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Interplay of Octahedral Rotations, Magnetic and Electronic Properties in Epitaxial $LaCoO_3$ Thin Films

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The corner sharing network of transition metal - oxygen octahedra (BO_6) in the ABO_3 perovskites enables a variety of octahedral tilt patterns which affect materials properties.[1] Recently, tilt discontinuities at interfaces became a topic of intense interest as a distinct instrument for engineering interface and thin film behavior, giving rise to novel magnetic and electronic properties not achievable in the bulk. However, identifying the effect of octahedral tilts on material or interface behavior can be challenging, because the corresponding effects can be extremely localized and thus not accessible by scattering methods. Quantitative aberration-corrected scanning transmission electron microscopy (STEM) is a powerful tool that enables unit-cell-by-unit-cell analysis of octahedral tilt patterns.

For example, $LaCoO_3$ (LCO) thin films show ferromagnetic ordering at low temperatures, while bulk LCO does not. It has been speculated that it is partly due to the effect of the octahedral tilts. To study this phenomenon, epitaxial LCO thin films of different thicknesses (5 u.c., 15 u.c., and 20 nm) were deposited by pulsed laser deposition onto a $SrTiO_3$ (STO) substrate. X-ray photoelectron spectroscopy studies of the films have demonstrated that Co 3p edges shift up to 2 eV for 15 u.c. and 20 nm films, indicating possible presence of 2D electron gas. STEM and electron energy loss spectroscopy (EELS) with atomic resolution were then performed to elucidate sources of difference in properties among the films of different thickness, including local structure in LCO and chemical intermixing at the interface.

Figures 1(a)-(c) show representative HAADF images from the 5 u.c, 15 u.c, 20 nm LCO films. Atomic position mapping from HAADF and BF/ABF images can reveal lattice spacing and octahedral tilt behavior with atomic resolution. 5 u.c. thin films showed no octahedral tilts, while 15 u.c. thin films were fully tilted, with tilts propagating into the first few layers of the STO substrate. La spacing modulation along the in-plane lattice direction (Fig.1 (d-f)) was also only present in the 15 u.c. film (image: (d), map: (e), profile: (f)). 20 nm films were no longer coherent, with orientational domain boundaries and Ruddlesden-Popper-like antiphase boundaries nucleating at a thickness of 15-17 unit cells. Density functional theory calculations were performed to understand the interplay between lattice strain, octahedral tilts, and the electronic/magnetic properties of the different thickness LCO thin films

Some degree of Ti/Co intermixing was observed by EELS core-loss mapping in the Fig 2(a), with mostly Ti atoms at Co site in 1^{st} LCO layer (Fig 2.(b)). A complex pattern of O *K* fine structure evolution at the interface was also observed, indicating multiple contributions to O *K* edge, such as hybridized O 2p to Co 3d electronic states;[2] using this data, different contributions to electronic structure could in principle be deconvolved via advanced simulations. However, interface intermixing appeared to be the same for the 5 u.c. and the 15 u.c. thin films, suggesting tilt behaviour as more likely origin of differences in properties between the two films.

References

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Figure 1. (a) 5 u.c., (b) 15 u.c, (c) 20 nm of $LaCoO_3$ film on $SrTiO_3$ substrate, respectively. (d-f)Atomic position mapping results from image (d): in-plane La spacing map (e) and profile (f).

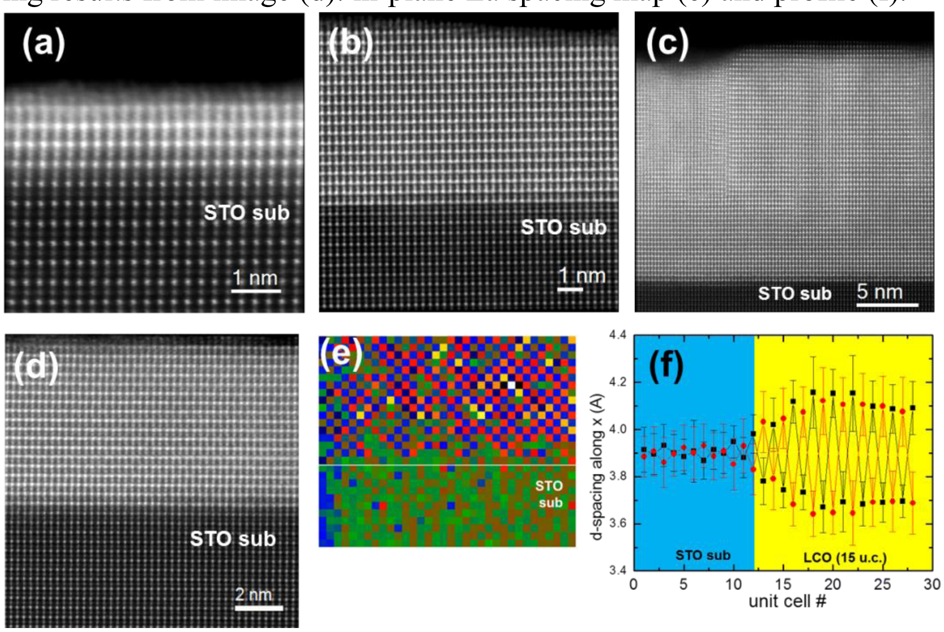
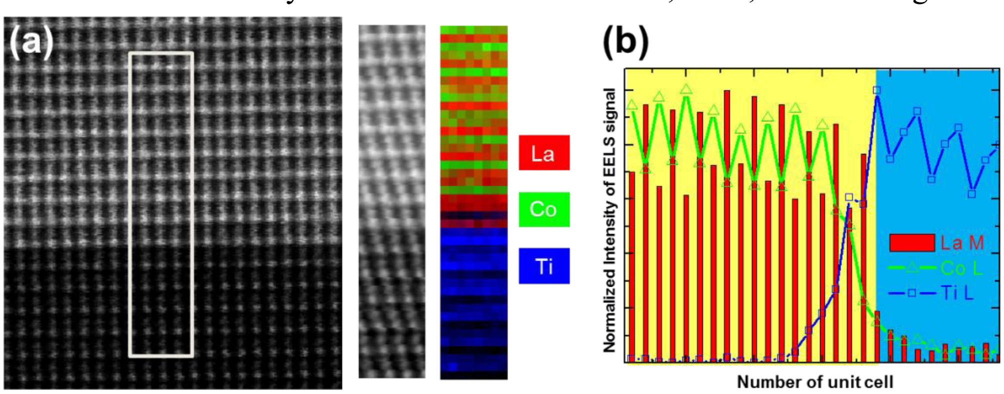


Figure 2. Core-loss EELS mapping of the area in the white box of HAADF image in fig. 2(a). Figure 2 (b) shows the normalized intensity of core-loss EELS for La M, Co L, and Ti L edges.



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