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 (FeGa) and Ti (TiGa) defects in $\beta$-Ga$_2$O$_3$. Using deep-level transient spectroscopy, we identify defect levels associated with Fe$_{Ga}$\textsubscript{0}/−GaI ($E_A = 0.66$ eV), Fe$_{Ga}$\textsuperscript{0}/−GaII ($E_A = 0.79$ eV) and Ti$^{+}$/0 GaII ($E_A = 1.03$ eV) in the $\beta$-Ga$_2$O$_3$ samples studied here. Accumulatively-recorded SSPC spectra reveal several defect levels labeled $T_{\text{EFG}}^{1}$–$T_{\text{EFG}}^{6}$ with onsets for optical absorption between 1.5 eV and 4.3 eV. The signature $T_{\text{EFG}}^{1}$ consists of several overlapping defect signatures, and is identified as being related to Fe$_{Ga}^{0}$/−GaI, Fe$_{Ga}^{0}$/−GaII and Ti$^{+}$/0 GaII 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 \cite{1, 2}. In recent years, many wide band gap semiconductors, such as monoclinic 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 \cite{3–6}. 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) \cite{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 \cite{8, 9}. Steady-state photo-capacitance (SSPC) measurements and related techniques \cite{1, 10} measure the optically-induced emission of charge carriers from traps, and are complementary 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\(_3\) [11–18]. 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-functionals, 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 Ga 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\(_3\) 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 \( \langle 201 \rangle \) 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 depositions. 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 \( \mu \)m, 600 \( \mu \)m and 900 \( \mu \)m. Subsequently, another layer of Ni with a thickness of 150 nm was deposited using a shadow mask with circular openings (diameter = 300 \( \mu \)m) which aligns with the first deposition 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 an 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\(_2\)O\(_3\) samples [1]. For analyzing CV measurements, a relative static dielectric constant (\( \epsilon_r \)) of 10.2 was assumed for \( \beta\)-Ga\(_2\)O\(_3\) [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 (\( \sigma_{\text{app}} \)) DLTS spectra were simulated using a python-based script, where the \( \lambda \)-correction was employed to obtain \( N_T \) [1, 32]. \( E_A \) is the sum of the classical activation energy for carrier capture (\( E_0 \)) and the thermodynamic charge-state transition level [1, 21]. \( \sigma_{\text{app}} \) depends both on \( E_0 \) and a prefactor (\( \sigma_0 \)) which is, for example, dependent on the charge state of the trap [21, 33–37]. 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 A.

SSPC measurements were performed with a setup described in detail in [28]. The photo-capacitance (\( C_{\text{illum}} \)) of the samples is recorded after illuminating the junction at a photon energy \( E \) for a time \( t_{\text{illum}} \), whereby \( t_{\text{illum}} \) between 30 s and 1200 s were employed for this study. \( C_{\text{illum}} \) is referenced to the capacitance
of the junction in the dark \((C_{\text{dark}})\). All capacitance values were measured at a fixed external bias \((V_{\text{ext}})\) of \(-8\) V. SSPC spectra \(S(E, t_{\text{illum}})\) were recorded by subsequently measuring \(C_{\text{illum}}(E, t_{\text{illum}})\) at different \(E\) after \(t_{\text{illum}}\). 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, \(S(E, t_{\text{illum}})\) was recorded at subsequent \(E\) without changing \(V_{\text{ext}}\), and the measurements were exclusively performed in ascending order of \(E\). In contrast, in non-accumulative SSPC measurements, \(V_{\text{ext}}\) is set to 0 V in-between measurements at subsequent \(E\).

3. Methodology

3.1. First-principles calculations based on hybrid-functional

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 et al [39, 40], and Gake et al [41], respectively.

The optical properties of FeGaI, FeGaII and TiGaII 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 \(E_{\text{ZPL}}\), 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 \(E_{\text{em}} = E_{\text{ZPL}} - \omega_{\text{FC}}^g\) and \(E_{\text{abs}} = E_{\text{ZPL}} + \omega_{\text{FC}}^e\), respectively, where \(\omega_{\text{FC}}^g\) and \(\omega_{\text{FC}}^e\) are the so-called FC shifts. The normalized absorption cross-section \(\sigma_{\text{n,norm}}^o(E)\), including temperature-dependent vibrational broadening, can be simulated using the effective vibrational frequencies, as outlined in [22, 24].

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

3.2. Simulation of steady-state photo-capacitance spectra

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

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

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 the 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.

\[ S(E, t_{\text{illum}}) = 2N_D \sum_i \frac{\Delta C_{\text{illum},i}}{C_{\text{dark}}} \frac{1}{1 + \exp \left( \frac{-E_i - E_i^*}{\gamma_i} \right)} \]  \hspace{1cm} (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 SSPC measurements can also be presented as derivative SSPC 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 β-Ga2O3, 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 \( N_{\text{tr,eff}} \) representing the steady-state concentration of ionized traps inside the probing volume. \( N_{\text{tr,eff}} \) is a sum of all \( N_{\text{tr,eff},i} \) representing the concentration of ionized traps \( i \) in steady-state. If optically-induced hole emission can be neglected, \( N_{\text{tr,eff},i} \) can be computed from \( N_{\text{tr,eff},i} \) via [1]:

\[ N_{\text{tr,eff},i} = \frac{N_{\text{tr,eff}}}{N_{\text{tr,eff}} - \frac{W}{x_{i,1}}} = c N_{\text{tr,eff}}^{\text{ss}}. \]  \hspace{1cm} (3)

\( N_{\text{tr,eff}} \) is the actual concentration of trap \( i \). \( W \) is the depth of the depletion layer at \( V_{\text{ext}}, x_{i,1} \) is the depth where the thermodynamic charge state transition level of trap \( i (E_{\text{th}}^i) \) crosses the Fermi-level \( E_F \), and \( W_{i,1} \) 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 SSPC measurements traps are only photo-ionized in part of the volume of the space-charge region, and will always be larger than 1. Notably, \( W_{i,1} \) will be smaller for a trap for which electron capture is more likely [1]. Here, \( W_{i,1} \) can be expected to be reduced for donor defects as compared to acceptor defects [34, 37]. Smaller values for \( W_{i,1} \) 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-sections 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 \( N_{\text{tr,eff}}^{\text{ss}} \) (see equation (1)). The time-evolution of \( N_{\text{tr,eff}}^{\text{ss}} \) is described by the following differential equation [1, 10]:

\[ \frac{dN_{\text{tr,eff}}^{\text{ss}}}{dt} = \sigma_n^a \Phi N_{\text{tr,eff}}^{\text{ss}} - \sigma_p^b \Phi N_{\text{tr,eff}}^{\text{ss}}. \]  \hspace{1cm} (4)

Here, \( N_{\text{tr,eff}}^{\text{ss}} \) denotes the concentration of traps occupied with electrons. \( \sigma_n^a \) 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:

\[ \frac{dN_{\text{tr,eff}}^{\text{ss}}}{dt} = \sigma_n^a \Phi N_{\text{tr,eff}}^{\text{ss}}. \]  \hspace{1cm} (5)

Here, \( N_{\text{tr,eff}}^{\text{ss}} \) is equal to \( N_{\text{tr,eff}}^{\text{ss}} - N_{\text{tr,eff}}^{\text{ss}} \). 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 an SSPC measurements. 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):

\[ S_{\text{acc}} (E^k, t_{\text{illum}}) = S (E^{k-1}, t_{\text{illum}}) + \left[ N_{\text{tr,eff}}^{\text{ss}} - S (E^{k-1}, t_{\text{illum}}) \right] \left[ 1 - \exp \left( -\sigma_n^a (E^k) \Phi (E^k) t_{\text{illum}} \right) \right], \]  \hspace{1cm} (6)
if one specific trap is assumed to be present in the space-charge region. Notably, k starts at 1, and S (E, t_{illum}) is set to zero.

For non-accumulative SSPC measurements, the corresponding expression is:

\[ S_{\text{non-acc}} (E, t_{illum}) = N_{t_{\text{eff}}} \left[ 1 - \exp \left( -\sigma^o_n (E) \Phi (E) t_{illum} \right) \right], \] (7)

if one specific trap is assumed to be present in the space-charge region. To solve equations (6) and (7), one needs to know \( \sigma^o_n (E) \) and \( \Phi (E) \). \( \sigma^o_n (E) \) can be defined as:

\[ \sigma^o_n (E) = \sum_n \sigma^o_{n,norm} (E^k). \] (8)

\( \sigma^o_{n,norm} \) can be obtained from first-principles calculations for a specific defect. The absolute value \( \sum_n \) 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, \( S_{acc} (E, t_{illum}) \) and \( S_{non-acc} (E, t_{illum}) \) are superpositions of contributions \( S_{acc,i} (E, t_{illum}) \) and \( S_{non-acc,i} (E, t_{illum}) \) 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 \( S_{acc} (E^k, t_{illum}) \) 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, a detailed derivation of equations (6) and (7) as well as comparisons between the theoretical expressions of \( S_{acc} (E^k, t_{illum}) \) (see equation (6)) and \( S_{non-acc} (E^k, t_{illum}) \) (see equation (7)) are shown.

### 4. Results and discussion

The CC diagrams for the charge state transitions Fe_{Gal}^{0/-}, Fe_{Gal}^{0/-} and Ti_{Gal}^{+/0} were calculated using hybrid-functional, and the parameters describing Fe_{Gal}^{0/-}, Fe_{Gal}^{0/-} and Ti_{Gal}^{+/0} are summarized in table 1 [8, 23]. The computed values are in accordance with other recent studies regarding Fe_{Gal}^{0/-} and Fe_{Gal}^{0/-} [48] as well as Ti_{Gal}^{+/0} [49]. Figure 2 displays results for \( \sigma^o_{n,norm} \) and \( \sigma^o_{p,norm} \) related to Fe_{Gal}^{0/-}, Fe_{Gal}^{0/-} and Ti_{Gal}^{+/0} in \( \beta\text{-Ga}_2\text{O}_3 \). A temperature of 120 K was assumed for the computations. For \( \sigma^o_{n,norm} \), calculated absorption cross-section spectra are shown with and without taking vibrational broadening into account, whereas only results including vibrational broadening are shown for \( \sigma^o_{p,norm} \). Calculated absorption cross-section spectra without vibrational broadening exhibit sharp onsets of absorption, and particularly, exhibit no absorption below the classical absorption energy \( E_{abs} \) [22], in contrast to what is expected in experiments. Hence, absorption cross-sections with vibrational broadening are used in the following. The calculated \( \sigma^o_{n,norm} \) and \( \sigma^o_{p,norm} \) are broad which is in accordance with previous computational results for \( \sigma^o_{n,norm} \), related to primary intrinsic defects in \( \beta\text{-Ga}_2\text{O}_3 \) [28]. Note that the \( \sigma^o_{n,norm} \) related to Fe^{0/-}_{Gal} and Fe^{0/-}_{Gal} show a significant overlap, while \( \sigma^o_{p,norm} \) related to Ti^{+/0}_{Gal} occurs at higher photon energies. Our computational results for \( \sigma^o_{n,norm} \) of Fe^{0/-}_{Gal} and Fe^{0/-}_{Gal} are in accordance with experimental photo-electron paramagnetic resonance studies performed by Bhandari et al [48, 50]. For Fe^{0/-}_{Gal}, Fe^{0/-}_{Gal} and Ti^{+/0}_{Gal}, optically-induced hole emission is only seen for photon energies close to \( E_g \), 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/-}_{Gal}, Fe^{0/-}_{Gal} and Ti^{+/0}_{Gal} 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 \( \beta\text{-Ga}_2\text{O}_3 \) crystal. Three defect signatures labeled as \( E_{Za} \) (\( E_A = 0.66 \) eV, \( \sigma_{na} = 4 \times 10^{-16} \text{ cm}^2 \)), \( E_{Zb} \) (\( E_A = 0.79 \) eV, \( \sigma_{na} = 3 \times 10^{-15} \text{ cm}^2 \)) and \( E_5 \) (\( E_A = 1.03 \) eV, \( \sigma_{na} = 1 \times 10^{-13} \text{ cm}^2 \)) are found to be present, in accordance with previous studies on EFG-grown \( \beta\text{-Ga}_2\text{O}_3 \) crystals [8, 23]. No other defect levels with smaller activation energies than 1.2 eV were present in

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**Table 1.** Summary of parameters describing the CC diagrams for Fe_{Gal}^{0/-}, Fe_{Gal}^{0/-} and Ti_{Gal}^{+/0} [8, 23].

| Defect | \( E_{Za} \) (eV) | \( \sigma^o_{p,norm} \) (eV) | \( \Delta Q \) (amu1/2Å) | \( \Omega_{exp} \) (meV) |
|--------|-----------------|------------------|------------------|------------------|
| Fe_{Gal}^{0/-} | 0.62 | 1.10/1.02 | 1.63 | 59/57 |
| Fe_{Gal}^{0/-} | 0.72 | 1.04/0.93 | 1.22 | 76/72 |
| Ti_{Gal}^{+/0} | 1.13 | 1.01/1.14 | 1.35 | 68/72 |
concentrations exceeding $1 \times 10^{15}$ cm$^{-3}$ in this sample. $E_{2a}$ and $E_{2b}$ have been assigned to $\text{Fe}^{0/-}/\text{GaI}$ and $\text{Fe}^{0/-}/\text{GaII}$, respectively [8, 23, 51], while $E_3$ is proposed to be related to $\text{Ti}^{+}/\text{GaII}$ [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$^{-3}$ ($E_{2a}$ or $\text{FeGaI}$), $2.32 \times 10^{16}$ cm$^{-3}$ ($E_{2b}$ or $\text{FeGaII}$) and $5.45 \times 10^{15}$ cm$^{-3}$ ($E_3$ or $\text{TiGaII}$), respectively (see table 2). Thus, using DLTS measurements, we are able to establish the presence and concentration of $\text{FeGaI}$, $\text{FeGaII}$ and $\text{TiGaII}$ 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 $T_{\text{EFG}}^1$ and $T_{\text{EFG}}^2$ are broad and partially overlap, and hence it is difficult to establish the respective onset position accurately. Interestingly, $T_{\text{EFG}}^1$ and $T_{\text{EFG}}^2$ 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].
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Table 2. Summary of the parameters used for the model displayed in figure 5. The values for \( N_{tr, eff}^{0} \) were determined from modeling accumulative SSPC spectra (see figure 5), while the values for \( N_{tr} \) were obtained from DLTS measurements (see figure 3).

| Defect level | \( \Sigma_{n}^{0} \) (10\(^{-14}\) cm\(^{2}\)) | \( N_{tr, eff}^{0} \) (10\(^{15}\) cm\(^{-3}\)) | \( N_{tr} \) (10\(^{15}\) cm\(^{-3}\)) |
|--------------|---------------------------------|---------------------------------|---------------------------------|
| Fe\(_{0}\)\(_{Gal}\) | 0.3 | 1.5 | 2.6 |
| Fe\(_{0}\)\(_{Gall}\) | 0.3 | 9.5 | 23.2 |
| Ti\(_{Gall}\) | 9.6 | 1.1 | 5.5 |

Figure 4. (a) SSPC spectrum recorded accumulatively on an EFG-grown \( \beta\)-Ga\(_{2}\)O\(_{3}\) crystal (\( t_{illum} = 300 \) s). The results are displayed as conventional SSPC spectrum (upper panel) and derivative SSPC spectrum (lower panel). Several defect-related signatures are present and their onset positions are marked with arrows. \( E_{0} \) marks a signature related to the band gap of \( \beta\)-Ga\(_{2}\)O\(_{3}\). (b) Comparison between derivative SSPC spectra recorded on an EFG-grown \( \beta\)-Ga\(_{2}\)O\(_{3}\) crystal accumulatively and non-accumulatively using two different \( t_{illum} \). Only the photon energy range where \( T_{1}^{0/0} \) and \( T_{2}^{0/0} \) occur is shown.

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 \( t_{illum} \). Data are only shown for the photon energy range where \( T_{1}^{0/0} \) and \( T_{2}^{0/0} \) can be seen. Features in \( dS_{acc} / dE \) are narrower than the corresponding features seen in \( dS_{non-acc} / dE \). Indeed, it is not possible to distinguish \( T_{1}^{0/0} \) and \( T_{2}^{0/0} \) in \( dS_{non-acc} / dE \). With increasing \( t_{illum} \), the signatures associated with \( T_{1}^{0/0} \) and \( T_{2}^{0/0} \) become significantly more narrow and shift to lower photon energies in \( dS_{acc} / dE \), while only minor changes are seen in \( dS_{non-acc} / dE \). Thus, using accumulative SSPC measurements with long \( t_{illum} \), the spectral resolution can be significantly improved. The spectral shape seen for \( T_{1}^{0/0} \) and \( T_{2}^{0/0} \) in \( dS_{acc} / dE \) recorded with \( t_{illum} = 1200 \) s clearly suggests the presence of several overlapping defect signatures.

As mentioned before, DLTS measurements confirm the presence of Fe\(_{0}\)\(_{Gal}\), Fe\(_{0}\)\(_{Gall}\) and Ti\(_{Gall}\) 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 0.4–1.2 eV as reported in \( \beta\)-Ga\(_{2}\)O\(_{3}\) previously [11, 12, 28], one expects the optical absorption related to Fe\(_{0}\)\(_{Gal}\), Fe\(_{0}\)\(_{Gall}\) and Ti\(_{Gall}\) to occur at around 1.1–2.2 eV. Thus, Fe\(_{0}\)\(_{Gal}\), Fe\(_{0}\)\(_{Gall}\) and Ti\(_{Gall}\)\(^{+}/0\) are all plausible candidates for \( T_{1}^{0/0} \). Further, the amplitude of \( T_{1}^{0/0} \) suggests an associated trap concentration in the range of \( 1 \times 10^{16} \) cm\(^{-3}\), corroborating the relation to Fe\(_{Gall}\), Fe\(_{Gall}\) and Ti\(_{Gall}\). 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 \( T_{1}^{0/0} \).

In order to assign \( T_{1}^{0/0} \) to Fe\(_{0}\)\(_{Gal}\), Fe\(_{0}\)\(_{Gall}\) and Ti\(_{Gall}\)\(^{+}/0\), however, it is necessary to compare the calculated results for \( \sigma_{norm}^{0} \) (see figure 2) to the recorded SSPC spectra. Particularly, it is necessary to take experimental parameters such as \( t_{illum} \) 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\(_{0}\)\(_{Gal}\), Fe\(_{0}\)\(_{Gall}\) and Ti\(_{Gall}\)\(^{+}/0\). The simulation has two free parameters for each defect signature: one pair of \( \Sigma_{n}^{0} \) and \( N_{tr, eff}^{0} \) for Fe\(_{0}\)\(_{Gal}\), Fe\(_{0}\)\(_{Gall}\) and Ti\(_{Gall}\)\(^{+}/0\), respectively. Increasing \( \Sigma_{n}^{0} \) will lead to a narrowing of the simulated defect signature and shift it to lower...
Figure 5. Accumulative SSPC spectra recorded on a EFG-grown β-Ga2O3 crystal using different $t_{\text{illum}}$. The spectra were modeled with equation (6), and the models are shown in solid lines. The model parameters are shown in table 2. A feature related to the spectral shape of $\Phi$ is marked in gray (see figure 1).

photon energies (see appendix A). Changing $N_{\text{ss tr,eff}}$ will scale the simulated defect signature (see appendix A). The parameters which give the model curve shown in figure 4(a) are shown in table 2. The model parameters yield an excellent fit to the recorded data even when modeling different $t_{\text{illum}}$ simultaneously, corroborating the validity of employing equation (6). Notably, it was not possible to model $T_{\text{EFG}}^2$ using the absorption cross-sections calculated for Fe0$^-$/GaI, Fe0$^-$/GaII and Ti$^+$/0GaII (not shown). Thus, we tentatively assign $T_{\text{EFG}}^1$ to Fe0$^-$/GaI, Fe0$^-$/GaII and Ti$^+$/0GaII. However, it is possible that other defects contribute to $T_{\text{EFG}}^1$ to a minor extent, i.e., from DLTS measurements, it cannot be ruled out that defects with a concentration below $1 \times 10^{15}$ cm$^{-3}$ are present in addition to FeGaI, FeGaII and TiGaII that might contribute to $T_{\text{EFG}}^1$.

Table 2 shows the comparison of values determined for $N_{\text{ss tr,eff}}$ and $N_{\text{tr}}$ of FeGaI, FeGaII and TiGaII from SSPC and DLTS measurements, respectively. Notably, all values obtained for $N_{\text{ss tr,eff}}$ are lower than the values determined for $N_{\text{tr}}$ by a factor of 2–5. Applying a probing volume correction to $N_{\text{ss tr,eff}}$ (see equation (3)) will bring the values determined from SSPC measurements closer to the ones obtained from DLTS measurements. Interestingly, a larger deviation between $N_{\text{ss tr,eff}}$ and $N_{\text{tr}}$ is seen for TiGaII, as expected for defects more likely to capture electrons. Indeed, TiGaII is a donor, and hence more prone to capture electrons compared to the acceptor defects FeGaI and FeGaII [34, 37]. In accordance, using DLTS, comparatively large apparent cross-sections for electron capture are determined for Ti$^+$/0GaII in contrast to Fe0$^-$/GaI and Fe0$^-$/GaII [8, 9, 23].

5. Summary and conclusion

In summary, we presented a new method to combine SSPC measurements with first-principles calculations which can be used to reveal the identity of optical charge-state transition levels related to defects in wide band gap semiconductors. A method to simulate SSPC spectra using defect-related optical absorption spectra obtained from first-principles calculations based on hybrid-functionals was proposed. The simulations take the experimental conditions for the accumulative SSPC measurements explicitly into account. The thermodynamic charge-state transition levels of Fe0$^-$/GaI, Fe0$^-$/GaII and Ti$^+$/0GaII in β-Ga2O3 were recently identified [8, 9, 23], and thus served as a test case for the method we developed. Accumulative SSPC measurements were performed on EFG-grown β-Ga2O3 crystals and several defect signatures labeled $T_{\text{EFG}}^1$–$T_{\text{EFG}}^6$ with onsets for optical absorption between 1.5 eV and 4.3 eV were unveiled. Indeed, we demonstrated how the simulation of accumulatively-recorded derivative SSPC spectra can be used to
identify the optical charge-state transition levels related to Fe$_{\text{Gal}}^{0/-}$, Fe$_{\text{Gal}}^{0/+}$, and Ti$_{\text{Gal}}^{+/-}$ in $\beta$-Ga$_2$O$_3$. Thus, we were able to assign the signature labeled $T_{\text{Gal}}^{\text{FEO}}$ to Fe$_{\text{Gal}}^{0/-}$, Fe$_{\text{Gal}}^{0/+}$ as well as Ti$_{\text{Gal}}^{+/-}$. Future applications of this approach, as well as its extension to account for optically-induced hole emission processes, may help elucidate the origins of other deep level signatures in $\beta$-Ga$_2$O$_3$ and other wide-band-gap semiconductors.

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Appendix A. Simulation of deep-level transient and steady-state photo-capacitance spectra

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 ($V_{\text{rev}} < 0$ V) and subjected to a voltage pulse ($V_{\text{pulse}} > 0$ V) at a time $t_0$ which lasts for a duration $t_{\text{pulse}}$. In the following, it is assumed that DLTS measurements are performed on a Schottky junction comprising an n-type semiconductor. Moreover, we assume that a trap exhibiting a concentration of $N_r$ 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 $V_{\text{rev}}$. 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 $V_{\text{rev}} + V_{\text{pulse}}$. After the end of the voltage pulse at $t_0 + t_{\text{pulse}}$, 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]:

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

Here, $T$ is the sample temperature, $E_A$ is the activation energy for thermally-induced electron emission from the trap, $\sigma_n$ 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 ($E_{th}$) [1, 21].

Assuming parabolic bands, $\beta$ can be computed by [1]:

$$\beta = 2\sqrt{3}\left(\frac{2\pi}{h^2}\right)^{\frac{1}{2}} k_B m_{n,\text{eff}}. \quad (A.2)$$

Here, $h$ is Planck’s constant and $m_{n,\text{eff}}$ 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 $m_{n,\text{eff}}$ [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]

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

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

| $\Sigma_r^0$ (m$^2$) | $\Phi$ (m$^{-2}$ s$^{-1}$) | $t_{\text{th}}$ (s) | $\Delta E$ (meV) | $N_{n,\text{eff}}$ (cm$^{-3}$) |
|----------------------|--------------------------|---------------------|-----------------|-----------------------------|
| $2 \times 10^{-20}$  | $10^{18}$                | $10/300$            | 20              | $10^{16}$                  |
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 $N_{tr,\text{probe}}$ 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]:

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

Here, $t_{\text{delay}}$ 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 $t_\text{transient}$ 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 $E_{\text{th}}$ (see figure 3 in the manuscript). The recorded $S_j(T)$ can be compared to simulations when combining equation (A.4) with equations (A.1) and (A.3). The free parameters of the simulation are the quantities $N_{tr,\text{probe}}, E_A$ and $\sigma_a$ which describe the concentration and properties of the trap. Often, one represents DLTS spectra as $2N_D \Delta C/C_{0,i}$ whereby $\Delta C = C_0 - C(t = 0)$. The recorded $S_j(T)$ can be compared to simulations when combining equation (A.4) with equations (A.1) and (A.3). The free parameters of the simulation are the quantities $N_{tr,\text{probe}}, E_A$ and $\sigma_a$ which describe the concentration and properties of the trap. Often, one represents DLTS spectra as $2N_D \Delta C/C_{0,i}$ whereby $\Delta C = C_0 - C(t = 0)$.

Figure A1. Graphical representation of equations (A.19) and (A.20). Results are shown in dependence of (a) $t$ and (b), (c) $E$. In (b) conventional SSPC spectra are shown, while in (c) derivative SSPC spectra are displayed. Here, the $\sigma_{\text{norm}}$ calculated for Ti$^{+}/$Ga$^{2+}$ 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: $\Delta E = 0.2$ eV, $\Sigma_{\text{norm}} = 2 \times 10^{-20} \text{m}^2$, $\Phi = 1 \times 10^{18} \text{m}^{-2} \text{sa}$ and $N_{N,i}^{\text{eff}} = 1 \times 10^{16} \text{cm}^{-3}$. 

Assuming $N_{tr} < N_D$ 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 $V_{\text{rev}}$ is applied. $N_D$ is the donor concentration and $N_{tr,\text{probe}}$ 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]:

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

Here, $t_{\text{delay}}$ 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 $t_\text{transient}$, 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 $E_{\text{th}}$ (see figure 3 in the manuscript). The recorded $S_j(T)$ can be compared to simulations when combining equation (A.4) with equations (A.1) and (A.3). The free parameters of the simulation are the quantities $N_{tr,\text{probe}}, E_A$ and $\sigma_a$ which describe the concentration and properties of the trap. Often, one represents DLTS spectra as $2N_D \Delta C/C_{0,i}$ where $\Delta C = C_0 - C(t = 0)$ can be calculated from $S_j(T)$ as outlined in [1, 55].
As mentioned above, \( N_{\text{tr,probe}} \) represents the effective trap concentration in-between \( x_2 \) and \( x_1 \). The actual trap concentration \( N_{\text{tr}} \) can be determined by using [1]:

\[
N_{\text{tr}} = \frac{W^2}{x_1^2 - x_2^2} N_{\text{tr,probe}}. \tag{A.5}
\]

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

### 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 \( t_{\text{illum}} \). In the following, it is assumed that SSPC measurements are performed on a Schottky junction comprising an n-type semiconductor. Moreover, we assume that a trap exhibiting a concentration of \( N_{\text{tr}} \) and a single thermodynamic charge-state transition level (\( E_t \)) is present in the semiconductor.

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

\[
S(E_k, t_{\text{illum}}) = 2 \frac{C_{\text{illum}}(E_k, t_{\text{illum}}) - C_{\text{dark}}}{C_{\text{dark}}} N_D = 2 \frac{\Delta C_{\text{illum}}(E_k, t_{\text{illum}})}{C_{\text{dark}}} N_D = N^*_{\text{tr,eff}}(E_k, t_{\text{illum}}). \tag{A.6}
\]

Here, \( \Delta C_{\text{illum}}(E_k, t_{\text{illum}}) \) denotes the change in (photo-)capacitance during illumination for \( t_{\text{illum}} \) at \( E_k \), and \( C_{\text{dark}} \) represents the capacitance of the junction measured in the dark. \( N^*_{\text{tr,eff}}(E_k, t_{\text{illum}}) \) 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 \( N_D \ll N_{\text{tr}} \) to be valid.

\( N^*_{\text{tr,eff}} = S(E_k, t_{\text{illum}}) \) is described by the following differential equation [10]:

\[
\frac{dN^*_{\text{tr,eff}}}{dt} = \sigma_o^\nu \Phi N_{\text{tr,eff}}, \tag{A.7}
\]

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), \( \sigma_n^o \) 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. \( \sigma_n^o \) and \( \Phi \) will be functions of \( E_k \). \( N_{tr,eff}^\ast \) is the concentration of defects inside the probing volume which are not ionized, and hence \( N_{tr,eff}^\ast \) is equal to \( N_{ss}^{tr,eff} - N_{\ast,eff}^{tr,eff} \). \( N_{ss}^{tr,eff} \) is the effective concentration of the defect inside the probing volume. Using this, equation (A.7) becomes:

\[
\frac{dN_{\ast,eff}^\ast}{dt} = \sigma_n^o \Phi N_{\ast,eff}^\ast - \sigma_n^o \Phi N_{\ast,eff}^\ast.
\] (A.8)

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

\[
\frac{dN_{\ast,eff}^\ast}{dt} = -\sigma_n^o \Phi N_{\ast,eff}^\ast.
\] (A.9)

This differential equation is solved by:

\[
N_{\ast,eff}^\ast = A \exp \left(-\sigma_n^o \Phi t \right).
\] (A.10)

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

\[
N_{\ast,eff}^\ast = N_{ss}^{tr,eff}.
\] (A.11)

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

\[
N_{\ast,eff}^\ast = N_{ss}^{tr,eff} + A \exp \left(-\sigma_n^o \Phi t \right).
\] (A.12)

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 \( N_{\ast,eff}^\ast \left(E_k, t = 0 \right) \) will be expressed by:

\[
N_{\ast,eff}^\ast \left(E_k, t = 0 \right) = 0.
\] (A.13)
Thus, $A$ will be equal to $-N_{\text{tr,eff}}$, and hence:

$$S_{\text{non-acc}}(E^k, t_{\text{illum}}) = N_{\text{tr,eff}}^{\text{ss}} - N_{\text{tr,eff}}^{\text{ss}} \exp \left( -\sigma_0^n \Phi t_{\text{illum}} \right)$$

$$= N_{\text{tr,eff}}^{\text{ss}} \left[ 1 - \exp \left( -\sigma_0^n \Phi t_{\text{illum}} \right) \right].$$  \hspace{1cm} (A.14)

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

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

$$S_{\text{acc}}(E^0, t_{\text{illum}}) = N_{\text{tr,eff}}^{\text{ss}} \left[ 1 - \exp \left( -\sigma_0^n \Phi t_{\text{illum}} \right) \right].$$  \hspace{1cm} (A.15)

For illumination at subsequent $E^k$, the following boundary condition holds:

$$N_{\text{tr,eff}}^{\ast}(E^k, t = 0s) = N_{\text{tr,eff}}^{\ast}(E^{k-1}, t_{\text{illum}})$$

$$= S_{\text{acc}}(E^{k-1}, t_{\text{illum}})$$  \hspace{1cm} (A.16)

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 $S_{\text{acc}}(E^{k-1}, t_{\text{illum}}) - N_{\text{tr,eff}}^{\text{ss}}$, and hence:

$$S_{\text{acc}}(E^k, t_{\text{illum}}) = N_{\text{tr,eff}}^{\text{ss}} + \left[ S_{\text{acc}}(E^{k-1}, t_{\text{illum}}) - N_{\text{tr,eff}}^{\text{ss}} \right] \exp \left( -\sigma_0^n \Phi t_{\text{illum}} \right)$$

$$= S_{\text{acc}}(E^{k-1}, t_{\text{illum}}) - N_{\text{tr,eff}}^{\text{ss}} \exp \left( -\sigma_0^n \Phi t_{\text{illum}} \right).$$  \hspace{1cm} (A.17)

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:
Figure A5. Graphical representation of equations (A.14) and (A.18) for various $N_{ss}^{\text{tr,eff}}$. Results are shown for (a) conventional and (b) derivative SSPC spectra. Here, the $\sigma_{o}^{n,norm}$ calculated for Ti$^{+}/$GaII 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 $\Delta E = 20$ meV.

Equations (A.14) and (A.18) can be expressed more general in the form $S_{\text{acc}} (E^k, t_{\text{illum}})$ and $S_{\text{non-acc}} (E^k, t_{\text{illum}})$. $S_{\text{acc}} (E^k, t_{\text{illum}})$ and $S_{\text{non-acc}} (E^k, t_{\text{illum}})$ describe the recorded SSPC spectrum after illumination for a time $t$ at $E^k$ while the junction was illuminated for a duration $t_{\text{illum}}$ at all photon energies $E$ for which $j < k$ is valid. $S_{\text{acc}} (E^k, t_{\text{illum}})$ can be expressed as:

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

This equation is valid for all $E^k$ if $S_{\text{acc}} (E^0, t_{\text{illum}})$ is set to 0.
while \( S_{\text{non-acc}}(E^k, t_{\text{illum}}, t) \) can be calculated by:

\[
S_{\text{non-acc}}(E^k, t_{\text{illum}}, t) = N_{\text{tr,eff}}^{\Phi} \left[ 1 - \exp \left( -\sigma^0_n \Phi t \right) \right].
\]  \hspace{1cm} (A.20)

\( \sigma^0_n \) is defined by:

\[
\sigma^0_n = \Sigma_n^o \sigma^o_{n,\text{norm}}.
\]  \hspace{1cm} (A.21)

Here, \( \sigma^o_{n,\text{norm}} \) can be obtained from first-principles calculations for a specific trap, while \( \Sigma^o_n \) is a free parameter of the simulation.

In the following, graphical representations of equations (A.14), (A.18–A.20) will be shown. Hereby, the calculated \( \sigma^o_{n,\text{norm}} \) of \( T_{\text{Gall}/0}^{1.70} \) 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 equations (A.19) and (A.20). Figure A1(a) shows the dependence on \( t \), while figures A1(b) and (c) show the corresponding dependence on \( E^k \). Notably, for the same experimental conditions, non-accumulative SSPC measurements will reach steady-state conditions for longer \( t_{\text{illum}} \) compared to accumulative SSPC measurements. Generally, longer \( t_{\text{illum}} \) are associated with steps in SSPC spectra shifting to lower photon energies and becoming steeper.

In figures 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 SSPC 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.

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**References**

[1] Blood P and Orton J W 1992 The Electrical Characterization of Semiconductors: Majority Carriers and Electron States (Techniques of Physics) (New York: Academic)

[2] Van de Walle C G and Neugebauer J 2004 First-principles calculations for defects and impurities: applications to III-nitrides *J. Appl. Phys.* 95 3851–79

[3] Pearton S J, Yang J, Cary P HIV, Ren F, Kim J, Tadjer M J and Mastro M A 2018 A review of Ga2O3 materials, processing, and devices *Appl. Phys. Rev.* 5 011301

[4] Higashiwaki M, Sasaki K, Murakami H, Kumagai Y, Koukitu A, Kuramata A, Masui T and Yamakoshi S 2016 Recent progress in Ga2O3 power devices *Sens. Actuators* 232 208–13

[5] Nakagomi S, Momo T, Takahashi S and Kokubun Y 2018 Iron and oxygen behavior in Ga2O3 power devices *Sens. Actuators* 233 201–4

[6] Nakagomi S, Sato T, Takahashi Y and Kokubun Y 2015 Deep ultraviolet photodiodes based on the β-Ga2O3/GaN heterojunction *Sens. Actuators* 231 5759–7192

[7] Lang D V 1974 Deep-level transient spectroscopy: a new method to characterize traps in semiconductors *J. Appl. Phys.* 45 3023–32

[8] Eide Ingebritsen M, Varley J B, Kuznetsova A Y, Svensson B G, Aliferi G, Mihaila A, Baerdtsünner U and Vines L 2018 Iron and intrinsic deep level states in Ga2O\(_3\) *Appl. Phys. Lett.* 112 042104

[9] Ingebritsen M E, Kuznetsova A Y, Svensson B G, Aliferi G, Mihaila A, Baerdtsünner U, Perron A, Vines L and Varley J B 2019 Impact of proton irradiation on conductivity and deep level defects in β-Ga2O3 *Appl. Mater. Lett.* 7 022510

[10] Chantre A, Vincent G and Bois D 1981 Deep-level optical spectroscopy in GaAs *Phys. Rev. B* 23 5335

[11] Farzana E, Ahmad E, James S S, Arehart A R and Ringel S A 2018 Deep level defects in Ge-doped (010) β-Ga2O3 layers grown by plasma-assisted molecular beam epitaxy *J. Appl. Phys.* 123 161410

[12] Zhong Z, Farzana E, Arehart A R and Ringel S A 2016 Deep level defects throughout the bandgap of (010) β-Ga2O3 detected by optically and thermally stimulated sweep capacitance spectroscopy *Appl. Phys. Lett.* 108 052105

[13] Farzana E, Chaiken M F, Blue T E, Arehart A R and Ringel S A 2019 Impact of deep level defects induced by high energy neutron radiation in β-Ga2O3 *Appl. Mater. Lett.* 7 022502

[14] Polyakov A Y, Smirnov N B, Shcherenkov I V, Yakimov E B, Yang J, Ren F, Yang G, Kim J, Kuramata A and Pearton S J 2018 Point defect induced degradation of electrical properties of Ga2O3 by 10 MeV proton damage *Appl. Phys. Lett.* 112 032107

[15] Polyakov A Y et al 2018 Defects responsible for charge carrier removal and correlation with deep level introduction in irradiated β-Ga2O3 *Appl. Phys. Lett.* 113 092102

[16] Polyakov A Y, Smirnov N B, Shcherenkov I V, Gogova D, Tarelkin S A and Pearton S J 2018 Compensation and persistent photocapacitance in homoepitaxial Sn-doped β-Ga2O3 *J. Appl. Phys.* 123 115702
