Decoupling a Thin Well-Ordered TiO$_2$(110) Layer from a TiO$_2$(110) Substrate with a Ti + Ta Mixed Oxide Interlayer

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ABSTRACT: A well-ordered TiO$_2$(110) thin film has been successfully prepared on a rutile TiO$_2$(110) single crystal substrate with a Ti + Ta mixed oxide interlayer. LEED and STM experiments show that the surface structure of the TiO$_2$ thin film is the same as that of a regular TiO$_2$(110) single crystal sample, and methanol TPD studies indicate that the chemical activities of the surfaces are also essentially identical. The Ti + Ta oxide interlayer hinders Ti diffusion, and therefore the TiO$_2$ film can quickly be reduced and oxidized due to the small layer volume without changing the state of the substrate notably. This permits to study fully oxidized defect-free electrically insulating TiO$_2$(110) surfaces with methods employing charged particles without surface charging. Also, strongly reduced layers can be prepared without substrate reduction.

INTRODUCTION

TiO$_2$ has attracted the interest of researchers because of its applications in gas-sensing technology,$^1$ as a white pigment,$^2$ in the coating industry,$^3$ in electric devices,$^4$ in solar cells,$^5$ in heterogeneous catalysis/photocatalysis,$^6,7$ and many other areas.$^8$ Being one of the most common polymorphs of titania, rutile with its stable (110) surface has been extensively studied.$^8−10$ Its surface structure has been well characterized,$^8,9$ and many surface chemistry studies have been conducted.$^9−11$ Such studies are usually performed with rutile single crystals which are reduced by thermal treatment and/or sputtering to make them electrically conductive so that experimental techniques employing charged particles such as photoelectron spectroscopy and scanning tunneling microscopy (STM) can be used.$^{12}$ Because of the quick diffusion of cations in rutile at elevated temperature,$^{13}$ this leads to a reduction not just at the surface but to a reduction of the whole sample which changes its color from colorless transparent for nonreduced samples to blue for low to medium degrees of reduction and black for strongly reduced samples.$^{12}$ However, many studies show that reduction affects the properties of TiO$_2$(110) since reduction leads to the presence of Ti interstitials and vacancies.$^8,9$ Therefore, even a just weakly reduced sample may not be suitable for certain studies.

It has been shown in many studies that thin layers can be studied with methods employing charged particles even when the material is electrically insulating.$^{14,15}$ Therefore, a way out would be the use of thin TiO$_2$(110) layers instead of massive single crystals. TiO$_2$(110) thin films have been grown on Ni$_2$Ti$_3$(110),$^{16}$ Mo(110),$^{17}$ Ni(110),$^{18}$ Ag(100),$^{19}$ and W(100)$^{20,21}$ by oxidation of the substrates or Ti deposition on the substrates with postoxidation. However, lattice mismatch commonly induces strain in the TiO$_2$ films. Most of the previously investigated films were reduced with a low level of nonstoichiometry.$^{18,20,21}$ Discrete islands rather than a continuous film were found at the substrate surface in many cases.$^{16−21}$ The resulting domain boundaries make the system complex and can affect the chemistry of the surface. Other defects such as crystallographic shear planes may also exist in the thin film.$^{18}$ Until now, preparation of a well-ordered TiO$_2$(110) thin film has not been reported.

In this paper we discuss a recipe for the preparation of thin well-ordered TiO$_2$(110) layers on TiO$_2$(110) single crystals with a mixed Ti + Ta oxide interlayer. The interlayer largely prevents Ti atom exchange between the substrate and the overlayer which essentially has two profitable aspects: (1) fully oxidized layers can be grown on a reduced substrate and studied with experimental methods employing charged particles, and (2) the overlayer can be reduced and oxidized, even strongly if required, without changing the state of the substrate to a comparable extent. Since the interlayer adapts to the structure of the substrate, high-quality well-ordered TiO$_2$(110) layers can be grown on it due to the absence of a notable interface strain.

EXPERIMENTAL METHODS

The experiments were performed in two different UHV (ultrahigh vacuum) chambers with base pressures of $\sim 1 \times 10^{-10}$ mbar. Both were equipped with a LEED (low-energy electron diffraction) system, a sputter gun for sample preparation, a quadrupole mass spectrometer with a pumped Feulner cup$^{22}$ for TPD (thermal desorption spectroscopy), and electron beam evaporators (Focus) for the deposition of tantalum and titanium. The deposition rates were calibrated...
with a quartz microbalance. One of the systems was additionally equipped with a rotatable electron energy analyzer for ARUPS (angular resolved ultraviolet photoelectron spectroscopy) using UV radiation from a He discharge lamp (21.22 eV). The other system was equipped with facilities for STM (Omicron STM1) and XPS (X-ray photoelectron spectroscopy) using Al Kα and Mg Kα radiation. An Omicron EA125 electron energy analyzer was employed to detect the photoelectrons. The energy scale of the analyzer was calibrated such that the Au 4f7/2 level of a Au(111) sample was at 84.0 eV.23 LEED and STM were used to examine the surface structure of the prepared thin films, and TPD experiments with methanol as the probe molecule were performed to test whether the surface reactivity of TiO2(110) layers and therefore their electronic and geometric structure differs from that of TiO2(110) single crystal surfaces. In the experiments presented here, 50 langmuirs (1 langmuir = 1 × 10−6 Torr·s) of methanol was dosed to the respective surfaces at room temperature via a pinhole doser. The latter consists of a tube with 10 mm diameter with the end opening positioned at a distance of ∼1 mm in front of the sample surface, which reduces the degree of chamber contamination by the dosed gas (methanol in the present case). Gas is introduced into the tube via a pinhole with 20 μm diameter that is located at the beginning of the tube near to the chamber flange. The pinhole acts as a pressure reduction stage, so that pressures in the gas-inlet system in the mbar range can be employed to dose under UHV compatible conditions. TPD spectra shown in this publication were recorded with a constant heating rate of 0.5 K s−1. The methane (m/z = 16), formaldehyde (m/z = 30), and water (m/z = 18) TPD traces shown in this publication are not raw data; they represent corrected data obtained via subtraction of the methanol contributions according to $C_{\text{compound}} \text{methanol mass}^{31} - C_{\text{compound}}$. The XPS matrix would leave the rutile type matrix intact, which is relevant for the growth of a well-ordered rutile layer on such a mixed oxide layer.

The suitability of Ta, W, and Pb (see Table 1) for such a blocking layer was tested. It was found that PbO2 tends to aggregate to form clusters which rendered it useless for the given purpose. W was found to diffuse to the top layer upon annealing at 800 K for 30 min. After several systematic tests Ta was selected since it was found to be more stable with respect to high-temperature treatment: Ta was only seen with XPS after annealing 10 h at 800 K or 2 h at 900 K. Introduction of Ta into the lattice of TiO2 is possible even up to concentrations of some 10% without a significant impact onto the crystal structure. Although a slight lattice expansion in the blocking layer (with respect to regular TiO2) is conceivable (we did not check this), high-quality uniform TiO2(110) thin films could successfully be grown on this layer. The thermal stability of the blocking layer was examined by checking the diffusion of Ta into the top TiO2(110) layer upon thermal treatment. Figure 1.

### RESULTS AND DISCUSSION

The interlayer preparation recipe was developed with the purpose of hindering the diffusion of cations through the layer (which is the origin of the term “blocking layer”) by stressing the layer via introduction of ions with a larger ionic diameter than that of the Ti4+ cations. Table 1 lists lattice parameters of oxides with rutile type structure which were tested with respect to their suitability for this goal. Metals forming rutile type structures were preferred since one might expect that introduction of cations of these metals into the rutile TiO2 matrix would leave the rutile type matrix intact, which is relevant for the growth of a well-ordered rutile layer on such a mixed oxide layer.

The TiO2(110) substrate (7 × 8 × 2 mm3, purchased from Crystal GmbH, Germany) was cleaned via repeated cycles of Ar+ sputtering at room temperature followed by annealing at high temperature (900 K) until no contamination was detectable with XPS. A Ti + Ta mixed oxide layer (Ti0.8Ta0.2O2, ~30 Å thick) was prepared on the TiO2(110) substrate by codeposition of Ta and Ti in an oxygen ambient atmosphere (1 × 10−6 mbar). Subsequently, an epitaxial TiO2(110) thin film (~100 Å thick) was grown on the Ti + Ta mixed oxide layer at the same oxygen pressure followed by annealing in a vacuum. During the deposition and annealing steps, the temperature of the substrate was maintained at 800 K measured with a K-type thermocouple fixed with a ceramic glue to a side of the crystal.

### Table 1. Structural Parameters of Some Oxides with Rutile Type Structure

<table>
<thead>
<tr>
<th>Compound</th>
<th>TiO2</th>
<th>β-PbO2</th>
<th>TaO2</th>
<th>WO3</th>
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<tbody>
<tr>
<td>cation radius</td>
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<td>0.92 Å</td>
<td>0.82 Å</td>
<td>0.80 Å</td>
</tr>
<tr>
<td>structure</td>
<td>tetragonal</td>
<td>tetragonal</td>
<td>monoclinic</td>
<td></td>
</tr>
<tr>
<td>lattice constant a</td>
<td>a = 4.59 Å</td>
<td>a = 4.91 Å</td>
<td>a = 4.96 Å</td>
<td>a = 5.56 Å</td>
</tr>
<tr>
<td></td>
<td>c = 2.95 Å</td>
<td>c = 3.39 Å</td>
<td>c = 3.39 Å</td>
<td>c = 5.66 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>β = 120.5°</td>
</tr>
</tbody>
</table>

“Data are from The Cambridge Structural Database, http://www.ccdc.cam.ac.uk/.

### Figure 1

XPS spectra (Al Kα: 1486.6 eV, normal emission) of the Ta 4d core level measured of (a) a freshly prepared TiO2(110) thin film, (b) the TiO2(110) thin film after annealing in a vacuum at 900 K for more than 2 h, and (c) the as-prepared Ti + Ta mixed oxide blocking layer.
displays XPS spectra of the Ta 4d energy range. The spectrum of the blocking layer (spectrum (c)) shows that the oxidation state of Ta is probably 4+, which would be compatible with Ta cations replacing Ti cations in the rutile lattice. In spectrum (b) a weak Ta signal (corresponding to a Ta concentration of less than 2% relative to Ti) shows up after annealing the sample at 900 K for more than 2 h, while spectrum (a) from the freshly prepared layer does not, as expected, show any indication of Ta 4d emission.

The diffusion blocking properties of the mixed oxide layer were tested with valence band photoelectron spectroscopy. Figure 2 displays highly surface-sensitive spectra of the TiO₂(110) band gap regime where the reduction-induced band gap state is located. Spectra (a) and (c) show that the intensity of this state essentially vanishes in the spectra of the oxidized TiO₂(110) substrate and the oxidized TiO₂(110) thin film. Both were prepared by annealing in oxygen (1 × 10⁻⁶ mbar) at 800 K for 10 min. On the other hand, the band gap state at ~0.8 eV below the Fermi level is observed with significant intensity in the spectra of the surfaces reduced by sputtering at room temperature and annealing at 800 K for 10 min [spectra (b) and (d)]. We note that the intensity of the band gap state in the spectrum of the reduced thin film is much higher than in the spectrum of the reduced substrate although both samples were prepared in the same way. After annealing the thin film in vacuo at 800 K for an additional 10 min, the intensity of the 0.8 eV state did not increase but remained the same as shown in spectrum (e).

The exact nature of the band gap state is still an actively discussed issue, but there is agreement that it is due to reduced cations. The spectra in Figure 2 indicate that the diffusion of these cations between the substrate and the top layer is blocked by the Ti + Ta mixed oxide interlayer, since otherwise the band gap state intensities for the thin layer and the single crystal surface would be identical and the second annealing step [spectrum (e)] would lead to a reduction of the band gap state intensity due to diffusion of the reduced cations into the substrate. With this blocking layer the epitaxial TiO₂(110) thin film is thus decoupled from the rutile (110) substrate: the travel of Ti ions from the layer into the substrate and vice versa are strongly hindered. This does probably not just apply to reduced cations ("Ti³⁺") but also to nonreduced cations ("Ti⁴⁺") since their diffusion would also lead to a balance of the degree of reduction between substrate and overlayer. Figure 3 compares TPD spectra of methanol on a TiO₂(110) thin film (solid lines) and on a reduced cation in the rutile lattice. In spectrum (b) a weak Ta signal (corresponding to a Ta concentration of less than 2% relative to Ti) shows up after annealing the sample at 900 K for more than 2 h, while spectrum (a) from the freshly prepared layer does not, as expected, show any indication of Ta 4d emission.

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It was also possible to fully oxidize the thin film while maintaining a reduced substrate. The surface structure of the layer after reduction and oxidation was studied with STM (Figure 3). Annealing the thin film in vacuum at 900 K for 20 min resulted in a reduced surface with a bridging oxygen vacancy concentration of ~15% per unit cell, higher than the density of oxygen vacancies (~7%) for the (110) surface of a bulk crystal prepared in the same way. Oxidation of the TiO₂(110) thin film was performed by annealing in O₂ (1 × 10⁻⁶ mbar) at 600 K for 10 min. The STM image in Figure 3b shows a flat (1 × 1) terrace with some bright features with a height of ~0.7 Å on the bright rows. Bridging oxygen vacancies are not visible.

When oxidizing a bulk crystal at 600 K, rosette-like structures and/or small islands of TiO₂ are usually formed at the surface (Figure 3c) through the reaction of O₂ with reduced cations diffusing from the bulk to the surface, making the surface rough. This is not the case for the thin film, which is another indication that the diffusion of reduced cations from the bulk to the top layer is inhibited by the blocking layer. The top TiO₂ layer may be fully oxidized as judged from the absence of bridging oxygen vacancies. The bright features on the 5-fold Ti sites are assigned to oxygen adatoms which have a height of 0.7 Å in STM images. The oxygen adatoms are assumed to originate from the dissociation of O₂ molecules at the bridging oxygen vacancies and Ti sites.

Methanol TPD was used to characterize the chemical reactivity of the thin films. Figure 4 compares TPD spectra of methanol on a TiO₂(110) thin film (solid lines) and on a reduced TiO₂(110) substrate. The blocking effect is clear from the absence of peaks at 1380 and 1730 cm⁻¹ corresponding to the C=O and CH₃ bending vibrations, respectively.
Other researchers found a formaldehyde desorption peak also when dosing is performed at low temperature (not shown in this study while it was dosed at room temperature in the present case. However, we observe the TPD peaks at 680 K of methanol or a formaldehyde desorption peak at 680 K, and water desorption was not observed in their experiment. We also did not observe a methane desorption peak at 680 K. No peak of methanol adsorption the samples were reduced by annealing in vacuo at 800 K for 10 min prior to methanol adsorption.

**Figure 4.** TPD spectra (mass-to-charge ratio 16, 18, 30, and 31) of methanol adsorbed at room temperature onto thin film TiO$_2$(110) (solid line, black) and a TiO$_2$(110) single crystal (dotted line, red). Both samples were annealed in a vacuum at 800 K for 10 min prior to methanol adsorption.

**Figure 5.** TPD spectra (mass-to-charge ratio 16, 18, 30, and 31) of CH$_3$OH adsorbed on a TiO$_2$(110) thin film annealed in O$_2$ at 600 K. Such layers can be reduced and oxidized without affecting the substrate, which permits to grow fully decoupled thin film surfaces without bridging oxygen vacancies which is decoupled from the rutile (110) substrate due to the presence of a Ti + Ta mixed oxide interlayer which blocks the cation exchange between the overlayer and the substrate. The decoupled thin film can be reduced and oxidized without significantly affecting the substrate, which permits to grow fully oxidized layers on a reduced substrate. Such layers can be studied with methods employing charged particles without surface charging. STM shows that the film is well ordered with groups at the bridging oxygen vacancies do not react with hydroxyl groups below 680 K. The stabilization of those methoxy groups is likely linked to the desorption of water at 520 K. Hydroxyl groups recombine to form water, which consumes the hydrogen at the surface, so that no hydrogen is left for the reaction with methoxy. By using the Redhead equation with a pre-exponential factor of $10^{13}$ s$^{-1}$ and a heating rate of 0.5 K s$^{-1}$, we obtain an activation energy of 1.96 eV for the reaction occurring at 680 K. This value is close to the energy barrier of 1.85 eV for the formation of formaldehyde on bridging oxygen vacancies obtained recently by Lang et al. with DFT (density functional theory).

Oxidized thin film surfaces without bridging oxygen vacancies exhibit a reactivity with respect to methanol adsorption which is also very similar to what is known for oxidized single crystal surfaces. **Figure 5** shows TPD spectra of methanol on a TiO$_2$(110) thin film that was annealed in O$_2$ at 600 K. The desorption states at 680 K are not visible anymore since there are no bridging oxygen vacancies, but new peaks at about 600 K arise. The desorption of methanol and formaldehyde from an oxidized TiO$_2$(110) single crystal surface at a similar temperature has been reported before by other researchers. The 600 K TPD peak has been assigned to formaldehyde formation from methoxy species bound to 5c-Ti sites in the presence of oxygen adatoms. The hydrogen released in this reaction does probably react with methoxy groups to methanol (see eqs 1 and 2). An activation energy of 1.73 eV for the reactions is estimated using the Redhead equation, which again fits quite well to the computed energy barrier of 1.76 eV obtained by Lang et al. with DFT.

**CONCLUSIONS**

We have successfully prepared a well-ordered TiO$_2$(110) layer which is decoupled from the rutile (110) substrate due to the presence of a Ti + Ta mixed oxide interlayer which blocks the cation exchange between the overlayer and the substrate. The decoupled thin film can be reduced and oxidized without significantly affecting the substrate, which permits to grow fully oxidized layers on a reduced substrate. Such layers can be studied with methods employing charged particles without surface charging. STM shows that the film is well ordered with

\[ \text{CH}_3\text{O} \rightarrow \text{H}_2\text{O} + \text{H}_2 \]  

(1)

This reaction produces H atoms as a byproduct. We propose that the concomitant desorption of methanol may be explained by a reaction of these hydrogen atoms with methoxy groups to produce methanol:

\[ \text{CH}_3\text{O} + \text{H}_2 \rightarrow \text{CH}_3\text{OH} \]  

(2)

Such a methanol production mechanism was also postulated by other researchers, with the reaction details being somewhat different. An interesting question is why the methoxy
large terraces, and methanol TPD experiments indicate that the chemical properties of the thin layer are essentially identical to those of a single crystal surface.

The blocking layer is not only able to block diffusion of titanium, but also the diffusion of other types of atoms may be blocked. This becomes relevant if doping with atoms that quickly diffuse in rutile TiO₂ comes into play. In fact, a well-mixed oxide layer of vanadia and titania has recently successfully been prepared based on this method.

This type of quasi-homoepitaxial growth of a decoupled layer is probably also suitable for other oxides, which may be relevant if the substrate is defective or contaminated (natural crystal) and a well-ordered noncontaminated surface is required or if other substrates for epitaxial growth are not known like in the present case of TiO₂(110).

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Notes

The authors declare no competing financial interest.

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**ABBREVIATIONS**

ARUPS, angular resolved ultraviolet photoelectron spectroscopy; LEED, low-energy electron diffraction; STM, scanning tunneling microscopy; TPD, thermal desorption spectroscopy; UHV, ultrahigh vacuum; XPS, X-ray photoelectron spectroscopy.

**REFERENCES**


