Morphology of the Cu₂O surface oxide phase formed on Cu(100) at high temperature

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(Received 6 February 2009; accepted 15 May 2009; published online 26 June 2009)

We have observed the nucleation and growth of the Cu₂O surface oxide on a Cu(100) surface at 870 K using low energy electron microscopy. Nucleating on a surface exhibiting the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -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 Cu₂O. 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 Cu₂O(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 photoemission 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 Cu₂O surface oxide phase which was formed at or above \sim 870 K.

The oxidation process on the (100) face of copper occurs at a wide range of temperatures and pressures.^{1–3} Studies of the oxidation of this surface report wide variations in the nature of the island structure with temperature from 423 to 1273 K.⁴ Variations in oxidation conditions, such as oxygen exposure and substrate temperature, can produce profound variations in surface morphology, oxygen adsorption states, and oxide phase.^{1,5} For most oxidation conditions, especially low-pressure oxidation, Cu₂O is the only oxide phase formed.⁶ Unlike some other oxide surfaces, the oxidizing copper surface nucleates epitaxial oxide islands which grow and coalesce into an oxide coating.⁷ The transition between the chemisorbed stage and the oxidation stage is marked by oxygen penetrating beneath the surface.3,8 Hirsimäki and Chorkendorff⁹ found that, once the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O/Cu overlayer has formed, oxygen exposure does not increase the surface oxygen coverage at temperatures up to \sim 570 K. Stefanov and Marinova,⁷ however, observed that at an oxygen exposure of $\sim 10^6$ L, the surface oxide did begin to form.

We have studied the initial growth of the oxide phase from the saturated $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -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,¹⁰ 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 $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -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.¹¹ 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 Elektronenmikroscopie GmbH in Clausthal-Zellerfeld, Germany. This system has been described in detail elsewhere.¹²

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 $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O phase and from the centered rectangular phase, which was described in detail in another paper.¹¹ This new phase was

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FIG. 1. 12-spot LEED pattern of hexagonal phase of oxygen on Cu(100), with electron energy of 96.1 V. The inner white circle traces through the first order spots of this pattern. The outer ring traces along the second order spots. The spots in the ring between these can be obtained by adding the vectors belonging to the first order spots on either side of the first order spot directly inward. The arrows illustrate this vector addition: the black arrow from the (0,0) spot to the first order circle was translated without lengthening or rotation, showing that the vector addition of two next-nearest neighbor first order spots results in a spot in the ring between the two white circles. The bright disk at the lower right is due to secondary electrons, which the LEEM optics do not exclude.

found on a surface with average oxygen coverage ≤ 2.6 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 $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -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 ± 0.3 Å for this hexagonal lattice. Since the lattice constant of the (111) face of Cu₂O 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 Cu₂O has a simple cubic structure. Shultz and Cox¹³ found that the LEED pattern of the (111) face of single crystal Cu₂O 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 $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -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.



FIG. 2. Dark-field LEEM images of the 12-spot surface. Image diameter is $\sim 25 \ \mu m$; imaging electron energy was 21.9 eV. (a) Image using one of the first order spots, and (b) image of the same area using an adjacent first order spot. Notice how most of the bright areas in (a) are dark in (b) and vice versa. To illustrate this difference, we have highlighted in white a shape in the lower half of each image.

Bright-field LEEM imaging has shown that this phase grows out of the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O phase and spreads across the surface. After a sample covered with the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -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 $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O



FIG. 3. Lattice structure of 12-spot hexagonal phase. The unfilled circles are copper atoms, the black dots are one rotational domain of the hexagonal phase, and the gray dots are the other domain, rotated from the first by 30°. This rotation is equivalent to reflecting the pattern across the indicated substrate mirror plane.



FIG. 4. (a) A small region of the Cu₂O surface oxide phase (bright area) growing out onto the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O surface (dark gray area). Note that it appears to be centered on the black holes. Image diameter was ~25 μ m and imaging electron energy was 4.1 eV. (b) Closeup image of above area, with 10 μ m image diameter. Note the smoothly curving, closely spaced step bunches outside the bright region, in comparison to the broader terraces and deeply curving bunches within the white region.

overlayer structure. These bright regions nucleated at large black islands and grew for many microns beyond the black islands. These black islands comprise a separate, hexagonal phase of oxygen on this surface, which is also insulating as seen by a shifting black aura around these islands in our LEEM images. This black island phase has not previously been observed. Our investigations of it showed that large islands of this phase also exhibit a hexagonal step structure. This phase is discussed in more detail elsewhere.¹¹ Brightfield images of such a region are shown in Fig. 4, where the oxide phase is growing out of a black hole, inside a larger region of $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O overlayer structure. As discussed below, it is clear that the bright regions grow out more quickly along the long direction of the steps, as the growing bright region is longer in that direction. The LEED pattern obtained when the electron beam is centered on one of these bright areas is identical to that shown in Fig. 1.

The step morphology within the bright oxide-covered areas is much different from the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O-covered area outside. Where the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O areas consist of narrow (~100 nm wide) terraces separated by tightly bunched and nearly straight steps, the oxide areas exhibit deeply curving step bunches with wide (~500-1000 nm wide) terraces. (See Fig. 5.) The terraces are often, but not always, littered with black spots, similar to those seen on the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O surface. Columns, or curving "rivers," of



FIG. 5. Bright-field LEEM image of the step morphology of the Cu₂O surface oxide phase. Note that a few of the terraces do not exhibit the small black dots seen on most terraces. Image diameter is \sim 25 μ m. Imaging electron energy was 5.3 eV.

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.

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 Cu₂O 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 Cu(100) lattice in Fig. 6.

In one instance of watching the growth of the oxide



FIG. 6. Schematic diagram showing centered rectangular lattice (medium gray circles) and hexagonal lattice (large black circles on bottom half of figure only) on Cu(100) (small open circles). The centered rectangular lattice has a primitive lattice vector of 13 Å, which is approximately double the primitive lattice vector of 5.9 Å for the hexagonal lattice.



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 or 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.

phase due to increasing sample temperature, the ($\sqrt{2}$ $\times 2\sqrt{2}R45^{\circ}$ -O, centered rectangular, and the oxide LEED patterns were all observed together on the same surface. Figure 7 is an example of the LEED pattern from this surface. When this LEED pattern was observed, these three phases must have coexisted in an area of $\sim 30 \ \mu m$ in diameter on the surface, as that is the size of the incident electron spot. As the imaging electron beam was panned across the surface, the centered rectangular pattern was usually the least prominent pattern and was sometimes not visible. The ($\sqrt{2}$ $\times 2\sqrt{2}R45^{\circ}$ -O pattern, on the other hand, was found more often. The oxide pattern was consistently observed over the entire surface. When this surface was heated above 870 K, however, both the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O and the centered rectangular patterns disappeared, leaving only the oxide pattern. We then cooled the sample to room temperature, and the other two phases reappeared, although less intensely and covering less of the surface area than prior to heating. Upon increasing the sample temperature above 870 K again, all patterns except that of the oxide phase disappeared again. The LEEM images of this surface were similar to images of surfaces which were observed to transform directly from the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O phase to the oxide phase.

The fact that the oxide was the only phase of the three coexisting structures to survive to 870 K suggests that the oxide is the most stable structure on this surface at high temperature. This is consistent with previous results regarding the centered rectangular phase, wherein that structure disappeared as the sample temperature reached 870 K.¹¹ The observed coexistence at lower temperatures also suggests that the centered rectangular phase may be an intermediate structure between the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O overlayer and the oxide. This is consistent with our observations of small islands of the centered rectangular phase coexisting with the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O overlayer, as noted previously.¹¹ We have, however, observed transitions of the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$

 $\times 2\sqrt{2}$)*R*45°-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 $(\sqrt{2} \times 2\sqrt{2})$ *R*45°-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 $Cu_2O(111)$ forms nonepitaxially on top of the square surface net of Cu(100). Sun and Yang¹⁴ and Zhou and Yang¹⁵ 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 Yang¹⁴ 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 Yang¹⁵ postulated that the hexagonal structure of the chemisorbed oxygen overlayer on Cu(111) served as a template for $Cu_2O(111)$'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 \sim 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 $Cu_2O(111)$ hexagonal net (5.9 Å). The bottom half of Fig. 6 shows how the $Cu_2O(111)$ 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 \sim 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

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, then centered rectangular, and finally $Cu_2O(111)$. Thus, one might expect always to observe the centered rectangular phase wherever the oxide phase was growing. In many of our observations, however, the centered rectangular phase was not observed in the LEED pattern of the growing oxide and the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O-covered area surrounding it. In these cases, however, the oxide phase appeared to grow outward from a central black island consisting of another surface oxygen phase, as discussed above. If the oxide grows outward into the region dominated by the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O phase, one would expect the oxygen concentration to rise sharply at the edge of the oxide phase. If excess oxygen over that necessary to form the ($\sqrt{2}$ $\times 2\sqrt{2}R45^{\circ}$ -O phase is only found along the outer edge of the oxide, and the centered rectangular phase forms only at that edge, these areas may be too small to contribute significantly to the LEED pattern. Obviously, however, further investigations are required to fully elucidate this transition to the oxide phase at 870 K and the role of the centered rectangular phase in that transition.

IV. CONCLUSIONS

We have observed the surface oxide phase, Cu₂O, on the Cu(100) surface. By XPS, we have measured an oxygen coverage of ≤ 2.6 ML on the surface for this oxide structure, which matches the (111) face of the bulk Cu₂O crystal. Surface morphological changes which accompanied the formation of this oxide phase included the widening of terraces and tighter step bunching, as well as pronounced curving of the step bunches. The overlayer structure of this oxide phase consists of a hexagonal net which is incommensurate with the Cu(100) substrate. Through a 30° rotation, equivalent to a reflection across a mirror plane of the substrate, two domains of this structure can be found on the surface, as shown by dark-field imaging. Of the three structures we have stud-

ied on this surface, with the other two being the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O and the centered rectangular phases, this structure is the most stable at 870 K.¹¹ We postulate that the centered rectangular phase, which has sometimes been observed to coexist with the oxide and $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -O phases, acts as a hexagonal template, causing the oxide to grow in the (111) structure, instead of forming epitaxial layers.

ACKNOWLEDGMENTS

We would like to thank Dr. Xiangdong Zhu for loaning us the copper crystal on which this work was done, and for useful discussions. We would also like to acknowledge helpful discussions with Dr. Michel Van Hove. This research was funded by National Science Foundation Grant No. DMR-95-12231 and by the University of California, Davis.

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