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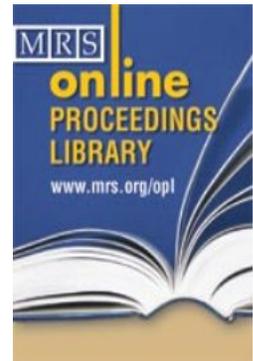
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Dramatic Effect of Temperature on Metal-oxide Nanostructures: Oxidation of Cu Films by *In situ* UHV-TEM

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ABSTRACT

We investigated the temperature effect on the Cu₂O morphology by oxidizing Cu(100) thin films at the temperature ranging from 350°C to 1000°C. We demonstrated that dramatically different morphologies of oxide nanostructures can be achieved by modifying the oxidation temperature. Quasi-one-dimensional Cu₂O structures with aspect ratios as large as 40:1 were formed at the oxidation temperature of 600°C. The *in situ* observation data on the elongation of Cu₂O islands agree with the energetic calculations based on the balance between surface and interface energies and the elastic stress relaxation in the three dimensional islands.

INTRODUCTION

From the standpoint of thermodynamics all of the metals exhibit a tendency to oxidize. The oxidation driving force depends on the free-energy change for oxide formation. But the morphological changes of oxides during oxidation depend on kinetics, and microstructural considerations. Visualizing the oxidation process will provide essential insights into the complex kinetics and energetics of nano-oxide formation [1,2]. Furthermore, oxidation can be viewed as a processing tool for creating self-ordered nanostructures and the understanding of exact formation process of oxide would provide the guidance to control the oxide nanostructures [3]. *In situ* ultra high vacuum transmission electron microscope (UHV-TEM) allows us to study the nucleation and growth processes of oxide at nanometer scale, provides a unique view of dynamic reactions, and enables us to understand and therefore manipulate surface reactions. Since Cu has been chosen by many investigators as a model system to understand oxidation kinetics [4-7], we chose Cu films as a model system to study the formation of the oxide nanostructures by *in situ* UHV-TEM. We have examined the dependence of island density, size distribution, morphology on the oxidation parameters, such as substrate temperature, oxygen pressure, and orientation of the substrate. The focus of this paper is the dramatic effect of temperature on the oxide morphology formed on Cu(100) thin films. Copper forms two thermodynamically stable oxides, Cu₂O and CuO. Cu₂O is simple cubic lattice (space group pn-3m) with 4Cu and 2O atoms in its basis, and a lattice parameter of 4.22Å. The Cu atoms form a FCC lattice and the O atoms form a BCC lattice, where each O atom is surrounded by a tetrahedron of Cu atoms. CuO has a monoclinic structure. Cu is a FCC metal with a lattice parameter of 3.6Å. For the temperatures and very low oxygen partial pressures used in our experiments, only Cu₂O is expected to form [8].

EXPERIMENTAL

The microscope used in this work was a modified JEOL 200CX [9]. 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. The microscope was operated at 100 KeV to minimize irradiation effects. Single crystal 99.999% pure (by referring to the purity of the originally evaporated material) 700Å Cu films were grown on irradiated NaCl(100) substrates in an UHV e-beam evaporation system where the chamber pressure was at $\sim 10^{-8}$ torr. The single crystal nature of the Cu films was determined by SAD in a TEM. The Cu films were removed from the substrate by dissolving the NaCl in de-ionized water. The native Cu oxide was removed inside the TEM by annealing the Cu films in methanol vapor at a pressure of 5×10^{-5} torr and 350°C, which reduces the copper oxides to copper [10]. Scientific grade oxygen gas of 99.999% purity can be admitted into the column of the microscope through a leak valve at a partial pressure between 5×10^{-5} torr and 760 torr. The specially designed sample holder allows for resistive heating at temperatures between room temperature and 1000°C.

RESULTS

We examined the Cu_2O island formation on Cu(001) as a function of oxidation temperature in the range of 350°C to 1000°C at constant oxygen pressure of 5×10^{-4} torr. The morphology of Cu_2O islands formed at different oxidation temperatures is shown in Figure 1 (bright field TEM images). At 350°C, only triangular geometry islands formed (Fig. 1a). The island size increased with continued oxidation, but the island shape did not change. At elevated temperatures, between 400°C 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 (Figure 1b).

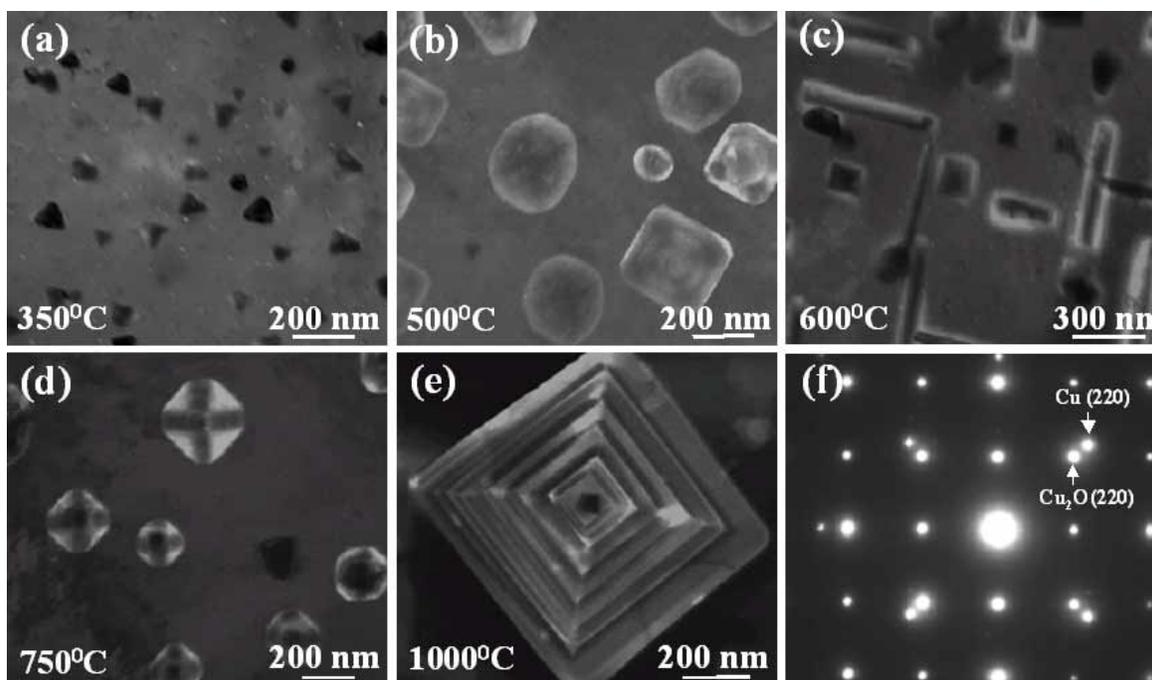


Figure 1. The morphology of Cu_2O islands formed during *in situ* oxidation of Cu(001) at a oxidation partial pressure of 5×10^{-4} torr and oxidation temperatures of (a) 350°C, (b) 500°C, (c) 600°C, (d) 700°C and (e) 1000°C.

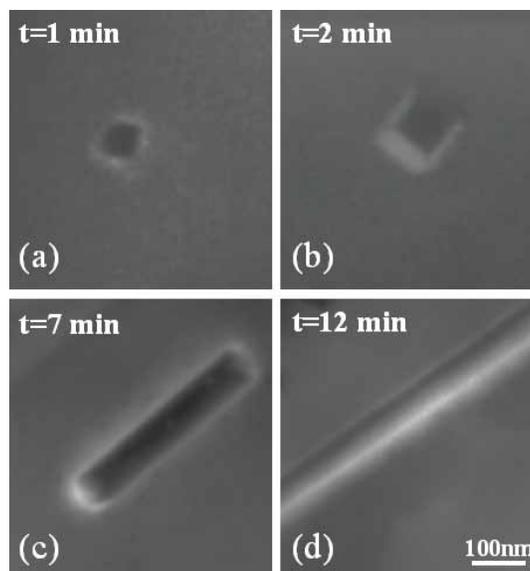


Figure 2. *In situ* TEM images of the four growth stages of a Cu_2O island as a function of oxidation time at constant oxygen partial pressure of 1×10^{-4} and temperature of 600°C .

In a narrow temperature regime near 600°C , elongated Cu_2O islands formed (Fig. 1c). These islands have varying lengths, but similar widths of $\sim 110\text{nm}$. The initial islands were square, and continued to grow uniformly, but showed a shape transition near 110nm to nanorods with continued oxidation. The elongation directions of the islands are along the two 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 $40:1$. In order to visualize the growth of one island for a long time without interference due to coalescence with neighboring islands, we oxidized the films at oxygen pressure of 1×10^{-4} torr. A sequence of images focusing on the growth of a single island is shown in Fig. 2. The initially formed island is square shaped (Fig. 2a), and continues to grow uniformly (Fig. 2b), when a critical size ($\sim 110\text{nm}$) is reached, the island shows a shape transition to nanorod (Fig. 2c, d). The contrast around the island is related to the strain in the island and the film. This was confirmed by AFM which indicates no dip around the island for the initial growth stages (Fig. 2a-c), and a very small dip $\sim 2\text{nm}$ for the larger island (Figure 2d).

Oxidation at temperatures between $650\text{-}800^\circ\text{C}$ resulted in the formation of pyramid islands, which have a distinctive cross-hatched pattern as shown in Figure 1d. When the Cu film was oxidized at temperatures between $800\text{-}1000^\circ\text{C}$, pyramids with flat terraces formed (Figure 1e). The pyramid terraces have roughly equal width and length distribution.

For all the temperatures that we have examined, the Cu_2O islands are epitaxial with Cu substrate as shown in Fig. 1f, i.e. $(001)\text{Cu}_2\text{O}/(001)\text{Cu}$ and $[100]\text{Cu}_2\text{O}/[100]\text{Cu}$. The SAD only confirms the crystal structure is cubic form of copper oxide (as compared to the monoclinic CuO), there is the possibility of nonstoichiometry of the Cu oxide. EELS is the one method probe this issue, and one future work will focus on the oxidation states of the Cu across the interface.

The accurate estimates of the island thickness are beneficial for understanding of the formation of the nanostructured Cu_2O . Unfortunately the *in situ* UHV-TEM modifications included modifications of the sample holder such that no tilt was available. Currently, we used

AFM for height measurements. A detailed structural characterization of the oxide islands by ex situ methods is necessary in the future work.

DISCUSSION

Many parameters affecting the kinetics and thermodynamics of growth depend sensitively on temperature, different oxide morphologies would be expected to form at various temperatures. During oxidation at low temperatures ($T < 400^\circ\text{C}$), the oxide islands adopt triangular shape, but at temperatures higher than 400°C , the islands have a more symmetrical geometry. 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 [11], indium-doped tin oxide films [12] and plasma enhanced chemical vapor deposition (PECVD) polycrystalline Si films [13]. Yet, only Afify *et al.* [12] 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 $\sim 200^\circ\text{C}$) than the temperature range we examined (350°C to 1000°C).

The oxide morphology is controlled by kinetic and thermodynamic factors during the oxidation. It is reasonable to expect that temperature would affect the kinetics and/or energetics of the oxide formation. The possible effects of temperature on 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, (3) the changes in mechanical properties.

Surface diffusion of oxygen plays an important role in the kinetics of the initial oxidation stage. [14] The rate of oxygen diffusion follows an Arrhenius relationship with temperature. The diffusion path of oxygen 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 Cu can diffuse quickly to form more thermodynamically, equilibrium shaped oxides, 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_2O islands will induce tensile stress in the Cu film due to the large lattice mismatch. Therefore, a strain field exists around islands, and this strain field could inhibit the island growth by creating additional activation barriers for the incorporation of atoms at island edges [15]. Cu_2O 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 the 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 more ductile. The enhanced ductility provides a mechanical mechanism for strain relaxation affecting the oxide morphology development.

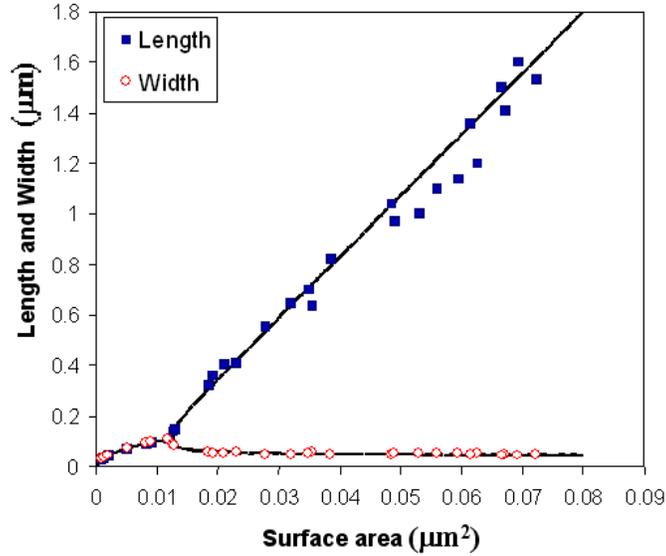


Figure 3. Dependence of both island length t (squares) and width s (circles) on the island surface area. The solid lines represent a theoretical fit based on Eq.(1). The initially square shaped island undergoes a shape transition at the critical size $s=t=e\alpha_0=114\text{nm}$. There is a reduction of the width to its optimal width, α_0 . The data points are obtained from the experimental results.

Particularly intriguing was the observed shape transition from square to elongated nanorods at a very narrow temperature range of 600°C . Tersoff and Tromp have shown that strained epitaxial islands may undergo a shape transition as they grow in size [16]. Below a critical size, islands have a compact symmetric shape. However, at a larger size, they adopt a long thin shape, which has an energy minimum for the system because of the tradeoff between surface/interfacial energies and stress relaxation in the islands due to the lattice mismatch between the substrate and epitaxial film. We compared our results with this theoretical model by using the analytical expression for the energy per unit volume of a strained epitaxial island [16].

$$\frac{E}{V} = 2\Gamma\left(\frac{1}{s} + \frac{1}{t}\right) + \frac{1}{h}(r_i + r_t - r_s) - 2ch\left[\frac{1}{s}\ln\left(\frac{se^{3/2}}{h\cot\theta}\right) + \frac{1}{t}\ln\left(\frac{te^{3/2}}{h\cot\theta}\right)\right] \quad (1)$$

where s , t , and h are the width, length, and height of the island, respectively; θ being the contact angle; Γ contains the surface and interface energies, $\Gamma = \gamma_e \csc\theta - (\gamma_t + \gamma_s - \gamma_i) \cot\theta$; γ_t , γ_s , and γ_e are the surface energies of the island's top, the substrate, and the island's edge facet, respectively; γ_i is the island-substrate interface energy. $c = \sigma_b^2(1-\nu)/2\pi\mu$, ν and μ are the Poisson ratio and shear modulus of the substrate, σ_b is the island bulk stress. The optimal balance between surface energies and strain is obtained through the minimization of the total energy expression for an island of constant height h with respect to both s and t . This gives a square island with $s=t=\alpha_0$, where the optimal size α_0 is given by

$$\alpha_0 = e\phi h \exp(\Gamma / ch) \quad (2)$$

where $\Phi = e^{-3/2} \cot\theta$. The island remains a square up to a critical size $s=t=e\alpha_0$. Due to continued oxidation, the island grows beyond this critical size, the square shape becomes unstable and a transition to rectangular shape takes place. As the island grows further, the aspect ratio increases.

To evaluate "c", we used standard values of μ_{Cu} (40GPa) and calculated σ_b for Cu_2O from the Young's modulus (30GN/m²) and Poisson ration (0.455) of Cu_2O . The contact angle, $\theta = 30^\circ$,

and height, $h=20\text{nm}$, were measured by the AFM. By fitting with the critical size, $e\alpha_0=114\text{nm}$, we can estimate Γ from Eqn. (2). These values are substituted into Eqn. (1) to determine the energy per unit volume as a function of width s and length t . A comparison of Tersoff and Tromp's model with our data shows excellent agreement for the size evolution of the island as shown in Fig.3. Furthermore, we have developed a kinetic model of oxidation based on oxygen surface diffusion to the perimeter of the oxide island. We have noted an excellent agreement of volume evolution of the island with the kinetic model that validates the growth of the Cu_2O islands is initially dominated by the surface diffusion of oxygen [17].

CONCLUSION

We demonstrated that oxidation temperature has a dramatic effect on the kinetics/energetics of oxide formation, which results in different morphologies of oxide nanostructures. Our *in situ* observation data on the elongation of Cu_2O islands agree with the energetic model.

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