in samples annealed at high temperatures and for long durations. The level $E_{1,\text{N}}$ is very shallow and can only be resolved fully at low temperatures using short rate windows.

When comparing the ($T_{\text{max}}$, $e_n$) pairs for the observed defect levels across samples subjected to different heat-treatments, it can be found that the following defect levels may have the same origin: $E_{2,\text{N}}$, $E_{2,\text{FG}}$, $E_{3,\text{N}}$, $E_{3,\text{FG}}$, and $E_{3,\text{H}_2}$, and $E_{4,\text{FG}}$, $E_{4,\text{N}}$, and $E_{3,\text{H}_2}$.

In Table II, an overview of the observed defect levels and their activation energy values, as well as apparent capture cross sections, is given. Due to the ambiguity concerning the value of the effective electron mass $m_e^*$, only orders of magnitude values are stated for $\sigma_a$.

IV. DISCUSSION

A. Experimental remarks

Generally, the Pd/TiO$_2$/InGa junctions display high rectification (see Fig. 1) as required for accurate space-charge spectroscopy measurements. In the case of highly doped samples, the CV characteristics resemble those expected for a depletion layer capacitance under uniform doping [see the linear $1/C^2$ - $V$ dependency in Fig. 2(a)]. However,
deviations from this behavior are evident for low doped samples [see Fig. 2(b)]. These deviations can be caused by a non-uniform doping concentration, a highly compensated interfacial layer. We found that their relative contribution depends on the sample and its particular treatment. By using comparatively small contact areas, the effect of the high series resistance can be minimized, 69-70.

Our set of data indicates that several of these causes contribute to the recorded CV characteristics, especially high series resistance and the presence of a highly compensated interfacial layer. We found that their relative contribution depends on the sample and its particular treatment. By using comparatively small contact areas, the effect of the high series resistance can be minimized, 69-70 and a detailed analysis of the CV characteristics and barrier heights of the Schottky junctions used in this work can be found in Ref. 48.

<table>
<thead>
<tr>
<th>Defect level</th>
<th>H2 gas annealed</th>
<th>N2 gas annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{1,FG}$</td>
<td>$E_{1,H2}$</td>
<td>$E_{2,N}$</td>
</tr>
<tr>
<td>[57, 76]</td>
<td>[49, 96]</td>
<td>[63, 93]</td>
</tr>
<tr>
<td>$E_{2,FG}$</td>
<td>$E_{1,H2}$</td>
<td>$E_{1,N}$</td>
</tr>
<tr>
<td>[69, 96]</td>
<td>[81, 104]</td>
<td>[82, 99]</td>
</tr>
<tr>
<td>$E_{3,FG}$</td>
<td>$E_{2,H2}$</td>
<td>$E_{2,N}$</td>
</tr>
<tr>
<td>[87, 111]</td>
<td>[92, 144]</td>
<td>[86, 109]</td>
</tr>
<tr>
<td>$E_{4,FG}$</td>
<td>$E_{3,H2}$</td>
<td>$E_{2,N}$</td>
</tr>
<tr>
<td>[104, 114]</td>
<td>[446, 471]</td>
<td>[110, 123]</td>
</tr>
<tr>
<td>$E_{5,FG}$</td>
<td></td>
<td>$E_{3,N}$</td>
</tr>
<tr>
<td>[111, 132]</td>
<td></td>
<td>[273, 313]</td>
</tr>
<tr>
<td>$E_{6,FG}$</td>
<td></td>
<td>$E_{4,N}$</td>
</tr>
<tr>
<td>[204, 218]</td>
<td></td>
<td>[365, 395]</td>
</tr>
<tr>
<td>$E_{1,FG}$</td>
<td>[10^13]</td>
<td>$E_{4,FG}$</td>
</tr>
<tr>
<td>[424, 630]</td>
<td>$E_{1,H2}$</td>
<td>[10^15, 10^17]</td>
</tr>
</tbody>
</table>

The interpretation of TAS and DLTS data is facilitated by uniform net carrier concentration versus depth profiles acquired at high measurement frequencies (\(\geq 10\) kHz). Indeed, this was confirmed for all the samples presented here prior to TAS and/or DLTS measurements. The validity of the TAS and DLTS analysis is furthermore corroborated by the applicability of Eqs. (2) and (4). For essentially all the observed defect levels, an Arrhenius dependence holds for the extracted electron emission rates. The exception is the shallow level $D_{1,FG}$, which is affected by charge carrier freeze-out.

### B. Origin of the observed defect levels

The data in Figs. 3-6 reveal the presence of some rather prominent shallow electron traps ($E_A \leq 130$ meV) and that charge carrier-freeze out is limited even at 28 K. Irrespective of the sample production batch and the post-growth heat treatment employed, three particular levels always occur. They exhibit similar electron emission rates as a function of temperature in each sample with $E_A \approx 70$ meV ($D_{4,FG}$, $E_{2,FG}$, $D_{1,H2}$, $D_{2,N}$, and $E_{2,N}$), $E_A \approx 95$ meV ($E_{3,FG}$, $D_{3,H2}$, $E_{1,H2}$, and $E_{2,N}$), and $E_A \approx 120$ meV ($E_{4,FG}$, $D_{3,H2}$, and $E_{4,N}$), respectively. This implies that these levels arise from intrinsic defects or defects involving omnipresent residual impurities. Generally, the absolute concentrations of defect levels in TiO$_2$ are difficult to determine with a high degree of accuracy because of the uncertainty in the dielectric constant (permittivity), 10-12,55-56. However, by assuming $\varepsilon_r = 100$ (as for the CV data), one arrives at values of $10^{15} - 10^{17}$ cm$^{-3}$ for most of the levels in Fig. 5.

Polaronic effects are strong in rutile TiO$_2$ and may be responsible for some of the observed levels via self-trapping of electrons on Ti sites. For instance, Frederikse\textsuperscript{24} and Deak \textit{et al.}\textsuperscript{23} as well as Janotti \textit{et al.}\textsuperscript{23} have reported experimental and theoretical indications, respectively, of such electron states with $E_A$ below 150 meV. Other prevalent intrinsic candidates anticipated in reduced rutile TiO$_2$ are the donor-like Ti$^3$ and V$_O$ centers.\textsuperscript{6,16,17,19} However, reports on the $E_A$ values for these two centers are scarce in the literature. Brandão \textit{et al.}\textsuperscript{14} suggested $E_A \approx 2.8$ meV for a V$_D$ donor-state based on electron paramagnetic resonance measurements, which is considerably lower than the thermal activation energy of our three “general” levels. On the other hand, rather recent
density functional theory (DFT) calculations by Janotti et al.\textsuperscript{23} predict single and double donor states of V\textsubscript{O} with E\textsubscript{\Lambda} equal to about 100 meV and 140 meV, respectively, for a configuration where the donor electrons are rather localized at neighboring Ti atoms (V\textsubscript{O}\textsuperscript{2+} + 2Ti\textsuperscript{3+}). Hence, V\textsubscript{O} cannot be excluded as the origin of our 95 meV and 120 meV levels. Furthermore, Deák et al.\textsuperscript{24} computed E\textsubscript{\Lambda} \approx 100 meV and \approx 1300 meV for the single and double donor states, respectively, of a V\textsubscript{O} configuration where the electrons are localized at the V\textsubscript{O} site. Mattioli et al.\textsuperscript{37} conducted similar calculations as in Ref. 24 but found a substantially lower E\textsubscript{\Lambda} value of about 300 meV for the double donor state. For thermally induced charge state transitions of Ti\textsuperscript{i} in rutile TiO\textsubscript{2}, Hubbard-U corrected DFT data by Mattioli et al.\textsuperscript{37} suggest that the single and double donor levels are resonant with the conduction band, whilst the triple and quadruple ones are located in the bandgap at \approx 70 meV and 400 meV below the conduction band edge. Thus, Ti\textsuperscript{i} may be an intrinsic candidate for the common level observed at 70 meV in our samples.

Main residual impurities found in all the investigated samples are H, Li, Al, Si, and Cr according to FTIR and SIMS measurements. Li displays a concentration below 10\textsuperscript{16} cm\textsuperscript{-3} and the three latter ones exhibit concentrations between 10\textsuperscript{16} and 10\textsuperscript{17} cm\textsuperscript{-3}. The H content is estimated to increase from the 10\textsuperscript{16} cm\textsuperscript{-3} range in the as-received samples to above 10\textsuperscript{19} cm\textsuperscript{-3} after the forming gas and H\textsubscript{2} gas anneals where the absorption signal saturates. Si substitutes for Ti in rutile TiO\textsubscript{2},\textsuperscript{71,72} and is not expected to introduce localized electronic states in the bandgap but rather to give rise to bandgap narrowing.\textsuperscript{60,72} Li in an interstitial configuration is potentially a shallow donor\textsuperscript{26,60} but the predicted E\textsubscript{\Lambda} value is only 30 meV and does not agree with those of our three common levels. Also, the anticipated electron trap positions associated with Cr in rutile TiO\textsubscript{2} deviate substantially from those of our three common levels, exhibiting values of 190 meV and 410 meV below the conduction band edge.\textsuperscript{46} Hence, both Li and Cr (as well as Si) are ruled out as likely candidates for the three common levels while Al in combination with V\textsubscript{O} appears to be a more plausible suggestion. Al itself substitutes for Ti and gives rise to an acceptor level in the lower part of the bandgap, i.e., Al on the Ti site acts as a p-type dopant.\textsuperscript{34,73} However, on the basis of generation noise recombination and temperature-dependent Hall effect measurements, it is argued by different authors\textsuperscript{60,74} that Al-related shallow acceptor states also occur close to the conduction band. In particular, Ackert and Volger\textsuperscript{60} have ascribed a level at \approx 50 meV below the conduction band edge to a 2Al\textsubscript{Ti} - V\textsubscript{O} complex which may be associated with our most shallow “general” defect level (E\textsubscript{\Lambda} \approx 70 meV) or alternatively with the prominent one at \approx 60 meV detected after forming gas and N\textsubscript{2} gas anneals only (D\textsubscript{2,FG}, D\textsubscript{2,N}).

Interstitial H is prevailing in all the studied samples, as manifested by its characteristic absorption line at \approx 3290 cm\textsuperscript{-1} in the acquired IR spectra. This holds already for the as-received samples and becomes even more clear after the forming gas and H\textsubscript{2} gas heat treatments. H\textsubscript{i} is a shallow donor in TiO\textsubscript{2}, and the 3290 cm\textsuperscript{-1} line originates from the local vibrational mode of an O-H bond oriented perpendicular to the c-axis of the crystal.\textsuperscript{30,53} Monitoring the free carrier absorption as a function of temperature and concurrently the transformation between neutral and positively ionized H\textsubscript{i}, Herklotz et al.\textsuperscript{30} determined E\textsubscript{\Lambda} to be 10 \pm 1 meV for the H\textsubscript{i} donor. This value is also corroborated by a muon spectroscopy study conducted by Shimomura et al.\textsuperscript{25} To the best of our knowledge, no corresponding theoretical estimates are available in the literature. Accordingly, H\textsubscript{i} can be excluded as the origin of any of the three “general” defect levels observed in the present samples. However, in addition to Ti\textsuperscript{i} and possibly V\textsubscript{O}, H\textsubscript{i} is an obvious candidate for the strong shallow donor activity found in our samples, exhibiting limited carrier freeze-out even at 28 K. That is, the dominant donor(s) must have an ionization energy below \approx 25 meV. Such very shallow donor states in reduced rutile TiO\textsubscript{2} have also been reported by other authors,\textsuperscript{9-13} and they are, indeed, expected to be due to intrinsic defect defects (like Ti\textsuperscript{i} and possibly V\textsubscript{O}) and/or common residual impurities (like H\textsubscript{i}). Here, it should also be noted that the abnormal decrease in the depletion capacitance observed at temperatures above 50–100 K in the TAS measurements (Fig. 3) is not caused by a decreasing concentration of ionized shallow donors but primarily attributed to the temperature variation of \epsilon\textsubscript{\text{r}} in rutile TiO\textsubscript{2}.\textsuperscript{55}

Finally, as demonstrated in Fig. 5, no common deep-level defect (E\textsubscript{\Lambda} \geq 200 meV) is found to be present in different samples. A rather prominent level with E\textsubscript{\Lambda} \approx 300 meV exists after N\textsubscript{2} gas annealing (E\textsubscript{\Lambda,N}) but not after forming gas and H\textsubscript{2} gas annealing. The opposite holds for the pronounced level with E\textsubscript{\Lambda} \approx 460 meV (E\textsubscript{\Lambda,FG} and E\textsubscript{\Lambda,H2}), present after forming gas and H\textsubscript{2} gas annealing but not after N\textsubscript{2} gas annealing. This indicates that these levels arise from (i) defects involving residual impurities with varying concentrations in different samples and/or (ii) complexes involving intrinsic defects being strongly influenced by the annealing conditions used. Further work needs to be pursued in order to resolve this issue.

V. SUMMARY

The DLTS and TAS techniques are demonstrated to be highly applicable for detailed investigations of electrically active defects in rutile TiO\textsubscript{2} single crystals. A comprehensive study of Pd/TiO\textsubscript{2}/InGa junctions has been performed using TiO\textsubscript{2} crystals post-growth heat-treated in FG, H\textsubscript{2}, or N\textsubscript{2} atmospheres. Irrespective of the sample production batch and the heat-treatment employed, three rather shallow levels occur in all the samples with E\textsubscript{\Lambda} \approx 70 meV, \approx 95 meV and \approx 120 meV, respectively. The origins of these levels are discussed in some detail where electron polarons and intrinsic defects such as Ti\textsuperscript{i} and V\textsubscript{O} appear as viable candidates and complexes involving common residual impurities, especially Al in combination with V\textsubscript{O}. Furthermore, TAS data display limited charge carrier freeze-out even at 28 K (minimum temperature reached) and evidence the presence of dominant and very shallow donors (E\textsubscript{\Lambda} \leq 25 meV). An obvious shallow donor is the omnipresent H\textsubscript{i}, as revealed by infrared absorption measurements of the studied samples, having an ionization energy of only \approx 10 meV. In contrast to the shallow defects, no common deep-level defect is found to be
present in different samples, possibly indicating a stronger
dependence on the annealing conditions used.

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Donors and polaronic absorption in rutile TiO$_2$ single crystals

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Appendices
Appendix A

Interaction between Light and Materials

Monochromatic light can be described as an electromagnetic wave with an electrical field vector \( \vec{E}(\vec{r},t) \) and a magnetic field vector \( \vec{B}(\vec{r},t) \) \[13\]. \( \vec{E}(\vec{r},t) \) is represented by
\[
\vec{E}(\vec{r},t) = Ae^{i(k \vec{r} - \omega t) + i\phi}.
\]
(A.1)
\( \vec{r} \) and \( t \) represent a specific point in space and time, respectively. \( \vec{k} \) is the wave vector and \( \omega \) the angular frequency of the light. The direction of \( \vec{E} \) determines the polarization of the light wave. \( \phi \) is the absolute phase of the light wave.

When two light waves with the same \( \omega \) and \( \vec{k} \) interfere, the difference in \( \phi \) will determine whether the interference is destructive or constructive. \( \phi \) will be different for two light waves, for example, if they traveled along paths with different lengths.

In the photon picture, \( \vec{k} \) is connected to the momentum \( \vec{p} \) of the photon via
\[
\vec{p} = \hbar \vec{k}
\]
(A.2)
while \( \omega \) is associated with the energy \( E_{\text{Ph}} \) of the corresponding photon according to:
\[
E_{\text{Ph}} = \hbar \omega.
\]
(A.3)
\( \omega \) is related to the frequency \( f \) and the wavelength \( \lambda \) of the light by
\[
\omega = 2\pi f = 2\pi \frac{c}{\lambda}.
\]
(A.4)
Here, \( c \) denotes the speed of light in the medium in which the light travels.

The interaction between matter and light is generally described by the complex refractive index \( \hat{n} \) of a material which can be expressed as
\[
\hat{n} = n + i\kappa.
\]
(A.5)

The absolute values of the wave vector in vacuum (\( |k_{\text{vac}}| \)) and inside a medium (\( |k_{\text{medium}}| \)) are connected by \( \hat{n} \) via
\[
|k_{\text{medium}}| = \hat{n}|k_{\text{vac}}|.
\]
(A.6)

An electromagnetic wave propagating from vacuum (\( \hat{n} = 1 \)) into a medium with semi-infinite thickness (see Fig. 2.4 (a)) can be described by:
\[
\vec{E}(\vec{r},t) = \begin{cases} 
\text{incident wave} & Ae^{i(k_{\text{vac}}|k_{\text{eff}} - \omega t)} \\
\text{reflected wave} & Be^{i(k_{\text{vac}}|k_{\text{eff}} - \omega t)} \\
\text{refracted wave} & Ce^{i(n|k_{\text{vac}}|k_{\text{eff}} - \omega t)} \\
\text{attenuation} & e^{-\kappa|k_{\text{vac}}|k_{\text{eff}} - \omega t}
\end{cases}, \text{ in vacuum}
\]
(A.7)
A. Interaction between Light and Materials

Figure A.1: Interaction between Light and Materials: (a) Illustration of reflection and refraction of an incident light beam at an interface between vacuum and a material of semi-infinite thickness. \( \alpha_i, \alpha_r \) and \( \alpha_{rf} \) are the angles of the incident, reflected and refracted beam measured against the surface normal, respectively. (b) Schematic illustration of the interaction between light and a slab of material with thickness \( d \). Multiple reflections will occur, and the overall intensity of the transmitted and reflected light will be a sum of the intensities of the individual transmitted and reflected light beams.

The incident wave propagates towards the interface between the vacuum and the medium with a wave vector \( |\vec{k}_{\text{vac}}| \hat{k}_i \). \( \hat{k}_i \) is a unity vector determining the direction of the incident light. Due to a breaking of symmetry at the interface, some portion of light is reflected back in a direction described by \( \hat{k}_r \). The angles between \( \hat{k}_i \) as well as \( \hat{k}_r \) and the surface normal are equal. The ratio between the amplitude coefficients \( A \) and \( B \) can be calculated via Fresnel’s equations [13]. The electromagnetic wave will penetrate into the medium and continue to propagate as refracted wave into a direction \( \hat{k}_{rf} \). Snell’s law connects the directions \( \hat{k}_{rf} \) and \( \hat{k}_i \) [13]. The amplitude \( C \) of the refracted wave can be calculated from \( A \) and \( B \).

If \( \kappa \) is larger than 0, the electromagnetic wave inside the medium will decrease in amplitude, i.e., it will be attenuated. Experimentally, one can often only measure the intensity \( I \) of the light, which is related to \( \vec{E} \) by

\[
I \sim |\vec{E}|^2, \quad (A.8)
\]

and hence

\[
I(\vec{r}) = \begin{cases} 
I_0 \sim |A|^2, & \text{for the incident wave} \\
I_r \sim |B|^2, & \text{for the reflected wave} \\
I_{rf} \sim |C|^2 e^{-\alpha_{rf} \vec{r}}, & \text{for the refracted wave}
\end{cases} \quad (A.9)
\]

is valid for light propagating from vacuum into a medium with semi-infinite thickness (see Fig. A.1 (a)). Here, the attenuation coefficient \( \alpha \) was introduced which is defined as

\[
\alpha = 2\kappa |k_{\text{vac}}|. \quad (A.10)
\]

The attenuation coefficient includes the physical processes of absorption (\( \alpha_{\text{abs}} \)) as well as scattering (\( \alpha_{\text{sc}} \)). Often, scattering is neglected. As mentioned before, \( A \)
and $B$ are connected via Fresnel’s equations. For, $|A|^2$ and $|B|^2$ phase relations are irrelevant, and the reflection coefficient $R$ can be introduced to connect both quantities via

$$I_t = R I_0.$$  \hspace{1cm} (A.11)

In the case of $\kappa \ll 1$ and light propagation between vacuum and a medium (or vice versa), $R$ can approximately be expressed by:

$$R = \left( \frac{n - 1}{n + 1} \right)^2.$$  \hspace{1cm} (A.12)

Fig. A.1 (b) illustrates the interaction between a light beam and a slab of material with thickness $d$. The light beam will undergo multiple reflections inside the material. The intensity of the transmitted light ($I_t$) and of the reflected light ($I_r$) have to be calculated from the sum of the individual transmitted and reflected beams. Light beams traveling inside the medium will be attenuated. The intensity of the transmitted light can be described by [359]:

$$I_t = I_0 \frac{(1 - R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)}.$$  \hspace{1cm} (A.13)

For, materials with weak absorption ($\alpha d \ll 1$), the following approximation is valid [359]:

$$I_t = I_0 (1 - R)^2 \exp(-\alpha d),$$  \hspace{1cm} (A.14)

and Eq. A.11 can be used.
Appendix B

Polarons

Figure B.1: Free charge carriers and polarons: Illustration of how the mobility of charge carriers in semiconductors can be understood in terms of free charge carriers and polarons. The upper panel shows how free electrons, large polarons and small polarons are distinguished by the localization of their corresponding wave function. The transport of free electrons and large polarons through the semiconductor is limited by scattering with, e.g., lattice vibrations (A) or ionized defects (B). The trapping of charge carriers (C) can also influence their transport (see Sec. 2.3.1). The transport of small polarons is determined by thermally-activated hopping. Free small polarons need to overcome a barrier $E_H$ to jump to a neighboring polaron site (D). Small polarons can also become bound to lattice defects. This may increase the energy required for making a jump to a value $E_T$ (E).

During their transport through a material, charge carriers can either be described as free charge carriers or polarons (see Fig. B.1). In both models, the charge carrier transport is described by quasi-particles that represent the
B. Polarons

charge carrier itself as well as as its interaction with the surrounding lattice. Free charge carriers are characterized by wave functions which are highly delocalized over many unit cells. Polarons are charge carriers that become localized in a material due to lattice distortions [183]. These distortions can occur either in an ideal region of the crystal (free polaron or self-trapped electron/hole) or close to defects (bound polaron). Notably, self-trapped holes or electrons will display features usually associated with defects in semiconductors [23, 31, 34, 383]. One usually distinguishes between small and large polarons. The distinction is based on how localized the polaron’s wave function is. The wave function of large polarons is is spread out over a few unit cells. In contrast, the wave function of a small polaron is often localized at or around a specific lattice site. In oxide semiconductors, electron polarons are usually localized at the cation, while hole polarons are localized at oxygen atoms [60, 251].

The mobility $\mu_i$ of charge carriers transported through a semiconductor can be described by:

$$
\mu_i = \frac{e^2 \tau_i}{m_{i,\text{eff}}} \quad (i = n, p).
$$

(B.1)

$m_{i,\text{eff}}$ is the effective mass of electrons ($i = n$) or holes ($i = p$). For free charge carriers, $m_{n,\text{eff}}$ is determined by Eq. 2.1 while $m_{p,\text{eff}}$ is calculated according to Eq. 2.2. For large polarons, the effective mass equals the polaron mass $m_{\text{polaron}}$ which is higher than what is expected from Eq. 2.1 or 2.2 [183].

The relaxation time $\tau_i$ describes the average time between scattering events. More scattering, will lead to a shorter relaxation time $\tau_i$, and hence lower mobility for charge carriers. Scattering can occur between charge carriers and ionized defects (for example, with ionized dopant atoms), lattice vibrations (phonons) or other charge carriers (see Fig. B.1). Defects can also trap charge carriers which will decrease the mobility (see Sec. 2.3.1).

Eq. 2.11 is generally used when charge carriers are transported through a material via extended electronic states, which implies fairly delocalized wave functions. Small polarons, however, are characterized by highly localized wave functions, and hence their transport is not described by Eq. 2.11. The transport of small polarons through a material occurs by hopping, and hence their mobility is thermally-activated and described by [183]:

$$
\mu_i \sim \exp \left( -\frac{E_H}{k_B T} \right) \quad (i = n, p).
$$

(B.2)

$E_H$ is the energy required for a polaron to jump from one site of localization to the next (see Fig. B.1). Bound polarons might experience a different binding energy than free polarons [183].
Appendix C

Junctions: Schottky Approximation

To compute the band diagram of a rectifying junction (see Sec. 3), one starts at Poisson’s equation:

$$\nabla^2 \Phi = -\frac{\rho}{\varepsilon_s \varepsilon_0}$$  \hspace{1cm} (C.1)

which connects the electrical potential $\Phi$ and the charge density $\rho$. Generally, Eq. C.1 can be solved iteratively and numerically, starting with an initial guess for $\Phi$ and $\rho$ [39, 40]. Eq. C.1 can, however, be solved analytically within the so-called Schottky approximation. For a $p$-$n$ homo-junction, it is assumed that the charge density $\rho$ can be described by:

$$\rho = \begin{cases} 
0, & \text{for } -W_p \geq x \\
-e N_A, & \text{for } -W_p \leq x \leq 0 \\
e N_D, & \text{for } 0 < x \leq W_n \\
0, & \text{for } x \geq W_n 
\end{cases} \quad p - \text{type side} \hspace{1cm} n - \text{type side}$$  \hspace{1cm} (C.2)

Here, $W_p$ and $W_n$ denote the width of the space-charge region at the $p$-type and $n$-type side of the junction, respectively. Thus, the Schottky approximation assumes sharp boundaries for the space-charge region. The charge density $\rho$ needs to satisfy overall charge neutrality. The width $W = W_n + W_p$ of the space-charge region can be calculated via

$$W_n = \sqrt{\frac{2 \varepsilon_0 \varepsilon_s}{e} N_A \frac{1}{N_D N_D + N_A} V_{bi}}$$  \hspace{1cm} (C.3)

and

$$W_p = \sqrt{\frac{2 \varepsilon_0 \varepsilon_s}{e} N_D \frac{1}{N_A N_D + N_A} V_{bi}}.$$  \hspace{1cm} (C.4)

Combining Eq. C.2 with Eq. C.1, one can compute $\Phi$ as

$$\Phi = \begin{cases} 
0, & \text{for } -W_p \geq x \\
\frac{1}{2} \frac{e N_A}{\varepsilon_s \varepsilon_0} (x + W_p)^2, & \text{for } -W_p \leq x \leq 0 \\
-\frac{1}{2} \frac{e N_D}{\varepsilon_s \varepsilon_0} (x - W_n)^2 + e V_{bi}, & \text{for } 0 < x \leq W_n \\
e V_{bi}, & \text{for } x \geq W_n 
\end{cases} \quad p - \text{type side} \hspace{1cm} n - \text{type side}$$  \hspace{1cm} (C.5)

$\Phi$ is connected to the electrical field $\mathcal{E}$ inside the junction via

$$\mathcal{E} = -\nabla \Phi,$$  \hspace{1cm} (C.6)
and hence

$$
\mathcal{E} = \begin{cases} 
0, & \text{for } -W_p \geq x \\
\frac{e N_A}{\varepsilon \varepsilon_0} (x + W_p), & \text{for } -W_p \leq x \leq 0 \\
\frac{e N_D}{\varepsilon \varepsilon_0} (x - W_n), & \text{for } 0 < x \leq W_n \\
0, & \text{for } x \geq W_n 
\end{cases}
$$

\text{\text{p-type side}}
\begin{cases} 
0, & \text{for } x \leq 0 \\
\frac{e N_D}{\varepsilon \varepsilon_0} (x - W_n), & \text{for } 0 < x \leq W_n \\
0, & \text{for } x \geq W_n 
\end{cases}

\text{\text{n-type side}} \quad \text{(C.7)}

From the electrical potential $\Phi$, the electro-chemical potential $\Psi$, and hence the band diagram can be obtained. For Schottky junctions, the same equations apply, when either $N_A \to \infty$ (junction between a metal and a $n$-type semiconductor) or $N_D \to \infty$ (junction between a metal and a $p$-type semiconductor) is used. Thus, one obtains the following equations for the case of a junction between a metal and a $n$-type semiconductor:

$$
\rho = \begin{cases} 
0, & \text{for } x \leq 0 \\
\frac{e N_D}{\varepsilon \varepsilon_0}, & \text{for } 0 < x \leq W_n \\
0, & \text{for } x \geq W_n 
\end{cases}
$$

\text{metal semi--}
\begin{cases} 
0, & \text{for } x \leq 0 \\
\frac{e N_D}{\varepsilon \varepsilon_0} (x - W_n), & \text{for } 0 < x \leq W_n \\
0, & \text{for } x \geq W_n 
\end{cases}

\text{conductor semi--} \quad \text{(C.8)}

$$
\mathcal{E} = \begin{cases} 
0, & \text{for } x \leq 0 \\
\frac{e N_D}{\varepsilon \varepsilon_0} (x - W_n), & \text{for } 0 < x \leq W_n \\
0, & \text{for } x \geq W_n 
\end{cases}
$$

\text{metal semi--}
\begin{cases} 
0, & \text{for } x \leq 0 \\
\frac{e N_D}{\varepsilon \varepsilon_0} (x - W_n)^2 + e \Psi_{bi}, & \text{for } 0 < x \leq W_n \\
\frac{e V_{bi}}{\varepsilon \varepsilon_0}, & \text{for } x \geq W_n 
\end{cases}

\text{conductor semi--} \quad \text{(C.9)}

and

$$
\Phi = \begin{cases} 
-\frac{1}{2} \frac{e N_D}{\varepsilon \varepsilon_0} (x - W_n)^2 + e \Psi_{bi}, & \text{for } 0 < x \leq W_n \\
\frac{e V_{bi}}{\varepsilon \varepsilon_0}, & \text{for } x \geq W_n 
\end{cases}
$$

\text{metal semi--}
\begin{cases} 
0, & \text{for } x \leq 0 \\
\frac{e N_D}{\varepsilon \varepsilon_0} (x - W_n)^2 + e \Psi_{bi}, & \text{for } 0 < x \leq W_n \\
\frac{e V_{bi}}{\varepsilon \varepsilon_0}, & \text{for } x \geq W_n 
\end{cases}

\text{conductor semi--} \quad \text{(C.10)}