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Atomic and electronic structures of the SrVO₃-LaAlO₃ interface

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The atomic and electronic structures at interfaces in thin films are typically different from the bulk and are vitally important in determining the physical properties of thin films. The interface between SrVO₃, chosen as a prototype for vanadium-based perovskite materials in this work, and LaAlO₃ substrate is investigated by scanning transmission electron microscopy, electron energy-loss spectroscopy, and theoretical multi-electron calculations. Extra electrons have been detected on the interface layer by comparing the energy-loss near-edge structures of V-$L_{3,2}$ edges to those from the film far from the interface. Monochromated EELS and theoretical calculations for SrVO₃, VO₂, and V₂O₃ support this conclusion. The extra electrons appear to originate from a change in the local bonding configuration of V at the La-O terminated substrate surface as determined by Z-contrast imaging. © *2011 American Institute of Physics.* [doi:10.1063/1.3601870]

Vanadium-based perovskite compounds, AVO_3, have attracted increasing interest because they form model correlated electron systems for understanding the fundamental connections between structure and properties. The interesting physical properties of the AVO_3 systems can be modified by incorporating different A cations which creates various distortions of the VO₆ octahedron and thus varies the electronic structures of these materials.[1–6] Recently, epitaxial growth techniques have been applied to AVO_3 systems, and interesting phenomena and properties in films and on interfaces that are different from that of the bulk were observed.[7–15] For example, high conductivity could be constructed at an insulator-insulator interface depending on the interface atomic configuration.[12,14] Because the properties and morphology of the thin films are strongly dependent on the type, orientation, and terminal plane of the substrate, detailed knowledge of the thin film/substrate interface at an atomic scale is indispensable to gain control over and design thin film AVO_3 systems.

On the other hand, atomic and electronic structures at the thin-film/substrate interface for AVO_3 have rarely been studied at atomic-scale spatial resolution. One possible reason is that previous techniques of analysis were not ideally suited to correlate specific atomic-level local structural features to the electronic structure due to the lack of high spatial resolution or bulk sensitivity.[4,5] An exception is a recent work reported by Kourkoutis *et al.* in which an insulator–insulator interface, LaVO₃/SrTiO₃, has been studied by using atomic resolution Z-contrast imaging.[13,16] In our work, SrVO₃ (SVO) is selected as the prototypical parent phase, exhibiting a simple cubic structure and a good starting point for exploring more complex perovskite vanadate systems.[17,18] Furthermore, SVO/LaAlO₃ (LAO) constructs a conductor-insulator interface, which should provide unique insights complementary to the insulator–insulator oxide interfaces that have been heavily studied recently.[9,12–14] This work is investigated by combining Z-contrast imaging, monochromated EELS, and first-principles multi-electron calculations to elucidate the interaction between the atomic and electronic structures at the interface.

The SrVO₃ thin film used in this research was grown on (001) LaAlO₃ by using pulsed laser deposition. X-ray diffraction revealed that the films were fully epitaxial both in and out of the plane of the film with the following lattice relationships [100]:$_{SVO}$//[100]lao, [010]svo//[010]$_{LAO}$, and [001]$_{SVO}$//[001]$_{LAO}$. The lattice parameters for SVO and LAO are 3.842 Å and 3.79 Å, respectively, with a lattice mismatch of ~1.35%.

A low-magnification STEM image is shown in Figure l(a). A sharp and flat interface exists over the entire specimen, indicating good epitaxial growth of the SVO film on the LAO substrate. This is confirmed by high-resolution

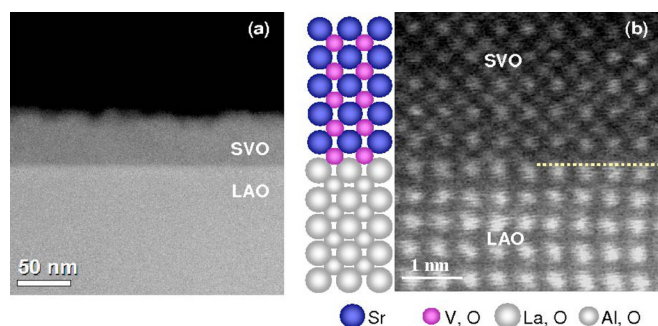a)Author to whom correspondence should be addressed. Electronic mail: chim@ornl.gov.

FIG. 1. (Color online) (a) Low-magnification HAADF-STEM image of $SrVO_3$ (SVO)/$LaAlO_3$ (LAO) shows that the interface is flat and smooth. (b) A typical high resolution Z-contrast image shows that the interface is atomically smooth and it terminates with V-O and La-O layers. The dotted line in (b) indicates the location of the interface.

Z-contrast imaging (Fig. 1(b)). which reveals atomically smooth interface. The stacking sequence across the interface is visible according to the contrast difference of different atomic columns, Sr-O, V-O, La-O, and A1-O. The atomic layer above the bright interfacial La-O layer (in Fig. 1) is brighter than Al-O layers in the LAO bulk while similar to V-O layers; this indicates that this interface is terminated with a V-O layer for the SVO side and a La-O layer for the LAO side. Such configuration has been observed on the entire interfaces of two TEM specimens ($\sim$4 μm length for each) that we have worked on. Terminating with La-O in this work most probably is resulted from the high temperature (700 °C) and oxygen-free ($<$1$\times$ 10^{-6} Torr) conditions used for film growth, which has been discussed and confirmed in prior reports.[19–21]

To investigate the electronic structures of the interface between the thin film and the substrate, EELS was performed across the interface and the recorded spectra are shown in Fig. 2. The interval between two neighboring spectra is $\sim$0.20 nm; the illuminated region of one EELS acquisition is around 0.26 nm due to specimen drift. Each spectrum thus covers the information from $\sim$1.5 atomic monolayers. The composition change crossing the interface can be clearly seen from the fine structure of the O-K edge. For example, the O pre-peaks A and B disappear on the LAO side due to the absence of unoccupied 3d-states in Al. The shape change of peaks C and D are from the hybridization of O_{2P} states with La and Al states. Therefore, spectrum "g" includes information about both sides according to the O signal variation.

The electronic structure of the interface can then be studied by comparing the fine structures of the V-L edges in spectrum "g" with those from the thin film (spectrum "a" and "b"). It is important to note that the V-L edges at the interface broaden toward lower energy. The splitting, as the width of the top of the L_3 peak, is $\sim$1.2 eV as indicated by the arrows (Fig. 2).

Because the ELNES profile is related to the atomic and electronic structures, two possible factors can be considered as the cause of the spectral difference: (1) the contributions of the atomic structure distortion at the interface and (2) the presence of multi-oxidation state of V at the interface. To discuss the cause, reference $V-L_{2,3}$ ELNES and calculated spectra were obtained for V_2O_3, VO_2, and $SrVO_3$.

$V-L_{2,3}$ ELNES from the reference compounds and the theoretical spectra are shown in Figs. 3 and 4, respectively. The experimental spectra of these oxides were acquired in monochromated and non-monochromated modes. These oxides have different oxidation states as well as different VO_6 octahedron distortions. Because vanadium oxides tend to be reduced by electron beam irradiation,[22] all EELS measurements were performed on a "fresh" area, which has been minimally exposed to the beam. In each case, more than 30 measurements were taken and compared to ensure that the spectra used in this work have not suffered radiation-induced structural changes. The calculated spectra were obtained by using first-principles multi-electron relativistic methods.[23,24] Model clusters used in our calculation were composed of one V ion and its coordinating six oxygen ions, which are embedded in a Madelung potential for the respective crystal. The multi- electron wave functions are expressed by a linear combination of Slater determinants made by fully relativistic molecular orbitals for V-2p and V-3d. The theoretical transition energy was corrected by taking orbital-energy difference between single-electron orbitals for the Slater's transition-state.

It is found that the spectral difference between VO_2 and $SrVO_3$ mainly appears at the lower energy side of L_2 and L_3 edges as indicated by arrows (Fig. 3(a)). Such difference can only be observed obviously when the monochromator is on. Concerning the peak position, although the local $[VO_6]$ octahedron in VO_2 is more distorted than that in $SrVO_3$, it can be seen that the positions of the main peaks of VO_2 and SVO are almost identical (Fig. 3(a)). Those features, the presence of a small shoulder in VO_2 and the same position of SVO and VO_2, are well reproduced by the calculations (Fig. 3(b)). Here it should be mentioned again that the SVO/LAO interface is atomically flat and the atoms across the interface are smoothly connected (Fig. 1), indicating that no large distortion is present at the interface. From these high-resolution images and calculated ELNES, it can be concluded that the distortion of $[VO_6]$ at the interface, which should be small, does not contribute to the spectral shift.

On the other hand, a chemical shift of approximately 1.4 eV is seen between the V^{4+} compounds and V_2O_3 in the experimental results (Fig. 3(a)), which is comparable to the shift of 1.2 eV by our calculations. This implies that the spectral shift observed at the interface is caused by the variation of oxidation state. To check the effect of both lattice distortion and variation of oxidation state on the spectrum, a hypothetic calculation for $SrVO_3$ with V^{3+} was also computed (Fig. 3(b)). The spectral shape for $SrVO_3$ with V^{3+} is very similar to that of V_2O_3 despite the distortion of the VO_6 octahedron in V_2O_3. The top of the L_3 peak for $SrVO_3$ with V^{3+} is $\sim$1.9 eV lower than that for $SrVO_3$ with V^{4+}. This result, in turn, indicates that the presence of V^{3+} in the SVO structure, even with no additional lattice distortion, contributes to the shift of the spectrum. Consequently, multiple valence states in the SVO are considered as the most probable cause of the spectral changes at the interface. If we assume that the shape change and energy shift of interfacial spectra are only contributed by the existence of multi-valences, the fractional contributions of V^{3+} and V^{4+} to the interfacial spectra can be estimated as 0.42 ± 0.09 and 0.58 ± 0.09, respectively, by
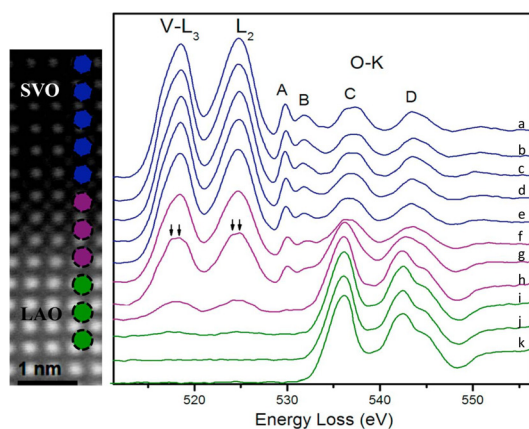
FIG. 2. (Color online) EELS line profile crossing the interface of SVO/LAO. Beam position for each spectrum is schematically marked in the left-side inset.

FIG. 3. (Color online) Comparison of the interface spectrum "g" from the line profile with the spectra of V_2O_3, VO_2, and SVO thin films reveals the existence of multi-valence of V on the interface; (b) Calculated V-$L_{2,3}$ ELNES of VO_2, V_2O_3, SV(+4)O and SV(+3)O.

using multiple linear least (see supplemental material[25]) squares (MLLS) fitting taking VO_2 and V_2O_3 as references.

Regardless of which factor dominates, the obvious left-shift of V-L peaks suggests that electronic reconstructions at the interface resulted from the multi-valence nature of V is observed. According to the spectra shown in Fig. 3(b), spectrum "g" is the spectrum containing the most insight into the nature of the interface. Although spectrum "h" also shows the signal from both sides, the V-L peaks are very weak compared with those of La and Al based on its O edge structure. Therefore the interface signal should be limited in one interval of this series of acquisition. This implies that the variation of V valence is only restricted to the interfaces V-O layer. One possible reason for the presence of multi-valence V at the interface is the existence of oxygen vacancies, which may arise from the reducing atmosphere for the film growth. However, as the LAO substrate has little potential to accommodate oxygen, and the valence state of V in the film is shown to be 4+, a more likely explanation for the multi-valence V at the interface is the bonding with La atoms from the La-O layer in the substrate. Because the formal valence of La is 3+ and that of Sr is 2+, to continue the perovskite structure from substrate to film, as imaged in the high-resolution Z-contrast work, more electrons will be found near the interface and will tend to be localized around the V atoms at the interface layer compared to the V far from the interface. This is similar to the substitution of La on Sr in SVO, which induces extra electrons to the VO_6 octahedron, and then affects the oxidation state of V. Further investigation on the electronic structures on the interface will be carried out by theoretical calculations and comparison with the spectra of $LaVO_3$.

In conclusion, we have studied the atomic and electronic structures of SVO/LAO experimental and theoretically. The terminated atomic layers on the interface are determined as V-O and La-O from Z-contrast imaging. Extra electrons were detected by ELNES on the interface layer. Monochromated EELS and theo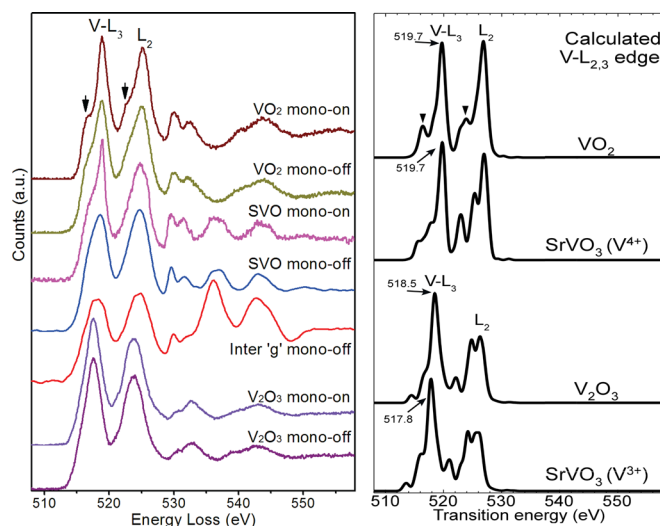retical calculations also have been carried out on V_2O_3, VO_2, and $SrVO_3$ for further confirmation. The origin of these extra electrons should be attributed to the bonding of V with La atoms on the interface.

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