

Oxygen-Induced Dissociation of Cu Islands Supported on TiO₂(110)

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Received: January 29, 2003; In Final Form: May 12, 2003

Scanning tunneling microscopy studies of Cu islands grown on TiO₂(110) demonstrate that these islands disappear from the STM images after exposure to oxygen gas (60–2000 Langmuir). Based on X-ray photoelectron spectroscopy experiments, the disappearance of the Cu islands cannot be explained by the loss of Cu from the surface or by a dramatic change in the electronic properties of the islands. The adsorption of oxygen appears to weaken the Cu–Cu bond, allowing two-dimensional (2D) islands to form on the surface at the expense of the existing three-dimensional (3D) islands. Thermodynamically, the conversion of 3D to 2D islands is favored by the lower surface free energy of the oxidized Cu compared to that of copper itself. This effect has also been observed for Ni islands, but the rate of island disappearance is slower even though Ni is more easily oxidized than Cu.

Introduction

The structure and morphology of supported metal particles are known to play a critical role in determining catalytic activity.¹ Understanding the adsorbate-induced changes in surface morphology is therefore important for relating ultrahigh vacuum studies of surface reactions to the higher pressure environments associated with real catalytic conditions. Previous scanning tunneling microscopy (STM) studies have shown that the morphologies of supported metal particles on TiO₂(110) can change dramatically upon exposure to adsorbate gases. For example, CO, NO, and O₂ promote the dissociation of Rh and Ir islands into metal atoms at room temperature for gas pressures between 8×10^{-4} and 8 Torr.^{2–6} For Ag islands on TiO₂(110), an O₂ pressure of 10 Torr at room temperature induces Ostwald ripening,⁷ and pressures (0.1–5 Torr) of O₂ or CO:O₂ also cause the sintering of Au islands at elevated temperatures.^{7,8} In this study, we report significant morphological changes in Cu islands on TiO₂(110) resulting from oxygen exposures as low as 430 Langmuir at room temperature (1 Langmuir = 1×10^{-6} Torr·s). STM was used to follow individual Cu islands during the oxygen-induced dissociation of three-dimensional (3D) islands into two-dimensional (2D) structures. Oxidation of the Cu islands thermodynamically favors 2D islands and promotes the mobility of Cu adatoms on the surface by weakening the Cu–Cu bonds.

Experimental Section

Experiments were carried out in an ultrahigh vacuum system ($P \leq 7 \times 10^{-11}$ Torr) equipped with an Omicron variable-temperature scanning tunneling microscope (VT-STM25), hemispherical analyzer for X-ray photoelectron spectroscopy (EA125), low-energy electron diffraction optics (Omicron Spec3), metal evaporator (EMF3), sputter gun (ISE10), and quadrupole mass spectrometer (Leybold-Inficon Transpector 2).^{9–11} All experiments were conducted on a rutile TiO₂(110) single crystal (Commercial Crystals), which was mounted on a standard Omicron sample plate. The crystal was heated by electron bombardment,

and the sample temperature was measured using a type K thermocouple spot-welded to the sample plate.¹⁰ The crystal was cleaned by Ar⁺ sputtering (1 keV, 3–4 μ A current to sample) followed by annealing at 1050 K, and the resulting surface exhibited a sharp (1×1) low-energy electron diffraction (LEED) pattern. STM images of the surface consisted of atomically flat terraces separated by steps of 3.2 Å, and higher resolution images showed bright rows separated by 6.5 Å, which is characteristic of the TiO₂(110)–(1×1) surface. The cleanliness of the crystal was verified by X-ray photoelectron spectroscopy (XPS). Metal deposition was achieved using a commercial evaporator for Cu and a home-built doser for Ni, which has been described elsewhere.¹² Metal coverages in monolayers (ML) with respect to the Cu(111) and Ni(111) surfaces were estimated from the island volumes and densities measured by STM; islands were assumed to have a paraboloid shape.

STM images were acquired with electrochemically etched tungsten tips using a tunneling current of 0.2 nA and a +1.7 V sample bias.⁹ XPS data for the Cu(2p_{3/2}), Ni(2p_{3/2}), O(1s), and Ti(2p_{3/2}) regions were collected with a Mg K α X-ray source. The Cu(2p_{3/2}) and Ni(2p_{3/2}) regions were averaged over three scans (0.2 s dwell time, 0.01 eV/step), whereas the O(1s) and Ti(2p_{3/2}) regions were collected over a single scan (0.2 s dwell time, 0.02 eV/step).

Results

Exposure of Cu islands to oxygen gas at room temperature causes the islands to gradually disappear from STM images of the surface. Figure 1a shows a 1.0 ML coverage of Cu islands deposited on TiO₂(110) at room temperature and quickly flashed to 715 K. The resulting islands are slightly larger than those formed without any postdeposition annealing,^{9,12} with sizes ranging from 5–12 Å in height and 33–60 Å in diameter. Immediately after oxygen is introduced into the chamber at a pressure of 1.0×10^{-7} Torr, the majority of Cu islands become noticeably smaller in the STM image (Figure 1b). Furthermore, some of the smaller islands completely disappear, as shown in the insets in Figure 1. These disappearing islands break up into grainy features on the surface that are 20 Å wide and 2–3 Å

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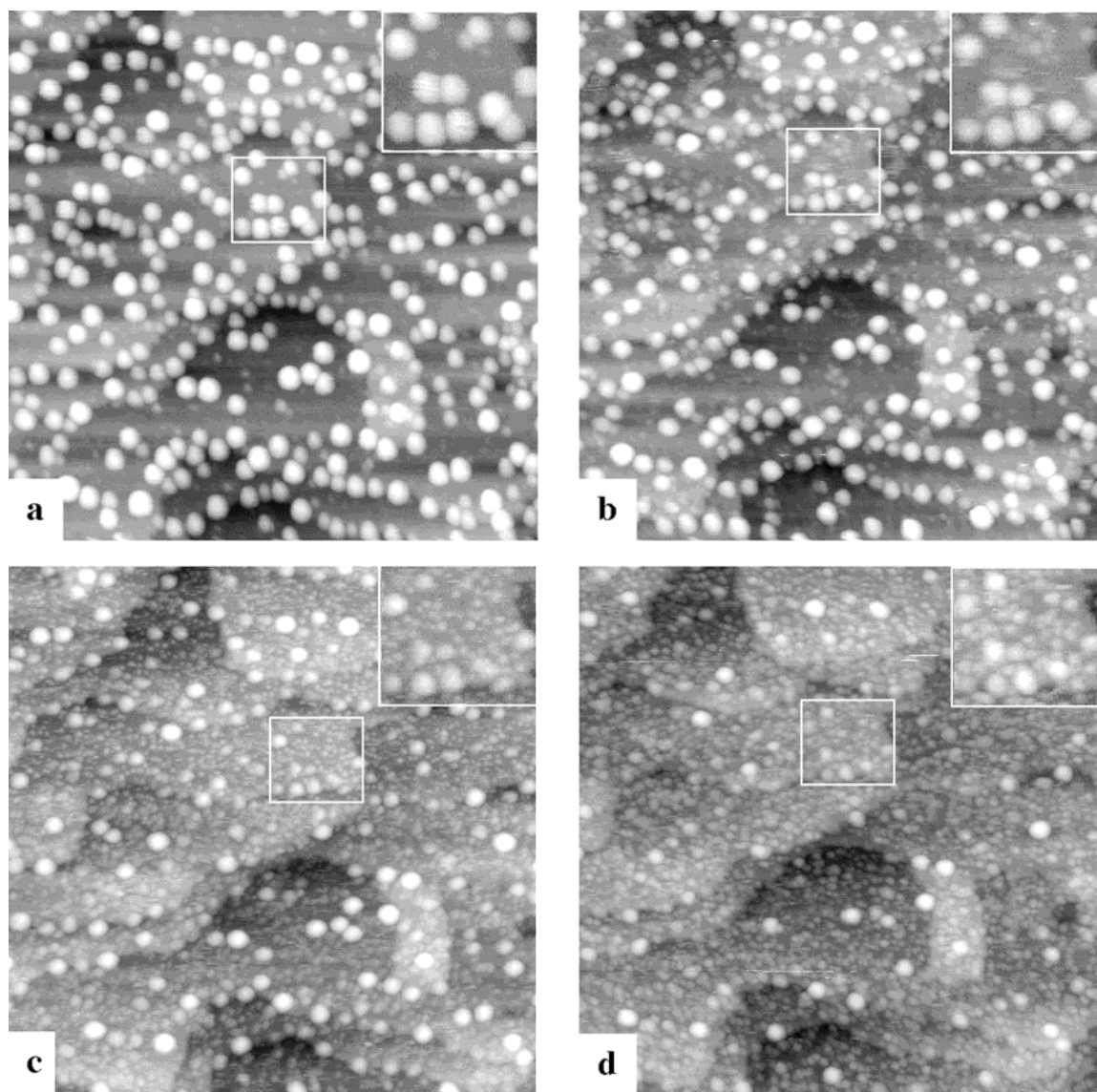


Figure 1. Scanning tunneling microscopy images of a 1.0 ML coverage of Cu deposited at room temperature on $\text{TiO}_2(110)$ at 0.22 ML/min and flashed to 715 K: (a) before exposure to oxygen; (b) immediately after introducing oxygen at pressure of $\sim 1 \times 10^{-7}$ Torr; and after oxygen exposures of (c) 57 min (427 L) and (d) 192 min (1363 L). All images are $1000 \text{ \AA} \times 1000 \text{ \AA}$, and the higher resolution insets shown in the top right corner of each image are $174 \text{ \AA} \times 156 \text{ \AA}$.

high, which is approximately the correct height for a 2D island. The oxygen exposure was continued at $(1.0\text{--}1.3) \times 10^{-7}$ Torr for over 3 h, and STM images of the surface were acquired approximately every 10 min. After a 57 min exposure (427 L), the Cu islands continue to decrease in size or completely disappear, and small grainy features cover the entire surface (Figure 1c). In most cases, islands are observed to dissociate into the grainy features, suggesting the latter could be 2D Cu islands. The positions of these grainy features change over time, indicating that they are mobile on the surface. As a control experiment, the $\text{TiO}_2(110)$ surface itself was imaged under the same oxygen exposure conditions, and grainy features covering the entire surface were *not* observed. Significant changes in island sizes and densities persist up to a 192 min exposure (1363 L), at which time only a small fraction of the original islands are still observed. As the oxygen exposure is increased, the surface also becomes more difficult to image, and some Cu islands appear to be picked up by the STM tip. The islands that disappear first have average sizes of approximately 5.9 \AA in height and 38.3 \AA in diameter. Larger islands with average sizes

of 11 \AA in height and 53.4 \AA in diameter are the ones that persist on the surface even after the highest oxygen exposure.

Island profiles as function of increasing oxygen exposure are shown for a large island (11.0 \AA height, 53 \AA diameter) and for a small island (7 \AA height, 43 \AA diameter) in Figure 2. In both cases, the island diameters are decreased by only 15% at the highest exposure while the island heights are decreased by 30% for the large island and by over 50% for the small island. For the large island, the immediate effect of oxygen is to decrease only the island height, but both the height and diameter then continue to decrease up to the highest exposure. In contrast, oxygen exposure immediately converts the small Cu island from 3D to 2D, while extended exposure has no further effect.

Possible explanations for the disappearance of the Cu islands include desorption of the Cu from the TiO_2 surface or a change in the electronic properties of the Cu islands due to oxidation, resulting in insufficient conductivity for imaging by STM. To explore these possibilities, XPS studies were conducted on the surface before and after oxidation. Cu islands with a coverage of 2.5 ML were imaged by STM before and after a 30 min, 1

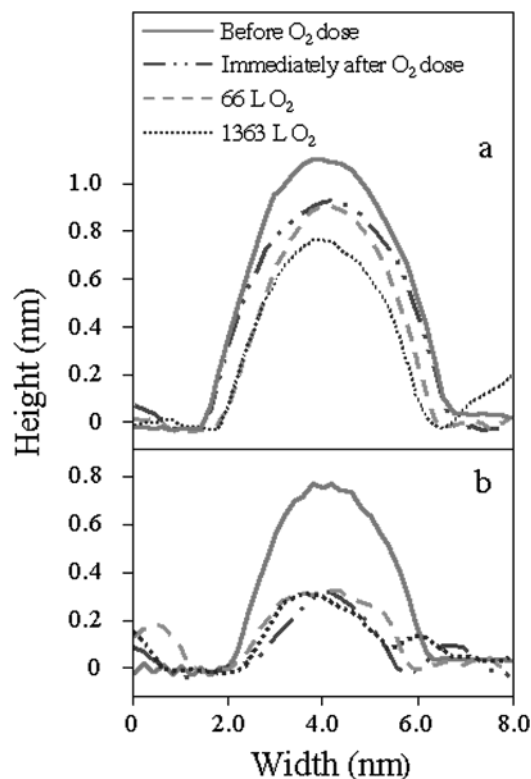


Figure 2. Island profiles from Figure 1 for: (a) one of the larger Cu islands (53 Å diameter, 11 Å height) that does not disappear upon oxidation and (b) one of the smaller Cu islands (43 Å diameter, 8 Å height) that disappears upon oxidation.

$\times 10^{-6}$ Torr (1800 L) oxygen exposure, and the Cu(2p_{3/2}), Ti(2p_{3/2}), and O(1s) regions were collected before and after oxygen treatment. As shown in Figure 3a, the position of the Cu(2p_{3/2}) peak does not shift after oxidation. This is not an unexpected result, given that previous XPS studies of the oxidation of bulk Cu surfaces¹³ and thin films¹⁴ also show no change in the Cu(2p_{3/2}) region; room-temperature oxidation resulted in the formation of Cu₂O, but the position and line shape of the Cu(2p_{3/2}) peak were the same as those of metallic Cu.¹³ Oxidation of the small Cu islands is similar to that of bulk Cu surfaces, which form Cu₂O and can still be imaged by STM. Consequently, there is no reason to believe that oxidation of the Cu islands induces dramatic changes in their electronic properties such that the islands are no longer conductive enough for STM studies. The slight decrease in Cu(2p_{3/2}) signal after oxidation, as shown in Figure 3, is *not* attributed to the desorption of Cu from the surface. In fact, a 20%–25% decrease in absolute integrated signal intensity is observed for the Ti(2p_{3/2}) and O(1s) peaks as well as the Cu(2p_{3/2}) peak after oxidation. The Cu:Ti and Cu:O ratios remain approximately the same before and after oxidation, indicating that Cu is not removed from the surface.

These oxidation experiments were then repeated on Ni islands grown on TiO₂(110).¹² XPS studies on a 2.5 ML coverage of Ni islands (Figure 3b) showed that the same exposure to oxygen has a much greater effect on the electronic properties of Ni compared to those of Cu islands. A change in the peak shape of the Ni(2p_{3/2}) signal accompanied by a 2.65 eV shift to higher binding energy is observed, consistent with strong binding of oxygen to Ni. Similar results have been reported for the oxidation of Ni thin films,¹⁵ which form NiO. If oxidation of metal islands is responsible for their disappearance in the STM images, then the Ni islands should disappear more quickly than

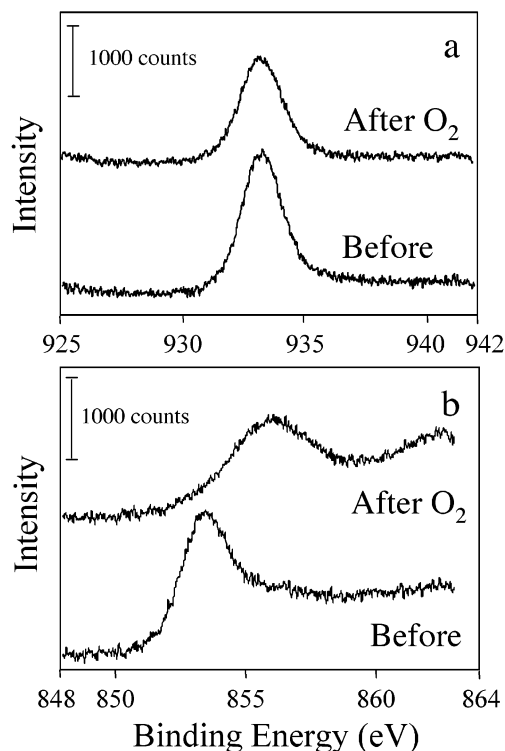


Figure 3. X-ray photoelectron spectra of 2.5 ML of Cu and Ni deposited at room temperature on TiO₂(110) for the: (a) Cu(2p_{3/2}) region and (b) Ni(2p_{3/2}) region, before and after oxygen exposure at $\sim 1 \times 10^{-6}$ Torr for 30 min (1980 L).

the Cu islands. However, STM experiments indicate that the Ni islands actually disappear more slowly (Figure 4). The decrease in Ni island density and size after a 2160 L oxygen exposure is comparable to what is observed for Cu island after a 427 L exposure. STM images collected as a function of increasing oxygen exposure (data not shown) demonstrate that the 3D Ni islands also dissociate into mobile, grainy features with heights of 2–3 Å.

Discussion

The disappearance of Cu islands in STM images after exposure to oxygen gas is attributed to an oxygen-induced dissociation of 3D Cu islands into 2D structures. A series of STM images acquired as a function of increasing oxygen exposure shows that Cu islands dissociate into grainy features, which have approximately the correct height (2–3 Å) to be 2D islands. Since the Cu(2p_{3/2}) peak in X-ray photoelectron spectrum does not shift when Cu is oxidized to Cu₂O, it is not possible to determine if the 2D structures are Cu or copper oxide islands. Previous studies of the growth of Fe on TiO₂(110)¹⁶ have shown that 3D Fe islands also dissociate into 2D islands upon relatively small exposures to O₂ (10 L), and X-ray photoelectron experiments indicate that the 2D islands are FeO rather than Fe.

The conversion of 3D Cu islands to 2D structures upon oxidation can be explained based on thermodynamics. The formation of 3D islands is favored when $\gamma_{\text{TiO}_2} < \gamma_{\text{m(o)}} + \gamma_{\text{m/TiO}_2}$, where γ_{TiO_2} , $\gamma_{\text{m(o)}}$, and $\gamma_{\text{m/TiO}_2}$ are the free energies of the TiO₂, metal or oxidized metal, and metal–TiO₂ interface, respectively.¹⁷ The greater surface free energy of Cu compared to TiO₂ (1.4¹⁸ vs 0.7 J/m²¹⁹) and the relatively weak Cu–TiO₂ interaction favor the formation of 3D islands in the absence of oxygen.^{9,17} However, the oxidation of Cu results in a decrease in surface free energy, with a only small amount of oxygen

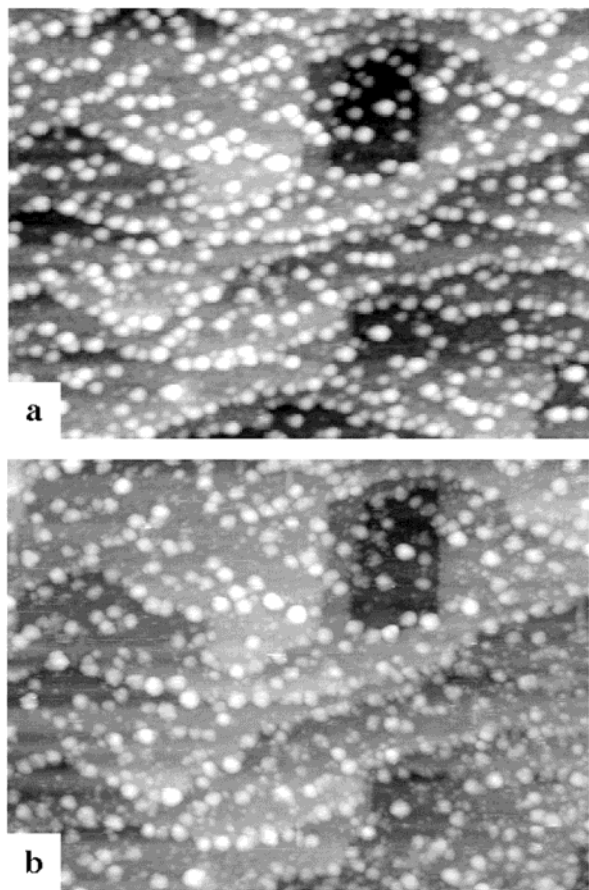


Figure 4. Scanning tunneling microscopy images of a 1.0 ML coverage of Ni deposited at room temperature on TiO₂(110) at 0.16 ML/min: (a) before oxygen exposure; and (b) after exposure to oxygen at 2×10^{-7} Torr for 3 h (2160 L). Both images are $1000 \text{ \AA} \times 744 \text{ \AA}$.

(0.88% weight oxygen) lowering the surface free energy to 0.53 J/m^2 .¹⁸ In the case of Cu, 2D islands become thermodynamically favorable because the surface free energy of oxidized Cu is not only lower than that of Cu but also lower than that of TiO₂. The slower conversion of oxidized Ni islands from 3D to 2D structures can also be understood in terms of thermodynamics. In the case of Ni, oxidation does decrease the surface free energy (1.1 J/m^2 for NiO²⁰ vs $\sim 1.7 \text{ J/m}^2$ for Ni¹⁷), but the surface free energy of NiO is still higher than that of TiO₂. Consequently, there is less driving force for the oxygen-induced dissociation of Ni islands compared to Cu.

The conversion of 3D to 2D islands also requires the Cu atoms to be mobile on the surface at room temperature. STM investigations in the literature demonstrate that Cu atoms on bulk Cu surfaces are indeed mobile at this temperature when adsorbed oxygen is also present.²¹ Previous studies of the sintering of Cu islands on TiO₂(110) at elevated temperatures have shown that the Cu–Cu bond is strong enough that Cu adatom detachment rather than diffusion is the rate-limiting step in island growth.¹² Since Cu islands are stable at room temperature in the absence of oxygen, it appears that adsorbed oxygen promotes Cu adatom detachment from existing 3D islands. Solymosi and co-workers have reported adsorbate-induced disintegration of Rh^{2–4} and Ir^{5,6} islands supported on TiO₂(110)–(1 \times 2), although much higher adsorbate pressures (0.1–0.001 Torr) were used. Disintegration of the metal islands was attributed to a weakened metal–metal interaction due to the formation of stronger metal–adsorbate bonds; adsorbates such as CO, O₂, and NO, which bind strongly to the metal

particles, caused island disintegration at room temperature while weakly interacting adsorbates such as N₂ and H₂ did not. Based on this argument, oxygen should also promote disintegration of Cu islands since the Cu–O bond (273 kJ/mol) is stronger than Cu–Cu (177 kJ/mol).²² The mobility of Cu adatoms is consistent with the fact that STM imaging of the Cu islands becomes more difficult at higher oxygen exposures, presumably due to interactions between the STM tip and mobile Cu atoms or clusters.

Other possible explanations for the disappearance of the Cu islands have been ruled out. For example, XPS studies show that Cu is not removed from the surface after oxidation at room temperature. Experiments involving the oxidation of Ni islands demonstrate that the disappearance of Cu islands is not due to a change in electronic properties that prevents STM imaging; while Ni islands are more easily oxidized than Cu, island disappearance is slower for Ni. Encapsulation of the Cu islands by TiO_x is also ruled out as a possible explanation for the disappearance of Cu islands at room temperature. Although encapsulation for Pd islands on TiO₂(110) subjected to similar O₂ exposures has been reported at temperatures $\geq 575 \text{ K}$,^{23,24} encapsulation was not observed at room temperature. Pd is also known to interact more strongly with the TiO₂ surface than Cu.^{25,26} Furthermore, encapsulation would result in a decrease in the Cu:O and Cu:Ti ratios, which are not observed in the XPS experiments.

Acknowledgment. We gratefully acknowledge financial support from the Department of Energy, Office of Basic Energy Sciences under a DOE/EPSCOR grant (DE-FG02-01ER45892), the National Science Foundation CAREER Award (CHE-0133926), and the U.S. Army Research Office Young Investigator Award (DAAD19-00-1-0557).

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