

## Interfacial Coupling and Polarization of Perovskite ABO<sub>3</sub> Heterostructures

Lijun Wu<sup>1</sup>, Zhen Wang<sup>1,2</sup>, Bangmin Zhang<sup>3</sup>, Liping Yu<sup>4</sup>, G.M. Chow<sup>3</sup>, Jing Tao<sup>1</sup>, Myung-Geun Han<sup>1</sup>, Hangwen Guo<sup>2</sup>, Lina Chen<sup>2</sup>, E.W. Plummer<sup>2</sup>, Jiandi Zhang<sup>2</sup>, and Yimei Zhu<sup>1</sup>

<sup>1</sup>. Condensed Matter Physics and Materials Science, Brookhaven National Lab, Upton, NY, USA

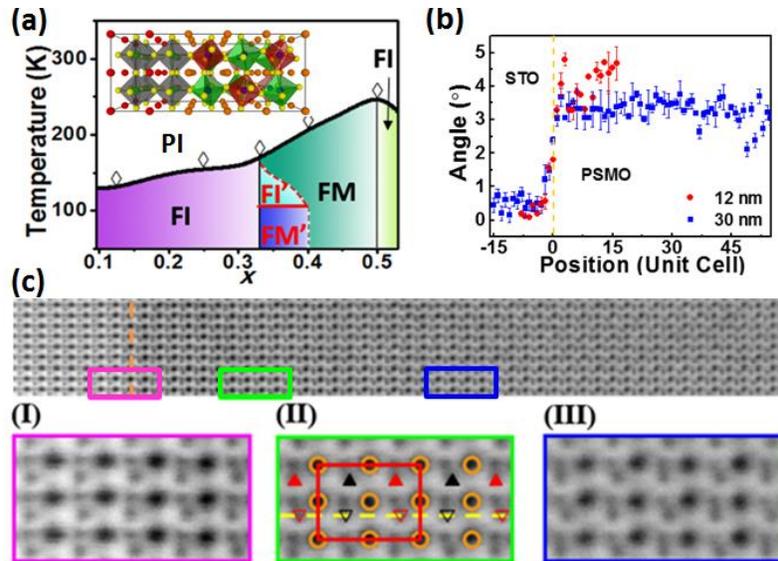
<sup>2</sup>. Department of Physics & Astronomy, Louisiana State University, Baton Rouge, Louisiana, USA

<sup>3</sup>. Department of Materials Science & Engineering, National University of Singapore, Singapore

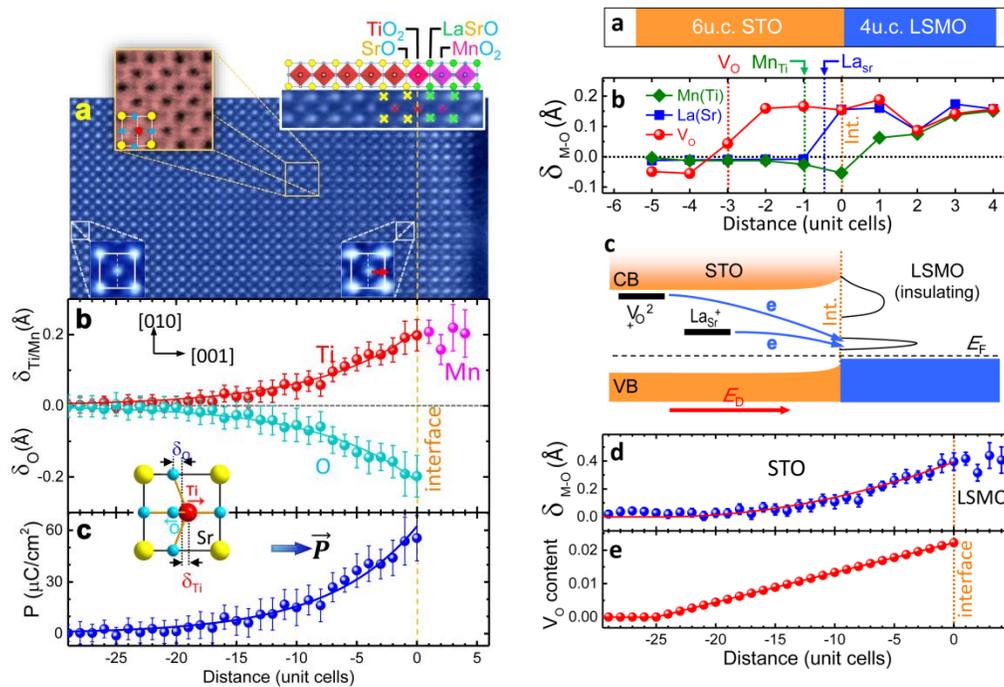
<sup>4</sup>. Department of Physics, Temple University, Philadelphia, Pennsylvania, USA

Interfaces with subtle difference in atomic and electronic structures in perovskite ABO<sub>3</sub> heterostructures often yield intriguingly different properties, yet their exact roles remain elusive. In this presentation, we report an integrated study of unusual transport, magnetic, and structural properties of Pr<sub>0.67</sub>Sr<sub>0.33</sub>MnO<sub>3</sub> (PSMO) films and La<sub>0.67</sub>Sr<sub>0.33</sub>MnO<sub>3</sub> (LSMO) films of various thicknesses on SrTiO<sub>3</sub> (STO) substrate. In particular, using atomically resolved imaging and electron energy-loss spectroscopy (EELS), we measured interface related local lattice distortion, BO<sub>6</sub> octahedral rotation and cation-anion displacement induced polarization. In the very thin 12nm PSMO film, an unexpected interface-induced ferromagnetic polaronic insulator phase was observed during the cubic-to-tetragonal phase transition of the STO substrate (Fig.1). We noted the interface induces significant asymmetrical MnO<sub>6</sub> tilt, resulting in a remarkable deviation of the bond length and angle from its bulk counterpart. However, this was not observed in thicker, say 30nm, films. Quantitatively measurements of the depth-profiles of MnO<sub>6</sub> octahedral tilt through mapping of the oxygen positions using ABF-STEM imaging revealed the film thickness dependent non-uniform interfacial environment. Such an environment enhances the site disorder strength ( $\Delta$ ) due to the random local TiO<sub>6</sub> tilt near the STO interface at the onset of cubic-tetragonal phase transition of STO near 110K. Increasing softening of the  $\Gamma_{25}$  phonon mode with decreasing temperature may strengthen electron-phonon interaction ( $\lambda$ ) of PSMO film through interfacial coupling by decreasing carrier relaxation time. Both enhanced  $\lambda$  and  $\Delta$  could lead to the formation of the theoretically predicted polaronic insulator FI<sup>†</sup> state in the 12 nm film (see Nano Lett. 16, 4174–4180 (2016)).

The interfaces of the ABO<sub>3</sub> heterostructures not only affect the structural integrity of the film but also the substrate. In ultrathin 4-unit-cell (u.c.) LSMO films we observed an interface induced remarkably deep polarization in non-ferroelectric STO substrate. Left panel of Fig.2 shows the atomic displacements of O ( $\delta_{\text{O}}$ ) and Ti ( $\delta_{\text{Ti}}$ ) as a function of distance from the interface. Based on the displacement the polarization density was determined to be about 54  $\mu\text{C}/\text{cm}^2$  at the position 1u.c. from the interface, being consistent with our off-axis electron holography measurement. Atomically resolved EELS measurements revealed that there is an off-stoichiometry of Sr at the interface and 1u.c. wide intermixing of Mn and Ti across the interface. We found substitutional Ti in the LSMO film has a reduced valence state, about 3.4<sup>+</sup>, compared with the 4<sup>+</sup> valence in STO. Small variation of the O-K edge fine structure was observed in the STO polarized region, indicating the existence of oxygen vacancies, which donate electrons to the interface. DFT based first-principles calculations using the generalized gradient approximation were carried out to elucidate the origin of the polarization in STO. We demonstrated that the Mn<sub>Ti</sub> defects (substitution of Mn on Ti site) result in rather small  $\delta_{\text{M-O}}$ ; in contrast, La<sub>Sr</sub> and V<sub>O</sub> defects induce large positive  $\delta_{\text{M-O}}$  in STO. The electron transferred from the donor defects to the LSMO empty state can build up an electric field ( $E_D$ ), which leads to polar-displacements of STO towards the interface (right panel of Fig.2). Combined with our experiments we propose that the observed deep polarization is induced by an electric field originating from low concentration of oxygen vacancies V<sub>O</sub> that extend beyond a dozen unit-cells from the interface (from ~2.2% at the interface to zero at 25u.c. away from the interface). Our study provide direct evidence of the role of defects in the emergent interface properties of transition metal oxides (see Phys. Rev B, 94 155307(2016)). Work at Brookhaven was supported by the US-DOE, BES-MSE, under Contract No. DESC0012704. Work at Louisiana State was supported by US-DOE under Grant No. DOE DE-SC0002136. Work at University of Singapore was supported by the Singapore NRF under CRP Award No. NRF-CRP10-2012-02. The calculations were performed at the Janus supercomputer supported by US NSF under Grant No.CNS-0821794 and the University of Colorado.



**Figure 1.** Phase diagram for 12 nm thick film of  $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$  (PSMO) on  $\text{SrTiO}_3$  (STO) showing the interface induced ferromagnetic insulating (FI') and ferromagnetic metallic (FM') phases. (b)  $\text{BO}_6$  octahedra a-/b- tilt angle as a function of distance from the interface for 12nm (red) and 30nm (blue) films. (c) Annular bright-field image of the 12nm film showing the asymmetric oxygen displacement and octahedral tilt across the interface (orange line marks the interface with PSMO on the left and STO on the right). Panel I, II, and III (left to right) correspond to the boxed area above. The triangles in II mark the oxygen positions while the circles and unmarked dots correspond to the Pr/Sr and Mn positions, respectively.



**Figure 2.** Left Panel: (a) A HAADF-STEM image of the interface region of 4u.c.  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  (LSMO) film on  $\text{SrTiO}_3$  (STO) viewed along the [100] direction. A zoom-in ABF-STEM and two HAADF-STEM images show distinct shifts of the Ti- and O-atoms. (b) Measured B-site (Ti, Mn) and O displacements as a function of position from the interface ( $x = 0$ ) with the exponential fitting profile (solid curves). (c) The polarization density  $p$  of STO derived from the atomic displacements in b, which is consistent with electron holography measurements. Right Panel: (a-b) DFT calculations of the  $\delta_{\text{M-O}}$  displacements induced by O-vacancy ( $\text{V}_\text{O}$ ), La-on-Sr ( $\text{La}_\text{Sr}$ ) and Mn-on-Ti ( $\text{Mn}_\text{Ti}$ ) defect, respectively. The locations of these defects are indicated by dashed vertical lines. (c) Schematic defect-level and band diagram. (d) The  $\delta_{\text{M-O}}$  displacements fitted with calculated one caused by  $\text{V}_\text{O}$  (red curve) with concentration shown in (e). The chemical defects near the interface used in calculations were determined by atomically resolved EELS measurements.