THE JOURNAL OF
PHYSICAL CHEMISTRY C

Article

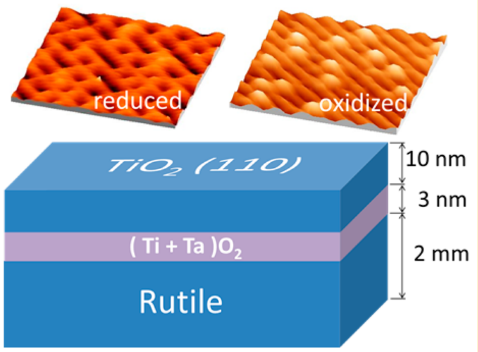
pubs.acs.org/JPCC

Decoupling a Thin Well-Ordered $TiO_2(110)$ Layer from a $TiO_2(110)$ Substrate with a Ti + Ta Mixed Oxide Interlayer

Xin Song, Elena Primorac, Helmut Kuhlenbeck,* and Hans-Joachim Freund

Chemical Physics Department, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany

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 $Ni_{94}Ti_6(110)$,[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 ∼1 × 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

Received: February 6, 2016
Revised: April 1, 2016
Published: April 1, 2016

DOI: 10.1021/acs.jpcc.6b01318
J. Phys. Chem. C 2016, 120, 8185−8190

Table 1. Structural Parameters of Some Oxides with Rutile Type Structure[a]

	TiO_2	β-PbO_2	TaO_2	WO_2
cation radius	0.75 Å	0.92 Å	0.82 Å	0.80 Å
structure	tetragonal	tetragonal	tetragonal	monoclinic
lattice constant	a = 4.59 Å	a = 4.91 Å	a = 4.96 Å	a = 5.56 Å, b = 4.90 Å
	c = 2.95 Å	c = 3.39 Å	c = 3.39 Å	c = 5.66 Å, β = 120.5°

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

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 $4f_{7/2}$ 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 $TiO_2(110)$ layers and therefore their electronic and geometric structure differs from that of $TiO_2(110)$ 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 $I_{\text{plotted}}^{\text{compound}} = I_{\text{raw}}^{\text{compound}} - C^{\text{compound}} I^{\text{methanol,mass31}}$ with C^{compound} being numbers derived from the fragmentation pattern of methanol and the sensitivity factors as reported by the manufacturer of the mass spectrometer (Thermo Scientific).

The $TiO_2(110)$ substrate ($7 \times 8 \times 2$ mm^3, 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 ($Ti_{0.8}Ta_{0.2}O_2$, ~30 Å thick) was prepared on the $TiO_2(110)$ substrate by codeposition of Ta and Ti in an oxygen ambient atmosphere (1×10^{-6} mbar). Subsequently, an epitaxial $TiO_2(110)$ 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.

■ 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 Ti^{4+} 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 TiO_2 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 PbO_2 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 TiO_2 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 TiO_2) is conceivable (we did not check this), high-quality uniform $TiO_2(110)$ 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 $TiO_2(110)$ layer upon thermal treatment. Figure 1

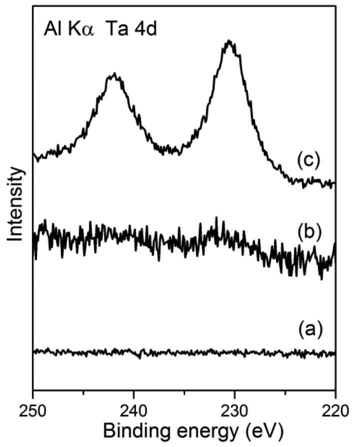


Figure 1. XPS spectra (Al Kα: 1486.6 eV, normal emission) of the Ta 4d core level measured of (a) a freshly prepared $TiO_2(110)$ thin film, (b) the $TiO_2(110)$ thin film after annealing in a vacuum at 900 K for more than 2 h, and (c) the as-prepared Ti + Ta mixed oxide blocking layer.

DOI: 10.1021/acs.jpcc.6b01318
J. Phys. Chem. C 2016, 120, 8185−8190

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.

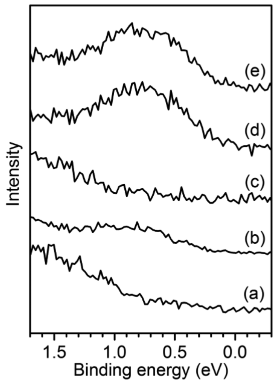


Figure 2. Surface-sensitive HeI UPS spectra (electron detection at 70° off-normal) of the $TiO_2(110)$ band gap region. (a) Single crystal annealed at 800 K in 10^{-6} mbar of O_2 for 10 min, (b) single crystal reduced by sputtering at room temperature and annealing at 800 K for 10 min, (c) $TiO_2(110)$ thin film annealed at 800 K in 10^{-6} mbar of O_2 for 10 min, (d) $TiO_2(110)$ thin film reduced by sputtering at room temperature and annealing at 800 K for 10 min, and (e) the layer produced in step (d) annealed for 10 more min at 800 K in a vacuum.

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 $TiO_2(110)$ 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 $TiO_2(110)$ substrate and the oxidized $TiO_2(110)$ 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 in a vacuum 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,[24] but there is agreement that it is due to reduced cations.[24−26] 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 $TiO_2(110)$ 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 ("Ti^{3+}") but also to nonreduced cations ("Ti^{4+}") since their diffusion would also lead to a balance of the degree of reduction between substrate and overlayer.

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 $TiO_2(110)$ thin film was performed by annealing in O_2 (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.

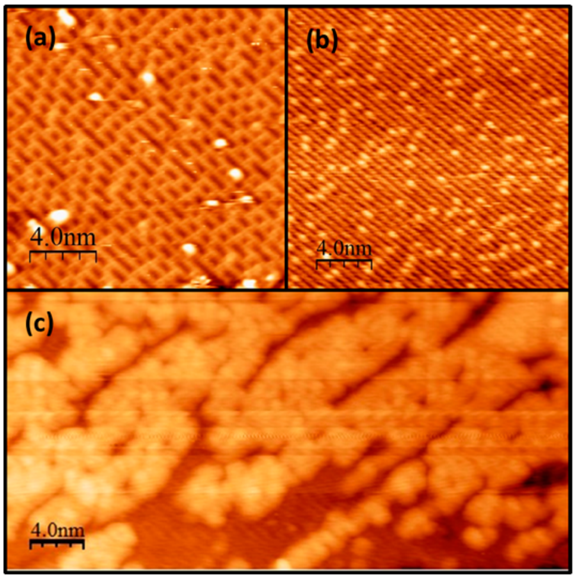


Figure 3. STM images (2.0 V, 0.1 nA) obtained after (a) annealing a $TiO_2(110)$ thin film in vacuum at 900 K for 20 min, (b) oxidizing a $TiO_2(110)$ thin film in 10^{-6} mbar of O_2 at 600 K for 10 min, and (c) oxidizing a regular $TiO_2(110)$ substrate in 10^{-6} mbar of O_2 at 600 K for 10 min. For the images shown in panels (b) and (c) the samples were annealed at 800 K in a vacuum prior to oxidation which resulted in flat surfaces with large terraces.

When oxidizing a bulk crystal at 600 K, rosette-like structures and/or small islands of TiO_2 are usually formed at the surface (Figure 3c) through the reaction of O_2 with reduced cations diffusing from the bulk to the surface, making the surface rough.[12] 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 TiO_2 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.[25,27] The oxygen adatoms are assumed to originate from the dissociation of O_2 molecules at the bridging oxygen vacancies and Ti sites.[25,27]

Methanol TPD was used to characterize the chemical reactivity of the thin films. Figure 4 compares TPD spectra of methanol on a $TiO_2(110)$ thin film (solid lines) and on a

DOI: 10.1021/acs.jpcc.6b01318
J. Phys. Chem. C 2016, 120, 8185−8190

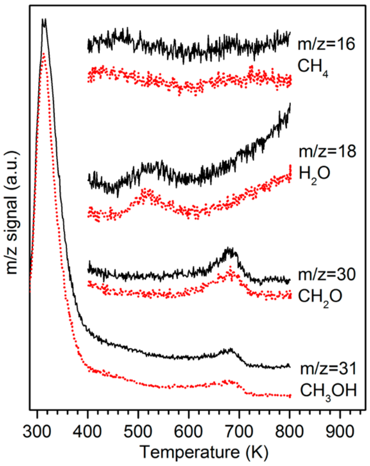


Figure 4. TPD spectra (mass-to-charge ratio 16, 18, 30, and 31) of methanol adsorbed at room temperature onto thin film $TiO_2(110)$ (solid line, black) and a $TiO_2(110)$ single crystal (dotted line, red). Both samples were annealed in a vacuum at 800 K for 10 min prior to methanol adsorption.

$TiO_2(110)$ single crystal (dotted lines). Prior to methanol adsorption the samples were reduced by annealing in vacuo at 800 K for 10 min. Spectra for different desorbing compounds are shown. They are apparently very similar for both surfaces, which clearly shows that the chemical properties of the thin film surface are very similar to those of the single crystal surface. A similar degree of surface reduction (the single crystal had a dark blue color) is responsible for the similar intensities in both sets of spectra. The large peak at 350 K in the $m/z = 31$ spectrum (methanol) is assigned to methanol produced by the recombination of methoxy and hydroxyl resulting from the dissociation of methanol on 5-fold-coordinated Ti sites at the TiO_2 surface.[28,29] Beside this intense peak, another methanol peak is found at 680 K. No peak of methane was observed but a prominent peak of water around 520 K. Additionally, formaldehyde ($m/z = 30$) is produced at 680 K.

Henderson and coauthors did also study methanol adsorption on reduced $TiO_2(110)$.[28] They did neither observe a methanol or a formaldehyde desorption peak at 680 K, and also water desorption was not observed in their experiment. We note that methanol was dosed at low temperature (~100 K) in this study while it was dosed at room temperature in the present case. However, we observe the TPD peaks at 680 K also when dosing is performed at low temperature (not shown here). Other researchers found a formaldehyde desorption peak at 680 K[30,31] but no methanol desorption at this temperature. The production of formaldehyde was explained through the decomposition of methoxy groups that were stabilized at bridging oxygen vacancies.:[32]

$$CH_3O_{(a)} \rightarrow H_2CO_{(g)} + H_{(a)} \tag{1}$$

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:

$$CH_3O_{(a)} + H_{(a)} \rightarrow CH_3OH_{(g)} \tag{2}$$

Such a methanol production mechanism was also postulated by other researchers, with the reaction details being somewhat different.[28,33] An interesting question is why the methoxy 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[34] 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.[35] 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.[28,33] 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.[28,30,31,33,36] 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.[28,33,36] 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,[34] which again fits quite well to the computed energy barrier of 1.76 eV obtained by Lang et al. with DFT.[35]

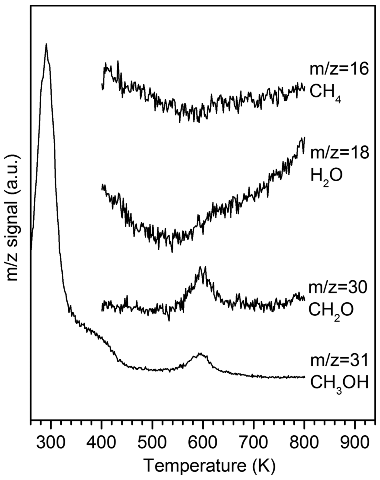


Figure 5. TPD spectra (mass-to-charge ratio 16, 18, 30, and 31) of CH_3OH adsorbed on a $TiO_2(110)$ thin film annealed in O_2 at 600 K.

■ 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 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 TiO_2 comes into play. In fact, a well-mixed oxide layer of vanadia and titania has recently successfully been prepared based on this method.[37]

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 $TiO_2(110)$.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail kuhlenbeck@fhi-berlin.mpg.de; Tel +49-30-8413-4222.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge the Deutsche Forschungsgemeinschaft (DFG) for funding through their collaborative research center 546, “Transition Metal Oxide Aggregates”.

■ 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

(1) Munuera, G.; Fernandez, A.; Soria, J.; Conesa, J.; Sanz, J. Mechanism of Hydrogen Gas-Sensing at Low Temperatures Using Rh/TiO_2 System. *Sens. Actuators* **1989**, *18*, 337−348.

(2) Johansson, L. Static SIMS Studies of Coated TiO_2 Pigments. *Surf. Interface Anal.* **1993**, *20*, 304−308.

(3) Sathiyanarayanan, S.; Azim, S. S.; Venkatachari, G. Corrosion Protection of Magnesium ZM 21 Alloy with Polyaniline-TiO_2 Composite Containing Coatings. *Prog. Org. Coat.* **2007**, *59*, 291−296.

(4) Yan, M. F.; Rhodes, W. W. Preparation and Properties of TiO_2 Varistors. *Appl. Phys. Lett.* **1982**, *40*, 536−537.

(5) Pandey, R. N.; Babu, K. S. C.; Srivastava, O. N. High Conversion Efficiency Photoelectrochemical Solar Cells. *Prog. Surf. Sci.* **1996**, *52*, 125−192.

(6) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. Environmental Applications of Semiconductor Photocatalysis. *Chem. Rev.* **1995**, *95*, 69−96.

(7) Fujishima, A.; Zhang, X.; Tryk, D. A. TiO_2 Photocatalysis and Related Surface Phenomena. *Surf. Sci. Rep.* **2008**, *63*, 515−582.

(8) Diebold, U. The Surface Science of Titanium Dioxide. *Surf. Sci. Rep.* **2003**, *48*, 53−229.

(9) Pang, C. L.; Lindsay, R.; Thornton, G. Structure of Clean and Adsorbate-Covered Single-Crystal Rutile TiO_2 Surfaces. *Chem. Rev.* **2013**, *113*, 3887−3948.

(10) Dohnálek, Z.; Lyubinetsky, I.; Rousseau, R. Thermally-Driven Processes on Rutile $TiO_2(110)$-(1×1): A Direct View at the Atomic Scale. *Prog. Surf. Sci.* **2010**, *85*, 161−205.

(11) Pang, C. L.; Lindsay, R.; Thornton, G. Chemical Reactions on Rutile $TiO_2(110)$. *Chem. Soc. Rev.* **2008**, *37*, 2328−2353.

(12) Li, M.; Hebenstreit, W.; Diebold, U.; Tyryshkin, A. M.; Bowman, M. K.; Dunham, G. G.; Henderson, M. A. The Influence of the Bulk Reduction State on the Surface Structure and Morphology of Rutile $TiO_2(110)$ Single Crystals. *J. Phys. Chem. B* **2000**, *104*, 4944−4950.

(13) Bowker, M. The Surface Structure of Titania and the Effect of Reduction. *Curr. Opin. Solid State Mater. Sci.* **2006**, *10*, 153−162.

(14) Freund, H.-J.; Pacchioni, G. Oxide Ultra-Thin Films on Metals: New Materials for the Design of Supported Metal Catalysts. *Chem. Soc. Rev.* **2008**, *37*, 2224−2242.

(15) Kuhlenbeck, H.; Shaikhutdinov, S.; Freund, H.-J. Well-Ordered Transition Metal Oxide Layers in Model Catalysis–a Series of Case Studies. *Chem. Rev.* **2013**, *113*, 3986−4034.

(16) Atrei, A.; Bardi, U.; Rovida, G. Structure and Composition of the Titanium Oxide Layers Formed by Low-Pressure Oxidation of the $Ni_{94}Ti_6(110)$ Surface. *Surf. Sci.* **1997**, *391*, 216−225.

(17) Lai, X.; Guo, Q.; Min, B. K.; Goodman, D. W. Synthesis and Characterization of Titania Films on Mo(110). *Surf. Sci.* **2001**, *487*, 1−8.

(18) Papageorgiou, A. C.; Pang, C. L.; Chen, Q.; Thornton, G. Low-Dimensional, Reduced Phases of Ultrathin TiO_2. *ACS Nano* **2007**, *1*, 409−414.

(19) Atrei, A.; Cortigiani, B.; Ferrari, A. M. Epitaxial Growth of TiO_2 Films with the Rutile (110) Structure on Ag(100). *J. Phys.: Condens. Matter* **2012**, *24*, 445005−445013.

(20) McCavish, N. D.; Bennett, R. A. Ultra-Thin Film Growth of Titanium Dioxide on W(100). *Surf. Sci.* **2003**, *546*, 47−56.

(21) Pang, C. L.; Grinter, D. C.; Matharu, J.; Thornton, G. A Scanning Tunneling Microscopy Study of Ultrathin Film Rutile $TiO_2(110)$ Supported on W(100)-O(2×1). *J. Phys. Chem. C* **2013**, *117*, 25622−25627.

(22) Feulner, P.; Menzel, D. Simple Ways to Improve “Flash Desorption” Measurements from Single Crystal Surfaces. *J. Vac. Sci. Technol.* **1980**, *17*, 662−663.

(23) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-Ray Photoelectron Spectroscopy*; Perkin-Elmer Corporation: Eden Prairie, MN, 1992.

(24) Yim, C. M.; Pang, C. L.; Thornton, G. Oxygen Vacancy Origin of the Surface Band-Gap State of $TiO_2(110)$. *Phys. Rev. Lett.* **2010**, *104*, 2−5.

(25) Wendt, S.; Sprunger, P. T.; Lira, E.; Madsen, G. K. H.; Li, Z.; Hansen, J. Ø.; Matthiesen, J.; Blekinge-Rasmussen, A.; Laegsgaard, E.; Hammer, B.; et al. The Role of Interstitial Sites in the Ti3d Defect State in the Band Gap of Titania. *Science* **2008**, *320*, 1755−1759.

(26) Di Valentin, C.; Pacchioni, G.; Selloni, A. Reduced and N-Type Doped TiO_2: Nature of Ti^{3+} Species. *J. Phys. Chem. C* **2009**, *113*, 20543−20552.

(27) Wendt, S.; Schaub, R.; Matthiesen, J.; Vestergaard, E. K.; Wahlström, E.; Rasmussen, M. D.; Thostrup, P.; Molina, L. M.; Lægsgaard, E.; Stensgaard, I.; et al. Oxygen Vacancies on $TiO_2(110)$ and Their Interaction with H_2O and O_2: A Combined High-Resolution STM and DFT Study. *Surf. Sci.* **2005**, *598*, 226−245.

(28) Henderson, M. A.; Otero-Tapia, S.; Castro, M. E. The Chemistry of Methanol on the $TiO_2(110)$ Surface: The Influence of Vacancies and Coadsorbed Species. *Faraday Discuss.* **1999**, *114*, 313−329.

(29) Li, Z.; Smith, R. S.; Kay, B. D.; Dohnálek, Z. Determination of Absolute Coverages for Small Aliphatic Alcohols on $TiO_2(110)$. *J. Phys. Chem. C* **2011**, *115*, 22534−22539.

(30) Wong, G. S.; Concepcion, M. R.; Vohs, J. M. Reactivity of Monolayer V_2O_5 Films on $TiO_2(110)$ Produced via the Oxidation of Vapor-Deposited Vanadium. *Surf. Sci.* **2003**, *526*, 211−218.

(31) Wang, Q.; Madix, R. J. Partial Oxidation of Methanol to Formaldehyde on a Model Supported Monolayer Vanadia Catalyst: Vanadia on $TiO_2(110)$. *Surf. Sci.* **2002**, *496*, 51−63.

(32) Kim, K. S.; Barteau, M. A.; Farneth, W. E. Adsorption and Decomposition of Aliphatic Alcohols on Titania. *Langmuir* **1988**, *4*, 533−543.

(33) Farfan-Arribas, E.; Madix, R. J. Different Binding Sites for Methanol Dehydrogenation and Deoxygenation on Stoichiometric and Defective $TiO_2(110)$ Surfaces. *Surf. Sci.* **2003**, *544*, 241−260.

(34) Redhead, P. A. Thermal Desorption of Gases. *Vacuum* **1962**, *12*, 203−211.

(35) Lang, X.; Wen, B.; Zhou, C.; Ren, Z.; Liu, L.-M. First-Principles Study of Methanol Oxidation into Methyl Formate on Rutile $TiO_2(110)$. *J. Phys. Chem. C* **2014**, *118*, 19859−19868.

(36) Price, S. P.; Tong, X.; Ridge, C.; Neilson, H. L.; Buffon, J. W.; Robins, J.; Metiu, H.; Bowers, M. T.; Buratto, S. K. Catalytic Oxidation of Methanol to Formaldehyde by Mass-Selected Vanadium Oxide Clusters Supported on a $TiO_2(110)$ Surface. *J. Phys. Chem. A* **2014**, *118*, 8309−8313.

(37) Duncan, D. A.; Kreikemeyer-Lorenzo, D.; Primorac, E.; Karslioğlu, O.; Naschitzki, M.; Unterberger, W.; Kuhlenbeck, H.; Woodruff, D. P. V-Doped $TiO_2(110)$: Quantitative Structure Determination Using Energy Scanned Photoelectron Diffraction. *Surf. Sci.* **2014**, *630*, 64−70.