

Charge Transfer at $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ / SrTiO_3 Interfaces Probed by Spectroscopic Imaging in an Aberration-Corrected STEM

Julia A. Mundy,^{*} Lena Fitting Kourkoutis,^{*} Yasuyuki Hikita,^{**} Takeaki Hidaka,^{**} Harold Y. Hwang,^{*,***} David A. Muller,^{*}

^{*} School of Applied and Engineering Physics, Cornell University, Ithaca, NY 14853

^{**} Dep. of Advanced Materials Science, University of Tokyo, Kashiwa, Chiba 277-8561, Japan

^{***} Japan Science and Technology Agency, Kawaguchi, Saitama 332-0012, Japan

As a function of temperature, pressure and magnetic field, transition metal oxides can access almost every physical ground state known [1]. Due to the close lattice matching of many materials in this class, engineered heterostructures can be created by epitaxially growing one oxide on another; the properties at this oxide-oxide interface can be wildly different from those in the bulk [2]. For the successful integration of these exotic phases into devices understanding the chemical and electronic reconstructions at the interface is crucial as it can dominate the properties of the thin films. Here, we show how atomic-resolution electronic structure information can be reliably extracted from spectroscopic imaging and related to physical and transport properties. Using these techniques we explore growth and intrinsic effects at interfaces of a series of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) oxides grown on 0.01 wt% Nb-doped SrTiO_3 (STO).

Scanning Transmission Electron Microscopy (STEM) in combination with Electron Energy Loss Spectroscopy (EELS) allows for spatially resolved, chemically sensitive investigations of oxide interfaces. We used a Nion 5th-order aberration corrected 100 keV dedicated STEM ($\alpha_{\text{max}} = 33$ mrad) to collect spectroscopic images of five LSMO / STO interfaces ranging from $x = 0$ (LaMnO_3) to $x = 0.5$ ($\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$). With both high spatial resolution ($\sim 1\text{\AA}$) and high usable collected beam current (nearly 300 pA), the two dimensional distribution of Ti, La and Mn atoms across the interface can be extracted in minutes as shown in Fig. 1. There is substantial chemical inter-diffusion in the LaMnO_3 interface (Fig. 1a) not manifest in the Sr doped samples ($x > 0$). In addition to understanding this chemical inter-diffusion, detailed analysis of the EELS fine structure across the interface lends insight into the corresponding electronic reconstruction.

In particular, we tracked the interfacial fine structure changes of the Mn $L_{2,3}$ edge as a function of doping. The formal Mn valence ranges from +3 to +3.5 as the Sr concentration is increased from $x=0$ to $x=0.5$. At the interface, we observe a decrease in the Mn valence, shown in Fig. 2, as expected from the polar discontinuity model [3]. To quantify this valence change, we used multivariate curve resolution (MCR) on the $\text{LaMnO}_3/\text{STO}$ interface to extract an interfacial Mn component, which is consistent with Mn^{+2} . All five spectroscopic images were then fit with a linear combination of the Mn +2, +3 and +3.5 reference spectra. This allows us to quantify the excess charge at the individual interfaces as shown in Fig. 3 to directly compare to the polar discontinuity model. We further connect the presence of this interfacial charge with transport measurements performed on the samples. [4]

1. E. Dagotto. *Science* 309 (2005) 257.

2. N. Reyren et al. *Science* 317 (2007) 1196.

3. N. Nakagawa, H. Y. Hwang, D. A. Muller. *Nature Materials* 5 (2006) 204.

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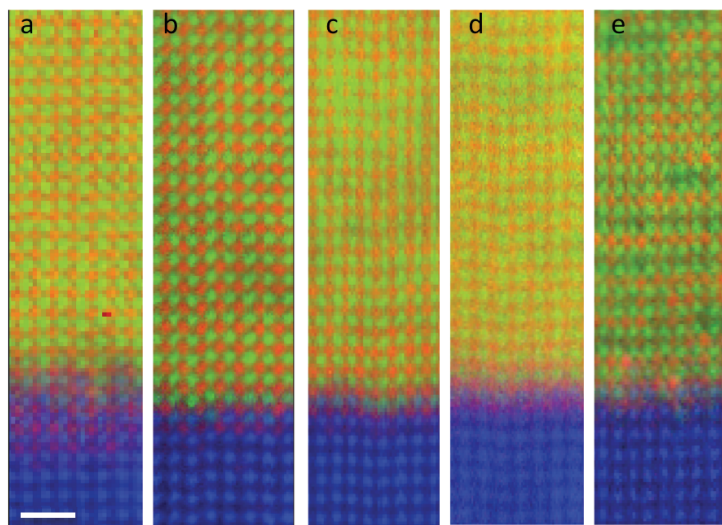


FIG. 1. EELS spectroscopic images of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ for x equal to 0, 0.1, 0.2, 0.3 and 0.5 in a – e respectively. The Mn concentration is plotted in green, Ti in blue and La in red. The scale bar is 1.5 nm.

FIG. 2. Bonding changes at the $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3/\text{SrTiO}_3$ interface (Fig. 1b). a) The Mn $L_{2,3}$ edge across the interface. b) A larger view of the interfacial region from the white box in a. c) Reference spectra of the bulk and interfacial component extracted from MCR. d) The 2-D fit of the reference spectra in b to the map (cropped from 1b due to space constraints) demonstrating atomic bonding information.

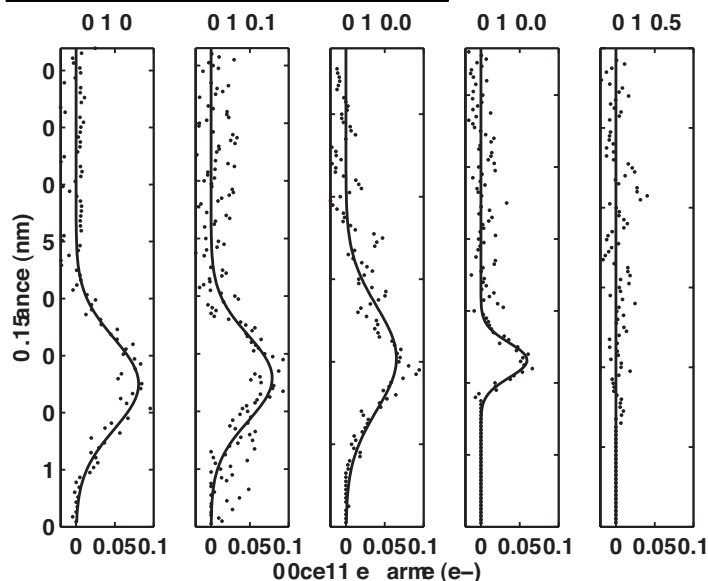
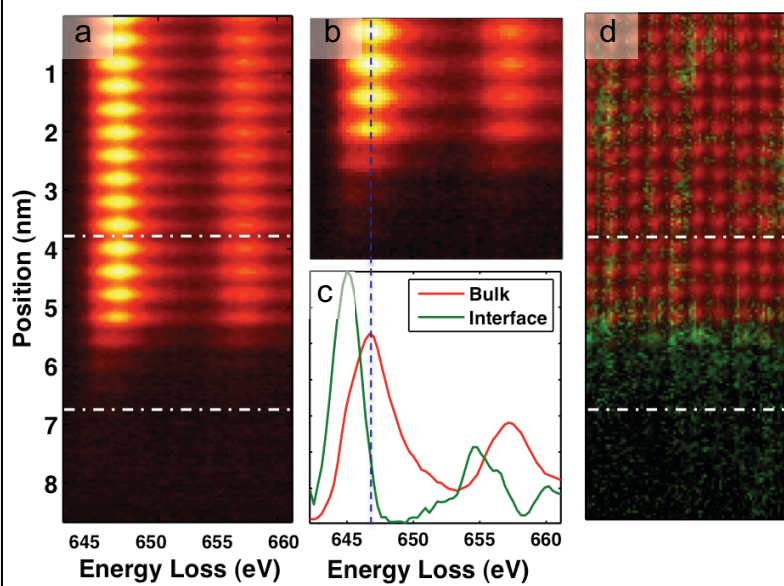


FIG. 3. Quantification of the difference between the mean Mn valence in the bulk and the observed valence at the interface for the samples in Figure 1 a-e. Excess charge is computed in electrons for direct comparison to polar discontinuity model. There is a trend towards decreasing interfacial charge as a function of the Sr doping (x).