Morphology of the Cu$_2$O surface oxide phase formed on Cu(100) at high temperature

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We have observed the nucleation and growth of the Cu$_2$O surface oxide on a Cu(100) surface at 870 K using low energy electron microscopy. Nucleating on a surface exhibiting the $(\sqrt{2} \times 2 \sqrt{2})$R45°-O overlayer, this phase caused the overall step morphology to change from long, mostly straight narrow-terraced step bunches to broad, deeply curved terraces with more highly bunched steps. Using x-ray photoelectron spectroscopy, we have measured an upper bound of 2.6 ML (monolayer) for the surface oxygen coverage at which we observed this oxide phase. The lattice constant of the observed oxide phase matches that of the (111) face of Cu$_2$O. We postulate that the oxide does not form epitaxially on this surface at this temperature due to interactions with the centered rectangular phase of oxygen, which provides a nearly hexagonal template for the Cu$_2$O(111) hexagonal structure. © 2009 American Institute of Physics. [DOI: 10.1063/1.3152799]

I. INTRODUCTION

We have used low energy electron microscopy (LEEM), low energy electron diffraction (LEED), and x-ray photoelectron spectroscopy (XPS) to investigate various phases of oxygen on Cu(100) and their high-temperature behavior. This paper discusses our observations of the formation, morphology, and behavior of the Cu$_2$O surface oxide phase which was formed at or above ~870 K.

The oxidation process on the (100) face of copper occurs at a wide range of temperatures and pressures. Studies of the oxidation of this surface report wide variations in the nature of the island structure with temperature from 423 to 1273 K. Variations in oxidation conditions, such as oxygen exposure and substrate temperature, can produce profound variations in surface morphology, oxygen adsorption states, and oxide phase. For most oxidation conditions, especially low-pressure oxidation, Cu$_2$O is the only oxide phase formed. Unlike some other oxide surfaces, the oxidizing copper surface nucleates epitaxial oxide islands which grow and coalesce into an oxide coating. The transition between the chemisorbed stage and the oxidation stage is marked by oxygen penetrating beneath the surface. Hirsimäki and Chorkendorff found that, once the $(\sqrt{2} \times 2 \sqrt{2})$R45°-O/Cu overlayer has formed, oxygen exposure does not increase the surface oxygen coverage at temperatures up to ~570 K. Stefanov and Marinova, however, observed that at an oxygen exposure of ~10$^5$ L, the surface oxide did begin to form.

We have studied the initial growth of the oxide phase from the saturated $(\sqrt{2} \times 2 \sqrt{2})$R45°-O/Cu(100) overlayer phase at 870 K. We have utilized the unique capabilities of LEEM to differentiate areas of differing surface structure and domain orientation via dark-field imaging, which allows nearly simultaneous measurements of both real-space microscopy images and structural information by diffraction from the same area on the sample. Viewing the surface with this remarkable tool, we have witnessed the growth of the oxide phase in islands from within the $(\sqrt{2} \times 2 \sqrt{2})$R45°-O/Cu(100) overlayer, causing marked terrace widening and step bunching. We have also verified the identity and surface lattice parameters of the oxide. In addition, we have demonstrated that two rotational domains of the oxide phase coexist, with each domain dominating its own terrace.

II. EXPERIMENTAL METHODS

These studies were conducted on a copper single crystal, which had a 1° miscut from the (100) plane. The details of the surface cleaning procedures used the measurement of surface oxygen and contaminants, and other experimental details have been given previously. Oxygen already present on the surface and in the bulk was the main contaminant. Oxygen coverage and other surface contaminants were measured by XPS in a chamber connected to the LEEM imaging chamber. Because of the presence of oxygen on the molybdenum sample holder cap and other measurement uncertainties, only an upper bound on surface oxygen coverage measurements could be determined. The LEEM used here was purchased from Elmitec Elektronenmikroskopie GmbH in Clausthal-Zellerfeld, Germany. This system has been described in detail elsewhere.

III. RESULTS AND DISCUSSION

For a Cu(100) surface annealed with oxygen present on the surface for over 1 h at or above 870 K, we found a surface structure distinct from the $(\sqrt{2} \times 2 \sqrt{2})$R45°-O phase and from the centered rectangular phase, which was described in detail in another paper. This new phase was
found on a surface with average oxygen coverage \( \leq 2.6 \text{ ML} \) (monolayer). Its LEED pattern consists of a ring of 12 spots around the \((0,0)\) spot, with the first order spots appearing at approximately 11 eV incident electron energy. (See Fig. 1.) This structure nucleated on the \((\sqrt{2} \times \sqrt{2})R45^\circ-O\) surface, described previously.\(^{11}\)

Using dark-field imaging, we have determined that every other spot around the innermost ring of 12 spots belongs to the same domain of this phase. As shown in Fig. 2, the images obtained from neighboring spots are negatives of each other, with the same area on the surface bright in one image and dark in the other. This reduced this 12-fold symmetric LEED pattern to a sixfold symmetric pattern. Thus, this is a hexagonal phase, with two domains. One domain is rotated 30° from the other, which is equivalent to mirroring this overlayer structure across a mirror plane of the substrate. The Bravais lattice of this structure is shown schematically in Fig. 3. The mirror plane is also noted in the figure.

Using this LEED pattern, we have derived a real-space lattice constant of 5.9 \(\pm 0.3\) Å for this hexagonal lattice. Since the lattice constant of the \((111)\) face of CuO is 5.96 Å, this strongly suggests that this “12-spot” phase is actually a layer of cuprous oxide on the surface. This face of the oxide presents a hexagonal surface net, since CuO has a simple cubic structure. Shultz and Cox\(^{13}\) found that the LEED pattern of the \((111)\) face of single crystal CuO is a six-spot ring with hexagonal symmetry, essentially a single domain of the surface phase was found in our observations.

The saturation coverage calculated from this structure is roughly 0.4 ML. Therefore, it is likely that this phase forms as a multilayer, as it occurs at a significantly higher oxygen coverage than the \((\sqrt{2} \times \sqrt{2})R45^\circ-O\) overlayer structure. This structure is also incommensurate with the Cu(100) square lattice, as shown in Fig. 3. This is expected, as it is well known that oxides of metals do not generally adopt the lattice constant of the substrate metal.

Bright-field LEEM imaging has shown that this phase grows out of the \((\sqrt{2} \times \sqrt{2})R45^\circ-O\) phase and spreads across the surface. After a sample covered with the \((\sqrt{2} \times \sqrt{2})R45^\circ-O\) phase was exposed to oxygen, as described previously,\(^{11}\) it was annealed for more than 1 h at 870 K, with probable segregation of oxygen from the bulk to the surface. At this point, bright regions appeared on the step terraces, surrounded by the less intense \((\sqrt{2} \times \sqrt{2})R45^\circ-O\)
The centered rectangular structure is another oxygen overlayer that we have observed on this surface, at oxygen concentrations between where we have found the \( (\sqrt{2} \times 2\sqrt{2})R45^\circ - O \) and the \( \text{Cu}_2\text{O} \) phases. The centered rectangular structure, similarly to the oxide, forms out of the \( (\sqrt{2} \times 2\sqrt{2})R45^\circ - O \) overlayer. A schematic diagram of the centered rectangular surface net is shown superposed on the \( \text{Cu}(100) \) lattice in Fig. 6.

In one instance of watching the growth of the oxide terraces that are free of black spots are sometimes seen to run between areas where all of the terraces have black spots.

The oxide phase grows out from the black holes in an interesting way. Figure 4 is an image of an area of the oxide phase (bright region), which nucleates at a black hole and grows out into the surrounding \( (\sqrt{2} \times 2\sqrt{2})R45^\circ - O \) overlayer (outer gray areas). The oxide phase region is elongated parallel to the step edges, suggesting that it grows more quickly along the length of the steps. This was observed during real-time observations of the growth.

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FIG. 7. LEED pattern showing the \((\sqrt{2} \times 2\sqrt{2})R45^\circ\)-O phase, centered rectangular, and oxide phases coexisting on a single surface. The Cu(100) spots are boxed, prominent \((\sqrt{2} \times 2\sqrt{2})R45^\circ\)-O spots are circled, and a circle is drawn through the first order ring of the oxide pattern. All spots inside the box formed by the Cu(100) spots that are not accounted for in the \((\sqrt{2} \times 2\sqrt{2})R45^\circ\)-O oxide pattern belong to the centered rectangular pattern. The astigmatism noticeable in the pattern is due to the fact that the LEEM optics were not optimized for LEED imaging for this image. Electron energy was 27.1 eV. Sample temperature was between 420 K and room temperature.

As the oxygen concentration increases on the Cu(100) surface at 870 K, the progression of surface phases is \((\sqrt{2} \times 2\sqrt{2})R45^\circ\)-O phase to the oxide without LEEM or LEED indications of the centered rectangular phase. Also, since the centered rectangular phase was not observed by other researchers in the phase transition between the \((\sqrt{2} \times 2\sqrt{2})R45^\circ\)-O phase and the oxide surface phase, we surmise that its formation is related to the high temperatures (~870 K) that this study has explored. Most other investigations involving LEED and similar surface analytical techniques were confined to significantly lower temperatures.

This observed coexistence between the centered rectangular and oxide phases may explain why we see a hexagonal surface net of the Cu2O(111) forms nonpepitaxially on top of the square surface net of Cu(100). Sun and Yang\(^{14}\) and Zhou and Yang\(^{15}\) have also observed the formation of Cu2O on various Cu surfaces, but their observations showed Cu2O forming epitaxially on the Cu(100), Cu(110), and Cu(111) surfaces, with the oxide having the same crystal face as the substrate. Their studies observed Cu(100) oxidation, however, only up to 620 K. Sun and Yang\(^{14}\) found that the oxidation kinetics on Cu(100) were significantly influenced by changes with temperature of the copper surface lattice beneath the oxide phase. Also, Zhou and Yang\(^{15}\) postulated that the hexagonal structure of the chemisorbed oxygen overlayer on Cu(111) served as a template for Cu2O(111)’s hexagonal structure, enabling very fast oxide island nucleation compared to the other faces of copper they studied.

Based on our observations, oxidizing at a temperature of ~300 K higher than previous studies changes the oxide growth to the (111) face. We propose that the structure of the adsorbed oxygen overlayer influences the oxide structure grown on it. Thus, the existence of the centered rectangular phase as an intermediate between the \((\sqrt{2} \times 2\sqrt{2})R45^\circ\)-O phase and the oxide phase may explain why the hexagonal (111) oxide face forms on the square Cu(100) lattice. We propose that the centered rectangular phase, with its pseudohexagonal lattice, provides a template for the growth of the hexagonal oxide surface lattice, similar to the way in which the chemisorbed overlayer provided a template for oxide growth on Cu(111). As shown in Fig. 6, the primitive lattice vector of this pseudohexagonal net is 13 Å, which is only slightly more than twice the primitive lattice vector of the Cu2O(111) hexagonal net (5.9 Å). The bottom half of Fig. 6 shows how the Cu2O(111) surface lattice would fit on top of the centered rectangular phase.

This explanation also provides a reason why Sun and Yang did not see the (111) oxide face, but instead observe the (100) face forming on this surface. We have only observed the centered rectangular phase on surfaces annealed to ~770 K and higher. Hence the lower temperature (up to only 620 K) study of Sun and Yang would not be expected to see the centered rectangular phase and its templating influence on oxide growth. Also, the fact that the (111) oxide phase grows faster parallel to the step edges than perpendicular to them may also be explained by this templating effect, as the centered rectangular phase has been postulated to nucleate at step edges and appears to be more stable near them.\(^{11}\)

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which matches the Cu average of consists of a hexagonal net which is incommensurate with the step bunches. The overlayer structure of this oxide phase and tighter step bunching, as well as pronounced curving of the step bunches, acts as a hexagonal template, causing the oxide to grow in the (111) structure, instead of forming epitaxial layers.

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