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Synthesis of TiO$_2$(110) ultra-thin films on W(100) and their reactions with H$_2$O

J. Matharu $^a$, G. Cabailh $^{a,b}$, G. Thornton $^a,^b$∗

$^a$ London Centre for Nanotechnology and Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, UK
$^b$ Institut des Nanosciences de Paris, Université Paris 6 – UPMC and CNRS, 4 Place Jussieu, 75005 Paris, France

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1. Introduction

Thin films can mimic the surfaces of their bulk counterparts [1] and provide a means to modify stoichiometry in a more controlled fashion. Epitaxial ultra-thin films can be grown on metallic substrates that are well-ordered and exhibit sufficient conducting character to enable study by electron spectroscopy and STM [2–6]. Both of these factors provide a motivation for the current work on TiO$_2$ ultra-thin films. Bennett et al. have previously grown thin films of TiO$_2$ using two deposition methods [7]: Ti deposition on a clean W(100) followed by post-oxidation and Ti deposition on a pre-oxidised W(100) surface. The latter method relies on the formation of a p(2 × 1)-O adlayer following exposure of W(100) to O$_2$ [8,9]. This results in a unit cell of dimensions 6.32 × 3.16 Å$^2$, which is comparable to the TiO$_2$ (110) unit cell, 6.49 × 2.96 Å$^2$, which is comparable to the TiO$_2$ (110) unit cell [10,11], Ni$_{64}$Ti$_{36}$ (110) [12], Mo(100), (110) and (112) [13–15] and more recently Ag(100) [16] as substrates. Here we look at the extension of the earlier work on thin films on W(100) [7] to the ultra-thin regime, using the reaction with water to provide additional characterisation to LEED and XPS. This complements previous work on ultrathin films on W(100) that examined XPS, UPS and infra-red spectra [17].

Defects in the form of O-vacancies on TiO$_2$(110) are known to be important in the reaction with H$_2$O [18,19]. Hence, one means of investigating the defect character of TiO$_2$(110) ultrathin films is to use H$_2$O as a probe molecule [20]. Surface science studies of the H$_2$O interaction with TiO$_2$(110) surface have built up a picture of the adsorption process and revealed evidence for the presence of surface hydroxyls (as a result of dissociation) at room temperature, accompanied by an increase in Ti$^{3+}$ states [21]. Experiments from Walle et al. suggest that both molecular and dissociative adsorption of H$_2$O occur when a monolayer of water is deposited on a nominally defect free rutile TiO$_2$(110) at 210 K [22]. Only dissociative adsorption of water is observed at room temperature, which involves dissociation at O-vacancies [22,23]. Recent first-principle simulations suggest that water does not dissociate on the defect free surface [24].

Scanning tunnelling microscopy (STM) and non-contact atomic force microscopy (NC-AFM) have provided insight into the mechanism of dissociation [23,25–28]. The currently accepted mechanism is that H$_2$O molecules adsorb at O vacancy sites (O$_{	ext{vac}}$) and dissociate, resulting in a pair of hydroxyls in the bridging row (OH$_b$): one in place of the original O$_{	ext{vac}}$, and a second formed from the dissociated H atom and another bridging row oxygen atom (O$_b$). The resulting OH$_b$ pair and its related charges play an important role in reactivity of the surface with O$_2$ [28]. Here we examine the morphology of TiO$_2$(110) ultra-thin films, their electronic structure as well as their reactivity with H$_2$O.

2. Experimental

Experiments were conducted in an ultra high vacuum (UHV) chamber with a base pressure of 3 × 10$^{-10}$ mbar. Data were recorded at room
temperature, using an unpolarised Mg Kα radiation source (hv = 1253.6 eV) and a VSW/Omicron EA125 hemispherical analyser. The angle of incidence of X-ray photons was 67.5° with respect to the surface normal, with photoelectrons collected at normal emission. A pass-energy of 40 eV was used, giving an energy resolution (full width at half maximum) of 0.3 eV. Binding energies are measured relative to the Fermi level, which was recorded from the Ta sample holder.

The W(100) crystal (Surface Preparation Laboratory) was cleaned by Ar⁺ sputtering, followed by repeated cycles of annealing in 1 × 10⁻⁷ mbar of high purity O₂ (SIP Analytical, 99.5%) at 1100 K and flash annealing in UHV to 2000 K to remove the principal contaminants (O and C) [29]. The clean surface was characterised by a sharp (1 × 1) LEED pattern and the absence of O 1s and C 1s peaks in XPS spectra.

Ti was deposited using a home-built electron beam evaporator. The doser was calibrated using the intensity ratios of the Ti 2p, W 4p and W 4d XPS peaks. Breakpoints in the ratios indicate monolayer coverage [30] and can be used to monitor the amount of Ti deposited. Oxidation of deposited Ti was achieved by annealing in 1 × 10⁻⁷ mbar O₂ at 800 K for 2 h. Films were characterised by a TiO₂(110) (1 × 1) LEED pattern with additional spots along the principal azimuths [7]. Film thicknesses were estimated from the areas of the Ti 2p and W 4d XPS peaks using the method described by Susaki et al. [31], correcting the peak areas to account for ionisation cross sections and for the analyser transmission function. One monolayer equivalent (MLE) is defined as the number of TiO₂ surface unit cells that will uniformly cover the surface of the W(100) substrate. De-ionised H₂O was degassed using freeze-pump-thaw cycles. The sample was exposed to H₂O after an initial ash annealing in UHV to 2000 K to remove the principal contaminants.

### 3. Results

#### 3.1. TiO₂ thin film growth

Three approaches to ultra-thin film growth were used, the first two being similar to those employed by Mc Cavish et al., who have studied a coverage regime from 5 to 30 monolayers [7]. In one approach, Ti was deposited in UHV onto a clean W(100) surface (two-stage growth). The second method consisted of depositing Ti in UHV onto a pre-oxidised W(100) surface (pre-oxidised growth) and the third depositing Ti in a second method consisted of depositing Ti in UHV onto a pre-oxidised W(100) surface (two-stage growth). The coverage regime from 5 to 30 monolayers [7]. In the case of pre-oxidised growth, where Ti is deposited on the W substrate, De-ionised H₂O is degassed using freeze-pump-thaw cycles. The sample was exposed to H₂O as well as O₂ by backfilling the chamber to a pressure of 1 × 10⁻⁷ mbar.

#### 3.2. TiO₂ growth on W(100)

In the case of pre-oxidised growth, where Ti is deposited on the W表面 previously annealed in 1 × 10⁻⁷ mbar O₂ at 800 K for 3 min, the Ti 2p XPS peaks are broader than for Ti deposited on the clean W surface (1.2 MLE film, Fig. 1(b)). This broadening can be assigned to the presence of oxidised species of Ti (i.e. Ti⁺⁺ and Ti⁺⁺⁺). The main peaks of these species are positioned at 457.1 eV (Ti⁺⁺⁺) and 453.4 eV (Ti⁺⁺). As for the case of the two-stage growth, these peaks shift to positions associated with Ti⁺⁺⁺ states after a 2 h anneal in O₂.

Depositing Ti in a background pressure of 1 × 10⁻⁷ mbar O₂ initially results in a Ti 2p XPS spectrum showing contributions from Ti⁺⁺⁺ states as well as reduced Ti⁺⁺⁺ and Ti⁺⁺⁺⁺ states, indicating incomplete oxidation [34] as shown for a 1.2 MLE film (Fig. 1(c)). After a 2 h anneal in O₂, the Ti 2p core level width decreases as Ti⁺⁺⁺ states (at 455.4 eV and 460.8 eV) are completely removed. By contrast the Ti⁺⁺⁺⁺ states are not completely removed, indicating that the film is slightly sub-stoichiometric.

TiO₂(110) films between 0.2 and 5.7 MLE thick were synthesised. In all cases, on deposition of Ti the observed LEED pattern has a very high background with faint (1 × 1) spots from the W(100) substrate. This indicates the absence of long range order associated with the deposited Ti using the three different growth methods. Following annealing in O₂, oxidised films produce LEED patterns (Fig. 2(c)) that are a composite of the (1 × 1) spots from the W(100) substrate (Fig. 2(a)) and the (1 × 1) spots from an ordered TiO₂(110) surface (Fig. 2(b)). For films of thickness ~1 MLE, the LEED beams are faint, likely due to incomplete coverage of the W(100) substrate and oxidation of regions of bare W. For films as thick as 5.7 MLE, the substrate diffraction spots are still visible, indicating that the thin films do not entirely cover the substrate surface.

Fig. 1. MgxKα XPS spectra (hv = 1253.6 eV) of W(100) showing (a) the shift in E₀ of the Ti 2p core levels after oxidation in 1 × 10⁻⁷ mbar O₂ for 2 h at 800 K for the two stage growth, (b) the broadened Ti 2p core levels of Ti deposited on an oxidised W(100) surface (bottom) and the shift to fully oxidised peaks after oxidation in 1 × 10⁻⁷ mbar O₂ for 2 h at 800 K (top) and (c) the mixed valence Ti states on depositing Ti in 1 × 10⁻⁷ mbar O₂ (bottom), and the removal of these states on oxidation in 1 × 10⁻⁷ mbar O₂ for 2 h at 800 K (top, blue). Spectra are normalised to the same maximum intensity and Shirley backgrounds have been subtracted. The peak at 449 eV corresponds to the Ti 2p satellites from Mg KαX-ray excitation. Ti 2p spectra were fitted with three doublets (Voigt functions) corresponding to the Ti⁺⁺ (light red), Ti⁺⁺⁺ (red) and Ti⁺⁺⁺⁺ (dark red) contributions, as shown for the reactive deposition method (c). The sum of the fitted contributions is represented by the black line and the experimental data by red dots. A polynomial plus Shirley background was subtracted. The peak widths, branching ratio, and spin-orbit-splitting were kept constant throughout and are summarised in Table 1.
The final pattern is a two-domain (2 × 1) with respect to the initial W(100) pattern, with two TiO$_2$ domains rotated 90° and aligned with the main directions of the substrate, as observed in the earlier work [7].

Examination of Ti 2p XPS spectra shows that films synthesised using the pre-oxidised method are not completely stoichiometric and that contributions from both Ti$^{3+}$ and Ti$^{4+}$ states are present (Fig. 3). Using the fitting parameters in Table 1, we use the Ti 2p spectrum to estimate the % Ti$^{3+}$ states (Table 2). Non-stoichiometry may arise due to strain in the films resulting from the lattice mismatch and from surface defects. A correlation between thickness and non-stoichiometry has been previously observed [7] with non-stoichiometry decreasing with increased thickness. Curve fitting of the corresponding O 1s XPS spectra reveals two contributions (Fig. 3), one centred around a binding energy of 530.4 eV that corresponds to oxygen in the selvedge, and a satellite peak, denoted S$_1$ shifted +1.4 eV from the main peak (fitting parameters shown in Table 1). S$_1$ was assigned to two-fold bridging oxygen atoms (O$_{b}$) on the TiO$_2$ surface in earlier work [36–38]. However, more recent studies have instead suggested that this peak is due to OH$_{b}$ arising from reaction with residual water in the background vacuum [11,39]. The S$_1$ contribution, expressed as a percentage of the total O 1s peak area, is greater in films < 1 MLE TiO$_2$ thick.

The nature of the substrate–film interface can be investigated by comparison of the W 4d XPS spectra for different stages of the growth process [7]. Upon adsorption of oxygen there is a slight broadening of the W 4d XPS peaks at higher binding energy compared with the clean surface (Fig. 4(a)). Streaking along the principal azimuths is also observed in the LEED pattern and with sufficient exposure to oxygen this sharpens to a (4 × 1) pattern as observed in [40]. There is no apparent change between the W 4d XPS spectra of the clean W surface and a Ti-deposited W surface (Fig. 4(b)). This is also the case between the W 4d spectrum of a fully oxidised TiO$_2$ film and the oxidised W surface (Fig. 4(c)).

### 3.2. Interaction with H$_2$O

As a preliminary measurement, a clean W(100) surface was exposed to up to 100 L H$_2$O (1 L = 1.32 × 10$^{-6}$ mbar s$^{-1}$). There has been a previous study of H$_2$O adsorption on W(100), which employed synchrotron radiation photoemission [41]. This indicated dissociative adsorption with formation of W–O bonds. Fig. 5(a) shows the changes in O 1s XPS spectra as H$_2$O exposure increases. Even with very thorough cleaning, a trace amount of oxygen is present on the nominally clean surface. The intensity of this peak increases on exposure to H$_2$O and it can be fitted with two Gaussian–Lorentzian singlet peaks at 530.5 eV and 532.9 eV. Using the area of these peaks and the area of the W 4d XPS spectra, the atomic concentration ratio of O and W is seen to increase exponentially (Fig. 5(b)) to a saturation limit of 0.15 and 0.05 for the peaks at 530.5 eV and 532.9 eV, respectively. The peak at 530.5 eV corresponds to what is expected for adsorbed atomic oxygen [42]. An E$_B$ of 532.9 eV corresponds to that expected for molecular water [41].

TiO$_2$ thin films prepared by the pre-oxidised W(100) method were exposed to ≤ 200 L H$_2$O in stages at 293 K. No change was observed in the LEED pattern, aside from attenuation of spots indicating adsorption without long range order. Changes to the stoichiometry of films upon H$_2$O exposure were monitored through the evolution of the Ti 2p XPS spectra. These are shown for two of the films, with thicknesses of 0.9 MLE TiO$_2$ (Fig. 6(a–c)) and 5.3 MLE TiO$_2$ (Fig. 7(a–c)). In both cases, there is an increase in the Ti$^{3+}$ concentration.

For the thinnest film, increases on the lower E$_B$ side of the Ti 2p doublet are apparent upon water exposure (see Fig. 6(a)). The difference spectrum for each exposure shows a doublet at 458.1 eV and 463.5 eV up to 187 L H$_2$O exposure, which evidences the presence of Ti$^{3+}$ states (Fig. 6(b)). For large exposure, the doublet peak in the difference spectra gains some asymmetry to lower E$_B$. This can be fitted with another
doublet at 455.4 eV and 460.8 eV and suggests the presence of Ti$^{2+}$ states [34]. By peak fitting and comparing peak areas, the relative concentration of Ti$^{3+}$ and Ti$^{2+}$ can be estimated (Fig. 8). Plotting these values against exposure (Fig. 6(c)) shows an increase in %Ti$^{3+}$, nearing a maximum at 37% Ti$^{3+}$ after 100 L exposure. A shallower increase to a maximum of 20% Ti$^{2+}$ is observed, with Ti$^{2+}$ features not present below 7 L exposure. In thicker films, no Ti$^{2+}$ features are observed.

Table 1

| Parameter | Position/eV | FWHM/eV |
|-----------|-------------|---------|
| Ti$^{4+}$ | 2p$_{3/2}$  | 459.0   | 2.16   |
|           | 2p$_{1/2}$  | 464.8   | 2.97   |
| Ti$^{3+}$ | 2p$_{3/2}$  | 457.1   | 2.20   |
|           | 2p$_{1/2}$  | 462.5   | 2.99   |
| Ti$^{2+}$ | 2p$_{3/2}$  | 455.4   | 2.22   |
|           | 2p$_{1/2}$  | 460.8   | 3.02   |
| O 1s      | 530.4       | 1.82    |
| S$_1$     | 531.8       | 2.06    |

peaks at 458.1 eV and 463.5 eV, corresponding to Ti$^{3+}$ features (Fig. 7(b)). The increase in %Ti$^{3+}$ features reaches a maximum of 18% at 60 L for the 5.3 MLE film.

Table 2

| TiO$_2$ thickness | Initial %Ti$^{3+}$ | Initial %S$_1$ | Saturation %Ti$^{3+}$ | Saturation %S$_1$ |
|-------------------|-------------------|----------------|-----------------------|-------------------|
| 0.9 MLE           | 5.0 ± 2.4         | 26.3 ± 1.2     | 37.2 ± 3.1            | 35.0 ± 1.8       |
| 1.6 MLE           | 6.6 ± 2.1         | 27.0 ± 1.3     | 15.3 ± 1.2            | 29.4 ± 1.0       |
| 4.2 MLE           | 4.5 ± 2.4         | 29.7 ± 1.4     | 15.3 ± 1.1            | 32.6 ± 1.1       |
| 5.3 MLE           | 0.0 ± 1.0         | 24.0 ± 2.7     | 17.5 ± 2.8            | 31.1 ± 1.4       |

Fig. 4. Comparison of the MgKα W 4d XPS spectra ($h\nu = 1253.6$ eV) after Shirley background subtraction of a 2.4 MLE thick TiO$_2$ film grown using the pre-oxidised W(100) method. (a) Ti 2p region showing contributions from Ti$^{3+}$ and Ti$^{4+}$ ions, as estimated by fitting with two Gaussian–Lorentzian doublets. Ti$^{3+}$ ions make up 9% of the overall Ti contribution. (b) O 1s region showing contributions from the main O 1s XPS peak and the S$_1$ satellite. The latter accounts for 27% of the total O 1s XPS peak area.
H2O at 300 K. Shirley backgrounds have been subtracted. (b) Atomic concentration ratio after subtraction of the 0 L H2O exposure spectrum (Figs. 6(e), 7(e)). This increase is more apparent in the difference spectra of each scan an EB of 531.8 eV, corresponding to the position of the S1 satellite re-

Changes in the O 1s XPS spectra are shown for the same two films: 0.9 MLE TiO2 (Fig. 6(d–f)) and 5.3 MLE (Fig. 7(d–f)). An increase at higher $E_B$ is observed upon increasing H2O exposure (Figs. 6(d), 7(d)). This increase is more apparent in the difference spectra of each scan after subtraction of the O 1 L H2O exposure spectrum (Figs. 6(e), 7(e)). Peak fitting of the difference spectra reveal an increase in a feature at an $E_B$ of 531.8 eV, corresponding to the position of the S1 satellite re-

a feature at an $E_B$ of 533.0 eV denoted $S_2$. Initial and saturation values of %$Ti^{3+}$ and %$S_1$ for the films are tabulated in Table 2.

4. Discussion

LEED data indicate that there is no long-range order associated with Ti deposited on W surfaces, but that ordered TiO2(110) films result post-oxidation. The LEED patterns are sharper for thicker films presumably because the TiO2 islands are larger and the strain due to the lattice mismatch between the substrate and the film decreases with increasing thickness. The similarity in the Ti 2p and O 1s XPS spectra for each of the growth methods used suggests that films produced by each route are more or less equivalent. At the temperature at which the films are annealed (800 K), oxygen can diffuse through TiO2 [43] and films can be completely oxidised regardless of initial conditions. Strain, as well as surface defects such as $O_{vac}$ can also explain the slight non-stoichiometry. The W 4d spectrum of the W/TiO2 interface is similar to the same spectrum for oxidised W, suggesting that the film layer at the substrate interface consists of O atoms rather than Ti.

The increase in Ti$^{3+}$ states on exposure to H2O suggests dissociation on the TiO2 thin film surface, with resulting charge transfer from hydroxyl species to Ti$^{4+}$ [21]. The O 1s XPS data is consistent with this picture, showing an increase in intensity of the OH peak (S1), with no increase of a feature at the position expected for molecular H2O (2.5 to 3.5 eV higher BE). For the 0.9 MLE film the increase in height of S2 will arise from molecular adsorption on bare areas of W(100)-O. The values of %Ti$^{3+}$ increase with H2O exposure for all films (Table 2), whereas Ti$^{2+}$ states are only detected for the exposure of the 0.9 MLE TiO2 thick film to H2O. Since the film is of <1 MLE thickness, the W(100)-O surface is not completely covered with TiO2 and the formation of lower oxides such as TiO is possible, especially at island edges. The asymmetry of the O 1s difference spectra upon H2O exposure for the 0.9 MLE film can also be explained by exposure of the W(100)-O surface to water (Fig. 6e). Changes in the S1 contribution (531.8 eV) as well as the feature arising from H2O adsorption on exposed W (532.9 eV), where H2O oxidises the W surface to WO3 and WO3$–x$ will contribute intensity to the difference spectra.

In the experiments presented here, the %$S_1$ increases exponentially to a maximum saturation value and is assigned to the presence of adsorbed hydroxyls. The presence of $S_1$ prior to H2O exposure will be due to dissociative adsorption of H2O from the residual vacuum [11].

5. Conclusions

Three methods of synthesising ultra-thin films of TiO2(110) on a W(100) substrate have been investigated using XPS and LEED. The resulting films have been found to be equivalent, with films between 0.2 and 5.7 MLE being synthesised. The reactivity of the TiO2(110) sur-

semble ordered TiO2(110) [10–16]. We note that ultra-thin TiO2 films grown on W(100) would be suitable for use in electron spin resonance experi-

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Fig. 6. MgKx XPS spectra (hν = 1253.6 eV) of W(100) after growth of a 0.9 MLE TiO₂ thin film (pre-oxidised growth). The spectra are presented as a function of H₂O exposure up to 187 L at 300 K: (a) Ti 2p region spectra at each exposure, (b) difference spectra showing changes compared with the film prior to H₂O exposure, (c) change in %Ti⁺³ upon H₂O exposure, (d) O 1s region spectra as a function of exposure; (e) difference spectra showing changes compared with the film prior to H₂O exposure; (f) change in %S1 and %S2 of the O 1s signal upon H₂O exposure.
Fig. 7. MgKα XPS spectra ($\hbar\nu = 1253.6$ eV) of W(100) after growth of a 5.3 MLE TiO$_2$(110) thin film (pre-oxidised growth). The spectra are presented as a function of H$_2$O exposure up to 100 L at 300 K: (a) Ti 2p region at each exposure; (b) difference spectra showing changes compared with the film prior to H$_2$O exposure; (c) change in Ti$^{3+}$ upon H$_2$O exposure; (d) O 1s region at each exposure; (e) difference spectra showing changes compared with the film prior to H$_2$O exposure; (f) change in S$\equiv$O 1s signal upon H$_2$O exposure. All spectra have had a Shirley background removed.
Fig. 8. MgKα XPS spectrum ($h\nu = 1253.6$ eV) of a 0.9 MLE TiO$_2$(110) film (pre-oxidised growth) on W(100) after exposure to 187 L H$_2$O at 300 K. The spectrum has been Shirley background subtracted. Contributions from Ti$^{2+}$, Ti$^{3+}$ and Ti$^{4+}$ ions are highlighted. They were estimated by fitting with three Gaussian–Lorentzian doublets. The concentrations of Ti$^{2+}$ and Ti$^{3+}$ are 20% and 37%, respectively.

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