

Experimental Investigation of Oxygen-Vacancy Defects in n -Type β -Ga₂O₃ (010) Single Crystals

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n 型 β -Ga₂O₃ (010) 単結晶の酸素空孔欠陥の実験的評価

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β -Ga₂O₃ is expected to be one of next-generation power semiconductors. However, knowledge of intrinsic point defects such as Ga- and O-vacancy (V_{Ga} , V_O) defects in β -Ga₂O₃ is very limited. In this study, we have electrically and optically investigated V_O -related defects in unintentionally-doped n -type β -Ga₂O₃ (010) single crystal substrates fabricated by an edge-defined film-fed growth method, employing variable-temperature photoluminescence (VT-PL), capacitance-voltage (C-V), and steady-state photo-capacitance spectroscopy (SSPC) techniques. Conventional spectral transmission measurements showed a strong optical absorption at ~ 4.5 eV in the band gap. VT-PL measurements exhibited a broad luminescence band at around ~ 3.30 eV probably due to self-trapped excitons at V_O sites. From C-V measurements, effective n -type carriers with their concentration of $\sim 1.3 \times 10^{17} \text{ cm}^{-3}$ were almost uniformly distributed over the measured depth range of 167 - 345 nm from the β -Ga₂O₃ surface. SSPC measurements revealed four dominant deep-level defects with their optical onsets at ~ 2.20 , ~ 3.88 , ~ 4.25 eV below the conduction band and at ~ 4.43 eV above the valence band. These deep-level defects tended to be more densely present with shallowing the probing depth range. Furthermore, the ~ 4.43 eV level was significantly enhanced after high-temperature vacuum annealing. Therefore, this defect level is probably attributable to the V_O -related defects.

Keywords : β -Ga₂O₃, Oxygen-vacancy defect, Steady-state photo-capacitance spectroscopy, Variable-temperature photoluminescence

1. Introduction

The monoclinic β -phase of gallium oxide (β -Ga₂O₃) is of increasing interest for UV transparent electrodes, UV photo detectors, and power field-effect transistors (FETs) because of its outstanding properties such as its ultra-wide bandgap of ~ 4.8 eV, high breakdown electric field of ~ 8 MV/cm, and good chemical and thermal stability.^{1,2)} A recent breakthrough in the low-cost mass production of native β -Ga₂O₃ bulk single-crystal

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substrates has attracted much more attentions in next-generation high-temperature and high-power devices superior to SiC- and GaN-based ones.³⁾ Depletion-mode β -Ga₂O₃-based metal-semiconductor FETs (MESFETs) and metal-oxide-semiconductor FETs (MOSFETs) using these native β -Ga₂O₃ substrates have been already demonstrated.^{1,4)} Most recently, enhancement-mode β -Ga₂O₃ wrap-gate fin FETs and MOSFETs on semi-insulating β -Ga₂O₃ substrates have been reported to show excellent device performances.^{5,6)} Thus, the development of β -Ga₂O₃-based power FETs begins rapidly to make advances. However, in order to further improve these device performances, it is needed to understand basic electronic properties of β -Ga₂O₃ such as carrier transport and electrically active point defects.⁷⁾ Especially, knowledge of intrinsic point defects such as V_{Ga} and V_O defects in β -Ga₂O₃ is very limited.^{8,9)} In this study, we have optically and electrically investigated V_O-related defects in unintentionally-doped (UID) *n*-type β -Ga₂O₃ (010) single crystal substrates, by using variable-temperature photoluminescence (VT-PL), capacitance-voltage (C-V), and steady-state photo-capacitance spectroscopy (SSPC) techniques.

2. Experimental

UID β -Ga₂O₃ (010) single crystal substrates fabricated by an edge-defined film-fed growth (EFG) technique were used in this study, which were obtained from a commercial vendor.³⁾ The size was 15 mm x 10mm x 0.5mm^t, as shown in Fig. 1. Here, note that high-temperature annealing was performed at 1450 °C in N₂ for fully activating residual donors as a final process.³⁾ In this study, to intentionally generate V_O-related defects, the β -Ga₂O₃ samples were annealed at 1000 °C for 20 min in vacuum by using a rapid thermal annealing system. The samples before and after the vacuum annealing were optically and electrically characterized. First, to estimate an optical absorption edge of the samples, spectral transmission measurements were conducted with a conventional UV-VIS spectrophotometry method. Additionally, variable-temperature photoluminescence (VT-PL) measurements were performed at temperatures between 15 and 300 K. Here, the 266 nm line with a power of 15 mW from a Nd:YAG laser (4 ω) was used as an excitation light source. Room-temperature C-V and SSPC measurements were performed at a frequency of 100 kHz with an ac modulation level of 50 mV on a Hg-probe system, using its lateral dot-and-ring Schottky barrier diode (SBD) configuration, as illustrated in Fig. 2. The Schottky metal dot was 1.231 mm in diameter. Here, note that the measurement bias voltage V_G was limited to be under reverse bias conditions. For the C-V measurements, the V_G was applied from +1.0 V to -10.0 V with a step voltage of 0.05 V. The depth profiles of effective carrier concentrations |N_D-N_A| were estimated from differential 1/C²-V plots. Here, N_D and N_A are donor- and acceptor-type carrier concentrations, respectively. The pristine samples showed typical *n*-type rectifying characteristics as confirmed by the C-V measurements in the dark. For the SSPC measurements, as illustrated in Fig. 3, photo-capacitance transients were measured as a function of incident photon energy from 0.78 eV (1600 nm) up to 5.17 eV (240 nm). The SBDs fabricated were illuminated from the back side with monochromatic light obtained from a 150 W Xenon lamp coupled with a high-resolution monochromator. The filling pulsed voltage V_P were set at +1.0 V for 3.0 s. The V_G was changed to be 0, -0.2, -0.5, -1.0, and -3.0 V to expand the probing depth range. For more details, refer to Refs. 10 - 12. In this study, the SSPC signal was defined as 2|N_D-N_A| Δ C/C₀, where |N_D-N_A| was the effective carrier concentration determined from the C-V measurements at each V_G, C₀ was the capacitance at each V_G before the optical excitation, and Δ C was the photo-capacitance variation which was determined as a saturation value of their transients recorded at each incident photon energy. The variation in 2|N_D-N_A| Δ C/C₀ between the optical onset and the saturation positions of the deep-level defect in SSPC spectra corresponds to its defect concentration.

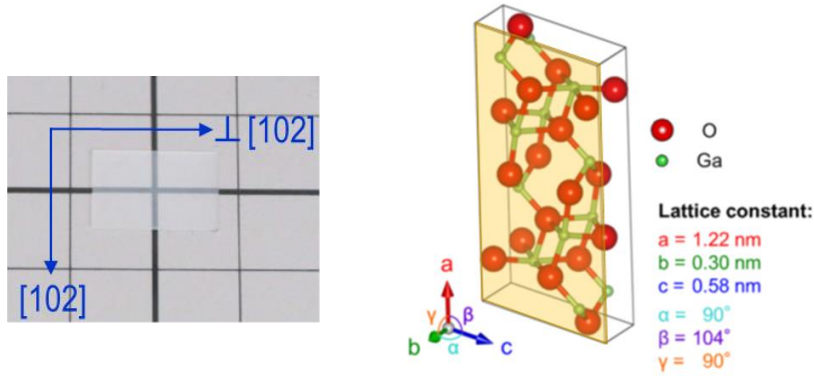


Figure 1. Photographed image of EFG-grown β -Ga₂O₃ (010) single crystal substrate, together with its unit cell of monoclinic crystal structure

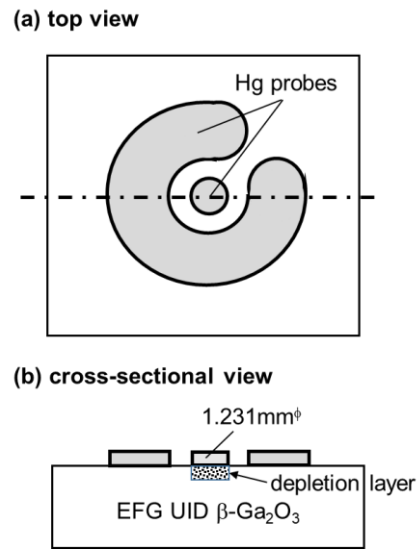


Figure 2. (a) Top view and (b) Cross-sectional view of lateral dot-and-ring SBD configuration for Hg-probe system

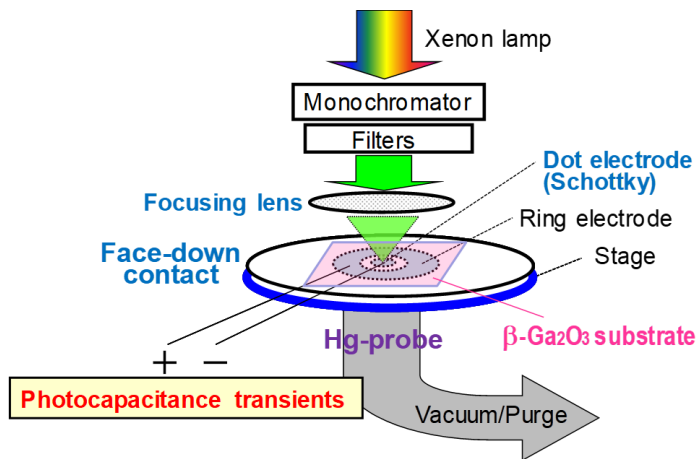


Figure 3. Setup of SSPC measurement apparatus equipped with Hg-probe system

3. Results and Discussion

Figure 4 shows typical Tauc plots of the β -Ga₂O₃ samples before and after the vacuum annealing, together with their optical transmittance spectra. Here, assume that β -Ga₂O₃ is a direct-gap material.¹³⁾ α is an optical absorption coefficient calculated from the spectral transmittance, and $h\nu$ is an incident photon energy. The both samples show a similar tendency of optical absorption; a linear relationship can be seen at around ~ 4.45 eV in the Tauc plots, corresponding to the sharp absorption in the optical transmittance spectra. This value is in good agreement with the experimental value determined from polarized transmittance and reflectance measurements.¹⁴⁾ Bearing in mind that β -Ga₂O₃ has a wide bandgap of ~ 4.8 eV, it most likely indicates a direct allowed optical transition within the bandgap via intrinsic defect levels such as V_O , rather than the optical bandgap.

Figure 5 shows typical VT-PL spectra of the β -Ga₂O₃ samples before and after the vacuum annealing. For the both samples, a broad luminescence band are clearly observed at around ~ 3.30 eV and its intensity increases significantly with increasing temperature up to 200 K. This strong luminescence is well known to be radiative recombination due to self-trapped excitons (STE) at V_O sites, which is characteristic of β -Ga₂O₃ with a strong exciton binding energy.^{15,16)} In addition, the high-temperature vacuum annealing is seen to enhance the STE luminescence. Simultaneously, a new PL peak shows up in the spectra at around ~ 4.29 eV, which peak intensity decreases monotonically with an increase in temperature. So, this PL peak is probably attributable to a bound-to-free (BF) transition via the V_O energy level. That is, these PL behaviors are most likely related to the introduction of V_O into the β -Ga₂O₃ bulk region by the vacuum annealing. Here, Arrhenius plots of measured temperature-dependent STE luminescence are displayed in Fig. 6. Negative thermal quenching of the STE luminescence is clearly observed in the temperature range between 76 and 152 K for the both samples.¹⁷⁻¹⁹⁾ The activation energies are roughly estimated to be small values of 22 - 23 meV regardless of the vacuum annealing. Comprehensive interpretation of the temperature variation of the STE luminescence and PL observed at ~ 3.30 and ~ 4.29 eV is as follows. With increasing temperature, the V_O energy level is more activated as a deep donor state, which leads to a disappearance of the PL peak at ~ 4.29 eV. Instead, the probability of the STE captured at the V_O sites seem to become high.

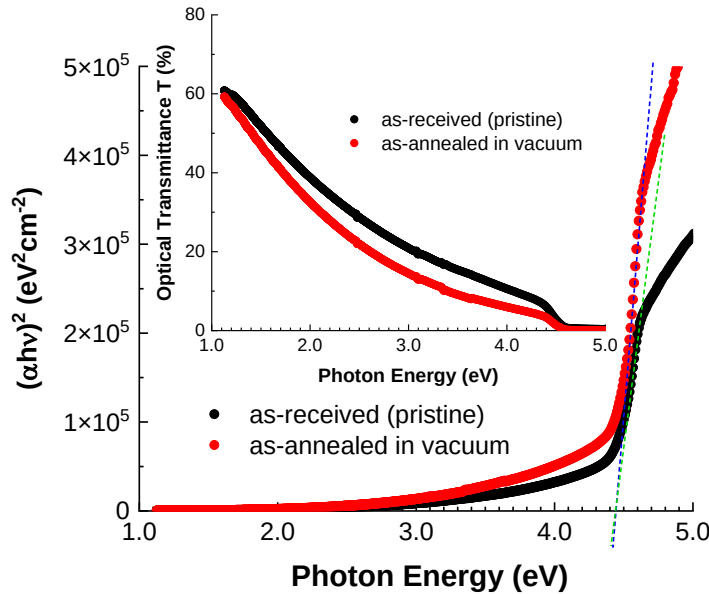


Figure 4. Tauc plots of β -Ga₂O₃ single crystals before and after annealing in vacuum. The inset shows UV-VIS transmittance spectra of β -Ga₂O₃ samples.

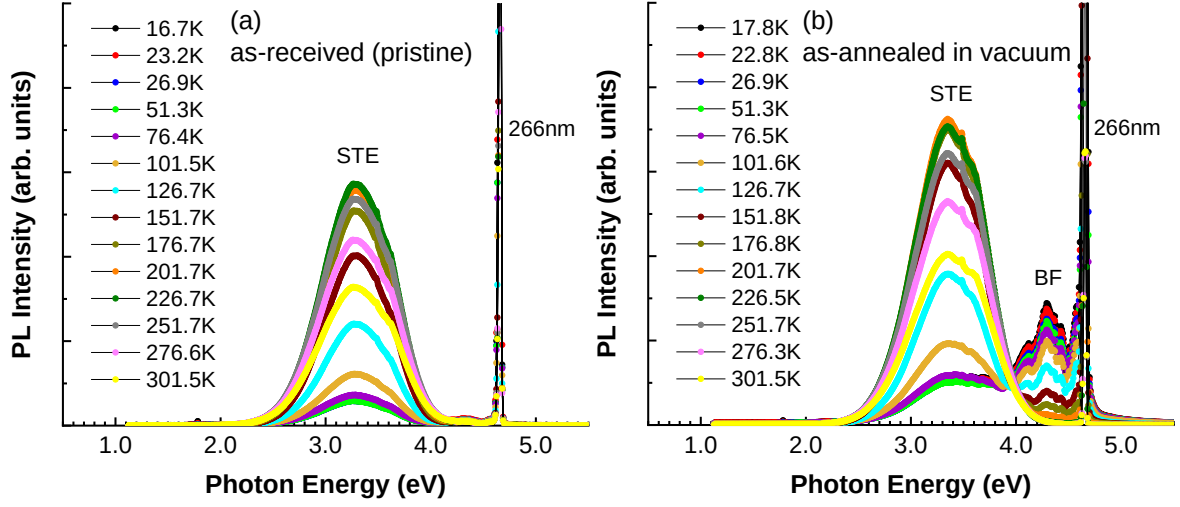


Figure 5. VT-PL spectra of β -Ga₂O₃ single crystals before and after annealing in vacuum

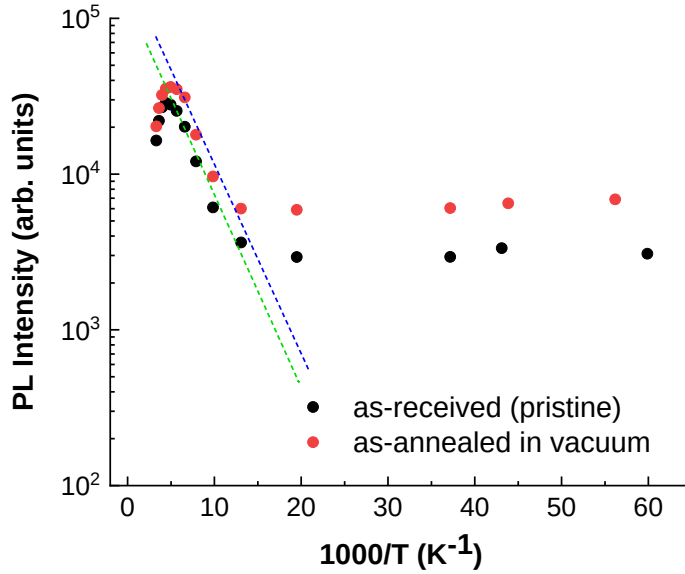


Figure 6. Arrhenius plots of measured temperature-dependent STE luminescence for β -Ga₂O₃ single crystals before and after annealing in vacuum

The inset of Fig. 7 shows typical $1/C^2$ - V characteristics of the Hg/ β -Ga₂O₃ samples before and after the vacuum annealing, together with lines fitted to their data. The fitted lines represent an ideal relationship expressed at $1/C^2 = 2(V_{bi} - V)/q\epsilon_s\epsilon_0|N_D - N_A|$, where C is the capacitance normalized by the Schottky contact area, V_{bi} is the built-in potential, ϵ_s is the relative permittivity of 10.2, ϵ_0 is the vacuum permittivity, and $|N_D - N_A|$ is the effective n -type carrier concentration. The depth profiles of $|N_D - N_A|$ determined from their local differentials are shown in Fig. 7. The average $|N_D - N_A|$ of the β -Ga₂O₃ samples before and after the vacuum annealing are respectively estimated to be $\sim 1.4 \times 10^{17}$ and 8.0×10^{16} cm⁻³, almost uniformly distributed over the measured depth ranges of 167 - 345 nm and 286 - 491 nm from the β -Ga₂O₃ surface. Considering that the $|N_D - N_A|$ of the pristine

sample is mainly due to Si incorporation into β -Ga₂O₃ from Ga₂O₃ source powder during the crystal growth process, this experimental result implies that the vacuum annealing definitely induces a decrease in $|N_D - N_A|$.³⁾ That is, V_O newly generated by the vacuum annealing is found to act as an electron-trapping center.

Figure 8 shows typical room-temperature SSPC spectra of the Hg/ β -Ga₂O₃ samples before and after the vacuum annealing at V_G of 0, -0.2, -0.5, -1.0, and -3.0 V. Under these V_G conditions, the corresponding edges of the depletion layers at these V_G are estimated to be located at ~ 191 , ~ 195 , ~ 202 , ~ 212 , and ~ 249 nm for the pristine sample and at ~ 309 , ~ 314 , ~ 322 , ~ 334 , and ~ 378 nm for the annealed sample, respectively, as determined from the C-V measurements. The β -Ga₂O₃ samples show four dominant photoemission states with their optical onsets at ~ 2.20 , ~ 3.88 , ~ 4.25 , and ~ 4.43 eV, respectively, denoted by T1, T2, T3, and T4. These photoemission states stem definitely from the deep-level defects existing in the β -Ga₂O₃ samples. For the T1, T2, and T3 levels, the dominant processes correspond to the optical transfer of electrons from the deep-level defects into the conduction band (E_c) because of their having positive photo-capacitance variations. On the other hand, for the T4 level, the optical transfer of electrons from the valence band (E_v) into the deep-level defect is dominant due to its negative photo-capacitance variation. For the both samples, all the deep-level defects tend to be more densely present with shallowing the probing depth range for the SSPC measurements. This suggests that most of the deep-level defects were introduced by the post annealing process, rather than the crystal growth one. In particular, the T1 and T4 levels is more res-shifted with shallowing the probing depth range for the both samples. Also, the T2 and T4 levels are seen to be significantly enhanced by the vacuum annealing. Combining with theoretical calculations of intrinsic defect models in β -Ga₂O₃ that have previously reported, the T1 and T4 levels are probably attributable to V_{Ga^-} and V_O -related defects, respectively.²⁰⁻²²⁾ Additionally, considering a possible mechanism of the intrinsic vacancy formation in β -Ga₂O₃, V_O defects should be first generated and then V_{Ga} defects will be finally created by the high-temperature vacuum annealing. In this study, the vacuum annealing caused no change in the T1 level corresponding to the V_{Ga} defects. So, the T2 level enhanced may be attributable to interstitial Ga_i defects on the way of the intrinsic-vacancy formation process.

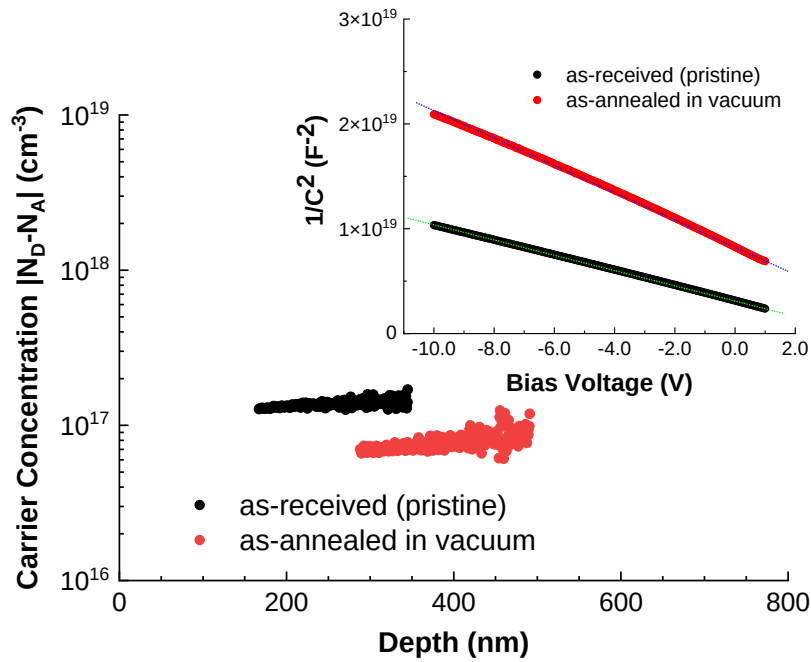


Figure 7. Depth profiles of $|N_D - N_A|$ for β -Ga₂O₃ single crystals before and after annealing in vacuum. The inset shows $1/C^2$ -V plots of β -Ga₂O₃ samples.

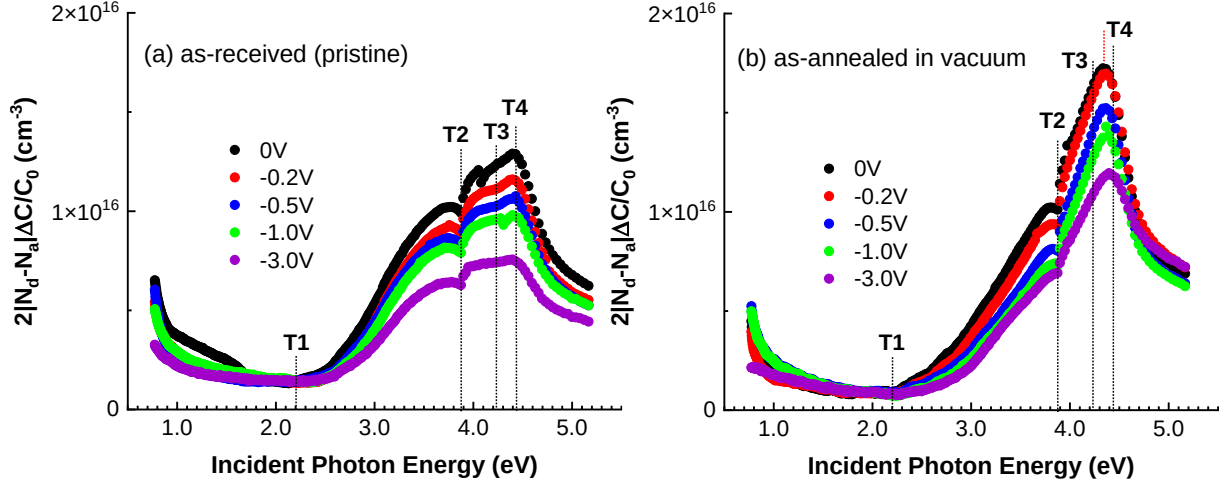


Figure 8. Room-temperature SSPC spectra at various V_G of Hg/ β -Ga₂O₃ single crystals before and after annealing in vacuum

4. Conclusion

Focusing on the V_O -related defects in β -Ga₂O₃, we have optically and electrically investigated the intrinsic deep-level defects in unintentionally-doped β -Ga₂O₃ (010) single crystal substrates before and after the high-temperature annealing in vacuum, by using VT-PL, C-V, and SSPC techniques. The defect level with its optical onset at ~ 4.43 eV above the E_v is probably attributable to the V_O -related defects. This level was found to dominate the optical and electronic characteristics of β -Ga₂O₃.

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