

In situ UHV-TEM investigation of the kinetics of initial stages of oxidation on the roughened Cu(1 1 0) surface

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Abstract

The initial stages of oxidation on roughened Cu(1 1 0) surface were explored by an in situ ultra-high vacuum transmission electron microscope (UHV-TEM). The dynamic observation of the nucleation and growth of Cu oxide islands shows a highly enhanced nucleation rate on the roughened Cu(1 1 0) surface. The kinetic data obtained from the initial stages of the oxidation indicate that oxygen surface diffusion plays a dominant role in the nucleation of the oxide islands; however, the growth of the three-dimensional oxide islands is caused by both oxygen surface diffusion and direct impingement.

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1. Introduction

A systematic investigation of crystal surfaces plays an important role in the understanding of many physical and chemical processes ranging from surface reconstructions to adhesion, wetting, catalysis, crystal growth, etc. The simplest surface one can conceive is an atomically smooth, low-index facet that separates a crystalline surface from the vapor. But the surface of a solid can go through different stages of disorder from the per-

fectly flat, zero temperature configuration up to the melting temperature of the bulk material. The low-index Cu(1 1 0) surface shows an anomalous thermal behavior and has received considerable interest both experimentally and theoretically [1–4]. Various surface probe techniques, such as low-energy ion scattering, inverse photoemission, thermal He scattering, X-ray scattering, high-resolution electron energy loss spectroscopy, have provided indirect evidence about the increase of disorder on Cu(1 1 0) between 227 and 727 °C [5–7]. The advent of UHV and modern surface analysis STM, low energy electron microscopy (LEEM) or surface X-ray diffraction have allowed observations of roughening phenomena down to atomic scales under well-controlled conditions [1–3,8,9]. In this work we present a direct, real time

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observation of the surface topology change of Cu(110) films at different temperatures and its effect on the oxidation kinetics by an in situ ultra-high (UHV) transmission electron microscope (TEM). Our in situ observation indicates that surface topology of Cu(110) thin films becomes rough at ~ 700 °C and this enhanced surface roughness can enhance the nucleation rate of the oxide islands and fasten the thickening rate of the oxide islands.

Oxygen reaction with Cu surfaces is considered to be a model system for the oxidation of metal surfaces and has consequently been studied extensively [10–16]. We have previously reported our investigations of the kinetics of the initial stages of Cu(100) and Cu(110) oxidation using in situ UHV-TEM [17–23]. We have demonstrated that oxygen surface diffusion is the dominant mechanism for the oxide formation during the initial oxidation in dry oxygen atmosphere where heteroepitaxial concepts describe surprisingly well the nucleation, and growth to coalescence of Cu_2O island on Cu(100) and Cu(110). Surface oxidation includes many complex processes, such as oxygen surface adsorption, oxygen induced surface reconstruction, oxygen surface diffusions, etc. Thus, surface roughening, a dramatic surface structural change, may affect the oxidation kinetics greatly. Therefore, this paper focuses on the oxidation of the roughened Cu(110) surface.

2. Experiment

Single crystal 99.999% pure 700 \AA Cu(110) films (by referring to the purity of the originally evaporated material) were grown on irradiated (110)NaCl in an UHV e-beam evaporator system, where the base pressure was 10^{-10} Torr. The copper film was removed from the substrate by floatation in deionized water, washed and mounted on a specially prepared Si mount. The Si mount and the specially designed sample holder allows for resistive heating at temperatures between room temperature and 1000 °C. The microscope used in this work was a modified JEOL 200CX. 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 cryoshroud inside the microscope column can reduce the base pressure to approximately 10^{-9} Torr when filled with liquid helium. The microscope was operated at 100 KeV in order to minimize irradiated effects. A leak valve attached to the column of the microscope permits the introduction of gases directly into the microscope. 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 5×10^{-5} and 760 Torr.

After removal from the Cu film growth chamber, the Cu film formed a native oxide on the surface due to exposure to air. 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 [24].

3. Results

3.1. Surface topology of Cu(110) at different temperatures

The surface topology of the Cu(110) films was observed to become rough at ~ 700 °C as shown in Fig. 1. Fig. 1(a) shows the surface morphology of Cu(110) after methanol cleaning at 400 °C, where the Cu film has a relatively flat surface. Fig. 1(b) shows the surface morphology of the rough Cu(110) film, where the surface resembled a hill-and-valley structure aligned along [001] direction over distances larger than 1000 nm. The spacing

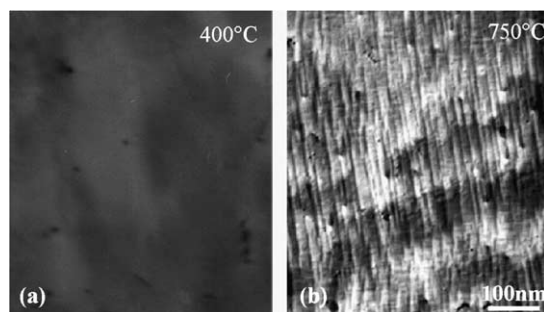


Fig. 1. Bright field images of Cu(110) surface: (a) flat surface; (b) rough surface at 750 °C.

between valleys or hills was typically 10 nm in the [1 1 0] direction.

Mochrie observed thermal roughening transition of Cu(1 1 0) surface at ~ 610 °C by surface X-ray diffraction [1]. According to his theoretical estimate, the roughening transition temperature for Cu(1 0 0) and Cu(1 1 1) is above Cu melting temperature ($T_M = 1083$ °C). However, Zeppendfeld et al. [2], by high resolution He-scattering, reported that surface roughening transition of Cu(1 1 0) was not observed up to 623 °C. In our investigation, the thermal stability of the Cu(1 0 0), Cu(1 1 0), Cu(1 1 1) thin films was followed from room temperature to 1000 °C by the in situ UHV-TEM, and only the surface topology of the Cu(1 1 0) thin films was observed to become rough at ~ 700 °C, which is consistent with Mochrie's theoretical prediction [1].

When the rough Cu(1 1 0) surface was allowed to cool to room temperature, it was found the rough surfaces do not become a completely flat surface as its initial state, it means that the surface topology roughening of the Cu(1 1 0) films in our investigation is not a completely reversible process. The ex situ AFM analysis of the roughened surface indicates that the step height is ~ 10 nm. In our experiment, the free standing Cu(1 1 0) films with thickness of ~ 70 nm were used, therefore, the free standing Cu films can exhibit roughening transition on both surfaces, which could make the

roughening behavior of thin films different from the semi-infinite bulk samples. Since this paper focuses on the effect of the surface roughness on the oxidation kinetics, for a deeper and quantitative understanding of the roughening transition of the Cu(1 1 0) thin films, extensive experimental work with carefully controlled condition and rigorous theoretical modeling are needed.

3.2. Nucleation on roughened (1 1 0) surface

The in situ observation of the island nucleation events on the roughened surface as a function of time provides significant insights into the effects of the enhanced surface roughness on the oxidation kinetics. Fig. 2 shows the in situ oxidation of the roughened Cu(1 1 0) surface, where the oxidation temperature is ~ 750 °C and the oxygen partial pressure is 5×10^{-4} Torr. Fig. 2(a) is a bright field (BF) TEM image of the copper film, where the surface topology of the film has become rough. No oxide islands are visible in this region. Fig. 2(b) and (c) show the corresponding BF images from the same region of the copper film as Fig. 2(a) at successive 2 min time increments after oxygen was leaked into the column of the microscope. The partial pressure of oxygen was 5×10^{-4} Torr and the temperature of the copper film was 750 °C. After the introduction of oxygen gas, Cu₂O nuclei appear after an incubation period of ~ 10 s. After

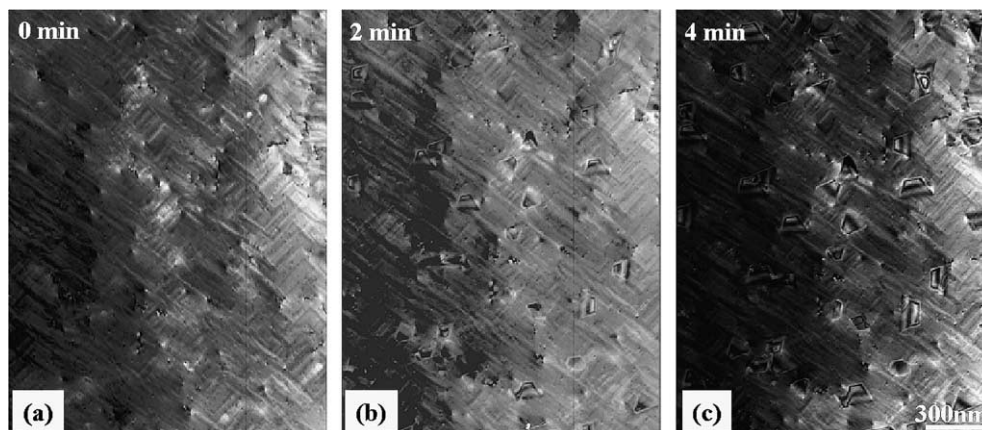


Fig. 2. Bright field images of the in situ oxidation on the roughened Cu(1 1 0) surface at the temperature of 750 °C and oxygen pressure of 5×10^{-4} Torr after (a) 0 min, (b) 2 min, and (c) 4 min.

4 min of oxidation, no new oxide islands formed and the island density has reached saturation.

If oxygen surface diffusion is the dominant mechanism for the nucleation of copper oxide islands, then the probability of an oxide nucleation event is proportional to the “zones of oxygen capture”, and the oxide nuclei density as a function of oxidation time has been determined to be [18]

$$N = \frac{1}{L_d^2} (1 - e^{-kL_d^2 t}) \quad (1)$$

where L_d^2 is the area of the zone of oxygen capture, $1/L_d^2$ is the saturation island density, L_d is much larger than the size of the initial nuclei, k is the initial nucleation rate, which depends on the probability for Cu and O to form Cu_2O , and t is the oxidation time. Fig. 3 shows the experimental data and theoretical fit to Eq. (1), the “zone of oxygen capture” model. A good match is noted where the fit parameters, the initial nucleation rate, k , is $5.29 \mu\text{m}^{-2} \text{min}^{-1}$, and the saturation island density, $1/L_d^2$, is $4.34 \mu\text{m}^{-2}$. In comparison, the oxidation on Cu(110) at the lower temperature of 350°C , but same oxygen pressure of 5×10^{-4} Torr revealed a larger saturation density of $9.01 \mu\text{m}^{-2}$, but a slower initial nucleation rate, k , $1.74 \mu\text{m}^{-2} \text{min}^{-1}$.

The early work regarding the oxidation of Cu(100) and flat Cu(110) surface indicates that

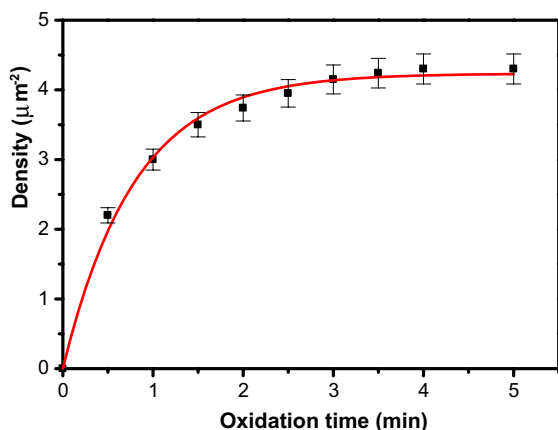


Fig. 3. Cu_2O island density as a function of oxidation time at constant oxygen partial pressure of 5×10^{-4} and temperature of 750°C .

there is a saturation island density and the saturation island density on a same surface structure at different oxidation temperatures follows an Arrhenius dependence on temperature for the oxide nucleation caused by oxygen surface diffusion [18,21]. We investigated the oxidation of the rough Cu(110) at different temperatures, and found that there is a saturation island density of the oxide islands at the different temperatures. But our experimental observation indicates that the roughness structure (hill-and-valley) of the surface topology of the Cu(110) films is different at the different temperatures. Therefore, the saturation island density has different temperature dependence at the different temperature due to the different surface structure.

3.3. Growth of oxide islands on roughened (110) surface

Orr [25], followed by Holloway and Hudson [26], has developed an oxidation model based on the assumption that oxygen surface diffusion plays a major role in the initial growth of the metal oxide. They assumed that the oxide islands grew on the metal surface, i.e. two-dimensional (2D) and obtained a parabolic growth rate law if oxygen surface diffusion and impingement on the island's perimeter is the dominant transport mechanism. We have extended Orr's model to incorporate the 3D growth and obtained a linear growth rate of the cross-sectional area of oxide islands for the oxygen surface diffusion controlled growth [19]. Therefore, based on the surface diffusion of oxygen, for 2D lateral growth of oxide islands with constant thickness, the cross-sectional area of oxide islands increases parabolically with respect to oxidation time. For 3D growth of oxide islands, the cross-sectional area of the oxide islands increases linearly with respect to oxidation time. It has been shown that the growth of oxide islands on Cu(110) surface have a 3D growth mode in the temperature range of $350\text{--}650^\circ\text{C}$ [21].

The evolution of cross-sectional area of the islands formed on the roughed surface was recorded in situ, and a sequence of images focusing on the growth of individual islands is shown in Fig. 4, where the Cu(111) reflection was used for the

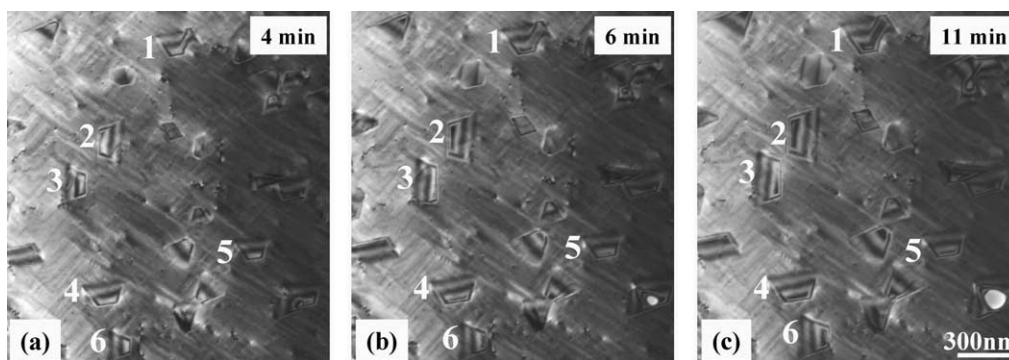


Fig. 4. In situ observation of the growth of oxide islands on the roughened surface at 750 °C and 5×10^{-4} Torr of oxygen pressure.

dark field image. About 30 s after the introduction of oxygen gas, Cu_2O islands were observed to nucleate rapidly followed by growth of these islands. After the initial nucleation of the oxide islands, ~ 4 min, the saturation density of the island nuclei was reached and no new nucleation event was observed, which is much faster than the oxidation at 350 °C, where the saturation is reached after 22 min oxidation. The selected area electron diffraction (SAED) pattern of the Cu_2O island and underlying $\text{Cu}(1\ 1\ 0)$ substrate revealed that the oxide islands are epitaxial with the underlying Cu film, where $(1\ \bar{1}\ 0)\text{Cu} \parallel (1\ \bar{1}\ 0)\text{Cu}_2\text{O}$ and $[0\ 0\ 1]\text{Cu} \parallel [0\ 0\ 1]\text{Cu}_2\text{O}$. The same epitaxial relationship was noted for the flat $\text{Cu}(1\ 1\ 0)$ surface at the lower oxidation temperatures [22]. The oxide islands formed on the roughened surface have a trapezoid cross-sectional shape which is similar as that formed at the lower temperatures [21,22]. It is noted that the TEM thickness fringes occurred in the oxide islands, and the periodicity of the thickness fringes increased with the continuous growth of the oxide islands. The growth of the oxide islands is accompanied by the conversion of copper atoms to Cu_2O islands along the $\text{Cu}/\text{Cu}_2\text{O}$ edge. The penetration of the islands into the Cu substrate creates inclined $\text{Cu}/\text{Cu}_2\text{O}$ interface that causes the TEM thickness fringe contrast.

According to the Howie–Whelan equations, the intensity from diffraction beam g is directly proportional to $\sin^2(\pi t/\xi_g)$ in Bragg condition, where t is sample thickness, and ξ_g is the extinction distance. Therefore, the sample thickness can be estimated by the periodicity of the thickness fringe

and ξ_g [27]. By applying this relationship, we estimated the island thickness at different oxidation times. In Fig. 4(a), two dark fringes plus one bright fringe or two bright plus one dark fringes occurred in the islands. Therefore, the periodicity of the thickness fringes is 1.5, i.e., $t/\xi_g = 1.5$, where $\xi_{\text{Cu}(111)}$ is used for imaging. Since $\xi_{\text{Cu}(111)}$ is 24 nm for the 100 kV electron beam, the thickness variation of the Cu film along the metal/oxide interface is close to 36 nm in Fig. 4(a). In Fig. 4(c), two or more dark/bright fringes occurred in the islands, therefore, the periodicity of the thickness fringes is 2 or larger, i.e., $t/\xi_g \approx 2$. The thickness variation of the Cu film along the interface should be close to 48 nm. During the oxidation time period, the lateral size of the islands increased from ~ 150 nm, (Fig. 3(a)), to ~ 200 nm, (Fig. 4(c)), and its thickness increased from 36 to 48 nm. Therefore, the oxide islands grow in three-dimension, not two-dimensional lateral growth, although the lateral growth rate is much faster than the thickening rate. Since the 3D growth of the oxide occurs, one way to know whether surface diffusion dominates oxide growth is to see if the island growth has a linear dependence on time t . If the time dependence is not linear, then another mechanism must contribute or dominate the initial oxide growth. The best power fit to the experimental data on the island growth is 1.4. This power law is higher than t —the predicted power law dependence for 3D growth by oxygen surface diffusion. To account for the deviation from a linear power law, other mechanisms besides oxygen surface diffusion were considered.

We expect that, the oxidation on the roughened Cu(110) surface at the high temperatures, the kinetics of island growth are as follows. As oxygen arrives on the surface and diffuse to the perimeter of oxide islands through surface diffusion, the oxygen atoms may be incorporated into Cu₂O islands by reacting with Cu atoms adjacent to the perimeter of the islands. Another likely possibility is the direct impingement of oxygen that is incorporated onto the oxide islands by bulk diffusion. The combination of surface diffusion of oxygen to the perimeter of the oxide island plus direct impingement of oxygen into the oxide island creates a growth rate of the island

$$\frac{dN}{dt} = c_1 f_1 \times L + c_2 f_2 \times S \quad (2)$$

where N is the number of oxygen atoms in Cu₂O island at time t , c_1 is the sticking coefficient for oxygen surface diffusion to the island perimeter, f_1 is the surface diffusion flux of oxygen to the island perimeter and has the dimension of atom/nm/s; c_2 is the sticking coefficient for oxygen direct impingement, f_2 is the flux of oxygen for direct impingement to the island surface area exposed to oxygen and has the dimension of atom/nm²s; L is the island perimeter on the Cu surface and S is the island surface area exposed to oxygen. Since the lateral growth rate of the oxide island is larger than its thickening rate, we assume the islands have an oblate shape (the cross-sectional area of the island on Cu surface has a circular shape) with radius r on the Cu surface and height/diameter aspect ratio of β that is determined by the lateral growth rate and thickening rate of the island. The perimeter, $L(t)$, of the island at time t is $2\pi r(t)$, the surface area, $S(t)$, of the island at time t is

$$\begin{aligned} \pi \times \left[2 + \frac{\beta^2}{\sqrt{1-\beta^2}} \times \ln \left(\frac{1 + \sqrt{1-\beta^2}}{1 - \sqrt{1-\beta^2}} \right) \right] \times [r(t)]^2 \\ = \pi \times \alpha \times [r(t)]^2 \end{aligned}$$

and the number of Cu atoms, $N(t)$, in the oxide island at time t is

$$\frac{(4/3)\pi\beta[r(t)]^3}{\Omega}$$

where Ω is the atomic volume of oxygen in Cu₂O. By solving the above differential equation (2), the cross-sectional area, A , of the oxide island increases with respect to oxidation time can be expressed as follows [19]:

$$\begin{aligned} \frac{1}{K_2\sqrt{\pi}} \times A^{1/2} - \frac{K_1}{K_2^2} \ln \left[\frac{K_2}{\sqrt{\pi}} \times A^{1/2} + K_1 \right] \\ = t - t_0 \end{aligned} \quad (3)$$

where

$$K_1 = \frac{c_1 f_1 \Omega}{2\beta}, \quad K_2 = \frac{c_2 f_2 \alpha \Omega}{4\beta}$$

In this equation, K_1 is the parameter related to the contribution of oxygen surface diffusion to the oxide island growth, K_2 is the parameter related to the contribution of oxygen direct impingement to the oxide growth. In this analysis, we do not consider desorption of oxygen from the surface. The characteristic length, which governs the fate of oxygen surface diffusion, is proportional to $\exp(\frac{E_a - E_d}{2kT})$, where E_a is the activation energy for oxygen adsorption, and E_d is activation energy for oxygen surface diffusion. The desorption of oxygen from surface may affect f_1 , the flux of oxygen surface diffusion, therefore, the fitting coefficient K_2 , but will not change the time dependence of the island growth. By using Eq. (3), we obtained a good fit to the combined surface diffusion and direct impingement model, as shown in Fig. 5.

Therefore, the growth rate of the oxide islands is broken into two components, one is related to the oxygen surface diffusion, the other one is related to oxygen direct impingement. The fit parameters related to these two components are given in Table 1. From the definition of K_1 and K_2 , we can estimate the sticking coefficients, c_1 and c_2 , if the surface diffusion flux of oxygen (f_1) and the flux of oxygen for direct impingement (f_2) are known. Based on the present data, it is difficult to estimate c_1 due to the unknown f_1 , however, we can calculate c_2 by using the kinetic gas theory. The flux of oxygen for direct impingement is $f_2 = \frac{P}{\sqrt{2\pi MRT}}$, where R is gas constant, P is the oxygen pressure, M is the molecular weight of oxygen and T is the temperature. The height/diameter aspect ratio (β) of the islands can be

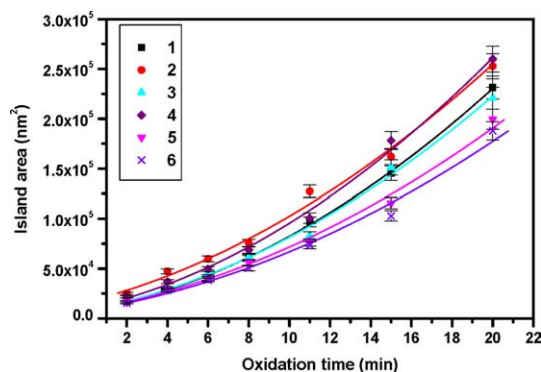


Fig. 5. Comparison of the experimental data and the theoretical function for the oxygen surface diffusion and direct impingement/interface diffusion for the 3-D growth of the six Cu_2O islands as marked in Fig. 4. (See the online paper for a colour version of the figure.)

estimated to be ~ 0.24 by measuring their lateral size and their thickness from the TEM images (Fig. 4). Therefore, the sticking coefficient for the oxygen direct impingement, c_2 , is estimated to be ~ 0.09 , which is in a reasonable range.

Our early work regarding the oxidation of $\text{Cu}(1\ 1\ 0)$ surface at $450\ ^\circ\text{C}$ has shown that oxygen surface diffusion is the main mechanism to the growth of oxide islands with the lateral size of up to $\sim 400\ \text{nm}$. It is reasonable to expect that oxygen surface diffusion initially dominates the oxide growth, and later oxygen direct impingement becomes significant when the oxide islands grow larger in size, especially for the Cu film with large coverage of the oxide islands. By considering an equal rate of oxygen surface diffusion and direct impingement from Eq. (3), we can make an estimation of the critical cross-sectional area, A_c , of an oxide island, where we need to consider oxygen direct impingement, as

$$A_c = \pi \times \left(\frac{K_1}{K_2} \right)^2 \quad (4)$$

where K_1 and K_2 have the same meaning as in Eq. (3). When the cross-sectional area of the oxide island is smaller than A_c , the island growth caused by oxygen direct impingement is insignificant, and we need only to consider the growth caused by oxygen surface diffusion. When the cross-sectional area of the island is larger than A_c , then the island growth caused by oxygen direct impingement also needs to consider. From the fit parameters in Table 1, we can know that the critical cross-sectional area of the oxide island is $\sim 300\ \text{nm}^2$ for the oxidation at $750\ ^\circ\text{C}$. Similarly, we have $\sim 1.2 \times 10^5\ \text{nm}^2$ of the critical cross-sectional area of the oxide island for the oxidation at $450\ ^\circ\text{C}$ [21]. It is noted from here that oxygen direct impingement becomes significant at a much smaller island size at $750\ ^\circ\text{C}$ compared to the oxidation at $450\ ^\circ\text{C}$. Bulk oxidation studies have shown that the rate limiting step for Cu oxidation at sufficiently high temperatures is lattice diffusion of point defects, (cations), through oxide scale, i.e., oxide growth at gas–oxide interface [14,15,28]. Therefore, this highly increased rate of oxygen direct impingement at $750\ ^\circ\text{C}$ is related to the highly enhanced diffusion of cations, which incorporate oxygen into the oxide islands at oxygen–oxide interface.

An earlier work regarding Cu halogenation showed that Cu halide nucleation was governed by diffusion of small Cu halide clusters rather than halogen diffusion [29]. Therefore, there is a particular question regarding the possibility of Cu–O as the surface diffusing species, rather than oxygen, i.e., oxygen reacting elsewhere to form a Cu–O species that then diffuses and collides with other Cu–O species to nucleate a Cu_2O island or add to an existing island to give the island growth, as observed for Cu halogenation. There are three possible diffusing species, Cu atoms, oxygen, and Cu–O, for the formation of oxide islands. If oxy-

Table 1

Comparison of fit parameters of the island growth on roughened $\text{Cu}(1\ 1\ 0)$ surface

	Island 1	Island 2	Island 3	Island 4	Island 5	Island 6
$K_1 \left(\frac{\text{atom nm}^2}{\text{s}} \right)$	79.72	106.88	81.23	93.10	74.93	70.74
$K_2 \left(\frac{\text{atom nm}}{\text{s}} \right)$	10.51	9.94	10.13	10.99	9.14	8.79

gen reacts with Cu substrate to form Cu–O species and then the Cu₂O island nucleation and growth are caused by surface diffusion of Cu–O species, then there will be a dramatic evolution of the Cu surface topology, such as the spacing between the hill-valley structure on the roughened surface, with the continuous formation and growth of the oxide islands. Our in situ TEM observation indicates that this case is not true, the surface topology of the Cu film almost does not change with the continuous oxidation, as shown in Figs. 2 and 3. Therefore, the possibility of Cu–O or Cu atoms as diffusing species in the initial stages of Cu oxidation is very small.

4. Discussion

The present result indicates that the nucleation of oxide islands on a roughened surface is still a surface controlled process, and the growth of oxide islands is caused by both oxygen surface diffusion and direct impingement. At present, we do not know the exact facets on the rough Cu(110) surface. But we notice that the oxide islands formed on the roughened Cu(110) surface show the similar cross-sectional shape (trapezoid) as that formed on the flat (110) surface [21]. The oxide islands formed on Cu(100) [23] and Cu(111) [30] have dramatically different morphology from that on Cu(110). Therefore, we believe that the Cu(110) thin films with rough surface topology still have (110) feature, and it is reasonable to compare these results with the oxidation on flat Cu(110) surfaces, and discuss the effects of surface roughness on the nucleation and growth kinetics of oxide islands.

4.1. Effect of surface roughness on nucleation kinetics

Since the nucleation is a surface process, surface structure of the underlying metal will have a major effect on the nucleation behavior. For a same surface structure, the surface diffusion of oxygen follows an Arrhenius relationship with temperature, i.e., higher mobility of oxygen at higher temperature. The attachment of oxygen to

Table 2
Comparison of fit parameters of Cu(110) oxidation on flat (350 °C) [21] and rough (750 °C) surface

Parameters	350 °C	750 °C
Initial oxidation rate ($\mu\text{m}^{-2} \text{min}^{-1}$), k	1.74	5.29
Saturation island density (μm^{-2}), $1/L_d^2$	9.01	4.34
Radius of oxygen capture zone (μm), L_d	0.33	0.48

existing islands is more favorable than the nucleation of new nuclei at high temperature. Hence, the dependence of saturation island density on temperature for the same surface structure follows a similar Arrhenius relationship on oxidation temperature. Table 2 summarizes the values of the fit parameters for the oxidation on Cu(110) at 350 °C (flat surface) and 750 °C (roughened surface). Differences in the initial oxidation rate, capture zone of oxygen, and saturation island density were noted. It is reasonable to expect that the initial oxidation rate k , and capture zone of oxygen, L_d become larger with the temperature increasing as shown in Table 2. But the changes in the rate constants in Table 2 is not as large as expected. The early work regarding the oxidation of Cu(100) and flat Cu(110) surfaces showed k and L_d have an Arrhenius dependency on temperature [18,21]. If the oxidation temperature of the Cu(110) films is increased to 750 °C from 350 °C, while the Cu film can still remain the same flat surface structure. From the Arrhenius temperature dependence of the saturation island density, the saturation density at 750 °C can then be deduced to be $\sim 0.01 \mu\text{m}^{-2}$, which is much smaller than the experimental measurement, $4.3 \mu\text{m}^{-2}$ for the same oxygen pressure (5×10^{-4} Torr). Therefore, we expect that the rough surface topology is the main factor causing this obvious increase in the saturation island density by over two orders of the magnitude. It is usually believed that increased surface roughness can increase the activation barrier for surface diffusion. The mobility of oxygen surface diffusion may decrease on the rough surface, which gives rise to a smaller capture zone of oxygen, and a higher saturation

island density. Our TEM observation also indicates that the density of the oxide islands on the roughened surface is closely related to the oxygen pressure, i.e., higher oxygen pressure, higher island density. In the oxidation of Cu(100), no preferential nucleation sites at dislocations or surface steps were observed. In the oxidation of Cu(110), repeated oxidation, reduction, followed by oxidation experiments were also performed, but no nuclei appeared at the same positions. Also, no preferential sites at dislocations or surface defects as oxide nucleation were clearly observed on Cu(110). Therefore, we believe that there are no special reactive sites for the nucleation of oxide islands on the roughened surface and the variation of defect densities on the surfaces would not significantly affect the nucleation behavior of the oxide. Thus, the increased surface roughness decreases the mobility of oxygen, but may not create special reactive sites for oxide nucleation.

The comparison of the oxidation of Cu(100) and (110) at the same oxidation temperature (350 °C) and oxygen pressure (5×10^{-4} Torr) indicated that Cu(110) surface has a much faster nucleation rate than Cu(100), and this was explained by the enhanced roughness of Cu(110) due to its O-chemisorption corrugation [21]. The present observation of the oxidation on the roughened Cu(110) surface is consistent with the same

argument, i.e., increased surface roughness enhances the oxide nucleation rate.

5. Effect of surface roughness on growth kinetics of oxide islands

The oxidation of Cu(110) at the different temperatures, (350–750 °C), resulted in the oxide islands with the similar cross-sectional shape, but different thickness contrast in the islands [21,22]. We compare the lateral size of the islands with the thickness fringes formed at the different oxidation temperatures. In the oxidation of the flat Cu(110) surface, no thickness fringe contrast appears in the oxide islands with the lateral size up to 500 nm when the oxidation temperature is lower than 500 °C [21]. When the oxidation temperature is at ~ 650 °C, thickness fringe contrast appears in the oxide islands with the lateral size of ~ 200 nm [22]. The thickness fringes appear in the oxide islands formed on the rough surface from much smaller size (~ 50 nm) as compared with the flat surface, as shown in Figs. 2 and 3(a). Fig. 6 shows the dark field TEM images of the oxide islands formed at 650 and 750 °C, where Cu(111) reflection was used for imaging. The islands formed on the flat surface, (650 °C), and roughened surface, (750 °C), have similar trapezoid cross-sectional shape. However, the islands formed at the two tempera-

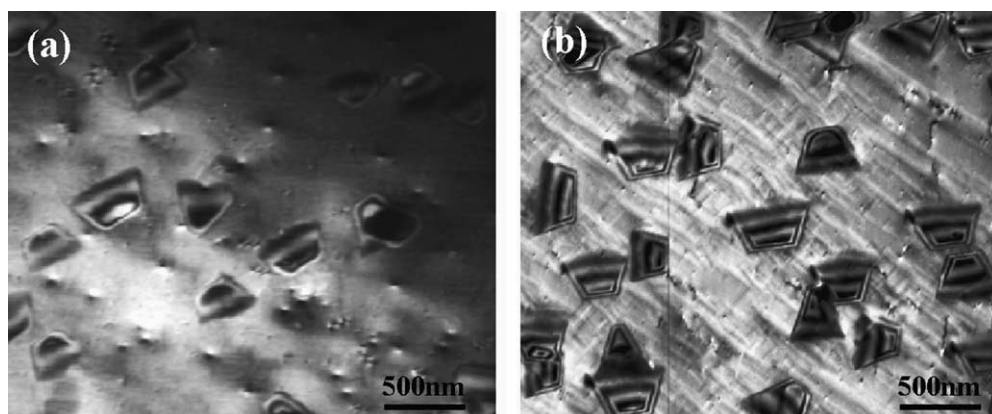


Fig. 6. The dark field images of oxide islands formed on (a) flat Cu(110) surface (650 °C); and (b) thermally roughened surface (750 °C) at the same oxygen pressure (5×10^{-4} Torr) and oxidation time (~ 10 min).

tures have different periodicity of the thickness fringes although they have similar lateral size. By applying Howie–Whelan relationship [27], we can make an estimation of the thickness of the islands in the substrate. In Fig. 6(a), one dark plus two bright fringes or one bright plus two dark fringes occur in the islands, therefore, the periodicity of the thickness fringes is ~ 1.5 and the thickness variation of the Cu film along the inclined Cu/Cu₂O interface is in the range of 24–36 nm. In Fig. 6(b), two or more dark/bright thickness fringes occur in the islands, i.e., the thickness variation of the Cu film along the inclined interface is approximately 48 nm or larger. Therefore, the oxide islands formed on the roughened surface have a deeper embedding than that on the flat surface for the similar lateral size. Fig. 7 is the schematics of the islands formed at the two different temperatures. The islands formed on the roughened surface (750 °C) have a larger embedding into the substrate, and a larger thickness variation of the Cu film along the inclined metal/oxide interface as compared to the oxidation at 650 °C.

The amount of the embedding of the oxide islands depends on the oxidation temperature, surface condition and oxidation time. We have determined the wedge slope of the islands formed on flat Cu(110) surface and found these thickness fringes are aligned with some particular Cu crystallographic directions [22]. The oxide islands formed on the roughened surfaces have the similar

trapezoid cross-sectional shape on Cu surface, same epitaxial growth, and same crystallographic relationship, but different amount of the embedding with the substrate as compared with the flat surface. The contact angles between the side facets of the island and Cu substrate can be measured by atomic force microscopy (AFM), we determined the island structural geometry by combining the epitaxial relationship between the oxide island and Cu substrate, as shown in Fig. 7(c), which has the same geometry as that on the flat surface [22]. This observation indicates that the increased roughness of the surface topology increases the amount of the island embedding, but does not change the island structure.

The formation of oxide islands with increased oxide thickness at the high temperatures is energetically favorable. The free energy change for the formation of oxide islands on surface is related to volume energy of Cu₂O (ΔG_{vol}), Cu₂O surface energy (γ_s), Cu surface energy (γ_{Cu}) and Cu/Cu₂O interfacial energy (γ_i), i.e., $\Delta G = \Sigma A_s \gamma_s + \Sigma A_i \gamma_i + \Delta G_{\text{vol}}(\text{Cu}_2\text{O}) - \Sigma A_{\text{Cu}} \gamma_{\text{Cu}}$. Cu is a FCC metal, with a lattice parameter of 3.61 Å, and Cu₂O is cubic with a lattice parameter of 4.22 Å. The thermal expansion coefficient of Cu₂O and Cu is 1.9×10^{-6} and $17 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$, respectively. With increasing temperature, the lattice mismatch ($\sim 15\%$) between Cu and Cu₂O is reduced due to their different thermal expansion coefficients. As a result, the lattice-mismatch induced interfacial energy is reduced. Thus, the islands tend to prefer the more compact structure, which is a thicker oxide with larger interface area, at high temperatures. Also, this thicker and more compact structure can decrease the island surface area, which reduces the surface energy of the islands. However, larger more 3D islands expose more of the Cu surface. Metals generally have higher surface tensions than oxides. It is generally believed that the first step for oxidation is the formation of a chemisorbed layer of oxygen on metal surface before the formation of oxide. This chemisorbed layer may decrease the surface energy of the Cu surfaces. Our experimental observation indicates that the interface energy seems to dominate the island geometry, but for a quantitative understanding the island geometry, more theoretical

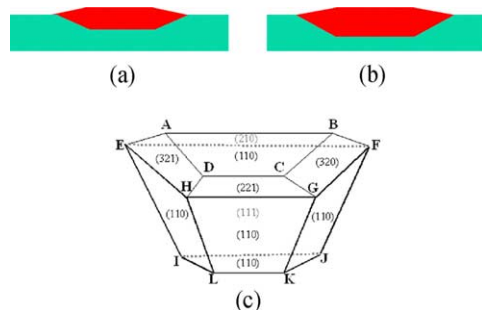


Fig. 7. Schematics of the oxide islands formed at (a) 650 °C; (b) 750 °C; (c) geometry of the island formed on rough Cu(110) surface.

modeling and calculation to quantitatively determine the surface and interface energy are needed.

6. Conclusions

The surface topology of Cu(1 1 0) films becomes rough at ~ 750 °C. The nucleation of the oxide islands on the roughened surface is dominated by oxygen surface diffusion. Compared to the nucleation of oxide islands on the flat Cu(1 1 0) surface, this enhanced surface roughness could hinder the mobility of oxygen on the surface, which gives rise to higher density of the oxide islands and slows lateral growth rate. The analysis of the kinetic data regarding the growth of the oxide islands indicates that the growth of the oxide islands is caused by both oxygen surface diffusion and direct impingement. Compared to the growth of the oxide islands on the flat surface, the islands on the roughened surface have a more compact structure where the oxide islands have a deeper penetration into the substrate.

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