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Formation of one-dimensional crystalline silica on a metal substrate

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Abstract

We have observed formation of one-dimensional silica structures of 0.5 nm in width on Mo(1 1 2) single crystal surface. Combination of high-resolution scanning tunneling microscopy, photoelectron and infrared spectroscopy, and density functional theory provides strong evidence for formation of paired rows of corner sharing [SiO$_4$] tetrahedra chemisorbed on a metal substrate.
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Preparation of well-defined oxide nanostructures, such as thin films and clusters, on metal substrates under controlled conditions is very important for an understanding of fundamental aspects of metal/oxide interaction. The metal substrate may provide not only a template for an epitaxial growth but may also be directly involved in stabilization of structures otherwise unstable like, for example, (1 1 1) surfaces of oxides with the rock-salt structure [1–3]. The metal/oxide interaction plays a crucial role in modern technologies, such as microelectronics, photonics and catalysis, where the dimension of "active zones" goes into the nanometer scale.

Silica (SiO$_2$) is well known as an important material in this "nano-world". In order to understand the structure and properties of silica-based systems on an atomic level, preparation of ultra-thin crystalline silica films grown on a Mo(1 1 2) substrate has been developed [4–6]. It has been recently established that the film consists of a monolayer of corner sharing [SiO$_4$] tetrahedra as a two-dimensional (2D) network, with one corner oxygen bonded to the Mo atoms

[7,8]. The structure of this silica film resembles the sheet structure of monolayer silicates [9], and the film surface exposes Si–O–Si bonds similar to internal surfaces of microporous silica modifications [10].

In this Letter, we report on the formation of crystalline silica with even further reduced dimensionality, i.e. as one-dimensional (1D) rows of corner sharing [SiO$_4$] units chemisorbed on a Mo substrate. The atomic structures of these silica "nanowires" have been determined by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), infrared reflection absorption spectroscopy (IRAS) and density functional theory (DFT).

The experiments were performed in an ultra high vacuum (UHV) chamber (base pressure below 1×10^{-10} mbar) equipped with STM, XPS, an IR-spectrometer and standard facilities for sample cleaning and preparation [5,7]. The IR spectra were measured with p-polarized light at 84° grazing angle of incidence (resolution $\sim$2 cm^{-1}). The binding energies (BE) in XPS spectra were calibrated relative to the Fermi edge of the clean Mo crystal. STM images were taken at room temperature and the bias voltage is given relative to the sample.

For formation of well ordered silica structures, the clean Mo(1 1 2) surface is exposed to oxygen, followed by Si

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vapor deposition in an oxygen ambient and subsequent annealing in vacuum at elevated temperature [4–7].

Fig. 1a shows an STM image of the sample possessing approximately a half of monolayer of Si deposited onto Mo(1 1 2) at 850 K in 5×10^{-8} mbar of O_2 and then annealed in UHV at 1000 K for 5 min. Formation of long features running along the $[\bar{1}\,\bar{1}\,1]$ crystallographic direction of Mo(112) is clearly seen. High-resolution images presented in Figs. 1b, c show that each stripe consists of two rows of protrusions, with distances between the protrusions of ~2.8 Å and ~4.5 Å in the $[\bar{1}\,\bar{1}\,1]$ and $[\bar{1}\,1\,0]$ directions, respectively. The distances match well the unit cell of the Mo(112) surface (2.73 Å × 4.45 Å). In addition, ill defined ridge-like features can be randomly observed between the silica stripes. These features were found in the blank experiments on the Si-free Mo(112) surface prepared at the same conditions. Therefore, they can be tentatively assigned to MoO_x species (see also XPS results below).

When the silica stripes coalesce, particularly at increasing Si coverage, islands exhibiting a honeycomb-like structure are formed as shown in Fig. 1b. STM images of these islands are identical to those previously observed for the dense silica film [7]. As determined by low energy electron diffraction, the unit cell of the silica film exhibits a $c(2 \times 2)$ structure with respect to Mo(112) as indicated in Fig. 1c.

Fig. 1c shows the STM image where both the stripes and the island are atomically resolved. The rectangular grid on this image represents a Mo(112) lattice. It is clear that the protrusions on the stripes and on the island surfaces are in a perfect registry, which implies the same nature of protrusions. Therefore, knowing the structure of the silica film one can determine the structure of the silica stripes as well. Here we recall the model of the silica film [7], which is schematically shown in Fig. 1d. In this model, the film is formed by a network of the corner sharing $[SiO_4]$ tetrahedra, with one oxygen (O3) atom pointing towards the protruding Mo rows of the substrate. Under tunneling conditions applied to the image in Fig. 1c, the protrusions show positions of the O2 atoms, which sit above the Mo atoms [7].

Based on the registry relationship observed by STM, a starting point for structural search is to mark two adjacent rows of the $[SiO_4]$ tetrahedra along the $[\bar{1}\,\bar{1}\,1]$ direction and to "unzip" them by removing the O1 atoms on both sides of this paired row. Then the dangling bond of the Si atoms, which lost the O1 atoms, flips over and couples with the counterpart Si atom on the other side of the row through the oxygen atom, which is again O1 in nature. This leads to the formation of stripes as schematically shown in Fig. 1d. However, within this model the distance between
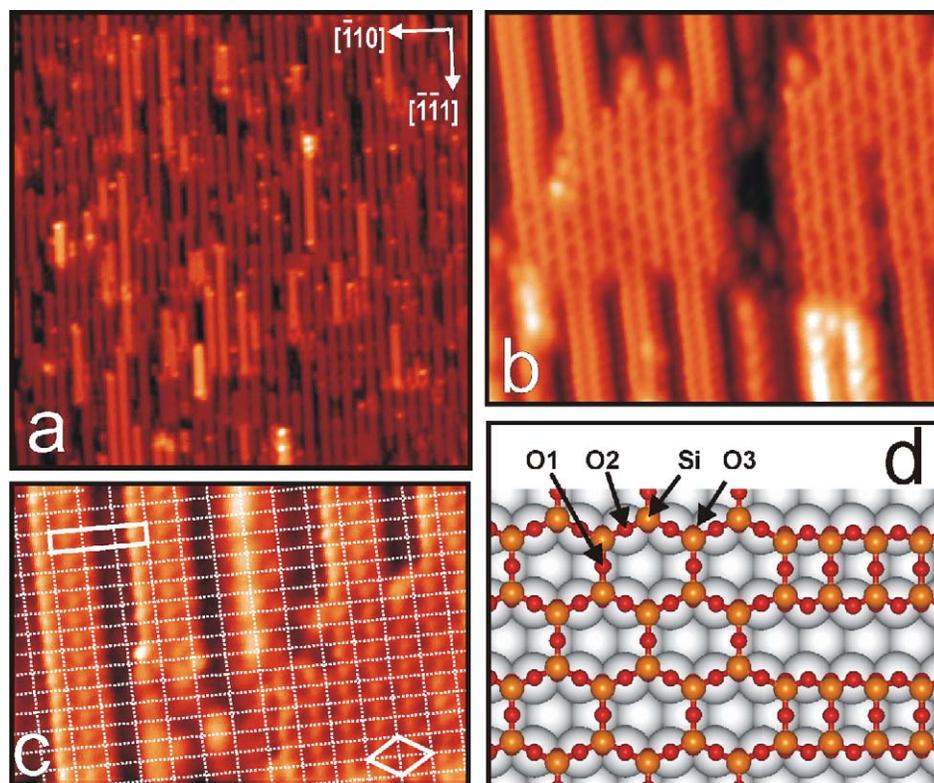
Fig. 1. (a–c) STM images of the silica stripes formed on Mo(112). Image (c) zooms in the region where both the stripes and the island of silica film is atomically resolved. The rectangular grid represents the Mo(112) lattice. The rhomb indicates the unit cell of the silica film, which forms a $c(2 \times 2)$ structure with respect to Mo(112). Image size and tunneling parameters are: (a) 50×50 nm^2, bias 3.9 V, current 0.2 nA; (b) 12.5×10.5 nm^2, −0.4 V, 0.4 nA; (c) 6.5×4.5 nm^2, −0.5 V, 0.4 nA. (d) Top view of the silica film model as determined in [7]. The right part of the figure only illustrates possible formation of the silica stripes by cutting the silica film along the O1 atoms in the $[\bar{1}\,\bar{1}\,1]$ direction of Mo(112); the correct model is shown in Fig. 2.

stripes is two times the Mo(112) substrate lattice in the [$\bar{1}$10] direction, which contradicts the experimentally measured by STM value of 13.4 Å (see Fig. 1c), that is three times the Mo(112) lattice. It is important to note that this spacing (13.4 Å) is the same as in the $p(2 \times 3)$ reconstruction observed on the O/Mo(112) surface prior to Si deposition [5,7]. This finding suggests that formation of silica stripes must be associated with the oxygen induced reconstruction of the Mo surface.

Based on the (1×3) unit cell observed by STM (see Fig. 1c) and the proposed structure of the silica stripes as paired rows of corner sharing [SiO$_4$] tetrahedra running along the [$1\bar{1}1$] direction (see Fig. 1d), we have applied density functional theory[1] to predict the thermodynamically most stable structure. We considered 50 structures in total, including models with (1×2), (1×3) and (2×3) periodicity as well as unreconstructed and "missing row" reconstructed Mo(112) surfaces. The models included different registry of silica stripes with respect to the Mo substrate atoms and varying amount of oxygen atoms chemisorbed directly onto the Mo(112) surface.

The relative stability of each structure was estimated using the energy of formation, ΔE_{form}, from clean Mo(112) surface, bulk silicon and molecular oxygen:

$$\text{Mo}(112) + m\text{Si} + n\frac{1}{2}\text{O}_2 \rightarrow (\text{SiO}_2)_m \cdot (n - 2m)\text{O}/\text{Mo}(112)$$
$$+ \text{Mo}^{bulk} \qquad (1)$$
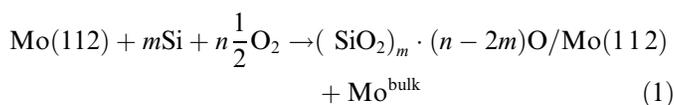
where m and n are the number of Si and O atoms in the unit cell. The term Mo^{bulk} appears only for the reconstructed surface, which is assumed to be in equilibrium with bulk Mo. However, the ΔE_{form} cannot be compared straightforward for structures having different chemical composition. To relate the stability of the structures to the conditions used in the experiments we define a surface related free energy change $\Delta\gamma$ defined per surface area S as

$$\Delta\gamma(T,p) = \frac{1}{S}[\Delta E_{form} - m\Delta\mu_{Si}(T,a_{Si}) - n\Delta\mu_O(T,p)] \qquad (2)$$

with $\Delta\mu_{Si}(T,a_{Si}) = \mu_{Si} - E_{Si}$ and $\Delta\mu_O(T,p) = \mu_O - 1/2E_{O_2}$, where μ_{Si} and μ_O are the silicon and oxygen chemical potentials, E_{Si} and E_{O_2} are energies of the bulk Si and molecular O$_2$. The chemical potentials of Si and O, $\Delta\mu_{Si}(T,a_{Si})$ and $\Delta\mu_O(T,p)$, respectively, can be related to silicon activity, a_{Si}, and oxygen partial pressure, p_{O_2} using standard thermodynamics [16,17].

Using this methodology, we have determined the structure, shown in Fig. 2, as the most stable stripe model at 5×10^{-8} mbar of O$_2$ and 1000 K applied in the experi-

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[1] Calculations were performed with the Vienna ab initio simulation package (VASP) [11,12] using the projector-augmented wave (PAW) method [13,14]. An energy cutoff of 400 eV and the Perdew–Wang (PW91) [15] exchange–correlation functional were applied. The Mo(112) surface was modeled using seven atomic layers with the four topmost fully relaxed and the three bottom layers kept frozen at their bulk positions.

Fig. 2. Perspective (a) and top (b) views of the thermodynamically most stable structure of silica stripes formed on a Mo(112) substrate. A simulated STM image is superimposed with the structure in order to show that the protrusions correspond to the position of the O$_2$ atoms. The (1×3) surface unit cell is indicated as a rectangle similar to that on image (c) in Fig. 1.

ments. In this structure the Mo surface is reconstructed and possesses oxygen adsorbed in pseudo threefold hollow (O*2), short-bridge (O*1) sites, and also in short-bridge (O*3) sites under the silica stripe. A simulated STM image of this structure, shown in Fig. 2, matches well the experimental STM images shown in Fig. 1.

Within this model, the electronic and vibrational properties of the silica stripes are expected to be similar to the silica film. Indeed, the Si 2p region in the XPS spectra (not shown) revealed only a single peak with a binding energy (BE) of 103.0 eV, which is characteristic for Si in an oxidation state 4+ [18]. The O 1s region for the silica stripes shows at least three different oxygen species (Fig. 3). Two components centered at 531.2 eV and 532.5 eV are essentially identical to those found for the 2D film. The higher BE component has been previously assigned to the oxygen atoms in the outmost layer (O1 and O2 in Fig. 1d) and the lower BE component – to the oxygen (O3) atoms bound to the Mo substrate. The third component at ~530.2 eV is observed for the Si-free surface, which is therefore assigned to oxygen chemisorbed on Mo(112).

Fig. 3. O 1s region of XPS spectra obtained for the silica structures formed on Mo(1 1 2). The spectrum for the Si-free surface prepared under the same conditions is shown for comparison. The spectra deconvolution for the stripes is performed using fitting parameters obtained for the silica film and Si-free surfaces.

Even stronger evidence for the proposed structure comes from the study of lattice vibrations, which are very sensitive to the silica structure and in particular to the registry between silica and Mo substrate [7]. The phonon region of the IRAS spectra taken for the silica stripes and the film are shown in Fig. 4. For the 2D film, we have previously assigned the most intense band at 1059 cm^{-1} to the asymmetric Si–O–Mo stretching,
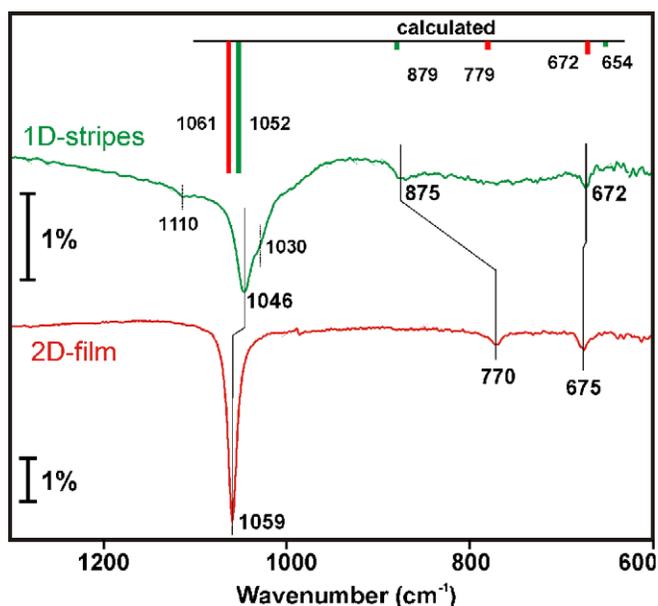
Fig. 4. IRAS spectra of silica structures formed on Mo(1 1 2). The frequencies calculated for the structure, shown in Fig. 2, are shown as bars with their height proportional to the vibration intensity (the colour code is the same as for the experimental spectra).

weak signals at 770 cm^{-1} to the Si–O–Si symmetric stretching coupled with Si–O–Si bending mode, and at 675 cm^{-1} to a coupling of Si–O–Si bending modes [7]. When silica stripes are formed, the spectra revealed a shift of the main signal to the lower wavenumbers (1046 cm^{-1}) and weak absorption bands at 875 and 672 cm^{-1}. (The weak signals at 1110 cm^{-1} and 1030 cm^{-1} (as a shoulder) can be attributed to silica particles and/or ill defined MoO_x structures (see Figs. 1b, c) present on the surface.)

Calculated harmonic vibrational frequencies[2] of the stripes model revealed three IRAS active modes at 1052, 879, and 654 cm^{-1}, which are in a good agreement with the experimental results as shown in Fig. 4. The origin of these modes is similar to those calculated for the 2D silica film [7]. The major difference between stripes and film is observed for the mode at 879 cm^{-1}, which is shifted by ~100 cm^{-1} towards higher wavenumbers as compared to the 2D film. This is due to the fact that this mode becomes essentially a Si–O–Si symmetric stretching vibration within the stripes, and has less Si–O–Si bending character than in the film. The mode calculated at 654 cm^{-1} is the Si–O–Si bending coupled with the Mo–O stretching involving the O atoms adsorbed directly on the Mo surface. This is in agreement with the previous study of the oxygen adsorption on the Mo(1 1 2) surface [19] which suggests that O atoms in threefold hollow sites exhibit a Mo–O stretching frequency in the range of 620–670 cm^{-1}. It should be mentioned that, similar to the 2D film, there are also a number of other vibrational modes undetectable in the experiments due to the selection rule applied in IRAS [20]. They include combinations of Si–O–Si asymmetric stretching vibrations in the range of 985–1206 cm^{-1} (1008–1195 cm^{-1} for the 2D film), the out-of-phase Si–O–Mo asymmetric stretching at 928 cm^{-1} (863–912 cm^{-1} for the film), and the coupled Si–O–Si bending with Mo–O3 stretching at 787 cm^{-1} as well.

In summary, we have shown formation of one-dimensional crystalline silica structures of 0.5 nm in width on a metal substrate. The atomic structure has been determined through a combination of experiment and theory, which provide strong evidence on the formation of silica "nanowires" as paired rows of corner sharing $[SiO_4]$ tetrahedra chemisorbed on a Mo substrate. Since silica nanowires have gained much interest owing to their potential use in microelectronics, photonics and sensors [21–23], we believe that our observation may open new technological applications. However, further studies on dielectric and electronic properties of these one dimensional silica structures remain to be done.

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[2] We used the harmonic approximation within the finite difference method with 0.02 Å displacements. The intensities were obtained from the dipole moment component perpendicular to the surface. A scaling factor of 1.0312 was applied to the frequencies (see [7]).

Acknowledgements

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