An investigation of the TiO$_x$–SiO$_2$/Mo(112) interface

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Received 3 August 2004; accepted for publication 21 October 2004
Available online 5 November 2004

Abstract

The interaction of TiO$_x$ with SiO$_2$/Mo(112) has been studied using high-resolution electron energy loss spectroscopy, Auger electron spectroscopy, low-energy electron diffraction, and molecular adsorption. Ti at varying coverages was deposited onto a SiO$_2$/Mo(112) surface followed by oxidation at 600 K and annealing at various temperatures. TiO$_x$ disperses and covers the SiO$_2$ surface after oxidation and annealing below 800 K, whereas TiO$_x$–SiO$_2$ interfaces undergo significantly restructuring when annealed to temperatures above 1000 K. Upon annealing a TiO$_x$-covered SiO$_2$(monolayer)/Mo(112) surface, SiO$_2$ diffuses to the surface and is bonded via Si–O–Ti linkages. SiO$_2$ in this bonding configuration decomposes and desorbs more easily than from a Mo(112) surface where the binding is via Si–O–Mo linkages. On the other hand, for a TiO$_x$-covered SiO$_2$(multilayer)/Mo(112) surface, TiO$_x$ prefers to phase separate into three-dimensional clusters, minimizing the contact area with the SiO$_2$ substrate. The annealing temperature is a key parameter in defining the properties of TiO$_x$–SiO$_2$ mixed oxide surfaces.

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Keywords: High-resolution electron energy loss spectroscopy (HREELS); Titanium oxides; Silica film; Mixed oxides; Surface structure morphology, roughness, and topography; Thin film

1. Introduction

TiO$_2$–SiO$_2$ mixed oxides or composites exhibit properties similar to TiO$_2$ yet have the high surface area and stability of SiO$_2$ and therefore have been

widely used as catalytic and photocatalytic materials [1,2]. The formation of Ti–O–Si linkages significantly modifies the electronic structure of TiO$_2$–SiO$_2$ [3] giving rise to unique catalytic properties [4]. The Ti–O–Si linkages in TiO$_2$–SiO$_2$ increase the band-gap to 4.1 eV from 3.3 eV for TiO$_2$ [5]. In addition, highly dispersed nanosized TiO$_2$ clusters either in or on high surface area SiO$_2$ exhibit unique properties that have been attributed to limited-size effects and/or to the high interface contact area [5,6].
It has been shown using NMR that at relative low concentrations of Ti atoms are incorporated into SiO$_2$ via four-fold oxygen coordination accompanied by significant restructuring of the SiO$_2$ lattice [7,8]. The catalytic behavior of atomically dispersed titanium oxide is completely different from that of bulk titanium oxide [9,10], i.e., the Ti–O–Si linkages at the TiO$_2$/SiO$_2$ interface strongly influence the catalytic properties. However, a thorough characterization of TiO$_2$/SiO$_2$ mixed oxides by electron spectroscopies has not been carried out because of the difficulties encountered in examining insulating metal oxides [11]. The use of thin films eliminates many of these problems, however, to date no studies have addressed ultra-thin TiO$_2$ films on SiO$_2$, although several other mixed oxide systems have been investigated including SiO$_2$/Al$_2$O$_3$ [12,13], NiO on MgO(100) [14,15] and on Al$_2$O$_3$ [16], MoO$_3$–Al$_2$O$_3$ [17], V$_2$O$_5$–Al$_2$O$_3$ [18], and VO–TiO$_2$ [19]. In these mixed oxide systems, the electronic properties such as the band-gap were found to be substantially different from either of the single component oxides [13,20].

In the studies described herein, varying amounts of TiO$_x$ were deposited onto mono- and multilayer SiO$_2$/Mo(112) surfaces. The SiO$_2$/Mo(112) surfaces have been characterized previously by high-resolution electron energy loss spectroscopy (HREELS) [21], and other surface analytical techniques [22,23]. The restructuring of the TiO$_x$–SiO$_2$ interface and the formation of the Ti–O–Si linkages were investigated using HREELS, Auger electron spectroscopy (AES), and adsorption of probe molecules. The conclusions drawn have important implications regarding the synthesis of TiO$_2$–SiO$_2$ mixed oxide catalysts.

2. Experimental

The experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of $2 \times 10^{-10}$Torr equipped with HREELS, a single-pass cylindrical mirror analyzer for AES, low-energy electron diffraction (LEED), and a quadrupole mass analyzer. The Mo(112) sample was cleaned by repeated cycles of oxidation at 1200 K followed by an anneal to 2100–2200 K, and characterized using AES and LEED. The substrate temperature was measured via a (W/5 wt%Re)/(W/26 wt%Re) thermocouple spot-welded to the back sample surface. A liquid-nitrogen cryostat and an electron beam heater allowed control of the sample temperature between 90 and 2300 K. The silica films were prepared by evaporating Si onto the Mo(112) surface from a tantalum filament in UHV at room temperature [21]. Briefly, a monolayer of SiO$_2$ on Mo(112), SiO$_2$(monolayer)/Mo(112), was prepared by depositing less than 1 monolayer (ML) Si onto a Mo(112)-p(2×3)–O surface, then oxidation/annealing at 800 K in a $1 \times 10^{-7}$Torr O$_2$ for 5 min, followed by an increase in the substrate temperature to 1200 K for an additional 5 min. This procedure (Si deposition/oxidation/annealing) was repeated until a constant Si/Mo AES ratio was achieved. Multilayer SiO$_2$ on Mo(112), SiO$_2$(multilayer)/Mo(112), was prepared by repeatedly depositing less than 0.5 ML Si onto a Mo(112)-p(2×3)–O surface followed by oxidation at 800 K in $5 \times 10^{-6}$Torr O$_2$ for 10 min; the procedure was repeated until the desired film thickness was obtained. After a sufficient thickness was reached, the film was annealed in $5 \times 10^{-6}$Torr O$_2$ in several steps; first 1000, then 1100 and finally to 1200 K, each for 10 min. Ti was evaporated from a wire wrapped Ta filament that was heated resistively. The coverage of Ti was estimated from the AES ratio assuming the Mo(112)-(8×2)–TiO$_x$ structure to be 1 ML [24].

Benzene (>99.0%, EM Science) and H$_2$O (doubly distilled) were degassed with numerous freeze-thaw cycles prior to exposure from the background to the sample at 90 K. Exposures were determined by an ion gauge with no correction for sensitivity. The benzene coverage was estimated from AES break points on a SiO$_2$(monolayer)/Mo(112) surface [25]. The energy resolution of the HREELS measurements was between 64 and 96 cm$^{-1}$ (8 and 12 meV) as determined by the full width at half-maximum (FWHM) of the elastic peak; the monochromatized electrons were incident at an angle of 60° with respect to the sample normal. The analyzer could be rotated about its
axis for on- and/or off-specular measurements; a primary energy \( E_p \) of \( \sim5\)eV was used.

3. Results

3.1. TiO\(_x\) on SiO\(_2\)(monolayer)/Mo(112)

Based on HREELS data the structure of SiO\(_2\)(monolayer)/Mo(112) exhibits a sharp c(2×2) LEED pattern and can be described as Mo(112)-c(2×2)-[SiO\(_4\)] since all four oxygen atoms in the [SiO\(_4\)] tetrahedral are bound to the Mo substrate [21]. Fig. 1 shows 1.5ML Ti on SiO\(_2\)(monolayer)/Mo(112). After oxidation at 600K in \(1 \times 10^{-7}\)Torr O\(_2\), the substrate Si–O asymmetrical stretching phonon mode at 131meV is significantly attenuated, suggesting that TiO\(_x\) forms two- and/or three-dimensional domains (2- and 3-D) and disperses on the SiO\(_2\) surface. Upon annealing at 1150 K, the intensity of the Si–O phonon stretching mode increases significantly, becomes well-resolved, and is accompanied by a 4meV red-shift. This red-shift is consistent with an interaction between TiO\(_x\) and SiO\(_2\) to form a Si–O–Ti linkage [21]. The Si–O–Ti linkage with a phonon mode at 127meV was confirmed by depositing a small amount of Si in \(2 \times 10^{-5}\)Torr O\(_2\) onto TiO\(_2\)(multilayer)/Mo(112) at 300 K. Note that this deposition leads to fully oxidized Si [26]. Upon annealing further to 1400K, the Si–O phonon feature completely disappears, and a single phonon feature appears at 84meV (Fig. 1d). This 84meV feature is attributed to a mixture of Ti\(^{3+}\)–O–Mo and Ti\(^{3+}\)–O–Ti\(^{3+}\) species [24]. The Si–O phonon feature disappears because the Si completely decomposes and desorbs from the surface as shown in the AES data of Fig. 1(insert). These results imply an interface restructuring sequence of SiO\(_2\)/Mo(112) → TiO\(_x\)/SiO\(_2\)/Mo(112) → Si–O–Ti/TiO\(_x\)/ Mo(112) → TiO\(_x\)/Mo(112) during annealing.

This interface restructuring sequence is more evident with the deposition of larger amounts of Ti as shown in Fig. 2, in which approximately 5ML Ti were deposited stepwise onto an ordered SiO\(_2\)(monolayer)/Mo(112) surface with subsequent oxidation in \(1 \times 10^{-7}\)Torr O\(_2\) at 600 K for 10min. After depositing TiO\(_x\) onto the SiO\(_2\) surface, the Si–O phonon feature is completely attenuated (see Fig. 2A). Upon annealing, the Si–O phonon feature reappears (red-shifted by approximately 4meV) with the intensity increasing as the anneal temperature is increased. The AES spectra of Fig. 2B, which correspond to the data of Fig. 2A, show the Si and Mo signals to be attenuated by the TiO\(_x\) overlayer after oxidation at 600K. Annealing at 800K causes a distinct increase in the intensities of the Si–O phonon mode at 127meV and a corresponding increase in the Si\(^{4+}\) AES features without an obvious increase in the intensities of the Mo features. These data are consistent with an interaction between SiO\(_2\) and TiO\(_x\) to form Si–O–Ti linkages, but with no significant change in the oxide film thickness. It is very likely that the restructuring of the TiO\(_x\) and SiO\(_2\)
interface leads to the formation of SiO$_2$-covered TiO$_x$ phases, consistent with the results of 1.5ML TiO$_x$ on SiO$_2$(monolayer)/Mo(112) and for the phase separations observed for TiO$_2$–SiO$_2$ where TiO$_2$ phases are covered by SiO$_2$ [1,27].

For the data of Fig. 3, 0.5ML Ti was deposited onto SiO$_2$(monolayer)/Mo(112) to assess the influence of submonolayer amounts of Ti on the Si–O phonon mode. Anneals of this surface to 800–1000 K caused no detectable shift in the Si–O phonon at 131 meV, whereas a shoulder at the lower loss energy side appears in the Si–O stretching double loss at 261 eV, implying an interaction between TiO$_x$ and SiO$_2$. With further anneals to 1050 and 1150 K, a red-shift of the Si–O mode from 131 to 127 meV (its double loss from 261 to 254 meV) is apparent, consistent with uniform dispersion of the TiO$_x$.

### 3.2. TiO$_x$ on SiO$_2$(multilayer)/Mo(112)

SiO$_2$(multilayer)/Mo(112) exhibits phonon features at 62 and 147 meV corresponding to the Si–O–Si bending and asymmetrical stretching modes as shown in Fig. 4A(a) [21], similar to bulk SiO$_2$ [28–30]. Stepwise deposition of 5ML Ti onto the SiO$_2$ surface with subsequent oxidation at 600 K completely attenuates the Si–O–Si phonon features at 62 and 147 meV as well as the AES features related to Si$^{4+}$ and Mo (Fig. 4). These data are consistent with TiO$_x$ covering the entire surface as seen for SiO$_2$(monolayer)/Mo(112). Upon annealing, Si–O–Si asymmetrical stretching phonon modes reappear at 147 meV and Si$^{4+}$ AES features are apparent whose intensities increase with an increase in the annealing temperature. The Si–O–Ti asymmetrical stretching phonon mode at 127 meV appears only after an anneal above 1250 K. These experiments show clearly that TiO$_x$ does not mix with SiO$_2$, but rather phase separates as in TiO$_2$–SiO$_2$ prepared by the sol–gel method [1,27]. Note that at the interface, Si–O–Ti linkages may form to a limited extent, however this may not be apparent due to attenuation of these features by the TiO$_x$ and/or SiO$_2$.

### 3.3. Adsorption of water and benzene

Since SiO$_2$(monolayer)/Mo(112) is coordinatively saturated [21], H$_2$O does not wet this sur-
On the other hand, because TiO$_2$ is coordinatively unsaturated, H$_2$O does wet this surface. H$_2$O, therefore, is an informative probe molecule for investigating oxide surfaces, including mixed oxides. The results for H$_2$O adsorption on SiO$_2$/TiO$_2$ are shown in Fig. 5, where only the double loss of the Si–O stretching mode at 261 meV was displayed together with HO–H vibrational mode. Dosing 10 L (approximately 3–4 ML) of H$_2$O on the well-ordered SiO$_2$(monolayer)/Mo(112) surface shows a weak HO–H stretching mode at 415 meV (3320 cm$^{-1}$) with residual Si–O phonon double loss intensity, implying the formation of H$_2$O 3-D clusters which occupy only a relatively small fraction of the SiO$_2$/Mo(112) surface. Note that the c(2 × 2) LEED pattern of the substrate SiO$_2$/Mo(112) was apparent even dosing H$_2$O with 20 L, confirming the formation of solid H$_2$O clusters on the SiO$_2$ surface which cover a relatively small fraction of the SiO$_2$/Mo(112) surface. With 0.25 ML of TiO$_x$ on the SiO$_2$ surface and dosing 10 L H$_2$O, a significant HO–H stretching mode is apparent, accompanied by attenuation of the Si–O phonon mode on those samples annealed at 800 and 900 K. This shows clearly that the topmost layer of Ti$^{3+}$ (δ = 3 or 4) plays an important role in binding H$_2$O and that the TiO$_x$ is highly dispersed on the surface. The samples annealed at relative high temperatures (>1000 K) show a weak HO–H stretching mode, with significant intensity in the Si–O asymmetrical stretching double loss, consistent with 3-D clustering of the water. Altogether these data suggest that the Ti is likely located below the [SiO$_4$] layer and bonded via Mo–O–Ti–O–Si linkages annealed above 1000 K. It is noteworthy that the 0.25 ML TiO$_x$ modified monolayer SiO$_2$ surface shows the same c(2 × 2) LEED pattern as the SiO$_2$(monolayer)/Mo(112) surface.

Benzene was also used as a probe molecule to investigate the TiO$_x$–SiO$_2$ surface. Fig. 6 shows 1 ML benzene adsorption on the SiO$_2$(monolayer)/Mo(112), 0.25 ML TiO$_x$ doped monolayer SiO$_2$ annealed at 1150 K, and a Mo(112)-(8 × 2)–TiO$_x$ surfaces. On the TiO$_x$/Mo(112) surface, a tilted geometry for benzene is suggested by a strong C–H stretching mode at 380 meV (Fig. 6c), the details of which will be discussed in a separate publication [36]. However, on monolayer SiO$_2$ and on a TiO$_x$-doped SiO$_2$ surface (Fig. 6a and b), only a weak C–H stretching mode at 380 meV appears, suggesting that benzene adsors with its molecular plane parallel to the surface. The specific geometry of benzene on the SiO$_2$(monolayer)/Mo(112) surface has been discussed in detail previously [25]. A slightly higher intensity in the C–H stretching mode on the TiO$_x$ doped surface compared with the SiO$_2$ surface suggests that Ti either modifies the SiO$_2$ film or partially forms small domains of TiO$_x$ on the Mo(112) surface [37].

4. Discussion

4.1. The oxidation state of TiO$_x$

The SiO$_2$(monolayer)/Mo(112) surface exhibits phonon features at 40, 86, 96 and 131 meV
Among these, the 86 and 96 phonons corresponding to Mo–O stretch modes are very close to those for TiO₂ at 88 meV [38] and TiO₂ at 94–98 meV [38, 39]. Accordingly, it is not possible to resolve Ti–O from Mo–O features at low TiOₓ coverages. However, at higher TiOₓ coverages, the Si–O and Mo–O phonon features are significantly attenuated (cf. Figs. 2 and 4), therefore the features between 80 and 100 meV can be used to differentiate Ti₂O₃ from TiO₂. Stepwise deposition of Ti to 5 ML on a monolayer SiO₂ surface followed by oxidation at 600 K leads to the appearance of a broad phonon feature corresponding to a Ti–O stretching mode near 98 meV (cf. Fig. 2), consistent with a TiO₂ phase. With annealing, the phonon feature red-shifts slightly, suggesting the formation of Ti₂O₃. On the multilayer SiO₂ surface (cf. Fig. 4), a phonon feature at 98 meV was also observed that corresponds to a TiO₂ phase. Annealing above 1050 K, the phonon feature shifts to 88 meV, i.e. Ti₂O₃, consistent with our previous data that shows conversion of TiO₂ to Ti₂O₃ upon annealing above 1100 K [38]. For Ti in a Ti–O–Si linkage, the oxidation state is assumed to be +4, since the phonon feature at 127 meV in TiOₓ–SiO₂/Mo(112) is the same as that for Si deposited onto a TiO₂ surface in O₂ where a Si⁴⁺–O–Ti⁴⁺ linkage formed. The asymmetrical stretching phonon mode of Si⁴⁺–O–Ti³⁺ should lie at a lower frequency relative to Si⁴⁺–O–Ti⁴⁺.

4.2. The dominant surface species: TiOₓ versus [SiO₄]

Attenuation of the Si–O phonon modes in HREELS and the Si⁴⁺ and Mo features in AES show definitively that TiOₓ covers the surface of TiOₓ–SiO₂ following oxidation at 600 K (cf. Figs. 1, 2 and 4). This is consistent with the data for H₂O adsorption (cf. Fig. 5) where H₂O wets more completely the TiOₓ-doped surface annealed to relatively low temperatures. Upon annealing to higher temperatures, the interface undergoes restructuring, depending upon the thickness of the SiO₂ films and the amount of TiOₓ deposited.
Such restructuring is indicated by changes in the AES ratio versus the annealing temperatures as shown in Fig. 7.

For 5ML TiO\textsubscript{x} on SiO\textsubscript{2}(monolayer)/Mo(112) (Fig. 7A), the Ti/Mo AES ratio does not change appreciably at annealing temperature lower than 1000 K, but quickly decreases at annealing temperatures >1000 K. A rapid decrease of the Ti/Mo ratio between 1000 and 1200 K likely correlates with the formation of 3-D TiO\textsubscript{x} clusters rather than the loss of Ti from the surface, particularly given the stability of TiO\textsubscript{x} \cite{38,40,41} and suggested by our HREELS studies \cite{42}. Annealing induces a marked increase in the Si/Mo AES ratio at low temperature and a decrease at high temperatures >900 K. Such changes cannot be explained by formation of 3-D TiO\textsubscript{x} clusters, since the AES Si and Mo signals should be equally attenuated. Thus, the significant increase of the Si/Mo AES ratio indicates an interaction of TiO\textsubscript{x} with SiO\textsubscript{2}, e.g. formation of Si–O–Ti linkages as evidenced by a phonon feature at 127 meV. Furthermore, it is likely that these Si–O–Ti linkages are at the outmost surface, as seen for sol–gel prepared TiO\textsubscript{2}–SiO\textsubscript{2} mixed oxides containing >10% Ti \cite{1,27}. Coating of the TiO\textsubscript{2} clusters by SiO\textsubscript{2} was evident in the rapid decrease of the Ti/Si AES ratio upon annealing. It should be noted that this decrease was not induced by formation of 3-D TiO\textsubscript{x} clusters since the Ti/Mo AES ratio remains essentially constant. For higher annealing temperatures, the Si/Mo AES ratio decreases rapidly, consistent with [SiO\textsubscript{4}] covering the 3-D clusters of TiO\textsubscript{x} that form between 1000 and 1150 K, coupled with the loss of Si from the surface at 1200 K (cf. Figs. 1, 3 and 7). The decomposition and desorption of Si from the TiO\textsubscript{x}-modified surface has been used to prepare ultra-thin TiO\textsubscript{x} films on Mo(112) \cite{24}.
Results similar to those described above are observed for 0.5ML TiO$_x$ on SiO$_2$(monolayer)/Mo(112) (Fig. 7B). However since the amount of TiO$_x$ is submonolayer, 3-D clusters formation is not indicated by changes in the Ti/Mo AES ratios. The significant increase of the Si/Mo AES ratio and a decrease of the Ti/Si AES ratio during annealing confirm that TiO$_x$–SiO$_2$ interactions form Si–O–Ti linkages at the surface. Such conclusions are consistent with results of the H$_2$O adsorption at 90K (cf. Fig. 5). Note, too, that H$_2$O does not wet the monolayer SiO$_2$ surface because the surface is coordinatively saturated [21]. H$_2$O adsorption is quite different with wetting indicated for a 0.25ML TiO$_x$-doped surface annealed below 1000K. The wetting of H$_2$O on TiO$_2$ surface is due to the coordinatively unsaturated surface sites [32–35]. In contrast to the tetrahedral [SiO$_4$] in SiO$_2$ whose surface can relax to achieve coordinative saturation [43], Ti atoms in Ti$_2$O$_3$ and TiO$_2$ are six-fold coordinated, thus at the surface the outermost atoms are unsaturated [44]. Therefore, if TiO$_x$ resides at the surface, H$_2$O wets. This contrast in the behavior of those samples annealed at relatively low and high temperatures likely relate to the nature of the coordination, i.e., unsaturated versus saturated, of the surface Ti and Si atoms. Assuming a saturated coordination number of 6 for TiO$_x$ versus 4 for SiO$_2$, it is reasonable that TiO$_x$ prefers a subsurface site whereas SiO$_2$ surface segregates. Because subsurface TiO$_x$ sites can achieve saturated coordination numbers whereas TiO$_x$ cannot when located at the outmost surface. However a tetracoordinated Si species, e.g. [SiO$_4$], can achieve saturated coordination both in the subsurface and at the outmost surface. Thus, a [SiO$_4$]-covered TiO$_x$ phase is energetically preferred to phase separated SiO$_2$ and TiO$_x$. On the other hand, bulk-like mixed oxides of SiO$_2$–TiO$_x$ are energetically less preferred due to the large mismatch in lattice and coordination. It is noteworthy that Ti–silicalites do not form under the conditions used in the present experiments.

That [SiO$_4$] is located at the surface is supported by the benzene adsorption data. Our previous data have demonstrated that benzene on the monolayer SiO$_2$ surface adopts a planar adsorption geometry due to the quasi-hexagonal arrangement of the outmost layer oxygen atoms [25]; on the TiO$_x$ well-ordered thin film a tilted adsorption geometry is assumed (cf. Fig. 5 and Ref. [36]). The parallel adsorption geometry on the TiO$_x$-modified SiO$_2$ surface annealed at 1150K demonstrates that Ti atoms are atomically dispersed on the surface without forming significant amounts of TiO$_x$, consistent with the observed Si–O phonon shift. And
furthermore, the arrangement of the outmost surface oxygen is similar to that of the monolayer SiO$_2$ surface [25] and also exhibits a sharp c(2 x 2) LEED pattern as that for SiO$_2$. These data support the conclusion that [SiO$_4$] units are located at the film surface.

4.3. Interactions between TiO$_x$ and SiO$_2$

The formation of Si–O–Ti linkages at the interface between TiO$_2$ and SiO$_2$ has been examined with IR [45] and XPS [5,46]. In the present studies, the Si–O phonon features suggest the formation of the Si–O–Ti linkages between TiO$_x$ and SiO$_2$. As shown in Fig. 3, 0.5 ML TiO$_x$ deposited on the monolayer SiO$_2$ surface induces a slight red-shift of the Si–O–Mo phonon feature at 131 meV for a sample annealed at 600 K due to the formation of Si–O–Ti linkages. With an anneal to >1000 K, a 4 meV red-shift of the 131 meV Si–O phonon feature is observed, similar to that seen for higher TiO$_x$ coverages (cf. Figs. 1 and 2) and consistent with complete dispersion. The formation of Si–O–Ti linkages was also confirmed by band-gap measurements as shown in Fig. 8. For 0.5 ML TiO$_x$ on the monolayer SiO$_2$ surface, oxidized and annealed at 600 K, a band-gap of approximately 4.5 eV is evident, a value much higher than 3.7 eV observed for 1.5 ML. This increase in band-gap occurs since small amounts of TiO$_x$ interact efficiently with the substrate SiO$_2$ to form Si–O–Ti linkages that have been shown to have a higher band-gap than TiO$_2$ [5]. Above 1 ML, TiO$_x$ forms 3-D structures in which the outmost layer of TiO$_x$ does not bind to Si, yielding a band-gap close to that of TiO$_2$. Annealing the 1.5 ML TiO$_x$/SiO$_2$ surface at 900 K yields a significant blue-shift of the band-gap from 3.7 to 4.5 eV. As discussed above, annealing at this temperature induces interface restructuring and the formation of Ti–O–Si linkages. These, in turn, induce a blue-shift in the band-gap.

In contrast to the monolayer SiO$_2$ surface, no significant Si–O–Ti phonon intensity was observed for the multilayer SiO$_2$ surface annealed to temperature less than 1200 K (cf. Fig. 4). These data demonstrate that TiO$_x$–SiO$_2$ mixed oxides are relatively unstable and tend to phase separate into single phase TiO$_2$ and SiO$_2$ [1,27]. Due to the formation of separate phases, the contact area between the two phases is small, therefore the Ti–O–Si linkages are minimized. Annealed at a temperature higher than 1200 K, multilayer TiO$_2$ decomposes and desorbs yielding monolayer SiO$_2$. Monolayer SiO$_2$, in turn, interacts with TiO$_x$ to form extensive Ti–O–Si linkages as evidenced by the significant increase in the intensity of the Si–O–Ti phonon feature at 127 meV (cf. Fig. 4).

5. Conclusions

Deposition of Ti onto mono- and multilayer SiO$_2$/Mo(112) surfaces with subsequent oxidation yields dispersed TiO$_2$ domains with Ti–O–Si linkages at the TiO$_2$–SiO$_2$ interface. Upon annealing, the monolayer TiO$_x$ becomes highly dispersed, while multilayer TiO$_x$ forms Si–O-covered TiO$_2$ phases on SiO$_2$(monolayer)/Mo(112). On SiO$_2$(multilayer)/Mo(112) TiO$_x$ disperses when annealed below 1000 K; when annealed above
1000 K, 3-D clusters form. The annealing temperature plays a key role in determining the surface properties of TiO$_x$–SiO$_2$ mixed oxides.

Acknowledgment

We acknowledge with pleasure the support of this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences and the Robert A. Welch Foundation.

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