Molecular-Scale Investigation of Reconstructed Copper Surface Induced by Dissociative Adsorption of O₂

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Oxidation of copper is known to occur during corrosion process, but if the oxidation is controlled under right condition, desirable oxide thin layers that can be applied in electronic devices, as protective layers against corrosion, and as heterogeneous catalysts for various chemical reactions could be generated.[1-8] To control the shape and thickness of oxide layers for the specific applications, fundamental understanding of oxide thin layers including growth mechanism on metal surface, their electronic properties, and atomic structures are prerequisite. Several research groups have reported the structures of Cu₂O layers on Cu(111) surfaces; exposure to gaseous oxygen at room temperature generates irregular shaped oxide islands on the surface whereas well ordered Cu₂O thin films on Cu(111) were prepared at the elevated temperature. However there have been discrepancies in the characterization of copper oxide formed at various annealing temperature.[9-11] For examples, Matsumoto *et al.*[10] reported that annealing at 573 K at a low pressure of O₂ produced the "44" superstructure, which was converted into "29" by subsequent annealing at 673 K. Contrary to this result, Wiame *et al.*[9] claimed that O₂ exposure at 573 K resulted in the formation of "29" superstructures. In order to clarify the actual surface structures, additional STM studies with atomic resolution are needed to further. Here, we report an investigation of oxide superstructures on Cu(111) induced by dissociative adsorption of O₂ at room temperature (RT) and 573 K.

All experiments were performed in UHV system, with a base pressure of 2×10^{-10} torr, equipped with a variable temperature scanning tunneling microscope (VT-STM). A clean Cu(111) surface was prepared after Ne$^+$ ion sputtering and subsequent annealing at 700 K. STM measurements were performed with electrochemically etched tungsten tips. All of the images shown here were taken at room temperature in the constant current mode at sample biases ranging from −3.0 V to +3.0 V.

Figure 1 shows a series of STM images recorded during an exposure of O₂ (pressure $\sim 5 \times 10^{-7}$ Torr) to the Cu(111) surface at room temperature. Figure 1(a) indicates a clean Cu(111) surface with a sharp step edge, having an apparent height of ~0.20 nm whereas (b), (c), and (d) correspond to exposures of 300 L, 600 L, and 900 L of O₂, respectively. The dashed arrows represent identical position on the

surface. Note that the diagonal ripple-marks (corrugations) in STM images are not real morphological features, but periodic noise from the differential pumping line to O₂ leak valve. An exposure of 300 L transformed the sharp step edge of the clean Cu(111) to be serrated, and the apparent depth of the region (designated as A) was measured as ~0.13 nm. The perimeters of the original clean step edges are clearly shown in Figure 1(b), and thus we were able to identify region A as an "oxide layer" of the upper terrace. Morphological changes of the lower terrace are also observed as triangular shaped dents with apparent depths of ~0.13 nm as shown in Figures (c) and (d), indicating that the inner structures of the triangular shaped dents most likely consist of the oxide layers. Exposure above 600 L of O₂ facilitated oxidation at both the step and terrace (Figs. (c) and (d)). The step oxides grow with a specific orientation along the close packed direction while the serrated etched steps merged into bigger triangular ones. Furthermore, the irregular shaped oxide islands designated as region B and C are clearly seen on both the upper and lower terrace. The height difference between
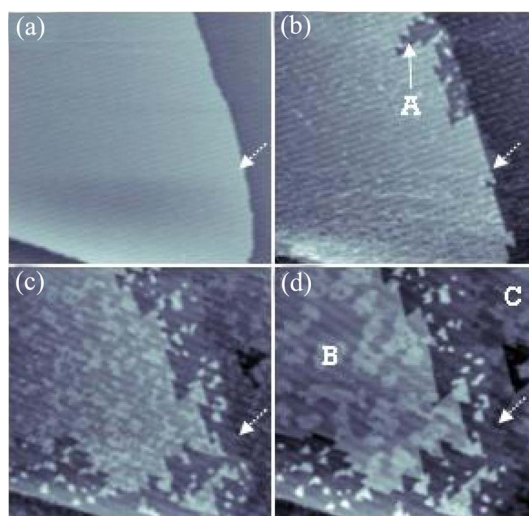
Figure 1. Sequential STM images (100 nm × 100 nm, V$_{sample}$ = 2.0 V, I = 0.1 nA) obtained during an exposure of clean Cu(111) surface to O₂ atmosphere (5×10^{-7} Torr) at room temperature. (a) Clean Cu(111) surface before exposure, (b) 300 L, (c) 600 L and (d) 900 L of O₂ exposure. The dashed arrows indicate identical surface position.
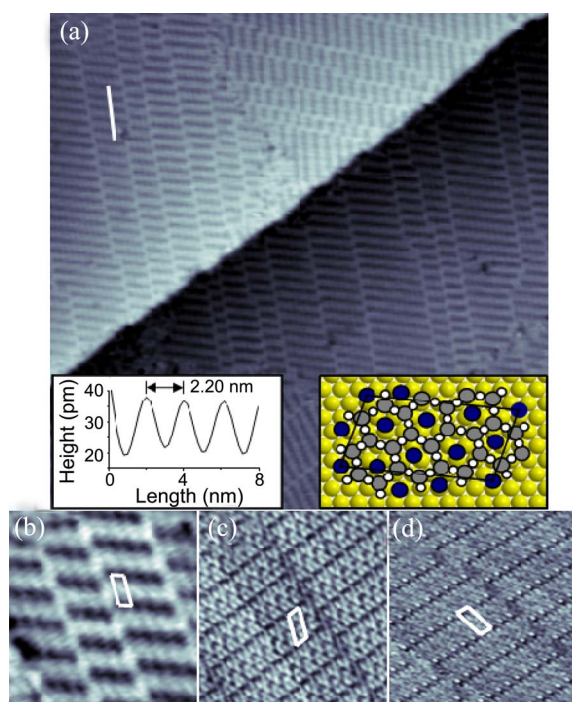
Figure 2. (a) A 100 nm × 100 nm STM image showing ordered Cu$_2$O layers on Cu(111) surface prepared by annealing the sample at 573 K in O$_2$ atmosphere (300 L, 5 × 10^{-7} Torr). The inset figures represent height profile and a ball model of "44" unit cell structure [Ref. 10]. (b)-(d) 15 nm × 15 nm STM images of Cu$_2$O layers on Cu(111) surface in Figure 2(a) with a imaging bias of (b) 3 V, (c) −1.5 V, (d) −3 V. The parallelograms represent a unit cell of "44" superstructure.

region B and C are close to actual step height of clean Cu(111) (~0.2 nm), implying that the oxide layers growing on both terraces are identical. It has been speculated that the O$_2$ can be dissociated on both the step and terrace of Cu(111) based on LEED and STM data.[12] Here we confirmed that O$_2$ molecules can not only consume the Cu atoms at the steps to build triangular shaped oxide layers, but dissociate on the terrace to form the irregular shaped oxide islands.

The oxidation of Cu(111) at higher temperature yields well ordered Cu$_2$O layers (Fig. 2). Since Matsumoto *et al.*[10] and Wiame *et al.*[9] controversially claimed that the oxidation of Cu(111) at 573 K produced "44" and "29" superstructures, respectively, we oxidized the surface at 573 K and performed bias dependent STM studies. Figure 2(a) shows an STM image of Cu$_2$O layers on Cu(111) after 300 L of O$_2$ dosed at 573 K. The surface contains a sharp step edge, which is in contrast to the serrated edges observed from annealing at RT as seen in Figure 1(b), and the flat terraces of Cu$_2$O can span as large as 50 nm separated by a domain boundary. Scanning tunneling spectroscopic (STS) measurements showed the existence of a band gap close to 1.4 eV (data not shown), supporting that the superstructures are oxide layers. The height profile in Figure 2(a) shows a peak to peak distance along the line where the average distance was measured to be 2.20 nm, close to the "44" superstructures (2.20 nm × 1.18 nm) as proposed by Jensen *et al.*[12] A ball model in Figure 2(a) shows the unit cell structure of

Cu$_2$O layer on the Cu(111) surface. The yellow circles represent a basal plane of the Cu(111) surface whereas the circles in white and dark blue show a Cu$_2$O layer and rest copper atoms, respectively. A high-resolution STM image of the Cu$_2$O layer is shown in Figure 2(b)-(d) where the Cu$_2$O layers were imaged at three different sample biases of 3 V, −1.5 V, and −3.0 V. At the positive sample biases (Fig. 2(b)), the unit cell of the Cu$_2$O layers can be clearly visualized. The rest Cu atoms (circle in dark blue) and Cu$_2$O structures (circle in white) appear as depressions and protrusions, respectively, indicating that the oxide layer increase the local density of empty electronic states. Scanning the surface at negative imaging biases inverts the topological features. The Cu rest atoms are now imaged as protrusions and electronic states of the oxide layers are outside the range of the bias. However, we can still see the retained unit cell of the "44" surface reconstruction. These STM images clearly demonstrate that the annealing of a Cu(111) surface at 573 K in O$_2$ atmosphere induces "44" reconstructions as proposed by Masumoto et al. and the morphology of the unit cell can be transformed depending on tunneling in the DOS of copper oxide.

In summary, O$_2$ adsorption on Cu(111) at RT and 573 K was investigated using STM. At room temperature, the gaseous O$_2$ reformed both the step and terrace into irregular shaped Cu$_2$O layers with an actual step height of Cu (111). Annealing Cu (111) at 573 K in O$_2$ atmosphere produced well ordered Cu$_2$O layers. The bias dependent STM studies clearly visualized a unit cell of the "44" superstructure.

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