Iron and intrinsic deep level states in Ga$_2$O$_3$


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Oxygen vacancies and donor impurities in $\beta$-Ga$_2$O$_3$
Iron and intrinsic deep level states in Ga$_2$O$_3$


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Using a combination of deep level transient spectroscopy, secondary ion mass spectrometry, proton irradiation, and hybrid functional calculations, we identify two similar deep levels that are associated with Fe impurities and intrinsic defects in bulk crystals and molecular beam epitaxy and hydride vapor phase epitaxy-grown epilayers of β-Ga$_2$O$_3$. First, our results indicate that Fe$_{Ga}$ and not an intrinsic defect, acts as the deep acceptor responsible for the often dominating E2 level at ~0.78 eV below the conduction band minimum. Second, by provoking additional intrinsic defect generation via proton irradiation, we identified the emergence of a new level, labeled as E2*, having the ionization energy very close to that of E2, but exhibiting an order of magnitude larger capture cross section. Importantly, the properties of E2* are found to be consistent with its intrinsic origin. As such, contradictory opinions of a long standing literature debate on either extrinsic or intrinsic origin of the deep acceptor in question converge accounting for possible contributions from E2 and E2* in different experimental conditions. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/), https://doi.org/10.1063/1.5020134

After the early work on gallium oxide (Ga$_2$O$_3$) in the mid-1900s, renewed interest has recently emerged on behalf of its prospects in power electronics and UV devices. Particularly, the monoclinic β-Ga$_2$O$_3$ phase attracts interest due to its bandgap of ~4.8 eV and n-type conductivity, and promising MOSFET devices have already been demonstrated. The control of the n-type charge carrier concentration can be achieved in the range of $10^{16}$–$10^{19}$ cm$^{-3}$ using Si or Sn as dopants, and semi-insulating materials can be made by substituting Ga with Fe, Mn, or Mg. The latter elements act as deep acceptors and thereby compensate the n-type dopants, although little is known of the exact positions of their electronic states within the bandgap. Knowledge of the identities and positions of these types of deep levels is critical for further developing Ga$_2$O$_3$-based optoelectronic devices.

In the literature, several deep levels have been described in β-Ga$_2$O$_3$ from observations by electrical characterization techniques like deep level transient spectroscopy (DLTS) and tentatively assigned to be either of intrinsic or extrinsic origin. In particular, Fe and Co—as the most common contaminants—were proposed to be involved in the levels appearing around 0.56 and 1.0 eV below the conduction band minimum (CBM). Another level appearing in the vicinity of 0.8 eV below the CBM, conventionally labeled E2, was identified in numerous samples grown from independent techniques and suggested to be the dominant source of compensation in the bulk crystals, Of the native defects, hybrid functional calculations have suggested that gallium vacancies (V$_{Ga}$) may be the acceptors that contribute to this electrical compensation, as well as their complexes with hydrogen. Initial calculations using HSE (Heyd-Scuseria-Ernzerhof) functionals predicted these levels to be around 1.6 and 1.8 eV below the CBM for (−2/−3) transitions related to the tetrahedrally coordinated V$_{Ga}$ (I) and octahedrally coordinated V$_{Ga}$ (II), respectively, while more recent calculations argue these levels to be closer to the conduction band, specifically around 0.67 and 1.0 below CBM. These results are consistent with positron annihilation studies that identify V$_{Ga}$-related defects to account for compensation in Si-doped Ga$_2$O$_3$ epitaxial films, but their concentration in bulk crystals remains to be determined. The oxygen vacancy (V$_O$) is also expected to be responsible for deep levels in the upper part of the bandgap, with the (0/+2) transition levels reported to fall between ~1.3 and 2.7 eV below CBM depending on the particular symmetry of the distinct V$_O$ (I), V$_O$ (II), and V$_O$ (III) lattice sites. Despite these experimental and theoretical efforts, unambiguous identification of the electrically active defects in β-Ga$_2$O$_3$ remains largely unresolved. Here, using a combination of deep level transient spectroscopy (DLTS), secondary ion mass spectrometry (SIMS), irradiation experiments, and hybrid functional calculations, we establish a strong link between the E2 level and the Fe content in a range of different samples. Our results suggest that Fe substitutional impurities are the dominant background acceptor in many bulk crystals and responsible for the E2 deep level 0.78 ± 0.04 eV below the CBM. We also identify an additional, distinct level at around 0.75 eV below the CBM that arises with irradiation and is likely attributed to a native defect or defect complex.

Experimentally, we studied bulk single crystals and homo-epitaxial β-Ga$_2$O$_3$ films synthesized by Tamura Corporation. The bulk crystals were fabricated with Edge-defined Film-fed Growth (EFG) and have surfaces oriented in the (010) or the (210) direction. These wafers were nominally undoped but exhibited n-type conductivity with charge carrier concentration.
concentrations (N_d) in the range of 0.6–2.6 × 10^{17} cm^{-3}. The homo-epitaxial films were grown on (010) oriented substrates by either molecular beam epitaxy (MBE) or hydride vapor phase epitaxy (HVPE) to thicknesses of 2 and 10 μm, respectively. The substrates for the films were doped with Sn, yielding charge carrier concentrations ~5 × 10^{18} cm^{-3}, while those in the films were found to be ~2 × 10^{16} and ~8 × 10^{16} cm^{-3} for the MBE and HVPE samples, respectively. Samples of the bulk single crystals will hereafter be referred to as bulk samples, while the epitaxially grown ones are labelled as MBE and HVPE. For electrical characterization, Schottky contacts were deposited through a shadow mask using e-beam evaporation of 150 nm Ni, yielding circular contacts of radii 400, 240, and 100 μm. Further, backside Ohmic contacts were prepared by e-beam deposition of a Ti and Al stack of 10 and 150 nm thickness, respectively. Barrier heights of the Schottky contacts as high as ~1.4 eV and ideality factors as low as 1.05 were observed from current-voltage characteristics with up to eight orders of magnitude rectification.\(^{12}\)

The (010) oriented bulk and the HVPE samples were exposed to an irradiation of 600 keV protons (H\(^{+}\)) at room temperature, with a projected range of about 4.3 μm as estimated by Monte Carlo simulations using the SRIM code.\(^{16}\) From these SRIM simulations, a close to homogeneous profile of vacancy generation is anticipated in the shallower depths relevant for DLTS characterization. Irradiation doses of 2 × 10^{13} and 3 × 10^{14} H/cm\(^2\) were used for the HVPE and bulk samples, respectively. These irradiation conditions caused strong charge carrier compensation, but the electrical conductivity was largely re-established during the first DLTS temperature scan up to 600 K. Subsequent capacitance-voltage measurements indicate flat charge carrier concentration profiles in the irradiated samples. The DLTS measurements were performed with a refined version of the system described in Ref. 17, with ~8 V reverse bias voltage and pulsing up to ~1 V. From this, analysis of the DLTS signal was done using lock-in and GS4 weighting functions applied to the transients in rate windows from (20 ms)\(^{-1}\) to (2560 ms)\(^{-1}\). The energy positions and capture cross sections of the deep levels were derived from Arrhenius plots of the peak positions. Identification of residual impurities and quantification of their concentrations in the samples were accomplished by SIMS using a Cameca IMS7f spectrometer equipped with Cs and O\(_2\) primary ion sources. Absolute concentration calibrations for the observed impurities were obtained using ion implanted reference samples. For the depth calibration, the sputtered crater depths were measured using a Dektak 8 stylus profilometer and a constant erosion rate was assumed.

Our modelling adopts the HSE06 screened hybrid functional,\(^{18,19}\) and projector-augmented wave (PAW) approach\(^{20}\) as implemented in the VASP code.\(^{21,22}\) We include semicore Ga 3\(d\) and Fe 3\(p\), 3\(d\), and 4\(s\) electrons as explicit valence states and set the fraction of screened Hartree-Fock exchange to 32%. This choice yields a bandgap of 4.85 eV and optimal lattice constants of 12.21, 3.03, and 5.79 Å for the \(a\), \(b\), and \(c\) lattice parameters, respectively, in excellent agreement with experimental values.\(^{2,24,25}\) To assess the favorability of incorporating Fe on a Ga site, we compute the formation energy \(E_f\) given by the expression

\[
E_f^{\text{Fe}_{Ga}^{q}} = E_{\text{tot}}^{\text{Fe}^{q}_{Ga}} - E_{\text{tot}}^{\text{Ga}_{2}O_{3}} + \mu_{Ga} - \mu_{Fe} + q\epsilon_F + \Delta^q, \tag{1}
\]

where \(E_{\text{tot}}^{\text{Fe}_{Ga}^{q}}\) represents the total energy of the supercell containing one substitutional Fe\(_{Ga}\) in the charge state \(q\), and \(E_{\text{tot}}^{\text{Ga}_{2}O_{3}}\) is the total energy of a perfect crystal in the same supercell. We vary the chemical potential of Ga \(\mu_{Ga}\) between the Ga-rich limit in which it is in equilibrium with bulk elemental Ga, and the O-rich limit in which it is bound by the stability condition of Ga\(_2\)O\(_3\) (e.g., \(\mu_{Ga} = 1/2 \Delta H_{\text{Ga}_{2}O_{3}} = -4.47 \text{ eV}\)). Similarly, the chemical potential of \(\mu_{Fe}\) is bound by the solubility-limiting phases of Ga\(_2\)Fe \((\Delta H = -1.03 \text{ eV})\) in the Ga-rich limit and Fe\(_2\)O\(_3\) \((\Delta H = -8.54 \text{ eV})\) in the O-rich limit.\(^{23}\) The electron chemical potential is defined by the Fermi level position \(\epsilon_F\), which we reference to the valence-band maximum (VBM). The \(\Delta^q\) term defines the finite-size correction for charged defects following the scheme of Refs. 26–28 for which we consider the dielectric tensor assuming electronic only \((\epsilon_{\infty})\) and electronic plus ionic \((\epsilon_{\text{DC}})\) screening contributions as a proxy for the uncertainty in our reported values.\(^{14,29}\) Specifically, these adopt values of 11.5 (3.8), 11.8 (2.8), and 11.1 (3.8) for the \(\epsilon_{xx}, \epsilon_{yy}, \text{ and } \epsilon_{zz}\) components of \(\epsilon_{\text{DC}} (\epsilon_{\infty})\) tensors.\(^{29}\)

Figure 1 shows DLTS spectra of four different samples: two spectra from the bulk samples having different surface orientations and two from the MBE and HVPE films. At least four signatures of deep level defects are observed; similar defect levels have previously been reported in the literature and labelled E1–E4.\(^{10,12}\) The energy positions for E1 to E4 in Fig. 1 are 0.56, 0.78, 1.01, and 1.48 eV below CBM, respectively. Of these levels, E1 occurs in the (010) oriented bulk sample and with a low concentration in the MBE sample. E3 is clearly resolved only in the bulk (010) sample, although it may also be found as part of the high temperature shoulder of the E2 level in the (201) bulk sample. In contrast, E4 is only seen in the bulk (010) sample. The level traditionally labelled as E2 is the most prominent one of all and particularly dominant in the (201) sample (note the large scale around the E2 region in Fig. 1). The expression on the y-axis of Fig. 1 (2\(N_D \times \Delta C/C\)) is an approximation valid for dilute...
deep level concentrations, typically considered up to 10%–20% of \((N_d)\). Note, however, that the concentration of E2 in the \((201)\) bulk sample is 30% of \((N_d)\) and thus the dilute approximation does not strictly hold, resulting in a slight overestimation of the E2 concentration.\(^{30}\) Nonetheless, the conclusion of a dominating presence in this sample over the other samples remains. In the HVPE sample, the E2 peak may be present at concentrations close to the detection limit of the measurement, \(<6 \times 10^{13} \text{cm}^{-3}\) in this sample, while the MBE sample has no discernible E2 peak above the noise level at \(\sim 1 \times 10^{14} \text{cm}^{-2}\). As such, the E2 intensity is prominently scaled in the different samples providing a suitable starting point of its identification.

Figure 2(a) shows the DLTS spectra detected in the 300–450 K range (shadowed area in Fig. 1) for the bulk (010) and HVPE samples, before and after irradiation with 600 keV \(H^+\) to doses of \(3 \times 10^{14}\) and \(2 \times 10^{13} \text{cm}^{-2}\), respectively. Prior to the irradiation (as already shown in Fig. 1), the bulk sample exhibits a dominating E2 signature at 0.78 ± 0.04 eV with a peak at 354 ± 4 K using a lock-in rate window of \((640 \text{ms})^{-1}\), while it is barely visible in the HVPE sample (with an absolute concentration on the order of \(\sim 6 \times 10^{13} \text{cm}^{-3}\) as deduced from the inset in Fig. 2). After the irradiation and an initial DLTS scan up to 650 K of the bulk sample, the amplitude of the peak at 354 K remains similar to that before the irradiation, while a new peak, labelled E2*, appears on the low temperature side (with a peak temperature of 317 ± 4 K). The energy position of the E2* is found to be 0.75 eV, i.e., similar to that of E2, but with a larger apparent capture cross section \((\sim 5 \times 10^{-14})\) as compared to E2 \((\sim 7 \times 10^{-15}\) cm\(^{-2}\)). A similar trend is observed in the HVPE sample, where the DLTS signature at 317 K emerges, while the trace of the 354 K peak appears as a shoulder on the high temperature side of the 317 K peak (still with a low concentration). Arrhenius plots of the two deep levels are presented in Fig. 2(b). The fact that the concentration of E2 is not significantly influenced by the generation of the intrinsic defects implies that this level is of extrinsic origin involving a residual impurity rather than an intrinsic defect only. E2*, on the other hand, shows a strong response on the irradiation as expected for a defect of intrinsic origin like \(V_{Ga}\) or a related complex. The energetic similarity of E2 and E2* helps to resolve the debate in the literature regarding the level identification in the energy range of E2.\(^{10,12,14}\)

In order to identify the residual impurity associated with E2, SIMS analysis was performed and revealed that Al, Si, Fe, and In are present in concentrations above the E2 concentrations in corresponding samples. Of these, only Si and Fe show the concentration variation resembling that of the E2 concentration variation that was discussed above. The relationships of the E2 concentration with Fe and Si concentrations are presented in Fig. 3. As discussed above, our DLTS measurements result in a small overestimation of the E2 concentration in the \((201)\) bulk samples. Indeed, taking this into account would improve the parallelism with the \([E2] = [Fe]\) line in Fig. 3. However, Si shows only a weak dependence and is excluded as a viable alternative. This is supported by the fact that Si is expected to act as a shallow donor and the observations of very low concentrations (or even absence) of E2 in the epitaxial films despite a strong Si presence. Hence, the remaining candidate accounting for the trend of the E2 content is Fe. Indeed, Fig. 3 shows the E2

FIG. 2. (a) DLTS signal \((2N_d \times \Delta C/C)\) using a \((640 \text{ms})^{-1}\) lock-in rate window versus temperature scans for the (010) oriented bulk and HVPE samples, before and after irradiation with 600 keV \(H^+\) to a dose of \(3 \times 10^{14}\) and \(2 \times 10^{13} \text{cm}^{-2}\), respectively. The inset shows an enlarged region of the DLTS signal from the HVPE sample (as-grown), indicating a minor presence of the E2 level already before irradiation. In (b), the corresponding Arrhenius plots of the electron emission rates are shown.

FIG. 3. E2 concentration as measured by DLTS versus Fe concentration (black squares) and Si concentration (red circles) as found by SIMS for bulk and epitaxial samples.
Calculated formation energies of the FeGa defects in Fig. 4. /C15 Thermodynamic transition level for the Fe$^{3+}$ configurations may also be anticipated to form in $\beta$-Ga$_2$O$_3$. As the Fe$^{2+}$ oxidation state, which preferentially adopts a high-spin configuration ($S=2$) and exhibits an outward relaxation of the bond lengths by $\sim$4–8% (similar to that reported for FeGa defects in GaN that are subjected to a different local lattice symmetry), the Fe$^{2+}$ has not been observed by EPR in $\beta$-Ga$_2$O$_3$, far higher Fe contents may be present than were previously assumed from EPR signals of the residual Fe$^{3+}$ impurities observed in bulk samples grown by independent groups and methods.\textsuperscript{10,32,33} Our calculated thermodynamic transition level for the Fe$^{3+}$/Fe$^{2+}$ [i.e., the $\epsilon(0/-)$ in Fig. 4] falls 0.61 eV below the CBM for Fe$\text{Ga}_{\text{II}}$ and 0.59 eV below the CBM for Fe$\text{Ga}_{\text{III}}$. If we assume the lower screening associated with the $\epsilon_{SC}$,\textsuperscript{14} these levels fall slightly higher, 0.40 and 0.36 eV below the CBM, respectively. While the agreement with experiment is better with $\epsilon_{DC}$, the levels computed assuming electronic-only screening is still in reasonable agreement with the measured E2 level.

Our results are also consistent with those of Irmscher \textit{et al.}\textsuperscript{10} and Zhang \textit{et al.}\textsuperscript{11} in Czocoralski and EFG-grown bulk crystals that exhibit Fe concentrations in excess of $10^{16}$ cm$^{-3}$ and are believed to be the dominant compensating acceptor. Considering the correlation with the Fe content (Fig. 3) and the calculated $E^F$ of the Fe impurities relative to that of other compensating acceptors like $V_{\text{Ga}}$ in $n$-type conditions and more Ga-rich growth environments,\textsuperscript{15,14} Fe$\text{Ga}_{\text{II}}$ appears to be a likely candidate for the E2 level. We note that while we predict Fe$\text{Ga}_{\text{II}}$ to also have a deep donor level 0.3–0.5 eV above the VBM, this level cannot be observed in the DLTS approach used in the present study.

In conclusion, our results strongly suggest that Fe$\text{Ga}_{\text{II}}$, and not an intrinsic defect such as $V_{\text{Ga}}$, acts as the deep acceptor responsible for the prominent E2 level at $\sim$0.78 eV below the CBM. Concurrently, by enhancing the intrinsic defect concentration via proton irradiation, a new deep level emerged, labeled as E2*, having the ionization energy very close to that of E2, but exhibiting an order of magnitude higher capture cross section. Importantly, the properties of E2* are found to be consistent with an intrinsic origin and are consistent with $V_{\text{Ga}}$ or related complexes as viable candidates, although an unambiguous assignment of the intrinsic origin of the E2* level will require further study. Perhaps ironically, the contradicting opinions of the literature debate on either extrinsic or intrinsic origin of the deep acceptor E2 converge by accounting for possible contributions from both E2 and E2* in different experimental conditions.

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