Deep level defect spectroscopies of complex oxide surfaces and interfaces

Cite as: J. Vac. Sci. Technol. A 39, 063215 (2021); https://doi.org/10.1116/6.0001339
Submitted: 06 August 2021 • Accepted: 30 September 2021 • Published Online: 20 October 2021

Jun Zhang, Kyle McNicholas, Snjezana Balaz, et al.

COLLECTIONS

Paper published as part of the special topic on Honoring Dr. Scott Chambers’ 70th Birthday and His Leadership in the Science and Technology of Oxide Thin Films

This paper was selected as an Editor’s Pick

ARTICLES YOU MAY BE INTERESTED IN

Diffusion of dopants and impurities in β-Ga2O3
Journal of Vacuum Science & Technology A 39, 060801 (2021); https://doi.org/10.1116/6.0001307

Reactor scale simulations of ALD and ALE: Ideal and non-ideal self-limited processes in a cylindrical and a 300 mm wafer cross-flow reactor
Journal of Vacuum Science & Technology A 39, 062404 (2021); https://doi.org/10.1116/6.0001212

Gas source molecular epitaxy of Ge1−ySny materials and devices using high order Ge4H10 and Ge5H12 hydrides
Journal of Vacuum Science & Technology A 39, 063411 (2021); https://doi.org/10.1116/6.0001253
Deep level defect spectroscopies of complex oxide surfaces and interfaces

Cite as: J. Vac. Sci. Technol. A 39, 063215 (2021); doi: 10.1116/6.0001339
Submitted: 6 August 2021 · Accepted: 30 September 2021 · Published Online: 20 October 2021

Jun Zhang,1 Kyle McNicholas,2 Snjezana Balaz,3 Zhao Quan Zeng,4 Darrell Schlom,5,6 and Leonard J. Brillson7,8,a)

AFFILIATIONS
1 Spears School of Business, Oklahoma State University, Stillwater, Oklahoma 74078
2 MIT Lincoln Laboratories, Lexington, Massachusetts 02421
3 Department of Physics, Astronomy, Geology, and Environmental Science, Youngstown State University, Youngstown, Ohio 44555
4 II-VI Incorporated, Warren, Pennsylvania 07059
5 Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853
6 Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853
7 Department of Electrical and Computer Engineering, The Ohio State University, Columbus, Ohio 43210
8 Department of Physics, The Ohio State University, Columbus, Ohio 43210

Note: This paper is a part of the Special Collection Honoring Dr. Scott Chambers’ 70th Birthday and His Leadership in the Science and Technology of Oxide Thin Films.

a)Author to whom correspondence should be addressed: brillson.1@osu.edu

ABSTRACT
Intrinsic point defects are commonly present in and can strongly affect the electronic properties of complex oxides and their interfaces. The near- and subsurface characterization techniques, depth-resolved cathodoluminescence spectroscopy and surface photovoltage spectroscopy, can measure the density distributions, energy levels, and optical transitions of intrinsic point defects in complex oxides on a near-nanometer scale. These measurements on SrTiO3, BaTiO3, and related materials reveal the sensitivity of intrinsic point defects to growth temperature, mechanical strain, crystal orientation, and chemical interactions. Spatial redistribution of these defects can vary significantly near surfaces and interfaces and can have strong electronic effects. The combination of these deep level spectroscopies along with other advanced characterization techniques provides an avenue to further expand the understanding and control of complex oxide defects in general.

Published under an exclusive license by the AVS.

I. INTRODUCTION
Complex oxides have emerged as exciting electronic materials over the past two decades due to their wide array of electromagnetic properties, particularly in ultrathin films and at their interfaces. The discovery of high conductivity at otherwise insulating complex oxide interfaces has attracted considerable interest in understanding their intrinsic physics and materials science.1–6 Extensive studies of complex oxides over the past decade have shown how sensitive their electronic properties are to specific epitaxial growth conditions, particularly at atomic-scale interfaces between epitaxially grown oxides. Thus, Chambers et al. showed that complex oxide interfaces can exhibit chemical interactions,7–10 just as Brillson et al. showed that such interface chemical reactions are common and systematic at metal-compound semiconductor interfaces.11,12 As expressed in Chambers’s Advanced Materials review, “Future scientific growth in this field depends critically on our ability to monitor and control both oxide epitaxial film growth processes and the film and interface structure and composition.”13

Due to their electrical activity, intrinsic point defects can strongly affect the electronic properties of complex oxide thin films and their interfaces. Extensive growth and transport studies have revealed the high sensitivity of such defects to epitaxial growth processes and chemical interactions on the atomic scale. We now know that intrinsic point defects are present in high densities...
within complex oxide semiconductors and insulators. These densities can be large enough to dominate free carrier densities, form significant dipoles at interfaces, and introduce conductive channels both at interfaces and across bulk films. In this article, we show how depth-resolved cathodoluminescence spectroscopy (DRCLS) and surface photovoltage spectroscopy (SPS), both near-surface and subsurface characterization techniques, can measure the density distributions, energy levels, and optical transitions of such defects on a near-nanometer scale. These measurements reveal the sensitivity of intrinsic point defects to growth temperature, mechanical strain, crystal orientation, and chemical interactions.

Measuring the physical nature, densities, and spatial distribution of these defects is challenging for most characterization methods due to the ultrathin dimensions of complex oxide films grown epitaxially on lattice-matched substrates. Thus, otherwise widely used capacitance techniques such as deep level transient spectroscopy and its variants are limited by the depletion regions involved, which can easily exceed film thicknesses. Spin-sensitive magnetic techniques such as electron paramagnetic resonance (EPR) and optically detected magnetic resonance are limited by the minimum number of spins required for detection, typically >10¹¹, and the absence of depth resolution. Optical spectroscopies are limited by 100 nm scale and poorer depth resolution, electrical spectroscopies by both poor depth resolution and the insulating nature of undoped complex oxides, and magnetic spectroscopies by the minimum material volumes at given spin densities required for detection. Cathodoluminescence spectroscopy (CLS) and DRCLS achieve both state-of-the-art sensitivity to defect densities, e.g., <10¹⁵ cm⁻³, as well as near-nanometer depth and lateral resolution. Furthermore, the incident electron beam enables excitation of optical emission with above bandgap energies exceeding those of lasers and other optical sources. This combination of sensitivity, nanometer-scale spatial resolution in three dimensions, and above bandgap excitation is very well suited to explore intrinsic point defects in complex oxides, where the presence and spatial distribution of charged imperfections and impurities at the nanoscale can determine the macroscopic electronic and magnetic properties of these materials.

After cathodoluminescence spectroscopy studies first made use of depth-resolved measurements in semiconductors, Brillson et al. applied DRCLS to study defects at ultrahigh vacuum (UHV)-cleaved surfaces of conventional semiconducting materials to examine their role in Schottky barrier formation. The extension of DRCLS to wide bandgap semiconductors demonstrated the role of interface-specific defects and chemical interactions in controlling Schottky barrier formation. The discovery of conducting interfaces between otherwise insulating electronic materials motivated the extension of DRCLS interface studies to a wide range of complex oxides.

DRCLS together with SPS provide the ability to measure optical transitions associated with deep level defects but also to determine the energies of these deep levels with respect to the semiconductor’s valence and conduction bands. Together with theoretical predictions of energy levels for specific defects, this information can help identify the physical nature of these defects. The intensity and physical redistribution behavior of these defects with thermal and chemical processing can provide further evidence to support such defect identification. And the measurement of these defects inside actual devices, even during operation, can help us understand electronic behavior at the nanoscale.

This article is structured as follows: Section II provides brief descriptions of the DRCLS and SPS techniques. Section III describes the application of these techniques to measure and identify deep level defects in SrTiO₃, BaTiO₃, and related materials. These results also show how specific defect densities and spatial distributions depend on chemical processing, growth stoichiometry, and epitaxial strain. Section IV discusses how these defects spatially redistribute due to orientation-dependent intrinsic electric fields and externally applied bias. Section V discusses the impact of specific defects in complex oxide electronic structures. Section VI discusses new directions for studies of intrinsic point defects in complex oxides.

II. EXPERIMENTAL TECHNIQUES

The DRCLS technique involves an incident electron beam that generates a cascade of secondary electrons by scattering with the semiconductor or the insulator lattice. Depending on the incident beam energy, these electrons lose energy sequentially to x rays, plasmons, and finally, electron-hole (e-h) pairs. Monte Carlo simulations including backscattering can provide depth distributions of the final positions of these electrons, which correspond to the energies of e-h excitation, recombination, and light emission to within the few Å of scattering length of these final, low-energy electrons. For incident beam energies ranging from 0.1 to 5 keV, excitation depths range from the sub-10 nm to the several 100-nm scale, depending on the density, atomic weight, and atomic number of the target lattice. The excited electrons and holes can recombine via band-to-band, band-to-defect, and defect-to-band transitions with a range of momenta. DRCLS can also detect higher lying conduction band transitions to the valence band maximum, given the relatively high incident beam energy.

SPS involves a vibrating Kelvin probe whose high impedance feedback circuit continuously monitors the electric potential difference between the probe and the sample surface as a function of increasing incident photon beam energy. The onset of photo-stimulated population of electrons from the valence band into states within a semiconductor or an insulator bandgap changes the initial surface band bending, the surface electric potential, and the contact potential difference (cpd) measured by the Kelvin probe circuit. Likewise, the onset of photo-stimulated depopulation from a state within the bandgap to the conduction band results in an opposite sign of band bending change, surface potential, and measured cpd. The onset of these transitions produces a slope change in cpd versus photon energy hv that correspond to the transition energy involved. Furthermore, the sign of slope change indicates the photopopulation or depopulation nature of the transition. The energy and sign of cpd slope change provide the position of a given defect level within the bandgap. Then by combining SPS with DRCLS intensity versus depth profiles of the same optical transition, one can determine both a specific defect’s energy level within the band and the depth distribution of that defect.

For DRCLS studies, we used an ultrahigh vacuum (UHV) chamber with a glancing incidence electron gun with constant...
beam current of 2 mA and incident beam voltages $E_B = 0.1–5$ keV. The optical detection system consisted of a CaF$_2$ focusing lens inside the UHV chamber, a sapphire viewport, an $f$-number matcher, a grating monochromator, and a charge couple detector (CCD). For SPS, we used a Park Systems XE-70 High Accuracy Small Sample probe microscope SPM in noncontact mode with conductive Cr-Au cantilever tips 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 17–18 kHz AC voltage to isolate the electrostatic signal. For KPFM, a variable DC tip bias is controlled with a lock-in amplifier feedback to null out the potential difference between the tip and the surface.

The SrTiO$_3$ samples that we studied were both commercially available single crystals and thin films grown by molecular beam epitaxy (MBE). The MBE samples were grown under a variety of controlled temperature, plasma-assisted oxygen, stoichiometry, and substrate conditions. Unless otherwise noted, SrTiO$_3$ films were epitaxially grown on SrTiO$_3$ substrates under $5 \times 10^{-7}$ Torr O$_2$ with 10% O$_3$ at a substrate temperature of 650 °C. The SrTiO$_3$ single crystal substrates were chemically cleaned using a standard substrate pretreatment method. No further processing was made for the unprocessed substrates, and the processed substrates were further annealed at the thin film growth condition for 100 min. (Ba,Sr)TiO$_3$ samples were grown by either MBE or pulsed laser deposition (PLD). For MBE growth, we grew 100 nm (Ba,Sr)TiO$_3$ epilayers on SrTiO$_3$ substrates by alternate deposition of Sr, Ba, and Ti layers. The TiO$_2$-terminated SrTiO$_3$ (100) substrates were treated with an aqua regia etch prior to (Ba,Sr)TiO$_3$ deposition. Source flux was calibrated by a quartz crystal microbalance and then by measuring in situ reflection high energy electron diffraction oscillations from a calibration sample grown in a 200 W, 5 × 10$^{-7}$ Torr oxygen plasma pressure (PO$_2$) at $T_G = 800$ °C. Films were grown with multiple, specific PO$_2$ and substrate temperatures as indicated below. SrTiO$_3$ DRCLS was performed with samples cooled with a helium cryostat to ~43 K. For PLD growth, we grew Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ with either 1 μm thickness on MgO substrates with high (100) orientation, which exhibited high dielectric loss, or on randomly oriented Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ on Mg substrates with 1% W, which exhibited lower dielectric loss.42–45

III. DEFECT MEASUREMENT AND IDENTIFICATION

Defects in complex oxides such as SrTiO$_3$, BaTiO$_3$, and related materials exhibit strong variations in DRCLS intensity and spatial distribution with growth conditions and subsequent processing. These systematic variations can help identify the physical nature of specific defects. Figure 1 illustrates DRCLS spectra with representative SrTiO$_3$ bulk features. Figure 1(a) illustrates spectra from a commercially available SrTiO$_3$ bulk crystal with $E_B = 1–5$ kV. Monte Carlo simulations yield maximum excitation depths, i.e., Bohr–Bethe ranges $R_B$, based on the kinetic energy decrease of an energetic incident electron along its path length after multiple scattering events and the electron’s final position in depth.46 This final depth increases from 20 to 210 nm with increasing excitation depth, consistent with bulk crystal uniformity. Optical emissions ranging from ~3.2 eV bandgap down to ~1.4 eV CCD cutoff show evidence of defect emissions at ~1.6, 2.1, and 2.6 eV. Defect emissions at 2.1 and 2.6 eV have intensities in excess of bandgap emission intensity, indicating relative high defect densities. Spectral features above ~3.2 eV bandgap correspond to optical transitions from higher lying conduction bands to the valence band edge. The broadness of defect emissions is attributed to multiple
Copyright © 2021, American Vacuum Society. Published under an exclusive license by The AVS.

The TiO₆ octahedra common to both TiO₂ and SrTiO₃ led to identifying similar emissions in SrTiO₃ with Ti³⁺ sites as well.⁵²,⁴,⁵⁸ Hence, these emissions in SrTiO₃ are properly termed Ti³⁺ ions on TiO₆ octahedral lattice sites. Likewise, sintering and photoemission studies suggested that losing oxygen atoms from the TiO₆ octahedra introduced states at 2.19 and 2.6 eV that were attributed to oxygen vacancies Vₐ and Vₐ complexes, respectively,⁴,³⁸ while ~2.9 eV emission has been attributed to self-trapped excitons⁴⁰ or Vₐ complexes as well. Indeed, photoinduced EPR studies demonstrate V₀ with unpaired spins localized on two neighboring titanium Ti³⁺ and a Ti²⁺ self-trapped electron, and a self-trapped hole shared by two adjacent oxygen ions.⁴₁ Isolated substitutional Fe³⁺, Al³⁺, and Cr³⁺ ion impurities⁴⁵ are common in bulk SrTiO₃ and can form multiple deep levels with different charge states. For Fe, several of these charge states include Fe⁴⁺/⁵⁺V₀, Fe²⁺/³⁺V₂O, and Fe⁴⁺/⁵⁺V₂O located 0.75, 1.06, and 1.35 eV above EV, respectively.⁴⁶ Their CL emissions exhibit narrow linewidths in contrast to the broader linewidths of intrinsic defect and band-to-band transitions presented in this study. For Fe impurities in SrTiO₃, their energies differ significantly from those of the intrinsic defects reported here as does their appearance as a multiple charge state group. See also supplemental information.⁴²

Thermal annealing MBE-grown SrTiO₃ produces DRCL spectral changes that support their identification with oxygen vacancies. Figure 2 shows spectra for 100 nm Sr₁.₂TiO₃ before and after a 700 °C, 1 h O₂ anneal. Previous DRCLS studies showed that Sr-rich growth increased defect emissions attributed to oxygen vacancies. Figure 2(a) shows that these Sr₁.₂TiO₃ emission intensities normalized to the 3.27 eV near band edge (NBE) increased by nearly an order of magnitude over those for SrTiO₃ in Fig. 1(b). Figure 2(b) shows how the O₂ anneal decreased defect emissions in the 2–3.3 eV range back to the range of SrTiO₃ normalized values, confirming the correlation with V₀-related defects.

Based on Fig. 2, Table II shows that the dominant 2.0 eV emission decreased by 5.3× within the outer 20 nm, by 4.0× within the outer 45 nm, and by 2.1× within the outer 85 nm of the 100 nm epitaxial growth. Likewise, the 2.6 eV emission strength decreased by 3.5× within the outer 20 nm, 3.8× within the outer 45 nm, and by 2.3× within the outer 85 nm. Table II indicates that these emissions all involve oxygen vacancy-related defects. Furthermore, the progression of highest to lowest defect reduction with increasing depth indicates that the removal of V₀ defect emissions occurs by diffusion of oxygen from the free surface into the bulk. In addition, the more pronounced reduction of 2.0 eV defect emission within the outer 20 nm suggests that it relates to a different V₀-related defect, possibly isolated V₀ rather than a V₀O-related complex. Similar analysis of stoichiometric SrTiO₃ subbandgap defect emissions by the same high temperature oxygen anneal also shows reduction of both 2.0 and 2.6 eV defect emissions at 45 and 85 nm depths.

Mechanical strain introduced during epitaxial growth can strongly affect defects in complex oxides. Figure 3 shows deep level defect spectra for epitaxial SrTiO₃ grown at different temperatures on substrates with varying lattice matches and strains. With higher growth temperature, more V₀O-related defects are expected as O incorporation in the epilayers during growth decreases. The orders-of-magnitude increase in defect emissions with increasing temperature supports this expectation.

<table>
<thead>
<tr>
<th>TABLE I. Comparison of interband transition energies measured by VUV, SE, and CLS techniques.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition assignment</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td>Bandgap (direct)</td>
</tr>
<tr>
<td>O₂p → Ti 3d t₂g</td>
</tr>
<tr>
<td>O₂p → Ti 3d t₂g</td>
</tr>
<tr>
<td>O₂p → Ti 3d t₂g</td>
</tr>
<tr>
<td>O₂p → Ti 3d t₂g</td>
</tr>
</tbody>
</table>

Published under an exclusive license by The AVS.
The substrate dependence of these spectra also highlights a strong dependence of defect densities on epitaxial strain. (LaAlO_3)_0.3(Sr_2TaAlO_6)_0.7 (LSAT), SrTiO_3 (STO) and DyScO_3 (DSO) all have the perovskite crystal structure and are commonly used as single crystal substrates for the growth of epitaxial complex oxide films. Substrate lattice spacings a_o for (LSAT), (STO), and (DSO) are 3.868, 3.905, and 3.952 Å, respectively. Epitaxial lattice match to these substrates with increasing lattice spacing introduces increasing tensile strain in the 100 nm overlayers. Lattice atom spacing can increase or decrease Ti^{3+} repulsion, making VO formation more or less likely. Missing O atoms between Ti atoms introduces more Ti^{3+}-Ti^{3+} repulsion, increasing their separation and expanding the lattice. Conversely, increased lattice spacing renders VO formation more energetically favorable. The apparent Ti^{3+}-related defect increase in Fig. 3(c) is consistent with such increased VO formation and the correlation of VO with neighboring Ti^{3+} atoms.57 Previously, studies of SrTiO_3 sintering established an increase in oxygen vacancies and increased lattice parameters with decreasing oxygen partial pressure.59 For SrTiO_3 grown at 650 °C, Fig. 3(c) also shows that Ti^{3+}-related normalized emission intensities increase with increasing tensile strain, consistent with increased VO density, even for this lowest growth temperature. For the 1000 °C V_O-rich growth, the compressive strain introduced by the LSAT substrate depresses both Ti^{3+} and V_O-related normalized defect intensities as expected. Interestingly, these defect intensities appear highest for STO on STO growth, regardless of growth temperature, suggesting some more complex lattice interaction. Thus, Fig. 3(c) illustrates a clear 35 meV upward energy shift of the 1.565 eV Ti^{3+} feature with compressive-to-tensile strain [smaller but also apparent in Fig. 3(d)] that may indicate an energy shift of this defect within the SrTiO_3 bandgap and the relative VO versus Ti^{3+} formation energies.

DRCLS measures strain effects on defect densities in other complex oxides as well. Figure 4 shows DRCLS spectra for Ba_{0.5}Sr_{0.5}TiO_3 grown by PLD on (a) MgO(100) oriented versus 1% WB a_{0.5}Sr_{0.5}TiO_3 randomly oriented on MgO(100). Here, the oriented Ba_{0.5}Sr_{0.5}TiO_3 displays high defect densities similar to those shown for SrTiO_3 defects in Figs. 1 and 2. Consistent also with the high defect density of Fig. 4(a), this (Ba,Sr)TiO_3 exhibits high RF dielectric loss of tan δ = 1.9 × 10^{-2}. In contrast, the much lower defect densities compared to bandgap emission in the spectra of Fig. 4(b) are consistent with this (Ba,Sr)TiO_3

<table>
<thead>
<tr>
<th>Depth (nm)</th>
<th>2.0 eV Preanneal</th>
<th>2.0 eV Postanneal</th>
<th>Δ2.0× reduced</th>
<th>2.6 eV Preanneal</th>
<th>2.6 eV Postanneal</th>
<th>Δ2.6× reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>12.9</td>
<td>2.4</td>
<td>5.3</td>
<td>4.2</td>
<td>1.2</td>
<td>3.5</td>
</tr>
<tr>
<td>45</td>
<td>20.4</td>
<td>5.1</td>
<td>4.0</td>
<td>6.6</td>
<td>1.8</td>
<td>3.8</td>
</tr>
<tr>
<td>85</td>
<td>23.2</td>
<td>11.0</td>
<td>2.1</td>
<td>7.4</td>
<td>3.3</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Figure 2 reduction of Sr_{1.2}TiO_3 subbandgap 2.0 and 2.6 eV defect emissions by high-temperature oxygen anneal. Pre- and postanneal values shown for both defects are normalized by 3.27 eV NBE values. Reduced values are pre- vs postratios for each defect.

FIG. 2. DRCLS spectra of 100 nm Sr_{1.2}TiO_3 (a) before vs (b) after a 700 °C, 1 h O_2 anneal. Annealing reduces subbandgap defect emissions in the hν = 2–3.27 eV energy range, indicating oxygen vacancy-related defects. Each colored spectrum corresponds to a maximum excitation depth R_b in nm as indicated.
compound’s \(2\times\) lower \(\tan \delta = 7.3 \times 10^{-3}\). The additional 1.76/1.83 eV peaks in these spectra can be identified with \(V_{Ba}\) defects, to be discussed below. The 2.8 eV peak identified as a self-trapped exciton in Fig. 4(b) may be obscured in Fig. 4(a) by the strong defect emission. Figure 4 provides an example of defect densities having a significant effect on electronic properties. These results in general provide evidence for the effect of epitaxial strain on defect densities in complex oxides.

With the association of optical transitions in SrTiO\(_3\) and (Ba,Sr)TiO\(_3\) with specific defects, SPS studies can provide energy levels associated with specific transitions within the semiconductor bandgap. Figure 5 insets illustrate photostimulated gap state depopulation and population, respectively. Figure 5(a) shows how contact potential difference \(\Delta cpd\) between the BaTiO\(_3\) free surface and the Kelvin probe tip exhibits changes in slope with increasing photon energy. Positive slope changes correspond to photostimulated decreases in band bending due to the removal of negative charge from the n-type semiconductor surface. The onset of these transitions occurs at energies below the conduction band as illustrated schematically in Fig. 5(b). Negative slope changes correspond to photostimulated increases in band bending due to the addition of negative charge to the free surface. These transitions appear at energies relative to the valence band. The large increase in \(cpd\) between 3.1 and 3.45 eV indicates band flattening due to valence-to-conduction band excitation that increases free electron and hole production.

Figure 5(b) shows that these transitions can all be matched as complementary pairs whose approximate sum adds up to the 3.1 eV
BaTiO₃ bandgap. (Note: the 0.7 eV complement to the 2.4 eV transition is outside the spectral range.) The TiO₆ octahedral correspondence between BaTiO₃, SrTiO₃, and (Ba,Sr)TiO₃ mentioned above suggests that approximately the same energies correspond to analogous defects in all three materials. Thus, the 1.60/1.75 eV pair can be associated with Ti³⁺-related states, while the 1.952/2.1 eV pair can be associated with Vₒ-related states. The 2.9 eV transition that appears in both DRCLS and SPS may also correspond to Vₒ-related (Vₒ-R) states based on its sensitivity to oxygen anneals shown in Fig. 2 and to growth temperature in Fig. 3.

FIG. 4. DRCL spectra of PLD-grown BaₓSr₁₋ₓTiO₃ (a) on MgO (100)-oriented and (b) on 1%W BaₓSr₁₋ₓTiO₃ randomly oriented on MgO. Each colored spectrum corresponds to an incident beam energy Eᵦ in kV and its corresponding maximum excitation depth Rₑ in nm as indicated.

FIG. 5. (a) Schematic illustration of BaTiO₃ photostimulated charge carrier depopulation (upper left) out of and population (upper right) of charge carriers into defect energy levels within the bandgap. Depopulation (population) transitions correspond to positive (negative) SPS cpd slope changes with increasing photon energy. (b) Schematic energy level diagram illustrating these transitions.
Both 2.9 and 1.95/1.15 eV pair SPS features can be related to specific defects based on CL measurements of sintered BaTiO$_3$ grains and theory of Koschek and Kubalek as reproduced in Fig. 6(a) based on earlier conductivity measurement-derived defect activation energies of Daniels and Härdtl. The proximity of Fig. 6(a)’s 1.95/1.15 eV pair to the 1.8/1.2 eV pair shown in Fig. 6(a) suggests their association with V$_{Ba}^-$. The Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ DRCL spectra in Fig. 4(a) indeed display a clear transition at 1.83 eV that can be related to this defect.

Based on Figs. 5(b) and 6(a), Fig. 6(b) suggests optical transitions into and out of energy levels within the BaTiO$_3$ bandgap. The 1.6 eV transition corresponds to an energy level of 1.6 eV below conduction band $E_C$ and can be identified with Ti$^{3+}$ states as discussed earlier.

Recent studies involving iterative feedback among atomic-layer-and stoichiometry-controlled thin-film epitaxy, hybrid density function theory, and high depth-resolution CL spectroscopy identified a functional cationic defect, the Ti antisite (Ti$_{Sr}$) defect with an energy of 1.74 eV. This work also attributed a 2.03 eV emission to V$_{Sr}^-$. However, previous work showed low 2 eV emission for Sr$_{0.5}$TiO$_3$, suggesting a stronger contribution from V$_{Sr}^-$. The 2.1 eV transition in Fig. 6(a) also suggests that transitions between V$_{O}^-$-V$_{Ba}^+$ donor-acceptor pairs can contribute to defect luminescence.

### IV. CRYSTAL ORIENTATION AND ELECTRIC FIELD EFFECTS ON SRTIO$_3$ INTRINSIC POINT DEFECTS

DRCLS results show how both complex oxide crystal orientation and applied electric fields can redistribute intrinsic point defects in complex oxides. Based on defect identifications of characteristic optical emissions obtained in Sec. III, DRCL spectra of bulk SrTiO$_3$ exhibit dominant emissions at 1.62 eV corresponding to Ti$^{3+}$ defects and 1.9–2.0 eV corresponding to V$_{O}$ defects. The strength of these defect emissions varies strongly with depth from the free surface on a scale of tens of nanometers. Furthermore, these depth distributions vary significantly with crystal surface orientation.

Figure 7(a) shows Ti$^{3+}$ and V$_{O}$ normalized depth distributions I(defect)/I(NBE) for SrTiO$_3$(111). Here, 2.0 eV V$_{O}$ CL intensity decreases steadily from bulk depths greater than 100 nm to less than a few nanometers of the free surface. The 1.62 eV Ti$^{3+}$ emission intensity also decreases steadily from the bulk but increases rapidly within $\sim$10 nm of the surface. As a result, the ratio of Ti$^{3+}$ to V$_{O}$ intensities increases by nearly 3x from approximately unity in the bulk to the surface. The near-surface defect distributions are significantly different for (110) and (100) orientations. Figure 7(b) shows that V$_{O}$ intensities are nearly an order of magnitude higher than Ti$^{3+}$ emissions at all depths but exhibit a steep decline within the outermost 10 nm to only I(2.0 eV)/I(1.6 eV) of only $\sim$2× V$_{O}$-rich. Figure 7(c) shows a
similar V_O-rich distribution to within ∼10 nm of the free surface but then nearly equal I(2.0 eV) and I(1.6 eV) intensities within the last few nanometers.

KPFM measurements of these different surface orientations showed significant differences in their absolute surface potential. The Kelvin probe used for these measurements was calibrated immediately beforehand with an air-stable, freshly cleaved, highly oriented, polycrystalline graphite surface.63 Surface potentials ϕ were 4.57, 4.22, and 4.23 eV for (111), (110), and (100) surface orientations, respectively. Interestingly, for Nb-doped SrTiO_3 (not shown), ϕ is 3.59 eV, i.e., with its Fermi level 0.6 eV higher than for the lowest work function for nominally undoped SrTiO_3 and consistent with its n-type, degenerate doping and Fermi level above its conduction band minimum versus inside the band gap without extrinsic doping. The 0.35 eV larger surface work function for the Ti^{3+}-rich (111) versus the more I(Ti^{3+})/I(V_O)-balanced (110) and
(100) surface orientations corresponds to a difference in surface dipole $\Delta \chi$ as shown in Fig. 7(d). This $\Delta \chi$ represents a voltage $V$ defined by capacitance $C = Q/V = \varepsilon A/d$, where $\varepsilon/\varepsilon_0 = 300$ nominally for SrTiO$_3$, $d$ is charge separation, $A$ is the surface area, charge $Q = q_n s$ is the surface charge, and $n_s$ is the surface charge density. Hence, $n_s = \varepsilon A \Delta \chi/qvd = 5.8 \times 10^{13} \text{ electrons cm}^{-2}$. For SrTiO$_3$ with lattice constant $a_0 = 3.905 \text{ Å}$ and surface atomic density $1/a_0^2 = 6.55 \times 10^{14} \text{ cm}^{-2}$, then $n_s = 8.9$ electrons per 100 surface atoms, equivalent to a volume charge density of $\sim 4 \times 10^{17} \text{ cm}^{-3}$ within the outer 10 nm depth. Hence, there is a massive defect segregation with defects attributed to Ti$^{3+}$ and VO tracking independently between orientations. Their opposite redistribution between (111) and (110) or (100) orientations contribute to significant surface dipoles. Photoemission spectroscopy studies of MBE-grown BaTiO$_3$/SrTiO$_3$ heterojunctions report even larger dipoles.64 The dramatic depletion of VO within the outer $\sim 10$ nm depth was also observed in electric field-induced VO migration studies$^{65}$ and is consistent with theoretical predictions.$^{66}$ Note that these KPFM measurements were performed in the dark and in air, independent of any extrinsic defects introduced by nonstoichiometry, chemical treatments, or other processing.$^{67,68}$

Previous studies of complex oxide surface polarity$^{69}$ considered II–IV perovskites such as SrTiO$_3$ with surface crystallographic orientations that are described according to Tasker notation$^{70}$ as type I Polar with Sr or TiO$_2$ surface termination for cubic (100) orientation or type III Polar with O$_2$ or BaTiO$_2$ surface termination for cubic (110) orientation or SrO$_2$ or Ti termination for cubic (111) orientation. Type I surfaces consist of a stack of neutral ionic planes. Type III surfaces consist of a stack of charge ionic planes that produce a net dipole. Significantly, the defect distribution plotted in Fig. 7(c) for the (100) surface orientation termed type I shows relatively equal intensities for the 1.9–2 eV VO and 1.62 eV Ti$^{3+}$ defects, whereas the defect distribution plotted in Fig. 7(b) for the (110) surface orientation termed type III and the defect distribution plotted in Fig. 7(a) for the (111) surface orientation also termed type III display asymmetric defect distributions—higher VO intensities for the (110) orientation versus higher Ti$^{3+}$ for the (111) orientation. Correspondingly, the (110) orientation has work function $\Delta \Phi = 4.22 \text{ eV}$, whereas the (111) orientation has work function $\Delta \Phi = 4.57 \text{ eV}$. The higher work function corresponds to a more negative (111) surface, consistent with the higher Ti$^{3+}$ versus VO near-surface ionic density. Thus, the near-surface defect distribution and work function differences versus crystal orientation can be viewed as either an electrostatic or a thermodynamic$^{66}$ effect.

V. ELECTRONIC EFFECTS OF COMPLEX OXIDE DEFECTS

Defects in complex oxides can strongly affect properties of electronic device structures—not only because of their deep level nature than can act as electrically compensating, tunneling, or recombination centers but because such defects in widely used materials such as SrTiO$_3$ or BaTiO$_3$ can diffuse under applied electric fields. The unique interface properties of these materials are particularly challenging since defects can form at or segregate to such junctions unless growth and processing conditions are well controlled.

One such example is Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ grown on SrTiO$_3$ by MBE. DRCLS shows that oxygen vacancies form at their interface as the growing Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ epilayer extracts O from the underlying substrate. Figure 8(a) illustrates this process schematically. DRCLS spectral features include the VO-R feature at 2.9 eV whose intensity depends strongly on O$_2$ pressure during the epilayer growth. With decreasing O$_2$ pressure, this feature increases by an order of magnitude as the Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ epilayer grows.$^{65}$ DRCLS
shows that this defect grows primarily in the SrTiO$_3$ at the interface with Ba$_2$Sr$_2$Ti$_2$O$_9$. Positron annihilation spectroscopy (PAS) confirms the depth location of this VO$_{R}$ growth in Fig. 8(c). PAS also provides semiquantitative defect densities, here estimated at $>10^{18}$ cm$^{-3}$. Such high densities are consistent with the dipole charge density described in Fig. 7. Figure 8(b) shows that DRCLS and PAS are natural complements since the depth dependences of incident electrons and positrons are the same. The extraction of substrate oxygen by growing oxide overlayers is well known from much earlier studies of high-temperature superconductors such as YBa$_2$Cu$_3$O$_{7-8}$ and other high-temperature superconductors as well as LaAlO$_3$ and TiO$_2$. Such oxygen outdiffusion is enabled by oxygen’s O$^{3+}$/O$^{4+}$ multiple charge states.

BaTiO$_3$ is a promising candidate for electrooptic and GHz RF devices due to its high tunable and anisotropic dielectric permittivity. Yet its dielectric loss can be limited by the presence of intrinsic point defects. Nevertheless, extended air anneals at high temperature reduce oxygen vacancies and other defects dramatically improve its RF performance at GHz frequencies.

The movement of V$_O$ under applied electric fields inside SrTiO$_3$ is a significant concern for its use for high-voltage capacitors since these defects can move macroscopic distances, forming conductive pathways and potentially contributing to dielectric breakdown.

Perhaps the most striking example of a defect contribution to interface effects has been for the LaAlO$_3$/SrTiO$_3$ interface. Here the control of oxygen vacancies by growth techniques has led to the observation of 2DHG. By strongly reducing oxygen vacancies in the SrTiO$_3$ epilayer on LaAlO$_3$, researchers could prevent the compensation of holes that would otherwise give rise to the formation of a two-dimensional hole gas (2DHG). This advance was recognized as enabling entirely new functionality in complex oxides by formation of dual 2DHG-2DEG structures. Other complex oxide interfaces such as LaNiO$_3$/La$_2/3$Sr$_1/3$MnO$_3$/SrTiO$_3$ heterostructures also exhibit unique interface-specific features that DRCLS could identify on a nanometer scale.

VI. CONCLUSIONS—NEW DIRECTIONS

The direct measurement and understanding of intrinsic point defects in complex oxides can further advance by combining DRCLS with other advanced characterization techniques. Figure 8 shows how DRCLS combined with PAS provides not only confirmation of interface-specific defect features but also calibrations (in Fig. 8, only a lower limit) of their defect densities. Positron annihilation spectroscopy can provide analogous information for complex oxides such as SrTiO$_3$. The combination of DRCLS with SPS shown here provides new information about the energy levels of depth-dependent defect densities as shown in Fig. 5. DRCLS combined with temperature-dependent Hall (TDH) measurements can correlate specific defects with donor and acceptor formation and their contribution to electrical properties. X-ray photoemission spectroscopy can define stoichiometries that correlate with specific defect emissions and their physical nature, for example, a nitrogen vacancy that acts as an Sc$_n$ impurity and oxygen doping precursor. Photo-EPR can provide energy level as well as spin-descriptive defect information. Impedance spectroscopy is yet another powerful tool for describing the electric transport properties of intrinsic point defects, particularly when combined with DRCLS in three dimensions. Finally, DRCLS combined with scanning TEM/electron energy loss spectroscopy line profiles provide powerful analytic techniques at the atomic scale that can reveal atomic composition and bonding configurations.

Overall, the results presented here show that the DRCLS and SPS techniques together can provide a powerful set of electronic, spatial, growth, and processing tools for detecting and characterizing intrinsic point defects in SrTiO$_3$, BaTiO$_3$, and other complex oxides. The combination of DRCLS with SPS with other advanced characterization techniques will further expand the understanding of these complex oxide defects and could lead not only to their physical control but also to new electronic device designs.

ACKNOWLEDGMENTS

L.J.B., J.Z., K.M., S.B., and Z.Q.Z. gratefully acknowledge support for this work by the National Science Foundation (NSF) Grant No. DMR-18–00130 (Tanya Paskova). The authors thank Lisa Alldredge, Wontae Chang, and Steven Kirchoefer at NRL for providing the (Ba,Sr)TiO$_3$ samples discussed here.

DATA AVAILABILITY

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

REFERENCES
