

Characterization of Two-Dimensional Electron Gas at the γ -Al₂O₃/SrTiO₃ Interface

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The interfaces between certain insulating transition-metal oxides exhibit a board range of properties, such as ferromagnetism, magnetoresistance, conductivity and superconductivity, making it possible to design all-oxide electronic devices [1]. The crystalline γ -Al₂O₃/SrTiO₃ forms a highly conductive layer (two-dimensional electron gas - 2DEG), attributed to oxygen vacancies, with a maximum room-temperature sheet-carrier density as high as $\sim 7 \times 10^{13} \text{ cm}^{-2}$ [2]. Here we use high-resolution TEM negative-Cs imaging (NCSI), high-angle annular-dark-field (HAADF) STEM imaging, energy-loss near-edge structure (ELNES) analysis, and off-axis electron holography, to characterize the nature of γ -Al₂O₃/SrTiO₃ interfaces, as grown by atomic layer deposition (ALD) and molecular beam epitaxy (MBE) at different temperatures. The effects of post-deposition annealing with or without the presence of oxygen, was also investigated.

Figures 1(a) and (b) show NCSI and HAADF images of a 2.1-nm-thick Al₂O₃ layer grown by ALD on a TiO₂-terminated STO (001) substrate at 345°C: this sample has a 2DEG at the interface. The NCSI (a) is taken at the [110] zone axis. The Sr and O mixed atomic columns in the substrate are the strong bright spots, the O atomic columns are the weak spots, and the Ti atomic column intensity is in between. The HAADF image (b) is taken at the [100] zone axis. The Sr atomic columns are bright spots, the Ti atomic columns are weaker, the Al atomic columns that form a square lattice are very weak, and the O atomic columns are not visible. From both images, it is clear that the interface at the substrate side is TiO₂-terminated, and the symmetry of the film is consistent with γ -Al₂O₃. The plots below the images are the auto-correlation results calculated from the images of the terminating TiO₂ layer, showing that the repeating patterns correspond to TiO₂. Figures 1(c), (d) are NCSI and HAADF images showing the sample grown by MBE at 600°C and annealed in air for an hour at 400°C. The 2DEG was not present in this sample after annealing. From the NCSI, the TiO₂-terminated layer at the interface is different from (a). The auto-correlation results also show that the repeating patterns of the TiO₂ surface layer have disappeared. From the HAADF image, the Ti contrast in the same layer has reduced, and the position of the invisible O atomic column shows some contrast. Both results indicate that Ti has diffused away from this layer, and that Al has diffused into this layer, thus suggesting the possibility that the disappearance of the 2DEG after annealing is related to the diffusion of Al and Ti atoms near the interface.

Figure 2 shows the ELNES scan across the interface of the sample shown in Figs. 1(a) and (b). Although extracting conclusive evidence of oxygen vacancies from imaging is not possible in these images, because the signal from random and/or low concentration of oxygen vacancies is submerged into the noise as well as unevenness in sample thickness, the ELNES signal clearly shows that the Ti oxidation state near the interface has changed, which could be taken as indirect evidence of oxygen vacancies. The

Ti⁴⁺ signals (with 4 peaks) in Figs. 2 (b) and (c) are very obvious in the substrate, while the Ti³⁺ signal (with 2 peaks) in Fig. 2 (a) shows up in a region less than one unit cell from the interface on the STO side. Figure 3(a) is a reconstructed thickness line profile from the sample shown in Figs. 1(a), (b), and Fig. 3(b) shows the reconstructed phase image. The thickness profiles of the substrate and the film (except near the surface) are almost constant. The arrow pointing at the positive curvature in the phase image indicates the position of the possible 2DEG. Further quantitative analysis and simulations are still in progress to better understand and interpret these results [3].

References:

- [1] Y.Z. Chen, *et al.*, Nature Communications **4** (2013) 1371.
 [2] K.J. Kormondy, *et al.*, J. Applied Physics **117** (2015) in press.
 [3] This work was supported by AFOSR Contract FA 9550-12-10494. We gratefully acknowledge the use of facilities within the John M. Cowley Center for HREM at Arizona State University.

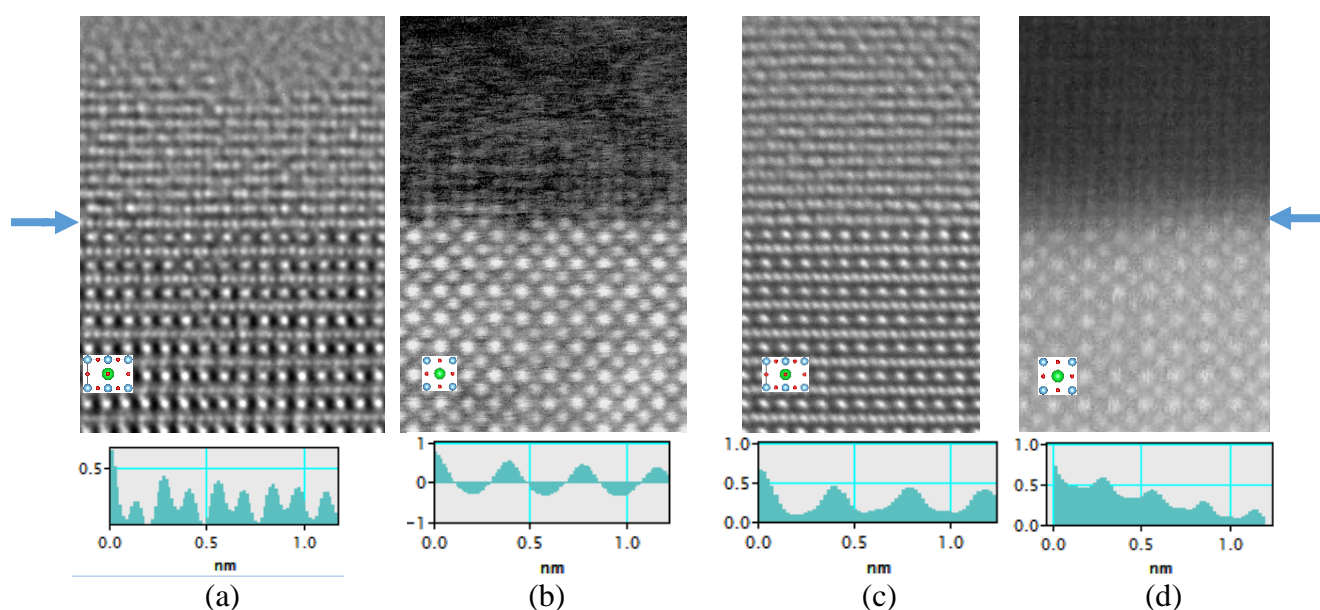


Fig.1. Images of γ -Al₂O₃/SrTiO₃ (001) interface. Sample with 2DEG: (a) NCSI; (b) HAADF. Sample without 2DEG: (c) NCSI; (d) HAADF. STO unit cell structure is superimposed on the image. Arrows point to the terminating TiO₂ layer. The plot below each image is the calculated auto-correlation result for the terminating TiO₂ layer.

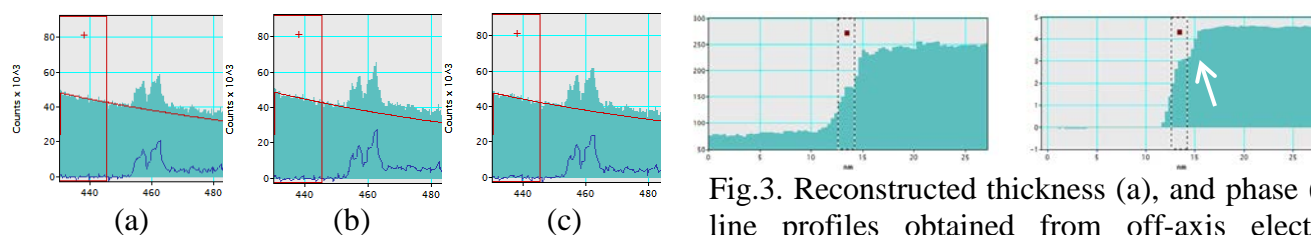


Fig.2. ELNES spectra near the interface at the STO side. Distance to interface: (a) within 1 unit cell; (b) 2 unit cells; (c) 3 unit cells.

Fig.3. Reconstructed thickness (a), and phase (b), line profiles obtained from off-axis electron holography. White arrow points to the positive curvature.