Ultrathin, ordered oxide films on metal surfaces

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Abstract

Metal oxides and oxide thin films are extensively used as active catalysts and catalytic supports, as well as in many other important technical applications. Unlike TiO\textsubscript{2}, which is a semiconductor and can be investigated using a variety of surface science techniques, most metal oxides are insulators, which seriously restricts their use as model surfaces with modern surface science techniques. This difficulty can be circumvented by synthesizing ultrathin oxide films a few nanometers in thickness with well-defined structures, that mimic the corresponding bulk oxides yet are thin enough to be sufficiently conducting. In this review, preparations, structures, electronic and chemical properties of four representative oxides, alumina, magnesium oxide, silica, and titania, are addressed. Of these MgO is found to grow in a layer-by-layer fashion, allowing preparation of crystalline thin film structures with varying thicknesses. Crystalline TiO\textsubscript{2} and Ti\textsubscript{2}O\textsubscript{3} can also be synthesized, whereas SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}, although amenable to synthesis as well-defined monolayer structures, have only been grown to date as amorphous multilayers.

(Some figures in this article are in colour only in the electronic version)

Acronyms used in the text

\begin{tabular}{ll}
AES & Auger electron spectroscopy \\
AFM & Atomic force microscopy \\
ARUPS & Angle resolved ultraviolet photoelectron spectroscopy \\
DFT & Density function theory \\
EELS & Electron energy loss spectroscopy \\
ESR & Electron spin resonance \\
FTIRS & Fourier transform infrared spectroscopy \\
HREELS & High-resolution electron energy loss spectroscopy \\
IR & Infrared \\
LEED & Low energy electron diffraction \\
LEIS & Low energy ion scattering spectroscopy \\
MIES & Metastable impact electron spectroscopy \\
ML & Monolayers \\
NC-AFM & Non-contact atomic force microscopy \\
PM-RAIRS & Polarization modulation reflectance absorption infrared spectroscopy \\
RAIRS & Reflectance absorption infrared spectroscopy \\
SFVS & Sum-frequency vibrational spectroscopy \\
STM & Scanning-tunneling microscopy \\
STS & Scanning-tunneling spectroscopy \\
TDS & Thermal desorption spectrometry \\
TPD & Temperature programped desorption \\
UHV & Ultrahigh vacuum \\
XPD & X-ray photoelectron diffraction \\
XPS & X-ray photoelectron spectroscopy \\
XRD & X-ray diffraction \\
\end{tabular}

1. Introduction

Oxides are fundamentally important in heterogeneous catalysis as active catalysts and as supports for metal clusters, and many other important applications [1]. Many of the traditional techniques used to study heterogeneous catalysts are limited with respect to atomic-level characterization of metal supported catalysts. Work over the last two decades has demonstrated that atomic-level surface science techniques...
can provide fundamental insights into the physics and chemistry of oxide surfaces by the synthesis of ultrathin oxide films [2–20]. Deposition of metal clusters onto these oxide films allows complexities of oxide-supported metal catalysts to be addressed. These specially prepared model systems offer advantages typically found for single crystals, while addressing important issues of supported catalysts such as metal cluster size effects and the role of the oxide support. Representative oxide thin films have been shown to mimic the chemical and physical properties of the corresponding bulk oxides, yet are electrically conductive [11]. The conductivity and planarity of these model catalysts allow study with various charged particle spectroscopies that comprise the core of modern surface science while being suitable for study with scanning-tunneling microscopy. Here we focus on recent results of well-defined, thin oxide films. Results for four prototype oxide supports, alumina, magnesia, silica, and titania, are addressed.

2. Alumina thin films

Aluminum oxide (Al$_2$O$_3$) is thermodynamically the most stable compound of aluminum over a wide temperature range, and is a widely used support for heterogeneous catalysts. Ultrathin Al$_2$O$_3$ ordered layers on alloys are used as templates for model catalysts, tunneling barriers in electronic devices, and corrosion-resistant layers. An ultrathin, well-ordered alumina film of 4–5 Å in thickness can be grown by dosing oxygen with a subsequent anneal on low-index terminations of NiAl alloys such as NiAl(110) [21, 22] and Ni$_3$Al(111) [23–25].

Epitaxial growth of highly ordered Al$_2$O$_3$ films on NiAl(110) at temperatures between 620 and 670 K has been demonstrated using LEED, EELS, HREELS, XPS, ARUPS, and STM [21, 26–28]. NC-AFM [29, 30] reveals atomic rows with a 9 Å periodicity for the well-ordered Al$_2$O$_3$/NiAl(110). The stoichiometry of the O–Al bonds during oxygen absorption and realignment during annealing are found to be important in the epitaxial growth of well-ordered crystalline films [28]. Oxygen adsorption on NiAl(001) at room temperature reaches saturation quickly after an initial high sticking probability [31]. Figure 1 (left panel) shows a series of HREEL spectra for increasing oxygen exposure at room temperature on NiAl(110) [21]. The related Al–O phonon shifts from 774 to 847 cm$^{-1}$ as a function of dosed oxygen up to saturation (1200 L). Annealing this oxygen saturated surface at 1000 K leads to a shift in the primary Al–O shifting to 880 cm$^{-1}$ as shown in figure 1 (middle panel). Because an α-Al$_2$O$_3$ single crystal exhibits only two loss features at 496 and 806 cm$^{-1}$ [32], a structural model similar to γ-Al$_2$O$_3$ was proposed. Four distinct loss features at 420, 603, 718 and 896 cm$^{-1}$ were identified for Al$_2$O$_3$/NiAl(001) as shown in figure 1 (right panel) [31]. Group theory predicts six normal vibrational modes for an octahedral structure, with only two being infrared active. For the tetrahedral structure there are also two infrared active modes with four normal modes. In α-Al$_2$O$_3$, Al$^{3+}$ ions occupy octahedral sites, resulting in two loss features at 496 and 816 cm$^{-1}$ [32]. Thus, it was concluded that in Al$_2$O$_3$ thin films, the Al$^{3+}$ ions occupy both octahedral and tetrahedral sites, as in γ-Al$_2$O$_3$ [31]. This conclusion is supported by XRD [33] and high-resolution soft XPS [34].
Based on XRD [33] and high-resolution soft XPS [34] data, the highly ordered Al2O3/NiAl(110) thin film is proposed to consist of a double layer of strongly distorted hexagonal oxygen ions with aluminum ions in octahedral and tetrahedral sites (see figure 2). DFT calculations [35] support a model with an almost coplanar Al–O layer, as predicted for terminated bulk single crystal alumina surfaces. The film structure is characterized by Al ions in different coordinative environments, i.e. octahedral and tetrahedral, and compares with the structure believed to exist on an oxygen deficient corundum surface. The stoichiometry of the film is estimated with the structure believed to exist on an oxygen deficient environments, i.e. octahedral and tetrahedral, and compares towards a variety of gas molecules, indicating no unsaturated surface bonds. Highly ordered and stoichiometric thin Al2O3 films with various thicknesses have also been prepared on a Mo(110) [45], Mo(100) [46] and Ru(0001) [47].

### 3. Magnesium oxide thin films

Magnesium oxide (MgO) is an ionic oxide of a rock-salt structure with alternation of ions with opposite charges [48]. MgO is often chosen as representative of metal oxides, due to its simple bulk and (100) surface structures. The (100) surface is stable, irreducible, nonpolar, and easy to prepare with well-defined stoichiometry [49–51]. Oxygen vacancies leave electrons trapped in the vacancy, i.e. a pair or a single electron as F or F+ centers, respectively. The oxygen vacancies are of great importance in defining the overall properties and chemical reactivity of MgO [52–55]. Well-ordered surfaces of MgO with low-defect density can be created by cleaving bulk single crystals. MgO is one of the most commonly used catalyst supports and is used in semiconductor devices as a high-k dielectric [56]. MgO(100) films have been prepared mainly on Mo(100) and Ag(100) substrates. Epitaxial MgO(100) with a thickness ranging from 2 to 100 ML can be grown by evaporating Mg onto Mo(100) at 300 K in 10−6 Torr of oxygen [57–67]. LEED indicates the growth of MgO(100) films with the MgO(110) oriented along the ⟨100⟩ direction of the Mo(001) substrate [68–70]. Despite the insulating nature of bulk MgO, films up to 15 ML thick have been imaged by STM [71, 72]. The films, stable up to 1300 K, are reduced at higher temperatures by the Mo substrate, forming MoO3 and Mg vapor. The electronic and vibrational structure of thin MgO films (see figure 3) are very similar to those of the bulk oxide [73–80]. The main difference between the thin films and bulk MgO(001) is the higher defect density in the former compared to the latter [81]. MgO(100)/Ag(100) systems have been prepared by evaporating metallic Mg from an alumina crucible in an oxygen background of 5 × 10−7 Torr at 350 K followed

![Figure 2. Structural models of ultrathin alumina films on (A) NiAl(110) and (B) Ni3Al(111).](image-url)
by annealing to 500 K [82–93]. As in the case of MgO(100)/Mo(100) [50, 57–61, 94–98] the as-prepared film appears to be free of point defects (color centers). Upon irradiation with electrons, color centers can be produced and detected by EELS. Exposure to oxygen quenches these defects indicating their presence within the surface layer. Low-temperature STM has been used to image the growth of the MgO(100) film on Ag(100) and the creation of color centers [84, 85, 88]; a series of images is shown in figure 4. MgO initially forms two-dimensional square islands homogeneously distributed on the surface. At 1 ML, approximately 60% of the substrate surface is covered by 2D domains. At MgO coverages of 2–3 ML, the surface is completely covered, with a typical terrace size of ∼20 nm. Layer-resolved differential conductance (dI/dU) measurements show that a three monolayer film has a band gap of ∼6 eV, comparable to a MgO(001) single crystal. Layer-resolved DFT calculations corroborate this finding [88]. This MgO film exhibits line defects by LEED profile analysis; point defects only become apparent via STS after electron bombardment; these paramagnetic surface colors centers have been detected using ESR spectroscopy [84]. These results can be directly compared with studies on powder samples [99–101]. On mono- and bilayer domains of MgO/Ag(001), the edges are mainly oriented along the (110) oxide direction, corresponding to polar perimeters, while on multilayer domains nonpolar perimeters appear, corresponding to the (100) orientation [102].

Thin MgO films (1–20 ML) synthesized by evaporating metallic Mg in an oxygen atmosphere onto Ag(100) exhibit a relative small lattice misfit (3.1%) between the (100) surface of fcc Ag and the MgO rock-salt structure. This lattice match facilitates epitaxial growth of MgO layers with (001)MgO parallel to (001)Ag and (100)MgO parallel to (100)Ag [87]. In spite of the weak interaction between the oxide overlayer and the substrate, there is significant tetragonal distortion of the MgO structure. At a substrate temperature of 450 K, a single-domain MgO film ([100] (film) || [100] (substrate)) grows heteroepitaxially on Ag(100) [103]. The in-plane lattice constant of the film changes continuously from the substrate value to that of the film. MgO adsorbs preferentially with the oxygen atom over the Ag atom and the Mg atom over the hollow site. The lattice constant increases gradually from bulk Ag(100) to that of bulk MgO(100). The lattice constant of the film is nearly equal to that of bulk MgO for films thicker than 20 ML.

The local atomic structure of MgO epitaxial layers on Ag(100) has been determined by polarization-dependent XAS at the Mg(K) and O(K) edges [104]. At the ultrathin limit, the local structure of the films is rock salt. An in-plane compressive strain, due to lattice mismatch with the Ag substrate, is present for the 3 ML film. The out-of-plane lattice constant is found to expand, in agreement with the expected behavior for a tetragonal distortion of the unit cell. This growth-induced strain is gradually released with increasing thickness and is almost completely relaxed at 20 ML. Any significant intermixing with the Ag substrate has been ruled out.

Figure 5 shows vibrational spectra for MgO films on Ag(100) as a function of MgO thickness [105]. Several features are present in the range between 400 and 700 cm⁻¹, with the position and intensity strongly dependent on film thickness. A phonon feature maximum at ∼524 cm⁻¹ appears for each film shifting little with thickness. The phonon at 572–677 cm⁻¹ appears after the growth of the second layer, with a significant intensity increase and a blue shift in peak position. For a thicker MgO film on Mo(100), a single phonon at 656 cm⁻¹ was observed. No specific vibrational modes
were assigned in [105]; however, various arrangements of the oxygen species, i.e. Mg–O–Ag and Mg–O–Mg, are likely at the ultrathin limit.

The growth of epitaxial and stoichiometric MgO(111) thin films on a Mo(110) surface has been demonstrated using LEED, XPS, AES, and LEIS [106, 107]. The MgO(111)/Mo(110) film is stable up to 1400 K, and is reduced by the Mo substrate at higher temperature, forming MoO3 and Mg vapor. By alternating the deposition of Mg and O2, layer-by-layer growth of polar MgO(111) ultrathin films with Mg-terminated or O-terminated surfaces has been successfully carried out on a Mo(110) substrate [108]. The geometric structure of MgO deposited on Fe(001) in UHV was determined in detail using XRD [109]. In contrast to the common belief that MgO grows in direct contact to the Fe(001) substrate, a FeO interface layer between the substrate and the growing MgO structure was proposed. MgO films with a thickness of 2 nm have been reported to grow on W(110) [110].

4. Silica thin films

Silica (SiO2) is an important support material used in many commercial catalyst systems [1]. Thin amorphous SiO2 films have been synthesized on Mo(110) and Mo(100) substrates [16, 111–113] by evaporating silicon onto the respective substrate at room temperature in < ~2 × 10−5 Torr O2 background followed by an anneal at < ~1300 K. The as-prepared film is predominantly silicon dioxide with a small fraction of suboxides (SiO) as indicated by AES, XPS and RAIRS. Annealing to approximately 1300 K yields a stoichiometric film of SiO2. The suboxides are believed to react further with oxygen to form SiO2 at elevated temperatures. The silicon oxide films prepared at room temperature exhibit additional low energy electron loss features at ~5 and 7 eV. These features are attributed to a local structure with broken Si–O bonds in tetrahedra of (SiO4) and the presence of some suboxide. After annealing at ~1200 K, these features disappear, yielding EELS features essentially identical to those of vitreous silica. These results are consistent with the formation of low-defect vitreous silica consisting of (SiO4) tetrahedra connected by an oxygen bridge to form a long-range 3D network. RAIRS (see figure 6) further illustrates that such structural changes occur when the silicon dioxide films are annealed. The asymmetric stretching mode of the Si–O bonds appears as a broad asymmetric peak centered at 1178 cm−1 in the RAIRS spectrum for the film prepared at a substrate temperature of 323 K. This peak gradually shifts to higher frequency upon heating and reaches a maximum of 1252 cm−1 as the silicon dioxide film is annealed to > ~1300 K. Furthermore, the line shapes, the peak energies of the AES electrons, and the EELS spectra are consistent with those of silicon dioxide. The SiO2 films are thermally stable up to 1600 K with the stability increasing with film thickness. At high temperatures, silicon dioxide is reduced by the Mo substrate to form volatile SiO and MoO3.

Ordered silica films have been grown on Mo(112) [114–117]. This film, which exhibits a sharp c(2 × 2) LEED pattern, was shown to have a thickness of 1 ML as estimated from AES intensity attenuation of the Mo(MNN) feature (187 eV) and to exhibit self-limited growth properties [118–120]. The orientation and growth of benzene and pyridine were used to characterize the quality of the SiO2 films via HREELS, AES and LEED [121]. A single vibrational mode corresponding to the Si–O asymmetric vibration was observed at ~1050 cm−1 as indicated in figure 6, which is significantly lower than that of ~1180 cm−1 observed for a thicker SiO2 films or single crystal. Regarding the fact that the film thickness is 1 ML, this mode at ~1050 cm−1 was assigned to the asymmetric vibration of Si–O–Mo [118]. The absence of the mode for the asymmetric vibration of Si–O–Si for this ultra thin film led to the conclusion that the film thickness was no greater than 1 ML, and to the conclusion that the structure consists of isolated (SiO4) units as shown in figure 7 (A) [118], a conclusion supported by DFT calculations [122]. In contrast a 2D network of SiO2 tetrahedra where one oxygen is bound to the metal substrate and the other three form a hexagonal honeycomb structure (see figure 7(B)) has been proposed [123–127]. This 2D network model in fact contradicts experimental results [118, 121, 128]. The axis of the Si–O–Si in the 2D network model is proposed to be parallel with the surface, thus the asymmetric vibrational mode of Si–O–Si should be infrared inactive, yet is absent in IRAS and on-specular HREEL spectra. Also off-specular HREEL shows no feature at ~1176 cm−1 characteristic of the asymmetric vibration of Si–O–Si (figure 8). Furthermore the bending mode of Si–O–Si in the proposed 2D network model lies perpendicular to the surface, i.e. infrared active, yet is not observed in HREEL data (see figure 6) [118, 128]. The DFT
Figure 6. Left panel: infrared reflection absorption spectra for a ∼5 nm silicon dioxide film on a Mo(110) annealed at various temperatures. Right panel: HREEL spectra of SiO₂ films on Mo(112) at various coverages. (a) 1 ML (solid line), (b) ∼1.2 ML (dotted line), (c) ∼1.8 ML, (d) ∼5 ML, and (top) from quartz(0001). The bottom four lines show the full spectra for (a)–(d).

Figure 7. Top- and side-view of the structural models of (A) isolated (SiO₄) and (B) 2D network for SiO₂ (1 ML)/Mo(112).

calculations in [123–125] are used to support the 2D network model, however, these calculation more consistently support the isolated (SiO₄) structural model as discussed in [128] and shown in figure 9. Furthermore, detailed atomically resolved STM features as shown in figures 10 and 11 support the isolated (SiO₄) model and are inconsistent with the 2D network model [120]. More recently, Kaya et al [132] have provided more experimental detail and summarized most of the related literature data in favor of the 2D network model. Unfortunately, Kaya et al [132] neglected to discuss an important piece of experimental information, i.e. the absence of an asymmetrical Si–O–Si vibrational mode in the off specular HREELS spectrum as well as the absence of a Si–O–Si bending mode in the HREELS spectrum [120, 128]. The absence of these modes is strong evidence against the 2D network model. Furthermore, the arguments used by Kaya et al in favor of the 2D network model essentially ignore the detailed atomically resolved STM data of Chen et al [120] that
are entirely inconsistent with the 2D network model. Therefore the detailed structure of monolayer SiO$_2$/Mo(112) is still an issue yet to be resolved.

H$_2$O molecularly adsorbs on low- and high-defect SiO$_2$/Mo(112), forming 3D water clusters even at low coverage. No evidence for dissociation of water was found [133, 134]. Various defect sites on SiO$_2$/Mo(112) have been characterized with MIES and UPS [80, 135, 136].

5. Titania thin films

Titanium dioxide (TiO$_2$) is the most thoroughly single-crystalline oxide investigated by surface science techniques, owing to its semiconducting properties. Rutile (110), (100), (001), and anatase surfaces have been studied. Among them, rutile (110) has been studied most extensively. Since TiO$_2$ is important for a wide range of technical uses, the bulk structure, defects, and electronic structure have been extensively studied and summarized [137]. A high-resolution STM image and schematic structural model of TiO$_2$(110) are shown in figure 12 [138].

Ultrathin (<10.0 nm) titanium oxide films can be synthesized on a Mo(100) surface [139]. Epitaxial growth with varying film thickness studied by LEIS, XPS, AES, and LEED show a (2√2 × √2)R45 diffraction pattern whereas STM images indicate that the TiO$_2$ films are ordered along the [010] and [001] directions of the Mo(100) substrate. XPS data reveals that unannealed titanium oxide films exhibit only a Ti$^{4+}$ valence state, whereas annealed titanium oxide films are partially reduced and exhibit Ti$^{3+}$ and Ti$^{2+}$ states. Ordered titanium oxide films can also be epitaxially grown on a Mo(110) substrate [140, 141]. Using various synthetic methods, TiO$_2$(100) or Ti$_2$O$_3$(0001) have been synthesized, as evidenced by (1 × 1) rectangular and (1 × 1) hexagonal LEED patterns, respectively, with supporting data from AES and XPS. STM indicates layer-by-layer growth at 900 K with the presence of flat terraces with three different orientations. The spacings between the neighboring atomic rows for all terraces were similar (0.65 nm), suggesting epitaxial growth of TiO$_2$(110)-(1 × 1). TiO$_2$ films have also been grown on Ni(110) [142, 143] and W(100) [144].

Titanium oxide thin films can also be grown on Pt(111) by vapor phase deposition of titanium metal followed by oxidation in 10$^{-6}$ Torr O$_2$ [145, 146]. A three-fold symmetric structure with a unit cell of 1.82 × 1.82 nm is observed at coverages ranging from 1.0 to 5.0 ML. XPS measurements of this phase show stoichiometric TiO$_2$. Heating in vacuum at 650–850°C leads to a new structure with a unit cell of 1.82 × 1.39 nm which is shown by XPS to have the stoichiometry of Ti$_3$O$_2$. Angle resolved XPS measurements indicate that reduced Ti$^{3+}$ is concentrated at the oxide/Pt(111) interface. By varying the Ti coverage and the annealing conditions, six different long-range ordered phases of TiO$_2$ are obtained. XPS binding energy and XPD data indicate that all the phases, except one (the stoichiometric rect-TiO$_2$), are one monolayer thick and composed of a Ti-O bilayer with interfacial Ti. Atomically resolved STM images confirm that these TiO$_2$ phases wet the Pt surface, in contrast to rect-TiO$_2$.

Surface structures formed by titanium oxide thin films at a Pt(100) surface have been studied by STM, LEED, AES, XPS, XRD and LEIS to explore and elucidate stable high-temperature structures that form at titania–Pt interfaces and provide a basis for characterizing the chemistry of titania thin films on Pt(100) [147]. Titanium oxide films were produced by two different methods, the first via oxidation of a Pt$_3$Ti surface alloy at 300 K using ozone (O$_3$) and annealing at 1000 K. Smooth thin films with a (3 × 5) structure were observed at 1 ML (monolayer) using this procedure. This (3 × 5) structure...
Figure 10. STM images of SiO$_2$ (1 ML)/Mo(112) at various sample bias voltages. All images are 3.5 nm × 3.5 nm. (a) $U_S = +2.5$ V, $I = 0.5$ nA; (b) $U_S = +1.0$ V, $I = 0.5$ nA; (c) $U_S = +0.8$ V, $I = 0.5$ nA; (d) $U_S = +0.6$ V, $I = 0.6$ nA; (e) $U_S = +0.45$ V, $I = 0.6$ nA; (f) $U_S = -2.5$ V, $I = 0.15$ nA; (g) $U_S = -0.8$ V, $I = 0.3$ nA; (h) $U_S = -0.6$ V, $I = 0.6$ nA; (i) $U_S = -0.4$ V, $I = 0.5$ nA. (j) and (k) the bias voltage was shifted from +0.6 to +2.5 V mid-way during the upward scan and shifted back from +2.5 to +0.6 V during the downward scan to complete the scan as indicated in the figure. Lower panel: $U_S = +0.6$ V, $I = 0.5$ nA; upper panel: $U_S = +2.5$ V, $I = 0.5$ nA. The $c(2 \times 2)$ unit is indicated in each image.

Figure 11. (a) STM image of SiO$_2$ (1 ML)/Mo(112) at $U_S = -3.0$ V, $I = 0.3$ nA. The image size is 5.5 nm × 5.5 nm. (b) Image A superimposed with thick and thin circles showing the oxygen atoms in the topmost layer and in the Mo(112) troughs in the isolated (SiO$_4$) model. (c) Top-view of the structural model of the 2D network highlighting the surface Si and oxygen atoms. (d) Top- and side-view of the modified structural model of isolated (SiO$_4$) for SiO$_2$ (1 ML)/Mo(112).

is a monolayer Ti$_2$O$_3$ film that is similar to the (1 × 2) strands formed on reduced TiO$_2$(110) surfaces. Structures prepared by this method show particularly ‘flat’ terraces without islands. A second method of synthesis is by Ti evaporation and deposition on Pt(100) in 6.7 × 10$^{-5}$ Pa O$_2$ followed by an anneal above 750 K in vacuum. A (3 × 5) structure was also produced for these films below 1 ML. A (4 × 3$\sqrt{5}$)R60$^\circ$ structure was observed after deposition of 2 ML and annealing at 850–1000 K. A model for this structure composed of TiO$_2$ tetragonal nets with a fraction of the O atoms in the second layer was proposed. The (4 × 3$\sqrt{5}$)R60$^\circ$ film changes to a (3 × 5) structure after annealing above 960 K in vacuum. TiO$_2$ clusters decompose to form a (2$\sqrt{2}$ × 2$\sqrt{2}$)R45$^\circ$ structure, proposed to be Ti$_5$O$_8$, and (3 × 5) domains after annealing at 1300 K. Based on this model, the composition of all titanium oxide ultrathin films on a Pt(100) surface is TiO$_{2−1.5}$.
observed for the (8 × 2) structure. This feature was assigned to TiO$_2$-Mo and/or TiO$_2$-Ti$_3$O$_8$ based on HREELS and XPS data [148–150]. A row spacing of 0.9 nm, corresponding to two rows of the Mo(112) trough along the [110] direction, is seen by STM (figure 13(a)), consistent with the observed (8 × 2) LEED pattern. High-resolution STM shows a double-row feature with a spacing of 0.9 nm. A proposed structural model for the Mo(112)-(8 × 2)-TiO$_2$ surface is shown in figure 13 in which seven Ti atoms decorate every eight Mo atoms along the Mo(112) trough (the [111] direction). The Ti atoms are bound to the surface via Ti–O–Mo bonds and to each other via Ti–O–Ti linkages [148, 149]. This is the first oxide support that Au completely wets forming well-ordered gold mono- and bilayer films, as shown in figures 13(b) and (c) [148, 151–155].

6. Conclusions

An abundance of recent studies has demonstrated the synthesis of a large family of ultrathin oxide films. These thin films are electronic conductive, which enable their exploration using a variety of surface techniques, and thus offer unprecedented opportunities to address the details of the structure, electronic properties, and chemistry of metal oxides at the atomic/molecular level. These thin films as model oxide supports provide a convenient method to study important aspects of supported metal catalysts such as cluster size effects, cluster morphology, and support–cluster interactions, and allow bridging of the pressure and material gaps of catalysis using operando techniques such as RAIRS, SFVS, etc.

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References

[64] Xu X, Oh W S and Goodman D W 1996 Langmuir 12 4877