Synthesis and characterization of titania films on Mo(110)

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Abstract

Ultra-thin titania films were grown on a Mo(110) substrate by vapor depositing Ti in an O₂ ambient (5 × 10⁻⁷ Torr) at 600 K, followed by annealing to 900–1200 K. X-ray photoelectron spectroscopy showed that titanium oxide films annealed to 900 K were partially reduced, exhibiting Ti⁴⁺, Ti³⁺ and Ti²⁺ species, whereas films annealed to 1200 K were fully oxidized and exhibited only Ti⁴⁺. Corresponding scanning tunneling microscopy measurements revealed layer-by-layer growth of titania films on Mo(110) at 900 K. Flat terraces with three different orientations were observed. The line spacings between the neighboring atomic rows for all terraces were ~6.5 Å, suggesting epitaxial growth of TiO₂(110)-(1 × 1). A further anneal of the films to 1200 K led to three-dimensional, rough surfaces for the fully oxidized films, indicating the formation of stable crystallites at high temperature. © 2001 Elsevier Science B.V. All rights reserved.

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As an active support, titanium oxide has been widely used in heterogeneous catalysis, photocatalysis, and gas sensors [1–3]. Substantial efforts have been focused on single-crystal titanium dioxide with these studies yielding considerable information regarding its chemical and physical properties [4–9]. Recently, there has been increasing interest in studying the role of titanium dioxide supports in modifying the catalytic activity of metal nanoclusters, such as Au and Ag [10–12]. In order to render the substrate suitable for electronic spectroscopic and scanning tunneling microscopy (STM) studies, titanium oxide samples must be made conductive via extensive sputtering and annealing to create oxygen defects. Oxygen removal from the surface creates Ti³⁺ and Ti²⁺ sites, resulting in an n-type semiconductor. Although suitable conductivity can be achieved with oxygen vacancies less than ~1 ppt, excessive oxygen removal can lead to significant modification of the bulk structure, such as added Ti₂O₃ rows and a (1 × 2) reconstruction on the TiO₂(110) surface [4,7,13]. This modification can fundamentally alter the surface properties of titania. These thin film syntheses were motivated by the need for single-crystalline TiO₂ samples closely coupled to a metallic substrate in order to carry out detailed temperature programmed desorption and elevated kinetic studies requiring accurate temperature measurements over a rather wide temperature range.
The vapor growth of oxide films on single-crystal metal substrates circumvents many difficulties presented in working with the corresponding insulating bulk oxides. Vacuum deposition of thin film oxides requires high-purity metal to be vaporized from a hot filament onto the surface of a single crystal in an oxygen ambient, followed by annealing to elevated temperatures for further oxidation and surface ordering. This procedure offers advantages in the control of film thickness, the degree of oxidation, surface structure and enhanced conductivity. This preparation method also enables the detailed study of the thin film growth mode and the rearrangement of surface atoms.

Recently, titanium oxide thin films have been successfully synthesized on various metal supports such as Mo(1 0 0), Rh(1 1 1) and Pt(1 1 1) [14-16]. In previous work in our laboratory, TiO2 thin films were synthesized on a Mo(1 0 0) substrate [14]; STM and low-energy ion scattering (LEIS) measurements showed the initial two-dimensional (2D) growth of TiO2 films on Mo(1 0 0). X-ray photoelectron spectroscopy (XPS) also showed that a substantial amount of Ti3+ and Ti4+ species existed in the annealed TiO2 surface. These TiO2 films were also examined qualitatively with low-energy electron diffraction (LEED) that showed a \((2\sqrt{2} \times \sqrt{2})R45^\circ\) reconstruction with respect to the TiO2(0 0 1) surface.

It is clear from these studies that the substrate plays an important role in controlling the oxide film structure. The preparation conditions, such as oxygen pressure and annealing temperature, significantly influence both the thin film surface morphology and the chemical composition. However, there has been relatively little work with scanning probe methods, exploiting the effect of varying the thin film composition on the surface structure. In this study, STM was primarily used to examine the temperature-dependent surface morphology of TiO2 films with respect to the film stoichiometry on a Mo(1 1 0) sample.

The experimental details for thin film growth on refractory metals have been published elsewhere [14,17]. Briefly, the experiments were performed in a UHV system with a base pressure of \(1.0 \times 10^{-10}\) Torr. The system is equipped with a double pass cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES) and XPS, reverse view LEED optics, mass spectrometer (MS), and an Omicron UHV-STM. In this study, thin titanium dioxide films were vapor grown on a freshly cleaned Mo(1 1 0) surface, which has a rhombic structure with \(a_0 = 0.314\) nm and \(b_0 = 0.272\) nm [18]. The Mo(1 1 0) crystal was 8 mm in diameter and 1 mm thick. The sample was mounted onto a Ta holder, heated by an e-beam filament. The Mo(1 1 0) substrate was cleaned by cycles of oxidation in \(2 \times 10^{-8}\) Torr of oxygen at 1000–1400 K and briefly annealed in vacuum to 2200 K. This procedure was repeated until no impurities could be detected by AES. A W–5%Re/W–26%Re thermocouple was spot welded to the edge of the Mo(1 1 0) single crystal. The thermocouple was used to measure the surface temperature and to calibrate an optical pyrometer (OMEGA OS3700) prior to its disconnection for the STM measurements. The pyrometer was then used to measure the temperature in subsequent annealing experiments. By using a wobble stick, the sample could be transferred to the STM chamber where the general surface morphology was assessed. The Ti doser was constructed by wrapping high-purity Ti wire (99.99%) around a W wire (0.010 in. diameter, H. Cross Co.) that was extensively outgassed prior to use. Metal coverages were reported in monolayers (ML), where one ML corresponds to \(2.3 \times 10^{15}\) atoms/cm². The growth of titanium oxide films was controlled at a rate of approximately 0.50 ML per minute.

Titanium oxide films were prepared by evaporating Ti onto the Mo(1 1 0) surface at 600 K substrate temperature in a \(5 \times 10^{-7}\) Torr O2 ambient, followed by annealing to 900 K. Fig. 1 shows the AES spectra for a clean Mo(1 1 0) substrate and that following deposition of a \(\sim 20\)-ML titanium oxide film onto the Mo(1 1 0) surface. The titanium dioxide film is free of any detectable impurities. At the 20-ML film thickness, the AES signal from Mo is highly attenuated and not detectable. The titanium oxide film was further stepwise annealed to 1200 K within the same O2 ambient. However, no obvious spectral change could be observed in subsequent AES measurements.

According to XPS measurements, titanium oxides of various chemical compositions exhibit dis-
crete core-level Ti 2p binding energies. The XPS spectra of the Ti 2p region of a ~20-ML titanium oxide film on Mo(110) are shown in Fig. 2 for various temperature treatments. The sample was heated to various temperatures and allowed to cool to 300 K for the XPS measurements. After the oxide film deposition under ambient O 2 and a 900 K anneal, three Ti chemical states are apparent. The major peak at 459.2 eV corresponds to the fully oxidized Ti 4+ chemical state. However, there are also pronounced broad shoulders on the low binding energy side of the Ti 2p 3/2 feature. The Ti 2p 3/2 binding energy for Ti 3+ is ~457.6 eV, whereas the Ti 2p 3/2 feature for Ti 2+ falls within the range of 455.0-455.5 eV. Our XPS results indicate a large concentration of Ti 3+ and Ti 2+ cations in the TiO 2 film after synthesis and anneal to 900 K. It is clear that the annealing temperature can alter the phases that, in turn, can play a critical role in the chemical reactivity of oxide thin films.

Repeated annealing to elevated temperatures in the O 2 ambient reduces the lower binding energy intensity and shifts the peak maximum to higher binding energy. Up to 1100 K, there is little change in the Ti 2p peak shape. However, the Ti 3+ and Ti 2+ shoulders completely disappear after an anneal to 1200 K, suggesting the formation of a fully oxidized TiO 2 film. Furthermore, the Ti core-level feature is also much narrower than that observed for the previous 900 K anneal.

Several recent studies of TiO 2 and other oxides have demonstrated that surface morphology can be dramatically influenced by elevated temperature anneals in oxygen ambient [14,17]. STM can be used to address the morphological changes at the atomic level of the titanium oxide films with respect to various chemical compositions. Generally, bulk, rutile TiO 2 has a bandgap of 3.1 eV. Since there are always to some extent reduced Ti 4+ and Ti 3+ cations in the synthesized films, TiO 2 films are conductive, and surface charging is usually negligible compared to bulk TiO 2, i.e., STM measurements can be performed on thick TiO 2 films without any imaging difficulties. An STM image is presented in Fig. 3 to show the general morphology of the 20-ML titanium oxide film prepared and annealed to 900 K. Although XPS suggests a
non-stoichiometric film due to a large concentration of reduced Ti cations in the film (pronounced Ti$^{2+}$ and Ti$^{3+}$ shoulders are apparent in XPS), the film morphology is surprisingly smooth. From the STM image, the titanium oxide film consists mainly of flat terraces crossed by well-defined mono- or multiple-atomic steps. Surface terraces are atomically smooth, consistent with 2D layer-by-layer growth of titania films on Mo(110). No large three-dimensional (3D) clusters are seen, consistent with significant lateral surface diffusion of the oxidized species at this temperature. However, compared to well-studied single-crystal TiO$_2$ surfaces [4,19], the terraces of the TiO$_2$ thin film are significantly smaller.

A magnified view of the TiO$_2$ film is shown in Fig. 4. Three different orientations of titanium oxide terraces can be clearly seen, each oriented at $\sim$120° with respect to the others (labeled A, B, and C in the image). The bright rows on the ordered terraces correspond to Ti cations since the image was acquired with a positive sample bias (2.0 V, 2.0 nA). There are also disordered regions at the juncture of the various oriented phases. Some small clusters, mainly one atom high, grow preferentially on the disordered regions rather than on the flat terraces. Examination of the size distribution for the titania nuclei shows that the largest clusters are $\sim$10 Å in diameter. The distances between the bright rows are shown in Fig. 5. The line profile indicates $\sim$39 Å across six row spacings, corresponding to $\sim$6.5 Å between the Ti rows. This is consistent with the terminal rutile (110)-(1 $\times$ 1) structure (the most stable TiO$_2$ surface) which has a spacing of $\sim$6.5 Å between the Ti- [001] rows. Furthermore, no added Ti$_2$O$_3$ row or (1 $\times$ 2) reconstruction (commonly formed on single-crystal TiO$_2$(110)) is observed for the thin film.

Apparently, the deposition of Ti atoms in an O$_2$ ambient at 600 K only leads to reduced TiO$_2$ films. The presence of oxygen during annealing is a critical factor for surface ordering. The growth of fully oxidized TiO$_2$ film is assumed to occur by diffusion of oxygen to the thin film subsurface at the higher annealing temperatures. At 900 K, the supply of oxygen to the subsurface interstitial Ti$^{2+}$ ions is kinetically limited, hence only Ti cations
near the surface region are first captured by the oxygen ambient at the surface and become fully oxidized. The topmost Ti atoms react with oxygen and form a new surface layer with the most stable TiO₂(1 1 0) lattice. However, since the oxide films are in transition between a metastable phase and the continuous, regular (1 × 1) surface, there are distinct regions of both the complete (1 × 1) phase as well as disordered patches.

The XPS results of Fig. 2 show that the titania films become fully oxidized after annealing to 1200 K. Surprisingly, the STM measurements show a very rough and disordered surface morphology after the corresponding anneal and oxidation treatments (Fig. 6). No smooth terraces and well-resolved atomic steps are observed. Protrusions (bright features) and indentations (dark areas) are randomly dispersed across the film surface. However, LEED measurements exhibit a slightly diffuse (1 × 1) rectangular pattern (not shown here). The surface morphology suggests the oxide films consist of 3D TiO₂ crystallites, rather than the 2D layers, after annealing in oxygen at 1200 K.

Based on STM and XPS results, a discrepancy arises between the chemical and structural properties of titanium oxide films during the synthesis. Reduced films prepared at lower temperatures (900 K) likely grow as a 2D layer-by-layer surface while fully oxidized films prepared at higher temperature (1200 K) more likely form 3D TiO₂ crystallites. The striking difference in the surface morphologies between the reduced and fully oxidized TiO₂ films can be explained in terms of temperature-dependent oxygen diffusion. It is well known that for single-crystal rutile TiO₂(1 1 0) samples, a smooth (1 × 1) surface can be acquired after cycles of anneal in the range of 900–1100 K in vacuum [4,17]. On the other hand, the TiO₂(1 1 0) surface will undergo reconstruction at temperatures above 1100 K [7]. The added Ti₅O₅ rows gradually appear and, if prevalent, lead to a (1 × 2) reconstruction. These temperature-dependent morphological changes have
been interesting topics for STM investigations and have undergone extensive study.

Following an anneal in O$_2$ ambient, the surface morphology is entirely different. To understand fully the role that oxygen adsorption plays in the modification of thin film chemical states, it is necessary to discuss the specific nature of the interaction of oxygen with TiO$_2$(110). STM studies have determined that elevated-temperature exposure of the TiO$_2$(110) surface to O$_2$ results in surface roughening and restructurings [8]. This is due to surface segregation of Ti cations induced by the presence of oxygen. Indeed, small 2D titania clusters usually grow and spread over the surface between 450 and 800 K at $1 \times 10^{-6}$ mbar O$_2$ pressure [5]. Clusterings and restructurings upon annealing in oxygen can eliminate energetically unfavorable states and lower the surface energy. Above some critical temperature where kinetic barriers should not limit the diffusion of oxygen into the deep subsurface, the less ordered region between the domains might well provide the nuclei for an inhomogeneous reconstruction process, leading to the 3D crystallite growth. Using LEIS,
Al$_2$O$_3$ films on Ru(0 0 0 1) and Re(0 0 0 1) that grew in a 2D fashion at 300 K switched to a 3D growth mode at 1170 K [20]. Similar effects have been observed in the synthesis of TiO$_2$ thin films. It has been reported that after annealing to 1200 K, rather than layer-by-layer growth, a 90 Å TiO$_2$ film mainly consists of 3D crystallites several hundred angstroms in diameter as determined by STM and LEIS measurements [14]. Based on the XPS measurements (Fig. 2), the extent of oxygen diffusion is sufficient to fully oxidize the TiO$_2$ films on Mo(1 1 0) at 1200 K. It is likely at this high temperature that 3D reconstruction takes place more significantly than does thermally activated lateral diffusion of surface species, necessary for the formation of ordered TiO$_2$(1 1 0) patches observed at 900 K. Therefore, a change in the surface morphology is observed from an initially terraced, atomically smooth surface to a 3D rough surface upon a change in the annealing temperature from 900 to 1200 K. These results have significant consequences for oxide film preparation. Oxide thin films are usually prepared via high-temperature annealing or low-temperature cooling in oxygen ambient. Consequently, the surface morphology and the chemical compositions will vary critically as the preparation conditions (oxygen pressure, temperature, annealing time, etc.) are changed.

In summary, atomic scale images of thin film TiO$_2$ on Mo(1 1 0) have been obtained and demonstrate the feasibility of using STM to probe oxide thin film surface structure and growth mode. Using STM to measure surface topography on a microscopic scale together with XPS for chemical composition, smooth surfaces with distinct flat terraces and well-defined step edges are found at 900–1100 K, while the oxide films remain partially reduced. In contrast, thin films annealed in oxygen to 1200 K are fully oxidized and exhibit a 3D rough surface morphology. We conclude that epitaxial growth of TiO$_2$ thin film is mediated by surface lateral diffusion of the oxidative species at
low temperature and 3D bulk crystallization at high temperature.

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