

Formation of Quasi-One-Dimensional Cu₂O Structures by *in situ* Oxidation of Cu(100)

Guangwen Zhou and Judith C. Yang

Department of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

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Epitaxial Cu₂O islands on a Cu(100) surface formed through oxidizing Cu(100) films at 600 °C in an ultrahigh vacuum transmission electron microscope were observed to undergo a shape transition from initially square shaped islands to elongated islands at a critical size of ~110 nm. Our experimental 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. We developed a kinetic model based on oxygen surface diffusion that fits well with the observed volume evolution of the Cu₂O islands.

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The fundamental understanding of oxidation mechanisms at the nanometer scale is essential, because these processes play crucial roles in a vast range of applications, including environmental stability, gate oxides, catalytic reactions, and fuel cell reactions. The driving force for oxidation of a given metal depends on the free-energy change for oxide formation. The structural changes of the oxides are dependent on the complex kinetics and energetics of the particular materials system. Furthermore, oxidation processes can be considered as a model system for surface chemical reactions and as a processing tool to create self-assembled nano-oxide structures.

Formation of self-assembled islands through a surface process has been intensively investigated because of potential applications and the intrinsic interest in structures with reduced dimension [1–4]. One intriguing aspect in these self-assembled systems is the tendency of the islands to change their shape as they increase in size. Tersoff and Tromp have given an analytical theory and shown that strained epitaxial islands, as they grow in size, may undergo a shape transition [5]. 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 three-dimensional islands due to the lattice mismatch between the substrate and epitaxial film. The formation of rectangular hut structures was observed by Mo *et al.* [4] during the initial growth stages of Ge on Si(100), and similar elongated island structures were also observed in many other systems created by molecular beam epitaxy [5–11]. Here we report the first observations of a surface chemical reaction where the nanorod transition is observed, thereby demonstrating a greater universality of the elastic strain relief model proposed by Tersoff and Tromp.

We have previously shown that the initial stages of copper oxidation (where the oxide thickness is less than 100 nm) are surprisingly similar to heteroepitaxy, where oxygen surface diffusion is the dominant mechanism [12]. We observed the formation of elongated Cu₂O islands on a Cu(100) surface through oxidizing the Cu(100) films in-

side an ultrahigh vacuum (UHV) transmission electron microscope (TEM). The microscope used in this work was a modified JEOL 200CX [13]. A UHV chamber was attached to the middle of the column, where the base pressure was less than 10⁻⁸ torr. Single crystal 99.999% pure 700 Å Cu films were grown on irradiated NaCl(100) substrates in an UHV e-beam evaporation system, then removed from the substrate by dissolving the NaCl in deionized water and mounted on a specially prepared TEM sample holder. 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 [14]. Scientific grade 99.999% purity oxygen can be admitted into the column of the microscope through a leak valve at a partial pressure between 5 × 10⁻⁵ and 760 torr. The specially designed holder allows for resistive heating between room temperature and 1000 °C. For the temperatures and oxygen partial pressures used in our experiments, only Cu₂O is expected to form [15], which was confirmed by selected area electron diffraction (SAD). We observed that the elongated islands formed only in a very narrow temperature regime near 600 °C; triangular, square, or round based pyramid islands formed at the other oxidation temperatures.

Figure 1 shows the morphology of Cu₂O islands formed on a Cu(100) surface under 8 × 10⁻⁴ torr of oxygen partial pressure at 600 °C. The islands are initially compact and become progressively elongated as they grow larger. These elongated islands have varying lengths, but similar widths. The islands grow epitaxially with the underlying Cu surface, as revealed by SAD, as shown in the inset of Fig. 1(a). The elongation directions of the islands are always along the two orientation pairs of the four crystallographic orientations, i.e., <001> and <00 $\bar{1}$ > or <010> and <0 $\bar{1}$ 0>, and roughly equally distributed. We have observed elongated islands with aspect ratios as large as 40 : 1. The island shapes were not observed to depend on oxygen pressure. Instead, the Cu₂O island density is closely related to the oxygen pressure. The island size is mainly determined by the oxidation time at this temperature. Atomic force microscopy (AFM) study as shown in Fig. 1(b) indicates that

the islands have a flat top, and the contact angle θ between their edge facets and the substrate varied from 20° to 35° at the different growth stages. The height of the islands above the Cu film surface is around 15 nm and remained almost constant during the island growth process. The total thickness of the islands was estimated to be about 20 nm by considering the conversion of the displaced copper atoms that had occupied the region of the Cu_2O island.

In order to visualize the growth of one island for a long time without interference due to coalescence with a neighboring island, we continuously oxidized the Cu(100) films at a low oxygen partial pressure of 1×10^{-4} torr. The

volume evolution of the islands is recorded *in situ*, and a sequence of images focusing on the growth of a single island is shown in Fig. 2. The initially formed island is square shaped as shown in Fig. 2(a), and it continues to grow uniformly in size [Fig. 2(b)]; when a critical size (~ 110 nm) is reached, the island shows a fascinating shape transition to a quasi-one-dimensional nanorod with the continued oxidation [Figs. 2(c) and 2(d)].

We compared our results with the theoretical model given by Tersoff and Tromp [5], who derived an analytical expression for the energy per unit volume (E/V) of a strained epitaxial island.

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

where s , t , and h are the width, length, and height of the island, respectively; θ is the contact angle; Γ contains the surface and interface energies, $\Gamma = \gamma_e \csc\theta - (\gamma_t + \gamma_s - \gamma_i) \cot\theta$ (units J/m^2); γ_t , γ_s , and γ_e are the surface energies (per unit area) of the island's top, the substrate, and the island's edge facet, respectively; γ_i is the island-substrate interface energy. It should be noted that the interface in this case is a dynamically growing metal/oxide, and the γ_i term incorporates the energy of this reaction front. $c = \sigma_b^2(1 - \nu)/2\pi\mu$; ν and μ are the Poisson ratio and shear modulus of the substrate, σ_b is the island bulk stress.

It is clear from Eq. (1) that the surface energy dependent term prefers to have a large interfacial area island for stability, while the strain relaxation energy term prefers to have islands with a smaller interfacial area for more stability. So 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 before increasing its size up to $s = t = e\alpha_0$. Because of continued oxygen exposure, the island grows beyond this critical size ($e\alpha_0$), the square shape becomes unstable, and a transition to rectangular shape takes place. As the island grows further, the aspect ratio, t/s , increases, i.e., reducing its width back to the optimal size α_0 , while rapidly increasing its length. Equation (2) implies an experimental observation of the critical size, at which the shape transition occurs, that determines the relative importance of the surface energy and the island stress.

To evaluate "c," we used standard values of μ_{Cu} (40 GPa) and calculated σ_b for Cu_2O from the Young's modulus ($30 \text{ GN}/\text{m}^2$) and Poisson ratio (0.455) of Cu_2O . The contact angle, $\theta = 30^\circ$, and height, $h = 20$ nm, were

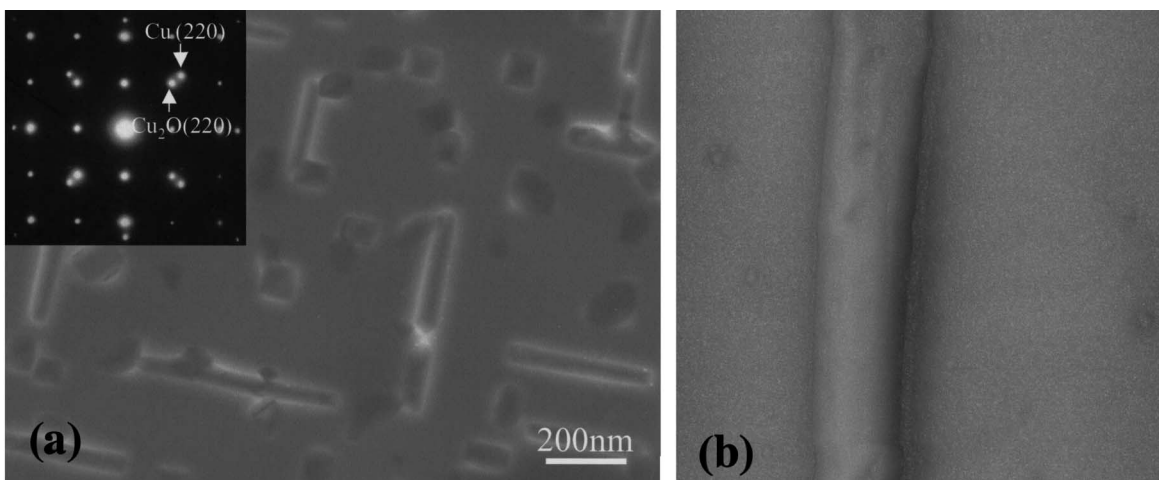


FIG. 1. (a) The Cu_2O islands formed by oxidation of Cu(100) at constant oxygen partial pressure of 8×10^{-4} and temperature of 600°C . The square shaped islands are smaller than or near to the critical size of ~ 110 nm. Elongated islands which have undergone shape transition are also observed. The SAD (inset) revealed the epitaxial relationship between Cu_2O and the Cu substrate. (b) AFM image ($0.6 \mu\text{m}$ by $0.6 \mu\text{m}$; z range, $0.3 \mu\text{m}$) of one elongated Cu_2O island.

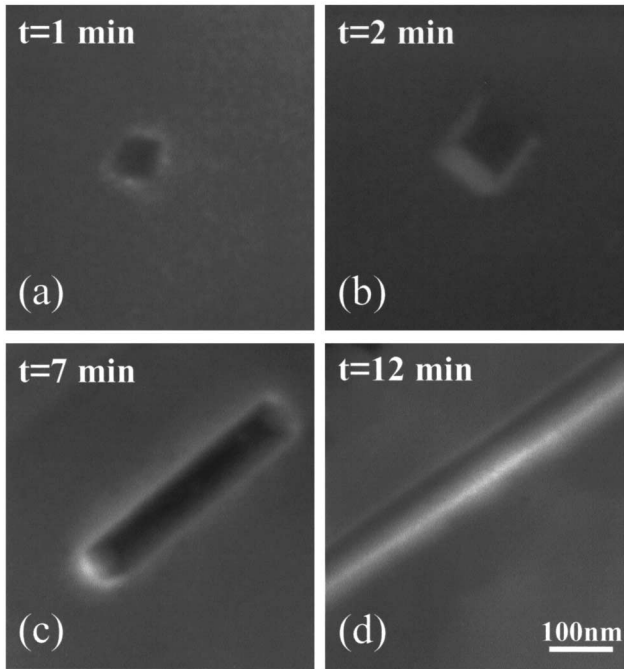


FIG. 2. *In situ* TEM images of the four growth stages of a Cu_2O island as a function of oxidation time at constant oxygen partial pressure of 1×10^{-4} and temperature of 600°C . The initially formed square shaped island is shown in (a). The island remains a square when increasing in size (b). A shape transition to rectangular islands has occurred, where its aspect ratio increases with continued oxidation (c) and (d).

measured by the AFM. By fitting with the critical size, $e\alpha_0 = 114 \text{ nm}$, we can estimate Γ from Eq. (2). Gamma (Γ) depends on the overall surface energies and interfacial energy, which were not readily available in the literature. The values can be substituted into Eq. (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. Figure 3 shows the evolution of width s and length t versus the island area obtained from Eq. (1). It is seen that the island grows as a square shape up to its critical size of 110 nm , beyond which there is a transition to a rectangular shape. With its continued elongation, there is a reduction in the island width.

The comparison of the island volume growth as a function of time provides significant insights into the oxidation kinetics. We assume that the dominant mechanism for the growth of three-dimensional Cu_2O islands is surface diffusion of oxygen to the perimeter of the island [16], $\frac{dN}{dt} = AK_S J_S$, where $N(t)$ is the number of oxygen atoms in a Cu_2O island at time t , K_S is the sticking coefficient, J_S is the diffusive flux of oxygen, and A is the perimeter of an island. The island volume evolution undergoes three different stages. (I) Before shape transition, the island has equal length and width. By solving the above differential equa-

tion, the island volume increases parabolically with respect to oxidation time before the shape transition

$$V^I(t) = \frac{(K_S J_S \Omega)^2}{4h} (t - t_0)^2, \quad (3)$$

where Ω is the atomic volume of oxygen in Cu_2O , and h is the island height. (II) As can be seen from Fig. 3, the width of the island reduces somewhat from $e\alpha_0$ to α_0 within a few minutes after the shape transition and then remains constant. Therefore, in stage (II) the island's width and length change simultaneously as a function of oxidation time. The island volume increase with respect to oxidation time can be expressed as follows:

$$V^{II}(t) = 2K_S J_S \Omega \int [s(t) + t(t)] dt, \quad (4)$$

where $s(t)$ and $t(t)$ are the island width and length. It should be noted that Eq. (4) is the general form of the volume dependence on time. To estimate the integrand, $2K_S J_S \Omega (s(t) + t(t))$, as a function of time, we used the experimental value of $s(t)$ and calculated the corresponding $t(t)$ from Tersoff and Tromp's model. The coefficient, $K_S J_S$, in Eq. (4) was determined from the fit of the experimental data prior to the shape transition to Eq. (3). Therefore, the island volume at time t in stage II, which is the integral of the formula $2K_S J_S \Omega (s(t) + t(t))$, can be numerically estimated as the area under the curve generated from this formula from the shape transition time to time t . (III) The island remains its optimal size α_0 of width and constant height, the length increases with time, we determine that the volume of the island increases

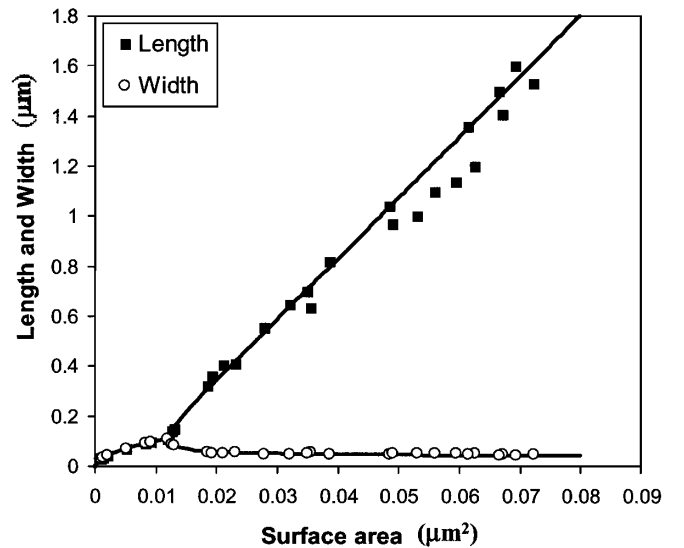


FIG. 3. Dependence of both island length t (squares) and width s (circles) on the island surface area. The solid lines represent a theoretical fit based on Eq. (1). The initially square shaped island undergoes a shape transition at the critical size $s = t = e\alpha_0 = 114 \text{ nm}$. There is a reduction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

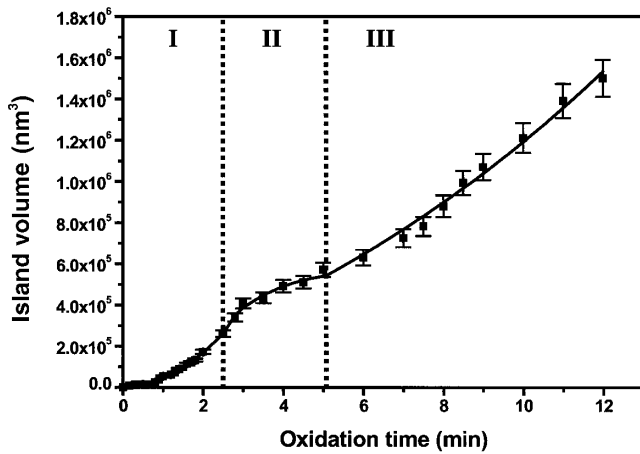


FIG. 4. The volume of the Cu_2O island with respect to time when the copper film was oxidized at 1×10^{-4} torr oxygen and 600°C . The solid line corresponds to the theoretical fit to the oxygen surface diffusion model.

exponentially:

$$V^{\text{III}}(t) = \frac{(\alpha_0 h)^2}{2K_S J_S \Omega} \left(e^{(2K_S J_S \Omega / \alpha_0 h)(t-t_0)} - \frac{2K_S J_S \Omega}{h} \right). \quad (5)$$

Figure 4 is the comparison of the experimental data of the oxide volume to this surface diffusion model. Prior to shape transition, the island volume increases parabolically with oxidation time as shown in region I. After shape transition, the island volume increases exponentially with the oxidation time as shown in region III. Region II corresponds to the transition zone of the island from compact to elongated structure, and the island changes its volume evolution behavior from parabolic to exponential dependency on time during this transition zone. The excellent agreement of volume evolution of the island with the kinetic model validates that the growth of the Cu_2O islands is initially dominated by the surface diffusion of oxygen.

In conclusion, highly elongated Cu_2O islands are formed on $\text{Cu}(100)$ surface by oxidizing $\text{Cu}(100)$ films at 600°C . Our experimental data are in excellent agreement with the theoretical model proposed by Tersoff and Tromp. The kinetic data on the volume evolution of the islands agree well with the model of surface diffusion of oxygen. Island formation during oxidation has been observed in several other metal systems, such as Ni, Fe, Al, Ti, Co, Pd,

Ir, and Sn, as well as in Cu. By carefully choosing the oxidation parameters, such as oxidation temperature, oxygen pressure, substrate orientation, etc., the self-assembly of quasi-one-dimensional oxide nanostructure arrays could be realized in these metal systems.

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