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Short communication

# Temperature effect on the Cu<sub>2</sub>O oxide morphology created by oxidation of Cu(0 0 1) as investigated by in situ UHV TEM

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## Abstract

The temperature effect on the Cu<sub>2</sub>O oxide morphology was investigated by oxidizing Cu(1 0 0) thin films at the temperature ranging from 150 to 1000 °C and constant oxygen partial pressure of  $5 \times 10^{-4}$  Torr. The evolution of the oxide island size and shape was followed inside an in situ ultrahigh vacuum transmission electron microscope (UHV TEM). Of particular interest, we find that the oxide morphology can be triangular, hut, rod or pyramid shaped depending only on the oxidation temperature. © 2003 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Understanding oxidation is of fundamental and practical interest for environmental stability as well as processing of oxide nanostructures and thin films. From the standpoint of thermodynamics, all of the structural metals exhibit a tendency to oxidize. The driving force for oxidation of a given metal depends on the free-energy change for oxide formation. But the rate of oxidation and the morphological changes during oxidation depend on complex kinetics, and microstructural considerations, not necessarily solely on thermodynamics. Understanding the exact formation process of an oxide at the nanometer scale will provide fascinating scientific information on the oxidation kinetics

of metals [1,2]. Furthermore, in the rapidly developing field of nanotechnology, the formation of ordered structures through surface processes can produce ordered quantum dots, quantum wires, or quantum wells. The quantum properties of dots, wires and wells will depend on their shape, size and distribution. Hence, the exact shape and size distribution of the nanostructures must be predictable. Such self-assembled quantum structures have been realized in semiconductor systems of Ge/Si [3,4], GeSi/Si [5], and InAs/GaAs [6,7]. The controlled formation of oxide nanostructures would also be technologically important for their potentially novel optical, magnetic and sensor properties. Oxidation can be viewed as a processing tool for creating such self-ordered nanostructures. Visualizing the oxidation process at the nanometer scale with in situ experiments under ultrahigh vacuum conditions will provide essential insights into the complex kinetics and energetics of nano-oxide formation.

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Since copper has been chosen by many previous investigators as a model system to understand oxidation kinetics [8–11], we chose Cu films as a model system to study the formation of the oxide nanostructures by in situ ultrahigh vacuum transmission electron microscopy (UHV TEM). In situ UHV TEM provides unique mesoscopic scale information, including the nucleation to the growth and coalescence of the nanostructures, permits visualization of the oxidation process in real time, and provides information about the nucleation and growth kinetics of the oxide structures at the nanometer scale. We have examined the dependence of island density, size distribution, morphology, etc., on the oxidation parameters, such as substrate temperature, oxygen pressure, and the orientation of the substrate. The focus of this report is the dramatic effect of temperature on the oxide morphology formed on Cu(1 0 0) thin films. Copper only forms two thermodynamically stable oxides, CuO and Cu<sub>2</sub>O. For the temperatures and very low oxygen partial pressures used in our experiments, only Cu<sub>2</sub>O is expected to form [12]. Cu<sub>2</sub>O has a direct bandgap of 2.0–2.2 eV and is a typical system for studying exciton effect due to its large binding energy between excitons. The formation of Cu<sub>2</sub>O nanostructured arrays provides an ideal system for studying quantum confinement effect and exciton effect in quantum structures.

## 2. Experimental

The microscope used in this work was a modified JEOL 200CX [13]. A leak valve attached to the column of the microscope permits the introduction of gases directly into the microscope. In order to minimize the contamination, a UHV chamber was attached to the middle of the column, where the base pressure was less than  $10^{-8}$  Torr without the use of the cryoshroud. Under the UHV conditions, the film surface is atomically clean at the start of the oxidation experiments, which is extremely important for quantitative understanding of growth kinetics. The microscope was operated at 100 keV to minimize irradiation effects. Single crystal 99.999% pure 700 Å Cu films were grown on irradiated NaCl(1 0 0) substrates in an UHV e-beam evaporation system, then removed from the substrate by dissolving the NaCl in de-ionized water. The native copper oxide was removed inside the TEM by annealing the Cu films in methanol vapor at a pressure of  $5 \times 10^{-5}$  Torr and 350 °C, which reduces the copper oxide to copper [14]. Scientific grade oxygen gas of 99.999% purity can be admitted into the column of the microscope through the leak valve at a partial pressure between  $5 \times 10^{-5}$  and 760 Torr. The specially designed sample holder allows for resistive heating at temperatures between room temperature and 1000 °C. After removal from the in situ TEM

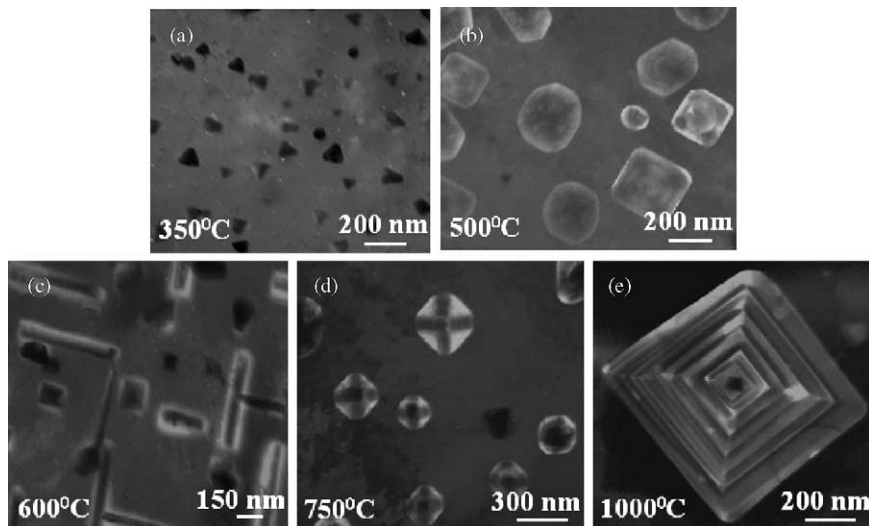


Fig. 1. The morphology of Cu<sub>2</sub>O islands formed during in situ oxidation of Cu(0 0 1) at a oxidation partial pressure of  $5 \times 10^{-4}$  Torr and oxidation temperatures of: (a) 350 °C; (b) 500 °C; (c) 600 °C; (d) 700 °C; (e) 1000 °C.

investigation, the samples were analyzed using a Digital Instruments NanoScope IIIa scanned probe microscope. Contacting-mode atomic force microscope (AFM) height images were employed to assess the sample topology.

### 3. Results

We examined the  $\text{Cu}_2\text{O}$  island formation as a function of oxidation temperature in the range of 150–1000 °C at constant oxygen partial pressure of  $5 \times 10^{-4}$  Torr. Oxide island formation was not observed for several hours at oxidation temperatures below 150 °C. Three-dimensional island formation was observed for oxidation at all temperatures higher than 150 °C. For all of the temperatures that we have examined, the selected area electron diffraction patterns revealed epitaxially oriented  $\text{Cu}_2\text{O}$  island on the Cu surface, i.e.  $\text{Cu}_2\text{O}(001)/\text{Cu}(001)$  and  $\text{Cu}_2\text{O}(100)/\text{Cu}(100)$ .

Fig. 1 are the bright field TEM images, which shows the morphology of  $\text{Cu}_2\text{O}$  islands formed on  $\text{Cu}(001)$  surface at different oxidation temperatures. At 350 °C, only triangular geometry islands formed (Fig. 1a). The island size increased with continued exposure to oxygen, but the island shape did not change. At elevated temperatures, between 400 and 550 °C, the islands exhibited a shape change from triangular to square- or round-based islands, as they increase in size due to the continued exposure to oxygen (Fig. 1b).

In a narrow temperature regime near 600 °C, elongated  $\text{Cu}_2\text{O}$  islands formed as shown in Fig. 1c. These elongated islands have varying lengths, but similar widths of  $\sim 110$  nm. Our in situ observation revealed that the initial islands formed at this temperature were square, and continued to grow uniformly in size, but showed a fascinating shape transition near 110 nm to a quasi-one-dimensional rod with the continued oxidation. The elongation directions of the islands are always along the two orientation pairs of the four crystallographic orientations, i.e.  $\langle 001 \rangle$  and  $\langle 00\bar{1} \rangle$ , or  $\langle 010 \rangle$  and  $\langle 0\bar{1}0 \rangle$ , and roughly equally distributed. We have observed elongated islands with aspect ratios as large as 40:1.

Oxidation at temperatures between 650 and 800 °C resulted in the formation of pyramid islands, which have a distinctive cross-hatched pattern as shown in

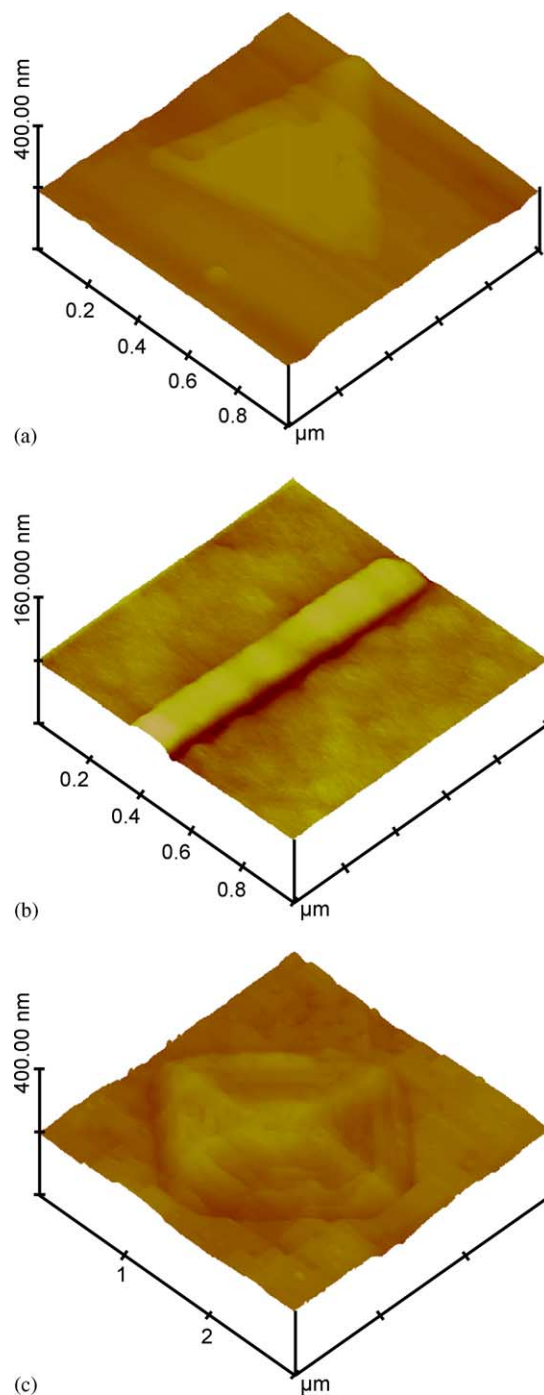


Fig. 2. AFM images of typical (a) triangular ( $T = 350$  °C), (b) elongated ( $T = 600$  °C), and (c) pyramid islands ( $T = 800$  °C).

**Fig. 1d.** When the Cu film was oxidized at temperatures between 800 and 1000 °C, pyramids with flat terraces formed (**Fig. 1e**). The pyramid terraces have roughly equal width and length distribution. Our in situ observation revealed that these terraced-pyramids developed by nucleating and growing new terraces underneath the base layer. The size of terraces was unchanged once a new terrace formed underneath it.

**Fig. 2** shows the AFM images of some typical Cu<sub>2</sub>O islands formed at different temperatures. **Fig. 2a** shows two oxide islands formed at  $T = 350$  °C. The larger island nucleated at an earlier time than the smaller island. The surface topology reveals that the large island has a flat top, and the small has a triangular top, where their height is approximately equal to 30 nm. **Fig. 2b** is the AFM image of an elongated island formed at  $T = 600$  °C. The surface profile shows that the island has a flat top with a height of 20 nm. **Fig. 2c** corresponds to an island formed at  $T = 800$  °C, where the island terraces are visible. The island height is 40 nm, which is much smaller than its lateral size.

Both in situ TEM and AFM investigation revealed that the edges of all of the square-shaped islands formed at higher temperature as shown in **Fig. 1b, d and e** are along Cu(0 0 1), Cu(0 0  $\bar{1}$ ), Cu(0 1 0) and Cu(0  $\bar{1}$  0), and they have roughly equal growth rates along these four equivalent crystallographic orientations, which results in the four-folded symmetry of the island.

#### 4. Discussion

The in situ UHV TEM observations show the dramatic sensitivity of the oxide island morphology to oxidation temperature. During oxidation at low temperatures ( $T < 400$  °C), the oxide islands adopt triangular shape, but at temperatures higher than 400 °C, the islands have a more symmetrical geometry. We have previously shown that the initial stages of copper oxidation are surprisingly similar to heteroepitaxy in thin film growth, where oxygen surface diffusion is the dominant mechanism [15]. Only a few investigators have examined the effect of the substrate temperature on the thin film growth and morphology such as Cr on Cu substrates [16], indium-doped tin oxide films [17] and plasma enhanced chemical vapor deposition

(PECVD) polycrystalline Si films [18]. Yet, only Afify et al. [17] noted a distinct change in the island morphology due to the substrate temperature, where dendritic growth was noted at higher temperatures for indium-doped tin oxide films. A possible reason why this dramatic effect of temperature on the film morphology has not been widely observed in other systems could be that the temperature ranges previously investigated were considerably smaller (only  $\sim 200$  °C) than the temperature range we examined (150–1000 °C).

The oxide morphology is controlled by kinetic and thermodynamic factors during the oxidation process. In situ observations can provide insights into distinguishing between morphologies due to kinetic or thermodynamic considerations. It is reasonable to expect that temperature would affect the kinetics and/or energetics of the oxide formation. The possible effects of temperature to the oxide morphology include: (1) the enhanced diffusion of copper and oxygen atoms; (2) the decrease in interfacial strain due to the differences in thermal expansion coefficients; and (3) the changes in mechanical properties.

It is known that the surface diffusion of oxygen plays an important role in the kinetics of the initial oxidation stage [15,19]. The coefficient of oxygen surface diffusion dependence on temperature follows an Arrhenius relationship:  $D_s = (1/4)a_j v_D e^{-\Delta E_s/k_B T}$ , where  $a_j$  is the distance per jump of oxygen molecules on Cu surface,  $\Delta E_s$  the activation energy for surface diffusion of oxygen molecules,  $k_B$  the Boltzmann's constant,  $v_D$  the surface vibration frequency. The diffusion distance of oxygen on Cu surface is larger at higher temperature, and oxygen atoms can migrate longer distances on the surface and hence are more likely to be captured by the oxide islands. Therefore, the islands are more likely to form the energetically favorable configuration with increasing temperature. At higher temperatures, both oxygen and copper can diffuse quickly to form more thermodynamically, equilibrium shaped oxides at the higher temperature oxidation, such as the four-fold symmetric islands observed above 450 °C. At lower temperatures, the oxide morphology is more likely to have low symmetry due to the slower kinetics, such as the triangular-shaped islands formed below 400 °C.

The formation of Cu<sub>2</sub>O islands will induce tensile stress in the Cu film due to the large lattice mismatch.

Copper is a face-centered cubic metal, with a lattice parameter  $a = 0.361$  nm, and  $\text{Cu}_2\text{O}$  is cubic with a lattice parameter  $a = 0.4217$  nm. Therefore, a strain field exists around each island, and this strain field could inhibit the island growth by creating additional activation barriers for the incorporation of atoms at island edges [20].  $\text{Cu}_2\text{O}$  has a thermal expansion coefficient of  $1.9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , and Cu has a thermal expansion coefficient of  $17 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ . With increasing temperature, the lattice mismatch becomes smaller, and this lattice mismatch induced strain becomes smaller too. This could explain the triangular shape at low temperatures, where the strain is high and so the interface area is minimized by this triangular shape. At higher temperatures, there is less lattice mismatch and therefore reducing interfacial strain with increasing temperatures. Hence, the chosen interfaces will be along the low energy interfaces (such as the low index planes). A third effect of temperature is on the mechanical properties of the oxide and substrate. At higher temperatures, the metal substrate and oxide become significantly more ductile. The enhanced ductility at higher temperatures provides a mechanical mechanism for strain relaxation that should affect the oxide morphology development.

Particularly intriguing was the observed shape transition from square to elongated nanorods at a very narrow temperature range of  $600 \text{ }^\circ\text{C}$ . The formation of elongated islands was observed in many systems such as Ag/Si(1 0 0) [21], Ge/Si(1 0 0) [4], GaAs/Si(1 0 0) [22], CoSi/Si(1 0 0) [23], Au/Mo(1 1 1) [24], InAs/InP(1 0 0) [25]. Tersoff and Tromp [26] predicted a universal property of strained systems is that square-based pyramid should be unstable with respect to ripening, and transform to elongated island spontaneously due to the elastic strain-relief mechanism. Our experimental data on the volume evolution of the island at this temperature has shown that the elongation of  $\text{Cu}_2\text{O}$  islands agrees well with the energetic calculations based on the balance between surface energy and stress relaxation in the three dimensional islands [27]. The surface/interface energies and strain energy within the island should be temperature dependent, and the oxidation at  $600 \text{ }^\circ\text{C}$  could provide an optimal condition for the formation of elongated island. Oxide morphologies depend on the kinetics or thermodynamics of the materials system. Since many parameters effecting the kinetics or thermodynamics of

growth depend sensitively on temperature, then different oxide morphologies would be expected to form at various temperatures.

## 5. Conclusion

We demonstrated that dramatically different morphologies of oxide nanostructures can be achieved by modifying the oxidation temperature. The oxidation temperature will effect diffusion, interfacial strain, surface and interface energies, and elastic properties, which all play a significant role in the development of the oxide morphology to pyramids, nanorods, domes or terrace-layered structure. Similar results could be realized in other metal systems such as Ni, Fe, Al, Ti, Co, Pd, Ir and Sn, where island formation has been observed during oxidation. These nanostructure arrays formed through this surface reaction process can serve as building blocks for the design and development of self-assembled, nano-optical, electronics and sensor devices.

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