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Correlative Aberration-Corrected STEM-HAADF and STEM-EELS Analysis of Interface-Induced Polarization in $LaCrO_3$-$SrTiO_3$ Superlattices

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Emergent phenomena at complex oxide interfaces have attracted considerable attention as the basis for a variety of next-generation devices, including photovoltaics and spintronics. Tremendous progress has been made toward understanding the role of interfacial defects, cation intermixing, and film stoichiometry in single heterojunction systems; however, the techniques commonly used to study these interfaces, such as X-ray photoelectron spectroscopy, are less effective to understand emergent interfacial behavior in superlattices. In this work we explore the induced ferroelectric polarization in superlattices of $LaCrO_3$ (LCO) and $SrTiO_3$ (STO) using a combination of aberration-corrected scanning transmission electron microscopy (STEM) and monochromated electron energy loss spectroscopy (STEM-EELS). We show that a correlative approach, utilizing an array of local and non-local probes, is necessary to fully understand the defect-mediated origin of the induced polarization in this system.

We have conducted detailed structural characterization of several LCO-STO superlattices, as shown in Figure 1. We employ high-angle annular dark field imaging (STEM-HAADF) to directly measure the induced ferroelectric polarization in the STO layers. We first acquire a relatively high-speed time series of multiple fast frames ($0.4\ \mu s\ px^{-1}$), which we then process using both rigid and non-rigid correction routines to remove both sample drift and scan noise. Using this procedure we are able to directly measure the induced ferroelectric polarization with picometer precision, as we have demonstrated elsewhere [1]. Our results reveal that the built-in asymmetric potential across the LCO / STO interfaces is sufficient to induce a sizable polarization, on the order of 40-70 $\mu C\ cm^{-2}$, in good agreement with density functional theory calculations [2].

We next perform detailed characterization of chemical intermixing and local fine structure changes to explore how defects affect the induced polarization. Figure 2 shows the result of monochromated EELS measurements of the Ti L_{23} edge fine structure, overlaid onto the integrated Ti L_{23} edge signal. We observe significant Ti intermixing through the superlattice, as well as subtle fine structure changes in the vicinity of the LCO layers. Mapping the Ti crystal field splitting across the film, we find evidence for a slight reduction in Ti valence from 4+ to 3+ in the vicinity of the LCO layers, likely the consequence of La^{3+} substitution for Sr^{2+}. Further evidence is provided by measurements of the Ti L_3 t_{2g} / e_g ratio, which we find is comparable to a 4+-like state in the middle of each STO layer. Moving toward the LCO the ratio begins to decrease within the intermixed region, indicating a redistribution of electrons from t_{2g} to e_g states, concomitant with a reduction in valence. Our results suggest that the induced ferroelectric polarization is robust against even sizable chemical intermixing and illustrate the importance of correlative, local characterization of superlattice structures.

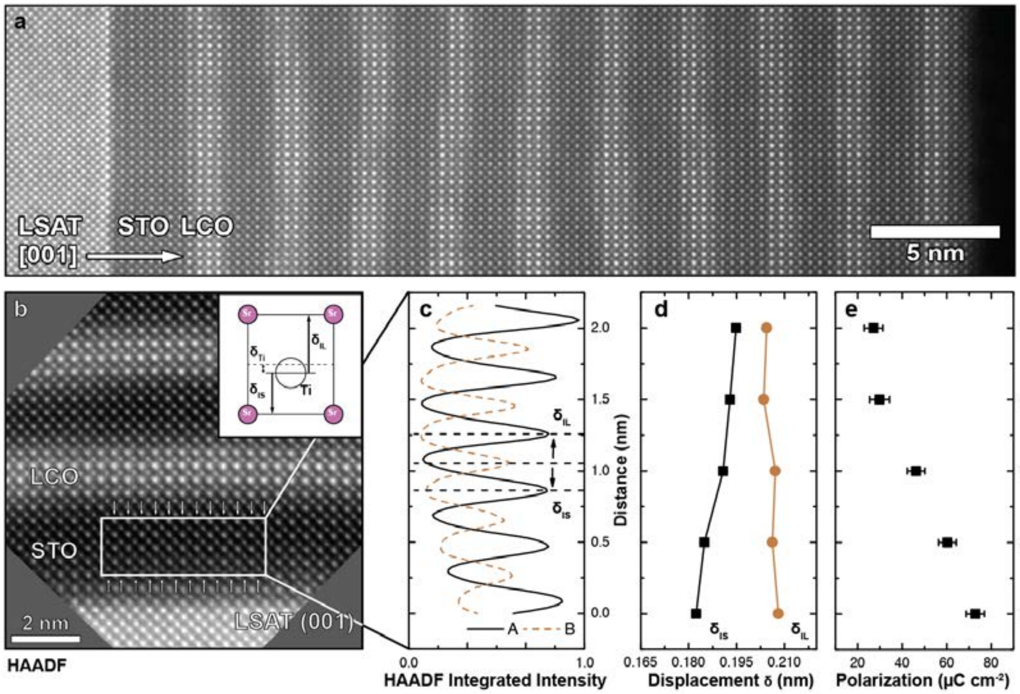

Figure 1: STEM analysis of induced polarization. A) Representative STEM-HAADF micrograph and model of 6 u.c. $SrTiO_3$- 3 u.c. $LaCrO_3$ superlattice with STO cap. B) Drift-corrected representative cross-sectional STEM-HAADF micrograph of the STO buffer layer, inset with an illustration of the unit cell. C) Average intensity profiles of the *A*- and *B*-site columns in A. D) Measurement of the short and long displacement vectors for each unit cell. E) Estimate of local polarization for each unit cell.

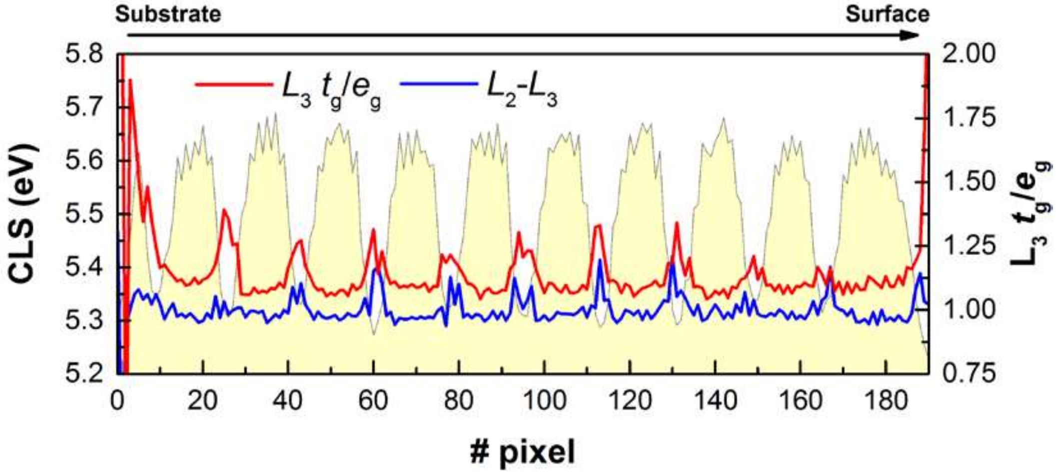

Figure 2: Monochromated EELS analysis. Measurement of Ti L_3 t_g / e_g peak ratio and Ti $L_2 - L_3$ crystal field splitting parallel to the superlattice growth direction, overlaid with integrated Ti L_{23} signal.

References

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