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Atomic-resolution EELS Study of Polarization of $BaTiO_3$ in the Interface With Metallic Manganite

Xuan Hu[1], Patrick Phillips[1], Robert Klie[1]

[1.] Department of Physics, University of Illinois at Chicago, Chicago, IL

Transition metal oxides have a wide variety of applications due to their outstanding electronic and magnetic properties, which mainly come from the electronically active *d* orbitals.[1] Understanding and controlling the *d* orbital occupancy and configurations are essentially important for the applications of these transition metal oxides. Our previous study demonstrated that the intrinsic displacements of ferroelectrics ($BaTiO_3$) can be transferred to the interfaces with $La_{1-x}Sr_xMnO_3$ (LSMO, x = 0.2) and modulate its orbital occupations.[2] Further modelling studies on the atomic-scale mechanisms of these effects are slow due to inconsistencies between experiment and theory for the accumulation state and depletion state. Using electron energy-loss spectroscopy (EELS) and high-angle annular dark field (HAADF) imaging, the electronic properties of Ti and O atomic columns within the $BaTiO_3$ (BTO) layer can be analysed to provide a complete picture of structural modulation and orbital occupancy.

A LSMO/BTO/LSMO sample consisting of 20 unit cells for each layer was grown on the TiO_2-terminated $SrTiO_3$ using molecular beam epitaxy (MBE). The aberration-corrected JEOL ARM200CF is utilized with a 200 kV cold field emission gun and post-column Gatan Enfina EELS spectrometer to acquire all the images and EEL spectra. Figure 1 shows an atomic-resolution HAADF image of BTO/LSMO interface. By taking the average of the lattice constants from different images which are acquired in the same area as Figure 1, we find that the in-plane and out-of-plane lattice constants for LSMO are a = 3.935 Å and 3.928 Å respectively, while the BTO has a similar in-plane constant a = 3.936 Å but a slightly larger out-of-plane constant a = 4.078 Å. Energy-dispersive X-ray spectroscopy (EDS) indicates that the sample has a sharp interface with BaO/MnO_2 termination. We find an average Ti-O displacement of 0.176 Å pointing away from the LSMO/BTO interface (each displacement is presented as the yellow arrows in Figure 1). We determine the polarization of this sample as the accumulation state, which means that additional charges have accumulated at the LSMO/BTO interface as a result of the electro-static polarization.

Figure 2a) shows the atomic-resolution EELS of Ti L-edge in the first and fifth layer BTO with respect to the LSMO/BTO interface. By comparing the Ti L-edge onset (458.2 eV) and the Ti $L_{3,2}$ edge splitting (5.1 eV) with reference spectra obtained from bulk $BaTiO_3$ (onset 459.5 eV, $L_{3,2}$ split 4.8 eV),[3] we find that all interfacial layers within BTO exhibit a Ti valence state of 4+. Figure 2b) shows atomic-resolution EEL spectra of the O *K*-edge taken from the first five layers and the bulk of BTO. Comparing the O *K*-edge fine-structure of the first layer BTO with that of the bulk BTO, we can see a shift towards higher energy and a wider pre-peak. The energy shift stems from the symmetry breaking as the result of the change of the intrinsic displacements in the interfaces. The wider pre-peak presents the change of the core-hole effects. The case of the depletion state shows the opposite trend.

The electron energy-loss near-edge structure (ELNES) simulations of O *K*-edge for the both states of BTO have been performed. The O *K*-edge of the accumulation state can be modelled using density functional theory in the $Z + 1$ approximation, while the Z approximation shows good agreement with the experimental data of the depletion state. The core-hole effects are strong (weak) in the accumulation

(depletion) state. The stronger core-hole effect means a more localized exciton with a longer lifetime which sharpens the pre-peak of the O *K*-edge at the interfaces (and vice versa). In this presentation, we will discuss our EELS results for the case of both the accumulation and depletion state and compare our experimental data with our ab-initio modelling results.[4]

References:

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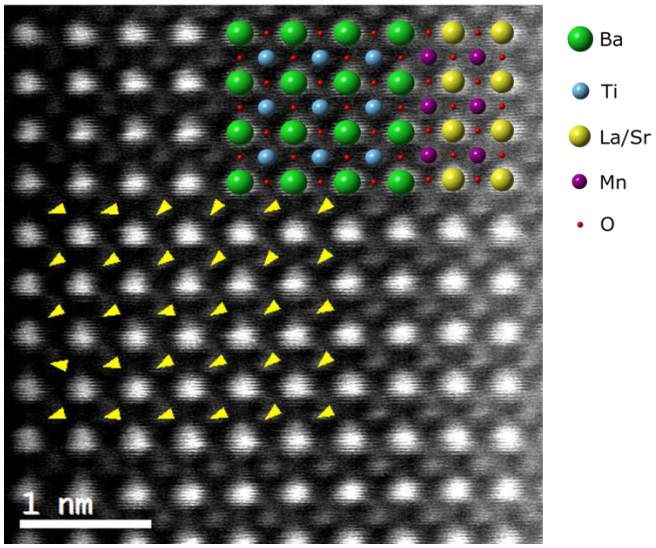
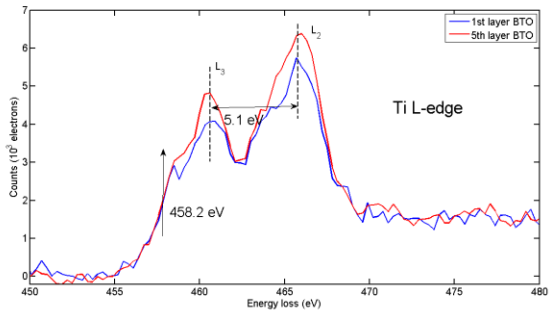


Figure 1. Atomic-resolution HAADF image of BTO/LSMO bottom interface. The image has been filtered by the radial wiener filter. The interface can be found to be BaO/MnO_2 termination. The yellow arrows present the displacements of Ti atoms from the center of nearby Ba atoms, which show that the sample is in the accumulation state.

a)



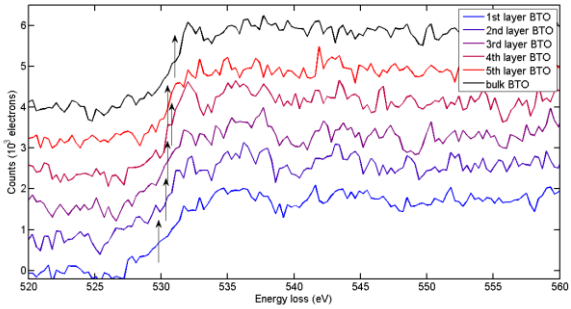


Figure 2. The electron energy-loss (EEL) spectra of a) Ti L-edge of the 1st layer BTO and 5th layer BTO from the bottom interface, b) O *K*-edge of the first five layers and bulk of BTO.

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