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Spectroscopic evidence of the formation of (V,Ti)O_2 solid solution in VO_2 thinner films grown on TiO_2(001) substrates

Y. Muraoka,[1,2,a)] K. Saeki,[1] R. Eguchi,[1,2,3] T. Wakita,[1,2] M. Hirai,[1,2] T. Yokoya,[1,2]
and S. Shin[3]
[1]*Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan*
[2]*Faculty of Science, Research Laboratory for Surface Science, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan*
[3]*RIKEN/SPring-8, 1-1-1 Kouto, Sayo, Hyogo, 679-5148, Japan*

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We have prepared VO_2 thin films epitaxially grown on TiO_2(001) substrates with thickness systematically varied from 2.5 to 13 nm using a pulsed laser deposition method, and studied the transport property and electronic states of the films by means of resistivity and *in situ* synchrotron photoemission spectroscopy (SRPES). In resistivity measurements, the 13-nm-thick film exhibits a metal-insulator transition at around 290 K on cooling with change of three orders of magnitudes in resistivity. As the film thickness decreases, the metal-insulator transition broadens and the transition temperature increases. Below 4 nm, the films do not show the transition and become insulators. *In situ* SRPES measurements of near the Fermi level valence band find that the electronic state of the 2.5-nm-thick film is different than that of the temperature-induced insulator phase of VO_2 itself although these two states are insulating. Ti 2*p* core-level photoemission measurements reveal that Ti ions exist near the interface between the films and TiO_2 substrates, with a chemical state similar to that in (V,Ti)O_2 solid solution. These results indicate that insulating (V,Ti)O_2 solid solution is formed in the thinner films. We propose a simple growth model of a VO_2 thin film on a TiO_2(001) substrate. Near the interface, insulating (V,Ti)O_2 solid solution is formed due to the diffusion of Ti ions from the TiO_2 substrate into the VO_2 film. The concentration of Ti in (V,Ti)O_2 is relatively high near the interface and decreases toward the surface of the film. Beyond a certain film thickness (about 7 nm in the case of the present 13-nm-thick film), the VO_2 thin film without any Ti ions starts to grow. Our work suggests that developing a technique for preparing the sharp interface between the VO_2 thin films and TiO_2 substrates is a key issue to study the physical property of an ultrathin film of "pure" VO_2, especially to examine the presence of the novel electronic state called a semi-Dirac point phase predicted by calculations. © *2011 American Institute of Physics*. [doi:10.1063/1.3549835]

I. INTRODUCTION

Vanadium dioxide VO_2, a $3d^1$ electron configuration system, undergoes a first-order metal-insulator transition (MIT) at 341 K accompanied by a structural change from a tetragonal rutile-type structure in a high-temperature metallic phase to a monoclinic structure in a low-temperature insulator phase.[1] The low-temperature insulator phase is characterized by the formation of distinct V–V dimmers along the *c* axis. Since the discovery of the MIT, numerous studies related to the transition have been done to elucidate the origin of the MIT. Despite of the intensive experimental and theoretical works, it is still under debate whether the MIT is driven mainly by an electron-phonon interaction (Peierls-type)[2,3] or an electron-electron interaction (Mott–Hubbard-type).[4]

Titanium dioxide TiO_2 has a rutile-type tetragonal structure in one of its polymorphs and is a $3d^0$ nonmagnetic band insulator. TiO_2 is technologically important because of its chemical stability and catalytic activity.

Recently, oxide multilayer nanostructures have received a great deal of attention because of their unexpected physical phenomena. A typical example is the $LaTiO_3/SrTiO_3$ (LTO/STO) multilayer nanostructure.[5] LTO is a Mott insulator with Ti $3d^1$ electron configuration while STO is a band insulator with Ti $3d^0$ electron configuration. In the LTO/STO multilayer nanostructure system, Ti 3*d* electrons are not confined within the LTO layer but are extended over neighboring STO layers, resulting in a metallic nature at the LTO/STO interfaces. Another example is the $LaAlO_3/SrTiO_3$ (LAO/STO) multilayer nanostructure.[6,7] Both LAO and STO bulk are band insulators. However, in the LAO/STO multilayer system, the interface between LAO and STO becomes metallic,[6] even superconducting, at low temperature.[7] For both systems, it is considered that the effects of having a polar interface come into play (called polar discontinuity), leading to unexpected physical phenomena. There are theoretical works that support the experimental observations.[8–10]

Very recently, Pardo and Pickett presented a theoretical study of the electronic behavior of the multilayer nanostructures of rutile-type $(TiO_2)_n/(VO_2)_m$ with first principles calculations.[11,12] Multilayer TiO_2/VO_2 nanostructures have

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[a)] Author to whom correspondence should be addressed. Electronic address: ymuraoka@cc.okayama-u.ac.jp.

d^0-d^1 interfaces with no polar discontinuity. In their calculations, the multilayer $(TiO_2)_5/(VO_2)_m$ nanostructures where m layers of VO_2 are sandwiched by 5 layers of insulating TiO_2 show a MIT with respect to the VO_2 layer thickness; for $m \geq 5$ layers the system becomes metallic while being insulating for $m = 1, 2$. Calculations also show that the MIT occurs through a two dimensional new electronic state called a semi-Dirac point phase for $m = 3, 4$. In this phase, the Fermi surface is pointlike and the electrons behave as massless fermions along the zone diagonal in k-space and as massive fermions along the perpendicular direction. Such a novel electronic state is considered to appear as a result of the effect of quantum confinement of VO_2 layers within insulating TiO_2. It is also shown from the calculation that the semi-Dirac point phase is half-metallic and show peculiar transport and thermodynamic properties.[13] Pardo and co-workers finally concluded that the multilayer $(TiO_2)_n/(VO_2)_m$ nanostructure system provides an example producing unexpected and unprecedented electronic states with no polar discontinuity.

Concerning the experimental works on TiO_2/VO_2 nanostructures, Muraoka and Hiroi prepared epitaxial thin films of VO_2 grown on TiO_2(001) substrates using a pulsed laser deposition (PLD) method.[14] In the films, the MIT temperature (T_{MI}) is reduced to 290 K while keeping the abrupt transition. This can be explained as a result of an in-plane tensile strain effects induced by the lattice mismatch between the films and TiO_2(001) substrates. Recently, Nagashima *et al.* studied the thickness dependence of the electrical property for VO_2 thin films on TiO_2(001) substrates in a range of film thickness from 3 to 15 nm.[15] They have found that as the thickness of the films decreases the T_{MI} increased with a loss of the steepness of transition accompanied with the increase in resistivity in the metallic phase of the films. Below 4 nm the abrupt MIT disappears and the films become insulator. It has been concluded that a minimum thickness of 5 nm (i.e., 15 layers) of VO_2 is needed to sustain an abrupt MIT. This experimental result does not agree with the theoretical one where metallic behavior is retained down to 5 layers of VO_2. Nagashima *et al*. claim that the interfacial structure between VO_2 thin films and TiO_2 substrates plays an important role in the electric properties of VO_2 thin films. However, the origin of insulating behavior for the VO_2 thinner films on TiO_2 substrates is not yet understood. It would be very beneficial to study the electronic properties of the VO_2 thinner films in order to not only elucidate the origin of the insulating behavior but also to assess the possibility of realizing the novel semi-Dirac point phase predicted by calculations.

Photoemission spectroscopy (PES) is a powerful experimental method to elucidate the electronic states of a material and has long played a central role in the measurements of the electronic properties of transition metal oxides (TMOs). Since PES is a surface sensitive technique, PES spectra are often affected by the disorder or segregation induced by surface preparation. Recently a synchrotron radiation photoemission spectroscopy (SRPES) system combined with a PLD chamber has been developed.[16] In this system, thin films prepared in a PLD chamber can be transferred into a PES chamber under high vacuum condition. Thus the film surface is kept clean and surface preparation is not necessary to be done. By using this system, one can perform *in situ* SRPES study of transition metal oxide thin films and obtain the PES data reflecting the intrinsic electronic state of TMOs.[17,18] It will be interesting to apply the *in situ* SRPES measurements to VO_2/TiO_2 (001) for the purpose of obtaining the intrinsic electronic states of the VO_2 thin films and valuable information on the origin of the insulating behavior in the VO_2 thinner films.

In this work, we prepared VO_2 thin films epitaxially grown on TiO_2(001) substrates with thickness systematically varied from 2.5 to 13 nm using a PLD technique, and studied the transport property and electronic states of the films by means of resistivity and *in situ* synchrotron photoemission spectroscopy in order to reveal the origin of the insulating behavior in the VO_2 thinner films.

II. EXPERIMENT

Experiments were carried out using a SRPES system combined with a PLD chamber at SPring-8 BL17SU. Epitaxial VO_2 thin films were grown on TiO_2(001) single crystal substrates by using a PLD technique with YAG laser ($\lambda = 355$ nm).[14] V_2O_3 was used as a target. During the deposition, the substrate temperature was kept at 573 K, and oxygen pressure was maintained at 1 Pa. After deposition, the films were cooled down to room temperature with same oxygen pressure. The prepared films were transferred into the PES chamber under a vacuum of 10^{-7} Pa without being exposed in air. The SRPES measurements were performed using a Gammadata-Scienta SES2002 spectrometer at temperatures of 270 and 390 K with a photon energy of 870 eV under an ultrahigh vacuum of 10^{-8} Pa. The total energy resolution was about 300 meV. The Fermi level (E_F) of VO_2 was referenced to that of a gold film evaporated onto the sample holder in all measurements.

We prepared the films with thickness of 2.5, 4, 5, 6, and 13 nm by controlling a number of laser pulse during film deposition. The film thickness was determined by a profilemeter for 6- and 13-nm-thick films. For the films with thickness less than 6 nm, the film thickness was estimated from the working curve between laser pulse number and film thickness made in advance. The surface morphology of the films was examined by atomic force microscopy in air and found to be smooth (for instance, a root mean square of 1.7 Å for a 13-nm-thick film). Epitaxy of the films was confirmed by reflection-high energy electron diffraction observations and also by a pole-figure obtained by x-ray measurements. Resistivity measurements were carried out using a standard four probe method in a physical properties measurement system (Quantum Design).

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of resistivity for the VO_2 thin films with various film thickness. For the 13-nm-thick film, an abrupt meal to insulator transition was observed around 290 K on cooling with a change of three orders of magnitudes in resistivity. As the film thickness decreased, the metal-insulator transition broadened and T_{MI} increased with a small jump in resistivity. Below 4 nm, the

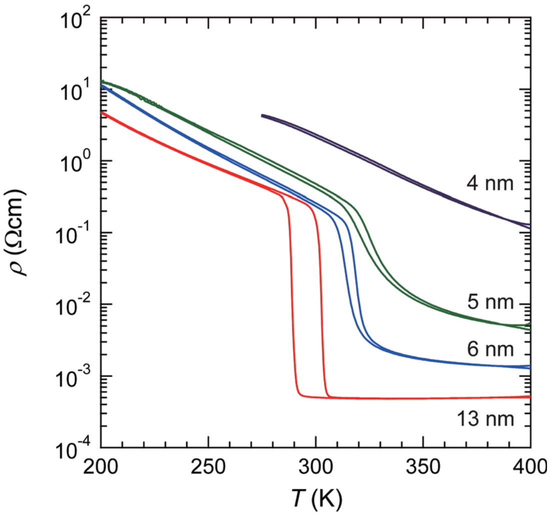

FIG. 1. (Color online) Temperature dependence of resistivity for the VO_2 thin films grown on $TiO_2(001)$ substrates with thickness of 4, 5, 6, and 13 nm.

films did not show the transition and became insulating. For the 2.5-nm-thick film, the resistance was too high to be measured using our apparatus. These results are in qualitatively good agreement with those reported previously.[15]

Figure 2 shows the valence band PES spectra across the MIT for the VO_2 thin film with a thickness of 13 nm, obtained from *in situ* SRPES measurements. The spectra were taken at 390 K for the metallic phase and at 270 K for the insulator phase. The cleanliness of the surface required for PES measurements can be confirmed by the absence of a hump structure around the binding energy of 8 – 10 eV which is often seen in the PES spectra on contaminated transition metal oxide surfaces.[19] The valence band spectra show a two-peak structure; a peak located at 0 – 2 eV is mainly due to the V 3*d* band and a broad band situated at 3 – 9 eV is mainly due to the O 2*p* band. The shape of the V 3*d* band drastically changes through the MIT, whereas the O 2*p* band shows no noticeable change. These results are in good agreement with those reported previously,[20–22] indicating that the reliable PES spectra of the VO_2 thin film are obtained in our measurements.

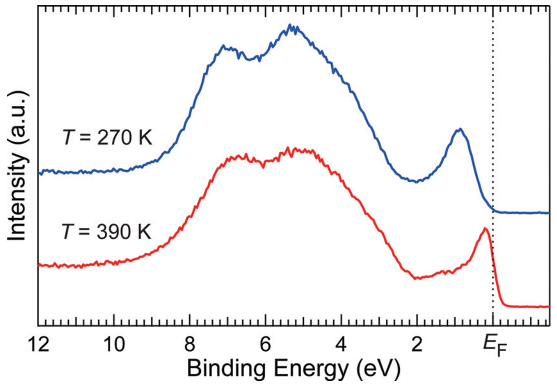

FIG. 2. (Color online) Valence-band PES spectra of the VO_2 thin film on $TiO_2(001)$ with thickness of 13 nm. The blue line shows the spectrum of the insulator phase measured at 270 K. The red line shows the spectrum of the metallic phase measured at 390 K. The spectra were taken at the photon energy of 870 eV.

Figure 3 shows the V 3*d* band PES spectra near E_F for VO_2 thin films with thicknesses of 2.5, 4, 5, 6, and 13 nm, measured at 390 K. The spectrum for the 13-nm-thick film showed a peak structure with the metallic Fermi edge as mentioned in Fig. 2. This spectral feature changed as the thickness of the films decreased; the intensity at E_F became weak with decreasing film thickness and finally disappeared in the 2.5-nm-thick film, accompanied with the shift of the peak position toward higher binding energy from 0.2 eV for the 13-nm-thick film to 1.1 eV for the 2.5-nm-thick film. The results indicate that the films become insulator as the film thickness decreases, which is consistent with the results from the resistivity measurements. Note that a finite intensity remained at E_F in the spectrum for the 4-nm-thick film. This means that the 4-nm-thick film was still metallic from a spectroscopic viewpoint although it showed insulating behavior in the resistivity measurements. This inconsistency can be explained on the assumption that the 4-nm-thick film contains a small fraction of metallic phase and a large fraction of insulator phase[23,24] and the insulating behavior in the resistivity measurements originates from the imperfection of the electric current path between metallic phases[23] while the metallic behavior in the SRPES measurements stems from the presence of a small fraction of the metallic phase. It is interesting to compare the spectrum of the 2.5-nm-thick film with that for the 13-nm-thick film at 270 K shown in Fig. 3. These two spectra are of insulating state. However, the

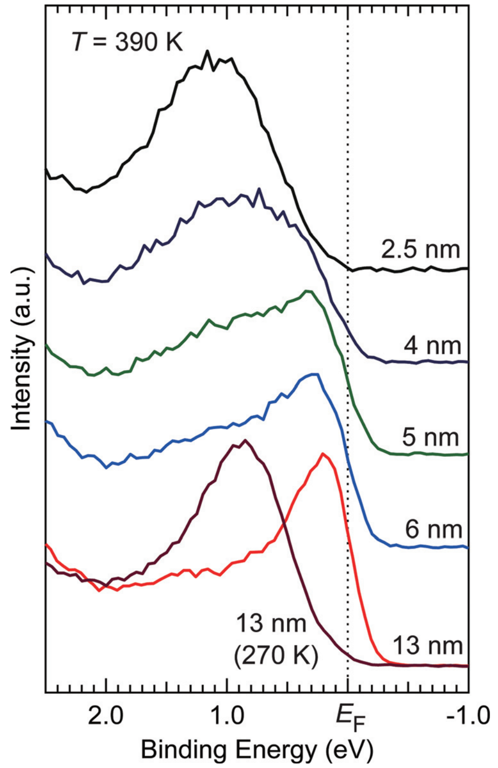

FIG. 3. (Color online) V 3*d* band PES spectra of the VO_2 thin films on $TiO_2(001)$ with thickness of 2.5, 4, 5, 6, and 13 nm measured at 390 K, together with V 3*d* spectrum of the 13-nm-thick film measured at 270 K for comparison.

spectrum of the 2.5-nm-thick film is not identical to that of the insulator phase for the 13-nm-thick film, namely, the peak position in the former spectrum is by 0.1 eV higher in binding energy than that in the latter one. This means that the electronic state of the insulating 2.5-nm-thick film is different than that of the temperature-induced insulator phase of VO_2 itself. Since the PES spectrum of the 2.5-nm-thick film reflects the electronic state near the interface between the VO_2 films and TiO_2 substrates, the obtained result indicates that the insulating electronic state which is different than the temperature-induced one appears near the interface.

We now consider the origin of the insulator phase near the interface between the VO_2 films and TiO_2 substrates. According to the previous work on the transport properties of $V_{1-x}Ti_xO_2$ thin films, the T_{MI} increases with disappearing the abruptness of transition and finally the films become insulator as the amount of Ti concentrations increase.[25] This change in transition behavior is quite similar to that observed in our resistivity measurements. In addition, more recent work on PES measurements of the VO_2 thin films with a rutile-type TiO_2 capping layer shows that the interdiffusion of Ti and V atoms occurs across the interface.[26] These results give us an idea that during VO_2 film deposition on TiO_2 substrates Ti atoms diffuse from the TiO_2 substrates into the VO_2 thin films to form insulating $(V,Ti)O_2$ solid solution near the interface. In order to confirm the idea, we performed SRPES measurements of the Ti $2p$ core-level for various thickness of the films.

Figure 4(a) shows the Ti $2p_{3/2}$ PES spectra for various thickness of the films measured at 390 K, together with those in insulating $(V_{1-x}Ti_x)O_2$ $(x = 0.6)$ solid solution bulk sample and $TiO_2(001)$ substrate for comparison. Since the escape depth of photoelectrons for the photon energy used is about 1 nm, our PES measurements provide the electronic state of the films within the depth of the nanometer order from the film surface. In the figure, each spectrum was normalized by the intensity of the O $1s$ spectrum. For the films with thicknesses of 2.5, 4, 5 and 6 nm, a finite intensity was observed in the Ti $2p_{3/2}$ core-level spectra. The intensity of the spectra became weak as the film thickness increased and no intensity was observed for the 13-nm-thick film. This result indicates that Ti ions exist near the interface between the films and $TiO_2(001)$ substrates and the amount of Ti ions in the film surface decreases with increasing the film thickness. The important fact is that the Ti $2p_{3/2}$ peak was situated at 458.41 eV for all spectra. This peak position is not close to that in the TiO_2 substrate itself, but to that in the $V_{0.4}Ti_{0.6}O_2$ solid solution, meaning that Ti ions in the films have chemical states that are similar to that in $V_{0.4}Ti_{0.6}O_2$ solid solution. The result indicates the formation of $(V,Ti)O_2$ solid solution near the interface, strongly supporting the proposed idea that Ti ions diffuse from the TiO_2 substrates into the VO_2 thin films near the interface to form $(V,Ti)O_2$ solid solution. We now estimate the diffusion distance of Ti ions along the direction of the film thickness. Here we consider that the intensity of the Ti $2p_{3/2}$ spectra corresponds to the amount of Ti ions, and the thickness of the films corresponds to the diffusion distance along the direction of the film thickness. We also consider that the intensity of the Ti $2p$ core-level spectrum for the 13-nm-thick film is zero and that in the TiO_2 substrate is 1. We plotted the intensity of the spectra with respect to the film thickness in Fig. 4(a). The intensity of the Ti $2p_{3/2}$ spectra decreased remarkably as the film thickness increased. The change in the intensity is well fitted by the function expressed as $\exp(-\alpha d^2)$ [see inset of Fig. 4(b)], where α is constant and d is the film thickness. Such a relationship between the amount of impurity atom (Ti ions in this work) and the diffusion distance in solid has been

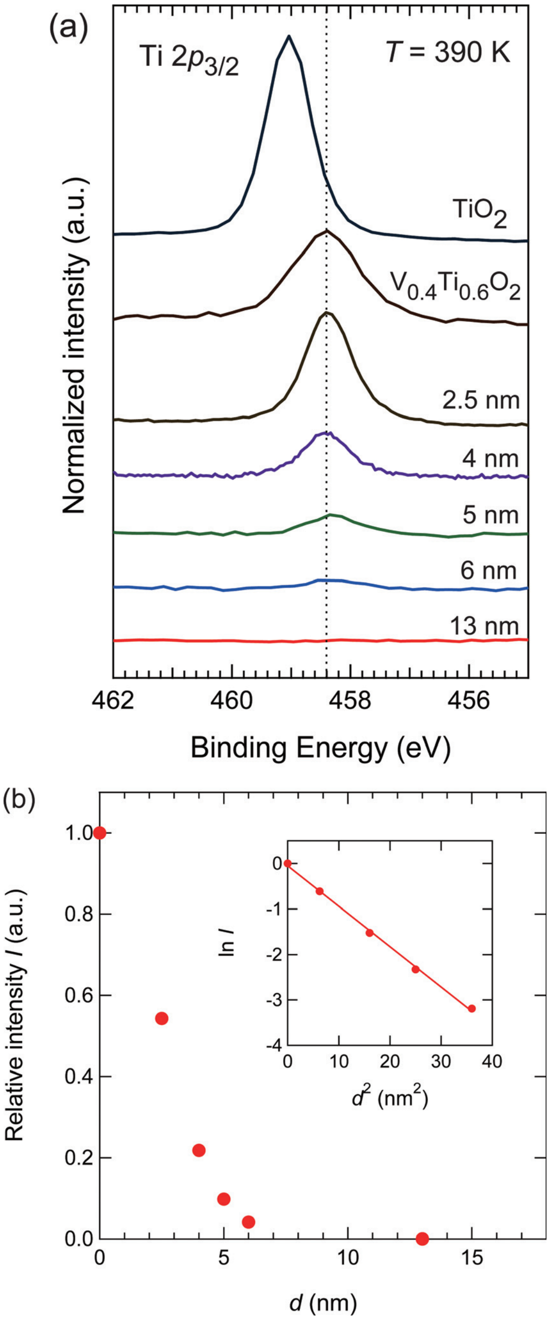

FIG. 4. (Color online) (a) Ti $2p_{3/2}$ core-level PES spectra of the VO_2 thin films on $TiO_2(001)$ with thickness of 2.5, 4, 5, 6, and 13 nm measured at 390 K, together with those of $V_{0.4}Ti_{0.6}O_2$ bulk and $TiO_2(001)$ substrate for comparison. Each spectrum was normalized by the intensity of the O $1s$ spectrum. (b) Relative intensity plot of the Ti $2p_{3/2}$ core-level spectra with respect to the film thickness d. The inset represents the logarithm plot of the relative intensity of the Ti $2p_{3/2}$ core-level with respect to the square of the film thickness d^2. Here, we consider the intensity of the Ti $2p$ core-level spectrum for the 13-nm-thick film as zero and that in TiO_2 substrate as 1.

observed in semiconductor systems like silicon[27] where the impurity atom on the surface of semiconductor diffuses into the interior of the semiconductor by thermal annealing. There might be some similarities in the diffusion mechanism between Ti-VO_2 and the semiconductor system. The intensity of the Ti $2p_{3/2}$ spectra reaches almost zero at about 7 nm in the horizontal axis in Fig. 4(a). This suggests that the diffusion distance of Ti ions from the interface toward the film surface is about 7 nm. This estimation also suggests that the VO_2 thin film without any Ti ions starts to be formed from thicknesses above 7 nm.

We now propose a simple growth model of a VO_2 thin film on a TiO_2(001) substrate as shown in Fig. 5. Near the interface, an insulating $(V,Ti)O_2$ solid solution is formed due to the diffusion of Ti ions from the TiO_2 substrate into the VO_2 film. The concentration of Ti in $(V,Ti)O_2$ is relatively high near the interface, decreases toward the surface of the film, and then becomes almost zero at a certain distance from the interface. Beyond a certain distance from the interface (about 7 nm in the case of our 13-nm-thick film), a VO_2 thin film without any Ti ions starts to grow. One may be reminded of the influence of the $(V,Ti)O_2$ formation on the epitaxial strain effect in the VO_2 thin films. Here, there is an important result of XRD measurements that the in-plane lattice parameter (*a*-axis length) of the 13-nm-thick film matches that of the TiO_2 substrate well (not shown in the paper, see Refs. 14 and 28). This indicates that both $(V,Ti)O_2$ near the interface and subsequently formed VO_2 film are epitaxially grown on the TiO_2 substrate. Thus it is considered that the in-plane tensile strain induced by the lattice mismatch between the film and TiO_2(001) substrate is retained in the whole of the film. In such an epitaxial film, the tensile strain effect can work in the whole of the film, resulting in the reduction of the metal-insulator transition temperature compared with the transition temperature in bulk. We would like to comment on the Ti $2p_{3/2}$ peak position in $(V_{1-x}Ti_x)O_2$. From our preliminary PES measurements for $V_{1-x}Ti_xO_2$ ($x = 0.4-0.8$) bulk samples under the same experimental condition as for film samples, we have found that the Ti $2p_{3/2}$ peak position shifts very slightly toward higher binding energy with increasing Ti concentration, namely, only about 0.1 eV from $x = 0.4$ to 0.8 in $V_{1-x}Ti_xO_2$. This result indicates that the Ti $2p_{3/2}$ peak position is nearly insensitive to the Ti concentration in $V_{1-x}Ti_xO_2$. When looking at Fig. 4(a), we see that the Ti $2p_{3/2}$ peaks from the films with different thickness do not shift from that of $V_{0.4}Ti_{0.6}O_2$, although the Ti concentration is different in the films at the PES detection depth. This insensitive peak shift behavior to the Ti concentration in the films is in good agreement with the result in the bulk mentioned above. When performing more detailed PES measurements, we will be able to see the change in the Ti $2p_{3/2}$ peak position with the Ti concentration (namely, the film thickness) in the films.

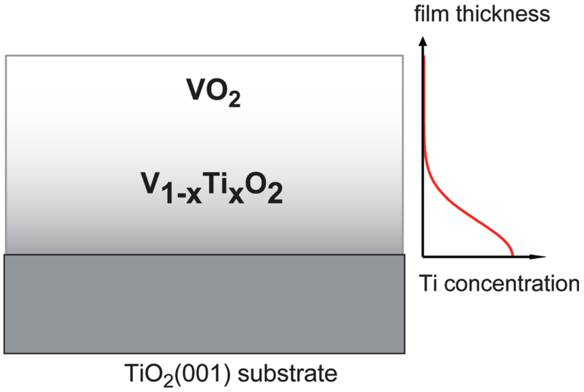

FIG. 5. (Color online) Schematic representation of a growth model of a VO_2 thin film on a TiO_2(001) substrate. Near the interface, $(V,Ti)O_2$ solid solution is formed due to the diffusion of Ti ions from the TiO_2 substrate into the VO_2 film. The concentration of Ti in $(V,Ti)O_2$ is relatively high near the interface and decreases toward the surface of the film. Beyond a certain film thickness, the VO_2 thin film without any Ti ions starts to grow.

Our work finds that the VO_2 thinner films grown on TiO_2(001) substrates become insulating because of the formation of $(V,Ti)O_2$ solid solution due to the diffusion of Ti ions from the TiO_2 substrates into the films during film deposition. Also, we would like to mention that *in situ* SRPES technique is effective to reveal the intrinsic electronic states of the thinner films in the VO_2/TiO_2(001) system. For the purpose of studying the physical property of a “pure” VO_2 thinner film, it is necessary to prepare a VO_2 thin film without any Ti ions. Such a film could be obtained when the film is prepared at substrate temperature as low as possible, because the diffusion distance of the ion generally becomes smaller at lower temperature. It would be also effective in film preparation to use a buffer layer whose constituent material is chemically nonactive to both TiO_2 and VO_2. Developing a method for film preparation with the sharp interface between the VO_2 films and the TiO_2 substrates will provide an opportunity not only to study the physical property of an ultrathin film of “pure” VO_2, but also to prepare multilayer nanostructures of rutile-type $(TiO_2)_n/(VO_2)_m$ and verify the presence of a semi-Dirac point phase in the $(TiO_2)_n/(VO_2)_m$ multilayer system predicted by calculations.

IV. CONCLUSIONS

We have prepared VO_2 thin films epitaxially grown on TiO_2(001) substrates with thickness systematically varied from 2.5 to 13 nm using a PLD method, and studied the transport property and electronic states of the films by means of resistivity and *in situ* synchrotron photoemission spectroscopy. In resistivity measurements, the 13-nm-thick film exhibits a metal-insulator transition at around 290 K on cooling with a change of three orders of magnitudes in resistivity. As the film thickness decreases, the metal-insulator transition broadens and the transition temperature increases. Below 4 nm, the films do not show the transition and become insulating. In *in situ* SRPES measurements, the V 3*d* band spectra near E_F show the decrease in the intensity of the Fermi level as the film thickness decreases. The SRPES measurements also find that the electronic state of the 2.5-nm-thick film is different than that of the temperature-induced insulator phase of VO_2 itself although these two states are insulating. Ti 2*p* core-level spectra measurements reveal that Ti ions exist near the interface between the films and TiO_2(001) substrates, possessing a chemical state similar to that in $V_{0.4}Ti_{0.6}O_2$ solid solution. These results indicate that insulating $(V,Ti)O_2$

solid solution is formed in the thinner films. Based on the obtained results, we propose a simple growth model of a VO_2 thin film on a TiO_2(001) substrate. Near the interface, insulating $(V,Ti)O_2$ solid solution is formed due to the diffusion of Ti ions from the TiO_2 substrate into the VO_2 film. The concentration of Ti in $(V,Ti)O_2$ is relatively high near the interface and decreases toward the surface of the film. Beyond a certain film thickness (about 7 nm in the present case of 13-nm-thick film), the VO_2 thin film without any Ti ions starts to grow.

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