The preparation and characterization of ultra-thin silicon dioxide films on a Mo(110) surface

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Ultra-thin silicon dioxide films have been deposited on an oxygen-covered Mo(110) surface at room temperature by evaporating silicon in an oxygen background ($\sim 1 \times 10^{-5}$ Torr). The growth mechanism and structural properties of the SiO$_2$ films were characterized with temperature programmed desorption, Auger electron, electron energy loss, and infrared reflection-absorption spectroscopies. The interaction of oxygen with Mo(110) was also investigated. The SiO$_2$ films grow a complete first layer before the growth of bulk film at room temperature. The gas phase precursor for the SiO$_2$ film is SiO, produced by oxidative etching of silicon. The as-deposited SiO$_2$ films are proposed to consist of short-ranged networks of [SiO$_4$]. Upon annealing to 1400 K, the small networks of [SiO$_4$] fuse together, with the films assuming the electronic and bonding structures of vitreous silica. The SiO$_2$ films are thermally stable up to 1600 K with stability increasing with film thickness. At high temperatures, silicon dioxide is reduced by the Mo substrate to form volatile SiO and MoO$_3$.

1. Introduction

There is a growing interest in the study of oxides using surface science techniques [1], particularly since oxides are widely used as catalysts and catalyst supports. Investigating the surface properties of oxides using the surface science approach, however, presents serious experimental difficulties related to sample mounting, sample heating and charging problems due to their insulating properties. Using thin films of oxides grown on a metal substrate circumvents many of these problems [1]. In addition, the interfacial properties of oxides and metal substrates themselves are of considerable interest. For example, it is well known that the catalytic properties of a metal can be altered by the interaction of the metal and the oxide support [2].

Silicon dioxide is one of the most widely used supports for metal catalysts thus, the interactions between silica and metals are of considerable interest [3]. There are few examples of studies of ultra-thin silicon dioxide films on metal surfaces; most studies have focused on metal oxides, such as TiO$_2$ [4], FeO$_x$ [5], AlO$_x$ [6] and MgO [7]. The interaction of ultra-thin silicon dioxide films with metals has been studied by the oxidation of silicon-containing platinum foil and Pt(111) [8,9]. The nucleation and growth of silicon monoxide films have been investigated on tungsten and rhenium crystals with field-emission microscopy [10,11], however, silicon dioxide was not included in these early studies.

We have previously reported that a thin stoichiometric silicon dioxide film can be prepared by depositing silicon onto a relatively cool Mo(110) substrate ($\sim 100^\circ$C) in an oxygen background ($\sim 1 \times 10^{-5}$ Torr) [12]. In this paper, we investigate further the silicon dioxide growth mechanism, the interaction of the film with the sub-
strate, and the effects of post-annealing on the properties of the SiO$_2$ films. Because of the oxygen background, the Mo(110) surface is saturated with oxygen during the SiO$_2$ deposition, therefore, the interaction of oxygen with Mo(110) is also described.

2. Experimental

These experiments were performed in two ultrahigh vacuum chambers. One chamber is equipped with a Perkin-Elmer double pass CMA for Auger electron (AES) and electron energy loss (ELS) spectrometries, a UTI quadrupole mass spectrometer (QMS), and an electron optics for low energy electron diffraction. The second chamber is equipped with AES, a QMS and a Mattson Cygnus 100 FTIR spectrometer for IR single reflection-absorption spectroscopy (IRAS) studies. In the ELS studies, the primary electron beam was 100 eV and the spectral resolution was 0.5 eV. A 2000 eV electron beam was used for AES. In the IRAS studies, a 4 cm$^{-1}$ resolution was used.

The Mo(110) substrates were mounted on manipulators capable of cooling to 90 K and heating to 2200 K. The Mo(110) surface was cleaned by heating in oxygen at 1200 K and flashing to 2200 K in vacuo. The crystal temperature was measured with a (W-5%Re/W-26%Re) thermocouple spot-welded to the back of the crystal. Resistive heating was used for heating up to 1500 K; electron beam heating was utilized for heating to 2200 K. The heating rate varied from 5 to 50 K/s.

The silicon evaporation source was made of a small silicon strip ($\sim 1 \times 1 \times 3$ mm) taken from a high purity silicon wafer and wrapped with a tantalum heating wire. After thorough outgassing of the evaporation assembly, a silicon film was deposited onto the Mo(110) substrate, positioned $\sim 4$ cm away from the source. The silicon film was determined to be pure within the AES detection limit ($\sim 1\%$). In addition, the Si(LVV, 91 eV) signal intensity was identical across the surface, demonstrating the uniformity of silicon flux. Research purity oxygen (99.997%, Matheson) was used without further purification.

3. Results and discussion

3.1. Temperature programmed desorption of oxygen from Mo(110)

Oxygen adsorption on Mo(110) has been previously studied by AES and LEED [13,14]. No TPD studies of this system have been reported; however, studies of the oxidation of Mo(100) and Mo(111) at high temperatures and the TPD for O/Mo(100) and O/Mo(111) have been reported [15]. These investigations have shown that molybdenum oxides are formed during the high temperature oxidation of Mo(100) and Mo(111).

Fig. 1 shows the TPD spectra of various masses from an oxygen-covered Mo(110) surface prepared by adsorbing 160 langmuir ($10^{-6}$ Torr · s)
of oxygen at 1000 K. Product desorption features are observed at ~1400, 1600, 1800 and 2100 K (fig. 1). It is noteworthy that both MoO$_3$ and (MoO$_3$)$_2$ desorption features were observed for this particular oxygen coverage, suggesting that the molybdenum substrate has been oxidized to molybdenum trioxide at 1000 K. Other products were monitored up to $m/q = 300$. Those observed to desorb concurrently within the 1400 K peak were $m/q = 288, 272, 256, 144, 128, 112$ and 96, corresponding to Mo$_2$O$_6^+$, Mo$_2$O$_5^+$, Mo$_2$O$_4^+$, MoO$_5^+$, MoO$_6^+$, MoO$^+$ and Mo$^+$, respectively. These ions are attributed to the fragmentation of (MoO$_3$)$_2$ and MoO$_3$ in the mass spectrometer, based on their identical desorption profiles within the 1400 K peak.

Both molybdenum trioxide monomers and dimers are believed to desorb at ~1400 K during TPD, since the peak temperature and lineshapes of the Mo$_2$O$_6^+$ and MoO$_5^+$ desorption features within this temperature range are somewhat different (fig. 1). The desorption of molybdenum trioxide is consistent with the previous studies of the high temperature oxidation of Mo(100) and Mo(111) [15]; however, in these studies the molybdenum trioxide dimer was not observed. The difference in these two experiments may be due to the different Mo crystal orientation, the specific oxygen coverage, or simply to the fact that the higher masses might not have been monitored in the previous studies.

Only the monomeric species, MoO$_3$, desorbs in the TPD feature at ~1600 K (fig. 1). Ions of the molybdenum trioxide dimer, Mo$_2$O$_6$, were not detected at ~1600 K. In addition, the lineshape and peak temperature of the MoO$_5^+$, MoO$_6^+$, MoO$^+$ and Mo$^+$ feature are identical, suggesting that these ions are derived from either one species or one process. MoO$_3$ is a layered compound with orthorhombic symmetry. The MoO$_3$ and (MoO$_3$)$_2$ desorption peaks at ~1400 K are attributed to the desorption of MoO$_3$ multilayers noting that the intensity of these features increases with oxygen exposure. The ~1600 K MoO$_3$ feature likely corresponds to desorption of the MoO$_3$ monolayer, since the intensity of this feature saturates with an oxygen exposure of ~80 L (fig. 2).

Molybdenum dioxide (MoO$_2$) is also desorbed in a broad peak between 1700 and 2000 K. In this

![Temperature programmed reaction of oxygen on Mo(110) as a function of oxygen exposure at 1000 K. The oxygen exposures are 2, 5, 20, 40, 80, 120 and 160 L, respectively. Only the MoO$_5^+$ and MoO$_6^+$ signals are shown.](image-url)
temperature range, there are no signals arising from MoO$_3$ or Mo$_2$O$_6$ (fig. 1). The small signal of MoO$^+$ ($m/q = 112$) above 1700 K is likely due to the fragmentation of MoO$_2$ in the mass spectrometer. The desorption of metallic molybdenum accounts for the increasing signal of Mo$^+$ above 2000 K (fig. 1).

The temperature programmed reaction spectra of oxygen on Mo(110) strongly depend on oxygen exposure at 1000 K (fig. 2). At low oxygen exposures (< 2 L), gaseous MoO$_3$ is not formed whereas MoO$_2$ is desorbed at ~2000 K. Upon an increase in the oxygen exposure to 5 L, MoO$_3$ desorption appears at 1700 K and the MoO$_2$ desorption saturates. A further increase in the oxidation exposure (20-40 L) results in a new MoO$_3$ desorption feature at 1600 K. At high oxygen exposures (> 80 L), Mo$_2$O$_6$ desorption is observed with its desorption intensity increasing with oxygen exposure. These data suggest that a molybdenum trioxide film is formed upon exposure of Mo(110) to sufficient oxygen (> 80 L) at 1000 K, whereas only chemisorbed oxygen (or low oxidation state molybdenum oxides) are formed at low oxygen exposures.

Exposing Mo(110) to oxygen at room temperature does not lead to deep oxidation. The oxygen uptake quickly reaches saturation at 300 K, and the TPD for saturation oxygen at 300 K is similar to the TPD for 2 L oxygen adsorbed at 1000 K. Therefore, during the preparation of SiO$_2$ film at room temperature in ~10$^{-5}$ Torr oxygen, the molybdenum substrate is saturated with oxygen, but is not further oxidized.

3.2. Preparation of SiO$_2$ thin films on Mo(110)

Silicon dioxide films were prepared by evaporating silicon onto the Mo(110) substrate at room temperature in oxygen ambient ($P_{\text{oxygen}} \approx 4 \times 10^{-6}$ Torr). Fig. 3 shows the Auger electron spectra for the silicon and silicon oxides films prepared with various oxygen background pressures. The AES features for silicon and silicon dioxide are distinctive: one main feature at 91 eV corresponding to the silicon LVV transition and several features at 76, 63 and 59 eV corresponding to silicon dioxide [16,17]. In addition, an Auger feature at ~85 eV has been observed for a SiO$_2$ species on platinum [8] and on silicon [18]. For oxygen background pressures < $1 \times 10^{-6}$ Torr, significant silicon and silicon dioxide are present in the films (fig. 3b), evidenced by two major Auger features at 91 and 76 eV. The feature at 91 eV is attributed to the reduced silicon whereas the features at 76, 63 and 59 eV are characteristic of silicon dioxide. An increase in the oxygen pressure leads to an increase in the relative amount of silicon dioxide. A pure silicon dioxide film is formed when the oxygen pressure is > $4 \times 10^{-6}$ Torr (fig. 3c). The Auger electron spectrum for the SiO$_2$ film is identical to the spectrum of bulk SiO$_2$. A further increase in the oxygen pressure does not noticeably alter the film composition, that is, the Auger ratio of the O(KLL) and Si(LVV) features remain constant.
The Auger spectrum shown in fig. 3c also suggests that the silicon oxide films are stoichiometric (SiO₂). The presence of SiO (silicon monoxide) in the silicon oxide films can be ruled out on the basis of the absence of the Auger transition at \( \sim 85 \) eV characteristic of SiO [8,18]. Other silicon–oxygen species, such as “\( \text{Si}_2\text{O} \)” and “\( \text{Si}_3\text{O}_3 \)”, are not likely formed, since these species do not exist as stable compounds; they have only been proposed to exist at the Si/SiO₂ interface [19,20]. Furthermore, the electron energy loss and IR spectra of the SiO₂ films are consistent with bulk silica.

The gas phase precursor to the SiO₂ film is a gas-phase oxygen-containing silicon species (likely SiO), not gas-phase silicon. The relative growth rate of the SiO₂ film increases linearly with respect to the oxygen pressure (in the range of \( (4-10) \times 10^{-6} \) Torr) (fig. 4). If only silicon were to be evaporated, the evaporation and deposition rate should not depend on the oxygen pressure at an identical source temperature. On the other hand, the rate of oxidative etching of silicon by oxygen to yield gaseous SiO is first order in the oxygen pressure at low pressures [21]. It is known that gaseous SiO can be produced by silicon oxidation at elevated temperatures and low oxygen pressures [21,22]. High oxygen pressures (> 2 mTorr) will cause thermal oxidation of silicon to silicon dioxide [21]. In addition, SiO₂ films have been prepared by laser ablation of a SiO target in an oxygen atmosphere [23]. Further oxidation of SiO to SiO₂ may occur on the Mo(110) surface.

Supporting evidence for gaseous SiO serving as the precursor to the SiO₂ films is the fact that silicon dioxide films can be made at a substrate temperature as low as 100 K. Thermal oxidation of silicon requires temperatures near 1000 K. Cycles of depositing silicon at 300 K for less than one monolayer followed by exposure to oxygen (1000 L) at \( \sim 600 \) K does not produce a silicon dioxide film. At an oxygen pressure less than \( 1 \times 10^{-6} \) Torr, Si evaporation competes with SiO formation/desorption, such that a film containing both silicon and silicon oxide is formed (fig. 3b).

3.3. Temperature programmed reaction of SiO₂ films on Mo(110)

Temperature programmed reaction spectra of silicon dioxide films show that silicon dioxide is reduced by the molybdenum substrate to produce volatile silicon monoxide and molybdenum oxides at \( \sim 1700 \) K (fig. 5). Reaction products were monitored up to \( m/q = 300 \) while heating the crystal. Four ions of molybdenum oxides: \( m/q = 96 \) (Mo⁺), 112 (MoO⁺), 128 (MoO₂⁺) and 144 (MoO₃⁺), and silicon monoxide \( (m/q = 44) \), are desorbed at the same peak temperatures and with identical lineshapes. No MOO₃ desorbed from a surface without silicon prepared with the same oxygen exposure, demonstrating that the evolution of molybdenum oxides from SiO₂/Mo(110) is due to the oxidation of the Mo(110) substrate by SiO₂. The relative intensities of the \( m/q = 96, 112, 128 \) and 144 desorption features agree with those features desorbing from a thin MoO₃ film (fig. 1), suggesting that only the MoO₃ species is produced from the reduction of the SiO₂ thin films. Only a small amount of volatile silicon dioxide \( (m/q = 60) \) is produced in the 1700 K peak. The \( m/q = 44 \) signal observed at \( \sim 1700 \) K is due to SiO⁺, rather than CO₂⁺, since the reaction of surface carbon and oxygen produces carbon monoxide below 1300 K. Further-
more, no carbon signal was detected with Auger electron spectroscopy for the SiO$_2$ films.

The evolution of volatile silicon monoxide and molybdenum trioxide from an ultra-thin SiO$_2$ film on Mo(110) is rate-limited by the reduction process. Molybdenum oxide itself desorbs at $\sim$1400–1600 K (fig. 1), a temperature significantly lower than the reduction temperature. Silicon monoxide has a vapor pressure of $\sim 2 \times 10^{-7}$ Torr at 1000 K [24]. In addition, the peak temperature and lineshape for the SiO and MoO$_3$ evolution are identical, demonstrating that SiO and MoO$_3$ are produced in the same step. The driving force for this reduction reaction is the formation of volatile products.

The SiO evolution and the stability of the SiO$_2$ films strongly depend on the film thickness. At low SiO$_2$ coverages (< 1 monolayer), the peak temperatures of SiO and molybdenum oxides (monitored at $m/q = 96$) increase with SiO$_2$ coverage but with overlapping leading edges (fig. 6). At high SiO$_2$ coverages, both the leading edges and the peak temperatures shift to higher temperature, suggesting a higher thermal stability for thicker SiO$_2$ film. The peak temperature of SiO evolution is at 1630 K for 0.2 ML SiO$_2$ on Mo(110), and shifts to 1700 K for 1 ML SiO$_2$. For a very thick SiO$_2$ film ($\sim 200 \text{ Å}$), the desorption product commences at 1900 K for SiO$_2$, 2000 K for SiO$_2$ (gas), and 2150 K for MoO$_3$. Thus thick SiO$_2$ films are relatively much more stable. The initial SiO and SiO$_2$ evolution for the very thick SiO$_2$ films is attributed to evaporation of silica. The much higher temperature of MoO$_3$ evolution than SiO is probably due to the fact that the reaction product at the SiO$_2$/Mo interface is confined below the thick silica layer.

Temperature programmed reaction of SiO$_2$/Mo(110) is sensitive to film impurities which induce new desorption features. For a surface contaminated with carbon, desorption of both SiO and SiO$_2$ are observed at $\sim$1300 K along with the production of carbon monoxide. When the film contains silicon, SiO desorption is also observed below 1400 K. It is known that carbon and silicon are able to reduce silicon dioxide to carbon monoxide and silicon monoxide at elevated temperatures [24]. Incorporation of metal impurities, such as tungsten, also introduces new desorption features. In addition to the main SiO peak at 1700 K, a small SiO peak is observed at 1500 K in the TPD when a small amount of tungsten is incorporated into the silicon oxide films. The SiO$_2$ films can become contaminated with tungsten, for example, when using a tungsten wire to heat silicon in oxygen since tungsten oxide has a relative low evaporation temperature. In these experiments, a tantalum heating wire was used to heat the silicon source.

3.4. SiO$_2$ film growth mechanism and coverage determination

The plot of the Auger intensities of Mo(186 eV) and Si(76 eV) peaks with respect to deposition time (fig. 7) suggests that silicon dioxide
Fig. 6. Temperature programmed reaction for SiO$_2$/Mo(ll0) as a function of SiO$_2$ coverage. The SiO$_2$ coverages are 0.2, 0.4, 0.6, 0.8 and 1.0 monolayer, respectively. Only two ions, SiO$^+$ and Mo$^+$ (for molybdenum oxides), are shown.

Auger breaks are more difficult to define for oxide-on-metal systems than for metal-on-metal systems [1]. The attenuation of the Mo(186 eV) intensity is also approximately exponential with respect to the deposition time (see the inset of fig. 7). A fit for the Mo(186 eV) Auger data yields a growth rate of $\sim 1$ Å/min for this particular condition, using a mean free path of the 186 eV electron in vitreous silica as $\sim 5$ Å [26,27]. Therefore, a $\sim 4$ Å thick film corresponds to one monolayer of SiO$_2$. No LEED patterns were observed for the SiO$_2$ monolayer on Mo(ll0), thus its detailed structure remains to be determined.

In section 3.1, we have shown that molybdenum trioxide dimer will desorb from heavily oxidized Mo(110) at a relatively low temperature ($\sim 1400$ K, fig. 1). Deposition of SiO$_2$ blocks (MoO$_3$)$_2$ desorption, thus the intensity of
The integrated \((\text{MoO}_3)_2\) temperature programmed desorption peak at 1450 K versus SiO\(_2\) deposition time. The Mo(110) was pre-adsorbed with 1000 L oxygen at 1000 K before SiO\(_2\) deposition. The substrate was at 300 K during deposition.

Fig. 8. The integrated \((\text{MoO}_3)_2\) temperature programmed desorption peak at 1450 K versus SiO\(_2\) deposition time. The Mo(110) was pre-adsorbed with 1000 L oxygen at 1000 K before SiO\(_2\) deposition. The substrate was at 300 K during deposition.

\((\text{MoO}_3)_2\) desorption should be proportional to the uncovered surface area. Fig. 8 shows that the integrated peak area of \((\text{MoO}_3)_2\) desorption from SiO\(_2\) partially covered O/Mo(110) (1000 L oxygen at 1000 K) decreases linearly with SiO\(_2\) deposition time, demonstrating that SiO\(_2\) grows two-dimensionally for the first layer on oxygen-covered Mo(110). The SiO\(_2\) deposition time for a full monolayer corresponds to that for the first Auger break in fig. 7. This two-dimensional growth mechanism contrasts the growth mode for SiO\(_2\) on Pt(111), where it has been proposed that SiO\(_2\) forms three-dimensional clusters [9]. This difference may be due to the growth conditions; the SiO\(_2\) on Pt(111) was prepared by annealing a silicon contaminated Pt(111) in oxygen [9].

3.5. Effect of annealing on the SiO\(_2\) film properties

Although the SiO\(_2\) films are stable up to 1600 K, the films undergo significant structural change upon annealing. Fig. 9 shows the electron energy loss spectra (first derivative) for the silicon dioxide films annealed to 350, 800 and 1200 K. The ELS features for the SiO\(_2\) films annealed to 1200 K are identical to those of vitreous silica. Vitreous silicon dioxide exhibits optical excitations at 10.3, 11.8, 14.0, 17.0 and 22–23 eV [28]. In addition, electron energy loss features at 10, 12, 14, 17, 20 and 23 eV have also been reported for thermally grown silicon dioxide on a silicon substrate [29,30]. The ELS for the 1200 K SiO\(_2\) films shows features at ~10, 12, 14, 17 and 20 eV (fig. 9). These ELS features are attributed to inter-band transitions in silicon dioxide whereas the 23 eV feature is due to a bulk plasmon excitation [31].

The silicon dioxide films prepared without post-annealing exhibit additional ELS features at ~5 and 7 eV (fig. 9). These features are attributed either to silicon suboxide [30,32] or to broken Si–O bonds in [SiO\(_2\)] tetrahedra [33]. The fact that the 5 and 7 eV features disappear upon annealing to 1200 K is consistent with these features being due to broken Si–O bonds in [SiO\(_2\)] units, since there are no volatile products below 1200 K. Defect-free vitreous silica consists of [SiO\(_4\)] tetrahedra connected by oxygen bridges to form a long range 3D network. Thus the ~5 and 7 eV ELS features indicate a substantial quantity of broken Si–O bonds, suggesting a less extensive network of [SiO\(_4\)].

The intensity of the ELS features at 5 and 7 eV significantly decreases with heating, and completely vanishes after annealing to 1200 K. Therefore, the silicon dioxide films undergo structural
re-organization during annealing, which reduces the density of broken Si–O bonds and increases the long range 3D network of SiO$_2$.

IR reflection–absorption spectroscopy (IRAS) of silicon dioxide films on Mo(110) further illustrates the structural changes which occur upon annealing (fig. 10). For a thin film with a thickness much less than the IR wavelength, the conductive metal substrate eliminates the absorption of the transverse-optical (TO) modes without reducing the absorption of the longitudinal-optical (LO) modes [34]. Since, the IRAS of the SiO$_2$ thin film on Mo(100) probes the LO modes, the IR reflection spectra are different than those obtained with transmission IR absorption spectroscopy, which probes primarily the TO modes [35,36]. Fig. 10 shows the IR absorption band associated with the asymmetric stretch motion of the Si–O bonds. The IR absorption features associated with local vibrational motion of the symmetric stretching ($\sim 810$ cm$^{-1}$) and rocking ($\sim 460$ cm$^{-1}$) modes for vitreous silica were not accessible due to the CaF$_2$ windows.

The IRAS data in fig. 10 show that the SiO$_2$ films annealed to 1400 K have a structure similar to that of fused quartz. Two absorption features are apparent for the SiO$_2$ film annealed to 1400 K: one feature at 1252 cm$^{-1}$ and one unresolved shoulder at 1160 cm$^{-1}$ are in excellent agreement with the longitudinal-optical modes of fused quartz [37]. Silica has two asymmetric stretching modes in this wavenumber regime, $\text{AS}_1$, corresponding to in-phase motion of adjacent oxygen atoms, and $\text{AS}_2$, corresponding to out-of-phase motion of adjacent oxygen atoms [37]. The LO modes are at 1256 cm$^{-1}$ ($\text{AS}_1$) and 1160 cm$^{-1}$ ($\text{AS}_2$), and the TO modes are at 1076 cm$^{-1}$ ($\text{AS}_1$) and 1200 cm$^{-1}$ ($\text{AS}_2$) [37,38]. The TO modes were not observed in the IRAS.

The broad asymmetric peak centered at 1178 cm$^{-1}$ for the unannealed SiO$_2$ film suggests a bonding structure markedly different from fused quartz, consistent with the ELS results which show broken Si–O bonds in the [SiO$_4$]. Furthermore, the increase in the peak frequency with annealing temperature for the SiO$_2$ films suggests some ordering of the SiO$_2$ film upon heating. The $\text{AS}_1$ and $\text{AS}_2$ modes for silica are coupled due to disorder in the SiO$_2$ [37,38]. The $\text{AS}_1$ mode is optically weak in crystalline $\alpha$-quartz and its intensity increases with a concomitant decrease in the $\text{AS}_1$ intensity in amorphous silicon dioxide [37]. Therefore, the increase of the intensity at 1250 cm$^{-1}$ and the decrease of the intensity at 1160 cm$^{-1}$ strongly indicate that the SiO$_2$ film becomes structurally more ordered with heating.

4. Conclusion

Thin stoichiometric silicon dioxide films can be deposited on a relatively cool Mo(110) substrate ($< 100^\circ$C) by evaporating silicon in a low pressure oxygen background ($\sim 1 \times 10^{-5}$ Torr). The growth of the SiO$_2$ film on the oxygen-covered Mo(110) at room temperature proceeds with a
complete monolayer followed by either layer-by-layer or three-dimensional growth. The gas-phase precursor for the SiO$_2$ film is gaseous SiO, which is produced by low pressure oxidative etching of a heated silicon surface in oxygen.

The SiO$_2$ films deposited at room temperature are amorphous and contain a substantial amount of broken Si–O bonds in the [SiO$_4$] units of vitreous silica. The low temperature films are proposed to consist of short ranged networks of [SiO$_4$]. Upon post-annealing, the broken Si–O bonds in the SiO$_2$ film are mended such that the [SiO$_4$] units are fused into long range networks. After heating the SiO$_2$ films to 1400 K, ELS and IRAS show the films to have electronic and bonding structures very similar to vitreous silica.

Relatively thin films (< 100 Å) of SiO$_2$ on Mo(110) are stable up to 1600 K. At temperatures higher than 1600 K, silicon dioxide is reduced by the molybdenum substrate to form volatile SiO and MoO$_3$. A very thick SiO$_2$ film (> 100 Å) is stable up to 1900 K.

References