Photoemission study of TiO_2/VO_2 interfaces

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We have measured photoemission spectra of two kinds of TiO_2-capped VO_2 thin films, namely, that with a rutile-type TiO_2 capping layer (r-TiO_2/VO_2) and that with an amorphous TiO_2 capping layer (a-TiO_2/VO_2). Below the metal-insulator transition temperature of the VO_2 thin films, ~300 K, TiO_2 and VO_2 form an interface between a band insulator with the d^0 electronic configuration and a Mott (or Mott-Peierls) insulator with the d^1 electronic configuration. Metallic states were, however, not observed at the interfaces, in contrast to the interfaces between the d^0 band insulator $SrTiO_3$ and the d^1 Mott insulator $LaTiO_3$. We discuss possible origins of the difference between TiO_2/VO_2 and $SrTiO_3/LaTiO_3$, and suggest the importance of the polarity discontinuity in the latter interface. The stronger incoherent part was observed in r-TiO_2/VO_2 than in a-TiO_2/VO_2, suggesting Ti-V atomic diffusion due to the higher deposition temperature for r-TiO_2/VO_2.

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I. INTRODUCTION

Strongly correlated electron systems, especially transition-metal oxides, have been the subject of numerous studies because of the variety of attractive behaviors including high-temperature superconductivity, giant magnetoresistance, and metal-insulator transition (MIT).[1] Among them, Ti and V oxides are typical systems in which MITs between Mott-Hubbard insulators and Fermi-liquid states have been studied.[1,2] Recently, high quality interfaces between transition-metal oxides have become available due to the development of epitaxial thin film fabrication techniques. Ohtomo *et al.*[3] have made an atomic-resolution electron-energy-loss spectroscopy study of layers of the Mott insulator $LaTiO_3$ (LTO) embedded in the band insulator $SrTiO_3$ (STO), and found that Ti $3d$ electrons are not completely confined within the LTO layer but are extended over the neighboring STO layers in spite of the chemically abrupt interfaces. Here, the Ti ion in LTO has the d^1 configuration, while that in STO has the d^0 configuration, i.e., the empty d band. Shibuya *et al.*[4] reported the metallic behavior of the STO/LTO interfaces by measuring the electrical resistivity of STO/LTO superlattices as a function of temperature. This metallic behavior is caused by the redistribution of electrons from the LTO into STO layers up to several monolayers, making the electronic structure of the interfaces analogous to that of the metallic $La_{1-x}Sr_xTiO_3$ alloy system.[5] Okamoto and Millis[6,7] have studied the spectral function of such systems by model Hartree-Fock and dynamical-mean-field-theory calculations and explained the novel metallic behavior at this interface between the two insulators, which they call "electronic reconstruction." Recently, Takizawa *et al.*[8] performed a photoemission spectroscopy study of LTO/STO interfaces using superlattice samples and, indeed, observed metallic behavior in the interface region. In this work, we have measured photoemission spectra of another series of interfaces formed between a d^0 band insulator, TiO_2, and a d^1 Mott (or Mott-Peierls) insulator, VO_2, in order to see whether the metallic behavior of the STO/LTO interfaces is a universal feature of band insulator and Mott insulator interfaces or not, and to gain further insight into the mechanism which causes the metallic behavior of these interfaces.

Vanadium dioxide (VO_2) is a well-known material which undergoes a transition between the high-temperature metallic phase and the low-temperature insulating phase.[9] In the high-temperature phase, the crystal has the tetragonal rutile-type structure, while in the low-temperature phase, the V atoms dimerize and twist, distorting the crystal from the tetragonal structure to a monoclinic one. Goodenough[10] first discussed the MIT based on a $d_{\parallel}$-d_{π} multiband model. Abbate *et al.*[11] directly observed the splitting of the unoccupied band into the $d_{\parallel}$ and d_{π} components in going from the metallic phase to the insulating phase by soft x-ray absorption spectroscopy. It has been debated for many decades whether the metal-insulator transition in VO_2 is derived by electron-lattice interaction (Peierls transition) or electron-electron interaction (Mott transition). The electronic structures of the metallic and insulating phases of VO_2 have been discussed emphasizing electron-phonon interaction,[12] electron-electron interaction,[13] and orbital degeneracy.[14,15] So far, several photoemission studies have been reported[16–20] on bulk VO_2 single crystals. Recently, Muraoka *et al.* prepared VO_2/TiO_2 thin films which undergo a MIT near room temperature.[21,22] By using thin films, it has become possible to perform detailed temperature-dependent photoemission spectroscopy (PES) studies utilizing the stability of the thin film surfaces.[23,24] In the present work, we have studied three samples: a VO_2 thin film capped with rutile-type TiO_2 (r-TiO_2/VO_2), a VO_2 thin film capped with amorphous TiO_2 (a-TiO_2/VO_2), and a VO_2 thin film without a TiO_2 capping layer. We observed no metallic states at the TiO_2/VO_2 inter-

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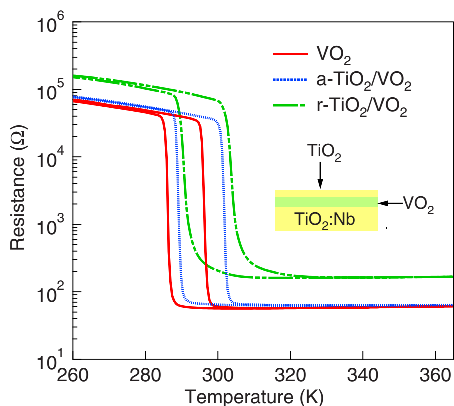

FIG. 1. (Color online) Electrical resistivity of the VO_2, a-TiO_2/VO_2, and r-TiO_2/VO_2 thin film sample.

face region for the low-temperature phase of VO_2 in contrast to the STO/LTO case.[8]

II. EXPERIMENT

The films were prepared using the pulsed laser deposition (PLD) technique on Nb-doped TiO_2(001) substrate.[21] V_2O_3 pellet was used as a target to prepare VO_2 thin films. During the deposition, the substrate temperature was kept at 733 K and the oxygen pressure was maintained at 1.0 Pa. The film thickness was about 10–15 nm and the surface roughness was estimated to be about 0.5 nm rms by atomic force microscopy. The r-TiO_2/VO_2 sample was prepared by depositing TiO_2 at 673 K on the VO_2 thin film. The a-TiO_2/VO_2 sample was prepared by depositing TiO_2 at room temperature. The thickness of the TiO_2 capping layer was 1–2 ML (monolayer), estimated from the deposition time. Although inhomogeneous growth of the TiO_2 layers could not be totally excluded and part of the VO_2 surface may have been exposed to air, part of the VO_2 surface should be covered by TiO_2 and a certain area of TiO_2/VO_2 interfaces should be created. The presence of the finite area of TiO_2/VO_2 interfaces is sufficient for the following argument to establish the absence of metallic features at the TiO_2/VO_2 interfaces. Resistivity of these samples are shown in Fig. 1. MIT was clearly observed in all the samples. The atomic structures of the TiO_2 capping layer were confirmed by comparing the Ti $2p$ x-ray absorption spectra with the previous results reported by Kucheyev *et al.*[2] as shown in Fig. 2. Due to the different TiO_2 deposition temperatures between r-TiO_2/VO_2 and a-TiO_2/VO_2, Ti and V atoms at the r-TiO_2/VO_2 interface may be more strongly interdiffused than those at the a-TiO_2/VO_2 interface as we shall see below. Epitaxial growth of r-TiO_2 on VO_2 film has been confirmed using the metal organic chemical vapor deposition technique, although in the present samples the atomic structure of the interfaces has not been characterized.[25,26]

PES measurements in the soft x-ray region were performed at BL-2C of Photon Factory, High Energy Accelerators Research Organization (KEK). The measurements were performed under an ultrahigh vacuum of $\sim 10^{-10}$ Torr from

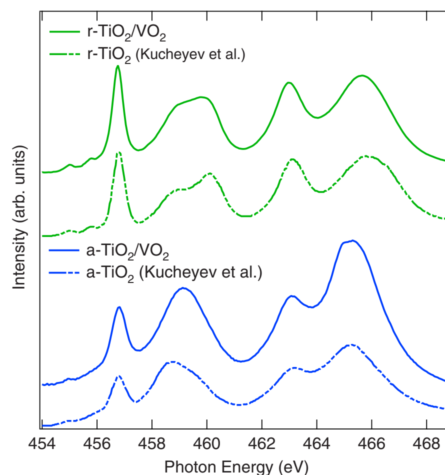

FIG. 2. (Color online) Ti $2p$ XAS spectra of r-TiO_2/VO_2 and a-TiO_2/VO_2 compared with spectra reported by Kucheyev *et al.* (Ref. 27).

room temperature down to 150 K using a Scienta SES-100 electron-energy analyzer. The total energy resolution was set to about 200 meV. Resonant photoemission spectroscopy (RPES) measurements at the V $2p \rightarrow$ V $3d$ absorption edge were performed to eliminate contributions from the TiO_2 capping layers. The Fermi-level (E_F) position was determined by measuring gold spectra. X-ray absorption spectroscopy (XAS) was performed in the total-electron-yield mode. The samples were transferred from the PLD chamber to the spectrometers through air, and no surface treatment was made. During the measurements, the samples were kept at room temperature (RT) to study the metallic phase, or at 220–250 K to study the insulating phase.

III. RESULTS AND DISCUSSION

Figure 3 shows the RPES spectra of a-TiO_2/VO_2 for different photon energies. The V $3d$ band was most strongly

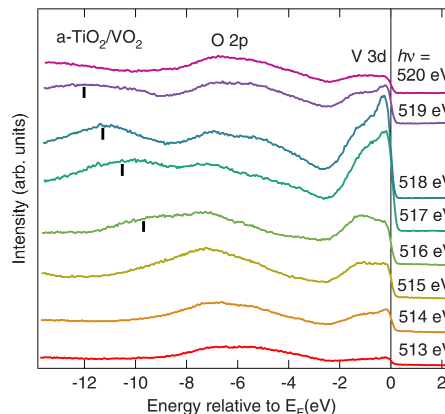

FIG. 3. (Color online) Valence-band V $2p \rightarrow 3d$ resonant photoemission spectra of a-TiO_2/VO_2 measured at room temperature. The V $3d$ band was strongly enhanced at 518 eV. Vertical lines indicate the LMM Auger peak position.

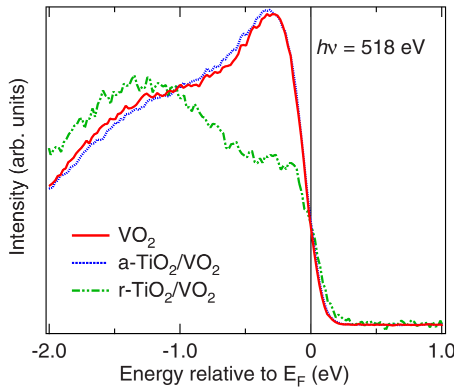

FIG. 4. (Color online) V $2p \rightarrow 3d$ resonant photoemission spectra of VO_2, a-TiO_2/VO_2, and r-TiO_2/VO_2 films in the V $3d$ band region. The photon energy corresponds to the V $2p \rightarrow 3d$ absorption edge and, therefore, these spectra were free from contributions from the TiO_2 capping layers.

enhanced at 518 eV due to V $2p \rightarrow 3d$ resonance. Hereafter, we show only V $2p \rightarrow 3d$ resonant photoemission spectra near E_F, where possible (Ti $3d$) contributions from the surfaces of the TiO_2 capping layers are masked by the resonantly enhanced V $3d$ emission. Figure 4 shows the RPES spectra of the VO_2, a-TiO_2/VO_2, and r-TiO_2/VO_2 samples in the V $3d$ band region measured at room temperature, i.e., spectra in which VO_2 was metallic. Each spectrum consisted of the coherent part (from −0.5 eV to E_F) and the incoherent part (from −2.0 to −0.5 eV). The spectra have been normalized to the integrated area in the V $3d$ band region. The spectrum of a-TiO_2/VO_2 was nearly identical to that of the VO_2 film. On the other hand, the spectra of r-TiO_2/VO_2 had stronger incoherent part than those of a-TiO_2/VO_2. Perhaps the amorphous TiO_2 layer did not form chemical bonding with the VO_2 surface and did not affect the electronic structure of the VO_2 film in the interface region.

In order to see the origin of the strong incoherent part for r-TiO_2/VO_2, the sensitivity of the photoemission measurements to the interface was varied by changing the emission angle as shown in Fig. 5. One can see that the incoherent part was enhanced as emission angle was increased, which indicates that the stronger incoherent part came from the interface region of r-TiO_2/VO_2. The different spectral weight distributions of the coherent and incoherent parts between r-TiO_2/VO_2 and a-TiO_2/VO_2 may have been caused by the different temperatures during the TiO_2 capping process. In the r-TiO_2/VO_2 sample, for which the TiO_2 capping layer was deposited at a higher temperature, Ti and V atoms may be interdiffused to some extent, and the interface region may become somewhat like $V_{1-x}Ti_xO_2$, which becomes less conducting as the Ti concentration increases.[28]

The temperature dependence of the V $3d$ valence-band spectra for r-TiO_2/VO_2 and a-TiO_2/VO_2 is shown in Fig. 6. In both samples, a metallic signature, namely, the Fermi edge, was not observed below the MIT temperature of the samples (Fig. 6) at the interface between the insulating TiO_2 and the insulating phase of VO_2, in contrast with the case of the STO/LTO interface,[8] although TiO_2 and VO_2 have d^0 and d^1 configurations, respectively, like STO and LTO.

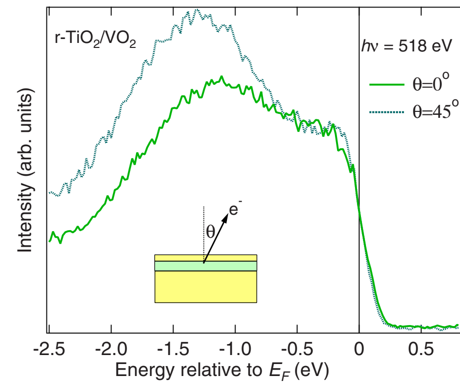

FIG. 5. (Color online) Angle dependence of the photoemission spectra of r-TiO_2/VO_2 in the V $3d$ band region. The result indicates that the strong incoherent part of r-TiO_2 arose from the interface region.

Since the metallic behavior of the STO/LTO interfaces comes from the extended distribution of electrons from the LTO to STO layers, the present result indicates that the electrons in VO_2 are confined within the VO_2 layer and are not redistributed into the TiO_2 capping layer. One possible explanation for the confinement of electrons can be made from the viewpoint of atoms constituting the interface: While TiO_2/VO_2 is composed of different transition-metal atoms, Ti and V, STO/LTO is composed of the same transition-metal atom, Ti. Therefore, the stronger attractive potential of the V atomic core than that of Ti may prevent electrons at the V site from being redistributed into the TiO_2 layer. From the crystal structure point of view, on the other hand, TiO_2/VO_2 has the rutile structure in which the d-band width is narrower than that of the perovskite structure and electrons may be more easily confined across the interface. The dielectric constant of the capping layer may also be important through the screening of electric potential: STO has a much larger dielec-

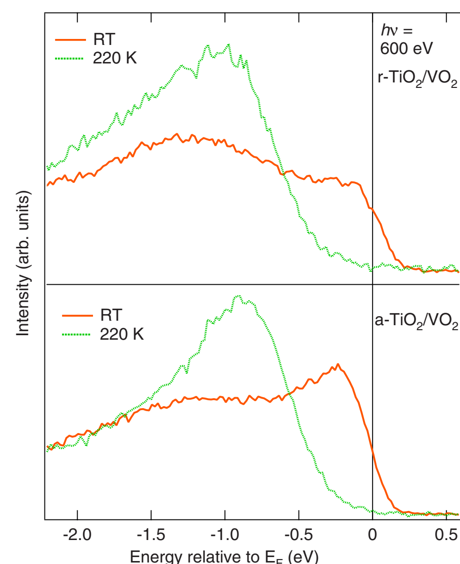

FIG. 6. (Color online) Photoemission spectra of r-TiO_2/VO_2 and a-TiO_2/VO_2 in the metallic and insulating phases of VO_2.

tric constant than TiO_2,[29] and may weaken the attractive potential of the Mott insulating layer compared to TiO_2. Moreover, the fact that VO_2 is not a simple Mott insulator but is a "Mott-Peierls insulator," where the Mott transition is accompanied by a crystal distortion, may also be important. The fact that $V_xTi_{1-x}O_2$ tends to be more insulating than VO_2 in contrast to $La_{1-x}Sr_xTiO_3$ being metallic may reduce the metallicity, if existed, of the TiO_2/VO_2 interfaces when there is atomic interdiffusion. Apart from the above various possibilities, we point out the fact that the penetration of electrons from the LTO to STO layers can be triggered by the polarity discontinuity at the interface: In order to avoid the macroscopic electric field generated across the polar LTO layer ($TiO_2^-/LaO^+/TiO_2^-/\ldots$), that is, in order to avoid the so-called polarity catastrophe,[30,31] part of the electronic charges should be transferred from the negatively charged TiO_2-layer side to the positively charged LaO-layer side of the LTO layer, causing the fractional occupation of the *d* band in both interface regions, and hence, the metallic state. In the case of the TiO_2/VO_2 interfaces, since the valence of V in VO_2 and that of Ti in TiO_2 are the same, such polarity discontinuity would not occur at the interface and the fractional occupancy of the *d* band would not occur. To confirm this scenario, systematic comparative studies of polarity discontinuous and continuous interfaces are necessary because the other possibilities including Ti-V atomic interdiffusion have not been completely ruled out at this stage.

IV. SUMMARY

We have performed photoemission measurements on TiO_2-capped VO_2 thin films. All the 3*d* band spectra showed the coherent and incoherent parts, and the coherent part disappeared in the insulating phase of VO_2. While *a*-TiO_2/VO_2 showed spectra almost identical to uncapped VO_2 thin film, the incoherent part was enhanced in *r*-TiO_2/VO_2, which we attribute to the interdiffusion of Ti and V atoms across the interfaces. Metallic state was not observed in the interfaces between the band insulator TiO_2 and the Mott-Peierls insulator VO_2 at low temperature for all the samples in contrast to the STO/LTO interfaces. We suggest that this is originated from the absence of polarity discontinuity at the TiO_2/VO_2 interface unlike the case of STO/LTO. In order to completely rule out the other mechanisms listed above, further systematic studies are necessary.

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