

## Hard x-ray photoemission study of LaAlO<sub>3</sub>/LaVO<sub>3</sub> multilayers

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We have studied the electronic structure of multilayers composed of a band insulator LaAlO<sub>3</sub> (LAO) and a Mott insulator LaVO<sub>3</sub> (LVO) by means of hard x-ray photoemission spectroscopy, which has a probing depth as large as  $\sim 60$  Å. The Mott-Hubbard gap of LVO remained open at the interface, indicating that the interface is insulating unlike the LaTiO<sub>3</sub>/SrTiO<sub>3</sub> multilayers. We found that the valence of V in LVO was partially converted from V<sup>3+</sup> to V<sup>4+</sup> only at the interface on the top side of the LVO layer and that the amount of V<sup>4+</sup> increased with LVO layer thickness. We suggest that the electronic reconstruction to eliminate the polarity catastrophe inherent in the polar heterostructure is the origin of the highly asymmetric valence change at the LAO/LVO interfaces.

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### I. INTRODUCTION

The interfaces of heterojunctions composed of transition-metal oxides have recently attracted great interest. For example, it has been suggested that the interface between a band insulator SrTiO<sub>3</sub> (STO) and a Mott insulator LaTiO<sub>3</sub> (LTO) shows metallic conductivity.<sup>1-3</sup> Recently, Takizawa *et al.*<sup>4</sup> measured photoemission spectra of this interface and observed a clear Fermi cutoff, indicating that an electronic reconstruction indeed occurs at this interface. In the case of STO/LTO, electrons penetrate from the layers of the Mott insulator to the layers of the band insulator, resulting in the intermediate band filling and hence the metallic conductivity of the interfaces. It is therefore interesting to investigate how electrons behave if we confine electrons in the layers of the Mott insulator. In this paper, we investigate the electronic structure of multilayers consisting of a band insulator LaAlO<sub>3</sub> (LAO) and a Mott insulator LaVO<sub>3</sub> (LVO). LAO is a band insulator with a large band gap of about 5.6 eV. LVO is a Mott-Hubbard insulator with a band gap of about 1.0 eV.<sup>5</sup> This material shows *G*-type orbital ordering and *C*-type spin ordering below the transition temperature  $T_{OO}=T_{SO}=143$  K.<sup>6</sup> From the previous results of photoemission and inverse photoemission spectroscopy, it was revealed that in the valence band there are O 2*p* bands at 4–8 eV and V 3*d* bands (lower Hubbard bands; LHB) at 0–3 eV and that above the Fermi level ( $E_F$ ) there are upper Hubbard bands of V 3*d* origin separated by a band gap of about 1 eV from the LHB.<sup>7</sup> Since the bottom of the conduction band of LAO has predominantly La 5*d* character and its energy position is well above that of the LHB of LVO,<sup>8</sup> the V 3*d* electrons are expected to be confined within the LVO layers as a “quantum well” and not to penetrate into the LAO layers, making this interface insulating unlike the LTO/STO case.<sup>1-4</sup> Recently,

Hotta *et al.*<sup>9</sup> investigated the electronic structure of 1–5-unit-cell-thick layers of LVO embedded in LAO by means of soft x-ray (SX) photoemission spectroscopy. They found that the V 2*p* core-level spectra had both V<sup>3+</sup> and V<sup>4+</sup> components and that the V<sup>4+</sup> was localized in the topmost layer. However, due to the surface sensitivity of SX photoemission, information about deeply buried interfaces in the multilayers is still lacking. Also, they used an unmonochromatized x-ray source, whose energy resolution was not sufficient for detailed studies of the valence band. In the present work, we have investigated the electronic structure of the LAO/LVO interfaces by means of hard x-ray (HX) photoemission spectroscopy ( $h\nu=7937$  eV) at SPring-8 BL29XU. HX photoemission spectroscopy is a bulk-sensitive experimental technique compared with ultraviolet and SX photoemission spectroscopy, and is very powerful for investigating buried interfaces in multilayers. Owing to the bulk sensitivity and the high energy resolution of HX photoemission, we succeeded in observing the V 3*d* bands at the deeply buried interfaces. A Mott-Hubbard gap of LVO was found to remain open at the interface, indicating the insulating nature of this interface. From the V 1*s* and 2*p* core-level spectra, the valence of V in LVO was found to be partially converted from

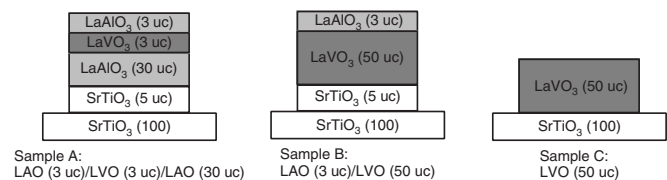


FIG. 1. Schematic view of the LaAlO<sub>3</sub>/LaVO<sub>3</sub> multilayer samples. Sample A: LaAlO<sub>3</sub> (3 uc)/LaVO<sub>3</sub> (3 uc)/LaAlO<sub>3</sub> (30 uc)/SrTiO<sub>3</sub>, Sample B: LaAlO<sub>3</sub> (3 uc)/LaVO<sub>3</sub> (50 uc)/SrTiO<sub>3</sub>. Sample C: LaVO<sub>3</sub> (50 uc)/SrTiO<sub>3</sub>.

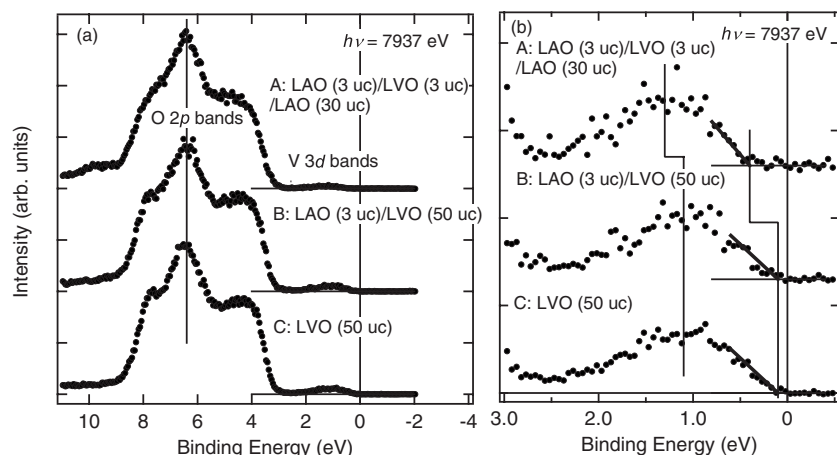


FIG. 2. Valence-band photoemission spectra of the  $\text{LaAlO}_3/\text{LaVO}_3$  multilayer samples. (a) Valence-band spectra over a wide energy range. (b) V 3d band region.

$\text{V}^{3+}$  to  $\text{V}^{4+}$  at the interface, confirming the previous study.<sup>9</sup> The observation of the V 1s core level, whose line shape is simpler than that of V 2p and allows less ambiguous analyses, has become possible only by HX photoemission spectroscopy. Furthermore, the amount of  $\text{V}^{3+}$  was found to increase with LVO layer thickness. We attribute this valence change to the electronic reconstruction due to polarity of the layers.

## II. EXPERIMENT

The LAO/LVO multilayer thin films were fabricated on  $\text{TiO}_2$ -terminated STO(001) substrates<sup>10</sup> using the pulsed laser deposition (PLD) technique. An infrared lamp was used for heating the substrates. The films were grown on the substrates at an oxygen pressure of  $10^{-6}$  Torr using a KrF excimer laser ( $\lambda=248$  nm) operating at 4 Hz. The laser fluency to ablate  $\text{LaVO}_4$  polycrystalline and LAO single crystal targets was  $\sim 2.5$  J/cm<sup>2</sup>. The film growth was monitored using real-time reflection high-energy electron diffraction (RHEED). Schematic views of the fabricated thin films are shown in Fig. 1. Sample A consisted of 3 unit-cell (uc) LVO capped with 3 uc LAO. Below the 3 uc LVO, 30 uc LAO was grown, making LVO sandwiched by LAO. Sample B consisted of 50 uc LVO capped with 3 uc LAO. Sample C was 50 uc LVO without LAO capping layers. Details of the fabrication and characterization of the films were described elsewhere.<sup>11</sup> The characterization of the electronic structure of uncapped  $\text{LaVO}_x$  thin films by x-ray photoemission spectroscopy will be described elsewhere.<sup>12</sup> HX photoemission experiments were performed at an undulator beamline, BL29XU, of SPring-8. The photoemission spectroscopy apparatus is described in detail in Refs. 13–15. All the spectra were measured at normal emission and at room temperature. The total energy resolution was set to about 180 meV. The  $E_F$  position was determined by measuring gold spectra.

## III. RESULTS AND DISCUSSION

Figure 2 shows the valence-band photoemission spectra of the LAO/LVO multilayer samples. Figure 2(a) shows the entire valence-band region. Compared with the previous photoemission results,<sup>7</sup> structures from 9 to 3 eV are as-

signed to the O 2p dominant bands and emission from 3 eV to  $E_F$  to the V 3d bands. The energy positions of the O 2p bands were almost the same in these three samples, indicating that the band-bending effect at the interface of LAO and LVO was negligible. Figure 2(b) shows an enlarged plot of the spectra in the V 3d-band region. A Mott-Hubbard gap of LVO remained open at the interface between LAO and LVO, indicating that this interface is insulating unlike the STO/LTO interfaces.<sup>1–4</sup> The line shapes of the V 3d bands were almost the same in these three samples, except for the energy shift in sample A. We estimated the value of the band gap from the linear extrapolation of the rising part of the peak as shown in Fig. 2(b). The gap size of sample B was almost the same ( $\sim 100$  meV) as that of sample C, while that of sample A was much larger ( $\sim 400$  meV) due to the energy shift of the V 3d bands. The origin of the enhanced energy gap is unclear at present, but an increase of the on-site Coulomb repulsion  $U$  in the thin LVO layers compared to the thick LVO layers or bulk LVO due to a decrease of dielectric screening may explain the experimental observation.

Figure 3 shows the V 1s core-level photoemission spectra of the LAO/LVO multilayer samples. The V 1s spectra had a main peak at 5467 eV and a satellite structure at 5478 eV. The main peaks were not simple symmetric peaks but exhibited complex line shapes. We therefore consider that the

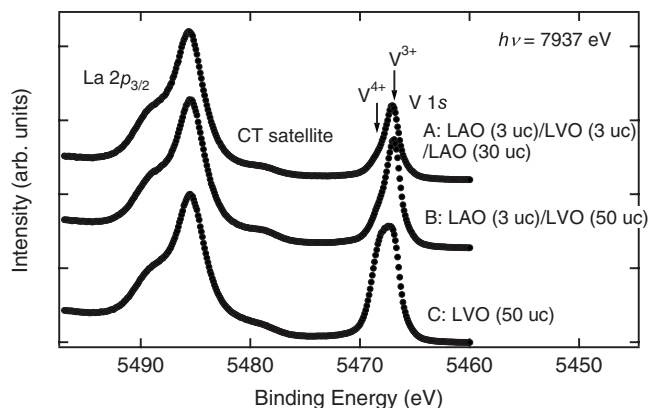


FIG. 3. V 1s core-level photoemission spectra of the  $\text{LaAlO}_3/\text{LaVO}_3$  multilayer samples.

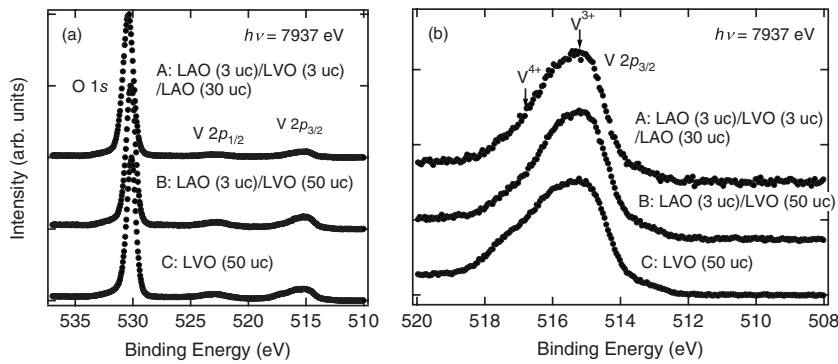


FIG. 4. O 1s and V 2p core-level photoemission spectra of the LaAlO<sub>3</sub>/LaVO<sub>3</sub> multilayer samples. (a) shows wide energy region and (b) is an enlarged plot of the V 2p<sub>3/2</sub> spectra.

main peaks consisted of V<sup>3+</sup> and V<sup>4+</sup> components. In sample C, there is a considerable amount of V<sup>4+</sup> probably due to the oxidation of the surface of the uncapped LVO. A satellite structure has also been observed in the V 1s spectrum of V<sub>2</sub>O<sub>3</sub> (Ref. 16) and interpreted as a charge transfer (CT) satellites arising from the 1s<sup>1</sup>3d<sup>3</sup> $\underline{L}$  final state, where  $\underline{L}$  denotes a hole in the O 2p band. Screening-derived peaks at the lower-binding-energy side of V 1s, which have been observed in the metallic phase of V<sub>2-x</sub>Cr<sub>x</sub>O<sub>3</sub>,<sup>16,17</sup> were not observed in the present samples, again indicating the insulating nature of these interfaces. The La 2p<sub>3/2</sub> core levels also appear near the V 1s core levels as shown in Fig. 3. The La 2p<sub>3/2</sub> spectra do not depend on the samples. This is because both LVO and LAO have LaO layers and there is no discontinuity for the A site. The differences of the electronic structures of these samples appear only at the V sites.

Figure 4 shows the O 1s and V 2p core-level photoemission spectra of the LAO/LVO multilayer samples. The O 1s spectra consisted of single peaks without surface contamination signal on the higher-binding-energy side, indicating the bulk sensitivity of HX photoemission spectroscopy. The energy position of the O 1s peak of sample A, whose LVO layer thickness was only 3 uc, was different from those of the rest because LAO and LVO have different energy positions of the O 1s core levels. Figure 4(b) shows an enlarged plot of

the V 2p<sub>3/2</sub> spectra. Here again, the V 2p<sub>3/2</sub> photoemission spectra showed complex line shapes consisting of V<sup>3+</sup> and V<sup>4+</sup> components, and no screening-derived peaks on the lower-binding-energy side of V 2p<sub>3/2</sub> were observed. The line shapes of the V 2p<sub>3/2</sub> spectra were very similar for samples A and B. The amount of V<sup>4+</sup> was larger in sample C, consistent with the case of V 1s and again shows the effect of the oxidation of the uncapped LVO.

We have fitted the core-level spectra of samples A and B to a Gaussian convoluted with a Lorentzian to estimate the amount of V<sup>3+</sup>, V<sup>4+</sup>, and V<sup>5+</sup> at the interface following the procedure of Ref. 9. Figure 5 shows the fitting results of the V 1s and V 2p<sub>3/2</sub> core-level spectra. Here, the spectra were decomposed into the V<sup>3+</sup> and V<sup>4+</sup> components, and the V<sup>5+</sup> component was not necessary. The full width at half maximum (FWHM) of the Lorentzian has been fixed to 1.01 eV for V 1s and to 0.24 eV for V 2p<sub>3/2</sub> according to Ref. 18. The FWHM of the Gaussian has been chosen 0.90 eV for both V<sup>3+</sup> and V<sup>4+</sup> of V 1s, 1.87 eV for V<sup>3+</sup> of V 2p<sub>3/2</sub>, and 1.25 eV for V<sup>4+</sup> of V 2p<sub>3/2</sub>. This reflects the larger multiplet splitting for V 2p than for V 1s and the larger exchange splitting for the V<sup>3+</sup> component than for the V<sup>4+</sup> component in the V 2p spectra. In Fig. 6, we summarize the ratio of the V<sup>4+</sup> component thus estimated, together with the results of the emission angle ( $\theta_e$ ) dependence of the V 2p core-level

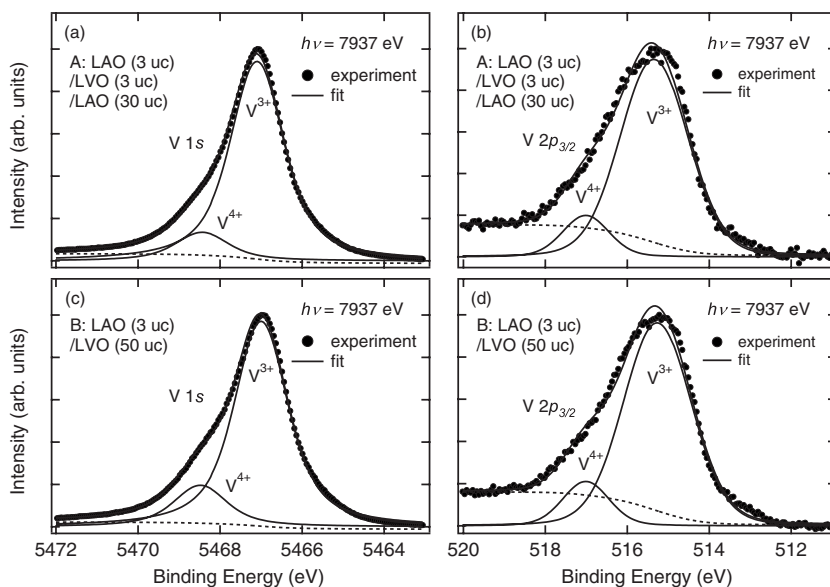


FIG. 5. Fitting results for the V 1s and 2p<sub>3/2</sub> core-level spectra. (a) V 1s core level of sample A (LaVO<sub>3</sub> 3 uc), (b) V 2p<sub>3/2</sub> core level of sample A (LaVO<sub>3</sub> 3 uc), (c) V 1s core level of sample B (LaVO<sub>3</sub> 50 uc), and (d) V 2p<sub>3/2</sub> core level of sample B (LaVO<sub>3</sub> 50 uc).

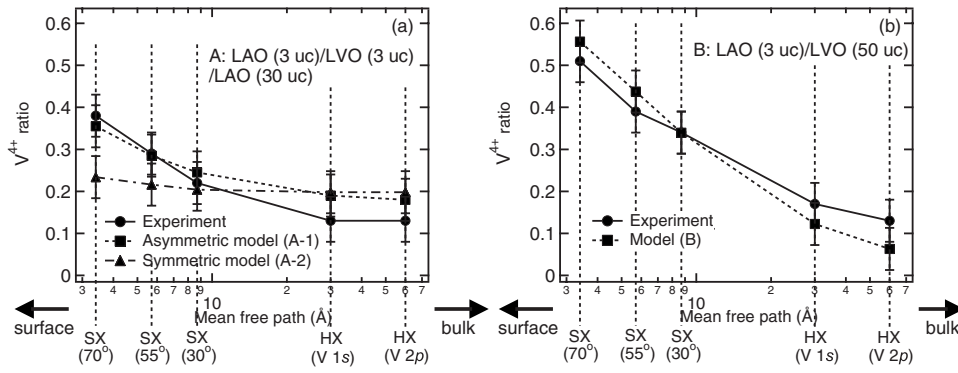


FIG. 6. Ratio of  $V^{4+}$  determined under various experimental conditions using hard x rays and soft x rays (Ref. 9). (a) Sample A (3 uc  $\text{LaVO}_3$ ) and (b) sample B (50 uc  $\text{LaVO}_3$ ). Here, SX is a result of soft x-ray photoemission and HX is of hard x-ray photoemission. In the case of SX, the values in the parenthesis denote the values of  $\theta_e$ .

SX photoemission spectra measured using a laboratory SX source.<sup>9</sup>

In order to interpret those results qualitatively, first we have to know the probing depth of photoemission spectroscopy under various measurement conditions. From the kinetic energies of photoelectrons, the mean free paths of the respective measurements are obtained as described in Ref. 19.<sup>20</sup> When we measure  $V 2p_{3/2}$  spectra with the  $\text{Mg } K\alpha$  line ( $h\nu = 1253.6$  eV), the kinetic energy of photoelectrons is about 700 eV and the mean free path is estimated to be about 10 Å. Likewise, we also estimate the mean free path in the HX case. The values are summarized in Table I. In the SX case, these values are  $(10 \cos \theta_e)$  Å. One can obtain the most surface-sensitive spectra under the condition of SX with  $\theta_e = 70^\circ$  [denoted by SX( $70^\circ$ )] and the most bulk-sensitive spectra for HX measurements of the  $V 2p_{3/2}$  core level [denoted by HX(V  $2p$ )]. From Fig. 6 and Table I, one observes a larger amount of  $V^{4+}$  components under more surface-sensitive conditions. These results demonstrate that the valence of V in LVO is partially converted from  $V^{3+}$  to  $V^{4+}$  at the interface.

In order to reproduce the present experimental result and the result reported in Ref. 9 (shown in Fig. 6), we propose a model of the V valence distribution at the interface as shown in Fig. 7. For sample A, we consider two models—that is, an asymmetric model and a symmetric model. In the asymmetric model (A1), no symmetry is assumed between the first and third layers. As shown in Fig. 6, the best fit result was obtained for the valence distribution that 50% of the first layer is  $V^{4+}$  and there are no  $V^{4+}$  in the second and third layers, assuming the above-mentioned mean free paths in Table I and exponential decrease of the number of photoelectrons. In the symmetric model (A2), it is assumed that the electronic structures are symmetric between the first and third layers. The best fit was obtained when 30% of the first and third layers are  $V^{4+}$ . In sample B, a model (B) where 70% of the first layer and 35% of the second layer are  $V^{4+}$  best reproduced the experimental result. One can see that the

thicker the LVO layer is, the more amount of  $V^{4+}$  there is at the interface. As shown in Fig. 6, for the 3-uc case, the model (A2) did not reproduce the experimental results well compared to (A1), which demonstrates that the valence distribution of V was highly asymmetric at these interfaces.

The origin of this highly asymmetric valence change from  $V^{3+}$  to  $V^{4+}$  at the interfaces can be interpreted in two ways. One possible scenario is a simple chemical effect during the fabrication process of the PLD technique. The topmost LVO layer spends a longer time before the next deposition of LAO than the rest LVO layers, and therefore, the oxidation process may easily proceed at the topmost layer. In this scenario, if we make samples under different oxygen pressures, the amount of  $V^{4+}$  at the interface may change greatly. In the other scenario, we consider that the polarity of the LAO/LVO multilayers plays an essential role. In the present samples, both the LAO and LVO layers are polar and do not consist of charge neutral layers; that is, they consist of alternating stack of  $\text{LaO}^+$  and  $\text{AlO}_2^-$  or  $\text{VO}_2^-$  layers. As recently discussed by Nakagawa *et al.*,<sup>23</sup> electronic reconstruction occurs during the fabrication of the polar layers in order to prevent the divergence of Madelung potential—i.e., so-called polar catastrophe.<sup>24</sup> We consider that the electronic reconstruction occurs in the present samples and that the valence change of V at the interface is a result of this reconstruction, although we cannot conclude whether the valence change occurs only

TABLE I. Mean free path of photoelectrons (in units of Å).

SX ( $70^\circ$ )	SX ( $55^\circ$ )	SX ( $30^\circ$ )	HX (V 1s)	HX (V 2p)
3.4	5.7	8.7	30	60

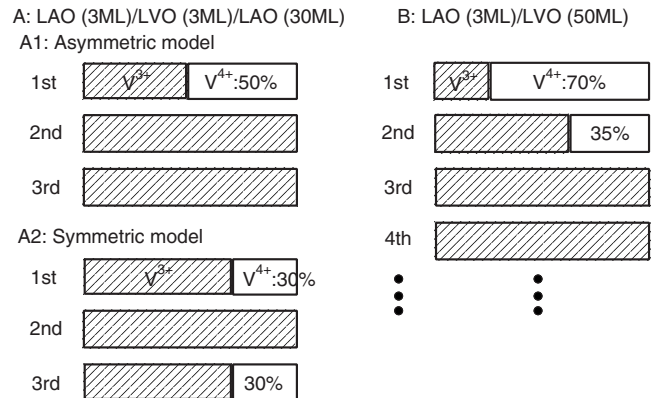


FIG. 7. Models for the V valence distributions in the  $\text{LaAlO}_3/\text{LaVO}_3$  multilayer samples. A:  $\text{LaVO}_3$  3 uc. A1 is an asymmetric model, whereas A2 is a symmetric model. B:  $\text{LaVO}_3$  50 uc.

at the top interface or continues to a few unit cells. This effect explains the 0.5 uc of  $V^{4+}$  for sample *A*, but we cannot explain the total amount of  $V^{4+}$  exceeding 0.5 uc for sample *B*, and we may also consider some chemical effects that V atoms are relatively easily oxidized at the topmost layer. Similar studies on samples with different termination layers will be necessary to test this scenario. Recently, Huijben *et al.*<sup>25</sup> studied STO/LAO multilayers and found a critical thickness of LAO and STO, below which a decrease of the interface conductivity and carrier density occurs. Therefore, changing the numbers of LAO capping layers may also change the valence of V at the interface. Further systematic studies, including other systems like LTO/STO<sup>1-4</sup> and LAO/STO,<sup>23,25,26</sup> will reveal the origin of the valence change at the interface.

#### IV. CONCLUSION

We have investigated the electronic structure of the multilayers composed of a band insulator LaAlO<sub>3</sub> and a Mott insulator LaVO<sub>3</sub> by means of HX photoemission spectroscopy. The Mott-Hubbard gap of LVO remained open at the interface, indicating that the interface is insulating and the delocalization of *3d* electrons does not occur unlike the LaTiO<sub>3</sub>/SrTiO<sub>3</sub> multilayers. From the V *1s* and *2p* core-

level photoemission intensities, we found that the valence of V in LVO was partially converted from  $V^{3+}$  to  $V^{4+}$  at the interface only on the top side of the LVO layer and that the amount of  $V^{4+}$  increased with LVO layer thickness. We have extended a model for the V valence distribution in order to explain the experimental result and concluded that the  $V^{4+}$  is preferentially distributed on the top of LVO layers in both thicker and thinner LVO cases. We suggest that the electronic reconstruction to eliminate polar catastrophe may be the origin of the highly asymmetric valence change at the interfaces.

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