Electronic Structure of the VO Film Grown on Ag(100): Resonant Photoelectron Spectroscopy Study

Yuichi Sugizaki, Hiroki Motoyama, and Kazuyuki Edamoto

Department of Chemistry, Rikkyo University, Toshima-ku, Tokyo 171-8501, Japan

Kenichi Ozawa

Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8551, Japan

(Received 11 November 2017; Accepted 24 April 2018; Published 7 June 2018)

The electronic structure of the VO film grown on Ag(100) has been studied by photoelectron spectroscopy (PES) utilizing synchrotron radiation. The Ag(100) surface covered by the VO film formed by V deposition in O₂ at 3.7 × 10⁻⁹ Torr and subsequent annealing at 450°C gave a (1 × 1) LEED pattern. In the PES spectra for the (1 × 1) VO film, the conduction band mostly composed of V 3d-components was observed at 0–2.5 eV. The valence band mostly composed of O 2p-components was formed overlapping with the substrate Ag 4d band, and the analysis of the resonant PES spectra revealed that the band existed at 4–10 eV. Both of the PES spectra for the VO film at room temperature and for that cooled to 4.86 K showed a clear cut-off at the Fermi edge, implying that the (1 × 1) VO film has a metallic electronic structure when the temperature is higher than 4.86 K.

Keywords: Synchrotron radiation photoelectron spectroscopy; Surface electronic phenomena; Silver; Vanadium oxides; Single crystal epitaxy

I. INTRODUCTION

Growth of vanadium oxide thin films on metal oxide substrates has attracted considerable attention not only due to their technological importance but also from a scientific viewpoint. From a technological viewpoint, it has been proposed that the catalytic activities of monolayer-thick vanadium oxide films are much enhanced as compared with those of bulk oxides [1]. In particular, vanadium oxides supported on titanium oxide are used as catalysts for a number of industrially important oxidation-reduction reactions such as the oxidation of α-xylene to phthalic anhydride [2]. From a scientific aspect, it was recently proposed that the VO₂ thin films grown on TiO₂(001) were not damaged when the films crossed the metal-insulator phase transition (MIT) repeatedly, which is impossible in the case of bulk crystals because MIT in VO₂ is a strong first order transition and the bulk crystal should be broken on passing through the MIT [3, 4]. Therefore, the growth of VO₂ thin films would allow us to measure the change in the electronic structure across MIT by photoemission spectroscopy (PES) without cracking the crystal. The growth of ultrathin vanadium oxide films on a metal substrate is also of interest because an oxide nanolayer on a metal substrate often exhibits functionalities different from those of bulk oxides [5]. When a vanadium oxide nanolayer is formed on a metal substrate, it has been found that various interface-mediated phases are realized according to preparation conditions. For example, the growth of the film on Pd(111) was found to be characterized by oscillating oxidation states; an interface-mediated V₂O₃ film is formed at the interface, on which VO₂ films are grown, and bulk-like V₂O₄ layers are formed when the film thickness is more than 3–4 layers [6–8]. The study of the growth of vanadium oxide films on Rh(111) revealed that two types of oxide films are formed in submonolayer coverage region depending on the preparation conditions; a film with a (√7 × √7)R19.1° structure is formed by reactive deposition, while a film with a (√13 × √13)R13.8° structure is formed by the postoxidation of a deposited V film [9, 10].

Recently our group found that at least three types of ordered vanadium oxide films can be formed on Ag(100) by a reactive deposition method [11]. When V atoms were deposited in O₂ at 3.7 × 10⁻⁹ Torr and the film was subsequently annealed at 450°C, the film with a (1 × 1) periodicity with respect to Ag(100) was formed [11]. On the other hand, when the O₂ pressure during the deposition was raised to 3.7 × 10⁻⁷ Torr, two types of ordered oxide films, which show hexagonal and (4 × 1) LEED patterns, were formed depending on the conditions of post annealing [11]. The films with (1 × 1) and hexagonal periodicities were investigated by PES and X-ray absorption spectroscopy (XAS), and these were ascribed to a VO(100) film and a corundum V₂O₃(0001) film, respectively [11]. The epitaxial growths of these films are thought to be enabled due to the well lattice matching; the lattice constant of VO(100) (0.407 nm) [12] is very close to that of Ag(100) (0.409 nm) [13], and the mean lateral distances of V–V and O–O in the (0001) plane of corundum V₂O₃ (0.287 nm) [14] are close to the interatomic distance in an Ag crystal (0.289 nm). At this point, very limited information is available on the physical properties, in particular on the electronic structures, of these films. In order to explore the functionalities of these systems, it is important to elucidate the electronic structures of the films. In this paper, we will show the results of the PES studies on the electronic structure in the valence band region of the (1 × 1) VO film formed on Ag(100).

II. EXPERIMENTAL

The Ag(100) surface was cleaned by several cycles of Ar⁺ ion sputtering (1 keV, 30 min) and annealing at 500°C for 30 min. The cleanliness of the surface was ex-
We have confirmed that the film showed a clear (1 1 1) LEED pattern at least up to $d = 1.2$ nm.

The PES measurements were performed at BL-3B and BL-13B of the Photon Factory (PF), High Energy Accelerator Research Organization (KEK) and at BL-5U of the UVSOR facility, Institute for Molecular Science. At BL-3B of PF, the photoelectrons were collected by a hemispherical electron energy analyzer (VSW HA54) with a microchannel-plate electron multiplier detector. The acceptance angle of the analyzer was $\pm 15^\circ$. The incidence angle of the light ($\theta_i$) was $45^\circ$ from the surface normal direction, and the photoelectrons emitted in the surface normal direction were collected for all measurements. The total experimental energy resolutions estimated from the Fermi edge in the spectra of a Ta sample holder were 0.20 eV at $\hbar \nu = 38$ eV and 0.28 eV at $\hbar \nu = 60$ eV. The spectra were normalized by the photocurrent of the final stage mirror. The base pressure in the vacuum system was $3.0 \times 10^{-10}$ Torr. The Ag 3d core-level PES spectra were measured at BL-13B of PF, KEK, using a hemispherical electron energy analyzer (Gamma Data/Scienta SES200). The axis of the analyzer lens system was parallel to the surface normal direction, and $\theta_i$ was $65^\circ$. The spectra presented below are measured at $\hbar \nu = 700$ eV, and normalized by the photon flux which is estimated by monitoring the photocurrent of the final stage mirror. The base pressure in the analysis chamber was $3.8 \times 10^{-10}$ Torr.

At BL-5U of UVSOR, the PES spectra were measured using a hemispherical electron energy analyzer (MB Scientific AB MBS A-1) in an angle-integrating mode with the acceptance angle of $\pm 18^\circ$. The spectra were measured for the sample at room temperature and for that cooled by a liq. He cooling system. The sample temperature in the latter case was measured by a monitor equipped with a Si diode, and was estimated to be 4.86 K. The total experimental energy resolutions were estimated from the Fermi edge in the spectra of an Au film attached to the sample holder, and those for the sample at room temperature and that cooled to 4.86 K were estimated to be 40 meV and 23 meV, respectively, at $\hbar \nu = 54$ eV. The base pressure in the analysis chamber was $8.0 \times 10^{-11}$ Torr.

### III. Results and Discussion

In this work, we made PES measurements for VO/Ag(100) to investigate the electronic structure of the film, and it is important to examine whether the spectra reflect the electronic structure of the VO film or that of a hybridized V–O–Ag system. We measured Ag 3d core-level spectra of Ag(100) before and after the film deposition, and confirmed that any features induced by the interaction with the film were not found in the spectra after the film deposition. In particular, if the substrate Ag atoms are oxidized, peaks with binding energies lower than those of the 3d levels of the Ag substrate by about 0.5 eV should appear [16, 17]. The magnified spectra of the clean and film-covered surfaces in the lower binding energy side of the Ag 3d$_{5/2}$ line are shown in Fig. 1(d) as black and red lines, respectively. In Fig. 1(d), the spectral intensities are adjusted so that they have the same peak heights. It is clearly shown that the oxidation-induced peaks do not appear after the film deposition, indicating...
that it is unlikely that hybridized V–O–Ag species are formed. We think that the chemical interaction between the film and the Ag(100) substrate is weak, and that the electronic structure of the film can be deduced from the valence band PES spectra qualitatively if the substrate component is subtracted adequately. The weak interaction of oxide films with Ag(100) has been also confirmed for the NiO/Ag(100) [18] and BaO/Ag(100) [19] systems, and Ag(100) is seemed to be a suitable substrate to study the electronic structure of the monolayer-thick metal oxide overlayer owing to its chemical inertness.

The normal-emission spectra of Ag(100) covered with the (1×1) VO film were measured at BL-3B of PF with various photon energies of 36–85 eV, and the spectra measured at $h\nu = 40–64$ eV are shown in Fig. 2. In the inset of Fig. 2, we show the spectrum of the Ag(100) clean surface (red line) and that of the surface covered with the (1×1) VO film (black line) measured at $h\nu = 54$ eV. For the clean surface, an intense Ag 4d band is observed at 4–8 eV overlapping with a flat 5sp band. As the surface is covered with the (1×1) VO film, a band appears at 0–2.5 eV. The band is ascribed to the partially filled conduction band mostly composed of V 3d components. Theoretical studies have predicted that the V 3d band in the occupied region is mostly composed of the $t_{2g}$ states [20, 21]. It is deduced from the results of resonant PES measurements that the valence band of the VO film mostly composed of O 2p components appears at 4–10 eV overlapping with the substrate Ag 4d band that is attenuated by the inelastic scattering of Ag 4d photoelectrons in the VO overlayer, as will be discussed later.

Figure 2 shows that both of the intensity of the band at 0–2.5 eV and that at 4–10 eV are maximized at $h\nu = 50–60$ eV. In Fig. 3, the integrated intensities of the band at 0–2.5 eV (open circles) and those of the band at 4–10 eV (filled circles) are plotted as a function of photon energy. The V 3p core-level spectrum of VO/Ag(100) is shown in the inset ($h\nu = 120$ eV).
The difference between the PES spectrum of (1×1) VO/Ag(100) measured at \( h\nu = 54 \) eV and 40 eV. The spectrum around \( E_F \) of VO/Ag(100) (red line) and that of the Ta sample holder (black line) measured at \( h\nu = 50 \) eV are shown in the inset.

The difference between the normal-emission spectra of VO/Ag(100) and that measured at \( h\nu = 4.86 \) K (b). The incident photon energy was 54 eV.

FIG. 4. Difference between the normal-emission spectra of VO/Ag(100) measured at \( h\nu = 54 \) eV and 40 eV. The spectrum around \( E_F \) of VO/Ag(100) (red line) and that of the Ta sample holder (black line) measured at \( h\nu = 50 \) eV are shown in the inset.

FIG. 5. Angle-integrated spectra of VO/Ag(100) (red lines) and of the Au film attached to the sample holder (black lines) measured for the sample at room temperature (a) and those measured for the sample at 4.86 K (b). The incident photon energy was 54 eV.

about 16 eV. This delayed onset of the resonance is consistent with the results of resonant PES studies for other V oxides in which the resonance maxima have been observed to be shifted from the V 3p photoexcitation threshold by 10–15 eV [24]. Similar results have been reported in resonant PES studies for Ti and Ti compounds [28], and this delayed onset of the resonance is seemed to be a general result for early transition metal compounds [29]. To our knowledge, the origin of this delay is still in dispute at this point; for example, the delay was interpreted to be caused by the exchange interaction in the \( p^5d^{n+1} \) configuration by Bertel et al. [30] while Fuentes et al. proposed that this was mainly caused by the Coulomb interaction between the 3p hole and the 3d electrons [28]. The intensity of the band at 4–10 eV shows a similar \( h\nu \)-dependent behavior to that of the V 3d-derived band, and has a maximum at \( h\nu = 52 \) eV. This result indicates the existence of the valence band of VO in this binding energy region, because the Ag 4d band does not show resonant behavior in the photon energy region of 40–70 eV [30]. We thus ascribe the band observed at 4–10 eV to the sum of emissions from the valence band of the VO film and those from the substrate Ag 4d band. The valence band of VO has been predicted to be mostly composed of O 2p components [20], and thus the resonance is interpreted to involve the interatomic Auger decay process in which the excited state formed by the V 3p → 3d excitation decays through the O 2p electron emission, as has been proposed in the resonant PES studies for the O 2p-derived valence band of TiO [31], Ti₂O₃ [23], and TiO₂ [32]. The process is believed to be enabled when the V 3d and O 2p orbitals are strongly hybridized [32].

The difference between the PES spectrum of (1×1) VO/Ag(100) measured at \( h\nu = 54 \) eV (resonance region) and that measured at \( h\nu = 40 \) eV (off-resonance region) is shown in Fig. 4. Since the Ag 4d band does not show the resonant behavior in this photon energy region [31], the difference spectrum qualitatively corresponds to the resonantly enhanced component of the emission from the VO film. The spectrum shows that the V 3d-derived conduction band in the occupied region and the O 2p-derived band are formed at 0–2.5 eV and 4–10 eV, respectively. This result is qualitatively reproduced by the theoretical study using GWA calculations in which these bands have been predicted to exist at 0–3 eV and 6–11 eV, respectively [20]. A clear cut-off is observed at the Fermi edge in the V 3d band, suggesting the metallic nature of the (1×1) VO film. In the inset of Fig. 4, we show the spectrum of (1×1) VO/Ag(100) (red line) together with that of the Ta sample holder (black line) in the region around the Fermi edge measured at \( h\nu = 50 \) eV. The energy scale of the spectrum is chosen to be the kinetic energy. We made the fitting of these spectra using Gaussian-convoluted Fermi distribution functions and the results show that the energy of the cut-off in the spectrum of (1×1) VO/Ag(100) and that of Ta are the same with each other (45.77 eV).

Since the photon energy is in the region near the resonance maximum where the intensity of the V 3d band is much higher than that of the Ag 5sp band, the spectral shape around \( E_F \) essentially reflects that of the V 3d band. Thus it is deduced from the results shown in the inset of Fig. 4 that the V 3d band has a cut-off at \( E_F \), which is the direct evidence for the metallic nature of the film.

It is known that many of the vanadium oxides undergo MITs, which are the first order phase transitions characterized by abrupt structural, electronic and magnetic transitions. The transitions have been found to occur, for example, at 530 K for V₂O₅ [33], at 340 K for VO₂ [24], and at 170 K for V₂O₃ [24]. A vast amount of experimental and theoretical studies have been made to elucidate the mechanism of MITs of V oxides. However, there has been very few studies on MIT in VO owing to the difficulty in synthesizing the single crystal, and even the most fundamental question as to whether MIT occurs in VO or not has not been cleared yet. Though the physical properties of an ultrathin film should be modified from those of bulk counterpart, the investigation of MIT in the (1×1) VO film should shed some light on the fundamen-
tal aspect of MIT in the VO crystal. As discussed in the previous paragraph, the electronic structure of the (1×1) VO film is metallic at room temperature, and thus the transition should be searched in the temperatures below room temperature. Figure 5 shows angle-integrated spectra of (1×1) VO/Ag(100) (red line) and that of an Au film (black line) measured at BL-5U of UVSOR in the region around the Fermi edge. The spectra were measured for the sample at room temperature [Fig. 5(a)] and that at 4.86 K [Fig. 5(b)]. The spectra are given with the energy scale of kinetic energy. The incident photon energy was chosen to be the resonance maximum of the V 3d photoemission (54 eV), and thus the spectral shape around $E_F$ is mostly determined by that of the V 3d components, as has been discussed in the previous paragraph. The spectra were fit with the Gaussian-convoluted Fermi distribution functions, and the results show that the energy of the cut-off in the spectrum of the VO film is 49.68 eV and that of the Au film is 49.69 eV at room temperature. The energy difference is below the total energy resolution (40 meV), and we conclude from the results that the VO film has the metallic electronic structure at room temperature, as has been deduced from the measurements in BL-3B of PF (Fig. 4). The fitting for the sample at 4.86 K revealed that the cut-off energies in the spectrum of the VO film and that of the Au film are both 49.69 eV, clearly indicating that the electronic structure of the VO film is metallic even at 4.86 K. Therefore, it is concluded that MIT does not occur in the (1×1) VO film at higher than 4.86 K, and it is likely that the (1×1) VO film in the ground state has a metallic electronic structure.

The electronic structures of 3d transition metal monoxides have attracted attention because these are promising candidates for the model systems to understand the properties of highly correlated electron systems owing to their structural and electronic simplicity. It has been revealed that the monoxides of Mn, Fe, Co, and Ni (group 7, 8, 9, and 10 transition metals, respectively) are antiferromagnetic insulators while TiO (group 4 transition metal monoxide) is a Fermi-liquid metal [21]. VO (group 5 transition metal monoxide) locates in the midst of these two groups, and the electronic structure has attracted attention. Some theoretical studies have been made to elucidate the electronic structure of VO, but it is still controversial whether the electronic structure is metallic or insulating. The metallic electronic structure has been predicted by Yamazaki and Fujiwara using GW calculations [20], while VO has been predicted to be an antiferromagnetic insulator by Mackrodt et al. using hybrid DFT calculations [34]. Rivadulla et al. made the study by the use of magnetic susceptibility and thermoelectric power measurements together with DFT calculations, and predicted that VO is a strongly correlated metal whose electronic structure is characterized by the existence of a pseudo gap around $E_F$ [21]. In this study, the PES studies clearly shows that, at least in the case of the ultrathin VO(100) film formed in this study, the electronic structure is metallic without a pseudo gap around $E_F$ at least above 4.86 K.

IV. CONCLUSION

The electronic structure of the (1×1) VO film formed on Ag(100) was investigated by PES utilizing synchrotron radiation. The conduction band mostly composed of V 3d-components was observed at 0–2.5 eV independent of the photon energy of 36–85 eV. The band intensity showed a resonant maximum at $h\nu = 54$ eV, which is characteristic of the photoionization cross section of the V 3d states. On the other hand, the valence band mostly composed of O 2p-components was formed overlapping with the substrate Ag 4d band, and the analysis of the resonant PES spectra revealed that the band existed at 4–10 eV. The band intensity also showed a maximum at $h\nu = 52$ eV, which is interpreted to be due to the resonance involving the interatomic Auger decay process. The energy position of the cut-off at the Fermi edge was identical to that in the spectra of the Au film attached to the sample holder both at room temperature and at 4.86 K, implying that the (1×1) VO film has a metallic electronic structure at these temperatures. Therefore, in the case of the (1×1) VO film, it is concluded that MIT does not occur at least above 4.86 K.

ACKNOWLEDGMENTS

We would like to thank the staff of the Photon Factory, High Energy Accelerator Research Organization, in particular Prof. K. Mase, for their excellent support. We also thank the staff of the UVSOR facility, Institute for Molecular Science, in particular Prof. K. Tanaka and Prof. S. Ideta, for their excellent support. This work has been performed with the approval of the Photon Factory Advisory Committee (Proposal No. 2017G017), and under the UVSOR Proposal (28-816). This work has been supported by the MEXT-Supported Program for the Strategic Research Foundation at Private Universities, 2013-2017, and by Grants-in-Aid for Scientific Research (No. 16K05409) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

[1] H. Bosch and F. Janssen, Catal. Today 2, 369 (1988).
[2] Q. Guo, S. Lee, and D. W. Goodmann, Surf. Sci. 437, 38 (1999).
[3] K. Okazaki, H. Wadati, A. Fujimori, M. Onoda, Y. Muraoaka, and Z. Hiroi, Phys. Rev. B 69, 165104 (2004).
[4] K. Saeiki, T. Wakita, Y. Muraoaka, M. Hirai, T. Yokoya, R. Eguchi, and S. Shin, Phys. Rev. B 80, 125406 (2009).
[5] J. Libuda and H.-J. Freund, Surf. Sci. Rep. 57, 157 (2005).
[6] S. Surnev, L. Vitali, M. G. Ramsey, F. P. Netzer, G. Kresse, and J. Hafner, Phys. Rev. B 61, 13945 (2000).
[7] S. Surnev, G. Kresse, M. G. Ramsey, and F. P. Netzer, Phys. Rev. Lett. 87, 086102 (2001).
[8] S. Surnev, G. Kresse, M. Sock, M. G. Ramsey, and F. P. Netzer, Surf. Sci. 495, 91 (2001).
[9] J. Schoiswohl, M. Sock, S. Eck, S. Surnev, M. G. Ramsey, F. P. Netzer, and G. Kresse, Phys. Rev. B 69, 155403 (2004).
[10] J. Schoiswohl, S. Surnev, M. Sock, S. Eck, M. G. Ramsey,
[11] T. Nakamura, Y. Sugizaki, S. Ishida, K. Edamoto, and K. Ozawa, Jpn. J. Appl. Phys. 55, 075501 (2016).
[12] M. D. Banus, T. B. Reed, and A. J. Strauss, Phys. Rev. B 5, 2775 (1972).
[13] C. Kittel, Introduction to Solid State Physics (Wiley, New York, 2004).
[14] M. Preisinger, J. Moosburger-Will, M. Klemm, S. Klimm, and S. Horn, Phys. Rev. B 69, 075423 (2004).
[15] S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Annal. 35, 268 (2003).
[16] L. H. Tjeng, M. B. Meinders, J. van Elp, J. Ghijsen, A. Sawatzky, and R. L. Johnson, Phys. Rev. B 41, 3190 (1990).
[17] V. I. Bukhtiyarov, M. Håvecker, V. V. Kaichev, A. Knop-Gericke, R. W. Mayer, and R. Schlögl, Phys. Rev. B 67, 235422 (2003).
[18] S. Yang, H.-K. Park, J.-K. Kim, S.-H. Phark, Y. J. Chang, T. W. Noh, H.-N. Hwang, C.-C. Hwang, and H.-D. Kim, Surf. Sci. 616, 12 (2013).
[19] T. C. Droubay, L. Kong, S. A. Chambers, and W. P. Hess, Surf. Sci. 632, 201 (2015).
[20] A. Yamasaki and T. Fujiwara, Phys. Rev. B 66, 245108 (2002).
[21] F. Rivadulla, J. Fernández-Rossier, M. García-Hernández, M. A. López-Quintela, J. Rivas, and J. B. Goodenough, Phys. Rev. B 76, 205110 (2007).
[22] J. Barth, F. Gerken, and C. Kunz, Phys. Rev. B 31, 2022 (1985).
[23] K. E. Smith and V. E. Henrich, Phys. Rev. B 38, 9571 (1988).
[24] S. 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).
[25] J. Lindström, P. A. P. Lindberg, L. I. Johansson, D. S. L. Law, and A. N. Christensen, Phys. Rev. B 36, 9514 (1987).
[26] G. A. Sawatzky and D. Post, Phys. Rev. B 20, 1546 (1979).
[27] S. Hufner, Photoelectron Spectroscopy (Springer, Berlin, 1995).
[28] G. G. Fuentes, P. Prieto, C. Morant, C. Quirós, R. Nuñez, L. Soriano, E. Elizalde, and J. M. Sanz, Phys. Rev. B 63, 075403 (2001); and references cited therein.
[29] L. C. Davis, J. Appl. Phys. 59, R25 (1986).
[30] E. Bertel, R. Stockbauer, and T. E. Madey, Phys. Rev. B 27, 1939(R) (1983).
[31] H. Kaneko, M. Tanaka, K. Ozawa, and K. Edamoto, Surf. Sci. 602, 2295 (2008).
[32] A. G. Thomas, W. R. Flavell, A. K. Mallic, A. R. Kumarasinghe, D. Tsoutson, N. Khan, C. Chatwin, S. Rayner, G. C. Smith, R. L. Stockbauer, S. Warren, T. K. Johal, S. Patel, D. Holland, A. Taleb, and F. Wiame, Phys. Rev. B 75, 035105 (2007).
[33] A. Chakrabarti, K. Hermann, R. Druzinic, M. Witko, F. Wagner, and M. Petersen, Phys. Rev. B 59, 10583 (1999).
[34] W. C. Mackrodt, D. S. Middlemiss, and T. Owens, Phys. Rev. B 69, 115119 (2004).