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Growth of ordered titanium oxide films on Ag(100)

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Abstract

Titanium oxide films grown on Ag(100) have been investigated with low-energy electron diffraction, X-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy. As Ti is deposited on Ag(100) at room temperature in an O_2 atmosphere at 10^{-5}–10^{-7} Torr, a disordered TiO_2-like film is formed. As the surface is subsequently heated at 600 °C, though the composition of the film is nearly unchanged, the film changes into an ordered film with (5 × 1) periodicity [(5 × 1) TiO_2 film]. On the other hand, as Ti is deposited in O_2 at 5.0×10^{-9}–1.0×10^{-8} Torr, a disordered TiO-like film is formed. As the surface is subsequently heated at 600 °C, the composition of the film is nearly unchanged and the film changes into an ordered film with (1 × 1) periodicity [(1 × 1) TiO film]. Ultraviolet photoelectron spectroscopy measurements show that the (1 × 1) TiO film has an electronic state around the Fermi level, and the state is ascribed to a partially filled Ti 3d state which has been theoretically expected to exist in a TiO crystal.

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Keywords: A. Thin films; C. Surface electron diffraction (LEED); E. Photoelectron spectroscopies

The Ti oxides have attracted much attention in recent years because of their technological importance. In particular, the physical and chemical properties of TiO_2 have been extensively studied because of its use as a catalytic support, photocatalyst, gas sensor and so on [1]. Ti monoxide (TiO) is also of interest because it has an interesting combination of useful properties such as extreme hardness, a high melting point and metallic conductivity [2]. In practical applications, TiO is expected to be useful as a diffusion barrier [3], anticorrosive coating material [3], gas sensor [4] and so on. To explore further the functionality of TiO, it is important to elucidate the electronic structure in the valence band region. Some theoretical studies have been reported on the band structure of TiO [2,5,6]; however, very few experimental investigations have been performed on the electronic structure of TiO. This is primarily due to the fact that TiO is rather unstable and it is difficult to synthesize the single crystal. Recently, Suzuki et al. found that a TiO single crystal film can be epitaxially grown on MgO(100) [7,8]. In order to explore the band structure, however, it is desirable to form the single crystal film on a conductive substrate. Recently, we have found that a TiO single crystal film can be formed on TiC(100), which is a conductive material, by heating the oxygen-adsorbed TiC(100) surface at ∼1000 °C [9]. The two-dimensional band structure of the film has been measured by angle-resolved photoemission spectroscopy (ARPES) [10]. However, the formed TiO layer passivates TiC(100) from further oxidation, and thus a very thin TiO film whose thickness is estimated to be 1.3–2.0 Å is formed on the TiC(100) surface [9]. Therefore, it is unclear whether the measured band structure is that inherent to TiO itself or that modified by the interaction with the TiC(100) substrate. In the present work, we tried to form a TiO epitaxial film on Ag(100) by Ti deposition in an O_2 atmosphere. The Ag(100) surface was chosen as a substrate because the Ag has a fcc-type crystal structure whose lattice constant is 4.09 Å [11], which is similar to that of the TiO crystal (4.18 Å [2]). In this work, it was found that the composition of the Ti oxide film on Ag(100) can be controlled by the O_2 pressure during Ti deposition, and

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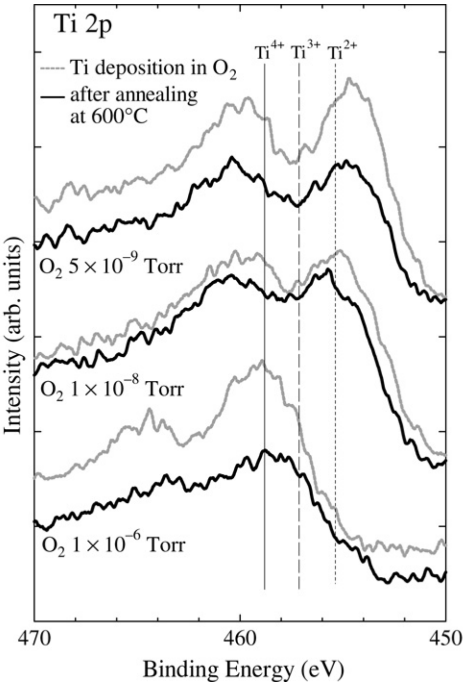

Fig. 1. Ti 2p spectra of the Ag(100) surface after Ti deposition in O_2 at 5.0×10^{-9}, 1.0×10^{-8} and 1.0×10^{-6} Torr (gray lines), and of the surfaces subsequently heated at 600 °C (solid lines). The energies of the Ti $2p_{3/2}$ levels of Ti^{2+}, Ti^{3+} and Ti^{4+} states [12] are shown as vertical bars.

that a TiO film is formed on Ag(100) by Ti deposition in O_2 at 1.0×10^{-8}–5.0×10^{-9} Torr.

The experiments were performed in an ultra-high vacuum chamber equipped with a dual anode X-ray tube, a He I discharge lamp, a 180° spherical-sector type electron energy analyzer (VG 100AX), and low-energy electron diffraction (LEED) optics. A Mg Kα radiation source was used for all X-ray photoelectron spectroscopy (XPS) measurements. The binding energy of the XPS spectra was calibrated by the energy position of the Ag $3d_{5/2}$ peak which is observed in the spectra at 368.2 eV. For ultraviolet photoelectron spectroscopy (UPS), the binding energy was calibrated by the Fermi cut-off in the spectra of the Ta sample holder. The base pressure in the vacuum system was 1.2×10^{-10} Torr.

The Ag(100) surface was cleaned by several cycles of Ar^+ ion sputtering and annealing at 600 °C. The cleanliness of the surface was checked by XPS. The prepared Ag(100) clean surface gives a sharp (1 × 1) LEED pattern (Fig. 2(a)). The Ti oxide films were grown on the Ag(100) surface at room temperature by Ti deposition in an O_2 atmosphere (5.0×10^{-9}–1.0×10^{-5} Torr). Ti was deposited onto the surface from an electron-beam evaporator (Omicron EFM3). During the deposition, the flux current of the Ti cations at the exit of the evaporation source was kept at ~10 nA, and the deposition time was 9 min for all experiments. During the deposition, the Ag(100) sample was kept at room temperature for all experiments.

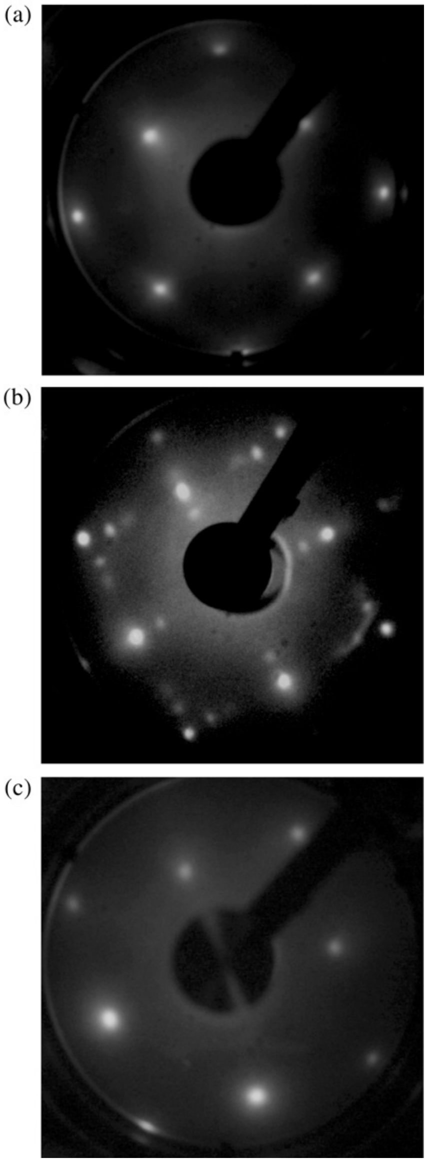

Fig. 2. LEED patterns of (a) the Ag(100) clean surface ($E_p = 55$ eV), (b) the surface after Ti deposition in O_2 at 1.0×10^{-8} Torr and subsequent heating at 600 °C ($E_p = 60$ eV), (c) the surface after Ti deposition in O_2 at 1.0×10^{-6} Torr and subsequent heating at 600 °C ($E_p = 58$ eV).

Fig. 1 shows Ti 2p spectra of the Ag(100) surface after Ti deposition in an O_2 atmosphere of 1.0×10^{-6}, 1.0×10^{-8} and 5.0×10^{-9} Torr (gray lines). When Ti is deposited in O_2 at 1.0×10^{-6} Torr, the Ti 2p peaks ($2p_{3/2}$, $2p_{1/2}$) are observed at (458.9, 464.5 eV). Nearly the same spectrum is observed independent of the O_2 pressure during 10^{-5}–10^{-7} Torr. As Ti is deposited in O_2 at 1.0×10^{-8} and at 5.0×10^{-9} Torr, the Ti 2p peaks are observed at (454.8, 460.0 eV) and (454.6, 459.5 eV), respectively. The Ti 2p peaks of Ti atoms in the oxidation state of Ti^{4+}, Ti^{3+} and Ti^{2+} have been observed at (458.8, 464.5 eV), (457.1, 462.8 eV) and (455.4, 461.1 eV), respectively [12]. Therefore, the Ti oxide films formed on the Ag(100) surface in O_2 at 10^{-5}–10^{-7} Torr are ascribed to a TiO_2-like film, and those formed in O_2 at 1.0×10^{-8} and at 5.0×10^{-9} Torr are ascribed to a TiO-like film. The ratios of the integrated intensities of the O 1s and Ti 2p peaks (I_{O1s}/I_{Ti2p}) are estimated to be 0.74, 0.40 and 0.26 for Ti oxide films formed in O_2 at 1.0×10^{-6}, 1.0×10^{-8} and 5.0×10^{-9} Torr, respectively.

By the correction using the photoionization cross sections of O 1s and Ti 2p levels [13], the compositions of the Ti oxides can be estimated from the ratio of the O 1s and Ti 2p peak intensities ($I_{\mathrm{O1s}}/I_{\mathrm{Ti2p}}$). The results show that the compositions of the Ti oxide films formed in O_2 at 1.0×10^{-6}, 1.0×10^{-8} and 5.0×10^{-9} Torr are $TiO_{2.1}$, $TiO_{1.1}$ and $TiO_{0.73}$, respectively, also suggesting that TiO_2-like film is formed in O_2 at 1.0×10^{-6} Torr while the TiO-like film is formed in O_2 at 1.0×10^{-8} and 5.0×10^{-9} Torr.

In Fig. 1, the Ti 2p spectra of the Ti oxide films after heating at 600 °C are also shown as solid lines. Fig. 1 shows that the spectral intensities are decreased while the peak energies are nearly unchanged upon heating at 600 °C for all measured films, indicating that the oxidation state of Ti in the oxide films is nearly unchanged by heating at $\leqq$600 °C. The surface covered with the Ti oxide films formed at room temperature gives diffuse LEED patterns with broadened (1 × 1) spots independent of the O_2 pressure during Ti deposition, and therefore the TiO_2-like film and TiO-like film formed at room temperature are thought to have structures with disorder over a long-range scale. However, when the surface covered with the TiO_2-like film is heated at 600 °C, the disordered pattern changes into a (5 × 1) pattern. The LEED pattern of the surface covered with the TiO_2-like layer formed by Ti deposition in O_2 at 1×10^{-6} Torr and subsequently heated at 600 °C is shown in Fig. 2(b). The surface gives a (5 × 1) pattern, and this film will be called a (5 × 1) TiO_2 film hereafter. On the other hand, when the surface covered with the TiO-like film is heated at 600 °C, the disordered pattern changes into a sharp (1 × 1) pattern. Fig. 2(c) shows the pattern of the surface on which Ti is deposited in O_2 at 1.0×10^{-8} Torr and subsequently heated at 600 °C. The surface gives a clear (1 × 1) pattern, indicating that the periodicity of the Ti oxide film after heating at 600 °C is the same as that of the Ag(100) surface. This film will be called a (1 × 1) TiO film hereafter. The thickness (d) of the ordered Ti oxide film is estimated from the measurements of the attenuation of Ag 3d peaks, using the equation $I/I_0 = \exp(-d/\lambda)$, where I_0 and I are the Ag 3d peak intensities in XPS spectra of the clean surface and of the surface covered with the oxide film, respectively, and λ is the inelastic mean free path of Ag 3d photoelectrons (λ is estimated to be 19.3 Å in TiO_2 and 17.8 Å in TiO [14]). The estimated thicknesses are 12.7 Å for the (5 × 1) TiO_2 film and 11.5 Å for the (1 × 1) TiO film.

TiO is known to have a NaCl-type crystal structure whose lattice constant (4.18 Å) is slightly larger than that of Ag (4.09 Å). Therefore, it is deduced from the XPS and LEED results that a slightly compressed TiO(100) single-crystal film is formed on the Ag(100) surface as the (1 × 1) TiO film when the surface covered by the TiO-like film is heated at 600 °C. It is more difficult to deduce the structure of the (5 × 1) TiO_2 film. If TiO_2 crystallizes into a rutile structure, the lattice constants are $a = 4.58$ Å and $c = 2.95$ Å [1], and thus the lattice is not commensurate with that of Ag(100). However, since the lattice constants a and c are close to $\frac{5}{3}r_{\mathrm{Ag}}$ and r_{Ag}, respectively, where $r_{\mathrm{Ag}} = 2.89$ Å is the nearest neighbor distance in Ag crystal, one of the possible models of the (5 × 1) TiO_2 structure is that the film has a distorted rutile TiO_2 structure whose lattice constants are $a = \frac{5}{3}r_{\mathrm{Ag}} = 4.82$ Å and $c = r_{\mathrm{Ag}} = 2.89$ Å with the a and c axes parallel to the [110] and $[1\bar{1}0]$ directions of Ag(100), respectively. In this case, the (5 × 1) LEED pattern (Fig. 2(b)) is interpreted as originating from the two types of (5 × 1) domains which are rotationally misaligned by 90°.

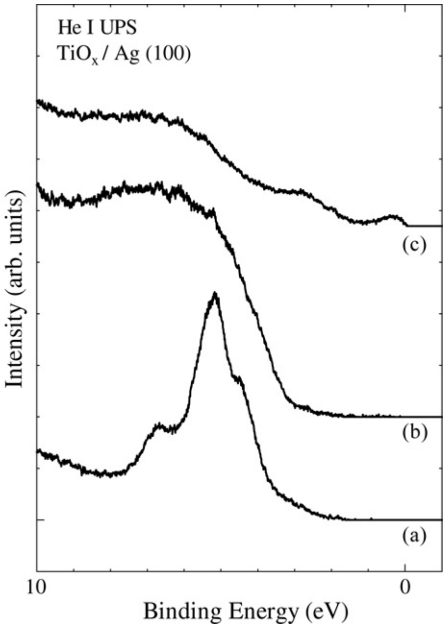

Fig. 3. He I UPS spectra of (a) the Ag(100) clean surface, (b) the surface after Ti deposition in O_2 at 1.0×10^{-6} Torr and subsequent heating at 600 °C and (c) the surface after Ti deposition in O_2 at 1.0×10^{-8} Torr and subsequent heating at 600 °C.

TiO_2 is a typical semiconductor with a band gap of ~3 eV [11], while TiO is expected to have metallic conductivity due to the existence of a partially filled Ti 3d band around the Fermi level (E_F) [2,5,6]. Therefore, the electronic states of the Ti oxide films, especially in the vicinity of E_F, are of interest. Fig. 3 shows UPS spectra of the Ag(100) clean surface and of the surfaces covered with Ti oxide films. For the clean surface (Fig. 3(a)), the Ag 4d band is observed at 4–7 eV and the spectrum is typical of the UPS spectra of Ag. As the Ag(100) surface is covered by the (5 × 1) TiO_2 film, the Ag 4d band emissions are suppressed and a broad band appears at 4–8 eV (Fig. 3(b)). The band at 4–8 eV has been typically observed in UPS spectra of TiO_2, and has been ascribed to the O 2p induced valence band [15,16]. Thus the UPS result is compatible with the model deduced from the XPS results that the Ti oxide film with (5 × 1) periodicity has a composition of TiO_2. Fig. 3(b) shows that there is no state in the vicinity of E_F in the spectrum of the (5 × 1) TiO_2 film, suggesting that the film corresponds to nearly stoichiometric TiO_2 with a negligible number of O vacancies. On the other hand, as the surface is covered by the (1 × 1) TiO film, the peaks appear at just below E_F, 2.8 eV, and ~6 eV (Fig. 3(c)). The O 2p band of a TiO film was observed at 6.5 eV and 6.4 eV in the spectra of TiO/MgO(100) [8] and of TiO/TiC(100) [10], respectively, and thus the band at ~6 eV is ascribed to the O 2p band of TiO. In contrast to the case of the (5 × 1) TiO_2

film, a peak is observed at just below E_F in the spectrum of the (1 × 1) TiO film. The peak is assigned as the partially filled Ti 3d state, which has been expected to exist in TiO from the theoretical calculations [2,5,6]. The peak just below E_F has also been observed in UPS spectra of the TiO/MgO(100) [8] and TiO/TiC(100) [10] systems, and thus the state is characteristic of the electronic structure of a TiO film. We think that the state is responsible for the metallic nature of the TiO crystal. The origin of the peak at 2.8 eV is unknown at present. In the case of TiO/MgO(100), a peak was observed at 3.5 eV and the peak was tentatively ascribed to the adsorbed oxygen on the TiO surface [8]. The existence of the ∼3 eV peak in the spectra of TiO/TiC(100) is not clear due to the existence of large emissions from the underlying TiC(100) substrate [10]. As discussed above, the spectrum of the (1 × 1) TiO film is essentially compatible with those of TiO/MgO(100) [8] and TiO/TiC(100) [10].

In conclusion, it was found that two types of ordered Ti oxide films can be formed on the Ag(100) surface; one is the (1 × 1) TiO film which is formed by Ti deposition in an O_2 atmosphere at 1.0×10^{-8}–5.0×10^{-9} Torr at room temperature and subsequent heating at 600 °C, and the other is the (5 × 1) TiO_2 film which is formed by Ti deposition in an O_2 atmosphere at 10^{-5}–10^{-7} Torr at room temperature and subsequent heating at 600 °C. Since the lattice constant of TiO is slightly larger than that of Ag, a slightly compressed TiO single-crystal film is thought to be formed as the former film. The UPS measurements showed that the electronic structure of the (1 × 1) TiO film is characterized by the existence of the state around E_F. The state is ascribed to the partially filled Ti 3d band which has been theoretically expected to be formed in a TiO crystal [2,5,6].

Acknowledgements

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