Ag growth on Mo(112)–O

A. K. Santra, B. K. Min, and D. W. Goodman

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012

(Received 26 March 2002; accepted 24 June 2002)

The growth of Ag clusters on preadsorbed oxygen and oxide-covered Mo(112) has been investigated using scanning tunneling microscopy (STM). The objective of these experiments is the synthesis of adjacent areas on a surface with distinctly different metal–support interactions in order to investigate the relationship between the morphology of a supported metal cluster and the strength of the cluster–support interaction. The STM results show that more highly dispersed Ag clusters with a greater number density are obtained on that surface that interacts to a greater extent with the metal.

Heating leads to the formation of two-dimensional–Ag nanostructures on oxygen-free Mo(112) (strong metal–support interaction) and three-dimensional cluster growth on oxide-covered Mo(112) (relatively weak metal–support interaction). © 2002 American Vacuum Society.

[DOI: 10.1116/1.1501581]

I. INTRODUCTION

The study of metal clusters on oxide supports has received considerable recent attention because of the technological importance of supported metal clusters, particularly in the area of heterogeneous catalysis.1–9 These studies have shown that the catalytic properties of ultrasmall metal clusters are clearly a function of cluster size. Therefore, considerable work has been directed toward understanding cluster growth and the role of the metal–support interaction in defining cluster morphology. Several simple models for the growth morphologies have been proposed for metal clusters deposited on various substrates. These models generally assume that the substrate contains randomly distributed nucleation sites and that the metal cluster size depends on the distribution of these fixed nucleation sites and the amount of metal deposited. For amorphous carbon substrates the number of nucleation sites are large. Egelhoff and Tibbetts10 proposed that on substrates with an abundance of nucleation sites deposition initially yields isolated adatoms. These isolated adatoms, in turn, diffuse randomly on the substrate, eventually coalescing with another adatom or adatom cluster. Since the nucleation sites are randomly distributed and the diffusion itself random, the result is a distribution of cluster sizes at each metal coverage. The diffusion of metal particles, however, along a surface depends critically on the metal–support interaction. For flat, well-ordered surfaces, in particular, the number of nucleation sites are relatively small, therefore, the cluster size distribution will show a marked dependence on the strength of the metal–support interaction. A surface with a relatively large metal–support interaction typically yields smaller clusters with high number densities. Large clusters with low number densities are typically found on surfaces with a relatively weak metal–support interaction. Since the metal adatom diffusion is critically dependent on the strength of the metal–support interaction and the surface temperature, increasing the surface temperature should enhance the rate of cluster sintering. Cluster growth morphology and thermal sintering have been studied thoroughly for various surfaces and various metal–support interaction strengths. However, due to the inherent irreproducibility in scanning tunneling microscopy (STM) experiments with respect to locating an identical area before and after heating, the data obtained thus far have been limited to comparisons of representative areas before and after specific surface treatments. In the experiments reported here, surfaces with two types of adjacent domains (several square nanometers in area) with distinctly different properties have been synthesized, facilitating a direct comparison of the cluster growth modes and sintering characteristics on these adjacent areas within the same STM image. Using this specially designed surface, the growth and thermal sintering of Ag clusters have been investigated with STM.

II. EXPERIMENT

Details of the ultra-high-vacuum (UHV) chamber equipped with STM, x-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES) with a base pressure <4 × 10−10 mb are found elsewhere.6 Briefly, a double-pass cylindrical mirror analyzer for AES and XPS, reverse-view LEED optics, and a room-temperature STM (Omicron) were used. Typically, the STM images were acquired in the constant current mode at ~1–2 V and 0.083 nA. Ultra-high-purity (99.999%) oxygen from MG industries and a Mo(112) crystal (from Matek) oriented within 0.25° of the desired crystal plane were used. The Mo(112) surface was cleaned initially by Ar+ ion sputtering (500 V, 5–10 μA) and annealing to 2100 K; C and O surface residuals were removed below the detectable level in AES and XPS by an oxygen treatment at 1000–1200 K followed by a flash to 2100 K. The surface prepared in this manner showed a very sharp rectangular p(1×1) LEED pattern. The coverages of Ag were estimated from a plot of the Ag/Mo AES ratio versus...
deposition time assuming layer-by-layer growth. Ag was deposited from a thoroughly outgassed tungsten filament wrapped with a high-purity Ag wire.

III. RESULTS AND DISCUSSION

A. Ag on p(1×3)-O reconstructed surface of Mo(112)

A recent study of the growth morphology of Ag on Mo(111) has shown that three-dimensional (3D) cluster growth occurs at room temperature, whereas two-dimensional (2D) Ag growth occurs upon heating.\textsuperscript{11} A different growth mode, however, was found for Co deposited on an oxygen preadsorbed Mo(110) surface.\textsuperscript{12} Recently, the preparation procedure for various oxygen-reconstructed Mo(112) surfaces has been investigated in detail.\textsuperscript{13,14} In order to investigate the growth mode of Ag metal on an oxygen precovered Mo(112) surface, the p(1×3)-O reconstructed surface (consisting of well-ordered terraces and steps) was prepared as shown in the large-area (200 nm×200 nm) STM image of Fig. 1(a). The p(1×3)-O surface was prepared by adsorbing 270 L O\textsubscript{2} at 1100 K and has been described in detail elsewhere.\textsuperscript{13} Deposition of 1.6 monolayer equivalents (MLE) of Ag at room temperature yielded relatively large (∼5.5 nm) 3D clusters [Fig. 1(b)] with a lower number density than that observed for Co on Mo(110).\textsuperscript{12} Annealing this surface at 750 K for 2 min leads to cluster sintering [Fig. 1(c)] and movement of the clusters to the step edges. A similar cluster behavior has been observed previously and explained in terms of an enhanced interaction of the clusters with the step edges.\textsuperscript{9}

B. Ag on the surface with adjacent MoO\textsubscript{2} and Mo(112) domains

A surface with adjacent MoO\textsubscript{2} and Mo(112) domains was prepared by vacuum annealing a p(1×2)-O reconstructed surface at 1400 K. The large-area (300 nm×300 nm) STM micrograph of Fig. 2(a) shows the simultaneous existence of two distinctly different types of surface morphologies. The enlarged STM image (100 nm×100 nm) of Fig. 2(b) shows that the domains of the type labeled as “1” consists of islands of thin layer MoO\textsubscript{2} on a Mo(112) surface and the domains of the type labeled as “2” consist essentially of clean Mo(112). The STM of Fig. 2(c), acquired after deposition of 1.6 MLE of Ag at room temperature onto the surface of Fig. 1(a), shows that Ag clusters grow very uniformly, with smaller size (∼3 nm) and with a higher number density relative to that of Fig. 1(b). This not only indicates that the surface has a higher average metal-support interaction compared to the oxygen preadsorbed surface [Fig. 1(b)] but also suggests that the two different regions (1 and 2) behave similarly with respect to the nucleation and growth of Ag clusters. A similar growth mode on the two regions could be due to the following factors: (a) similar metal-support interaction strengths; and/or (b) sufficiently large metal-support interactions at room temperature such that the clusters underwent very little surface diffusion. To check for the relative contribution of (b), the surface temperature was increased by increments in order to increase the rate of cluster surface diffusion. In Fig. 2(d), a STM image (200 nm×200 nm) is shown after annealing the surface at 750 K for 10 min. The

Fig. 1. STM image of (a) p(1×3)-O reconstructed Mo(112) surface (200 nm×200 nm), (b) 1.6 MLE Ag deposited on the same surface at room temperature (200 nm×200 nm), and (c) after annealing the surface at 750 K for 2 min (200 nm×200 nm).
image shows that the metal clusters have diffused and sintered to form 2D-Ag nanostructures with elongated shapes. More interestingly, the 2D-Ag nanostructures are preferentially located on the bare metal sites. To verify this behavior, a second experiment was carried out in which 0.8 MLE Ag was deposited at room temperature, followed by an anneal to 650 K for 10 min. In Fig. 2(e), the STM image of the surface confirms that the Ag clusters not only transform into 2D-Ag nanostructures but also preferentially decorate the edges of the oxide islands. This set of experiments shows that the bare metal areas have a higher relative metal–support interaction than do the MoO$_2$ areas, hence, the metal clusters preferentially move toward the bare metal sites if sufficient energy is available.

C. Ag on domains of varying thicknesses of MoO$_2$ on Mo(112)

A surface with MoO$_2$ layers with varying thicknesses was prepared by vacuum annealing a $p(1 \times 3)$-O reconstructed surface of the type shown in Fig. 1(a) at 1400 K. The large-area STM image (400 nm×400 nm) of Fig. 3(a) shows that the surface consists of MoO$_2$ layers of varying thicknesses. This surface has been used to address the role of oxide thickness in controlling Ag cluster growth. As anticipated, the thinner oxide layers, because of geometrical strain due to

![Image](image1.png)
lattice mismatch with the substrate, have a higher surface free energy compared with the thicker layers, and thus interact more strongly with adsorbed metal clusters. The high-resolution STM image of Fig. 3(b) shows the ordered growth of MoO$_2$ and the variation in the thickness of the oxide films. A STM image following the deposition of 1.6 MLE Ag at room temperature is shown in Fig. 3(c). The STM image shows clearly two distinctly different regions with variations in the cluster-size distribution due to the variation of the strength of the metal–support interaction. As expected, on the thicker oxide domains, the average cluster size is largest (~4.5 nm) with a lower number density, while on the relative thin oxide domains the cluster size is relatively small (~3 nm) with a relatively high number density. This is consistent with the results of Fig. 2(c), which show that at room temperature the cluster size and shape on bare Mo$_{112}$ and domains of the thin oxide layer of MoO$_2$ are indistinguishable.

IV. CONCLUSIONS

Detailed STM investigation on a specially designed Mo$_{112}$ surfaces have led to the following conclusions:

(a) Ag clusters on oxygen preadsorbed Mo$_{112}$ surfaces are highly mobile compared with oxygen-free Mo$_{112}$ or MoO$_2$ surfaces, and undergo rapid sintering. This likely occurs via the formation of an Ag$_{5x}$O phase $[\text{Mo}(112) - \text{O}_a + x\text{Ag} \rightarrow \text{Ag}_{5x}\text{O} + \text{Mo}]$$_a$. The mechanism has been proposed previously by us$^9$ to explain the sintering of Ag particles on a TiO$_2$(110) surface at higher oxygen pressures.

(b) The metal–support interaction of MoO$_2$ islands is significantly less than that of the clean Mo$_{112}$ surface.

Therefore, preferential movement of clusters to step edge and to bare metal sites occurs with an increase in the surface temperature, finally leading to 2D-Ag nanostructures.

(c) First-layer MoO$_2$ or relatively thin oxide layers exhibit a greater metal–support interaction compared to relatively thick oxide films. This is likely because of the strain-induced instability of the thin films due to the lattice mismatch with the substrate.

ACKNOWLEDGMENTS

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

$^1$M. Baumer and H. J. Freund, Prog. Surf. Sci. 61, 127 (1999), and references therein.