Synthesis of TiO₂(110) ultra-thin films on W(100) and their reactions with H₂O

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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 TiO₂ ultra-thin films. Bennett et al. have previously grown thin films of TiO₂ 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 O₂ [8,9]. This results in a unit cell of dimensions 6.32 × 3.16 Å², which is comparable to the TiO₂ (110) unit cell, 6.49 × 2.96 Å², and the mismatch between these two cells is 2.7% × 6%. In the earlier work, Bennett et al. show that their TiO₂ thin films have the rutile structure when using both preparation methods.

Previous structural characterisation work on ultra-thin (<1 nm thickness) films of rutile TiO₂(110) is restricted to the use of Ni(110) [10,11], Nb₃SiP₆ (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 TiO₂(110) are known to be important in the reaction with H₂O [18,19]. Hence, one means of investigating the defect character of TiO₂(110) ultrathin films is to use H₂O as a probe molecule [20]. Surface science studies of the H₂O interaction with TiO₂(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 Ti³⁺ states in a pair of hydroxyls in the bridging row (OHb) [21]. Experiments from Walle et al. suggest that both molecular and dissociative adsorption of H₂O occur when a monolayer of water is deposited on a nominally defect free rutile TiO₂(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 tunneling 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 H₂O molecules adsorb at O vacancy sites (Ovac) and dissociate, resulting in a pair of hydroxyls in the bridging row (OHb): one in place of the original Ovac, and a second formed from the dissociated H atom and another bridging row oxygen atom (O₂). The resulting OHb pair and its related charges play an important role in reactivity of the surface with O₂ [28]. Here we examine the morphology of TiO₂(110) ultra-thin films, their electronic structure as well as their reactivity with H₂O.

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 as well as O₂ by backfilling the chamber to a pressure of 1 × 10⁻⁷ mbar.

### 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 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.

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In the case of pre-oxidised growth, where Ti is deposited on the W surface 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. Ti⁵⁺ and Ti⁶⁺). The main peaks of these species are positioned at EB = 457.1 eV (Ti⁴⁺) and 455.4 eV (Ti⁵⁺). As for the case of the two-stage growth, these peaks shift to positions associated with Ti⁴⁺ 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 Ti⁵⁺ states as well as reduced Ti⁴⁺ and Ti⁶⁺ 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 Ti⁵⁺ states (at EB = 455.4 eV and 460.8 eV) are completely removed. By contrast the Ti⁴⁺ and Ti⁵⁺ states are not completely removed, indicating that the film is slightly 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 (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 Kα excitation. Ti 2p spectra were fitted with three doublets (Voigt functions) corresponding to the Ti⁴⁺ (light red), Ti⁵⁺ (red) and Ti⁶⁺ (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.

**Fig. 1.** MgKα XPS spectra (hv = 1253.6 eV) of W(100) showing (a) the shift in Eb 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 Kα excitation. Ti 2p spectra were fitted with three doublets (Voigt functions) corresponding to the Ti⁴⁺ (light red), Ti⁵⁺ (red) and Ti⁶⁺ (dark red) contributions, as shown for the reactive deposition method (c).
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. However, an increase in Ti$^{3+}$ concentration is still observed in the Ti 2p spectra (Fig. 7(a)). The doublet peak appearing in difference spectra is more symmetric and can be fitted with a single doublet with XPS 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 1
Parameters used in Ti 2p (Figs. 1, 3 and 8) and O 1s (Fig. 3) fitting procedures, showing peak position and Gaussian–Lorentzian (Voigt function) full-width at half-maximum (FWHM) values.

<table>
<thead>
<tr>
<th></th>
<th>Position/eV</th>
<th>FWHM/eV</th>
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<tr>
<td>Ti$^{4+}$</td>
<td>2p$3/2$</td>
<td>459.0</td>
</tr>
<tr>
<td>Ti$^{4+}$</td>
<td>2p$1/2$</td>
<td>464.8</td>
</tr>
<tr>
<td>Ti$^{3+}$</td>
<td>2p$3/2$</td>
<td>457.1</td>
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<td>462.5</td>
</tr>
<tr>
<td>Ti$^{2+}$</td>
<td>2p$3/2$</td>
<td>455.4</td>
</tr>
<tr>
<td>Ti$^{2+}$</td>
<td>2p$1/2$</td>
<td>460.8</td>
</tr>
<tr>
<td>O 1s</td>
<td></td>
<td>530.4</td>
</tr>
<tr>
<td>$S_1$</td>
<td></td>
<td>531.8</td>
</tr>
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Table 2
Summary of initial values for %Ti$^{3+}$ and %S$_1$ for TiO$_2$(110) ultra-thin films on W(100) of varying thickness prepared by the pre-oxidised method. The corresponding figures are given for the spectra following a saturation exposure to water at 1 × 10$^{-8}$ mbar.

<table>
<thead>
<tr>
<th>TiO$_2$ thickness</th>
<th>Initial %Ti$^{3+}$</th>
<th>Initial %S$_1$</th>
<th>Saturation %Ti$^{3+}$</th>
<th>Saturation %S$_1$</th>
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</thead>
<tbody>
<tr>
<td>0.9</td>
<td>5.0 ± 2.4</td>
<td>26.3 ± 1.2</td>
<td>37.2 ± 3.1</td>
<td>35.0 ± 1.8</td>
</tr>
<tr>
<td>1.6</td>
<td>6.6 ± 2.1</td>
<td>27.0 ± 1.3</td>
<td>15.3 ± 1.2</td>
<td>29.4 ± 1.0</td>
</tr>
<tr>
<td>4.2</td>
<td>4.5 ± 2.4</td>
<td>29.7 ± 1.4</td>
<td>15.3 ± 1.1</td>
<td>32.6 ± 1.1</td>
</tr>
<tr>
<td>5.3</td>
<td>0.0 ± 1.0</td>
<td>24.0 ± 2.7</td>
<td>17.5 ± 2.8</td>
<td>31.1 ± 1.4</td>
</tr>
</tbody>
</table>

Fig. 3. MgKα XPS spectra (hv = 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.

Fig. 4. Comparison of the MgKα W 4d XPS spectra (hv = 1253.6 eV) for (a) W(100) and W(100)-(2 × 1)-O surfaces, (b) W(100) and Ti-deposited (3.9 MLE Ti) W(100) surfaces, and (c) W(100)-(2 × 1)-O surface and a fully oxidised TiO$_2$(110) thin film on W(100) (grown using the two-stage method). Shirley backgrounds have been subtracted and spectra are normalised to the same maximum intensity.
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 at an EB of 531.8 eV, corresponding to the position of the S1 satellite. This increase is due to a saturation limit of 0.15 and 0.05 for the peaks at 532.9 eV (red) and 530.5 eV (blue), respectively.

Fig. 5. (a) MgKα XPS spectra (hv = 1253.6 eV) of the O 1s region for W(100) exposed to H2O at 300 K. Shirley backgrounds have been subtracted. (b) Atomic concentration ratio \( C_{\text{O}}/C_{\text{W}} \) as a function of exposure to H2O, where \( C_{\text{O}} \) and \( C_{\text{W}} \) correspond to the peak areas of O 1s and W 4d, respectively. The ratio in atomic concentration increases exponentially to a saturation limit of 0.15 and 0.05 for the peaks at 532.9 eV (red) and 530.5 eV (blue), respectively.

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 0 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 referred to above. This increases to a maximum value of 35% of the total O 1s area for the 0.9 MLE film and 31% for the 5.3 MLE film. The higher increase for the thinner film can be related to the higher increase in Ti3+ states which are twice as large for the 0.9 MLE film (~32%) compared to the thicker films (~16%). For the 0.9 MLE film, an increase is also seen in a feature at an \( E_B \) of 533.0 eV denoted S2. Initial and saturation values of \%Ti3+ and \%S1 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 routine 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 Ovac 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 Ti3+ states on exposure to H2O suggests dissociation on the TiO2 thin film surface, with resulting charge transfer from hydroxyl species to Ti4+ [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 \%Ti3+ increase with H2O exposure for all films (Table 2), whereas Ti2+ 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 is also explained by exposure of the W(100)-O surface to water (Fig. 6(e)). 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 %S1 increases exponentially to a maximum saturation value and is assigned to the presence of adsorbed hydroxyls. The presence of S1 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) surface has been examined by exposing to H2O. An increase in adsorbed hydroxyls, OHb, accompanies an increase in Ti3+ states, consistent with an increase in excess charge on the TiO2(110) surface. Molecular H2O was not observed spectroscopically except for films of <1 MLE TiO2 thickness, where regions of exposed WO3 are present and can be hydrated, as shown by exposure of a clean W surface to H2O. The findings of this study are in line with experiments previously reported in the literature using native surfaces of TiO2 and on ultra-thin films of TiO2(110) [10–16]. We note that ultra-thin TiO2 films grown on W(100) would be suitable for use in electron spin resonance experiments, since the substrate is paramagnetic.

Acknowledgements

This work was supported by the EPSRC (UK) and COST1104. In addition, GT acknowledges the support of a European Research Council Advanced Grant (ENERGYSURF) and a Humboldt Research Award.
Fig. 6. MgKα XPS spectra ($h\nu = 1253.6$ 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 Ti²⁺ 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.

References

Fig. 7. MgKα XPS spectra (hv = 1253.6 eV) of W(100) after growth of a 5.3 MLE TiO2(110) thin film (pre-oxidised growth). The spectra are presented as a function of H2O 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 H2O exposure; (c) change in %Ti3+ upon H2O exposure; (d) O 1s region at each exposure; (e) difference spectra showing changes compared with the film prior to H2O exposure; (f) change in %O 1s signal upon H2O exposure. All spectra have had a Shirley background removed.
Fig. 8. MgKα XPS spectrum ($\hbar \nu = 1253.6$ 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.