

X-ray Absorption Spectroscopy of Reconstruction in V-oxide Heterostructures

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Introduction

The interfaces of hetero-junctions composed of transition-metal oxides have recently attracted great interest. For example, the interface between two band insulators, SrTiO₃ (STO) and LaAlO₃ (LAO), is especially interesting due to its metallic [1] and even superconducting properties [2]. In this study, we investigated the electronic structure of multilayers consisting of a band insulator, LAO and a Mott insulator, LaVO₃ (LVO).

Experiment

The LAO/LVO multilayer thin films were fabricated on TiO₂-terminated STO or LAO (001) substrates using the pulsed laser deposition (PLD) technique. Schematic views of the fabricated thin films are shown in Figure 1. X-ray absorption experiments (XAS) were performed at the SGM beamline 11ID-1. The spectra were measured both in the total-electron-yield (TEY) and fluorescence-yield modes. There was almost no difference between the spectra of these two modes discussed here, so only the TEY spectra are shown. All measurements were taken at room temperature.

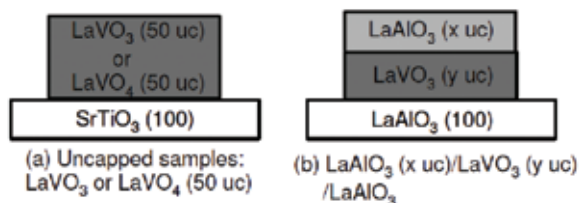


Figure 1: Schematic view of the samples. (a) LaVO₃ (50 uc) or LaVO₄ (50 uc)/SrTiO₃, (b) LaAlO₃ (x uc)/LaVO₃ (y uc)/LaAlO₃.

Results and Discussion

Figure 2 shows the V 2p XAS spectra of 50 unit cells (uc) LVO and LaVO₄ thin films on STO (001). These two spectra look very different. The spectrum of LVO was broad and composed of V³⁺, V⁴⁺ and V⁵⁺, which shows that the surface of LVO was oxidized and/or valence redistribution occurred to avoid the “polar catastrophe” of the polar layers of LaO⁺ and VO₂⁻. The spectrum of LaVO₄ was sharp, characteristic of d⁰ (V⁵⁺) configuration.

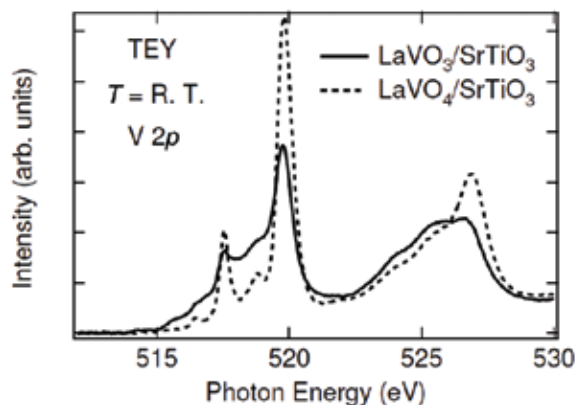


Figure 2: V 2p XAS spectra of 50 uc LaVO₃ and LaVO₄ thin films on SrTiO₃ (001).

Figure 3 shows the V 2p XAS spectra of LAO-sandwiched LVO thin films. As seen from Figures 3 (a) and (b), the V 2p XAS spectra do not depend on the thickness of LVO but on the thickness of LAO capping layers. The V 2p XAS spectrum of LAO (8 uc)/LVO/LAO was mostly V³⁺, and that of LAO (3 uc)/LVO/LAO was a combination of V³⁺, V⁴⁺ and V⁵⁺.

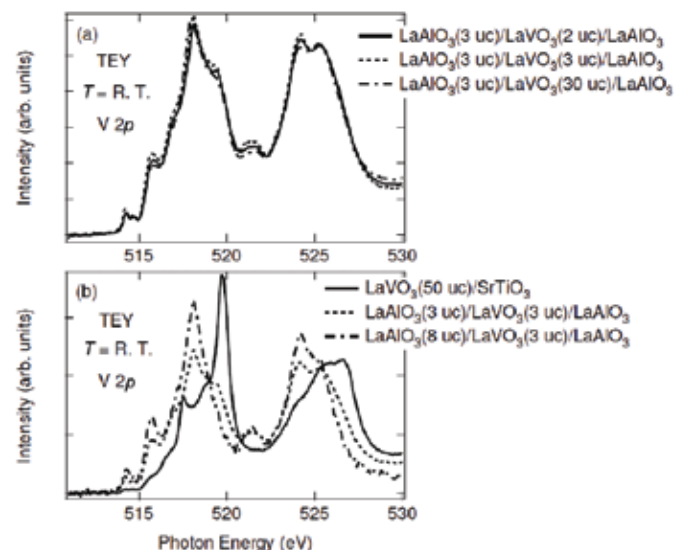


Figure 3: V 2p XAS spectra of LAO (x uc)/LVO (y uc)/LAO. (a) Dependence of LVO thickness. (b) Dependence of LAO thickness.

Here we confirmed the assignments of V³⁺, V⁴⁺, and V⁵⁺ by comparing the experimental spectra with cluster-model calculations. Figure 4 shows the comparison of the experimental spectra with the cluster-model calculation. As

shown in Figure 4 (a), there is a good agreement between the V 2p XAS spectra of LAO (8 uc)/LVO (3 uc)/ LAO and the V³⁺ (O_h) calculation, demonstrating that the valence of V is mostly 3+ in LAO (8 uc)/LVO (3 uc)/ LAO. Similarly, Figure 4 (b)

shows that a good agreement is obtained between the V 2p XAS spectra of uncapped LVO with the V⁴⁺ (O_h) calculation, indicating that the valence of V is mostly 4+ at the surface of uncapped LVO thin films. Figure 4 (c) shows that the V 2p XAS spectra of uncapped LaVO₄ can be better described by V⁵⁺ (T_d) than V⁵⁺ (O_h), consistent with the monazite structure of this material.

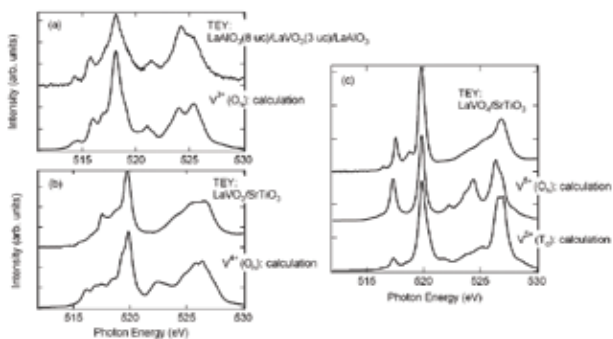


Figure 4: Comparison of the experimental spectra with the cluster-model calculation. (a) V 2p XAS spectra of LAO (8 uc)/LVO (3 uc)/ LAO with V³⁺ (O_h) calculation. (b) V 2p XAS spectra of uncapped LVO with V⁴⁺ (O_h) calculation. (c) V 2p XAS spectra of uncapped LaVO₄ with V⁵⁺ (O_h and T_d) calculation.

Finally we will discuss why the valence of V depends on the thickness of LAO. In the present samples, both the LAO and LVO layers are polar, and consist of alternating stacks of LaO⁺ and AlO₂⁻ or VO₂⁻ layers. Electronic reconstruction [3] occurs during the fabrication of the polar layers in order to prevent the divergence of Madelung potential, i.e., so-called polar catastrophe. Figure 5 shows schematic diagrams describing the polar catastrophe and electronic reconstruction in the case of LAO/LVO/STO. Panel (a) shows an unreconstructed case, leading to a polar catastrophe. Panel (b) shows the case of ionic reconstruction, where the divergence of V (z) disappears. Panel (c) shows the case of electronic reconstruction, where the divergence of V (z) disappears in the LVO layers, but V (z) diverges in the LAO layers. Our results can be explained by the transition from “electronic reconstruction” to “ionic reconstruction” involving O vacancies with increasing thickness of LAO capping layers.

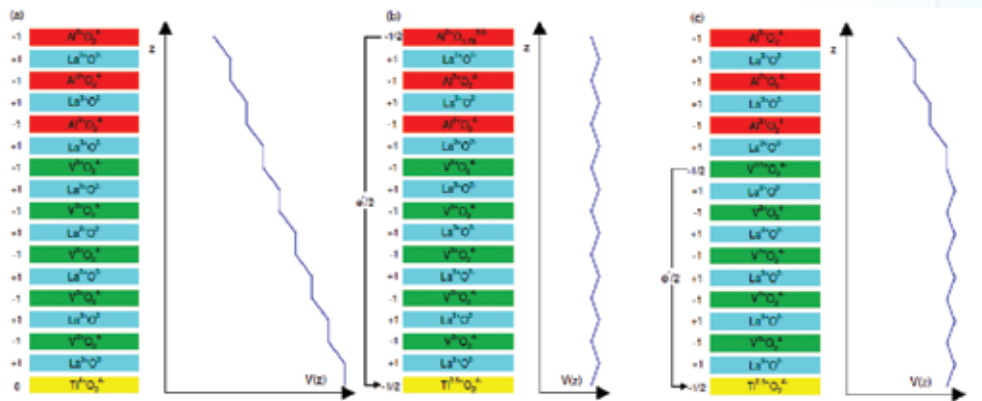


Figure 5: Polar catastrophe, ionic reconstruction and electronic reconstruction in LaAlO₃/LaVO₃/SrTiO₃. (a) Unreconstructed case. The electric potential V (z) diverges with thickness, leading to a polar catastrophe. (b) Reconstructed case (Ionic reconstruction). The divergence of V (z) disappears. (c) Reconstructed case (Electronic reconstruction). The divergence of V (z) disappears in the LaVO₃ layers, but not in the LaAlO₃ layers.

Conclusion

We performed an X-ray absorption study of the dependence of the V oxidation state on the thickness of LVO and capping LAO in the multilayer structure of LVO sandwiched between LAO layers. We present evidence that there is an abrupt change from electronically reconstructed interfaces to ionic reconstruction as the layer thickness of LAO on top increases. This provides a possible mechanism for the abrupt change in the electrical properties of similar heterostructures as a function of the layer thickness.

References

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