The structure of monolayer SiO$_2$ on Mo(112): A 2-D [Si–O–Si] network or isolated [SiO$_4$] units?

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Abstract

In this letter, atomically resolved scanning tunneling microscopic (STM) images obtained from monolayer SiO$_2$/Mo(112) are presented. The results are consistent with a previously proposed structural model of isolated [SiO$_4$] units based on vibrational features observed by high-resolution electron energy loss spectroscopy (HREELS) and infrared reflection–absorption spectroscopy (IRAS), and oxygen species identified by ultra-violet photoemission spectroscopy (UPS). These results are inconsistent with a structural model that assumes a two-dimensional (2-D) [Si–O–Si] network. These data illustrate that a metal substrate, although coated with an oxide thin layer, can be directly imaged at the atomic-scale with STM.

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SiO$_2$, TiO$_2$, and Al$_2$O$_3$, are extensively used as catalytic supports. Unlike TiO$_2$, which is a semiconductor and can be investigated using a variety of surface science techniques, bulk SiO$_2$ is an insulator and of limited utility in model catalytic studies. Amorphous SiO$_2$ films have been synthesized on Si [1–4] and Mo(110) [5,6]; however, an important step for the preparation of model SiO$_2$ surfaces as a catalyst support is the synthesis of well-defined, ultra-thin SiO$_2$ films. Such films are required to have a thickness sufficient to exhibit the surface properties of bulk SiO$_2$ yet thin enough to facilitate the use of surface science techniques. Ordered SiO$_2$ films yielding a sharp c(2×2) low-energy electron diffraction (LEED) pattern and a single mode at 1048–1056 cm$^{-1}$ in infrared reflection–absorption spectroscopy (IRAS), corresponding to the asymmetric vibration of Si–O, have been grown on Mo(112) by annealing multilayer SiO$_2$ films at 1200–1250 K [7,8]. Using stepwise deposition of submonolayer Si to an oxygen-covered Mo(112) surface, oxidation at ~800 K followed by an anneal at 1200 K, a SiO$_2$ film with identical vibrational features (Fig. 1a) and LEED pattern was obtained [9,10]. This is a self-limited preparation method, i.e., the final thickness is independent of the initial coverage once the surface is completely covered [9]. The specific thickness of this ordered film was determined to be only one monolayer based on Auger electron attenuation and the single phonon feature for the Si–O asymmetric vibration observed by high-resolution electron energy loss spectroscopy (HREELS) (see Fig. 1a) [9]. For a monolayer film there are a limited number of possible structures with a c(2×2) arrangement on Mo(112): isolated [SiO$_4$] units (Fig. 1b), a one dimensional (1-D) chain-like structure, and a two-dimensional (2-D) network structure (Fig. 1c) [9]. Since the film is a single layer in thickness, the SiO$_2$ layer must bind to the substrate Mo atoms, i.e., there must be Si–O–Mo linkages. The features at 1048 cm$^{-1}$ in HREELS [9] and 1056 cm$^{-1}$ in IRAS [10] were assigned to the asymmetrical vibrational mode of Si–O–Mo [9]. Since no modes were observed at ~1176 cm$^{-1}$ in HREELS (Fig. 1a) [1–3,9] or at 1200–1250 cm$^{-1}$ in IRAS [6,10,11] corresponding to the asymmetrical vibrational modes of a
Si–O–Si species, the 1-D chain-like and 2-D network models were rejected, the only viable model being the one with isolated [SiO₄] units [9]. This was confirmed by identification of an oxygen species with ultra-violet photoemission spectroscopy (UPS), where a single feature at a binding energy of 10.5 eV, corresponding to an oxygen species in the Si–O–Mo linkage, was evident. No evidence was seen at or near 11.5 eV for an oxygen species corresponding to Si–O–Si linkages [10]. Density-functional calculations (DFT) offer support for isolated [SiO₄] units [12] and the 2-D network model [13,14] structures. In this letter, we present direct atomically resolved images of the isolated [SiO₄] and 2-D network for SiO₂(1 ML)/Mo(112) surface that are entirely consistent with the isolated [SiO₄] structural model and inconsistent with the 2-D network model.

The experiments were carried in an ultra-high vacuum (UHV) chamber with a base pressure of ~1 x 10⁻¹⁰ Torr and equipped with scanning tunneling microscopy (STM: Omicron room temperature), low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), X-ray photoemission spectroscopy (XPS) and temperature programmed desorption (TPD). The substrate temperature was measured directly with 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 Mo(112) sample was cleaned by repeated cycles of oxidation at 1200 K for an additional 10 min. Following this procedure, a (p2 × 3)-O surface was obtained. The silica films were prepared by depositing less than 1 ML Si onto a Mo(112)-p(2 × 3)-O surface, followed by annealing at 800 K in 1 x 10⁻⁷ Torr O₂ for 5 min then increasing the temperature to 1200 K for an additional 5 min. This Si deposition/oxidation/annealing procedure was repeated several times until a constant Si/Mo AES ratio was achieved [9]. The so-formed surface exhibits a sharp c(2 × 2) LEED pattern indicating a well-ordered surface structure.

Fig. 2 shows STM images of the SiO₂(1 ML)/Mo(112) surface that indicate a smooth surface with large terraces. Furthermore, the images also display a well-ordered surface arrangement with low defect density (Fig. 2b). The heights of the steps and islands on the terraces (see the insert of Fig. 2a) are approximately 1.2–1.5 Å, close to the layer spacing of 1.25 Å for Mo(112). Since the layer spacing for SiO₂ is ~3 Å, the height difference between the steps is therefore induced by the Mo substrate rather than the formation of different layers of SiO₂, consistent with the thickness of the film being one monolayer [9].

Fig. 3 shows STM images obtained at room temperature for SiO₂(1 ML)/Mo(112) at various sample bias voltages. The most characteristic feature of the STM image is the single spot in each Mo(112)-c(2 × 2) unit found at relatively high positive or negative sample bias voltages (+1.5 to +4.0 V in Fig. 3a and −2.5 V in Fig. 3f). It is general agreed that at relative high positive sample bias voltages the protruding spots of STM images of oxide surfaces correspond to the positively charged surface atoms [15–17] in this case, Si⁴⁺. The single spot seen at positive bias voltages (+1.5 to +4.0 V) indicates that there must be one cation that is significantly different from the others in each Mo(112)-c(2 × 2) unit. There are two identical Si atoms and three essentially identical oxygen atoms in a c(2 × 2) unit in the 2-D SiO₂ network model (Fig. 1c), but only one Si atom, i.e., one [SiO₄] group, in each unit of the isolated [SiO₄] model (Fig. 1b). Therefore, the 2-D network model is inconsistent with these single-spot images. The single-spot seen at negative bias voltage of −2.5 V (Fig. 3f) likely corresponds to the [SiO₄] group in the isolated model (Fig. 1b). Indeed, a single spot indicative of the [SiO₄] structure was observed at a bias voltage of −0.8 V (Fig. 3g). Note that the detail arrangements of the Si, O and surface Mo atoms may be different from the schematic shown for the isolated [SiO₄] model in Fig. 1b.

At lower bias voltages, +0.45 V (Fig. 3e), −0.8 V (Fig. 3g), −0.6 V (Fig. 3h), and −0.4 V (Fig. 3i), the (1 × 1) structure of the Mo(112) substrate, in addition to an appar-
ent single spot, was imaged. The images obtained at low bias voltages (Fig. 3d, e, h and i) clearly show (1 x 1) arrangements of the Mo(112) substrate with two spots in each lattice unit. This observation cannot be explained by any structural model proposed for SiO$_2$(1 ML)/Mo(112) including the 2-D network or the isolated [SiO$_4$] unit models [9] considering the surface oxygen and Si atoms (see Fig. 1b and c). An interpretation of these features, i.e., four spots in a Mo(112)-c(2 x 2) unit with an arrangement identical to the substrate Mo(112) with one being distinguishable from the other three, requires that the substrate Mo atoms contribute to the observed STM image. The variation in

Fig. 2. STM images of SiO$_2$(1 ML)/Mo(112): (a) 100 nm x 100 nm, (b) 20 nm x 20 nm. The insert shows a line scan profile of the white line indicated in the image. $U_s = +3.0$ V, $I = 0.5$ nA.

Fig. 3. STM images of SiO$_2$(1 ML)/Mo(112) at various sample bias voltages. All images have dimensions of 3.5 nm x 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, $I = 0.5$ 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 V to +2.5 V half-way of the upward scan and shifted back from +2.5 V 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 x 2) unit is indicated in each image.
the protruding spots may arise from variation in the binding of these sites with oxygen atoms. Indeed, contributions from the metal substrate to the observed STM image of an oxide overlayer at relatively low bias voltages have been discussed in detail for MgO(1 ML)/Ag(100) [18,19], and Al₂O₃/γ-TiAl(111) [20]. Fig. 3 j and k show the reversibility of the effects of bias voltages, where a full scan consists of upward and downward scans. The bias voltage was shifted from +0.6 V to +2.5 V at the half-way point of the upper scan then back to +0.6 V at the half-way point of the downward scan. The image before the shift to +2.5 V is identical with that acquired after the shift back to +0.6 V, demonstrating that different images observed at various bias voltages are due to tip bias rather than tip condition.

At a bias voltage of −3 V, another detailed arrangement of surface atoms was observed as shown in Fig. 4a. In each Mo(112)-c(2 × 2) unit, two pairs of protruding spots are apparent, one brighter than the other. This arrangement is different from that of Mo(112)-(1 × 1), and from either surface oxygen (red balls) or Si (blue balls) atoms in the 2-D network model in Fig. 4b. Since this image was only seen at relatively high negative bias voltages (−3 V), near the energy level of the O 2p state (−3 eV below the Fermi level), the protruding spots likely correspond to surface O₂⁻ sites. The pair of bright spots in the c(2 × 2) unit likely correspond to the two oxygen atoms at the topmost surface in the isolated [SiO₄] model. The pair of less intense spots on the other hand likely corresponds to the two oxygen atoms in the Mo(112) trough, as shown in Fig. 4c and d. A superposition of oxygen atoms onto the image shows a clear domain boundary where the Mo–Mo distance is evident, as indicated by the dash-line in Fig. 4a and b.

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Fig. 4. (a) STM image of SiO₂(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 topmost layer and in the Mo(112) troughs in the isolated [SiO₄] model. (c) Top-view of the structural model of the 2-D network highlighting the surface Si and oxygen atoms. (d) Top- and side-view of modified structural model of isolated [SiO₄] for SiO₂(1 ML)/Mo(112).

1 For interpretation of colour in Fig. 4, the reader is referred to the web version of this article.
According to the STM images, the axis of the pair of the topmost oxygen atoms is inclined to the [−1 1 0] direction. Based on these data the isolated [SiO₄] structural model of Fig. 1b was modified to best fit the observed STM images. The modified structure shown in Fig. 4d adequately explains the STM images of Figs. 3 and 4.

Relevant to the DFT results of Refs. [13,14] that support 2-D network model in Fig. 1c is the question regarding which modes of the Si–O asymmetrical vibrations, i.e., the transverse optical (TO) and/or longitudinal optical (LO), are observed for a monolayer SiO₂/Mo(112) in infrared reflection–absorption spectroscopy (IRAS) using p-polarized, grazing incidence IR light. The TO modes reported in [13,14] were calculated using DFT and compared with the experimental frequencies obtained by IRAS with a grazing incidence angle of 84° (from the surface normal) and p-polarized light. However, it is well-established that for dielectric thin films only the TO mode is observed in transmission and reflection IR using normal incident light, while both the TO and LO modes are observed with grazing incident light, with the intensity of the LO mode increasing with an increase in the grazing angle [5,10,21–26]. Furthermore, the intensity of the LO mode is enhanced significantly using p-polarized light [24]. For an ultra-thin oxide film with the thickness less than the Berreman thickness, ~100 nm, the TO modes are completely suppressed using grazing incidence and p-polarized IR light [21,22]. This has been demonstrated in previous studies of thin SiO₂/Mo(110) films (thickness < 10 nm) [6] and more recently with SiO₂/Mo(112) (thickness < 1 nm) [10] where only LO modes of the Si–O asymmetric vibrations were observed.

In summary, in view of the vibrational features observed in IRAS and HREELS, the unique oxygen species identified by UPS, and the bias-dependent STM images acquired for monolayer SiO₂/Mo(11 2), we suggest that the detailed structure of monolayer SiO₂/Mo(1 1 2) remains in question, and, in fact, the most viable model is one consisting of isolated [SiO₄] units rather than a 2-D network.

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