Probing the Origin of Interfacial Carriers in SrTiO$_3$–LaCrO$_3$ Superlattices

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Supporting Information

ABSTRACT: Emergent phenomena at complex oxide interfaces could provide the basis for a wide variety of next-generation devices, including photovoltaics and spintronics. To date, detailed characterization and computational modeling of interfacial defects, cation intermixing, and film stoichiometry have helped to explain many of the novel behaviors observed at a single heterojunction. Unfortunately, many of the techniques employed to characterize a single heterojunction are less effective for a superlattice made up of a repeating series of interfaces that induce collective interfacial phenomena throughout a film. These repeating interfaces present an untapped opportunity to introduce an additional degree of complexity, such as confined electric fields, that cannot be realized in a single heterojunction. In this work, we explore the properties of SrTiO$_3$–LaCrO$_3$ superlattices to understand the role of defects, including variations in cation stoichiometry of individual layers of the superlattice, intermixing across interfaces, and interfacial oxygen vacancies. Using X-ray photoelectron spectroscopy (XPS) and scanning transmission electron microscopy electron energy-loss spectroscopy (STEM-EELS), we quantify the stoichiometry of individual layers of the superlattice and determine the degree of intermixing in these materials. By comparing these results to both density functional theory (DFT) models and STEM-EELS measurements of the Ti and Cr valence in each layer of the superlattice, we correlate different types of defects with the associated materials properties of the superlattice. We show that a combination of ab initio modeling and complementary structural characterization methods can offer unique insight into structure–property relationships in many oxide superlattice systems.

Research into epitaxial complex oxide films and interfaces over the past few decades has broadened our understanding of fundamental physics and offered applications across a wide range of useful devices. Research on perovskite oxide thin films with the general formula of ABO$_3$ has played a major role in the field over this time. Interfaces between polar and nonpolar materials are particularly intriguing for the emergent properties they exhibit. Since the initial observation of a two-dimensional electron gas (2DEG) at the interface between films of the polar band insulator LaAlO$_3$ (LAO) and nonpolar STO substrates,† much work has focused on understanding the phenomena that occur at polar/nonpolar interfaces. In an idealized model of LAO–STO, a 2DEG is predicted to form to compensate the polar discontinuity at a nearly atomically abrupt interface, with the surface of the LAO film donating an electron to the STO at the interface.‡ However, investigations of interface composition have revealed that cation mixing is more extensive than originally thought, introducing a plethora of defects whose role in promoting conductivity is still poorly understood.§,∥ Moreover, various works have shown that the 2DEG behavior occurs only in the case of Al-rich off-stoichiometric LAO film growth under certain conditions.‡,§,∥ It is only through careful characterization of the film stoichiometry using Rutherford backscattering (RBS) and X-ray photoelectron spectroscopy (XPS) that a plausible mechanism to explain the varying behaviors between samples emerged.‡,§,∥ These studies underscore the need for thorough interface characterization using a variety of techniques before drawing definitive conclusions about the physical mechanism(s) that lead to emergent behavior.

One of the broadest fields of study of perovskite oxides is that of ferroelectricity, where materials exhibit a spontaneous
remnant electrical polarization. Ferroelectric materials are used in novel technologies including ferroelectric random access memory (FeRAM).\textsuperscript{7} Epitaxial strain can be used in thin-film growth to induce a ferroelectric phase transition in a material that is otherwise paraelectric, such as SrTiO$_3$ (STO).\textsuperscript{8} In particular, recent work has shown that when STO is grown with a slight Sr deficiency on the A-site in an ultrathin (less than a few nanometers) film, dipoles due to TiSr antisite defects will align to yield a ferroelectric polarization.\textsuperscript{9} On the other hand, others have shown that strain-induced ferroelectricity in STO grown on (La,Sr)(Al,Ta)O$_3$ (LSAT) is highly sensitive to stoichiometry and that ferroelectric response degrades rapidly when the Sr:Ti ratio is not unity.\textsuperscript{10} These results illustrate the wide range of structural handles to control emergent functionality but also show that an understanding of the defects present in oxide films is necessary to explain novel phenomena observed in oxide thin films and heterostructures.

Oxide superlattices in particular have generated significant interest due to the high density of interfaces present in such systems. In this sense, these composite materials may be thought of as exhibiting the behavior of a single interface, but having many interfaces in parallel produces “bulk-like” properties. Previous observations of a built-in potential gradient across LCO thin films grown on STO substrates make this combination of materials particularly interesting for further exploration.\textsuperscript{11} Our team has recently examined induced polarization in STO through the growth of STO$-$LaCrO$_3$ (LCO) superlattices with asymmetric positively and negatively charged interfaces.\textsuperscript{12} We found that the alternating positive and negative charges on the interfaces produce a built-in electric field within the STO that could be used to separate photoexcited electron−hole pairs for renewable energy applications. As in the case of the induced ferroelectricity in off-stoichiometry STO films\textsuperscript{9} and the defect-induced 2DEG at the LAO$-$STO interface,\textsuperscript{7} however, careful characterization of the possible defects present in the materials and understanding of the resulting effects induced by them is critical. Unfortunately, measurements of superlattice stoichiometry cannot be easily performed with the same precision as in a single heterojunction because of the lack of depth resolution. For example, due to interfacial intermixing, the large number of interfaces in superlattices, and the close overlap in atomic number of Cr and Ti,\textsuperscript{13} RBS models would have large

Figure 1. Cross-sectional STEM-EELS mapping of local composition and valence. (a) STEM-HAADF image of the overall film structure acquired during EELS mapping. (b) Composition map of the Ti $L_{23}$, Cr $L_{23}$, and La $M_{45}$ (red, green, and blue, respectively) edges constructed using multiple linear least-squares fitting (MLLS). (c) Line profile of the integrated Ti $L_{23}$ edge intensity. (d) Line profile of the Ti $L_{13}$ and $L_{23}$ edge separation $\Delta E_{Ti L_{13}-L_{23}}$ used to estimate local Ti valence; this profile falls within the bounds of a Ti$^{4+}$ state (marked by the dashed lines). (e) Line profile of the integrated Cr $L_{23}$ edge intensity. (f) Line profile of the O $K$ and Cr $L_{3,2}$ edge energy loss separation ($\Delta E_{Cr L_{3,2}-O K}$), used to estimate local Cr valence; this profile falls within the bounds of a Cr$^{3+}$ state (marked by the dashed lines). (g, h) O $K$/Cr $L_{23}$ and Ti $L_{23}$ edge spectra, respectively, extracted across the LCO/STO/LCO layers in the middle of the superlattice (dashed lines added to guide eye).
measurements of the Ti and Cr valence and the La results to cross-sectional scanning transmission electron and a single-crystal STO substrate. We then compare these

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intermixed Ti. This

evaluation increases

uncertainties in the stoichiometry of the individual layers of the superlattice. Alternative techniques employing XPS and cross-sectional electron microscopy to measure and model the composition of the superlattice are therefore extremely valuable.

In this work, we examine the composition, structure, and electronic properties of STO–LCO superlattices grown by molecular beam epitaxy on (La,Sr) (Al,Ta)O$_3$ (LSAT) (001) substrates. We have previously shown that a polarization within the STO layers of the superlattice throughout the samples is induced by alternating positively charged TiO$_2^{6−}$–LaO$^\circ$ and negatively charged CrO$_2^{−}$–SrO$^0$ interfaces in the structures. However, we also observe free carriers and conductivity in the system that was not expected based on our first-principles modeling. Using ex situ XPS sputter depth-profiling, we measure the stoichiometry of individual layers throughout the film via comparisons to an RBS-calibrated LCO reference film and a single-crystal STO substrate. We then compare these results to cross-sectional scanning transmission electron microscopy electron-energy loss spectroscopy (STEM-EELS) measurements of the Ti and Cr valence and the La–Cr stoichiometry to link how defects in individual superlattice layers mediate the overall composite behavior. In light of density functional theory (DFT) modeling, we explore the origin of interface-induced free carriers in these superlattices. We broadly categorize the interfacial defects into two categories: those which suppress a built-in electrostatic field and those which do not. We show that this combined approach is highly useful for gaining deeper insight into the behavior of superlattice materials in general. This knowledge provides an approach to control the magnitude of the field by tuning the growth protocols and, vice versa, enabling formation of preferential defects via control of field-producing structural blocks.

## RESULTS

Interfacial Phenomena. We have conducted extensive STEM-EELS mapping to provide a detailed local picture of interfacial composition and valence. Figure 1a,b shows a representative high-angle annular dark field (HAADF) STEM image and simultaneously acquired EELS chemical map of the entire heterostructure, a superlattice with repeating units of 6 STO unit cells and 3 LCO unit cells (STO$_6$–LCO$_3$). These images confirm the structure and regularity of the LCO and STO layers and reveal no apparent structural defects or imperfections in the film. Moreover, they directly confirm that the asymmetric termination of each layer is preserved throughout the superlattice. Figure 1c,d shows line profiles averaged in plane for the integrated Ti $L_{2,3}$ edge intensity and Ti $L_{1,2}$ $\Delta E_{\text{Ti}L_{2,3}}$ crystal field splitting ($\Delta E_{\text{Ti}L_{3}-\text{L}2}$), respectively, while Figure 1e,f shows similar line profiles for the integrated Cr $L_{2,3}$ edge intensity and the O $K$–Cr $L_3$ edge energy loss separation ($\Delta E_{\text{O}K3-\text{O}L3}$), respectively. The former two profiles (Figure 1c,e) indicate that Ti is present in all 3 unit cells of each LCO layer and that there is a finite Cr concentration present in all 6 unit cells of each STO layer, albeit at a lower level than the intermixed Ti. This finding is further supported by Ti $L_{2,3}$ $O_\circ$, and Cr $L_{2,3}$ edge EEL spectra extracted from an STO/LCO/STO region in the middle of the film, shown in Figure 1g,h.

Such behavior is consistent with our earlier studies of LCO–STO interfaces and suggests that Ti out-diffusion increases the thermodynamic stability of the interface. The differing Ti and Cr intermixing concentrations are primarily attributable to the difference in thickness between the STO (6 unit cells) and LCO (3 unit cells) repeating layers.

To determine whether this intermixing has any effect on valence, we have measured changes in the Ti and Cr edges, which result from transitions from spin–orbit split 2p$^{1/2}$ and 2p$^{3/2}$ core levels to unoccupied portions of the valence band with 3d character. The Ti $L_{2,3}$ edge is further split into $t_2$ and $e_g$ states by the crystal field and is highly sensitive to local valence state. While the white-line ratio method is a well-accepted means of characterizing valence, it is difficult to compare to the literature, owing to the range of background subtraction methods used, and can sometimes show a complex spatial dependence. By measuring the separation of the Ti $L_{3}$ and $L_2$ edges, we are able to explore trends in valence independent of energy drift, without the need for simultaneous background fitting. We map $\Delta E_{\text{Ti}L_{3}-\text{L}2}$ at each pixel of the spectrum image and average in the plane of the film to generate the line profile shown in Figure 1d. This measurement indicates an average separation of ~6.5 eV, similar to values reported in the literature (~6.1–6.7 eV). We find that $\Delta E_{\text{Ti}L_{3}-\text{L}2}$ decreases in the vicinity of each LCO layer to a value near that of Ti$^{4+}$, and furthermore, that the overall profile trends slightly toward a lower separation near the film surface; this result supports a slight reduction in Ti valence. One possible explanation for this is that excess La$^{3+}$, accumulated during LCO layer growth, has diffused into the STO layer and substituted for Sr$^{2+}$, acting as an electronic donor and resulting in Ti valence changes. However, we note that Ti coordination can also significantly affect the Ti edge fine structure. More work is needed to disentangle octahedral rotations from intermixing effects.

The use of the white-line ratio method is also problematic for the Cr $L_{2,3}$ edge, where the O $K$ edge continuum overlaps with the onset of the Cr $L_3$ peak, precluding an accurate background subtraction. We therefore map the energy loss separation between the Cr $L_3$ peak and O $K$ edge prepeak ($\Delta E_{\text{O}K3-\text{O}L3}$), which we and others have previously shown to be an accurate indicator of Cr valence. Figure 1f shows a line profile of $\Delta E_{\text{O}K3-\text{O}L3}$ that has been integrated in the plane of the film. The separation across each of the LCO layers falls well within the range for Cr$^{3+}$ (~46.25–46.75 eV), but we see indications of a slight reduction in Cr valence at each STO interface. This behavior is consistent with our earlier study and suggests that Cr may partially reduce to compensate the Ti$^{4+}$ cations in the adjacent STO layer, though other defects (such as antisites) may also drive reduction.

To determine whether free carriers are indeed present at the buried interfaces, spectroscopic ellipsometry was performed on the STO$_6$–LCO$_3$ superlattice shown in Figure 1, along with a pristine STO thin film on LSAT and STO$_{30}$–LCO$_{20}$ and STO$_{40}$–LCO$_{20}$ superlattices. These results are shown in Figure 2. The Drude peak at low binding energy for all three superlattices indicates that free carriers are present in the system. The presence of free carriers is confirmed by electrical transport measurements, which yield sheet resistances of 1–20 k$\Omega$/square at room temperature when measured using the van der Pauw method. The Drude peak intensity scales with interface density, with the smallest peak found in the STO$_{40}$–LCO$_{20}$ film that has the lowest interface density, suggesting that the carriers are primarily present at the interfaces of the superlattices. We also note that the shoulder between 2.5 and 3.5 eV scales with interface density. This shoulder can be attributed to Cr–O–Ti bonds across the interface, as we have previously observed in...
La, Cr codoped SrTiO₃ films that exhibit visible light absorption. The observed conductivity and free carrier concentrations are not predicted to occur in the idealized superlattices, suggesting that they may be the result of defects or nonidealities during the film growth process. These could include variations in cation stoichiometry in the layers of the superlattice or interfacial oxygen vacancies. In the following sections, we explore the effects of both of these mechanisms on the polarization in the superlattice by detailed characterization and ab initio modeling.

**Film Stoichiometry.** To probe the stoichiometry of the superlattice, depth-profile X-ray photoelectron spectroscopy measurements were performed on the STO₈−LCO₄ superlattices. The results were compared to measurements made using the same sputter energy on a LaCrO₃ reference film grown on a SrTiO₃ substrate with the La:Cr ratio verified to be 1.00(5) using Rutherford back scattering spectrometry measurements. The Sr 3d, Ti 2p, Cr 2p, and La 3d peak areas were measured and compared for both samples and are summarized in Figure 3. The STO ratios were averaged using a simple boxcar average over a period of one layer of the superlattice, while the LCO ratios were measured at the point of greatest peak area for the La 3d peak. This approach for LCO takes into account the different escape depths for photoemitted electrons from the high binding energy La 3d (~834 eV) and Cr 2p (~570 eV) from the 3 unit cell thin layers. In the case of the thicker 6 unit cell STO layers, the escape depths are greater for Ti 2p (~459 eV) and Sr 3d (~133 eV), meaning that a boxcar average over one period of the superlattice provides a reasonable measure of the stoichiometry through the entire depth of the layer. The gradual decay in peak intensity in Figure 3b is most likely due to roughening of the film surface during Ar⁺ sputtering, which reduces electron escape depth and overall peak intensity. A similar trend of overall peak intensity in the Ti 2p and Sr 3d ratio is observed for the STO peaks in Figure 3a (not shown).

In Figure 3a, we see that the STO ratio remains with the measurement range for stoichiometric STO throughout the STO₈−LCO₄ film.

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**Figure 2.** Extinction coefficient, k, derived from spectroscopic ellipsometry for the STO₈−LCO₄, STO₆−LCO₄, and STO₄−LCO₄ superlattices and an STO reference.

**Figure 3.** Sputter depth-profile XPS analysis of (a) SrTiO₃ and (b) LaCrO₃ stoichiometry throughout the STO₈−LCO₄ film.
Figure 4. Substitutional dopant models of impact of (a) variations in SrTiO$_3$ stoichiometry; (b) variations in LaCrO$_3$ stoichiometry; and (c) oxygen vacancies induced by Cr-rich LaCrO$_3$ layers. Key: La, purple circles; Sr, yellow circles; Cr, red octahedral; Ti, green octahedral; O, light blue circles. The difference in B-site bond length is equal to the length of the B–O bond between the apical oxygen above the B site ion in the figure minus the length of the B–O bond between the apical oxygen below the B site ion.

layer-by-layer growth process and the relatively long deposition times for each unit cell (86 s/unit cell), this diffusion to the surface is likely to be facile. Collectively, these results suggest that cation vacancy concentrations are likely to be low when compared to other defects that may be present in the system. This also means that any variations in the stoichiometry for either LCO or STO are likely to produce substitutional dopants in the neighboring layers while leaving the overall A-to-B site ratio close to the ideal value. We refer to this as “off-stoichiometry” within a single superlattice unit in the models that follow.

Substitutional doping due to off-stoichiometry in the LCO or STO layers of the superlattice can occur at either the nominally positively charged LaO+/TiO$_2$ interface or at the negatively charged SrO−−CrO$_2^-$ interface. The structural model for these defects and corresponding geometrical parameters of the superlattice are summarized in Figure 4a,b, with (a) showing the effects of off-stoichiometry within the STO layer and (b) showing the effects of off-stoichiometry within the LCO layer. Substitutional dopants at both interfaces are considered for each case, with the ± notation used to describe the interface at which the substitution is made (i.e., Cr$_{Ti}$ to indicate Cr substituted for Ti at the LaO+/TiO$_2$ interface). The graphs show the difference in the B–O bond lengths along the c-axis (growth direction), which is directly correlated with a built-in electric field in the material. A schematic showing how the difference in B–O bond lengths in the figure is calculated is provided in the Supporting Information (Figure S4). Any La$_{Sr}$ substitution would electron-dope the STO layer, while a Sr$_{La}$ substitution would hole-dope the LCO layer. Each could conceivably screen the electric field and eliminate the polarization. Cr$_{Ti}$ substitutions replace a $d^5$ Ti$^{4+}$ cation with a $d^3$ Cr$^{3+}$ ion with an available hole at the top of the valence band, while Ti$_{Cr}$ substitutions replace a $d^3$ Cr$^{2+}$ with a $d^5$ Ti$^{4+}$, which adds an electron to the LCO layer near the conduction band of the neighboring STO layer. In both cases, these substitutions may add carriers to the system at room temperature, as the holes and electrons are weakly bound. Somewhat surprisingly, we find from the models that the built-in polarization is preserved in the majority of cases. Only in cases of hole-doping at the positively charged interface (Sr$_{La}$ or Cr$_{Ti}$) do we see screening of the electric field. Indeed, in both cases a hole at the positively charged interface will be electrostatically repelled toward the negatively charged interface. The substitutional Cr$_{Ti}$ ion at the positively charged interface adopts the charge states of 3+ while a Cr in LCO at the negatively charged interface adopts a +4 charge state. A Sr$_{La}$ substitution at the positively charged interface yields an analogous charge redistribution. Both substitutions cancel out the electric field due to the hole on the Cr$^{3+}$ ion at the negatively charged interface, which screens the polarization. This eliminates the polarization in the material, as can be observed in the case of the Sr$_{La}$ and Cr$_{Ti}$ bond distortion curves in Figure 4. Furthermore, these configurations are found to have a lower total free energy than the opposite case of hole-doping at the negatively charged interface, suggesting that a screened polarization is energetically favorable. Interestingly, the converse does not hold, in that an electron donated from La$_{Sr}$ or Ti$_{Cr}$ substitutions does not screen the field, regardless of the interface where the defect occurs. Given that we experimentally observe cation distortions and a built-in field in good agreement with the theoretical predictions, this suggests that any free carriers are likely to be electrons rather than holes, which would screen the field.

The observed polarization in slightly Cr-rich LCO layers, which may be present deeper within the film based on our XPS depth profile, raises questions as to the effects that we observe, since hole-doping is expected to screen the electric field in the Cr-rich regime where holes would be expected. Given the instability of octahedrally coordinated Cr(IV) and the presence of a hole at the top of the valence band that can readily be neutralized through the formation of an oxygen vacancy, a defect pair formed by a substitutional Cr$_{Ti}$ and an oxygen vacancy needs to be considered. We have modeled additional configurations for each Cr$_{Ti}$ substitutional case with a...
neighboring oxygen vacancy at two locations: in the equatorial BO$_2$ plane, and in the neighboring axial AO plane found to be most energetically favorable. These configurations are shown in Figure 4c, along with the original Cr$_{Ti}$ substitutional cases. We note that a single oxygen vacancy adds two electrons to the system but that only one Cr ion is present to be reduced, so an additional electron is added to the system. In each case, through analysis of the charge and spin distributions in the models, we find that the substitutional Cr ion is reduced to Cr$^{3+}$ as expected. Furthermore, we see that the electric field and bond length distortions are preserved. The additional electron contributes charge over both neighboring Ti and Cr, reducing each toward Ti$^{3+}$ and Cr$^{2+}$. Given that we have observed no spectroscopic evidence in either our previous XPS analysis or in the EELS data presented in this work for Cr$^{4+}$, we suggest that in the case of excess Cr in the LCO layers that interface oxygen vacancies form and the polarization is preserved.

**Oxygen Vacancies.** Direct measurement of interfacial oxygen vacancies is notoriously difficult, but their presence is often inferred from the observed chemical valence or electronic behavior of these materials.$^{13}$ Our observations of free carriers and evidence of interfacial Ti$^{3+}$ suggest that oxygen vacancies are likely to be present, either due to cation off-stoichiometry, such as excess Cr in the LCO layers, or due to incomplete STO oxidation at the interface. To understand the effects of oxygen vacancies in an otherwise ideal lattice, DFT models of various oxygen-deficient configurations were constructed with oxygen vacancies in each AO and BO$_2$ plane in the superlattice. Oxygen vacancies were found to be most energetically stable near the interfaces compared to the bulk, though a side-by-side energy comparison between a fully oxidized film and the oxygen deficient structures is not possible using this method to determine if oxygen vacancy formation would be preferred to the fully oxidized case. The results of these simulations are shown in Figure 5, with schematics of the four oxygen deficient structures shown in (a) and Bader ionic charge$^{34}$ and the bond length differences shown in (b) and (c), respectively.

We find that the polarization is preserved in three of the four cases, with an oxygen vacancy in the TiO$_2$ plane adjacent to the SrO−CrO$_2$ negatively charged interface (referred to as TiO$_2$ in Figure 5c) as the lone exception where the polarization is screened. In this case, the oxygen vacancy donates two electrons to the system, and the population analysis indicates that they are distributed with one electron lying on a Ti$^{3+}$ ion at each interface. This electronic configuration neutralizes the electric field and completely screens the polarization, with no change in the Cr valence. Conversely, in the case of an oxygen vacancy in the AO planes at each interface, one electron is donated to the nearest-neighbor Ti ion, while the other lies on the neighboring Cr ion, as can be seen by the purple square and yellow diamond with charge of $\sim$1.2e in the LCO region of Figure 5. Similar Bader charge behavior was predicted in the DFT model for the Cr$_{Ti}$ substitution at the negatively charged interface with an oxygen vacancy in the SrO plane (Cr$_{Ti}$−VO$_{ox}$ in Figure 4c). This Bader charge corresponds to a 2+ formal charge on the Cr ion, in agreement with the trend observed in the Cr STEM-EELS data in Figure 1 and observed previously.$^{23,25}$

### DISCUSSION

Our experimental and computational results have allowed us to produce quantitative estimates of the stoichiometry of each layer of a STO−LCO superlattice. Based on the detailed STEM-EELS analysis, we can correlate the film stoichiometry with the observed interfacial valence phenomena and the built-in polarization to better understand the source of free carriers in the system. Our depth-profile XPS analysis showed that the STO stoichiometry is essentially ideal throughout the superlattice. While we have not considered the effects of cation vacancies or antisite defects in the STO, these would not be expected to suppress the observed polarization.$^{9}$ However, we do not observe any measurable deviation in the STO stoichiometry, suggesting that these defects are unlikely to be the main driver of our observed polarization.

Near the film surface, we detect a possible excess of La ions relative to Cr in the LCO layers of a few atomic percent in the depth profile XPS analysis. In this region, we also observe a more pronounced trend of Ti reduction at the Ti L$_{2,3}$ edge, indicating that excess La has donated electrons in the STO layer. This trend alone could be sufficient to explain the free carriers that are observed. Our ab initio simulations indicate...
that free electrons donated by excess La may reduce the polarization near the interfaces but do not eliminate the effect, which is in agreement with our previous experimental observations.12

Beyond effects due to cation stoichiometry, the observed valence changes near the interface suggest that oxygen vacancies may be present even in regions where the cation stoichiometry is nearly perfect. Our models indicate that these vacancies would reduce both the Ti and Cr ions near the interface, in agreement with our STEM-EELS observations. It is also likely that any Cr excess in an LCO layer would promote the formation of oxygen vacancies. In this case, the vacancy would donate one electron to reduce the excess Cr ion to a 3+ formal valence, while the second electron from the vacancy could either compensate a second excess Cr ion or contribute a free electron to the system. This type of behavior is qualitatively similar to what has been observed in the case of Al-rich LAO films grown on STO, where carrier concentrations increased in the cases of Al-rich films.5,6

■ CONCLUSION

Using complementary X-ray spectroscopy and electron microscopy techniques, we have shown a new approach to characterize the stoichiometry of a LaCrO3−SrTiO3 superlattice on a layer-by-layer basis. This understanding of the properties of each layer of the superlattice allows us to study the effects of various defects and nonidealties in the materials using a combination of density functional theory modeling and electron energy-loss spectroscopy. We find that excess La ions in the LCO layer of the superlattice contribute free carriers to the neighboring STO layers. Meanwhile, excess Cr ions promote the formation of interfacial oxygen vacancies. These vacancies produce a combination of Cr2+ and Ti3+ ions while also preventing the formation of a Cr4+ hole that would screen the built-in polarization in the superlattice.

■ METHODS

Film Synthesis. Epitaxial superlattices were synthesized via molecular beam epitaxy using atomic fluxes from metal effusion cells containing each cation element using a technique described previously.7 The effusion cells were initially calibrated using a quartz crystal rate monitor to ~5% precision to achieve a growth rate of 43 Å per atomic layer (AO or BO2 plane). Prior to superlattice growth, a homoepitaxial SrTiO3 lattice on a layer-by-layer basis. This understanding of the properties of each layer of the superlattice allows us to study the effects of various defects and nonidealties in the materials using a combination of density functional theory modeling and electron energy-loss spectroscopy. We find that excess La ions in the LCO layer of the superlattice contribute free carriers to the neighboring STO layers. Meanwhile, excess Cr ions promote the formation of interfacial oxygen vacancies. These vacancies produce a combination of Cr2+ and Ti3+ ions while also preventing the formation of a Cr4+ hole that would screen the built-in polarization in the superlattice.

X-ray Photoelectron Spectroscopy. Author: Angle-resolved measurements were performed on the sample after growth by transferring under ultrahigh vacuum to an appended XPS chamber with a Scienta R3000 analyzer and monochromated Al Kα source. An electron flood gun was used to prevent charging due to the insulating nature of the substrate. The Cr and Ti 2p core levels were measured at normal emission and over an angular range from 0° to 80° off-normal to vary the degree of surface sensitivity. Measurements were also made on the Sr 3d and La 4d peaks and showed analogous behavior, though incomplete charge compensation by the flood gun affected the quality of some of the data. Depth profile measurements of the Cr 2p, Ti 2p, La 3d, and Sr 3d were made using a PHI Quanta X-ray Microprobe XPS system with a focused monochromatic Al Kα (1486.7 eV) source. Ar+ ions with energies of 500 eV were used to sputter through the superlattice slowly, with data acquired at a density of one to two scans per perovskite unit cell in the superlattice (~2–3 Å/scan). Depth profile measurements through an STO single crystal and LCO film with stoichiometry calibrated using Rutherford back scattering were used to determine the peak sensitivity factors. Background reduction and depth-profile measurements using a traditional Shirley background,62 and the peak area ratios were then calculated over the relevant energy range.

Scanning Transmission Electron Microscopy. Samples were prepared for TEM using an FEI Helios NanoLab Dual-Beam Focused Ion Beam (FIB) microscope and a standard lift out procedure, with initial cuts made at 30 kV and final polishing done at 5 kV/5 s6 and 2 kV/6° incidence angle.63 An additional reference sample for bulk valence states was prepared from a thick (~40 nm) LaCrO3 film deposited on SrTiO3. EELS maps and STEM-HAADF images were collected on a Cs-corrected Nion UltraSTEM 100 operated at 100 keV, with a convergence angle of 30 mrad. The HAADF inner and outer collection semiangles were 182 and 190 mrad, respectively. Additional mapping was performed on a Cs-corrected Nion UltraSTEM 100MC operated at 100 keV, with a convergence angle of 30 mrad. The EELS collection semiangle was 44 mrad. Spectra were collected with 0.5 eV ch⁻¹, 0.3 eV ch⁻¹, and 0.2 eV ch⁻¹ dispersions, yielding effective energy resolutions of 1.5, 0.9, and 0.6 eV, respectively. No plural scattering correction was performed since zero loss measurements confirm that the samples are sufficiently thin (t/L ≈ 0.5 MFP). Maps of ∆Ep=1.1L and ∆Ep=0.3L were calculated using the STIsTools plugin2 for Digital Micrograph.

Density Functional Theory. We employed the density functional theory (DFT) with the exchange-correlation functionals of Perdew–Burke–Enzerhof80 and modified for solids (PBEsol)80 to examine ideal [SrTiO3]6/[LaCrO3]3 system various structural models were constructed with oxygen vacancies, substitutional dopants, and intermixed interfaces. We first examined the stability of a single oxygen vacancy and the vacancy-induced charge redistribution as a function of its position in the heterostructure. The charge redistribution was analyzed using the method proposed by Bader.84 To examine the effect of the vacancies on the internal electrostatic field, we employed the same methodology as in the idealized model. Similar calculations and analysis were performed for the Ti ⇔ Cr and Sr ⇔ La intermixed cation configurations as well as for the off-stoichiometric configurations for both n- and p-type interfaces. In the latter case we considered defects formed by excess Ti occupying the Cr site (Tic) in LCO and vice versa (Cr3T) and, similarly for the site of the lattice, Sr1 and La1. Cr1 substitutions with a correlated oxygen vacancy were also modeled.

■ ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmate.6b04329.

Experimental and computational studies of cation intermixing in the behavior of these samples and atom
probe tomography of the superlattices to study cation intermixing and stoichiometry (PDF)

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