Abstract

Ordered titanium oxide films were prepared on an Mo(110) substrate under ultrahigh vacuum conditions and characterized by various vacuum surface analytical techniques. Using different preparation methods, the titanium oxide films exhibit two low-energy electron diffraction patterns: a (1×1) rectangular pattern and a (1×1) hexagonal pattern. Auger electron spectroscopy, high-resolution electron loss spectroscopy, and X-ray photoelectron spectroscopy results indicate that the titanium oxide films grow epitaxially on Mo(110) as either TiO$_2$(100) or Ti$_2$O$_3$(0001), depending upon the particular preparation method. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

There is considerable interest in titanium oxides owing to their importance in many areas, such as photo-assisted oxidation, heterogeneous catalysis, and gas sensors [1-3]. Studies on powdered and single crystalline samples of titanium oxide using a variety of techniques, including ultrahigh vacuum (UHV) surface spectroscopies, have yielded considerable information regarding its chemical and physical properties [4-24]. Generally, studies using electron spectroscopies are of limited use on metal oxides because of surface charging. However, certain oxides, including those of titanium, can be prepared as semiconductors and hence are amenable to electron probes. In order to prepare conducting TiO$_2$, oxygen defects are created by annealing, a process that fundamentally alters its physical and chemical properties. It is informative, then, to compare ordered oxide films and the corresponding single crystalline samples. A limited number of studies on titanium oxide films can be found in the literature; however, most of these are polycrystalline films [25-28]. Recently, ordered metal oxide films supported on metals have been successfully prepared, including layered binary oxide films [29-42].

In this paper, results are presented for ordered TiO$_2$ and Ti$_2$O$_3$ films grown on an Mo(110) substrate. The films were characterized using Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), high-resolution electron energy loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS).

2. Experiments

The experiments were carried out in two UHV chambers. The first chamber has a base pressure
of 2 × 10⁻¹⁰ Torr and is equipped with reverse view optics for LEED, electron optics with a single-pass cylindrical mirror analyzer (CMA) for AES, and an LK-2000 model HREELS spectrometer for electron energy loss studies. The second chamber has a base pressure of 5 × 10⁻¹⁰ Torr and is equipped with dual-anode (Mg and Al) X-ray sources for XPS, optics for LEED, and an electron gun for AES.

The Mo(110) sample used as the substrate had a diameter of 8 mm and a thickness of 1.5 mm. The sample was mounted with Ta wire and could be resistively heated to 1500 K. The sample could also be heated to 2500 K by an electron beam heater at the backside of the sample, and cooled to 90 K by liquid N₂. A W–5%Re/W–26%Re thermocouple was spot welded to the edge of the Mo(110) sample.

The substrate was prepared by cycles of annealing to 1200 K in 2 × 10⁻¹⁰ Torr O₂ and subsequently flashing to 2000 K, until no impurities could be detected by AES. The Mo(110) surface has a rhombic structure with \( a_0 = 0.314 \) nm and \( b_0 = 0.272 \) nm. Titanium oxide films were prepared in two ways. The first method consists of evaporating Ti in 2 × 10⁻⁷ Torr O₂ onto Mo(110) at 600–700 K followed by annealing to 800 K in \( 30 \) MLE titanium oxide film (film A) grown on the Mo(110) surface using the first method. The second method consists of initially dosing ≤1 ML Ti in UHV onto the substrate, subsequently evaporating Ti in 2 × 10⁻⁷ Torr O₂ at 600–700 K, and then annealing to 800 K in \( 10⁻⁷ \) Torr O₂. Films produced by both methods were further annealed to 800 K in vacuum to order the surface. Hereafter, the films will be referred to as ‘film A’ if prepared by the first method and ‘film B’ if prepared by the second method.

A single crystal of TiO₂(110) was also used in this study. This crystal was approximately 5 × 10 mm² in size, 1 mm thick, and was epitaxially polished and cleaned ultrasonically with acetone before insertion into the UHV chamber. The single crystal was annealed at \( \sim 1200 \) K for 10 to 20 min in UHV. In some cases, the sample was annealed using 10⁻⁶ Torr O₂ at about 1000 K for reoxidation of the surface. After several cycles of annealing, LEED exhibited a sharp (1 × 1) rectangular periodicity, with no impurities detected by AES.

A primary energy of 3 keV was used in the AES measurements. To minimize electron beam damage, a low beam current of 10–15 mA was used; the collection time for each AES spectrum was less than 50 s. The X-ray source used for XPS was Mg Kα; the collector pass energy was 11.75 eV. The binding energy (BE) was calibrated to 90 K by liquid N₂. A W–5%Re/W–26%Re thermocouple was spot welded to the edge of the Mo(110) sample.

3. Results and discussion

3.1. TiO₂(100) on Mo(110)

Fig. 1a shows a (1 × 1) LEED pattern from a clean Mo(110) substrate. Molybdenum has a body-centered cubic (bcc) close-packed crystal structure with a lattice constant of \( a_0 = 0.314 \) nm [43]. The Mo(110) surface has a rhombic structure with \( a_0 = 0.314 \) nm and \( b_0 = 0.272 \) nm. A ~30 MLE titanium oxide film (film A) grown on the Mo(110) surface using the first method detailed above gives a (1 × 1) rectangular periodicity, as shown in Fig. 1b. Fig. 2 shows the AES results for the Mo(110) substrate (Fig. 2a) and a ~30 MLE titanium oxide of film A (Fig. 2b). The titanium oxide film is free of any detectable impurities by AES. With increasing deposition of Ti in O₂ ambient, the AES signal from Mo was gradually attenuated.

The common titanium oxides, TiO, Ti₂O₃, and TiO₂, must be considered as possible phases for our titanium oxide films. TiO has the NaCl crystal...
value (1.55) expected for TiO\(_2\) (100). Since LEED (Fig. 1b) shows weak streaking along the [010] direction, some local reconstruction of the surface may occur; however, the likely structure of film A is TiO\(_2\) (100).

Several examples of the use of AES to differentiate titanium oxides are found in the literature. A TiO\(_2\) (100)-(1\(\times\)3) surface exhibits an O(510 eV)/Ti(380 eV) AES ratio of 1.7, whereas a TiO\(_2\) (100)-(1\(\times\)7) surface shows a ratio of 1.5 [44]. An Ar ion-bombarded TiO\(_2\) (110) surface yields an O(510 eV)/Ti(380 eV) AES ratio of 1.3, and an annealed TiO\(_2\) (110) surface a ratio of 1.7 [45]. For film A, the O(510 eV)/Ti(380 eV) AES ratio was 1.7–1.8, consistent with the film being TiO\(_2\).

The Ti LMM and Ti LMV AES fine structure can also be used to distinguish titanium oxides. In the case of TiO\(_2\), for instance, the Ti LMV Auger transition exhibits a shoulder in the region 410–415 eV [46]. Fig. 3 shows the Auger spectra from film A (solid line in Fig. 3) and from a TiO\(_2\) (110) single crystal (open circles in Fig. 3). A shoulder on the low energy side of the Ti LMV transition at 413 eV has been observed for both TiO\(_2\) (100) and TiO\(_2\) (110). The identical AES line shapes of the film and the TiO\(_2\) single crystal, as shown in Fig. 3 indicate that film A is very

Various titanium oxides exhibit different core-level Ti 2p BEs in XPS. In general, higher titanium oxidation states exhibit larger BEs. The Ti 2p\(_{3/2}\) BE of TiO falls within the range 458.5–459.3 eV [47–50]. Fig. 4 shows the XPS results at 110 K for ~50 MLE of film A. A Ti 2p\(_{3/2}\) BE of 459.1 eV, and a splitting between the Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\) features of 5.7 eV in Fig. 4, strongly supports film A being TiO. Surface defects can give rise to a pronounced feature on the low BE side of the Ti 2p\(_{3/2}\) feature; however, such was not observed for film A. The favorable comparison of the XPS results for film A with the XPS results of stoichiometric TiO\(_2\), with respect to BE and peak shape [9,10], strongly suggests that film A is stoichiometric TiO\(_2\).

Fig. 5 shows the HREEL spectrum acquired for ~30 MLE of film A. The spectrum was obtained
Fig. 2. Auger spectra: (a) Mo(110) surface prior to film growth, (b) ~30 MLE titanium oxide film on Mo(110). The primary energy was 3 keV; the spectra were collected at 100 K.

Fig. 3. AES fine structure of Ti LMM and Ti LMV. Solid line is for film A with a (1 × 1) rectangular LEED pattern; the open circles are for TiO$_2$(110).
Fig. 4. XPS of film A with a (1 × 1) rectangular LEED pattern at 110 K. The film thickness is ~50 MLE.

Fig. 5. HREELS spectra at room temperature: (a) titanium oxide film (film A) with ~30 MLE thickness on Mo(110); (b) TiO$_2$(110) single crystal. $E_p$ = 4.7 eV.
at room temperature at an incidence angle of 60° at the surface normal. Fundamental phonons of 54 meV ($v_1$) and 95 meV ($v_2$), as well as overtone losses and combinations are observed. The loss at 149 meV, for instance, is due to $v_1 + v_2$ and the loss at 245 meV is due to $v_1 + 2v_2$. The anatase form of TiO$_2$ can be ruled out for film A since this phase exhibits fundamental surface phonons at 48 meV and 92 meV for the (001) surface and at 44 meV and 98 meV for the (100) surface [51]. The vibrational spectrum for rutile TiO$_2$(110) was also acquired with the same experimental conditions (Fig. 5b). This spectrum is consistent with previously published HREELS spectra for TiO$_2$ single crystal surfaces [16,52]. The similarities in the HREELS spectra between film A and bulk TiO$_2$ add further support to the assignment of film A to TiO$_2$(100).

There are a number of valence band studies of titanium oxides [20,44,45,48–50,53–55]. For TiO$_2$, the valence band consists primarily of two features related to the O 2p band, although various crystalline faces yield slightly different BEs. For TiO$_2$(001), features at ~5.0 and ~7.0 eV, corresponding to the bonding and non-bonding components of the O 2p bands respectively, are observed [48]. Following Ar-ion bombardment in O$_2$ in UHV, the photoemission spectrum of TiO$_2$(100) shows features at 5.2 and 6.5 eV [44]. One report shows two major features at 5.4 and 7.9 eV for a (1 × 1) TiO$_2$(110) surface, sputtered and annealed at 700 K [53]. For Ti$_3$O$_7$, on the other hand, the Ti 3d feature is at ~1 eV, whereas the peak shape of the O 2p band is quite different from that for TiO$_2$ [54]. The X-ray-induced (Mg Kα) valence band spectra for film A is shown in Fig. 6. Features are evident at 6.1 and 8.3 eV with a structureless region between the Fermi level and 2 eV, characteristic of TiO$_2$.

3.2 Ti$_3$O$_7$(0001) on Mo(110)

Using the second synthesis method detailed above, film B was prepared on Mo(110). With this method, ~1 ML of Ti was deposited on the Mo(110) prior to growth of the titanium oxide film. Fig. 7 shows the LEED data from film B, which exhibited a (1 × 1) hexagonal periodicity and clearly exhibited a different LEED periodicity compared with film A. The LEED pattern of film B was very similar to that of ordered aluminum. 

Fig. 6. Valence band spectrum of film A obtained with an Mg Kα source.
The fine structure of the Ti LMV AES feature from film B is shown in Fig. 8 (solid line). For comparison the corresponding AES spectrum from film A is also shown (Fig. 8, open circles). As discussed above, the Ti LMV Auger line shape of film A (TiO$_2$) has a shoulder between 410 and 420 eV, a feature not observed for TiO [46,56,57]. In Fig. 8 the Ti LMV Auger line shape of film A is broader than that for film B. Also, the Ti(LMM)/Ti(LMV) ratio of film A is slightly larger than that for film B. For film B, a small shoulder on the low energy side of the Ti LMV oxide (Al$_2$O$_3$) films grown on Mo(110) [41], for which LEED indicated a lattice constant corresponding to the oxygen-oxygen bond distance (~0.28 nm) of Al$_2$O$_3$(0001). Possible structures of film B with a hexagonal symmetry are corundum Ti$_2$O$_3$(0001) or cubic TiO(111). However, TiO is unstable relative to Ti$_2$O$_3$, and can be easily identified by XPS as discussed below. From Fig. 7, the lattice constant of film B can be estimated to be 0.29 nm (the oxygen-oxygen bond distance). The corundum structure of Ti$_2$O$_3$(0001) has a lattice constant of $a_0$ = 0.515 nm, with an oxygen-oxygen distance of 0.3 nm, consistent with film B being Ti$_2$O$_3$(0001).

Surface optical phonons from film B were observed, as shown in Fig. 9. Film B (~40 MLE) was heated to 1100 K for 28 min in UHV prior to the HREEL spectrum. The main losses are located at 47 and 88 meV, an overtone at 175 meV is also seen in Fig. 9. These losses are quite different from...
Fig. 9. HREEL spectrum of film B (40 MLE) on Mo(110) at 100 K ($E_p = 5$ eV). The surface was annealed to 1100 K for 28 min prior to acquisition of the spectrum.

Fig. 10. XPS of titanium oxide film (film B) with a (1 × 1) hexagonal LEED pattern as shown in Fig. 7.
Fig. 11. XPS of the O 1s region for the indicated titanium oxide films. The solid line is for film A, the open circles are for film B.

Fig. 12. Valence band spectrum of film B obtained with an Mg Kα source.
XPS results of titanium oxides indicate that lower oxidation states exhibit lower Ti 2p BEs. Fig. 10 shows the XPS core-level spectrum of film B (~80 MLE). The Ti 2p3/2 BE is 458.1 eV, 1 eV lower than that from film A (Fig. 4). The Ti 2p features of film B are much broader than those from film A, and their peak shapes identical to those previously reported for Ti₂O₃ [59]. The O 1s feature of film B (Fig. 11) is also quite different from that of film A. The O 1s BE from film A is 530.7 eV, with a symmetric peak. The O 1s BE from film B is 531.0 eV with a broad shoulder on the high BE side. The BE position from film B is very close to the value reported previously for Ti₂O₃(1012) (531.2 eV) [60]. The O 1s feature of film B is also asymmetric and broad, characteristic of Ti₂O₃ [60]. Therefore, LEED, AES, XPS, and HREELS results are all consistent with the assignment of film B to Ti₂O₃(0001).

Previous work has shown that the valence band electronic structure of Ti₂O₃ consists of an O 2p band from 4 to 10 eV and a Ti 3d band extending from the Fermi level to 1.5 eV [45]. Fig. 12 shows the X-ray-induced valence band spectrum of film B. A feature extending from the Fermi level to ~3 eV is clearly visible and characteristic of Ti₂O₃. This feature is absent in the corresponding valence band spectrum of film A (see Fig. 6). It is also noteworthy that the O 2p band of film B does not show the two-peak structure seen for film A.

3.3. Thermal stability

The thermal stability of the films was also investigated by annealing the films to successively higher temperatures, cooling between annealings to acquire AES spectra. In general, thermal stabilities vary with film thicknesses, thus the thermal stabilities of both films were studied at identical thicknesses (~20 MLE). Fig. 13 presents AES spectra of film A (Fig. 13A, curve a) and film B (Fig. 13B, curve a) as prepared. After flashing film A to 1100 K for several seconds, an Mo(110) substrate signal is evident in the AES spectrum (Fig. 13A, curve b). However, AES from film B, annealed to 1100 K for 28 min, showed no signal from the Mo(110) substrate (Fig. 13B, curve b), indicating that film B is thermally more stable.
than film A. After annealing film B at 1350 K for 2 min an Mo signal was observed (Fig. 13B, curve d). Further annealing to 1450 K for 1 min resulted in prominent AES Mo features (Fig. 13B, curve e). It is reasonable that film B is more thermally stable than film A since the melting point of TiO$_2$ is 305 K higher than that of Ti$_2$O$_3$.

4. Conclusion

Two different titanium oxide films have been prepared on Mo(110). The films were characterized by LEED, AES, HREELS and XPS. The results indicate that the titanium films grow on Mo(110) as either TiO$_2$(100) or Ti$_2$O$_3$(0001), depending on the particular preparation method.

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