

Band dispersion near the Fermi level for VO₂ thin films grown on TiO₂ (001) substratesK. Saeki,¹ T. Wakita,² Y. Muraoka,^{1,2} M. Hirai,^{1,2} T. Yokoya,^{1,2} R. Eguchi,³ and S. Shin³¹*Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka, Tsushima, Kita-ku, Okayama 700-8530, Japan*²*Faculty of Science, Research Laboratory for Surface Science, Okayama University, 3-1-1 Tsushima-naka, Tsushima, Kita-ku, Okayama 700-8530, Japan*³*RIKEN/SPring-8, 1-1-1 Kouto, Sayo, Hyogo 679-5148, Japan*

(Received 7 May 2009; revised manuscript received 17 July 2009; published 10 September 2009)

We have performed angle-resolved photoemission spectroscopy (ARPES) measurements of VO₂ using epitaxial thin films and observed the band dispersion near the Fermi level (E_F) for this compound. The VO₂ thin films have been grown on TiO₂ (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 features in the binding-energy range of 3–8 eV along the Γ –Z direction. Also, the V 3*d* state shows two dispersive bands around the Γ point near E_F , indicative of two electron pockets centered at the Γ point. Both electron pockets have an occupied bandwidth of about 0.4 eV. Assuming the parabolic energy bands around the Γ point, the effective-mass ratios of the two electron pockets are estimated to be about 0.2 and 1. The present work indicates that the ARPES measurements using epitaxial thin films are promising for determining the band structure of VO₂ and thus would play a crucial role to elucidate the mechanism of the MIT in VO₂.

DOI: [10.1103/PhysRevB.80.125406](https://doi.org/10.1103/PhysRevB.80.125406)

PACS number(s): 71.30.+h, 79.60.–i, 71.20.–b

I. INTRODUCTION

Vanadium dioxide VO₂ is a 3*d*¹ electron-configuration system and exhibits a first-order metal-insulator transition (MIT) at $T_{\text{MI}}=341$ K accompanied by a structural change.¹ In a high-temperature metallic phase, VO₂ has a rutile-type (*R*) tetragonal structure while in a low-temperature insulator phase it has a monoclinic (*M*₁) structure 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, VO₂ has attracted much attention in terms of an electron-phonon interaction (Peierls-type) versus electron-electron interaction (Mott-Hubbard-type) driven MIT.

Goodenough² proposed the model of electronic structure and described that the lowest-energy *t*_{2*g*} states split into the *d*_{||} band and the π^* bands. In the *R* phase, the *d*_{||} band overlaps the π^* band. In the *M*₁ phase, the zigzag-type pairing consists of a tilting of the V-V pairs which lifts the π^* band above the Fermi level (E_F), and the *d*_{||} band opens up a gap because of the splitting into a filled bonding and empty antibonding band caused by V-V pairing. Since this band picture also explained the nonmagnetic properties of insulating VO₂, it was considered that VO₂ was a typical case of a Peierls insulator, namely, the electron-phonon interaction was essential for opening the gap in *d*_{||} band. This idea was supported by Raman-scattering and x-ray diffraction studies. Also the first-principle band calculations³ showed that a crystallographic transition can be explained by the formation of charge-density waves that are accompanied by lattice distortion and subsequent consideration of phonons.

On the other hands, Pouget *et al.*⁴ showed that minute amounts of Cr substitutions, as well as, uniaxial stress applied to *pure* VO₂ lead to a new phase (*M*₂) in which only

half of the V atoms dimerize, while the other half forms chains of equally spaced atoms behaving as spin-1/2 Heisenberg chains. This phase is also insulating, strongly suggesting that the physics of VO₂ is very close to that of a Mott-Hubbard insulator. Zylbersztein and Mott,⁵ Sommers and Doniach,⁶ and Rice *et al.*⁷ suggested that Coulomb repulsion indeed plays a major role in opening the gap.

Recently, Biermann *et al.*⁸ explained the crucial role of strong Coulomb interactions and structural distortions using the cluster dynamical mean-field theory calculations. More recently, Haverkort *et al.*⁹ claimed that the V 3*d* orbital occupation changes across the MIT, thus the MIT of VO₂ can be ascribed as orbital-assisted collaborative Mott-Peierls transition.

Besides above studies, various experimental and theoretical studies related to the transition have been reported. Despite these intensive works, the mechanism of the MIT is still under discussion. This is mostly because there is no report on the *experimentally determined* electronic band structure of VO₂. The lack of the experimental data makes it difficult to verify and improve the proposed ideas for the MIT. Angle-resolved photoemission spectroscopy (ARPES) is one of the most powerful methods to determine the band structure. Thus applying this method to VO₂ is highly encouraged. However, few ARPES measurements of VO₂ single crystal have been reported so far. This is mainly due to the difficulty in obtaining a chemically stable cleavage plane in VO₂ single crystal with the three-dimensional crystal structure. In addition, since the transition is strongly first order with relatively large volume change in unit cell, VO₂ single crystal is cracked easily on passing through the MIT. One can go through the transition only once for one sample.

Recently, it has been reported that epitaxial thin films of transition-metal oxides are available for ARPES measurements, even though the oxides have a three-dimensional crystal structure. For instance, perovskite-type oxides such as

(La,Sr)MnO₃ (Refs. 10 and 11) and (La,Sr)FeO₃ (Ref. 12) were prepared in the form of epitaxial thin films on SrTiO₃ substrates using the pulsed laser deposition method and their band structure were determined from the ARPES measurements without any surface problem seen in single crystals. By analogy with these works, it is expected that the epitaxial thin film of VO₂ is also available for the ARPES measurements. Muraoka *et al.*¹³ prepared high-quality epitaxial thin films of VO₂ grown on TiO₂ (001) single-crystal substrates by using a pulsed laser deposition technique. The T_{MI} of the films was reduced to 300 K due to an in-plane tensile strain effect induced by the lattice mismatch between the film and the substrate. Okazaki *et al.*¹⁴ performed angle-integrated photoemission spectroscopy (PES) measurements of the VO₂ thin films using the Mg $K\alpha$ line and He I resonance line as light sources. They found that a clean surface obtained by thermal annealing remained fairly stable during measurements and also that the films were not damaged even when the films crossed the MIT many times. They presented detailed temperature-dependent PES studies of the films. More recently, Eguchi *et al.*^{15,16} presented a synchrotron-radiation PES study of the VO₂ thin films. Their works motivate us to perform ARPES measurements using VO₂ thin films. In this paper, we report on the ARPES measurements using VO₂ thin films and demonstrate the band dispersion of oxygen 2*p* and vanadium 3*d* states near the Fermi level (E_F) in the metallic phase.

II. EXPERIMENT

Epitaxial thin films of VO₂ were fabricated on TiO₂ (001) single-crystal substrates using a pulsed laser deposition technique with yttrium aluminum garnet laser ($\lambda=355$ nm) as described in Ref. 13. A V₂O₃ bulk pellet was used as a target material. During the deposition, the substrate temperature was kept at 683 K and oxygen pressure was maintained at 1.0 Pa. After deposition, the films were cooled down to room temperature in 30 min under the same oxygen pressure. A deposition rate was about 0.18 nm/min. 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 was determined to be 2.844 Å which is in good agreement with that obtained previously.¹³ 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 (root mean square of 1.7 Å). 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 VO₂ 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. Here we note a short explanation of normal-emission ARPES measurements. In angle-resolved photoemission measurement, we view the

exciting process in the direct-transition picture. In a direct transition, it is assumed that the momentum of an electron excited from one band to another band is unchanged. Thus,

$$E_f = E_i + h\nu,$$

$$k_f = k_i,$$

where E_f and E_i are the final- and initial-state energies of the electron in the solid, $h\nu$ is the photon energy, and k_f and k_i are the final- and initial-state wave vectors, respectively. When we assume a free-electron final state inside the crystal, we have

$$E_f(k_f) = \hbar^2 k_f^2 / 2m - V_0 (V_0 > 0),$$

where m is the mass of the electron and V_0 is a constant positive inner potential referenced to the vacuum level which defines the zero of the free-electron final-state band. Since upon exciting the solid the component of k_f parallel to the surface, k_{\parallel} , is conserved to within a surface reciprocal-lattice vector, when only electron emitted normal to the surface are detected, we have

$$k_{\parallel} = 0,$$

$$k_{i\perp} = k_{f\perp} = 0.51(E + V_0)^{1/2} \text{ \AA}^{-1},$$

where the free-electron mass is assumed and E and V_0 are expressed in eV. Thus as the photon energy is varied, we obtain different values of $k_{i\perp}$, and can measure the electronic state along a direction in k space normal to the surface.

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 $\sim 10^{-7}$ Pa using a VSW hemispherical analyzer with an acceptance angle of $\pm 1^\circ$. The Fermi level position was determined by measuring gold spectra. The deviation of photon energy was estimated from the Fermi-level position before and after taking the spectra to be within ± 100 meV. Before measurements, the films were annealed at 100 °C under the ultrahigh vacuum for 1h to obtain a clean surface.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the temperature dependence of the resistivity for the VO₂ thin films grown on TiO₂ (001) substrates. A large jump in resistivity is observed at 305 K on cooling and 315 K on heating due to the MIT. 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 quite similar to those reported previously.¹³ Fig. 1(b) shows the valence-band photoemission spectra of the VO₂ thin films across the MIT for a photon energy of 150 eV. The upper line represents the spectrum in the insulator phase measured at 300 K and the lower line in the metallic phase at 350 K. 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

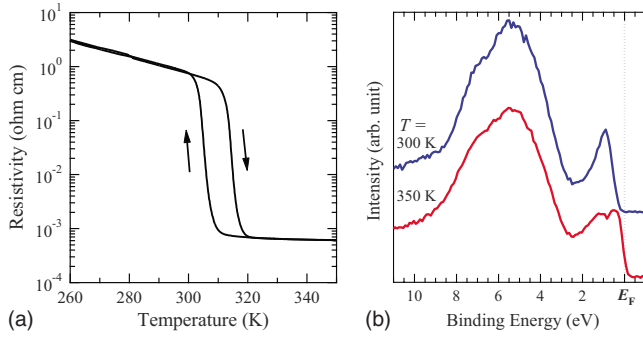


FIG. 1. (Color online) (a) Temperature dependence of resistivity for the VO₂ thin films grown on TiO₂ (001) substrates. (b) Valence-band PES spectra of the VO₂ thin films. The upper line shows the spectrum of the insulator phase measured at 300 K. The lower line shows the spectrum of the metallic phase measured at 350 K. The spectra were taken at the photon energy of 150 eV.

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,^{14–17} indicating that the surface preparation described above is enough for obtaining PES spectra of VO₂.

Figure 2(a) shows ARPES spectra of the VO₂ thin films in the metallic phase at 350 K measured by changing photon energy from 50 to 200 eV in a step of 5 eV in the normal-emission mode. As seen in Fig. 2(a), 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 VO₂ thin films along the Γ –*Z* direction in the Brillouin zone of the rutile-type tetragonal structure. Figure 2(b) shows the

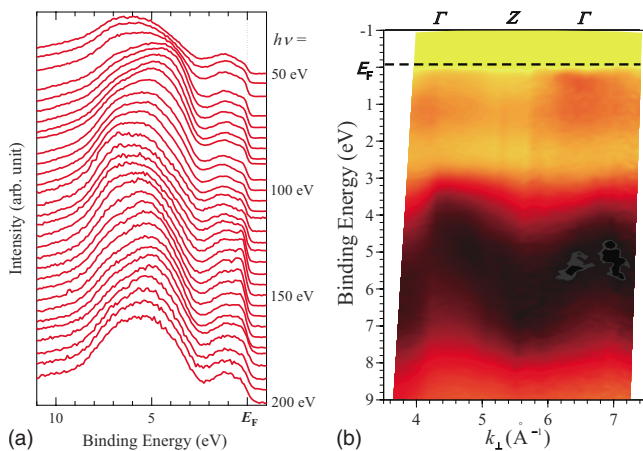


FIG. 2. (Color online) (a) Normal emission ARPES spectra of the VO₂ thin films in the metallic phase measured at 350 K for various photon energies. (b) Experimental band structure in the Γ –*Z* direction of the VO₂ thin films obtained from the ARPES measurements. Dark parts correspond to the energy bands. Γ point shown here is determined from the ARPES measurements of the V 3*d* state (see text).

experimental band structure of the VO₂ thin films derived from the present normal-emission ARPES measurements. The ARPES spectra are plotted in a color scale as a function of k_{\perp} and the binding energy. The inner potential used here is estimated from the detailed ARPES measurements of the V 3*d* state as will be mentioned later. Dark parts correspond to the energy bands. 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 VO₂ thin films. The overall feature of the experimental band structure is similar to the band-structure calculations,^{18,19} supporting that we have succeeded in observing the dispersive band of the O 2*p* state in the metallic VO₂ thin film. On the other hands, at first glance there seems to be no dispersive band near E_F . However, when looking at near E_F carefully, we find a small portion of a dispersive band around the Γ point, suggesting the existence of an electron pocket predicted by the band-structure calculations.^{3,18,19} In order to see more clearly the dispersive band near E_F , we performed the detailed ARPES measurements of the V 3*d* band in the binding-energy range of 0–2 eV.

Figure 3(a) shows ARPES spectra of the V 3*d* band for the VO₂ thin films in the metallic phase at 350 K, measured with photon energy changing from 137.5 to 172.5 eV in a step of 2.5 eV. We find that the ARPES spectra exhibit systematic changes as a function of photon energy; distinct dispersive features exhibit in the binding-energy range of 0–0.5 eV. A peak structure in the spectrum at $h\nu=155$ eV, which has a bottom binding-energy position of about 0.4 eV moves toward E_F with decreasing and increasing photon energy and crosses E_F around $h\nu=150$ and 162.5 eV. Outside of this dispersion, we can see another distinct peak structure which also approaches E_F with changing photon energy and crosses E_F around $h\nu=140$ and 170 eV. These results indicate that there are at least two electron pockets in the V 3*d* band.

In order to determine the energy position of the peak structures precisely, the ARPES spectra are divided by the Fermi function. After moderate smoothing, the energy position of the peak structures was determined from a peak or structure in the smoothed spectrum as shown in Fig. 3(b). We can see two dispersive bands symmetric with respect to photon energy of 155 eV in the binding-energy range of 0–0.5 eV; one is a small band closer to E_F and the other is a relatively weak dispersive band outside the small band. These two bands exhibit a concave shape with a Fermi cutoff. The obtained result clearly indicates the presence of electron pockets in the Γ –*Z* direction and also that electron carriers are responsible for the conductivity in the metallic VO₂. Although the presence of electron carriers in the metallic VO₂ has been reported from Hall measurements²⁰ and Seebeck coefficient measurement,²¹ our observation is the spectroscopic evidence of electron carriers in metallic VO₂. This is a direct experimental observation of the electron pockets of the V 3*d* band in metallic VO₂ which is predicted by the band-structure calculations.

The presence of the dispersive bands crossing E_F can be clearly shown by the momentum distribution curve (MDC).

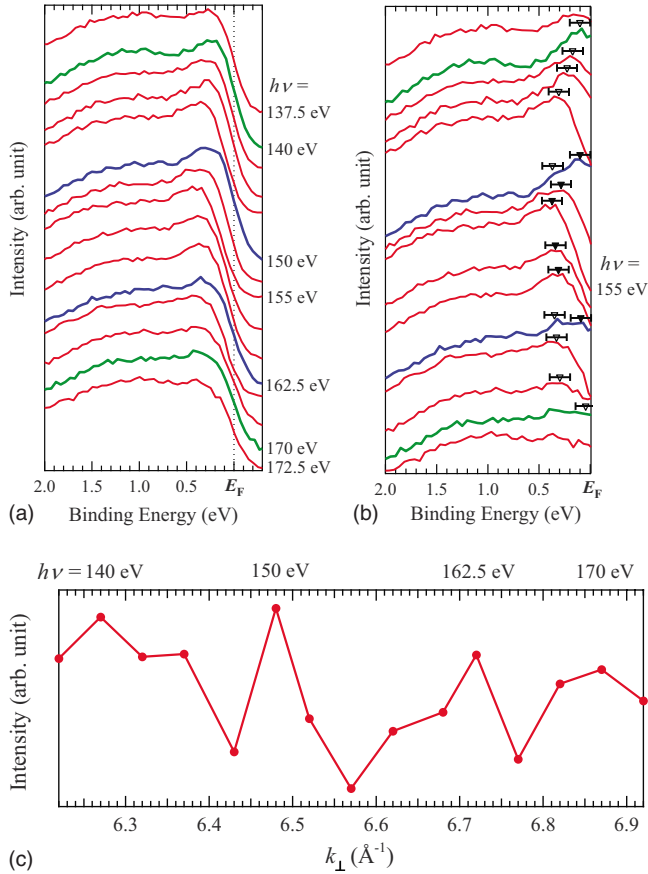


FIG. 3. (Color online) (a) Normal emission ARPES spectra of the metallic VO₂ thin films in the binding-energy range of 0–2 eV measured at 350 K. The spectra at photon energy of $h\nu=150$ and 162.5 eV show the blue line and the spectra at $h\nu=140$ and 170 eV show the green line. (b) The ARPES spectra divided by the Fermi function. Solid and open triangles represent the energy position of the band structure. The line segments indicate the upper and lower bounds for the dispersive features. (c) A momentum distribution curve at E_F as a function of wave number k_{\perp} along the Γ – Z direction.

Figure 3(c) displays a plot of the MDC at E_F of the ARPES spectra in Fig. 3(a). We can see two pairs of peaks, namely, a pair of peaks obtained from the spectra at $h\nu=150$ and 162.5 eV and another pair of peaks obtained from the spectra at $h\nu=140$ and 170 eV. Both pairs of peaks are symmetrical to a certain wave number k_{\perp} . Since the intensity at E_F becomes maximal just when the dispersive band crosses E_F , the result indicates the existence of two bands crossing E_F in the Γ – Z direction. According to the band-structure calculations of metallic phase in VO₂,^{3,18,19} electron pockets in the Γ – Z direction are centered at the Γ point. Thus we estimate the Γ point and inner potential to be 6.6 Å⁻¹ and 16 eV, respectively.

Figure 4 shows the energy position in Fig. 3(b) plotted with respect to the wave number k_{\perp} along the Γ – Z direction. Two electron pockets are observed around the Γ point near E_F . According to the previous ultraviolet photoemission spectroscopy study by Shin *et al.*,¹⁷ the high density of states at E_F is originated from the π^* band. Thus observed electron pockets can be ascribed to the π^* band. Assuming the para-

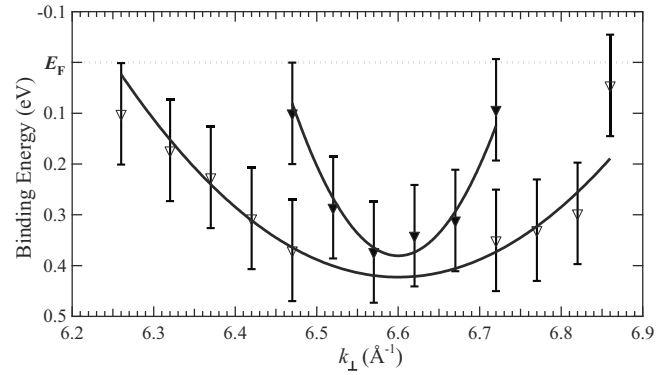


FIG. 4. Energy position of the bands in the ARPES spectra in Fig. 3(b) plotted against the wave number k_{\perp} along the Γ – Z direction. The error bars represent a rough estimate of the energy where the energy band may exist, namely, the upper and lower bounds of the energy band.

bolic energy dispersions around the Γ point for two pockets, the small electron pocket has a bandwidth of 0.38 eV and the large electron pocket has that of 0.42 eV. The effective-mass ratio m^*/m_0 is estimated to be ~ 0.2 for the small electron pocket and ~ 1 for the large electron pocket. Both values are smaller than that reported from other physical property measurements such as Hall measurements ($m^*/m_0=3.5$) (Ref. 20) and reflectance measurements ($m^*/m_0=3.3$).⁵ This implies that there would be other electron pockets with a larger effective-mass ratio in the same or other direction. When looking at band-structure calculations, one may think that some of band calculations for metallic phase are not correct because one sees about the correct bandwidth of the electron pockets but also sees no essential difference in the effective-mass ratio for different electron pockets. However, we should be careful about conclusion because in our results we only see a part of band structure along the Γ – Z direction. In order to conclude whether some of calculations are correct or not, we need to perform further detailed ARPES measurements and determine the whole of band structure along Γ – Z direction.

Finally, we would like to anticipate that combination of the epitaxial thin films with ARPES measurements is a promising method to determine the band structure of VO₂. By using this method, we could determine whole of the band structure of VO₂ for both metal and insulator phases. Actually, in preliminary ARPES study, we succeed in observing dispersive band feature along the Γ – M direction in the metallic phase and also observing the distinct band structure in the insulator phase. The experimentally determined band structure makes it possible to reveal Fermi-surface topology and also to compare with the band-structure calculations, both of which are crucial to understand the mechanism of the transition and establish the proper model for the MIT in VO₂. For instance, it is said that there is some degree of Fermi-surface nesting in the [101] lattice direction of tetragonal metallic phase (Γ – R direction in the Brillouin-zone notation for metallic VO₂). From Fermi-surface topology of metallic VO₂ determined by the present method, we can examine the presence of such a nesting vector and discuss the possibility of the Fermi-surface instability (Peierls transition) as an ori-

gin of the MIT. We believe that the present ARPES method using epitaxial thin films will play a crucial role to understand the underlying physics of the MIT in VO₂.

IV. CONCLUSION

In summary, we have performed ARPES measurements in a metallic phase of VO₂ using the thin films grown on TiO₂ (001) substrates and demonstrated a dispersive feature of the O 2*p* and V 3*d* bands 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. In the V 3*d* band, two electron pockets are found around the Γ point, namely, a small dispersive band and relatively large dispersive band outside the small one. These bands are ascribable to the π^* band. The effective-mass ratio of the small and large electron pockets is estimated to be about 0.2 and 1, respectively, both

of which are smaller compared with the effective-mass ratio deduced from Hall measurements and reflectance measurements. 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 VO₂ with no chemical stable cleavable planes. We believe that ARPES study using this technique would provide crucial information to reveal an origin of the mechanism of the metal-insulator transition in VO₂.

ACKNOWLEDGMENTS

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.

-
- ¹F. J. Morin, Phys. Rev. Lett. **3**, 34 (1959).
²J. Goodenough, Solid State Chem. **3**, 490 (1971).
³R. M. Wentzcovitch, W. W. Schulz, and P. B. Allen, Phys. Rev. Lett. **72**, 3389 (1994).
⁴J. P. Pouget, H. Launois, T. M. Rice, P. Dernier, A. Gossard, G. Villeneuve, and P. Hagenmuller, Phys. Rev. B **10**, 1801 (1974).
⁵A. Zylbersztejn and N. F. Mott, Phys. Rev. B **11**, 4383 (1975).
⁶C. Sommers and S. Doniach, Solid State Commun. **28**, 133 (1978).
⁷T. M. Rice, H. Launois, and J. P. Pouget, Phys. Rev. Lett. **73**, 3042 (1994).
⁸S. Biermann, A. Poteryaev, A. I. Lichtenstein, and A. Georges, Phys. Rev. Lett. **94**, 026404 (2005).
⁹M. W. Haverkort, Z. Hu, A. Tanaka, W. Reichelt, S. V. Streltsov, M. A. Korotin, V. I. Anisimov, H. H. Hsieh, H.-J. Lin, C. T. Chen, D. I. Khomskii, and L. H. Tjeng, Phys. Rev. Lett. **95**, 196404 (2005).
¹⁰M. Shi, M. C. Falub, P. R. Willmott, J. Krempasky, R. Herger, K. Hricovini, and L. Patthey, Phys. Rev. B **70**, 140407(R) (2004).
¹¹A. Chikamatsu, H. Wadati, H. Kumigashira, M. Oshima, A. Fujimori, N. Hamada, T. Ohnishi, M. Lippmaa, K. Ono, M. Kawasaki, and H. Koinuma, Phys. Rev. B **73**, 195105 (2006).
¹²H. Wadati, A. Chikamatsu, M. Takizawa, R. Hashimoto, H. Kumigashira, T. Yoshida, T. Mizokawa, A. Fujimori, M. Oshima, M. Lippmaa, M. Kawasaki, and H. Koinuma, Phys. Rev. B **74**, 115114 (2006).
¹³Y. Muraoka and Z. Hiroi, Appl. Phys. Lett. **80**, 583 (2002).
¹⁴K. Okazaki, H. Wadati, A. Fujimori, M. Onoda, Y. Muraoka, and Z. Hiroi, Phys. Rev. B **69**, 165104 (2004).
¹⁵R. Eguchi, S. Shin, A. Fukushima, T. Kiss, T. Shimojima, Y. Muraoka, and Z. Hiroi, Appl. Phys. Lett. **87**, 201912 (2005).
¹⁶R. 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, and S. Shin, Phys. Rev. B **78**, 075115 (2008).
¹⁷S. Shin, S. Suga, M. Taniguchi, M. Fujisawa, H. Kanzaki, A. Fujimori, H. Daimon, Y. Ueda, K. Kosuge, and S. Kachi, Phys. Rev. B **41**, 4993 (1990).
¹⁸E. Caruthers, L. Kleinman, and H. I. Zhang, Phys. Rev. B **7**, 3753 (1973).
¹⁹V. Eyert, Ann. Phys. (Leipzig) **11**, 650 (2002).
²⁰W. H. Rosevear and W. Paul, Phys. Rev. B **7**, 2109 (1973).
²¹C. N. Berglund and H. J. Guggenheim, Phys. Rev. **185**, 1022 (1969).