Depth-resolved cathodoluminescence and surface photovoltage spectroscopies of gallium vacancies in β-Ga₂O₃ with neutron irradiation and forming gas anneals **9**

Cite as: J. Vac. Sci. Technol. B 39, 052205 (2021); doi: 10.1116/6.0001240		Ċ.					
Submitted: 28 June 2021 · Accepted: 29 July 2021 · Published Online: 13 August 2021		Export Citation	CrossMark				
Hantian Gao, ¹ ^[] Shreyas Muralidharan, ² Md Rezaul Karim, ² ^[] Lei R. Cao, ^{3,4} ^[] Kevin D. Leedy, ⁵ ^[] Hongping Zhao, ^{2,6} ^[] Siddharth Rajan, ^{1,6} David C. Look, ^{5,7} ^[] and Leonard J. Brillson ^{1,2,a} ^[]							
AFFILIATIONS							

¹Department of Physics, The Ohio State University, Columbus, Ohio 43210

- ²Department of Electrical and Computer Engineering, The Ohio State University, Columbus, Ohio 43210
- ³Nuclear Reactor Lab, The Ohio State University, Columbus, Ohio 43210
- ⁴Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, Ohio 43210
- ⁵Air Force Research Laboratory, Wright-Patterson AFB, Ohio 45433
- ⁶Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio 43210
- ⁷Semiconductor Research Center, Wright State University, Dayton, Ohio 45435.

Note: This paper is a part of the Special Topic Collection on Physics and Chemistry of Surfaces and Interfaces. ^{a)}Electronic mail: brillson.1@osu.edu

ABSTRACT

The gallium vacancy is one of the dominant native point defects in β -Ga₂O₃, one that, together with its complexes, can have a major effect on free carrier densities and transport in this wide bandgap semiconductor. We used a combination of depth-resolved cathodoluminescence spectroscopy and surface photovoltage spectroscopy to identify the optical and energy-level properties of these defects as well as how their defect densities and spatial distributions vary with neutron irradiation and temperature-dependent-forming gas anneals. These studies reveal optical signatures that align closely with theoretical energy-level predictions. Likewise, our optical techniques reveal variations in these defect densities that are consistent with hydrogen passivation of gallium vacancies as a function of temperature and depth from the free Ga₂O₃ surface. These techniques can help guide the understanding and control of dominant native point defects in Ga₂O₃.

Published under an exclusive license by the AVS. https://doi.org/10.1116/6.0001240

I. INTRODUCTION

Ga₂O₃ has emerged as a next-generation, wide bandgap semiconductor for high power microelectronics^{1–5} due to its extremely high breakdown voltage predicted to be ~8 MV and its large single crystal manufacturability.^{6,7} An identification of deep-level defects in Ga₂O₃ is important since these defects are electrically active with energy levels that can produce compensation, recombination, and scattering of free carriers. The nature and energy levels of deeplevel defects may also play a role in Schottky barrier formation at metal–Ga₂O₃ interfaces.^{8,9} Depth-resolved cathodoluminescence spectroscopy (DRCLS)¹⁰⁻¹² and surface photovoltage spectroscopy (SPS)¹³⁻¹⁶ have proved useful in identifying the energy levels of deep-level point defects in semiconductors and their physical nature. Our ability to measure the spatial distribution and physical nature of specific defects using nanoscale cathodoluminescence spectroscopy¹⁷ in three dimensions,¹⁸ coupled with donor/acceptor densities and free carrier mobilities using temperature-dependent Hall effect measurements,^{19,20} enables us to identify and quantify defect and degenerate doping densities on a near-nm scale, relate them to transport and dielectric properties on a macroscopic scale, and potentially inform growth and processing methods to control them. Both DRCLS and SPS are well suited for studies of native point defects in Ga₂O₃, whose 4.85 eV bandgap enables a clear optical observation of transitions to and from deep-level defects in the visible and near-visible energy ranges.

DRCLS involves an electron beam incident on an electronic material that generates a cascade of secondary electrons extending into the solid. These electrons scatter and multiply into a cascade with a range of momenta, steadily losing energy with each scattering event until their energy permits only impact ionization of single electron-hole pairs. For semiconductors, this minimum energy corresponds to ~14/5 of the semiconductor bandgap EG due to momentum conservation.^{21,22} At these energies, electron scattering occurs within a few Å23 so that simulations of scattered electron densities versus penetration depth^{24,25} provide depthdependent profiles of electron-hole excitation intensity within this few Å precision. The excited electrons have a range of energies and can initially populate multiple conduction bands, from which they can drop to lower-energy, previously empty conduction band levels, recombine with valence band holes, and emit light at corresponding transition energies. Conduction electron recombination occurs primarily with holes at the valence band maximum due to a rapid recombination of excited holes deeper below with valence electrons.

SPS involves measurement of a semiconductor's surface electric potential using a capacitor in a closed feedback circuit to monitor the potential variation between the semiconductor surface and a vibrating electrode, in this case, an atomic force microscopy probe tip as a function of incident photon energy hy. With this capacitor in a closed feedback loop and scanning from low to high photon energy, the contact potential difference (cpd) between semiconductor surface and probe tip changes when hy reaches energies sufficient to produce photostimulated population or depopulation of states within the semiconductor bandgap. Transitions that change the n- or p-type majority carrier density near the semiconductor surface cause changes in band bending, the Fermi level EF position within the bandgap at the surface, and thereby the semiconductor work function Evacuum-Ep. The onset of photopopulation of states from the valence band into a gap state or depopulation from states in the bandgap to the conduction band produces slope changes in cpd versus hv plots, i.e., the surface photovoltage spectra. The sign of these slope changes at specific energies identifies the conduction or valence band nature of the optical transition. In turn, the transition energy hv indicates the energy difference between the gap state and either the conduction or valence band. As an example, for an n-type semiconductor with the usual upward band bending toward the surface in its depletion region, photopopulation would add more negative charge to the surface, which increases the upward band bending and lowers the surface EF in the bandgap. This increases Evacuum-EF and changes cpd accordingly. Photodepopulation would remove negative charge from the surface, producing the opposite cpd change.

Both SPS and DRCLS provide energies of optical transitions involving defect states within the semiconductor bandgap. In addition, SPS provides the defect energy levels relative to conduction or valence band edges, while DRCLS provides defect densities as a function of depth from the free surface. Energy-level positions can be compared with theoretical predictions of specific defects and defect complexes. The behavior of specific defects with various surface and bulk processing can indicate specific defect behavior. Both energy-level positions within the bandgap and defect depth dependence within the semiconductor are useful in determining the physical nature of specific defects.

II. EXPERIMENT

For SPS, we used a Park Systems XE-70 High Accuracy Small Sample probe microscope SPM in noncontact mode, which is an amplitude-modulated rather than a frequency-modulated measurement method, e.g., the system responds to changes in the amplitude of cantilever oscillation when vibrated near its resonant frequency using an internal lock-in amplifier. Conductive Cr-Au cantilever tips had stiffness k = ~5 N/m and resonant frequency f = ~160 kHz in order to perform electrostatic force microscopy, i.e., Kelvin probe force microscopy, KPFM. We used a Stanford Research Systems SR830 lock-in amplifier to apply an additional AC voltage between 17 and 18 kHz to isolate the electrostatic signal. For KPFM, a variable DC tip bias is controlled via lock-in feedback mode to null out the potential difference between the tip and the surface. For scanning KPFM this continuous feedback yields a potential map. In order to avoid charging for some insulating Ga2O3 samples, we obtained SPS spectra by probing inside the openings of a grounded copper grid in contact with the semiconductor.

We used an ultrahigh vacuum (UHV) chamber equipped with a glancing incidence electron gun for DRCLS excitation with incident beam voltages capable of operating from 0.1 to 5 keV. The optical train consisted of a CaF_2 focusing lens in UHV to maximize solid angle light collection, a sapphire viewport, an *f*-number matcher outside the UHV chamber, a grating monochromator, and a charge-coupled device detector.

In order to identify gap state features that are representative of Ga_2O_3 in general, we performed SPS and DRCLS measurements on Ga_2O_3 grown by molecular beam epitaxy (MBE), low-pressure chemical vapor deposition (LPCVD),^{26,27} pulsed laser deposition (PLD), and edge-fed growth (EFG). All three epitaxial films were grown on EFG substrates, and an EFG bulk crystal was also directly analyzed.

We irradiated LPCVD- and PLD-grown Ga₂O₃ samples at The Ohio State University Research Reactor (Columbus, OH) facility. Initially, Ga₂O₃ samples were exposed to neutrons in the central irradiation facility reactor for 41 min at 2 kW power, which produced a neutron dose $n = 2.27 \times 10^{14} \text{ cm}^{-2}.^{28}$ Higher doses denoted as 2xn, 4xn, 10xn, 500xn, and 2000xn increased linearly with exposure time at constant power. Ga₂O₃ samples after 2000xn dose irradiation were furnace-annealed in forming gas (FG) (3% H₂ in Ar₂) over a range of temperatures.

III. RESULTS

A. SPS of β-Ga₂O₃

Figure 1 presents SPS results for an MBE-grown, $2.6 \times 10^{19} \text{ cm}^{-3}$ Si-doped Ga₂O₃ for which CPD slope changes are

avs.scitation.org/journal/jvb





FIG. 1. SPS spectrum of MBE-grown, Si-doped β-Ga₂O₃, and schematic photoinduced population (2.4, 3.0, 3.5 eV) and depopulation (1.4, 2.0, 2.6, 3.8 eV) transitions from the valence band or to the conduction band, respectively.

commonly observed in samples grown by other methods. Also shown here are schematic illustrations of the photopopulation (red) and depopulations (blue) transitions involving the valence and conduction bands, respectively. The corresponding energy labels indicate negative and positive slope changes, respectively, at energies of these photostimulated transitions. Positive slope changes appear at 1.4, 2.0, 2.6, ~3.8, and 4.7-4.8 eV, corresponding to defect levels at E_C-1.4 eV, E_C-2.0 eV, E_C-2.6 eV, E_C-3.8 eV, and the β-Ga₂O₃ bandgap. Negative slope changes appear at 2.4, 3.0, and 3.5 eV, corresponding to defect levels at these energies above the valence band maximum. Because of Ga2O3's very large bandgap, these SPS spectra required very long (hours) scan times to accommodate the slow response times for the charge to fully redistribute and establish clear and reproducible slope changes. The gradual slope decrease that starts at 2.4 eV indicates the start of gap state filling, while the change to a more positive slope that starts at 2.6 eV indicates the start of emptying that state. Note that the spectrum proceeds in time from low to high energy so that filling first followed by the emptying afterward is expected. Slope changes at 2.0, 3.0, and 3.5 eV are quite clear. Less so is the slightly positive slope at ~3.8 eV, similar to a weak 3.8 eV CL feature shown below, which may correlate with the negative slope at ≤1.1 eV but which remains to be investigated further. The positive slope change at 4.7-4.8 eV is consistent with absorption measurements of the β-Ga2O3 bandgap, which can vary from values of 4.56, 4.59, and 4.85 eV for electric field polarization ([[001]), ([[100]), and ([[010]), respectively7.

Table I shows positive and negative slope changes for each of the clear transitions paired to indicate possible complementary transitions into and out of the same gap state level. These SPS slope changes correspond to photopopulation and depopulation into and out of the same deep-level defect. Bandgap complements may slightly exceed the actual bandgap due to slightly higher photoexcitation thresholds for electrons into a partially filled gap state. These SPS features indicate the presence of at least three energy levels deep within the Ga₂O₃ bandgap.

TABLE I. Complementary SPS transition energies.

+ SPS slope change (eV)	$E_{C} - E_{defect}$ (eV) (+)	$E_{defect} - E_V$ (eV) (-)	E _g complement (eV) (+)+(-)
~+1.4, -3.5	~1.4	3.5	~4.9
+2.0, -3.0	2.0	3.0	5.0
+2.6, ~ -2.4	2.6	~2.4	5.0

B. DRCLS of β-Ga₂O₃

The energy dependence of DRCLS excitation enables measurements that distinguish electronic structures within a few nanometers from the free surface to depths of several hundred nanometers with incident electron beam energies $E_B = 0.5-5 \,\text{kV}$, respectively. Monte Carlo simulations can provide distributions of final electron positions²⁵ including backscattering. These distributions are based on energy loss per unit path length, momentum transfer with the material's scattering centers based on its density ρ , atomic weight A, and atomic number Z that yield energy loss per unit path length.^{30,31} At their final positions, these electrons produce impact ionization³² and electron-hole pair creation with their remaining energy. Figure 2 illustrates these distributions for Ga₂O₃ for this range of E_B and corresponding depths. A differential form of DRCLS, termed DDRCLS, provides finer depth resolution between higher energy spectra.³³

Figure 3 shows DRCL spectra of Ga_2O_3 grown by four different techniques—MBE, EFG, PLD, and LPCVD. Sample dopings were:~ 2×10^{19} cm⁻³ Si (MBE), UID (EFG), 1.97×10^{20} cm⁻³ Si (PLD), and 2.6×10^{19} cm⁻³ Si (LPCVD). High doping enables temperature-dependent Hall (TDH) measurements of just the epilayers and introduced no additional DRCLS or SPS features. Each spectrum displays peak features that yield the energies shown as well as integrated peak areas after spectrum deconvolution. For each growth method, DRCL spectra exhibit identical 3.0 and 3.5 eV peak energies and nearly identical 2.3–2.5 and 3.8–4 eV peak



FIG. 2. Monte Carlo simulations of electron distributions vs E_B for Ga₂O₃.



FIG. 3. DRCL spectra acquired at E_B = 4 keV of β-Ga₂O₃ grown by the MBE, EFG, PLD, and LPCVD techniques.

energies. Each of the spectra also exhibit low-intensity, broad emission in the 4.5-5 eV range, corresponding to bandgap recombination. The high-intensity 3.0 and 3.5 eV transitions match closely with the corresponding SPS slope change energies in Table I. The 2.3–2.5 eV shoulders in Fig. 2 may correspond to 2.4 and 2.6 eV onsets listed in Table I. The 3.8 eV shoulder evident in Fig. 3 for all growth methods also appears to have an ~3.8 eV counterpart in Fig. 1.

Furthermore, the close agreement of DRCLS energies shown in Fig. 3 with the SPS photoexcited onsets shown in Fig. 1 is also consistent, with neither technique requiring a Franck–Condon correction,^{34,35} otherwise required for photoluminescence spectroscopy, since neither DRCLS nor SPS involves momentum-conserving instantaneous optical transitions. Thus, DRCLS and SPS results representative of Ga₂O₃ single crystals grown by a variety of techniques exhibit optical transitions that correspond to at least three midgap energy levels at 3.5, 3.0, and ~2.4 eV above the valence band maximum. Furthermore, these energy levels correlate closely³⁶ with charge state transition energies predicted theoretically³⁷ for V_0^* (III) at 3.52 eV, VGa(II) at 3.0 eV, and VGa(II)-H at 2.55 eV above E_V.

C. Neutron irradiation and forming gas anneals of $\beta\text{-}Ga_2O_3$

In order to confirm the identification of Ga vacancy (VGa) optical features, we performed DRCLS and SPS studies on Ga2O3 under conditions designed to alter the densities of these defects. Specifically, (1) we used controlled neutron irradiation to systematically increase V_{Ga} defect densities and (2) we used subsequent forming gas anneals to decrease VGa densities while increasing densities of VGa complexes with hydrogen (VGa-H). Previous EPR studies have demonstrated that neutron irradiation increases the densities of VGa-related defects.38 Density function theory (DFT) with hybridized functionals^{39–41} yields thermodynamical energies versus Fermi level (EF) position with charge state transition energies for different native point defects. These results predict energies for Ga vacancies in Ga_{II} sites at 3.0 eV and Ga_{II} vacancies complexed with hydrogen (VGaII-H) at ~2.4-2.5 eV.37 Indeed, both Fig. 3 and Table I show a close correlation between these theoretical assignments and our DRCL spectra. Neutron irradiation and FG annealing can provide further confirmation of the experimental and theoretical assignments of gap state energies associated with VGa and VGaII-H complexes.

Of the three dominant midgap defect emissions in Ga₂O₃, DRCLS studies have already identified the 3.5 eV emission with oxygen vacancies. Near-surface optical and electronic measurements have shown that surface exposure to remote oxygen plasma (ROP) treatment removes oxygen vacancies in many semiconductors, including ZnO,⁴² and SrTiO₃.^{43,44} Previously, we used severalhour ROP treatments of Ga₂O₃ to fill oxygen vacancies where 3.5 eV peak signals decreased monotonically with proximity to the free surface and extended further into the bulk with increasing ROP exposure.³⁶ Such exposures did not significantly affect the spatial distributions of other defects. Those results provided direct evidence that the 3.5 eV DRCLS is related to oxygen vacancies.

While ROP exposure is limited by the diffusion of activated oxygen into the Ga_2O_3 lattice—typically 50–100 nm, depending on temperature and time of exposure—neutron irradiation is far more penetrating as well as damaging to the crystal lattice. Figure 4 shows that neutron irradiation produces similar changes in defect emissions at both near-surface (<10 nm) and bulk (>130 nm) depths, indicating that neutron irradiation generates these defects uniformly with depth in this range, as expected for neutron irradiation's penetrating nature. Furthermore, Fig. 4 shows that both ~2.5 and 3.0 eV emissions increase relative to 3.5 eV emissions, suggesting both their relation to a common physical defect and their difference from oxygen vacancy emission.

Figure 5 shows a similar effect of neutron irradiation on PLD-grown Ga₂O₃ deep levels located in the bulk. From Fig. 2, these spectra acquired at $E_B = 5 \text{ keV}$ correspond to defects located up to ~150 nm below the free surface. These spectra before and after neutron irradiation display peak features at 2.4, 3.0, and 3.5 eV and a 3.8 eV shoulder, as shown in Fig. 3. Deconvolved peak



FIG. 4. DRCL spectra of 2.5, 3.0, and 3.5 eV defects in PLD-grown, Si-doped Ga_2O_3 before and after irradiation at near-surface and bulk depths. Irradiation increases emissions at ~2.5 and 3.0 eV relative to 3.5 eV at both depths.

intensities of both 2.4 and 3.0 eV features increase significantly relative to 3.5 eV peaks with increasing radiation. All three peak emissions increase in intensity when normalized to a weak but observable band emission centered at 4.8 eV.



FIG. 5. DRCL spectra for a Si-doped PLD-grown Ga₂O₃ as-received, after 10xn, and after 2000xn neutron irradiation. Deconvolutions show individual peak components and their energies.

DFT calculations of thermodynamic formation energies of defects versus E_F in Ga₂O₃ include charge state transitions at 2.5 and 3.0 eV for V_{GaII}-H and V_{GaII}, respectively. FG anneals can provide a test of the physical nature of the defect emissions at these energies. With FG anneals at temperatures up to ~550 °C, emissions due to H-passivation gallium vacancies are expected to increase and emissions due to unpassivated gallium vacancies are expected to decrease. At higher temperatures, such passivation is expected to reverse as hydrogen begins to dissociate from the Ga₂O₃ lattice. Figure 6 displays variations in the deconvolved 2.5 and 3.0 eV peak areas attributed to V_{Ga}-H and V_{Ga}, respectively, with FG {3% H in Ar} anneal temperatures of 400, 550, and 700 °C for 10 min each.

Figure 6(a) before annealing shows a relatively constant 2.5 eV peak area normalized to the ~4.6 eV near bandgap emission. After a 400 °C anneal, this bulk ratio increases steadily from ~40 nm below the surface, nearly doubling at the free Ga_2O_3 surface. A 550 °C anneal produces a similar increase but starting slightly deeper at ~60 nm below the free surface. These peak area ratios decrease overall at 700 °C but still display a gradual increase toward the free surface extending from a similar depth.

In contrast to these increases in 2.5 eV emission, the deconvolved 3.0 eV peak ratio displays opposite behavior. Figure 6(b) shows a gradually decreasing 3.0 eV peak ratio from the bulk to the surface before annealing, while a 400 °C produces a nearly 50% decrease from ~40 nm to the free Ga₂O₃ surface. The 550 °C FG anneal produces less of a 3.0 eV decrease and from only ~30 nm from the free Ga₂O₃ surface. A 700 °C FG anneal displays a gradually decreasing 3.0 eV peak ratio from the bulk to the surface, similar to the decreasing depth profile before annealing. Error bars in Figs. 6 and 7 are 10%–20% of the measured values, i.e., standard deviations are significantly smaller than the measured subsurface variations.

Figure 7 shows expanded depth profiles obtained for an undoped, LPCVD-grown Ga_2O_3 after a 750 °C anneal. Similar to Fig. 6(a), the 2.5 eV defect emission attributed to hydrogen passivated V_{Ga} increases toward the free surface. For this undoped Ga_2O_3 , the slightly higher temperature anneal introduces an even larger 2.5 eV increase that extends even further (>150 nm) into the bulk. Figure 7(b) shows the 3.5 eV depth profile for this undoped





FIG. 6. Normalized area ratios of (a) 2.5 and (b) 3.0 eV defect emissions vs FG anneal temperature for Si-doped, LPCVD-grown Ga₂O₃ after 2000xn neutron irradiation. Emissions attributed to V_{Ga}-H (V_{Ga}) increase (decrease) at 400 and 550 °C and reverse at 700 °C. Error bars are 10%-20%.

Ga₂O₃. The decrease in this feature for all depths suggests a decrease in oxygen vacancies.

valence band maximum. These energy levels are in close agreement with the charge state transition energies calculated previously for V_{GaII} -H complexes and isolated V_{GaII} in Ga_2O_3 .

IV. DISCUSSION

The SPS and DRCLS results for Ga_2O_3 before and after neutron irradiation and forming gas anneals confirm the physical nature of ~2.5 and 3.0 eV optical absorption and emission features in Ga_2O_3 . The agreement between SPS photoexcitation thresholds shown in Table I with the optical emissions that dominate cathodoluminescence features in Fig. 3 establish the presence of native point defects with energies located ~2.5 and 3.0 eV above the Figures 4 and 5 show that neutron irradiation increases the relative density of these defects uniformly across our measurable depth range, consistent with the expected penetrating nature of the fast and thermal neutrons used and the increase in V_{Ga} reported previously.²⁰ Figure 6 shows that subsequent FG anneal at 400 °C increases the ~2.5 eV emission attributed to V_{GaII} -H in the near-surface region extending ~40 nm below the Ga₂O₃ bulk, consistent with the limited diffusion of H into the solid and low hydrogen outdiffusion typical of other semiconductors at this temperature.



FIG. 7. Depth profiles of (a) 2.5 and (b) 3.5 eV normalized peak area ratios for an undoped LPCVD-grown Ga₂O₃ with 2000xn neutron irradiation before and after 750 °C FG anneal. Error bars are 10%–20%.



Correspondingly, the 3.0 eV emission attributed to VGaII decreases under these conditions as expected for H passivating some of these defects.

The higher-temperature FG anneal at 550 °C also increases 2.5 eV emission and extends deeper, indicating further hydrogen indiffusion and suggesting that hydrogen outdiffusion remains low. At the even higher 700 °C FG anneal temperature, however, this 2.5 eV increase is no longer apparent, suggesting some hydrogen outdiffusion. However, FG annealing at 750 °C for 10 min of an undoped Ga2O3 sample shown in Fig. 7(a) shows an even higher (2.5 eV) emission in the near surface region, suggesting that highertemperature passivation may be possible for undoped Ga2O3. Figure 7(b) shows that such annealing can also reduce 3.5 eV emission attributed to oxygen vacancies extending over the same depth range. One possible explanation for this ~30% decrease may be that hydrogen can passivate oxygen vacancies as well as $V_{\rm Ga}$ forming $V_{\rm O}\text{-}H$ complexes, which are energetically favorable^{36} acting as shallow donors⁴⁵ and reducing deep-level V_O emission. Unlike these FG anneals, however, O2 anneals can affect VGa,46 as can N2 anneals,47 but only at much higher temperatures. See also a recent review of VGa-H complexes.48

Overall, these neutron irradiation and FG anneal results show that neutron irradiation and forming gas anneals produce controllable changes in defect densities attributable to V_{Ga} and V_{Ga}-H complexes that are consistent with chemical passivation and temperature-dependent hydrogen diffusion/dissociation.

V. CONCLUSIONS

SPS and DRCLS measurements of ~2.5 and 3.0 eV defect emissions in Ga₂O₃ with neutron irradiation and FG anneals provide physical and chemical evidence that can be used to identify their physical nature as VGa-H complexes and VGa native point defects, respectively. Agreement between SPS photoexcitation energy thresholds and DRCLS luminescence transition energies places these VGa-related defects at 2.5 and 3.0 eV above the valence band maximum, respectively, in agreement with theoretical predictions. These results were enabled by the near-surface sensitivity of SPS to band bending associated with gap state occupancy and the sensitivity of DRCLS to native point defects below the surface with near-nanometer depth resolution.

ACKNOWLEDGMENTS

H.G. and L.J.B. gratefully acknowledge support from AFOSR under Grant No. FA9550-18-1-0066 (A. Sayir). LJ.B. and D.C.L. acknowledge support from the National Science Foundation (NSF) under Grant Nos. DMR-18-00130 and DMR-18-00139, respectively (T. Paskova). H.Z. acknowledges support from the NSF under Grant No. DMR-1755479. S.R. acknowledges support for this work by the Department of Energy/National Nuclear Security Administration under Award No. DE-NA0003921. L.R.C. acknowledges support by the U.S. Department of Energy, Office of Nuclear Energy under DOE Idaho Operations Office Contract No. DE-AC07-051D14517 as part of a Nuclear Science User Facilities experiment. We acknowledge the support of The Ohio State University Nuclear Reactor Laboratory and reactor staff member Susan White for the irradiation services provided.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

¹M. Higashiwaki, K. Sasaki, A. Kuramata, T. Masui, and S. Yamakoshi, Appl. Phys. Lett. 100, 013504 (2012).

²M. Higashiwaki et al., Appl. Phys. Lett. 108, 133503 (2016).

³J. Yang, S. Ahn, F. Ren, S. J. Pearton, S. Jang, J. Kim, and A. Kuramata, Appl. Phys. Lett. 110, 192101 (2017).

⁴M. Higashiwaki and G. H. Jessen, Appl. Phys. Lett. 112, 060401 (2018).

⁵M. Mastro, A. Kuramata, J. Calkins, J. Kim, F. Ren, and S. J. Pearton, ECS J. Solid State Sci. Technol. 6, P356 (2017).

⁶Akito Kuramata, K. Koshi, S. Watanabe, Y. Yamaoka, T. Matsui, and S. Yamakoshi, Jpn. J. Appl. Phys. 55, 1202A2 (2016).

⁷Z. Galazka, Semicond. Sci. Technol. 33, 113001 (2018).

⁸E. Farzana, Z. Zhang, P. K. Paul, A. R. Arehart, and S. A. Ringel, Appl. Phys. Lett. 110, 202102 (2017).

⁹Y. Yao, R. F. Davis, and L. M. Porter, J. Electron. Mater. 46, 2053 (2017).

¹⁰L. J. Brillson, H. W. Richter, M. L. Slade, B. A. Weinstein, and Y. Shapira, . Vac. Sci. Technol. 3, 1011 (1985).

¹¹L. J. Brillson, J. Vac. Sci. Technol. 19, 1762 (2001).

- 12L. J. Brillson, J. Phys. D: Appl. Phys. 45, 183001 (2012).
- ¹³H. C. Gatos and J. Lagowski, J. Vac. Sci. Technol. 10, 130 (1973).
- ¹⁴J. Lagowski, C. L. Balestra, and H. C. Gatos, Surf. Sci. 29, 203 (1972).
- ¹⁵L. J. Brillson, J. Vac. Sci. Technol. 12, 249 (1975).

16L. Kronik and Y. Shapira, Surf. Sci. Rep. 37, 1 (1999).

17T. J. Asel, H. Gao, T. J. Heinl, D. Adkins, P. M. Woodward, J. Hoffman, A. Bhattacharya, and L. J. Brillson, J. Vac. Sci. Technol. B 33, 04E103 (2015).

¹⁸Chung-Han Lin, Tyler A. Merz, D. R. Doutt, Jungwoo Joh, Jesus A. Del Alamo,

U. K. Mishra, and Leonard J. Brillson, IEEE Trans. Electron. Devices 59, 2667 (2012). 19G. M. Foster, G. Faber, Y.-F. Yao, C. C. Yang, E. R. Heller, D. C. Look, and L. J. Brillson, Appl. Phys. Lett. 109, 143506 (2016).

20H. Gao, S. Muralidharan, Md Rezaul Karim, S. M. White, L. R. Cao, K. Leedy, H. Zhao, D. C. Look, and L. J. Brillson, J. Phys. D: Appl. Phys. 53, 465102 (2020). ²¹E. B. Yakimov et al, Appl. Phys. Lett. 118, 202106 (2021).

²²C. A. Klein, J. Appl. Phys. 39, 2029 (1968). ²³M. P. Seah and W. A. Dench, Surf. Interface Anal. 1, 2 (1979).

²⁴P. Hovington, D. Drouin, and R. Gauvin, Scanning 19, 1 (1997).

²⁵D. Drouin, A. R. Couture, D. Joly, X. Tastet, V. Aimez, and R. Gauvin, Scanning 29, 92 (2007).

265. Rafique, L. Han, A. T. Neal, S. Mou, and H. Zhao, Phys. Status Solidi A 215, 1700467 (2018).

27Z. Feng, M. R. Karim, and H. Zhao, APL Mater. 7, 022514 (2019).

28See https://reactor.osu.edu/research-reactor for The Ohio State University Research Reactor (OSURR), a pool-type neutron reactor with multiple beam ports and dry tubes as irradiation facilities. ²⁹F. Ricci, F. Boschi, A. Baraldi, A. Filippetti, M. Higashiwaki, A. Kuramata,

V. Fiorentini, and R. Fomari, J. Phys. Condens. Matter 28, 224005 (2016).

³⁰T. E. Everhart and P. H. Hoff, J. Appl. Phys. 42, 5837 (1971).

³¹L. J. Brillson, Surface and Interfaces of Electronic Materials (Wiley-VCH, Weinheim, 2010), Chap. 16, ISBN:978-3-527-40915-0.

32A. Rose, RCA Rev. 27, 600 (1966).

³³S. Shen, Y. Liu, R. G. Gordon, and I. J. Brillson, Appl. Phys. Lett. 98, 172902 (2011).

34J. Franck, Trans. Faraday Soc. 21, 536 (1926).

35E. Condon, Phys. Rev. 28, 1182 (1926).

³⁶H. Gao, S. Muralidharan, Md R. Karim, S. M. White, L. R. Cao, K. Leedy,

H. Zhao, D. C. Look, and L. J. Brillson, Appl. Phys. Lett. 112, 242102 (2018).

³⁷J. B. Varley, H. Peelaers, A. Janotti, and C. G. Van de Walle, J. Phys. Condens. Matter 23, 334212 (2011).



³⁸B. E. Kananen, L. E. Halliburton, K. T. Stevens, G. I. Foundos, and N. C. Giles, Appl. Phys. Lett. **110**, 202104 (2017). ³⁹J. L. Lyons and C. G. Van de Walle, NPJ Comput. Mater. **3**, 1 (2017).

40Q. Yan, A. Janotti, M. Scheffler, and C. G. Van de Walle, Appl. Phys. Lett. 105, 111104 (2014).

⁴¹C. G. Van de Walle, J. L. Lyons, and A. Janotti, Phys. Status Solidi A 207, 1024 (2010).

42H. I. Mosbacker, Y. M. Strzhemechny, B. D. White, P. E. Smith, D. C. Look, D. C. Reynolds, C. W. Litton, and L. J. Brillson, Appl. Phys. Lett. 87, 012102 (2005).

- ⁴³J. Zhang, S. Walsh, C. Brooks, D. G. Schlom, and L. J. Brillson, J. Vac. Sci. Technol. B 26, 1466 (2008).
- 44H. Lee et al., Nat. Mater. 17, 231 (2018).
- 45A. Janotti and C. G. Van de Walle, Nat. Mater. 6, 44 (2007).
- ⁴⁶J. Jesenovec, M. H. Weber, C. Pansegrau, M. D. McCluskey, K. G. Lynn, and J. S. McCloy, J. Appl. Phys. 129, 245701 (2021).
 ⁴⁷N. T. Son, Q. D. Ho, H. Abe, T. Ohshima, B. Monemar, Y. Kumagai,
- T. Frauenheim, and P. Deák, Appl. Phys. Lett. 117, 032101 (2020).
- 48Y. Qin, M. Stavola, W. B. Fowler, P. Weiser, and S. J. Pearton, ECS J. Solid State Sci. Technol. 8, Q3103 (2019).