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 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 $d$ 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$_2$O$_3$ 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$_2$O$_3$ substrate due to the lattice mismatch between the VO$_2$ and Al$_2$O$_3$. 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$_2$O$_3$ 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 $h\nu$=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

<table>
<thead>
<tr>
<th>Film thickness</th>
<th>Lattice constant ($b$-axis)</th>
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<tbody>
<tr>
<td>55.54 nm</td>
<td>4.636 Å</td>
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<tr>
<td>126.30 nm</td>
<td>4.481 Å</td>
</tr>
<tr>
<td>157.63 nm</td>
<td>4.480 Å</td>
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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 2$p_{3/2}$ 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 2p and O 1s core levels of VO₂ thin film as a function of film thickness.

Fig. 3 V 2p XAS spectra of VO₂ 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 2p XAS spectra of VO₂ thin film with film thickness of 55.54 and 154.63 nm. The V 2p XAS corresponds to the transition from the V 2p core level to the unoccupied V 3d state. The V 2p XAS spectra consist of 2p3/2 (L₃) and 2p1/2 (L₂) states. Although the spectral shape do not depends on the film thickness, the intensity of eₓ⁺ (peak B) is lower and those of a₁g (peak C) and eₓ⁻ (peak D) are higher in 55.54 nm. This is considered to be due to the change of V 3d DOS with the lattice distortion and oxygen vacancies.

Figure 4 shows the resonant-PES spectra of VO₂ thin film with film thickness of 55.54 nm measured at various excitation energies of Fig. 3.

α₁g and eₓ⁻ states of V 3d. The DOS at E_F is not observed in these spectra. This indicates that the thin film is Mott-insulator at room temperature. The VO₂ 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 VO₂ thin film is closely related with the lattice distortion.

4 Summary
We have studied the electrical resistivities and electronic structures of VO₂ thin films with various film thickness on Al₂O₃ 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

Research Achievements

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