Electronic Structure of the Ultra-Thin TiO$_2$ Film on Ag(100):
Resonant Photoemission Spectroscopy Study$^*$

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The electronic structure of the (5×1) TiO$_2$ film on Ag(100) has been investigated with photoemission spectroscopy utilizing synchrotron radiation. The film was prepared by Ti deposition on Ag(100) at room temperature in an O$_2$ atmosphere at 5×10$^{-6}$ Torr and subsequent annealing at 600°C for 3 min. The valence band of the film was observed in the binding energy region of 4-10 eV. The spectral intensity of the valence band of the film was maximized at the photon energies of 48 eV and 54 eV, which were ascribed to the resonances caused through the interference between the normal photoemission process and the process including Ti 3p → 3d and 3p → 4s excitations, respectively. Resonant photoemission measurements showed that the valence band of the film in the region of 5-10 eV are formed by hybridization of the O 2p orbitals with both the Ti 3d and 4s orbitals, while the top region of the valence band is mostly composed of the O 2p components.

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I. INTRODUCTION

The properties of titanium dioxide (TiO$_2$) have been the subject of numerous studies in the past few decades because it is a promising material for catalytic support, photocatalyst, gas sensor, and so on [1]. In particular, two-dimensional (2D) TiO$_2$ nanosheets have recently attracted much attention because they are expected to achieve advanced functions such as unidirectional electron or energy transfer, higher photocatalytic activity, and higher photovoltaic efficiency due to the reduced electron-hole recombination rates [2]. The 2D TiO$_2$ nanosheets were found to be formed by delamination of layered titanates [3]. Structural analyses revealed that these crystallize into a 2D crystal in which octahedrally coordinated Ti cations form a double layer with a rectangular unit cell of 0.38 nm × 0.30 nm [3, 4]. This structure is similar to that of a 3D crystal of the lepidocrocite type [3, 4], and thus will be called a lepidocrocite-like structure, hereafter. It has recently been shown that the TiO$_2$ thin film with the lepidocrocite-like structure can also be formed epitaxially on (1×2)-Pt(110) through reactive deposition of Ti in O$_2$ atmosphere [5, 6]. This process can be viewed as a bottom-up route to form the 2D TiO$_2$ nanosheets, which is alternative to the top-down route to form the nanosheets by exfoliation of layered titanates. The formation of the film on a metal substrate is expected to enable the microscopic characterization of the atomic and electronic structures of the metal by the use of the variety of surface analytical methods, and therefore the possibility for the formation of the TiO$_2$ nanosheets with the lepidocrocite-like structure on other metal surfaces is worth exploring.

Our previous study showed that TiO and TiO$_2$ films can be formed selectively on Ag(100): an ordered TiO$_2$ film with (1×1) periodicity with respect to Ag(100) is formed by Ti deposition in O$_2$ at 5.0×10$^{-9}$-1.0×10$^{-8}$ Torr and subsequent annealing at 600°C, while an ordered TiO$_2$ film with (5×1) periodicity is formed by Ti deposition in O$_2$ at 10$^{-5}$-10$^{-7}$ Torr and subsequent annealing at 600°C [7, 8]. The TiO film was proposed to be a thin 2D sheet with a NaCl-type structure which is commensurate with the Ag(100) lattice with the (1×1) periodicity from the analysis of the angle-resolved photoemission spectra [8]. On the other hand, the information on the structure of the (5×1) TiO$_2$ film was not obtained in our study, and the lattice of the film was tentatively ascribed to that of a distorted rutile TiO$_2$(001) [7].

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FIG. 1: LEED patterns of (a) the (1×1)TiO film on Ag(100) ($E_p = 60$ eV), and (b) the (5×1) TiO$_2$ film on Ag(100) ($E_p = 58$ eV).

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structure of the (5×1) TiO$_2$ film on Ag(100) has recently been studied in detail by Atrei et al. by means of scanning tunneling microscopy (STM), X-ray photoelectron diffraction (XPD), and low-energy electron diffraction (LEED) intensity analysis as well as the density functional theory (DFT) calculations [9], and they have proposed that the crystal structure of the (5×1) TiO$_2$ film on Ag(100) is the lepidocrocite-like structure [9]. The functionalities of the TiO$_2$ nanosheets should be closely related to the electronic structure, and the formation of the ordered 2D nanosheet on a metal substrate enables the investigation of the electronic structure by the use of photoemission spectroscopy (PES). In this work, we investigated the electronic structure of the (5×1) TiO$_2$ film on Ag(100) by PES utilizing synchrotron radiation.

II. EXPERIMENTAL

The ARPES measurements using synchrotron radiation were performed at the beamline 3B of the Photon Factory, High Energy Accelerator Research Organization (KEK). Photoelectrons were collected by an electron-energy analyzer (VSW HA54) with a microchannel-plate electron-multiplier detector. The acceptance angle of the analyzer was ±1°. The total energy resolution was estimated from the Fermi edge in the spectra of the Ta sample holder, and it was estimated to be 0.24 eV at $h\nu = 35$ eV and 0.29 eV at $h\nu = 60$ eV. The spectra presented below are normalized by the photocurrent of the final stage mirror. In this work, the incidence angle of the light ($\theta_0$) and the detection angle of photoelectrons ($\theta_d$), both of which are given relative to the surface normal, are 45° and 0° (normal-emission), respectively, and the incidence light was polarized in the incidence plane for all measurements. The work function was estimated from the width of photoemission spectra, which is deduced from the measurements of the Fermi level and the secondary electrons cut-off. The sample was biased at −9.80 eV when the secondary electrons cut-off was measured. The base pressure in the vacuum system was 1.0×10$^{-10}$ Torr.

The Ag(100) surface was cleaned by several cycles of Ar$^+$ ion sputtering (1 kV, 30 min) and annealing at 400°C for 30 min. The cleanliness of the surface was checked by Auger electron spectroscopy (AES). The Ti oxide films were grown on Ag(100) by Ti deposition from an electron-beam evaporator (Omicron EFM3) in O$_2$ atmosphere at 5.0×10$^{-5}$ Torr. During the deposition, the flux current of the Ti cations at the exit of the evaporator was kept at 0.5 nA, and the deposition time was 15 min for all experiments. The Ag(100) sample was kept at room temperature during deposition. The (5×1) TiO$_2$ film was formed by annealing the deposited film at 600°C for 3 min. The thicknesses of the film ($d$) was estimated to be 0.45 nm assuming the exponential decay of the Ag MNN Auger peak ($I/I_0 = \exp(-d/\lambda)$, where $\lambda$ is the inelastic mean free path of Ag MNN Auger electrons in the film). The value of $\lambda$ in the TiO$_2$ film is estimated to be 1.016 nm by the use of the TPP-2M equation [10]. The thickness of the film formed in this study is comparable to that of the (5×1) TiO$_2$ monolayer sheet with the lepidocrocite-like structure on Ag(100) obtained by Atrei et al. (0.5 nm) [9].

III. RESULTS AND DISCUSSION

First, we briefly discuss the periodicity and the composition of Ti oxide films grown on Ag(100). As Ti is deposited onto Ag(100) at room temperature in O$_2$ at 5.0×10$^{-9}$-1.0×10$^{-8}$ Torr, a TiO-like film with a diffused LEED pattern is formed. Our previous XPS study showed that the binding energy of the Ti 2p peak (454.6-454.8 eV for 2p$_{3/2}$) was compatible with that of TiO$_2$ (454.8 eV [11]), and that the O 1s and Ti 2p peak intensity analyses suggested that the composition of the film was TiO$_x$ (0.73 < $x$ < 1.1) [7]. As the surface covered with the TiO-like film is annealed at 600°C, the composition of the film is nearly unchanged and the LEED pattern changes to a clear (1×1) pattern independent of the film thickness below 1.2 nm. The LEED pattern of the (1×1) TiO film on Ag(100) with the thickness of 1.2 nm is shown in Fig. 1(a). Our previous ARPES study showed that a metallic band composed of mostly Ti 3d orbitals are formed in the TiO film, and the Ti 3d-induced states show two-dimensional band dispersions which are compatible with the (1×1) periodicity with respect to the Ag(100) substrate [8]. According to these results, it is shown that a TiO(100) film with a NaCl-type crystal structure is formed on Ag(100) epitaxially. On the other hand, as Ti is deposited in O$_2$ at 10$^{-5}$-10$^{-7}$ Torr a TiO$_2$-like film with a diffused LEED pattern is formed. Our previous XPS study showed that the binding energy of the Ti 2p peak (458.9 eV for 2p$_{3/2}$) was compatible with that of TiO$_2$ (458.8 eV [11]), and that the O 1s and Ti 2p peak intensity analyses suggested that the composition of the film was TiO$_{2.1}$ [7]. As the surface covered with the TiO$_2$-like film is annealed at 600°C, the composition of the film is nearly unchanged and the LEED pattern is changed into a (5×1) pattern independent of the film thickness below 1.3 nm. The LEED pattern of the (5×1) TiO$_2$ film on Ag(100) with the thickness of 1.3 nm is shown in Fig. 1(b). In this paper, our interest is focused on the electronic structure of the (5×1) TiO$_2$ film.

Figure 2(a) shows normal-emission spectra of the...
Ag(100) clean surface and of the surface covered by the (5×1) TiO$_2$ film with the thickness of 0.45 nm. The spectra are measured at $h\nu = 50$ eV. The spectrum for the clean surface consists of an intense band at 4-7.5 eV and a plateau between the Fermi level ($E_F$) and the intense band, which are ascribed to the Ag 4d band and 5sp band, respectively. As the surface is covered with the TiO$_2$ film, the spectral shape in the Ag 4d band region is modified; the band intensity around 4-5 eV is decreased and an additional band appears around 8-10 eV. The band around 8-10 eV is associated with a part of the valence band of the TiO$_2$ film, since the valence band of bulk TiO$_2$ has been observed at 4-10 eV [12]. The intensity of the Ag 5sp-induced plateau is also decreased and a slight band peaked at 1 eV appears. The band around 1 eV has been observed in the PES spectra for both anatase and rutile TiO$_2$, and has been ascribed to the state composed of the 3d components of the Ti$^{3+}$ species which are induced by the formation of oxygen vacancies [12]. The appearance of this peak thus suggests that the film formed in this study also includes oxygen vacancies. In Fig. 2(b), the Ti 3p spectra of the surface covered by the as deposited film and that covered by the film after annealing at 600°C (the (5×1) TiO$_2$ film) are shown. The Ti 3p band is slightly shifted to the higher binding energy side and is slightly decreased in intensity by annealing at 600°C, suggesting that oxidation of the Ti proceeds but slight amount of Ti atoms are desorbed by the present annealing procedure. The peak is observed at 37.6 eV after annealing, which is close to that observed for the anatase and rutile TiO$_2$ surfaces (38 eV) [12]. In Ti 3p spectra for the anatase and rutile TiO$_2$ surfaces, the components due to the Ti$^{3+}$ species adjacent to the oxygen vacancies have been observed around 36 eV [12]. The Ti 3p spectrum for the (5×1) TiO$_2$ film also shows a shoulder around 36 eV as shown in Fig. 2(b), also indicating that some oxygen vacancies exist in the film.

As shown in Fig. 2(a), the valence band of the TiO$_2$ film is substantially overlapping with the Ag 4d band, and it is difficult to observe the electronic structure of the film selectively. Therefore, we try to measure the resonant enhancement of the photoemission intensity of the valence band in the TiO$_2$ film. Figure 3 shows normal-emission spectra of Ag(100) covered by the (5×1) TiO$_2$ film with the thickness of 0.45 nm measured at various photon energies (36-80 eV). A series of spectra in Fig. 3 show that the spectral shape of the band at 4-10 eV is dependent on photon energy. In Fig. 4, we plot the intensity of the band at 4-10 eV in each spectrum as a function of photon energy (open circles). In order to estimate the band intensity, the background drawn by the Shirley procedure is subtracted from each raw data, and then the spectral intensity is integrated. The intensities are normalized to that measured at $h\nu = 36$ eV. In Fig. 4, we also plot the spectral height at 8.3 eV each difference spectrum between the spectrum of Ag(100) covered by the (5×1) TiO$_2$ film and that of the Ag(100) clean surface (filled circles). The intensities are normalized to that at $h\nu = 48$ eV. As shown in Fig. 2(a), the spectrum for the (5×1) TiO$_2$ film covered surface has a shoulder peak at 8.3 eV, while only a weak tail of the Ag 4d band exists around 8.3 eV in the spectrum of Ag(100), indicating that the spectral height at 8.3 eV reflects mostly the intensity of the TiO$_2$ valence band at this energy. The peak height at 8.3 eV clearly shows a maximum at $h\nu = 48$ eV. Previous resonant photomission studies for the anatase and rutile TiO$_2$ surfaces have concordantly shown that the intensity of the valence band is maximized at $h\nu = 47$ eV [12–15]. Since...
the photon energy corresponds to the Ti 3p → 3d optical absorption edge, the maximum has been interpreted to arise from the interference between a direct photoemission process and the process including Ti 3p → 3d excitation. However, the valence band of TiO$_2$ is mostly composed of O 2p components, and it is unlikely that the prominent increase of the valence band emission at $h\nu = 47$ eV [12–15] is induced by the enhancement of the emissions from the Ti 3d components. Therefore the maximum of the valence band intensity has been interpreted to arise from the interference between the direct photoemission process of the O 2p-induced state and the process including the 3p → 3d excitation followed by the emission from the O 2p-induced states via an interatomic deexcitation process [12–15];

$$\text{Ti}_3p^53d^6\text{O}_2p^6 + h\nu \rightarrow [\text{Ti}_3p^53d^4\text{O}_2p^6]^* \rightarrow \text{Ti}_3p^53d^6\text{O}_2p^5 + e^-.$$

(1)

The process is believed to be enabled when the Ti 3d and O 2p orbitals are strongly hybridized. The existence of the maximum at 48 eV is thus indicative of the strong hybridization between the Ti 3d and O 2p orbitals also in the (5×1) TiO$_2$ film around 8.3 eV. The plot of the peak height at 8.3 eV also shows a shoulder peak at around 54 eV. Previous resonant photoemission studies for the TiO$_2$ surfaces have also shown that the valence band intensity has an additional maximum around 54 eV, and the maximum has been attributed to the resonance arising from the interference between the direct photoemission process and the process including Ti 3p → 4s excitation [12–15]. The decay process after Ti 3p → 4s excitation is thought to include an interatomic deexcitation process, which is believed to occur when the O 2p and Ti 4s orbitals are strongly hybridized [12–15]. The existence of this maximum thus implies that the hybridization between the O 2p and Ti 4s orbitals should also contribute to the formation of the valence band of the film. The resonant behavior of the peak height at 8.3 eV is qualitatively agreement with those observed in CIS spectra of rutile and anatase TiO$_2$ at the initial state of 8.2 eV [12, 15]. However, the plot of the peak at 8.3 eV has an additional small peak at 60 eV, which has not been observed in CIS spectra at 8.2 eV for rutile and anatase TiO$_2$ [12, 15]. To our knowledge, a corresponding final state is not existing for TiO$_2$, and the origin of this peak is unknown at present.

Figure 4 shows that the plot of the integrated intensity in the band at 4-10 eV as a function of photon energy also shows a maximum at 48 eV and a weak maximum at around 54 eV. The $h\nu$-dependence of the Ag 4d band intensity in the PES spectrum for the Ag(100) clean surface has been reported in our previous paper [8], and it has been proved that $h\nu$-dependent modulation of the Ag 4d band intensity is relatively weak; no resonant peak is observed at 35-70 eV [8]. Therefore, the intensity maxima at 48 and 54 eV should arise from the resonances induced by Ti 3p → 3d and Ti 3p → 4s excitations, respectively, of the photoemission from the valence band of the TiO$_2$ film.

In Fig. 5, the normal-emission spectra of the (5×1) TiO$_2$ film covered surface measured at $h\nu = 48$ eV (Ti 3p → 3d resonance region), 54 eV (Ti 3p → 4s resonance region), and 78 eV (off-resonance region) are shown. The resonant enhancements of the intensities of the band in 4-10 eV at $h\nu = 48$ eV and 54 eV are clearly shown. Since the Ag 4d band does not have resonant behavior in this energy region [8], the difference between the spectrum measured by the photon with the energy in a resonance region and that measured by the photon with the energy in an off-resonance region should qualitatively correspond to the resonantly enhanced component of the emission from the TiO$_2$ film. The difference between the spectrum measured at 48 eV and that measured at 78 eV is shown in the upper part of Fig. 5, together with the difference between the spectrum measured at 54 eV and that measured at 78 eV. These correspond to the enhanced photoemission components due to the resonance including Ti 3p → 3d and 3p → 4s excitations, respectively. A dip is observed at around 4 eV in both difference spectra, and the dip arises from the fact that the substrate Ag 4d emission around 4 eV is relatively intense at 78 eV as shown in the inset of Fig. 5, in which the normal-emission spectra of Ag(100) measured at 48 eV and 78 eV are shown (the background drawn by Shirley procedure has been subtracted from each raw data). Peaks are observed at 5.0, 6.3, and 8.4 eV in both difference spectra. The spectral features are in good agreement with the normal-emission spectra of He I UPS measured for the lepidocrocite-like TiO$_2$ thin film epitaxially grown on...
The surface covered by the (5×1) TiO$_2$ film (red line) measured at $h\nu = 50$ eV and $\theta = 45^\circ$, and the difference between the latter and former spectra (blue line).

FIG. 6: Normal-emission spectra in the valence band region of the Ag(100) clean surface ($\times 0.350$, black line) and of the surface covered by the (5×1) TiO$_2$ film (red line) measured at $h\nu = 50$ eV and $\theta = 45^\circ$, and the difference between the latter and former spectra (blue line).
these two work function changes are equilibrate with each other in the case of the (5×1) TiO$_2$ film covered Ag(100). In this work, the valence band is observed at 4-10 eV (Figs. 5 and 6). The valence bands of rutile and anatase TiO$_2$ have been observed in nearly the same binding energy region (4-10 eV) [12, 15], and thus the valence band width of the (5×1) TiO$_2$ film on Ag(100) is nearly identical to that of rutile and anatase TiO$_2$, though the film is formed as an ultra-thin film (0.45 nm). Previous resonant PES study has revealed that the valence band in the resonance region is found to have also three peaks (5.0, 6.3 and 8.2 eV in Fig. 5, and 5.1, 6.8 and 8.3 eV in both case) [12]. These have been ascribed to the O $2p$ non-bonding, Ti–O $\pi$-bonding, and Ti–O $\sigma$-bonding states, respectively [12]. In this work, the valence band in the resonance region is found to have also three peaks (5.0, 6.3 and 8.2 eV in Fig. 5, and 5.1, 6.8 and 8.3 eV in Fig. 6). These results suggest that the binding energies of the Ti–O $\sigma$-bonding and $\pi$-bonding states are nearly the same as those of rutile and anatase TiO$_2$, while the O $2p$ non-bonding state seems to be formed in the lower binding energy region as compared with that of rutile and anatase TiO$_2$. According to a structural model for lepidocrocite-like TiO$_2$ nanosheets, all the Ti atoms are fully coordinated by O atoms while the outermost O atoms are not fully coordinated [2]. In this case, the O $2p$ non-bonding band should include the O $2p$ components which are not stabilized through the formation of bonds with Ti orbitals. The shift of the lowest binding energy peak in the valence band of the TiO$_2$ film toward the lower binding energy side relative to the that in the spectra for rutile and anatase TiO$_2$ is thus thought to be due to the fact that the film includes O atoms which are not fully coordinated.

**IV. CONCLUSIONS**

The electronic structure of the (5×1) TiO$_2$ film on Ag(100) was investigated by resonant photoemission spectroscopy. The valence band of the film was deduced by two different methods; one was the extraction of the resonantly enhanced component, and the other was taking the difference between the spectrum of the film covered surface and that of Ag(100) multiplied by the decay factor. The results were qualitatively in agreement with each other; the valence band of the film was observed in the binding energy region of 4-10 eV. The spectral profiles were in good agreement with the He I UPS spectrum of the lepidocrocite-like film on (1×2)-Pt(110) [6]. The spectral intensity of the valence band of the film was maximized at the photon energies of 48 eV and 54 eV, which were ascribed to the resonances caused through the interference between the normal photoemission process and the process including Ti 3$p$ → 3$d$ and 3$p$ → 4$s$ excitations, respectively, followed by interatomic deexcitation processes. Resonant photoemission measurements showed that the valence band of the film in the region of 5-10 eV are formed by hybridization of the O 2$p$ orbitals with both the Ti 3$d$ and 4$s$ orbitals, however, the top region of the valence band is mostly composed of the O 2$p$ components forming non-bonding states.

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