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Electronic Structure of VO_2 Thin Film with Lattice Distortion Probed by Soft-X-Ray Spectroscopy

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The electronic structure of VO_2 thin film with the lattice distortion has been studied by soft-X-ray spectroscopy. The as-deposited VO_2 thin film prepared by sputtering has the mixed valence states of V^{4+} and V^{3+}. The valence band is mainly composed of the O2*p* state hybridized with the V 3*d* state. The coherent and incoherent bands are observed at near the Fermi level (E_F) in the thin film with small lattice distortion. The photoemission spectrum of the thin film with large lattice distortion does not exhibit DOS at E_F at room temperature. These results indicate that the bandwidth is closely related with the metal-insulator transition.

1 Introduction

Vanadium dioxide VO_2 single crystal with d^1 configuration occurs the metal-insulator transition (MIT) at ~340K. The VO_2 has rutile structure above 340K and monoclinic structure below 340K. The structural and electrical properties have been studied in the single crystal and thin film forms. For a long time, the MIT has been described in term of single-band Hubbard model, which contributes to the delicate balance of bandwidth and on-site Coulomb energy. The MIT temperature can control by pressure, carrier doping and introduction of V vacancies. Such controls may possible the change of bandwidth. Therefore, the relationship between MIT and bandwidth of VO must be clarified in term of electronic structure.

In this study, the authors have prepared the VO_2 thin films on (0001) Al_2O_3 substrates by sputtering and probed their electronic structures by X-ray absorption spectroscopy (XAS) and high-resolution photoemission spectroscopy (PES). The lattice distortion of VO_2 thin film, which corresponds to the effect of pressure for VO_2 single crystal, exists on Al_2O_3 substrate due to the lattice mismatch between the VO_2 and Al_2O_3. In this paper, the authors present the valence state of Vanadium and electronic structures of the valence band and Fermi level regions on the VO_2 thin films with several film thickness.

2 Experiment

VO_2 thin films were deposited on (0001) Al_2O_3 substrates by RF magnetron sputtering using oxygen radical and V-metal target. During the deposition, the deposition pressure, the RF power of V-metal target and substrate temperature were fixed at 5 mTorr, 60 W, and 600°C, respectively. The oxygen radical with unpaired electron was used as reactive gas for sputtering deposition [1]. The prepared thin films were crystallized without postannealing. The VO_2 thin films exhibited the (020) single phase. The lattice constant of *b*-axis is shown in Table 1.

The electronic structures were studied by XAS and PES installed at an undulator beamline BL2C. The energy resolutions of XAS and PES at *hν*=800eV were 60 meV and 100 meV, respectively.

3 Results and Discussion

Figure 1 shows the electrical resistivity of VO_2 thin films as a function of the film thickness. The VO_2 thin film with 55.54 nm occurs MIT at ~340 K, which corresponds to the single crystal. The thin films with 126.30 and 157.63 nm do not exhibit MIT, although the resistivities slowly increase with decreasing temperature. This result may indicates that the change of lattice constant of *b*-axis is closely related with MIT.

Table 1 Lattice constant of *b*-axis for the film thickness

Film thickness	Lattice constant (*b*-axis)
55.54 nm	4.636 Å
126.30 nm	4.481 Å
157.63 nm	4.480 Å

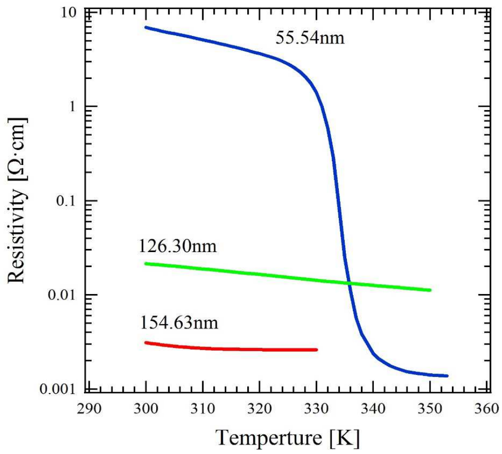

Fig.1 Electrical resistivity of VO_2 thin films as a function of the film thickness.

Figure 2 shows the XPS spectra in the O 1*s* and V 2*p* core levels of the VO_2 thin films as a function of the film thickness. The peak positions of O 1*s* and V 2*p* core levels do not depend on the film thickness. The V $2p_{3/2}$ core level consists of double peaks of V^{4+} and V^{3+}, which corresponds to the mixed valence states of V^{4+} and V^{3+}. The intensity of V^{3+} increases and that of V^{4+} decreases with the film thickness. This indicates that the amount of oxygen vacancies increase with the film thickness.

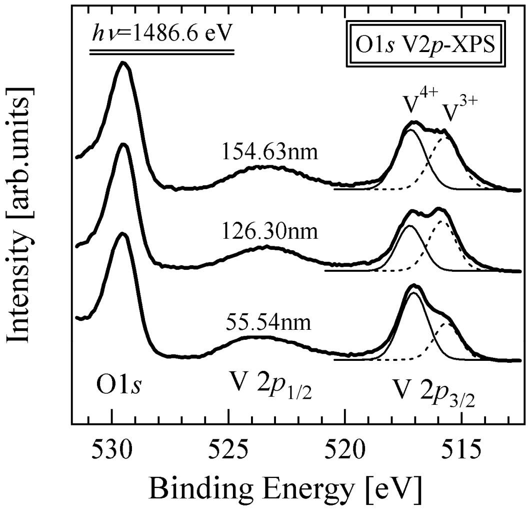

Fig. 2 XPS spectra of V 2*p* and O 1*s* core levels of VO_2 thin film as a function of film thickness.

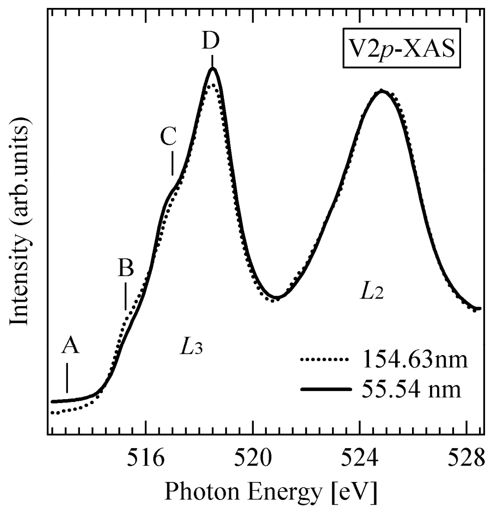

Fig. 3 V 2*p* XAS spectra of VO_2 thin film with film thickness of 55.54 and 154.63 nm. The labels A, B, C, and D are the excitation energies for resonant-PES measurements.

Figure 3 shows the V 2*p* XAS spectra of VO_2 thin film with film thickness of 55.54 and 154.63 nm. The V 2*p* XAS corresponds to the transition from the V 2*p* core level to the unoccupied V 3*d* state. The V 2*p* XAS spectra consist of $2p_{3/2}$ (L_3) and $2p_{1/2}$ (L_2) states. Although the spectral shape do not depends on the film thickness, the intensity of e_g^{π} (peak B) is lower and those of a_{1g} (peak C) and e_g^{σ} (peak D) are higher in 55.54 nm. This is considered to be due to the change of V 3*d* DOS with the lattice distortion and oxygen vacancies.

Figure 4 shows the resonant-PES spectra of VO_2 thin film with film thickness of 55.54 nm. The off-resonance spectrum A reflects the O 2*p* DOS in the valence band region. The spectra B, C, D exhibit apparent resonance effect of V $3p \rightarrow 3d$ at ~1.8 eV, which corresponds to the incoherent band. The peak position depends on the excitation energy. These peak positions accord with the

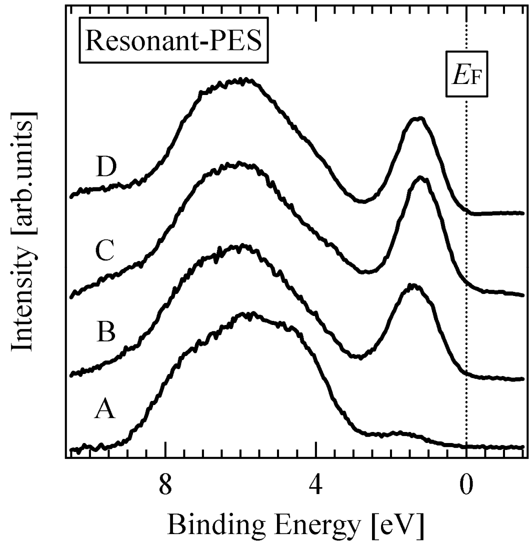

Fig. 4 V 2*p* resonant PES spectra of VO_2 thin film with film thickness of 55.54 nm measured at various excitation energies of Fig. 3.

a_{1g} and e_g^{π} states of V 3*d*. The DOS at E_F is not observed in these spectra. This indicates that the thin film is Mott-insulator at room temperature. The VO_2 thin film with film thickness of 154.63 nm, which exhibits the low electrical resistivity, has an apparent Fermi edge, although the spectral data are not shown in this paper. These results indicate that the MIT of VO_2 thin film is closely related with the lattice distortion.

4 Summary

We have studied the electrical resistivities and electronic structures of VO_2 thin films with various film thickness on Al_2O_3 substrates. The MIT is controlled by lattice distortion and oxygen vacancies. The corresponding spectral data were obtained in this study.

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References

[1] Y. Shimazu *et al.*, Jpn. J. Appl. Phys. **53** (2014) 06JG01.

Research Achievements

1. T. Inoue, T. Okumura, Y. Shimazu, E. Sakai, H. Kumigashira, T. Higuchi; Jpn. J. Appl. Phys. **53** (2014) 06JG03.
2. Y. Shimazu, T. Okumura, A. Shimada, K. Tanabe, K. Tokiwa, E. Sakai, H. Kumigashira, T. Higuchi; Jpn. J. Appl. Phys. **53** (2014) 06JG05.
3. K. Usui, T. Okumura, E. Sakai, H. Kumigashira, T. Higuchi; J. Phys.: Condens. Matter. **502** (2013) 012001.

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