Fundamental studies of titanium oxide–Pt(100) interfaces
I. Stable high temperature structures formed by annealing
TiO$_x$ films on Pt(100)

Taketoshi Matsumoto $^1$, Matthias Batzill $^2$, Shuchen Hsieh $^3$, Bruce E. Koel $^*$

Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482, United States

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Abstract

Surface structures formed by titanium oxide thin films at a Pt(100) surface have been studied by STM (scanning tunneling microscopy), LEED (low energy electron diffraction), AES (Auger electron spectroscopy), XPS (X-ray photoelectron spectroscopy), XPD (X-ray photoelectron diffraction) and He$^+$-ISS (He$^+$ ion scattering spectrometry) in order to explore and elucidate stable high-temperature structures that may be formed at titania–Pt interfaces and provide a basis for characterizing the chemistry of titania thin films on Pt(100). Titanium oxide films were produced by two different methods. First, titanium oxide films on Pt(100) were produced by oxidation using ozone (O$_3$) on a Pt$_3$Ti surface alloy at 300K and annealing at 1000K. Smooth thin films with a (3·5) structure were observed at 1ML (monolayer) using this procedure, and we propose that the (3·5) structure is due to one layer of a Ti$_2$O$_3$ film that is similar to the (1·2) strands formed on reduced TiO$_2$(110) surfaces. Structures prepared by this method showed particularly “flat” terraces without islands. Second, TiO$_x$ films were formed by Ti evaporation and deposition on Pt(100) in 6.7 $\times$ 10$^{-5}$Pa O$_2$ and annealing the substrate above 750K in vacuum. A (35) structure was produced also for these films below ~1ML. A (4·3·5/60°) structure, referred to as the “24-structure”, was observed after deposition of ~2ML and after annealing at 850–1000K. We propose a model for this structure composed of TiO$_2$ tetragonal nets with some O atoms in the second layer. The (4·3·5/60°) film changed to one with a (3·5) structure after annealing above 960K in vacuum. TiO$_2$ clusters were observed in our investigations, but mainly after Ti deposition sufficient to form several monolayers and after annealing at 1000K. Under those conditions, a small number of (3·5) domains were observed also, but it was surprising that clean (1·1)- and (5·20)-Pt(100) domains still existed over ~2% of the surface. TiO$_2$ clusters decomposed to form a (2√2·2√2)R45° structure, which we propose to be Ti$_7$O$_8$, and (3·5) domains after annealing at 1300K. Within our models, the composition of all titanium oxide ultrathin films on a Pt(100) surface are TiO$_{2-x}$ after

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$^*$ Corresponding author. Tel.: +213 740 4126; fax: +213 740 3972.
E-mail address: koel@usc.edu (B.E. Koel).

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1 Present address: Laboratory for Entrepreneurship, University of Tsukuba, Ibaraki 305-8573, Japan.
2 Present address: Department of Physics, Tulane University, New Orleans, LA 70118, United States.
3 Present address: NIST, Gaithersburg, MD 20899, United States.

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annealing at 850–1300 K. Chemical changes occurring during annealing of titanium oxide films include Ti dissolution (alloying) into the bulk of the Pt(100) crystal. We suggest that these results will have important consequences for the understanding and modeling of catalysis of related systems.

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1. Introduction

Many metal catalysts are dispersed on oxide supports, and SMSI (strong metal support interaction) has been reported as an important effect to alter their catalytic behavior [1]. Pt/TiO2 catalysts are typical systems exhibiting SMSI for CO hydrogenation after high temperature reduction. Reduced Pt/TiO2 surfaces have been investigated using many techniques, including XPS (X-ray photoelectron spectroscopy), AES (Auger electron spectroscopy), XRD (X-ray diffraction), NMR (nuclear magnetic resonance), IR (infrared spectroscopy), ISS (ion scattering spectrometry), and EXAFS (extended X-ray absorption fine structure) [1–6]. These studies lead to the conclusion that a reduced titania (TiO1.5–0.9) film covers Pt surfaces and this suppresses CO and H2 chemisorption. SMSI has also been reported for Pt/TiO2 catalysts used for the selective hydrogenation of crotonaldehyde [7,8].

Some researchers have also been concerned with Ti diffusion into the Pt clusters on the catalysts. The possibility of Pt–Ti alloy formation was suggested by Pt 4f peak shifts or narrowing in XPS spectra or characteristic EXAFS peaks. These results were observed for Pt clusters produced from Pt films deposited on TiO2 [3,9,10], Pt clusters on carbon black impregnated with TiO2 [11], a Pt + TiO2 co-sputtered sample [10], and Pt clusters formed on TiO2/Ti(0001) [12], but not for 2% Pt clusters supported on TiO2 powder [13]. Investigations of polycrystalline Pt surfaces containing TiOx films have produced mixed results [6,14]. Theoretical analysis has also suggested Pt–Ti alloy formation [15,16], but experiments have not yet provided a decisive answer to questions about the conditions required for alloying.

A few STM (scanning tunneling microscopy) experiments have been attempted to observe thin films of titanium oxide on Pt surfaces and Pt active sites with SMSI at atomic resolution. Two ordered structures of TiO2 and Ti4O7 were found on Pt(111) that were similar to the rutile TiO2(110) surface [2]. Deposition of Pt on TiO2(110) and annealing in vacuum formed TiO1.1 films on flat (111) tops of Pt clusters [17,18]. It was also suggested that active Pt sites might be the sides of Pt clusters floating on TiO2-like “icebergs”. However, titanium oxide thin films on Pt(100) or Pt(110) have not been studied. In related studies, AES and LEED (low electron energy diffraction) experiments have indicated TiO, TiO1.2, and TiO2 thin films on Pt3Ti(111) and (100) bulk alloy surfaces after annealing in O2 [19]. Another study on Pt3Ti(111) using XPS indicated formation of TiO2 following O2 oxidation below 673 K and Ti2O3 after oxidation above 723 K [20].

The clean Pt(100) surface is known to reconstruct to a hexagonal (5×20) structure after annealing to 1000 K [21]. The first layer of the (5×20)-Pt(100) surface contains an excess atomic density of ~20% over that of the second layer in the (1×1) structure [22]. This reconstruction is lifted, with the excess Pt atoms incorporated into the adlayer, with the adsorption of CO, H, O [23–25] and C2H4 [26] at 300 K or the deposition of other materials such as Sn [27], Ag [28], Sm [29], Ge [30], Ti [31] and FeO [32]. Such deposition can give islands, “flat” alloys with square structures, or a flat (1×1)-Pt(100) substrate.

In this study, oxidation of a Pt3Ti surface alloy and deposition of Ti in an O2 ambient were used to create ultrathin films of titanium oxide on a Pt(100) crystal substrate. These surfaces were characterized by STM, LEED, AES, XPS, XPD (X-ray photoelectron diffraction) and He+–ISS
(He$^+$ ion scattering spectrometry) under varying conditions of film thickness and annealing temperature. While speculative, we have proposed some reasonable structural models for these films. Thermal stability of the titanium oxide films is also discussed.

2. Experimental

Experiments were carried out by using the same single crystal in two UHV (ultra high vacuum) chambers. One chamber was equipped with STM, LEED and AES [33], and the other with LEED, ISS, XPS, and XPD [34]. The clean Pt(100) surface was prepared by many cycles of Ar$^+$-ion sputtering and annealing in O$_2$ and flashing to 1000 K in vacuum. The clean surface was checked by STM, LEED, AES, and/or XPS. Titanium was evaporated from a Ti rod by electron bombardment after outgassing for 10 min, and AES and XPS subsequent to the deposition showed a clean Ti film with good reproducibility. AES ratios of Pt, Ti, and O were obtained by using the peak-to-peak heights of the Pt(237 eV), Ti(387 eV) and O(510 eV) transitions obtained in d$N$/d$E$ spectra. Sensitivity ratios for these peaks is estimated to be 1:2:2.4 for Pt:Ti:O [35]. All STM images were acquired in constant-current mode with the sample at 300 K. The coverage where one layer of a TiO$_x$ film effectively covers the Pt(100) substrate, as determined by STM is defined to be 1 ML. As discussed later, this condition is also where TiO$_2$ assigned to the second layer starts to be detected in XPS.

3. Results

3.1. Oxidation of a Pt$_3$Ti surface alloy on Pt(100)

Oxide thin films with a coverage near 1 ML were easily produced by 6 L O$_3$ (ozone) oxidation of a Pt$_3$Ti surface alloy on Pt(100), denoted as Pt$_3$Ti/Pt(100), at 300 K. The clean Pt$_3$Ti surface alloy was produced before oxidation by Ti evaporation on Pt(100) and annealing to 900 K in vacuum. The AES ratio of Pt/Ti was 1/2. LEED showed a c(2×2) pattern (Fig. 1(a)), and STM images (Fig. 1(b)) reveal homogeneous c(2×2) terraces with sizes smaller than ~30 nm. Some small pits and bumps (possibly due to TiC [36]) can also be observed.

After annealing such an oxide film to 800–900 K, LEED showed a (4×3$\sqrt{5}$)R60° pattern as seen in Fig. 2(a) and simulated in Fig. 2(b). This unit cell is 24 times larger than that of (1×1)-Pt(100),
and we denote this as the “24-structure” (as will be discussed further in Section 3.3). The rectangle in Fig. 2(b) shows the reciprocal unit cell, and the pattern derives from the two equivalent domains that exist because of symmetry on the (1×1)-Pt(100) surface.

Sharp (3×5) spots appeared in LEED after annealing such oxide films at 1000 K. This pattern is shown in Fig. 3. The AES ratio of Pt:Ti:O was 1:1.5:1.2. STM revealed flat terraces that were ~100 nm wide with a (3×5) atomic structure without islands, as shown in Fig. 4(a). Domains of (5×20)-Pt(100) were also observed, with a concentration of ~5%, as marked by the “A”. The magnified image of Fig. 4(b) more clearly shows the homogeneous structure of these films. Fig. 4(c) is an STM image of these films at atomic resolution. A symmetric, ordered (3×5) structure was observed, and the rectangle superimposed on
the image shows this unit cell. The apparent corruga-
tion of this structure was small, only 0.03 nm. Oxida-
tion with 1000 L O₂ rather than O₃ resulted in a similar LEED pattern but many spots were broad or missing.

3.2. TiOₓ deposition on Pt(100) to form a (3 × 5) structure

Titanium oxide films with a (3 × 5) structure were produced by deposition of Ti on Pt(100) at 300 K in an O₂ ambient of 6.7 × 10⁻⁵ Pa and annealing in vacuum. After deposition and annealing below 750 K, a (1 × 1) LEED pattern appeared with diffuse spots. Annealing at 750–850 K produced additional LEED spots which became sharper by heating above 900 K. An STM topograph of such a (3 × 5) film with a coverage of 0.3 ML is shown in Fig. 5(a). The Pt:Ti:O AES ratio of this surface was 1:1:1. The LEED pattern showed a mixture of (3 × 5) and (5 × 20) spots. STM images revealed patches of oxide wider than 50 nm on flat terraces. A line scan shown in Fig. 5(a) is given below the STM image and a model is provided to interpret this cross-section of the surface. Fig. 5(b) provides an expanded view of the highlighted square area in Fig. 5(a). A rectangle indicating the (3 × 5) unit cell is superimposed on this image. In Fig. 5(a), domains B1, B2, and B3 are assigned to the (3 × 5) oxide film and the region A1 is
assigned to a (5 × 20)-Pt(100) terrace [22]. Oxide islands were produced on the middle of terraces (B1) and on terraces adjacent to step edges, both below (B2) and above (B3) the step edges. Step edges run along the close packed [011] direction, and other equivalent directions. The apparent height of these (3 × 5) oxide films is 0.06 nm. Islands (A2) and small clusters around oxide domains (B1, B2, and B3) are assigned to 1 ML thick, Pt islands. These have an apparent height of 0.2 nm, which is the same as that of A1. No ordered structure was observed on the Pt-island (A2) surfaces. The coverage of these Pt islands and clusters was ~0.02 ML.

In an attempt to completely cover the Pt(100) surface with the (3 × 5) oxide film, additional TiOx was deposited at 300 K and then annealed. Practically, we never succeeded in this endeavor. The STM topograph in Fig. 6 was acquired on a Pt(100) surface upon which a few monolayers of TiOx film had been deposited at 300 K and then annealed to 1000 K. The Pt:Ti:O AES ratio of this surface was 1:4:4, and the (3 × 5) LEED pattern was the same as that shown in Fig. 3(a). The

![Fig. 5. STM topographs of (3 × 5) films at a coverage of 0.3 ML. The surface was prepared by Ti deposition in O2 on Pt(100) at 300 K and annealing at 1000 K. (a) (3 × 5) patches (B) and bare-Pt(100) domain (A) (Vt = –0.14 V, It = 0.86 nA). The domains A1, A2, B1, B2 and B3 indicate Pt(100) terraces, Pt islands, (3 × 5) films on terraces, (3 × 5) films along step edges, and (3 × 5) films sharing step edges, respectively. The dashed, square area is amplified in (b). A cross-section along the superimposed straight solid line is inserted in (a) along with a schematic model used to explain the tunneling current. (b) Expanded view of the highlighted area in (a) (Vt = –0.14 V, It = 0.98 nA). The superimposed rectangle indicates one unit cell.](image1)

![Fig. 6. STM topograph of titanium oxide films at a coverage of 2–3 ML (Vt = 0.3 V, It = 1.5 nA). The surface was prepared by Ti deposition in O2 on Pt(100) at 300 K and annealing at 1000 K. The arrow shows a typical oxide island with an apparent height of 0.4–1 nm. The inserted STM topograph is an expanded view of a flat domain between islands (Vt = 0.34 V, It = 0.17 nA). The superimposed rectangle indicates one unit cell.](image2)
STM image of this surface (Fig. 6) showed many islands which had disordered structures. The apparent height of these islands was 0.4 to 1 nm higher than that of the (3 × 5) oxide surface, indicating that the islands have a thickness of several layers of titanium oxide. The inset in Fig. 6 reveals a (3 × 5) terrace between islands. The superimposed rectangle indicates a (3 × 5) unit cell. If the surface was only annealed to 850 K, in contrast to the behavior for lower coverage oxide films, we observed the 24-structure.

We used He⁺-ISS to characterize a titanium oxide film that just covered the Pt substrate. He⁺-ISS reveals uniquely the composition of the outermost layer of the substrate. The TiOₓ coverage after deposition and annealing to 1000 K was determined to be ~1.2 ML from XP spectra (as discussed in Section 3.4). LEED showed a sharp (3 × 5) pattern. Fig. 7 shows that the Pt peak at \( E/E₀ \approx 0.9 \) is completely eliminated for the oxide-covered surface and only Ti \( (E/E₀ \approx 0.7) \) and O \( (E/E₀ \approx 0.35) \) peaks were observed. This establishes that the outermost layer of the (3 × 5) oxide surface consists of only Ti and O atoms.

For the identical oxide surface, XPD spectra were also obtained along the [011], [032], [031] and [010] azimuths. Fig. 8(a) and (b) provide the XPD spectra for the [011] and [001] azimuths. No forward scattering peaks for Ti(2p) or O(1s) photoelectrons were observed, and the Pt(4f) forward scattering peaks were similar to those for the clean Pt(100) surface (not shown). Data acquired for the [032] and [031] azimuths were consistent with these observations. Because we know that the oxide surface has an ordered structure, these results indicate that the (3 × 5) oxide film is only one layer thick [37]. These data also eliminate any substantial concentration of Ti in the near-subsurface region, due to appreciable alloying with Pt [31], under these conditions.

Heating any coverage of the (3 × 5) oxide film in an ambient of \( 6.7 \times 10^{-5} \) Pa O₂ to give a 100 L O₂ exposure with the surface at 300–1000 K made no significant difference in either the LEED or STM results.
3.3. TiO$_x$ deposition on Pt(100) to form a (4 × 3$\sqrt{3}$R60°) structure

Deposition and annealing of titanium oxide films to produce a (4 × 3$\sqrt{3}$R60°) structure, denoted as the 24-structure, was investigated. Ti deposition was carried out on Pt(100) at 300K in 6.7 × 10$^{-5}$ Pa O$_2$ to produce an ~2ML titanium oxide film and then the film was annealed at 850–1000K. The Pt:Ti:O AES ratio of this surface was 1:2:2 and LEED showed the 24-structure pattern.

The STM image in Fig. 9 characterizing the 24-structure shows domains C1 and C2 which are assigned to the oxide film with the 24-structure on the Pt(100) substrate and a Pt island, respectively. This was inferred from their surface structures and a height difference of 0.2 nm. Oxide terraces with the 24-structure are 20–50 nm in width. The unit cell of the 24-structure is illustrated schematically by the white parallelogram superimposed on the image. Domains D1–D5 at different levels by 0.07 nm contain partially ordered row structures. Typical row separations are ~0.045 nm, close to that of the rutile TiO$_2$(001) surface reported as 0.046 nm [38]. This is larger than the 0.54 nm row separations of the 24-structure. A structure similar to that of domains D1–D5 was observed on a reconstructed TiO$_2$(001) film produced on Mo(110) [39].

Flat oxide films with the 24-structure were prepared by annealing at 1000 K after Ti deposition in an O$_2$ ambient on a Pt$_3$Ti surface alloy. The Pt:Ti:O AES ratio of this surface was 1:2:2 also. The STM image of this surface shown in Fig. 10 revealed that domains of the 24-structure increased to 30–50 nm in width without the formation of islands. Disordered domains were observed with similar concentrations to the 24-structure domains.

Fig. 11 provides an expanded STM image of the 24-structure oxide film. A (4 × 3$\sqrt{3}$R60°) unit cell is superimposed on the image. The cross-section along the thick straight line shows an apparent height difference of 0.06 between the grooves (i) and (ii), and an apparent height difference of 0.12 nm between the grooves (ii) and bright spots. The rows of bright spots, labeled as (iii) in Fig. 11 correspond to the bright rows in Fig. 10.
3.4. TiO\textsubscript{x} deposition on Pt(100) to form a thick layer with (3\times5) domains

Thick films were produced by Ti deposition on Pt(100) at 300 K in 6.7\texttimes10\textsuperscript{-5} Pa O\textsubscript{2} and annealing at 1000 K. LEED showed diffuse (3\times5) spots, as shown in Fig. 12(a). The highlighted spots correspond to those in Fig. 3(b). The Pt:Ti:O AES ratio of this surface was 1:7:8. STM topographs, such as shown in Fig. 12(b), show that the surface is covered by many 3D clusters that are without any ordered surface structure. The corrugation of these clusters is 0.5–2 nm, and this implies that they have a thickness exceeding several monolayers. During scanning of several hundred areas across the surface, a few sites were found with structures as shown in Fig. 12(c) and (d). Domains labeled as B are assigned to (3\times5) oxide film structures. Surprisingly, even small domains of (1\times1)-Pt(100), labeled as F in Fig. 12(c), and (5\times20)-Pt(100) surface, labeled as A in Fig. 12(d), were observed.

Thick titanium oxide films produced by Ti evaporation in O\textsubscript{2} onto Pt(100) at higher temperatures of 600–900 K showed no significant differences in STM, LEED or AES observations from those described above. Thus, we never produced a smooth titanium oxide film on the Pt(100) surface under these conditions.

3.5. XPS of titanium oxide films on Pt(100)

XPS investigations of ultrathin titanium oxide films on Pt(100) were performed to characterize the chemical state of Ti in these films and address the film composition. Figs. 13–15 show XPS spectra of the Pt 4f, Ti 2p and O 1s core levels, respectively. These figures include spectra of deeply oxidized titanium oxide films (the (4\times13) and (2\sqrt{2} \times 2\sqrt{2})R45\textdegree films discussed precisely in [40]), titanium oxide films at different coverages, Pt\textsubscript{3}Ti surface alloy, thick Ti film, and a clean Pt(100) surface. The (4\times13) and (2\sqrt{2} \times 2\sqrt{2})R45\textdegree films were produced by oxidation at 600 K with NO\textsubscript{2} and then annealing at 900 or 1000 K, respectively. Three (3\times5) oxide-film surfaces were produced by Ti evaporation in an O\textsubscript{2} background on Pt(100) at 300 K and annealing at 1000 K in vacuum, and these were: submonolayer coverage, ~1 ML as was used for the ISS and XPD experiments, and a film that was several layers thick. The latter, thick oxide film showed diffuse (3\times5) spots, as shown in Fig. 12(a), and is labeled in Figs. 13–15 as “thick film + (3\times5)”. We note that STM images of the 24-structure oxide film always showed the presence of other phases accompanying this structure, and so XPS spectra for this oxide structure could not be obtained cleanly. For the thick, pure-Ti film, Ti was evaporated onto Pt(100) at 300 K without contamination until the Pt 4f\textsubscript{7/2} peak in XPS had almost disappeared, as shown in Fig. 13. Fig. 13 also shows that the Pt 4f core level peaks were not shifted (<0.1 eV) by producing any of the titanium oxide films. XPS spectra were calibrated relative to the Pt 4f\textsubscript{7/2} peak of clean Pt(100) set at 70.6 eV BE [23,41].
Fig. 14 provides information on the Ti 2p core levels for a number of surfaces, and this data is summarized in Table 1. The Ti 2p3/2 peak at 453.6 eV BE for the thick, pure-Ti film was within 0.1 eV of that reported previously for thick, heterogeneous Ti metal films [43]. The (4·13) oxide film showed a broad Ti 2p3/2 peak at 457.6 eV BE, and this is assignable to Ti4+ based on previous studies as indicated by the dark band at the top of the figure. Two peaks at 457.8 and 455.7 eV BE were observed for the (3·5) oxide films, and peaks from Ti4+ appeared at 458.7–458.1 eV BE with increasing coverage. Thus, we assign the (4·13) structure to TiO2, (2√2×2√2)R45° structure to TiO2−1.5, (3·5) structure to Ti2O3 and thick oxide islands to TiO2 with possibly some Ti2O3. The coverage of the (3·5) oxide film that was used for the ISS and XPD experiments can be estimated to be ~1.2 ML from the Ti4+ to Ti3+ peak ratio in the middle curve of Fig. 14.

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The O 1s spectra shown in Fig. 15 from four different oxide films, i.e., (4·13), (2√2×2√2)R45°, submonolayer (3·5) and thick oxide film, gave peaks at 529.9–529.1 eV BE, with widths of 1.4, 1.5, 2.0 and 1.1 eV FWHM, respectively.
Both of the Ti\textsuperscript{4+} 2p and O 1s peaks shifted to higher binding energy for the thick film by 0.6–0.9 eV.

### 3.6. Thermal stability of titanium oxide films

The thermal stability of an ultrathin titanium oxide film on a Pt(100) substrate was studied with AES, LEED and STM. This involved a titanium oxide film with a coverage of \(\frac{1}{2}ML\) produced by Ti deposition in an O\textsubscript{2} ambient on Pt(100) and annealing in vacuum. Following deposition, only a disordered structure was observed in LEED. The LEED pattern of the 24-structure was observed after annealing at 850K. Fig. 16 summarizes changes observed in the AES ratios of Ti/Pt, O/Pt and O/Ti after annealing. Heating to 850K only changed the Ti/Pt ratio, indicating that excess Ti dissolved into the bulk [45]. Annealing at 1000 and 1200 K caused the appearance of the (3 x 5) LEED pattern and disordered TiO\textsubscript{2} clusters (as shown in the STM images in Fig. 6).
This further decreases the Ti/Pt AES ratio, and also now a large change in the O/Pt AES ratio. Heating to 1300 K formed the $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$ LEED pattern [38]. STM topographs showed fewer TiO$_2$ clusters and more $(5 \times 20)$-Pt(100) area along with $(3 \times 5)$ and $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$ domains. This behavior was also observed for the thick films, as seen in Figs. 6 and 12. However, $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$ domains were not observed after annealing the flat 24-structure to 1300 K, as shown in Fig. 10.

We attempted to perform TPD on these samples, but no clear O$_2$ or Ti desorption peak was observed prior to 1300 K was seen, although a large increase in the background signals occurred near 1200 K and this could possibly indicate some desorption from the sample. This differs from O$_2$ TPD results from SnO$_x$/Pt(111) [44] where O$_2$ desorption peaks were observed prior to 1200 K.

4. Discussion

Our goals include identifying the stable, high-temperature structures that are formed by heating TiO$_x$ films at Pt(100) surfaces. Elucidation of the chemical state of Ti in these films is essential in this regard. We begin our discussion of the characterization and structure of these films by considering the results from XPS.

![XPS spectra of several titanium oxide films, thick Ti film and clean (5 × 20)-Pt(100) surface.](image)

**Fig. 15.** O 1s XPS spectra of several titanium oxide films, thick Ti film and clean (5 × 20)-Pt(100) surface.

<table>
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<th>Species</th>
<th>Material</th>
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<th>Reference</th>
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<td>TiO$_2$/Pt foil</td>
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<td>458.6-457.9</td>
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4.1. Chemical state identification from XPS

4.1.1. Ti binding energies in alloy and oxide films on Pt

Alloying Ti with Pt causes an increase in the Ti 2p3/2 peak binding energy compared to that in Ti metal, apparently due to an increase in oxidation state of the Ti. Pt–Ti alloys are formed with electron transfer from Ti to Pt [36, 56].

Reactions of Ti with oxygen to form titanium oxides increase the Ti oxidation state to Ti2+, Ti3+ and Ti4+, and further increase the Ti 2p3/2 peak binding energy. Identification of small amounts of Ti2+, or TiO, is difficult in Pt–Ti bimetallic systems because of the difficulty in distinguishing this phase from the Pt–Ti alloy phase on the basis of the Ti 2p3/2 peak binding energy. However, TiO is not a major species in any of the TiOx films that we prepared and investigated on Pt(100).

Based on XPS, we conclude that Ti3+, or Ti2O3, comprises most of the (3 × 5) structure on Pt(100). Also, XPS indicates that that Ti4+, or TiO2, comprises most of the (4 × 13) structure on Pt(100). Spectra from the (2√2 × 2√2)R45° structure showed two peaks, both Ti3+ and Ti4+, and this oxide film is assigned to TiO2−1.5. Thick oxide islands are assigned to TiO2 with possibly some Ti2O3.

The Ti 2p peaks for the (4 × 13), (2√2 × 2√2)R45° and submonolayer (3 × 5) films showed lower binding energies by 0.2–0.6 eV than those of TiO2 and Ti4O7 films on Pt(111) [2]. The O 1s XPS peaks also appeared at 530.6 eV for TiO2(110) [57] and 530.2–529.6 eV for thin TiOx films on a Pt polycrystalline sample [6], and at 529.9–529.1 eV for TiO2−1.5/Pt(100). The titanium oxide films on Pt(111) were two-layer films, and the lower binding energies that we observed for monolayer oxide films on Pt(100) implies either that the oxide films on Pt(100) are more reduced oxide phases or increased final-state screening effect occur in the monolayer films.

We note that the Pt 4f peaks did not shift for any of titanium oxide films studied. This phenomenon was also observed for 2% Pt catalysts supported on TiO2 powder [12].

4.1.2. Peak shifts with increasing oxide film thickness

Simultaneous positive shifts (to higher binding energies) of Ti 2p and O 1s peaks were observed for thick titanium oxide films on Pt(100). The same shifts were reported for Al2O3/Ru(001) [46] and Al2O3/Al/Re(0001) [47], and this is explainable by two effects [46]. One effect, the screening effect, is that holes formed in photoemission are compensated by free electrons in the metal substrates to stabilize the final state and lower the photoelectron binding energy. More electrons can be supplied from the metal into thinner oxide films which have better conductivity. The other effect, the band-bending effect, is that phenomena that occurs for semiconductors on metals. N-type semiconductors have higher Fermi levels than those of most transition metals. Their contact results in electron transfer from the semiconductor to the metal to achieve thermal equilibrium and this causes downward band bending in the semiconductor. This in turn causes an apparent increase in binding energy of emitted photoelectrons. This effect produces simultaneous positive shifts of all of the XPS peaks from thicker films. (Simultaneous negative shifts for thicker oxide films have been reported on MgO/Mg/Ru(001) [48] and MgO/Mg/Mo(100) [49], and those are explained by upward band bending because the Fermi level of Mg is higher than that of MgO.)

Fig. 16. Influence of temperature on the AES ratios for Ti/Pt, O/Pt and O/Ti of a titanium oxide film on Pt(100). The observed LEED patterns are also indicated.
For the TiO$_2$/Pt(100), the work functions of Pt(100) and TiO$_2$(001) are 5.75 eV [50] and 5.5 eV [51], respectively. Ti$_2$O$_3$ surfaces or slightly reduced TiO$_2$ are known as n-type semiconductors and show smaller work functions of 4 eV [52–54] and 4.6 eV [55], respectively. The higher Fermi levels of TiO$_x$ compounds than that of Pt(100) support the downward band-bending model [28] and can explain the observed simultaneous positive shifts of Ti 2p and O 1s peaks for thick titanium oxide films on Pt(100). Note that Ti 2p and O 1s peaks assigned to the same chemical species can occur over a fairly wide range of binding energies because of band bending and screening effects. Broadening occurs in thick films also if these films are not homogeneous.

4.2. A proposed model of the (3×5) oxide film structure

The most difficult aspect of this work involves determining the atomic structure of the oxide films. The hazards of proposing structures of oxide films on metals, even with the support of theoretical calculations, is generally appreciated. However, to stimulate discussion and calculations, we propose several reasonable models for the ordered titanium oxide films that at least are consistent with all of our characterization data.

A proposed model of the (3×5) structure is depicted in Fig. 17(a) and (b). The composition of this film is Ti$_2$O$_3$ as indicated by XPS. Typical values of 0.134, 0.28 and 0.277 nm are used for the diameters of Ti$^{3+}$, O$^{2-}$ and Pt, respectively [58]. This structure consists of pairs of Ti$_2$O$_3$ rows, as marked with a bracket at the top of the drawing, that are similar to the (1×2) strands found on reduced TiO$_2$(1 1 0) [45,59] and SrTiO$_3$(0 0 1) [60] surfaces. Most Ti and O atoms are placed near fourfold Pt sites at similar heights. The darkest and brightest points in the STM image are assignable to O 1 and T 1, respectively, which correspond to oxygen adatoms located in the deepest hollow sites and titanium adatoms located at the topmost sites. This assignment is possible because Ti atoms are observed brighter than O atoms in the same level [46] and the corrugation of this surface is only 0.03 nm. The densities of Ti and O atoms relative to the (1×1)-Pt(100) unit cell are 8/15 = 0.53 and 12/15 = 0.8, respectively. Thus, O$_3$ oxidation of the Pt$_3$Ti/Pt(100) surface alloy, which has 0.5 ML Ti atoms in the second layer, requires complete dealloying, or abstraction of alloyed Ti into the adlayer, to form a monolayer oxide film of the (3×5) structure.
4.3. A proposed model of the \((4 \times 3\sqrt{3}R60^\circ)\) oxide film structure

The 24-structure is proposed to correspond to a two-layer TiO\(_2\) film, as depicted in Fig. 18(a) and (b). This model is much less certain because STM does not clearly reveal information on the first-layer structure in contact with the Pt(100) surface. The diameters of Ti\(^{4+}\) and O\(^{2-}\) ions are 0.12 and 0.28 nm, respectively [58]. Parallelograms show the unit cells in both of the first and second layers. Dark lines in the STM image correspond to the grooves (i) and (ii) in the schematic drawing. These are proposed to be O atoms near fourfold sites and near on-top sites, respectively. Their height difference of \(\sim 0.06\) nm is reasonable morphologically. \(^{4}\) One bright spot in the bright rows marked as (iii) is assignable to two O atoms (O1 and O2) sitting on top of Ti atoms (T1 and T2) in the first layer since the height difference of 0.12 nm between (ii) and (iii) is equal to the diameter of Ti\(^{4+}\) ions. These on-top O atoms take similar positions to sulfur adatoms on fivefold Ti at the TiO\(_2\)(110) surface which was produced by sulfur deposition at 300 K [61] without diffusion of interstitial Ti atoms [62]. The O adatoms (O3) in the second layer bonding to two Ti atoms (T3 and T4) in the first layer are observed as gray rows in the STM image. The O atoms (O4–O8) are arranged tetragonally with two Ti atoms (T1 and T2).

The 24-structure could also be produced by Ti deposition in O\(_3\) at 900 K. This procedure, but with less Ti deposition, gives the \((4 \times 13)\)-TiO\(_2\) film at submonolayer coverages [40] and implies that the composition of the 24-structure is also TiO\(_2\). This is useful information because XPS spectra for this oxide structure could not be obtained cleanly since STM images of the 24-structure oxide film always showed the presence of other phases accompanying this structure. The densities of Ti and O atoms relative to the \((1 \times 1)\)-Pt(100) unit cell are 16/24 = 0.67 and 32/24 = 1.33, respectively. Ti atoms are packed 26\% more densely than those in the \((3 \times 5)\) structure.

Our model for the 24-structure is different from the polar trilayers of TiO\(_2\)/Cu(100) [63] and also TiO\(_2\)(001)/Mo(100) [39]. This indicates a strong influence of the substrate on the TiO\(_2\) film structure, and clearly theoretical analysis is essential to determine the exact structure formed on a given substrate.

4.4. Comparisons of the structure and reactivity of titanium oxide films on Pt

The \((3 \times 5)\)-Ti\(_2\)O\(_3\) film on Pt(100) is more stable in O\(_2\) than the Ti\(_4\)O\(_7\) film on Pt(111). While these films have similar structures, the surface structure of Ti\(_4\)O\(_7\)/Pt(111) at 773–973 K in \(1.33 \times 10^{-4}\) Pa O\(_2\) changed [2], but the surface structure of \((3 \times 5)\)Ti\(_2\)O\(_3\)/Pt(100) did not change under similar conditions. This additional stability may arise because the \((3 \times 5)\) structure is a monolayer film and the Ti\(_4\)O\(_7\) film is two layers thick. If the oxidation mechanism is similar to that on reduced TiO\(_2\)(110), where interstitial Ti atoms [62] are considered to migrate around \((1 \times 2)\)-Ti\(_2\)O\(_3\) strands to form the \((1 \times 1)\)-TiO\(_2\) surface in \(1 \times 10^{-5}\) Pa O\(_2\) on TiO\(_2\)(110) at 800 K [59], Ti\(_2\)O\(_3\) strands at the two-layer Ti\(_4\)O\(_7\)/Pt(111) surface provide mobility of Ti atoms in the layer below to reconstruct the surface and stabilize a TiO\(_2\) surface.

Our results for TiO\(_x\) ultrathin films on a bulk, Pt single crystal, and the differences with previous studies on Pt clusters deposited on the TiO\(_2\)(110) and bulk crystals of Pt\(_3\)Ti(111) and (100), highlight the importance of Ti and Pt interdiffusion and the overall concentration of Ti in Pt–Ti alloy phases. Changes such as these will occur in TiO\(_2\)-supported Pt catalysts as a function of Pt-particle size and number of oxidation and reduction cycles or time on-stream. Films of mostly TiO\(_2\)–1.5 were formed on Pt(100) single crystal surfaces after annealing at and above 850 K, with dissolution of excess Ti into the bulk of the Pt crystal. However, more reduced titanium oxides such as TiO, TiO\(_1.1\) and TiO\(_1.2\) were formed on Pt clusters deposited on TiO\(_2\)(110) crystals and oxidized bulk.
crystals of Pt$_3$Ti(111) and (100) surfaces [17,18,64]. The more reduced oxides are formed because of the increased concentration of Ti near the surface in these latter systems and the lower propensity to have Ti dissolve into the Pt phase.

4.5. Formation of homogeneous titanium oxide films on Pt(100)

It was surprising to us to observe how difficult it was to prepare flat, homogeneous, titanium oxide films that completely covered the Pt(100) surface at near monolayer coverages. Homogeneous films were not produced by Ti deposition in O$_2$ on Pt(100) and annealing in our studies. Also, we could find bare-Pt sites surrounded by titanium-oxide islands even for multilayer titanium oxide films. CO TPD, which probes only adsorption at Pt sites indicated concentrations of 0.02 ML [40]. These bare-Pt sites were rarely found to be (1×1)-Pt(100) domains from the STM images. These domains are considered to be too small to undergo the hex-reconstruction to the (5×20)-Pt(100) structure. These bare-Pt sites, especially the irregular (1×1)-Pt(100) domains, that are not covered by the oxide film could be important.

Fig. 18. Proposed model of the (4 × 3√5R60°) oxide film or “24-structure”. The superimposed solid parallelogram indicates the unit cell, and the superimposed small circles and big circles indicate a Ti and O atoms, respectively: (a) STM topograph with a superimposed unit cell and (b) schematic model of the 24-structure on Pt(100). The left half of the drawing shows only the first layer. This structure consists of O atoms in the second layer (O1–O3), and Ti (T1–T3) and O (O4–O8) atoms in the first layer.
as active sites in catalysts exhibiting SMSI, and these could now be studied at atomic resolution.

Another surprise was the observation that many straight step edges are shared between Pt and (3 \times 5)–Ti$_2$O$_3$ domains, as can be seen in Fig. 5(a). The Pt patches on the terraces correspond to one-third of the excess Pt from the first layer of the (5 \times 20)-Pt(100) hex-reconstructed surface [22–32], but these patches might also include some atoms evaporated from step edges [65,66]. This observation indicates that Ti, O and Pt atoms stop diffusing at a similar temperature during cooling from 1000 K. The Pt patches produced in this mechanism are stable under the oxide film (see C2 in Fig. 9) even after annealing at 850 K. When we heated the oxide film at 1000 K to remove the Pt patches, more than 15% of the Ti dissolved into the bulk of the Pt crystal, as shown in Fig. 16. Thus, some excess Ti deposition is necessary to create a flat and homogeneous oxide film, but this of course can always be accompanied by the formation of TiO$_2$ islands, as shown in Fig. 6 or Fig. 9. Thermal decomposition and reduction of these TiO$_2$ clusters resulted in formation of local (2√2 \times 2√2)R45° domains. More details about the thermal reduction mechanism are discussed elsewhere [40]. Thick titanium oxide films grow as clusters after annealing at 1000 K. This is different from the thick TiO$_2$(001) films produced on the Mo(100) surface [39].

The morphology of oxide films is expected to sensitively control chemical reactions at their surfaces. Step edges are often reported as being more active [36,67–81], and flat homogeneous films without defects might be catalytically uninteresting (unreactive), or in contrast, free from undesirable side reactions. We expect that the interfaces probed in these studies are important to understand in order to control surface reactions in systems having TiO$_2$/Pt interfaces.

5. Conclusion

We have investigated the thermally stable, ordered surface structures that were formed for ultrathin titanium-oxide films on a Pt(100) surface produced by either O$_2$ or O$_3$ oxidation of Pt–Ti alloys and/or deposition of Ti in O$_2$ or O$_3$ background gas. The focus was on morphological and structural characterization of the ordered nanostructures formed. In particular, Ti evaporation in 6.7 \times 10^{-3} Pa O$_2$ on Pt(100) at 300 K and subsequent annealing at 750–1300 K in vacuum produced several different interfaces characterized as: (3 \times 5)-Ti$_2$O$_3$, (4 \times 3\sqrt{5}R60°)-TiO$_2$, and TiO$_2$ clusters.

A (3 \times 5) monolayer oxide-film structure, identified as Ti$_2$O$_3$, was produced from deposited TiO$_x$ films after annealing at 750–1300 K. O$_3$ oxidation of Pt$_3$Ti surface alloy at 300 K and annealing at 1000 K in vacuum produced the same (3 \times 5) structure, with the special property that this was a smooth film, “flat” over relatively large areas of 100 \times 100 \text{nm}^2. O$_3$ oxidation leads to more ordered oxide films that did O$_2$ oxidation, highlighting the importance of the oxygen potential. A model was proposed for the (3 \times 5) structure that is similar to the (1 \times 2) strands on the TiO$_2$(110). The Ti$^3+$ sites in this Ti$_2$O$_3$/Pt(100) structure were not oxidized by O$_2$, exhibiting a greater stability than that of a reduced TiO$_2$(110) surface or the Ti$_4$O$_7$/Pt(111) film structure.

A (4 \times 3\sqrt{5}R60°) oxide-film structure, identified as TiO$_2$ with a thickness of ~2 ML was produced from deposited TiO$_x$ films on Pt(100) after annealing at 850–1000 K. This film transformed to the (3 \times 5) oxide structure above ~960 K. We proposed a tentative model for the (4 \times 3\sqrt{5}R60°) structure in which the first layer is considered as tetragonal Ti–O– nets with some O adatoms arrayed in the second layer. Ti deposition in O$_2$ on the Pt$_3$Ti surface alloy and annealing resulted in “flatter” films with the (4 \times 3\sqrt{5}R60°) structure.

TiO$_2$ clusters that were more than several layers thick were mainly produced following deposition of several layers of Ti in an oxidizing background gas on Pt(100). Surprisingly, under these conditions and after annealing to 1000 K, bare-Pt (1 \times 1)- and (5 \times 20)-Pt(100) domains were observed at concentrations of ~2% of a monolayer, along with (3 \times 5) oxide monolayer films between the TiO$_2$ clusters. The TiO$_2$ clusters decomposed near 1300 K to form (3 \times 5)-Ti$_2$O$_3$ islands and other reduced, ordered oxide phases. The composition of the titanium oxide film was always Ti$_{2–1.5}$O$_2$.
after annealing at 850–1300 K, with dissolution of excess Ti into the bulk of the Pt(100) crystal. These stable, high-temperature structures formed for ultrathin titania thin films on Pt(100) have important consequences for the understanding and modeling of catalysis of related systems. We observed that thermal decomposition of titania films lead to irreversible dissolution (alloying) of Ti in the Pt(100) crystal. However, no trace of a Pt–Ti alloy was found at interfaces between titania thin films and the Pt(100) substrate. Characterization of these oxide-film structures also provides important benchmarks for theoretical calculations and a basis for understanding the chemistry of titania thin films on Pt(100).

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References
