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Optical signatures of deep level defects in Ga$_2$O$_3$

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We used depth-resolved cathodoluminescence spectroscopy and surface photovoltage spectroscopy to measure the effects of near-surface plasma processing and neutron irradiation on native point defects in β-Ga$_2$O$_3$. The near-surface sensitivity and depth resolution of these optical techniques enabled us to identify spectral changes associated with removing or creating these defects, leading to identification of one oxygen vacancy-related and two gallium vacancy-related energy levels in the β-Ga$_2$O$_3$ bandgap. The combined near-surface detection and processing of Ga$_2$O$_3$ suggests an avenue for identifying the physical nature and reducing the density of native point defects in this and other semiconductors. Published by AIP Publishing. https://doi.org/10.1063/1.5026770

The ultra-wide bandgap semiconductor Ga$_2$O$_3$ has now become a promising candidate for next generation high power electronics. The ability to grow Ga$_2$O$_3$ by multiple techniques and to manufacture large-size, high-quality bulk wafers has led to rapidly expanding applications chiefly because its large bandgap enables high breakdown electric fields estimated at 7–8 MV/cm, yet n-type doping ranging from intrinsic to degenerate is achievable. These properties can be impacted by deep level defects that compensate free carriers, increase scattering that reduces carrier mobility, form gap states that “pin” Fermi levels, and initiate trapping that limits breakdown voltage. Multiple defect features that vary with growth and processing have been reported, but the nature of native point defects in Ga$_2$O$_3$ is relatively unexplored. We have now used nanoscale depth-resolved cathodoluminescence spectroscopy (DRCLS) and surface photovoltage spectroscopy (SPS) with plasma processing and neutron irradiation, combined with temperature-dependent Hall effect measurements, to correlate the spectral features of deep level defect gap states in Ga$_2$O$_3$ with their physical and donor/acceptor nature. The energy levels associated with these features display close correspondences with those predicted theoretically and measured using capacitance spectroscopies.

We used DRCLS and SPS to measure the energy level positions of electrically active defects within the outer tens of nanometers of Ga$_2$O$_3$ grown by various techniques, including low pressure chemical vapor deposition (LPCVD), molecular beam epitaxy (MBE), pulsed laser deposition (PLD), and edge-defined film-fed growth (EFG). We used surface remote oxygen plasma (ROP) processing, neutron irradiation, and forming gas (FG) anneals to manipulate deep level defects, i.e., oxygen vacancies (Vo) and gallium vacancies (V$_{Ga}$), from the free semiconductor surface into the bulk, measuring their depth distribution with several nanometers or less resolution.

We used SPS to measure the energy levels of defects within the Ga$_2$O$_3$ bandgap and DRCLS to measure the luminescent transitions involving these defects and their bandgap—normalized intensity variations with excitation beam energy $E_b$ and depth, i.e., defect profiles, of Ga$_2$O$_3$ as-received and after each processing treatment. For β-Ga$_2$O$_3$ grown by LPCVD, MBE, PLD, and EFG, DRCLS and SPS spectra exhibit common optical features (supplementary material) corresponding to transitions into and out of multiple deep level defect states within the bandgap. Individual spectra exhibited multiple peak features that were deconvoluted using Fityk (V.0.9.8) and MagicPlot (V.2.7.2) to reveal Gaussian peaks on a linear baseline across the spectral range detected. Figure 1 illustrates spectra of an LPCVD-grown sample after 1.5 h ROP treatment. Four major, broad features at 2.5, 3.0, 3.5, and 3.8 eV appear in each spectrum, likely corresponding to transitions between

![FIG. 1. DRCL spectra of LPCVD Ga$_2$O$_3$ after 1.5 h ROP with sub-bandgap features, 4.6 eV, bandgap shoulder, and changes with depth. The dashed line outlines Gaussian peak deconvolutions for the $E_b = 0.5$ keV spectrum.](image-url)
gap states and the conduction or valence band. The 4.5–4.7 eV shoulder represents the $\beta$-Ga$_2$O$_3$ conduction-to-valence band transition, consistent with the conclusions of previous studies.\textsuperscript{3}

Figure 2 shows SPS features of MBE-grown $\beta$-Ga$_2$O$_3$. The contact potential difference (cpd) increase at 4.7–4.8 eV represents band flattening due to bandgap excitation, similar to the 4.5–4.7 eV bandgap feature in DRCL spectra. The four negative $\Delta$cpd slope changes at 2.4, 3.0, 3.5, and 4.0 eV signify photo-population of four defect states from the valence band. Two positive $\Delta$cpd slope changes at 2.0 and $\sim$3.8 eV indicate photo-depopulation of two deep level states to the conduction band.

We combined DRCLS with near-surface chemical processing and bulk neutron irradiation to characterize the physical nature of the deep level defects. We used Monte Carlo simulation software CASINO (V. 2.4.8.1) to model the depth dependence of electron-hole excitation in DRCLS.\textsuperscript{40} The CASINO\textsuperscript{41} simulations yield the final relative densities of electrons at the end of their multiplication and cascade, where they finally lose energy to impact ionization and electron-hole pair creation. For beam energies $E_B = 1$, 2, 3, 4, and 5 keV, excitations have Bohr-Bethe maximum range $R_B = 20, 40, 80, 120, \text{ and } 160 \text{ nm}$, respectively. Staged exposure to ROP caused systematic spectral changes identified with filling of oxygen vacancies.\textsuperscript{32,42} From deconvolved peak areas similar to those in Fig. 1 normalized to the $\sim$4.5–4.7 eV near band edge (NBE) area, Fig. 3(a) shows 3.5 eV depth profiles for the LPCVD Ga$_2$O$_3$ as-received, after 1/4 h ROP, and after 3/4 h ROP. Of all the samples after ROP treatment, the LPCVD samples showed the most prominent ROP effect. The area ratios for each profile are renormalized to the $E_B = 5.0 \text{ keV}$ bulk ratios since all ROP changes occur at shallower depths. For as-received Ga$_2$O$_3$, the 3.5 eV feature is nearly constant with depth, indicating a uniform 3.5 eV defect distribution. After 1/4 h ROP, the 3.5 eV depth profile at 80 nm decreases by 33% toward the surface. After 3/4 h total ROP, it decreases over 65% from 100 nm to 10 nm. In contrast, the analogous depth profiles for the 2.5 eV and 3.0 eV normalized defect areas show no effect after 1/4 h ROP treatment. The decreasing 3.5 eV surface content and deeper penetration suggest that this feature is related to $\beta$-Ga$_2$O$_3$ oxygen vacancies that are filled by activated oxygen atoms entering the lattice from the surface. Furthermore, this 3.5 eV area ratio increases with $N_2$ annealing (not shown), consistent with O outdiffusion and increased oxygen vacancy-related defect formation, similar to the case of other metal oxides.\textsuperscript{42}

We used neutron irradiation to identify DRCLS peaks associated with Ga vacancies. Previously, electron paramagnetic resonance (EPR) studies showed that neutron irradiation produced VGa defects.\textsuperscript{43} Figure 4 shows normalized DRCL spectra of a 1/4 h ROP treated LPCVD $\beta$-Ga$_2$O$_3$ epilayer after neutron irradiation at the Ohio State University Research Reactor (Columbus, OH) under nearly identical conditions to those reported previously. Similar to Fig. 1 spectra but on a linear scale, Fig. 4 shows the two most prominent defect features at 3.0 and 3.5 eV. Peaks at 2.5 and 3.8 eV are almost invisible due to linear scaling. The appearance of two VGa defect emissions may be related to two inequivalent Ga sites in the Ga$_2$O$_3$ unit cell, tetrahedrally and octahedrally coordinated Ga(I) and Ga(II), respectively.\textsuperscript{43} After neutron irradiation, both the 2.5 eV and 3.0 eV peak intensities increase significantly when compared to the 3.5 eV peak—an average of 20% for the 2.5 eV peak and
with a neutron irradiation increase of an EC/C2 of 0.5 values of ND and NA in bulk Ga2O3 to be 2.5 respectively. By comparison, we have found typical background CL that extend continuously from the surface to correspondingly 2.5 eV and 3.0 eV defect increases with neutron irradiation that extend continuously from the surface to correspondingly 2.5 eV and 3.0 eV defect increases with neutron irradiation. Neutron irradiation increases the 2.5 eV normalized defect by 30% for the 3.0 eV peak. These increases are evident for both 0.5 keV near-surface and 5.0 keV bulk excitation in Figs. 3(a) and 3(b), respectively. When normalized to the NBE emission area for E\textsubscript{B} = 0.5–5 keV, depth profiles reveal corresponding 2.5 eV and 3.0 eV defect increases with neutron irradiation that extend continuously from the surface to the bulk, consistent with neutron penetration throughout the sample (see supplementary material). Neutron irradiation increases the 2.5 eV normalized defect by ~90% consistent with a neutron irradiation increase of an E\textsubscript{C} < 2 eV deep level transient spectroscopy (DLTS) level by ~10\textsuperscript{16} cm\textsuperscript{-3}.44 Unlike these features, the 3.5 eV normalized defect decreases by >2× over the same depth range. A defect density calculated using transient SPS\textsuperscript{55,45} yields a density for the E\textsubscript{V} + 2.4 eV transition of ~5×10\textsuperscript{15} cm\textsuperscript{-3} for LPCVD Ga2O3 before irradiation. ~5× higher than trap densities measured for a similar level in EFG Ga2O3 by DLTS.\textsuperscript{44} Overall, these irradiation-induced 2.5 eV and 3.0 eV emission increases indicate that both are related to gallium vacancies in Ga2O3.

Hall effect measurements of the neutron irradiated Ga2O3 after forming gas anneals provided information on the donor/acceptor nature of the 2.5 and 3.0 eV features. Initially, both as-grown and irradiated LPCVD β-Ga2O3 samples were too resistive for accurate measurements. However, after each sample was annealed for 10 min at 750 °C in forming gas (FG), free carrier density n and mobility μ strongly increased for the irradiated sample but not for the as-grown one. A theoretical fit of Hall-effect n vs. 1/\textsuperscript{46} after irradiation and anneal gave donor and acceptor concentrations N\textsubscript{D} = 4.6×10\textsuperscript{17} and N\textsubscript{A} = 2.7×10\textsuperscript{17} cm\textsuperscript{-3}, respectively. By comparison, we have found typical background values of N\textsubscript{D} and N\textsubscript{A} in bulk Ga2O3 to be 2.5×10\textsuperscript{17} and 0.5×10\textsuperscript{17} cm\textsuperscript{-3}, respectively. (Since our irradiated sample and the bulk Ga2O3 were grown by different techniques, the agreement between the increases in N\textsubscript{D} – N\textsubscript{A} is merely fortuitous. In general, n is not equal to N\textsubscript{D} – N\textsubscript{A} but instead depends on compensation ratio K = N\textsubscript{A}/N\textsubscript{D} and activation energy, which are not the same for these two samples.) Annealing above 500 °C improves Hall measurement accuracy and increases both n and μ, which can happen if acceptors such as V\textsubscript{Ga} are preferentially destroyed or passivated during the annealing process. Reliable mobility values starting at 500 °C in 50 °C increments up to 750 °C were 3.5, 5.0, 6.5, 10.1, 11.7, and 11.3 cm\textsuperscript{2}/V s. Mobility values for Ga2O3 vary greatly with growth and processing treatments, but literature values of mobility for neutron irradiated Ga2O3 are not readily available.\textsuperscript{47} Interestingly, DRCL spectra after irradiation and FG anneal exhibit a peak increase at 2.5 eV (possibly passivated Ga vacancies) but a decrease at 3.0 eV (possibly unpassivated Ga vacancies).

Figure 2 photo-stimulated population and depopulation SPS threshold energies and matching Fig. 1 CL transition energies correspond to specific energy levels in the Ga2O3 bandgap. Figure 5(left) shows an energy level diagram with these SPS and CL optical transitions. Horizontal black lines indicate energy levels corresponding to 2.0 eV photo-depopulation (blue) and 2.4, 3.0, and 3.5 eV photo-population (red) SPS transitions. The 2.0 eV photo-depopulation transition and 3.0 eV population transition could be complementary, i.e., their respective energies sum to ~4.9 eV, the bandgap. Darker red arrows signify CLS transitions, which match the energy levels determined by SPS almost exactly as indicated by dotted lines. Without a clear energy level assignment, the 3.8 eV CL feature in Fig. 1 could correspond to a transition 3.8 eV below the conduction band or 3.8 eV above the valence band, the latter close to a defect level reported using deep level optical spectroscopy (DLOS).\textsuperscript{48}

These levels can be compared in Fig. 5(right) with those predicted theoretically for transition energies between above mid-gap charge states calculated for V\textsubscript{O}, V\textsubscript{Ga}, and V\textsubscript{Ga}-H. Also shown are deep level gap states measured experimentally by deep level transient/optical spectroscopies (DLTS/DLOS).\textsuperscript{48} Energy levels are calculated for V\textsubscript{O}\textsuperscript{+} in the geometry of the V\textsubscript{O}\textsuperscript{0} configuration for three different lattice configurations (VdW)\textsuperscript{49} using density functional theory (DFT) with hybrid functionals that provide the β-Ga2O3 bandgap observed experimentally.\textsuperscript{50} While unambiguous identification of a specific configuration requires additional microscopic evidence and notwithstanding possible screening effects,\textsuperscript{51} Fig. 5 shows that the 3.5 eV SPS photo-population transition and the 3.5 eV CLS transition agree closely with the 3.52 eV V\textsubscript{O}\textsuperscript{+} (III) energy transition level predicted theoretically.\textsuperscript{49} While not definitive, the V\textsubscript{O}\textsuperscript{+} (III) configuration is more thermodynamically stable that its V\textsubscript{O}\textsuperscript{+} (I) and V\textsubscript{O}\textsuperscript{+} (II) counterparts for intermediate-doped Ga2O3.

Also shown in Fig. 5(right) are energy levels calculated for Ga vacancies V\textsubscript{Ga} and their hydrogenated V\textsubscript{Ga}-H counterparts.\textsuperscript{14} None of these transition energies overlap the 3.5 eV V\textsubscript{O}-related emission. Instead, the 2.5 and 3.0 eV spectral features appear to correlate with the 2.55 eV V\textsubscript{Ga}-H(II) and either the 2.9 eV V\textsubscript{Ga}-H(I) or 3.0 eV V\textsubscript{Ga}(II), the latter being thermodynamically less stable than its hydrogenated counterpart.\textsuperscript{14} These alignments indicate that the 2.5 eV and 3.0 eV features in Fig. 1 are consistent with V\textsubscript{Ga}-related defects while the 3.5 eV peak is due to V\textsubscript{O}-related defects. Again, unambiguous identification of a specific configuration requires additional microscopic evidence. Overall, all five DRCLS features correspond to energy levels measured by SPS, while nearly all SPS transitions correlate with energy levels predicted theoretically or measured by DLTS/DLOS.

In summary, we used DRCLS and SPS to measure the effects of near-surface plasma processing and neutron irradiation on native point defects in LPCVD-grown β-Ga2O3. The near-surface sensitivity and depth resolution of these optical techniques enabled us to identify spectral changes associated with removing or creating these defects, leading...
to spectral correlations with one $V_O^-$ and two $V_{Ga}$-related energy levels in the $\beta$-Ga$_2$O$_3$ bandgap. In addition, these results suggest processing methods to reduce $V_O^-$-related densities by ROP processing and $V_{Ga}$-related densities by FG anneals. Defect reductions can be monitored spatially in three dimensions by DRCLS as processing parameters are varied systematically. The combined near-surface defect detection and processing of Ga$_2$O$_3$ suggests an avenue for characterizing and reducing native point defects in $\beta$-Ga$_2$O$_3$ and other semiconductors.

See supplementary material for representative measurements across growth types and pre- and post-irradiation depth profiles.

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FIG. 5. Ga$_2$O$_3$ defect level transitions (left) measured by CL and SPS vs. (right) predicted by theory and/or measured by DLTS/DLOS.


