Zimmermann, Christian; Frodason, Ymir Kalmann; Barnard, Abraham Willem; Varley, Joel Basile; Irmscher, Klaus; Galazka, Zbigniew; Karjalainen, Antti; Meyer, Walter Ernst; Auret, Francois Danie; Vines, Lasse

Ti-A nd Fe-related charge transition levels in β-Ga2O3

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ABSTRACT

Deep-level transient spectroscopy measurements on $\beta$-Ga$_2$O$_3$ crystals reveal the presence of three defect signatures labeled $E_{2a}$, $E_{2b}$, and $E_3$ with activation energies at around 0.66 eV, 0.73 eV, and 0.95 eV below the conduction band edge. Using secondary ion mass spectrometry, a correlation between the defect concentration associated with $E_3$ and the Ti concentration present in the samples was found. Particularly, it is found that $E_3$ is the dominant Ti-related defect in $\beta$-Ga$_2$O$_3$ and is associated with a single Ti atom. This finding is further corroborated by hybrid functional calculations that predict Ti substituting on an octahedral Ga site, denoted as TiGaII, to be a good candidate for $E_3$.

Moreover, the deep level transient spectroscopy results show that the level previously labeled $E_2$ and attributed to Fe substituting on a gallium site (FeGa) consists of two overlapping signatures labeled $E_{2a}$ and $E_{2b}$. We tentatively assign $E_{2a}$ and $E_{2b}$ to Fe substituting for Ga on a tetrahedral or an octahedral site, respectively.

Monoclinic gallium sesquioxide ($\beta$-Ga$_2$O$_3$) has attracted considerable attention in recent years due to its wide bandgap and exceptionally high break-down electrical fields, rendering it a potential candidate for applications in UV sensors and power electronics. Defects, however, influence the optical and electrical properties of the material and need to be understood for $\beta$-Ga$_2$O$_3$ to live up to its potential. For example, defects can pin the Fermi-level in semiconductor–metal or semiconductor–insulator–metal junctions and hence influence the performance of devices for power electronics.

Intentional and unintentional impurities are particularly relevant defects in $\beta$-Ga$_2$O$_3$. For example, iron (Fe) is commonly used to achieve semi-insulating $\beta$-Ga$_2$O$_3$ needed for obtaining field effect transistors based on $\beta$-Ga$_2$O$_3$, while titanium (Ti) is often used as Ohmic contact on $\beta$-Ga$_2$O$_3$. Furthermore, Ti in $\beta$-Ga$_2$O$_3$ was also proposed as a promising defect for quantum information processing. Fe and Ti are believed to give rise to deep electronic states in $\beta$-Ga$_2$O$_3$. Indeed, several defect-related electronic levels have been observed by deep level transient spectroscopy (DLTS). In particular, the defect levels commonly labeled as $E_1$, $E_2$, and $E_3$, with energy level positions at 0.56 eV, 0.78 eV, and 1.01 eV below the conduction band edge, respectively, have all been proposed to be related to impurities due to their lack of response to irradiation. Indeed, $E_2$ has been identified as being related to FeGa using DLTS in combination with secondary ion mass spectrometry (SIMS) and hybrid functional calculations.

In this study, we report on a combined DLTS and SIMS study. Using both techniques, we were able to tentatively identify a defect level with an activation energy of 0.95 eV below the conduction band edge to be associated with Ti substituting on an octahedral gallium (Ga) site and denoted as TiGaII. The corresponding level is commonly observed in commercially available $\beta$-Ga$_2$O$_3$ and is often labeled...
as \( E_3 \). Our identification is corroborated by hybrid functional calculations as \( E_3 \). Our identification is corroborated by hybrid functional calculations and associated with \( \text{FeGa}_\text{ox} \), indeed consists of at least two defect signatures.

\( \beta\)-Ga\(_2\)O\(_3\) bulk crystals grown by edge-defined film-fed growth (EFG)\(^\text{1,2,3}\) and the Czochralski method (CZ)\(^\text{4,5}\) were used for this study. The EFG crystals were purchased from Tamura Corporation, and the CZ crystals were obtained from Novel Crystal Technology Inc. were used as reference materials with a low impurity content. All samples were prepared for DLTS measurements, and hence, Ohmic contacts (Ti/Al or InGa eutectic alloy) and Schottky contacts (Ni or Pt) were deposited on the back and front sides, respectively. The resulting junctions exhibited a rectification of at least two orders of magnitude and a series resistance never exceeding 1 k\( \Omega \). The samples displayed donor concentrations ranging from \( 5 \times 10^{15} \text{ cm}^{-3} \) to \( 7 \times 10^{16} \text{ cm}^{-3} \). Further details regarding the fabrication of Schottky diodes can be found in Ref.\(^\text{25}\) for the CZ crystals and in Refs.\(^\text{12, 15, and 20}\) for the EFG and HVPE samples.

DLTS measurements were performed on two different setups described in detail elsewhere,\(^\text{20,26}\) with one setup covering the temperature range from 20 K to 400 K and one high-temperature setup enabling measurements between 150 K and 700 K. In short, a reverse bias of \(-10 \text{ V} \) and a filling pulse of 10 V were deployed for conventional DLTS measurements, while Laplace DLTS was performed at a reverse bias of \(-2 \text{ V} \) and a filling pulse of 1.8 V. Laplace DLTS measurements were analyzed with a software written by Dobaczewski et al.\(^\text{27,28}\) A GS4 filter was utilized to construct the conventional DLTS spectra in order to better resolve the defect signatures \( E_2 \) and \( E_3 \), and the spectra were simulated with a python-based script. Parameters such as the trap concentration \( N_t \), the activation energy \( E_a \), and the apparent capture cross section \( \sigma_{na} \) of the individual traps were obtained from Laplace DLTS measurements by constructing an Arrhenius plot,\(^\text{27,28}\) while these parameters were extracted from conventional DLTS measurements from the afore-mentioned simulations. In both cases, the extracted value for \( \sigma_{na} \) can be expected to exhibit a large uncertainty. For calculating \( N_t \), the \( \lambda \)-correction was included.\(^\text{27,28}\)

SIMS measurements were performed using a Cameca IMS 7f instrument with a primary beam of 10 ke V O\(_2\) ions. For Ti, the absolute concentration was determined using an implanted reference sample. Crater depths were measured using a Dektak Stylus Profilometer to convert sputtering time to depth.

First-principles calculations were performed using the projector augmented wave method\(^\text{1,3}\) and the Heyd–Scuseria–Ernzerhof (HSE)\(^\text{33}\) screened hybrid functional, as implemented in the VASP code.\(^\text{33}\) The fraction of screened Hartree–Fock exchange was adjusted to \( z = 0.33 \), resulting in a direct bandgap of 4.9 eV.\(^\text{33}\) The experimentally determined bandgap value can be expected to exhibit an uncertainty of around \( \pm 0.1 \text{ eV} \).\(^\text{33}\) The Ga-3d and Ti-3p, -3d, and -4s electrons were included as valence states. For defect calculations, we used 160-atom supercells, a plane wave energy cutoff of 300 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.\(^\text{34}\) For charged defects, we adopted the anisotropic Freysoldt, Neugebauer, and Van de Walle scheme to correct formation energies\(^\text{35}\) and the method recently proposed by Gake et al. to correct vertical transition energies.\(^\text{36}\) Nonradiative carrier capture barriers were estimated by using the one-dimensional configuration coordinate (CC) model.\(^\text{37}\) The CC diagrams were derived from the calculated one-dimensional CC model parameters by using a harmonic approximation.\(^\text{38}\)

Figure 1(a) shows DLTS spectra recorded on an EFG-grown \( \beta\)-Ga\(_2\)O\(_3\) crystal. Three defect signatures are observed labeled as \( E_{2a} \), \( E_{2b} \), and \( E_{3} \). The samples displayed donor concentrations \( \sigma_{na} \) of \( 4 \times 10^{-16} \text{ cm}^{-2} \). The defect signatures similar to \( E_{2a} \) and \( E_{2b} \) were found in EFG- and CZ-grown \( \beta\)-Ga\(_2\)O\(_3\) crystals and HVPE-grown \( \beta\)-Ga\(_2\)O\(_3\) thin-films, while \( E_{3} \) was only found in EFG- and CZ-grown \( \beta\)-Ga\(_2\)O\(_3\) crystals. Notably, on similar samples, the \( E_{3} \) values of around 1.04 eV (Ref.\(^\text{25}\)) and 1.01 eV (Ref.\(^\text{20}\)) have been reported previously for \( E_{3} \). Hence, an uncertainty of around 0.1 eV can be assumed for the values of \( E_{3} \) stated here. Considering the previously reported values for \( \sigma_{na} \) of \( E_{2a} \) and \( E_{2b} \), an uncertainty of around \(+/−\) an order of magnitude can be expected.

Figure 1(b) displays the results obtained performing Laplace DLTS on an EFG-grown \( \beta\)-Ga\(_2\)O\(_3\) crystal. The corresponding results corroborate the findings presented above and in Fig. 1(a). Three defect signatures were revealed: \( E_{2a} \) (\( E_a = 0.56 \text{ eV}, \sigma_{na} = 1 \times 10^{-17} \text{ cm}^{-2} \)), \( E_{2b} \) (\( E_a = 0.70 \text{ eV}, \sigma_{na} = 4 \times 10^{-16} \text{ cm}^{-2} \)), and \( E_{3} \) (\( E_a = 0.98 \text{ eV}, \sigma_{na} = 4 \times 10^{-14} \text{ cm}^{-2} \)). These parameters match well with the results obtained from simulations of conventional DLTS spectra. The defect parameters extracted from conventional and Laplace DLTS measurements are summarized in Table 1. In previous studies, the signatures \( E_{2a} \) and \( E_{2b} \) were observed as a single defect signature labeled \( E_{2} \). \(^\text{15,25,26,28}\) which was attributed to \( \text{FeGa}_\text{ox} \). \( E_{2a} \) and \( E_{2b} \) are present in a variety of commercially available \( \beta\)-Ga\(_2\)O\(_3\) crystals and thin-films.\(^\text{15,25,26}\) Notably, neither \( E_{2a} \) nor \( E_{2b} \) has been found to be affected by irradiation with protons.\(^\text{15,25}\)
The charge transition level of around 0.75 eV below the conduction band edge is typically significantly lower than in CZ- or EFG-grown Ga2O3, suggesting a different origin. Moreover, the trap concentrations associated with E2a and E2b exhibit a ratio of approximately 1:5 (not shown). Notably, a similar ratio is expected for the two configurations of FeGa, assuming a difference in the formation energy of 0.3 eV (Ref. 15) at the melting point temperature.44,45 Notably, an electron paramagnetic resonance (EPR) study also found a ratio of 1:5 for the two different crystallographic configurations of FeGa in β-Ga2O3.46 Hence, we suggest that E2a and E2b arise from the tetrahedral and octahedral configuration of FeGa, respectively.

Figure 2(a) shows an overview over DLTS spectra recorded on a variety of Schottky junctions including CZ-, EFG- and HVPE-grown β-Ga2O3. The trap concentration in HVPE-grown β-Ga2O3 is generally significantly lower than in CZ- or EFG-grown β-Ga2O3 as reported earlier.15 For some CZ-grown β-Ga2O3 crystals [see CZ A in Fig. 2(a)], it was not possible to model the region where E2a and E2b are present with only two defect signatures, indicating the presence of additional defect signatures in this temperature region in DLTS measurements. The modeling of conventional DLTS spectra described the signature related to E2a, suggesting that, indeed, only one defect contributes to this defect signature, as corroborated by Laplace DLTS [see Fig. 1(b)].

A wide range of concentrations associated with E2a, E2b, and E3 are found in CZ- and EFG-grown samples as reported previously, rendering them suitable candidates for the identification of impurity-related defects. SIMS measurements reveal that Ti, Fe, Mg, Al, and Si are present in at least some of the investigated samples. In addition to the correlation between E2 and Fe reported previously,16 the concentration of E3 was found to correlate solely with that of Ti. Figure 2(b) displays the correlation between the Ti concentration [Ti] as determined by SIMS and the E3 trap concentration [E3] as determined by DLTS (square brackets denote concentration). A linear relationship between [Ti] and [E3] can be seen. Notably, all data points fall close to the line expected for [Ti] = [E3], suggesting that E3 is the dominant Ti-related trap and associated with a single Ti atom. Importantly, in HVPE-grown β-Ga2O3, the concentration of both Ti and E3 was found to be below the detection limit of our systems, further corroborating the correlation between Ti and E3.

To gain insights into the formation of defects involving Ti in β-Ga2O3 and corroborate the observed correlation between [E3] and [Ti], we have performed hybrid functional calculations. Only results for the TiGa configurations are presented since TiGa and TiGaII configurations were found to have significantly higher formation energies (not shown). Figure 3(a) displays the formation energy diagram for TiGa and TiGaII, where GaI and GaII denote the tetrahedral and octahedral Ga sites in the β-Ga2O3 lattice. TiGaII has the lowest formation energy regardless of the Fermi level position: the difference is 0.34 eV and 0.86 eV for the positive and neutral charge states, respectively. This means that TiGaII is expected to be the dominant configuration for TiGa, which is consistent with EPR studies performed on β-Ga2O3 crystals, where only TiGaII was identified.13,14,16 A recent study reporting first-principles calculations on Ti in β-Ga2O3 found very similar results for TiGaII,19 Furthermore, the solubility of Ti is expected to be around 1.5 at. % in β-Ga2O3,51 which is consistent with the low formation energy found here for TiGaII. Notably, the amount of unintentionally incorporated Ti will strongly depend on both the amount of Ti present and the experimental conditions during growth.

TiGa is predicted to act as a deep single donor on both lattice sites. In the neutral charge state, the donor electron occupies a localized defect state within the bandgap, showing mainly Ti 3d character. The calculated thermodynamic (+/0) charge state transition level of TiGa in TiGaII occurs at 0.60 eV and 1.13 eV below the conduction band minimum (CBM), respectively. To enable a more direct comparison with the DLTS results, we have estimated the classical capture barrier for electrons E2 as constructed by a CC diagram,52 as shown in Fig. 3(b). The excited state potential energy surface corresponds to the ionized...
donor plus an electron at the CBM ($E_{\text{CBM}}$), and the ground-state curve corresponds to the charge-neutral donor ($E_{\text{TiGaI}}$). The two curves are vertically displaced by the thermal ionization energy $E_i$, i.e., the Fermi level position of the thermodynamic (+/0) charge-state transition level relative to the CBM. In this classical picture, the activation energy for electron emission corresponds to the sum of $E_i$ an $E_0$, which is taken as the energy required to reach the crossing point between the two potential energy curves. For $E_{\text{TiGaI}}$, we obtain a capture barrier of 0.09 eV, whereas no barrier was found for $E_{\text{TiGaII}}$. Note that the activation energy will be lower if its temperature-dependence is taken into account. Thus, we arrive at 0.69 eV and 1.13 eV as the upper limit for the activation energy of $E_{\text{TiGaI}}$ and $E_{\text{TiGaII}}$, respectively. Hence, the calculated transition level for $E_{\text{TiGaI}}$ agrees within the errors of experimental and theoretical calculation with the activation energy found for $E_0$ (0.95 eV), further strengthening the assignment of $E_0$ to Ti. The calculated defect parameters for $E_{\text{TiGaI}}$ are summarized in Table II.

In summary, conventional DLTS measurements on selected EFG- and CZ-grown $\beta$-Ga$_2$O$_3$ crystals reveal the presence of three defect signatures labeled $E_{\text{TiGaI}}$, $E_{\text{TiGaII}}$, and $E_{\text{TiGaIII}}$ with activation energies of 0.66 eV, 0.73 eV, and 0.95 eV below the conduction band edge. The defect concentration associated with Fe substituting for Ga on a tetrahedral or an octahedral site, respectively. The defect concentration associated with $E_0$ is found to be correlated with the Ti concentration present in the samples as measured by SIMS. Particularly, it is shown that $E_3$ is the dominant Ti-related defect in $\beta$-Ga$_2$O$_3$ and is associated with a single Ti atom. This is further supported by hybrid functional calculations where Ti substituting on an octahedral Ga site denoted as $E_{\text{TiGaIII}}$ is shown to be an excellent candidate for $E_3$.

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REFERENCES
