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Lepidocrocite-like TiO_2 and $TiO_2(110)$-(1 × 2) supported on W(100)

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Ultrathin films of TiO_2 were grown on a W(100)-O(2 × 1) substrate and characterised with a combination of scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). In addition to islands of rutile $TiO_2(110)$ with (1 × 1) termination that were reported previously, we also observed rutile $TiO_2(110)$ islands with a (1 × 2) film termination. A lepidocrocite-like TiO_2 nanosheet was also observed on the W(100) surface. High-resolution STM images show that the nanosheet grows in the principal orthogonal directions of the W(100) substrate and forms a commensurate (1 × 7) coincident cell.

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1. Introduction

There is great interest in the study of oxide surfaces.[1] This is due to their use in a multitude of applications, including catalysis and electronics.[2-5] In many of these studies, thin oxide films are used.[2,6] Thin film alternatives to bulk oxides supported on conducting substrates are typically employed to make insulating oxides sufficiently conductive to allow charged-particle techniques, such as scanning tunneling microscopy (STM) to be used on otherwise insulating oxides.[7,8] In some cases, such as for anatase TiO_2, high quality crystals are difficult to grow and ultrathin and thin films provide an alternative to natural crystals.[9-12] Structures with no bulk-counterparts are of great interest as new material properties may be discovered and exploited.[3,4]

As the most thermodynamically stable face of rutile TiO_2, the (110) face has been studied extensively.[13] Ultrathin rutile TiO_2(110) islands have been grown on various substrates and are usually terminated by the (0.30 nm × 0.65 nm) (1 × 1) surface,[8,14-23] but if the deposited Ti is not completely oxidised, the reduced (0.30 nm × 1.30 nm) (1 × 2) reconstruction can also be observed, where the unit cell mesh is doubled in the $[\bar{1}10]$ direction.[16] As mentioned above, ultrathin films of anatase TiO_2 have also been grown. The (001) surface generally displays a (1 × 4) reconstruction,[9-12] consistent with measurements of the single crystal.[24,25]

TiO_x films have also been reported that have no bulk counterpart, such as a quasi-hexagonal TiO_x phase on $Ni_{94}Ti_6$(110)[26] or Ni(110)[15,23] and TiO_x nanodots on Ni(110).[23] A series of TiO_x phases have also been grown on Pt(111),[27,28] several of which are related to encapsulation layers observed on TiO_2(110)-supported nanoparticles.[29,30] Of particular relevance to this paper are the family of lepidocrocite-like films that have been observed on Pt(110)-(1 × 2), Ni(110), Ag(100), and Pt_3Ti(111).[15,17,18,27,31,32] This film is so-named due its structural similarity to the FeO(OH) lepidocrocite bilayer.[33] In calculations, the lepidocrocite-like structure forms spontaneously from a (001) anatase bilayer,[18,31,34,35] the top layer displacing by half a unit cell. The substrate-free bilayer has lattice parameters of ~0.375 nm × 0.300 nm.[15,17,18,27,31,36]

Here, we have studied ultrathin TiO_2 films grown on W(100)-O(2 × 1) surfaces using STM and low energy electron diffraction (LEED). The W(100)-O(2 × 1) reconstruction is formed by removing (or adding) alternate rows of W along [001] or [010] to create {110} microfacets that contain O in the 3-fold hollow sites.[37] This gives a primitive surface unit cell of 0.63 nm × 0.32 nm that is nearly lattice matched with rutile TiO_2(110). Apart from the (1 × 1) phase which was previously observed,[19] we observed a TiO_2 lepidocrocite-like structure as well as the TiO_2(110)-(1 × 2) reconstruction for the first time on W(100).

2. Experimental

The experiments were conducted in an ultrahigh vacuum (UHV) system comprising a preparation and analysis chamber with base pressures in the 10^{-10} mbar range, equipped with quadrupole mass spectrometers for residual gas analysis (RGA). The analysis chamber housed an *Omicron* UHV AFM/STM, calibrated with a TiO_2(110) single crystal, and rear-view LEED optics that were also employed for retarding field Auger electron spectroscopy (AES). The films were grown in the preparation chamber, which was equipped with an ion sputter gun, an electron bombardment sample heater, and metal evaporators. Prior to the growth of the films, the W(100) sample (*Surface Preparation Laboratory*) was prepared by cycles of argon sputtering and annealing to ~1173 K in 2×10^{-8} mbar O_2 and UHV, followed by flashing to 1500-1600 K, until a well-ordered W(100)-O(2 × 1) was identified in LEED and STM and any contamination was below the detection limit of AES.[19]

STM images were recorded at room temperature using positive sample bias (tunneling into empty sample electronic states) and either etched tungsten or mechanically formed PtIr tips. Estimates of coverage are given in monolayer equivalents (MLE) where 1 MLE is defined as complete coverage of the surface by a single layer of TiO_2 that has a thickness of 0.325 nm. Likewise for the TiO_2 lepidocrocite-like phase, 1 MLE is defined as the complete coverage of the surface by a bilayer, the thickness being estimated at 0.5 nm.

The first step of the film preparation was the deposition of 2-3 monolayers (ML) of Ti (determined retrospectively from the film coverages) onto the W(100)-O(2 × 1) surface at room temperature from the vapour of a metal wire (*Goodfellow*) using a commercial evaporator (*Omicron* EFM) with a deposition rate of 10^{-2} MLs^{-1}. The second step consisted of annealing under 2-7 × 10^{-7} mbar O_2 at 800-850 K between 1-1.5 hours, followed by cooling to room temperature in UHV. The final step was a UHV anneal to 920-980 K for 10 minutes. Sample temperatures were measured with an optical pyrometer (*Minolta*). Three TiO_2 films were studied, each grown under slightly different conditions: (1) A TiO_2(110)-(1 × 1) ultrathin film was formed by annealing to 840 K under 2-7 × 10^{-7} mbar O_2 for 1 hour and annealing in UHV at 970-990 K. (2) A TiO_2(110)-(1 × 2) ultrathin film was formed by annealing in 2-7 × 10^{-7} mbar O_2 for 1.5 hours at 840 K and annealing to 920 K in UHV. (3) A TiO_2(110)-(1 × 1)/lepidocrocite-TiO_2 ultrathin film was annealed at 840 K at 2-7 × 10^{-7} mbar O_2 for 1 hour, then annealing to 920 K in UHV.

3. Results and Discussion

3.1 TiO_2(110)-(1 × 1) Ultrathin Film

STM images are displayed in Fig. 1. In the large area (100 × 85 nm^2) image of Fig. 1*a*, islands with mean heights of 2 nm, lengths of 15-20 nm, and widths of 7-10 nm can be seen, the coverage being ~2.4 MLE. The heights corresponds to six TiO_2(110) layers and the islands are elongated in the principal directions of the W(100) substrate. In the high resolution STM image (Fig. 1*b*) taken from the top of one of the TiO_2(110) islands, the characteristic TiO_2(110) topography can be observed. Point defects resolved between bright rows of Ti atoms are consistent with the observations of Pang *et al*..[19] Given that the film was left in a UHV chamber with a background water pressure of 2 × 10^{-11} mbar (estimated from RGA) for 76 hr after forming the film (~3 Langmuirs), we assume that the defects are bridging hydroxyl (OH_b), the coverage being 0.19 ML, where 1 ML is the density of Ti_{5c} sites.[13]

3.2 TiO_2(110)-(1 × 2) Ultrathin Film

The second film was prepared in a similar manner to the (1 × 1) film described in the previous paragraph except the final UHV anneal was at a reduced temperature of 920 K (as compared to 970-990 K). In some areas, islands of rutile TiO_2 (110)-(1 × 1) were observed with the same characteristics as in Fig. 1. In other regions the islands have a different structure. Fig. 2*a* depicts a large area image of the film. As with the (1 × 1) islands, these are also elongated in the [001] and [010] directions of W(100). Within the islands, rows can be observed and these run parallel to the direction of elongation. This row structure is more apparent in the high-resolution image in Fig. 2*b* and it is apparent that the rows have a spacing of 1.25 nm ± 0.05 nm which is consistent with the rutile TiO_2(110)-(1 × 2) reconstruction.[38-51] The coverage of the film is 3.1 MLE. In Fig. 2*b*, the surface shown contains three different layers, all displaying the (1 × 2) reconstruction. The line profile in Fig. 2*c* shows that the height of the step (0.30 nm ± 0.02 nm) is consistent with a step edge of TiO_2(110). This is the first time, to our knowledge, the (1 × 2) surface reconstruction has been observed on an ultrathin TiO_2 film on W(100). The (1 × 2) reconstruction is a reduced phase of TiO_2 and is thought to be composed of added rows of Ti_2O_3.[45,47]

Such a film containing a (1 × 2) reconstruction has been previously reported in connection with a Ni(110) substrate,[16] where its appearance was attributed to incomplete oxidation of the as-deposited Ti. The growth conditions for the (1 × 2) film involved a longer oxidation step than for the (1 × 1) film, and a final anneal step at a lower temperature. The lower temperature of the final anneal step may lead to incomplete oxidation of the Ti.

3.3 TiO_2(110)-(1 × 1)/lepidocrocite-TiO_2 Ultrathin Film

Fig. 3*a* shows a large area STM image of the film. Two distinct overlayers were observed with quite different mean heights. The taller of these overlayers corresponds to islands of rutile TiO_2 (110). The islands have mean heights of 2-2.5 nm. Co-existing with these islands is a pseudo-2D or 'nanosheet' overlayer that has a uniform height of ~0.5 nm. This nanosheet has a similar appearance and height to the lepidocrocite-like phases reported previously.[15,17,18,27,31,36] The rutile islands have an area coverage of 25% and the nanosheet 42%. This corresponds to MLE coverages of 1.7 MLE and 0.42 MLE, respectively.

Higher resolution images of the nanosheet recorded from a different region of the sample are displayed in Fig. 4. Fig 4*a* is a large area image and shows a long-range periodicity of ~2.0 nm along the [010] direction of the W(100) substrate. This periodicity is more apparent in the zoomed-in image of Fig 4*b*. The image in Fig. 4*b* resembles a Moiré pattern with a short lattice and a superlattice that is periodic in the W(100) [010] direction. The short lattice has dimensions of 0.37 nm ± 0.02 nm in the W(100) [010] direction while being exactly matched with the substrate at 0.30 nm ± 0.02 nm in the W(100) [001] direction. The superlattice is 2.20 nm ± 0.02 nm (or six times the short lattice) in the W(100) [010] direction.

Fig. 5 shows LEED patterns simulated from the real-space lattice parameters together with a photograph of a LEED pattern recorded at 50 eV. Fig. 5*a* and 5*b* depict two orthogonal W(100)-O(2 × 1) reflexes which are calculated from the lattice parameters of W(100)-O(2 × 1). Fig. 5*c* and Fig. 5*d* show two orthogonal patterns with (1 × 7) periodicity with respect to W(100). These are assigned to the superlattice of the nanosheet phase. Fig. 5*e* is a superposition of all of these, which reproduces accurately the LEED pattern presented in Fig. 5*f*. The {0 , ½} reflexes are consistent with either TiO_2(110) or W(100)-O(2 × 1). According to our interpretation of the LEED pattern, the superlattice should be seven times the W(100) lattice (0.316 nm) which gives the periodicity of the superlattice as 2.21 nm, consistent with the STM measurement.

A simple model derived from the LEED and STM data is shown in Fig. 6. The substrate W(100)-(1 × 1) lattice is shown with black circles. Superimposed on this is the nanosheet layer. With respect to the azimuths of the W(100), in the [001] direction, the two are exactly matched, whereas in the [010] direction, the nanosheet layer does not coincide and has a spacing of 0.369 nm. This leads to a commensurate (1 × 7) lattice that has a period of six times the lattice parameter of the nanosheet layer and seven times the W(100) lattice.

The theoretical lattice parameters for the substrate-free TiO_2 lepidocrocite-like phase is calculated at 0.373 nm × 0.302 nm by Vittadini *et al*.[34] and 0.3766 nm × 0.3007 nm by Atrei *et al*..[18] Thus the long side of our nanosheet unit cell would only represent a very modest contraction of 1.1-2.1% from the calculated values of the lepidocrocite-like phase. This compares to an expansion of 3.4-4.4% to 0.39 nm for the lepidocrocite-like phase on Pt(110)-(1 × 2)[35] and a contraction of 3.2-4.2% to 0.361 nm for the same film on Ag(100).

The short side of our nanosheet unit cell (0.316 nm) also only represents a small expansion from the theoretical values of 4.3-5%. For comparison, the lepidocrocite-like phase on Ag(100) has a maximum contraction of 4-4.6% to 0.289 nm, making the short direction commensurate with the substrate. The short side of lepidocrocite-like phase unit cell on Pt(110)-(1 × 2), was measured in STM to have a length of 0.30 nm. This had an identifiable ×14 super cell with respect to the substrate in the [001] azimuth (0.277 nm).

As for the height of our nanosheet film, this was measured in STM to be 0.5 nm ± 0.05 nm. This is in agreement with the height of the lepidocrocite-like film on Ag(100) as determined by X-ray photoelectron spectroscopy and LEED intensity measurements.[18] On the other hand, Agnoli *et al*.[35] report an apparent height in STM of ~0.15 nm on Pt(110)-(1 × 2) but attribute this to electronic effects.

From this comparison, we conclude that our nanosheet phase is also a lepidocrocite-like phase. If the underlying substrate was W(100)-O(2 × 1) this would imply a ×3.5 coincident lattice in the W(100) [010] direction. As such, we believe the oxygen from the W(100)-O(2 × 1) is incorporated into the lepidocrocite-like phase which is then formed directly on the W(100) surface.

Poor stability of a delaminated titanate bilayer was observed previously by a transformation into anatase crystallites above 1070 K,[52] and we tested this on our film by annealing the sample to 1000 K. The (1 × 7) LEED spots were considerably weakened in intensity. Likewise, whereas before annealing the lepidocrocite-like overlayer had area coverage of 42 %, this was reduced to 3.3 % after annealing. The formation of the lepidocrocite-like phase may be related to the lower temperature of the final UHV step in comparison with the (1 × 1) film. In the two studies by Atrei *et al.,*[17,18] for the same growth conditions, the lepidocrocite-like phase was observed for up to one ML of Ti deposition, beyond which rutile TiO_2(110) islands co-exist on the surface. Thus another explanation for the appearance of the lepidocrocite-like phase in the current work could be related to the lower coverage of Ti used to make this film in comparison to the two rutile TiO_2 films presented.

4. Conclusion

We used STM to image rutile TiO_2(110)-(1 × 2) islands supported on W(100)-O(2 × 1). In addition, a TiO_2 lepidocrocite-like nanosheet was also shown to grow on W(100) and was characterised by STM and LEED. The unit cell of the film was 0.369 nm × 0.316 nm. The short side of the lattice was directly coincident with the W(100) substrate in one of the principal directions. A commensurate superstructure with respect to the substrate of 2.21 nm × 0.316 nm was observed. The modulation in height observed in STM had a period of 2.21 nm, six times the unit cell of the film and seven times the unit cell of the W(100) substrate.

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Figure Captions

1

STM images (+1.6 V, 0.05 nA) of the TiO_2(110)-(1 × 1)/ W(100)-O(2 × 1) film.

a) A large area (100 nm × 85 nm) image, showing the rutile TiO_2(110) island morphology with a coverage of 2.4 MLE. The azimuths are defined with respect to the W(100) surface. b) A high resolution (6.2 nm × 5.5 nm) image of the surface of a rutile island, six layers thick. The image is characteristic of the native TiO_2(110)-(1 × 1) surface: bright rows are Ti atoms, with point defects between on the bridging oxygen rows. The blue circle highlights a bridging hydroxyl (OH_b). The azimuths are defined with respect to the rutile TiO_2(110) surface.

2

STM images (+1.6 V, 0.05 nA) of the TiO_2(110)-(1 × 2)/W(100)-O(2 × 1) film.
a) A large area (100 nm × 100 nm) image of a 3.1 MLE titania film, displaying the TiO_2(110)-(1 × 2) surface reconstructed islands. Azimuths are defined with respect to the W(100) surface. b) A 9.5 nm × 9.5 nm image zoomed-in from the light-blue square in a displaying the (1 × 2) reconstruction. Azimuths are defined with respect to the rutile TiO_2 (110) surface. c) Line profiles taken from the image in b. The black profile displays the step edge on the island (0.30 nm ± 0.02 nm) and the light-blue profile shows the 1.25 nm ± 0.05 nm periodicity in the $[\bar{1}10]$ **direction, as well as another 0.30 nm ± 0.02 nm step edge.**1. …

3

STM images (+1.6 V, 0.05 nA) of the TiO_2/W(100)-O(2 × 1) film.
a) A large area 100 nm × 75 nm image of the titania film. TiO_2(110) islands are present together with the lepidocrocite-like TiO_2 nanosheet. A hole in one island is circled in green, and is presumably due to some interaction with the tip. The rutile TiO_2(110) islands and lepidocrocite-like film have coverages of 1.7 MLE and 0.42 MLE, respectively. b) The line profile taken from the line indicated in a, shows the heights of a rutile TiO_2(110)–(1 × 1) island and the lepidocrocite-like phase, which are 2.0-2.5 nm and 0.5 nm, respectively.

4

STM images (+1.6 V, 0.05 nA) of the W(100)-O(2 × 1)-lepidocrocite-like film. Islands of 0.5 nm height, orientated in the principal directions of the W(100) crystal are observed, azimuths are defined with respect to the W(100) surface. a) A large area (25 nm × 15 nm) STM image shows the islands have periodic stripes separated by ~2 nm, with the islands elongated perpendicular to these stripes. b) A (8 nm × 6 nm) filtered image zoomed in from the green rectangle in a, where the primary unit cell and superlattice are visible (identified by black rectangles). The minor and major ticks on the blue line highlight this further. d) Line profile taken from black line in b displaying the [001] direction unit cell spacing of the lepidocrocite-like phase (0.30 nm ± 0.02 nm). c) Line profile taken from the light blue line in b depicting the periodicity of the superlattice (2.20 nm ± 0.02 nm) in the [010] direction.

5

LEED patterns of the TiO_2 and lepidocrocite-like films on W(100)-O(2 × 1).

a,b) Schematics of the two orthogonal, calculated LEED patterns of W(100)-O(2 × 1), with a real space unit cell of (0.316 nm × 0.632 nm). c,d) Schematics of the two orthogonal, calculated LEED patterns of a lepidocrocite-like film (L-TiO_2) that has (1 × 7) periodicity with respect to W(100) and a real space unit cell of (0.316 nm × 2.21 nm). e) A superposition of schematics in a-d forming the predicted LEED pattern. f) LEED pattern of the film at 50 eV, which compares favorably with e. Azimuths are defined with respect to the W(100) surface.

6
TiO_2 lepidocrocite overlayer schematic.
A schematic representation of the TiO_2 lepidocrocite-like phase in red circles (0.369 nm × 0.316 nm) superimposed on top of the W(100)–(1 × 1) surface (0.316 nm × 0.316 nm) in black circles. These parameters were derived from the STM and LEED data. Azimuths are defined with respect to the W(100) surface.