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Ag clusters on ultra-thin, ordered SiO$_2$ films

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Abstract

Scanning tunneling microscopy (STM) and low energy electron diffraction have been used to optimize the key synthetic parameters for the preparation of oriented, SiO$_2$ films on Mo(112). Extremely flat, ultra-thin, single-crystalline SiO$_2$ films have been prepared via deposition of silicon, its subsequent oxidation, followed by an anneal. Highly resolved STM images have been obtained for the first time on these films. At room temperature, Ag clusters grow two-dimensionally on these oriented films with a preferred orientation and sinter with a bimodal size distribution upon exposure to elevated pressures (160 mb and 60 min) of oxygen. Annealing the as-deposited Ag clusters at elevated temperatures (>600 K) in ultra-high vacuum also leads to sintering.

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Metal clusters on oxide supports have received considerable attention because of their relevance in heterogeneous catalysis [1–14]. Models of supported-metal catalysts have been prepared by vapor depositing metals onto oxide supports [4–6, 10]; however, the insulating character of most oxide supports render them unsuitable for use with many surface science probes. To circumvent this difficulty, ultra-thin films of oxides on refractory metal substrates have been synthesized and found amenable to study by a variety of surface science techniques [4–6,10]. These films are thin enough to prevent surface charging yet exhibit electronic and chemical properties comparable to their bulk analogs. Work in our group has addressed the synthesis of a variety of oxide thin films including SiO$_2$ [14]. Very recently, Freund and co-workers [8,9] have shown that an epitaxial, single-crystalline SiO$_2$ film of most likely β-tridymite type can be prepared on Mo(112) by deposition of Si, oxidation, followed by annealing. These workers have also shown the growth of Pd particles on such films using scanning tunneling microscopy (STM) [10]. In this communication, using STM as a diagnostic, we report a slightly modified method for the preparation of an extremely flat, well-ordered SiO$_2$ film on Mo(112). The growth and sintering behavior of Ag metal clusters on this support are also described.

The ultra-high vacuum (UHV) chamber (base pressure < 4 × 10$^{-10}$ mb), equipped with STM, X-ray photoelectron spectroscopy (XPS), low energy
electron diffraction (LEED) and Auger electron spectroscopy (AES), is described in detail elsewhere [11]. Briefly, the system contains a double-pass cylindrical mirror analyzer for AES and XPS, reverse view LEED optics, and a room temperature STM (Omicron). Typically the STM images were acquired in the constant current mode at \( \sim 1-2 \) V and 0.083 nA. Ultra-high purity (99.999\%) oxygen from MG industries was used. The Mo-(112) crystal, purchased from Matek, was oriented within \(<0.25^\circ\) of the indicated plane. LEED results for the clean surface showed a very sharp rectangular \( p(1\times1) \) pattern; wide terraces and steps were observed in the STM images confirming the accuracy of the crystal orientation. SiO\(_2\) films were grown via a rather simple method consisting of the deposition of 0.5 monolayer equivalents (MLE) of Si at 300 K followed by oxidation in \( 1 \times 10^{-7} \) mb of O\(_2\) (5 min) at 800 K. This process was repeated several times depending upon the desired film thickness. Finally the film was annealed at 1100 K in \( 1 \times 10^{-7} \) mb O\(_2\) for 30 min. The annealing process is slightly different from that followed by Freund and co-workers [8,9] who used a two-step annealing procedure. The thicknesses of SiO\(_2\) films were calculated from the relative attenuation of Mo AES intensity [12] while the coverage of Ag was estimated from quantitative Auger calibration curves using the ratio of Ag/Mo relative intensities versus the deposition time assuming layer-by-layer growth. Typically the optimum deposition rates were found to be near 12 min/MLE. Ag was deposited from a thoroughly out-gassed tungsten filament wrapped with a high-purity Ag wire.

A goal of the experiments was the optimization of the parameters crucial to the preparation of high-quality SiO\(_2\) films, i.e., silicon deposition flux, oxidation time and exposures, and the temperature/time of the final anneal to establish film quality. Films prepared using this recipe grow in a layer-by-layer manner oriented along the \([11\bar{1}]\) rows of Mo(112). Absence of any Si or SiO related features in the AES and XPS confirmed that the films grow stoichiometrically [4]. A constant current STM image (400 nm \( \times \) 400 nm) of a representative SiO\(_2\) film (0.5 nm) is shown in Fig. 1 in which the wide terraces and steps of an extremely flat SiO\(_2\) film are apparent. The dark areas in this image are likely due to the stacking faults that occur during film growth. The lower-left inset of Fig. 1 shows an highly resolved (10 nm \( \times \) 10 nm) image of a SiO\(_2\) film (at the early stage of growth) with epitaxial growth along the \([11\bar{1}]\) rows of the substrate Mo(112). The sharp hexagonal LEED pattern in the upper-right inset of Fig. 1 was observed for film coverages \( >0.9 \) nm. It is noteworthy that during our investigation sharp hexagonal LEED patterns were also observed for SiO\(_2\) films prepared by several other methods, however, these alternative preparations did not produce uniformly flat films as determined by STM. Thus a sharp hexagonal LEED pattern is insufficient evidence for a high-quality, flat film.

An investigation of the growth of Ag clusters on oriented, SiO\(_2\) films with varying thicknesses was also carried out. In Fig. 2, a typical STM image (100 nm \( \times \) 100 nm) is shown of Ag clusters (0.8 MLE) deposited at room temperature on a SiO\(_2\) film of 0.5 nm thick. The Ag particles grow in a 2D manner as reported previously for a TiO\(_2\)(110)
substrate [13]. More interestingly, the 2D Ag clusters are not circular but rather are elongated and oriented along the direction of the SiO2 rows, i.e., the [1 1 1] direction. Metal clusters growing with this orientation can be explained only by assuming a relatively strong interaction between the metal and the substrate.

Fig. 3A, shows a typical STM image (200 nm × 200 nm) of 3 MLE Ag, deposited on SiO2 (0.5 nm). It should be noted that by increasing the Ag coverage from 0.8 MLE (Fig. 2) to 3 MLE (Fig. 3A), the particle size and density are significantly enhanced. The Ag clusters, however, preserve their orientation with respect to the SiO2 rows as well as their elongated shape. The changes that occur in the morphology of these Ag clusters because of the elevated gas pressure and/or temperatures have been followed by STM. Recently, we have reported [13] that the sizes of Ag clusters deposited on a TiO2(1 1 0) substrate and exposed to 13 mb of O2 gas at room temperature change significantly, i.e., the larger clusters grew at the expanse of small clusters leading to a bimodal distribution (Ostwald ripening). In the present study, the clusters shown in Fig. 3A, when exposed to relatively high oxygen pressures (160 mb and 60 min), alter their size distribution (Fig. 3B). More interestingly, we see that along with the change in cluster size, cluster shape and orientation have also dramatically changed. This change in shape (2D to 3D hemispheres) and the loss of orientational ordering is consistent with the explanation given previously that an Ag2O phase is involved in the sintering process [13].

It is well known that metal clusters of model catalysts undergo sintering concurrently with a dramatic change in the reactivity at elevated temperatures [13]. We have therefore carried out a detailed investigation of the sintering behavior of the Ag clusters on these well-defined SiO2 films as a function of temperature. The following points are noteworthy: (a) a threshold temperature for sintering in UHV is evident near 600 K; and (b) the ultimate size, shape and decoration of the particles depends strongly on the heating rate, time and temperature. Fig. 3C shows a typical STM image of the Ag clusters after annealing the surface shown in Fig. 3A at 700 K for 2 min in UHV. As shown previously [13] and as seen in Fig. 3C, the cluster size increases and the cluster shape and orientation are altered. However, the average cluster size in Fig. 3C is much larger compared to the clusters of Fig. 3B. An area with a high density of steps was chosen purposefully to show the preferential decoration of the Ag clusters near the step-edges, i.e., the strong cluster–substrate interaction at these sites. It is noteworthy that the same surface showed almost uniform decoration on the extended terraces indicating that the clusters sense the steps only in their vacinity.

In summary, atomically resolved STM images show that very high-quality, flat SiO2 films can be prepared in a layer-by-layer manner on an atomically clean Mo(1 1 2) surface by silicon deposition, oxidation, and annealing. However, a sharp hexagonal LEED pattern can be obtained at film coverages >0.9 nm. At room temperature, Ag clusters grow along the direction of the SiO2 rows, consistent with a relatively strong interaction between the metal and support. Exposure to 160 mb oxygen at room temperature leads to a bimodal distribution of the clusters as reported previously [13]. However, preferential decoration of the clusters occurs around areas of very high step density.
only after annealing the as deposited clusters in UHV at 700 K.

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References


Fig. 3. A STM image of Ag (3 MLE) deposited on a SiO2 (0.5 nm): (A) as-deposited at 300 K, (B) after exposure to 160 mb of O2 for 60 min, and (C) as-deposited clusters after annealing at 700 K for 2 min under UHV.