Angle-resolved photoemission spectroscopy for VO_2 thin films grown on TiO_2 (001) substrates

Y. Muraoka,[1,2] K. Saeki,[1] Y. Yao,[1] T. Wakita,[2] M. Hirai,[1,2] T. Yokoya, [1,2]

R. Eguchi,[3] S. Shin[3]

[1] *Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan*

[2] *Faculty of Science, Research Laboratory for Surface Science, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan*

[3]*RIKEN/SPring-8, 1-1-1 Kouto, Sayo, Hyogo, 679-5148, Japan*

Abstract

We present the results of angle-resolved photoemission spectroscopy (ARPES) measurements of metallic VO_2 thin films. The VO_2 thin films have been grown on TiO_2 (001) single crystal substrates using pulsed laser deposition. The films exhibit a first-order metal-insulator transition (MIT) at 305 K. In the ARPES spectra of the metallic phase for the films, the O 2*p* band shows highly dispersive feature in the binding energy range of 3 – 8 eV along the Γ - *Z* direction. The periodicity of the dispersive band is found to be 2.2 $Å^{-1}$ which is almost identical with the periodicity expected from the *c*-axis length of the VO_2 thin films. The overall feature of the experimental band structure is similar to the band-structure calculations, supporting that we have succeeded in observing the dispersive band of the O 2*p* state in the metallic VO_2 thin film. The present work indicates that the ARPES measurements using epitaxial thin films are promising for determining the band structure of VO_2.

Keywords: ARPES, VO_2, thin film

Vanadium dioxide, VO_2, exhibits a metal-to-insulator transition (MIT) at 341 K[1] which is a first-order phase transition accompanied by a structural change from a high-temperature rutile-type tetragonal form to a low-temperature monoclinic form with zigzag-type pairing of V atoms along the *c* axis. Magnetically, the metallic phase shows the enhanced magnetic susceptibility while the insulator phase shows nonmagnetic. Since the first observation 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 by an electron-phonon interaction (Peierls-type)[2,3] or electron-electron interaction (Mott-Hubbard-type)[4].

Angle-resolved photoemission spectroscopy (ARPES) is one of the most powerful methods to determine the band structure of materials. Thus ARPES measurements of VO_2 are highly encouraged. However, few ARPES measurements of VO_2 single crystal have been reported so far. This is mainly because of the difficulty in obtaining a chemically stable cleavage plain in VO_2 single crystal with the three-dimensional crystal structure. Recently, a high-quality epitaxial thin film of VO_2 was prepared on TiO_2(001) single crystal substrates by a pulsed laser deposition technique[5]. The T_{MI} of the film was reduced to 300 K due to in-plain tensile strain effect induced by the lattice mismatch between the film and the substrate. Okazaki[6] and Eguchi[7] performed angle-integrated photoemission spectroscopy (PES) measurements of the VO_2 thin film and obtained the PES spectra without any surface problem seen in single crystals. Their works motivate us to perform ARPES measurements using VO_2 thin films. In this paper, we report on the ARPES measurements using VO_2 thin films and demonstrate the band dispersion of oxygen 2*p* state near the Fermi level (E_F) in the metallic phase.

We fabricated VO_2 thin films epitaxially grown on TiO_2 (001) single crystal substrates using a pulsed laser deposition technique with YAG laser ($\lambda = 355$ nm)[5]. The film thickness was measured by a profilometer to be 10 nm. The prepared films were examined by x-ray diffraction measurements and found to be an (001)-oriented single phase. The *c*-axis length of the films was determined to be 2.844 Å which is smaller than that of bulk material (2.855 Å). This compression of the *c*-axis length is

plausible due to an in-plane tensile stress (lattice mismatch: 0.86 %). The surface morphology of the films was examined by atomic force microscopy and the surface was found to be smooth enough for the ARPES measurements. The epitaxy of the films was confirmed by reflection high-energy electron diffraction observations and also by pole figure obtained by x-ray measurements. Resistivity measurements were carried out using a standard four-point probe method.

ARPES measurements were performed on the beamline BL-5, at Hiroshima Synchrotron Radiation Center in Hiroshima University. In the present measurements, the (001) surface of VO_2 thin films was situated normal to the analyzer, and the ARPES spectra were taken with changing the excitation photon energy $h\nu$ from 50 to 200 eV. The total energy resolution was about 200 – 300 meV depending on the photon energy used. ARPES spectra were measured at 300 K for an insulator phase and at 350 K for a metallic phase under an ultrahigh vacuum of ~10^{-7} Pa using a VSW hemispherical analyzer with an acceptance angle of ±1˚. The Fermi level position was determined by measuring gold spectra. Before measurements, the films were annealed at 100 °C under the ultrahigh vacuum for 1h to obtain a clean surface.

Figure 1 shows the temperature dependence of the resistivity for $VO_2/TiO_2(001)$ thin film. A large jump in resistivity is observed at 305 K on cooling and 315 K on heating due to the MIT. T_{MI} is lower by 30 K than that for bulk material. The decrease in T_{MI} is considered to be due to an in-plane tensile stress at the interface between the films and the substrates. The thermal hysteresis is due to the first-order nature of the phase transition. A large and sharp change in resistivity observed at the transition indicates the high quality of the films. These results are in good agreement with previous ones[5].

Figure 2 shows the valence band photoemission spectra of the VO_2 thin films across the MIT for a photon energy of 150 eV. In the valence band spectra, 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. The obtained results are in good agreement with those reported previously[6-9], indicating that the surface preparation described above is enough for obtaining PES spectra of VO_2.

Figure 3 shows ARPES spectra of the VO_2 thin films in the metallic phase measured at 350 K. The spectra were taken by changing photon energy from 50 to 200 eV in a step of 5 eV in the normal emission mode. As seen in Fig. 3, the ARPES spectra exhibit considerable and systematic changes as a function of photon energy; highly dispersive feature is observed in the O 2*p* band with the binding energy range of 3 – 8 eV. Since the photon energy can be converted to the wave vector perpendicular to the crystal surface $k_\perp$, the spectral change with photon energy directly represents the band structure of the VO_2 thin films along the Γ- *Z* direction in the Brillouin zone of the rutile-type tetragonal structure. Figure 4 shows the experimental band structure of the VO_2 thin films derived from the present normal emission ARPES measurements. The ARPES spectra are plotted as a function of $k_\perp$ and the binding energy. The inner potential used here is 16 eV which is estimated from the detailed ARPES measurements of the V 3*d* state (not shown in this paper). As expected from ARPES spectra shown in Fig. 2(a), dispersive band structure is observed in the O 2*p* state in the binding energy of 3 – 8 eV. It is also observable that the band structure shows a periodical feature along the Γ - *Z* direction. The periodicity of the dispersive band is found to be 2.2 $Å^{-1}$ which is almost identical with the periodicity expected from the *c*-axis length of the VO_2 thin films. The overall feature of the experimental band structure is similar to the band-structure calculations[10,11], supporting that we have succeeded in observing the dispersive band of the O 2*p* state in the metallic VO_2 thin film.

In summary, we have performed angle-resolved photoemission (ARPES) measurements in a metallic phase of VO_2 using the thin films grown on TiO_2 (001) substrates, and demonstrated a dispersive feature of the O 2*p* band along the Γ- *Z* direction. The dispersion periodicity of the O 2*p* band is consistent with that expected from the *c*-axis length of the films. Our study indicates that the combination of the epitaxial thin films with ARPES measurements can be a useful experimental technique for determining the electronic band structure of VO_2 with no chemical stable cleavable planes.

Acknowledgements

The authors are very grateful to A. Chainani for film preparations, J. Takada and T.

Fujii for x-ray measurements, and K. Oshima and T. Kambe for resistivity measurements. This research was supported by JST, CREST and The Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] F. J. Morin, Phys. Rev. Lett. 3 (1959) 34.

[2] J. Goodenough, Solid State Chem. 3 490 (1971).

[3] R. M. Wentzovitch, W. W. Schultz, P. B. Allen, Phys. Rev. Lett. 72 (1994) 3389.

[4] J. P. Pouget, H. Launois, T. M. Rice, P. Dernier, A. Gossard, G. Villeneuve, P. Hagenmuller, Phys. Rev. B 10 (1974) 1801.

[5] Y. Muraoka, Z. Hiroi, Appl. Phys. Lett. 80 (2002) 583.

[6] K. Okazaki, H. Wadati, A. Fujimori, M. Onoda, Y. Muraoka, Z. Hiroi, Phys. Rev. B 69 (2004) 165104.

[7] R. Eguchi, S. Shin, A. Fukushima, T. Kiss, T. Shimojima, Y. Muraoka, Z. Hiroi, Appl. Phys. Lett. 87 (2005) 201912.

[8] R. Eguchi, M. Taguchi, M. Matsunami, K. Horiba, K. Yamamoto, Y. Ishida, A. Chainani, Y. Takata, M. Yabashi, D. Miwa, Y. Nishino, K. Tamasaku, T. Ishikawa, Y. Senba, H. Ohashi, Y. Muraoka, Z. Hiroi, S. Shin, Phys. Rev. B 78 (2008) 075115.

[9] S. Shin, S. Suga, M. Taniguchi, M. Fujisawa, H. Kanzaki, A. Fujimori, H. Daimon, Y. Ueda, K. Kosuge, S. Kachi, Phys. Rev. B 41 (1990) 4993.

[10] E. Caruthers, L. Kleinman, H. I. Zhang, Phys. Rev. B 7 (1973) 3753.

[11] V. Eyert, Ann. Phys. (Leipzig) 11 (2002) 650.

Figure captions

FIG. 1. Temperature dependence of resistivity for the VO_2 thin films grown on TiO_2 (001) substrates.

FIG. 2. Valence-band PES spectra of the VO_2 thin films. The upper line shows the spectrum of the insulator phase measured at 300 K and the lower line shows the spectrum of the metallic phase measured at 350 K. The spectra were taken at the photon energy of 150 eV.

FIG. 3. ARPES spectra in the normal emission mode of the VO_2 thin films in the metallic phase measured at 350 K.

FIG. 4. The band structure in the Γ-Z direction of the VO_2 thin films obtained from the ARPES measurements. Dark parts correspond to the energy bands. The white curves are the calculated dispersion energies[11] reduced 20 % and shifted by 1.6 eV.

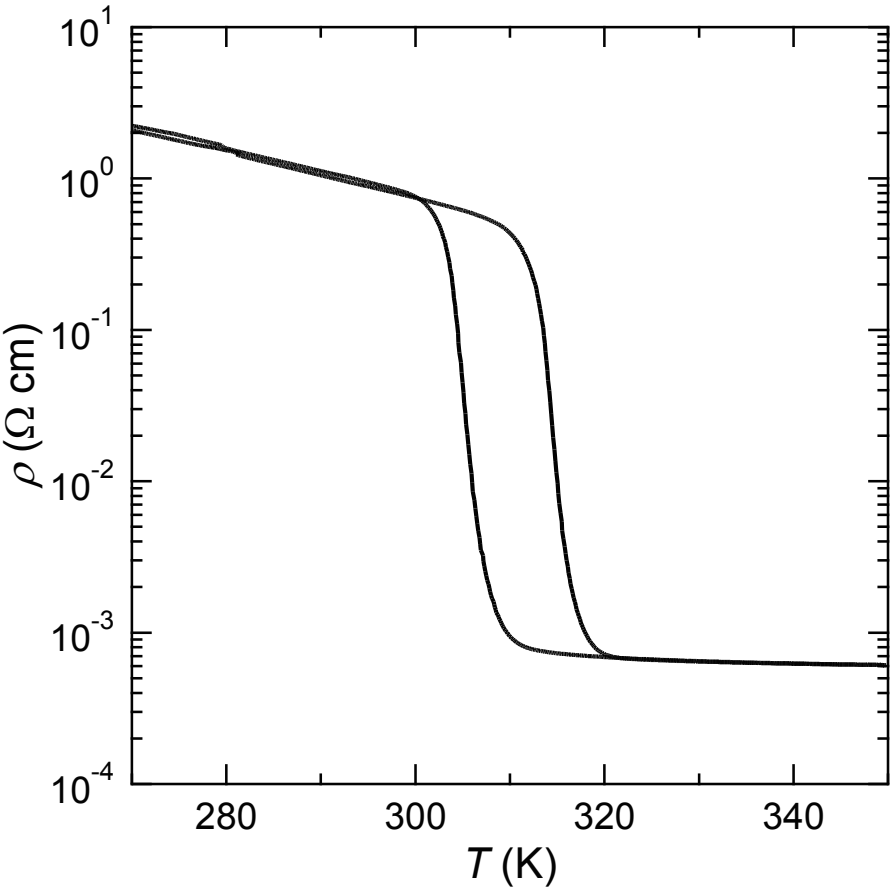

Fig. 1 Y. Muraoka et al.

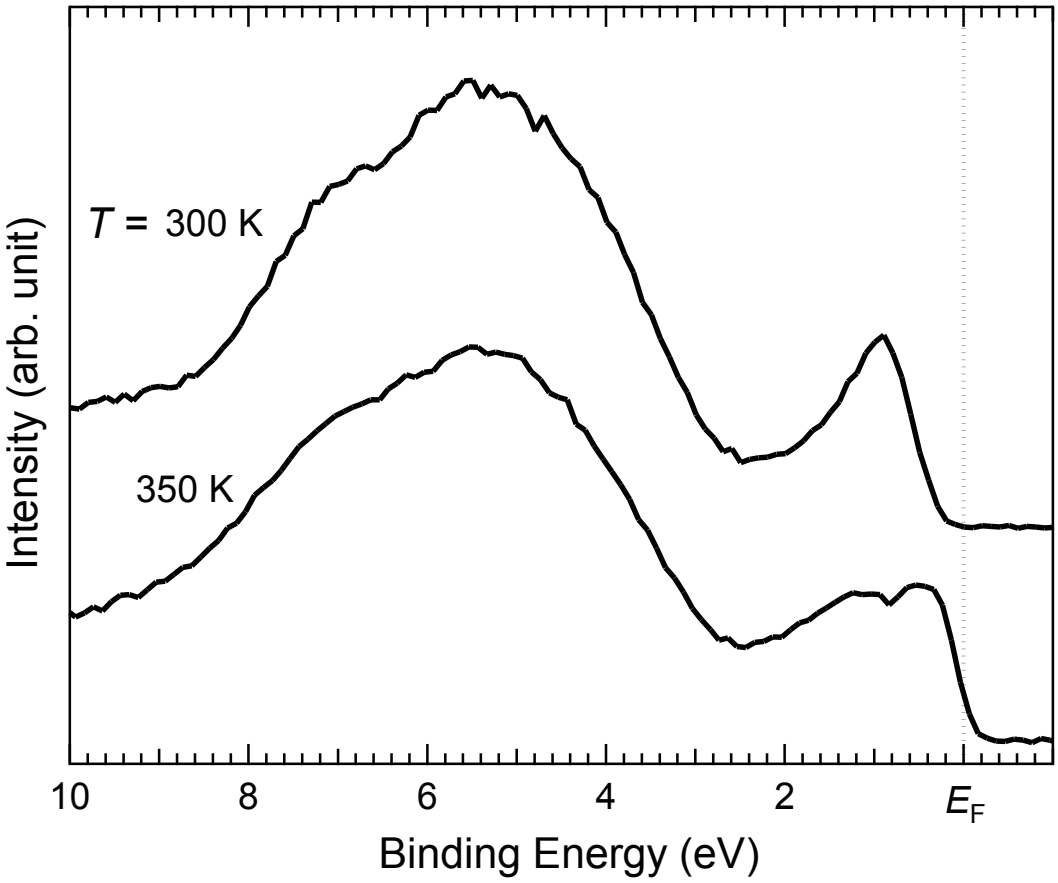

Fig. 2 Y. Muraoka et al.

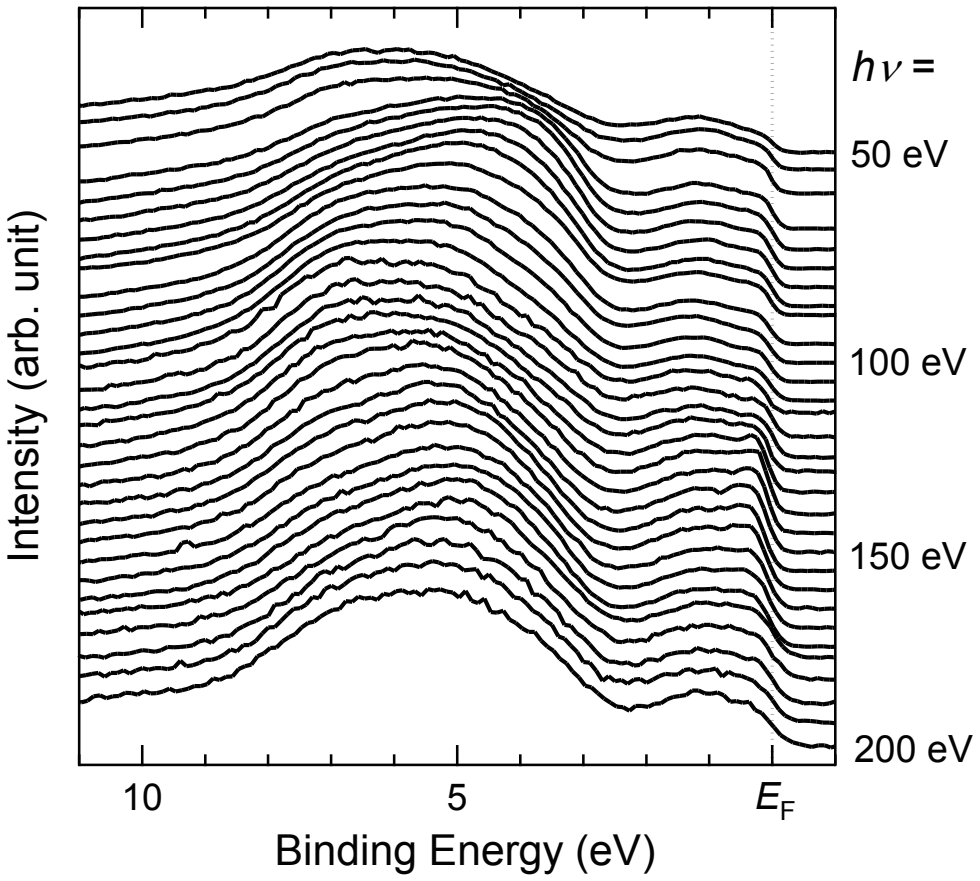

Fig. 3 Y. Muraoka et al.

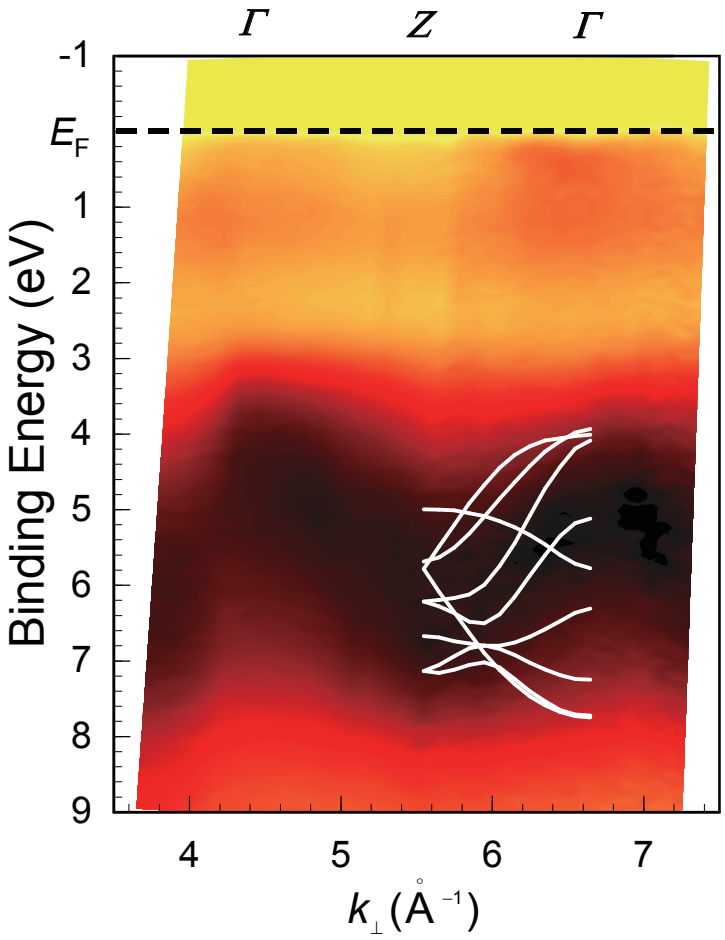

Fig. 4 Y. Muraoka et al.