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Formation of Oxide Nanostructures Investigated by *In Situ* UHV-TEM

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In the rapidly developing field of nanotechnology, the controlled formation of oxide nanostructures is 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. However, so far few studies exist concerning the initial oxidation stage-from the nucleation to the initial growth of metal oxides. Hence, we have used *in situ* ultra high vacuum transmission electron microscopy (UHV-TEM), to study the initial stages of oxidation, in order to gain insights into the oxidation kinetics with controlled surface conditions.

We have studied the oxidation of Cu(100) at temperatures below 350 ^{o}C in order to extend our previous studies, which centered on oxidation mechanisms that occurred at temperatures at and above 350^{o}C [1]. For the temperature range we examined (200 to 350 ^{o}C), epitaxial Cu_2O islands form with a triangular in cross-section shape that had rounded edges when Cu(100) was exposed to dry oxygen at $5x10^{-4}$ torr *in situ*. Figures 1 shows *in situ* bright field TEM images of the growth of Cu_2O islands as a function of time at 250^{o}C. As shown in Figures 1, one edge of the Cu_2O triangular islands is along <110> direction. The other two edges are along the directions with high indices which can vary from island to island. The light contrast feature around each Cu_2O island is the result of lattice mismatch induced strain between Cu_2O islands and Cu substrate. The atomic force microscopy (AFM) image of a typical Cu_2O island formed at 200^{o}C is shown in Figure 2. The surface topology reveals that the oxide island has a rounded top and the island height is approximately equal to 2.6nm. According to the heteroepitaxial model of surface diffusion of oxygen, which was originally developed by Yang et al.[1], the saturation island density N_s could follow an Arrhenius relationship with temperature and the 3-D island growth adopts a linear growth rate law, Figure 3 shows the saturation density of nuclei versus inverse oxidation temperature, where the activation energy, E_a, was determined to be 0.5±0.13 eV. Figure 4 shows the average oxidation island cross-section area and the island growth rates data at different temperatures and fit to the 3-D surface diffusion model. The experimental data indicates our initial analysis on the nucleation and growth of these three-dimensional Cu_2O islands agree well with the heteroepitaxial model of surface diffusion of oxygen[1].

Our previous result of Cu50%Au *in-situ* oxidation has showed that double pyramid Cu_2O islands form with cube-on-cube crystallographic orientation with respect to the film at temperature range from 550^{o}C to 750^{o}C. Comparing with Cu(100) nano-oxidation, Cu50％Au alloy has much slower kinetics toward oxidation and longer incubation time at the same temperature[3]. The initial stage of oxidation of CuAu(100) at different component (CuAu5%, CuAu15% and CuAu38%) at the higher temperature range (800 ^{o}C-1000 ^{o}C) will be studied in order to extend our earlier studies. Other alloy such as CuTi and CuTa which are viewed as a novel scheme to prevent the formation of Cu oxide in the integrated circuit will also be studied. In these alloys the additive element Ti and Ta have limited solid solubility in Cu and may diffuse to the free surface. This outward diffusion of Ti and Ta will strongly influence the oxidation of Cu, which will be investigated by our *in situ* UHV-TEM[4].

References

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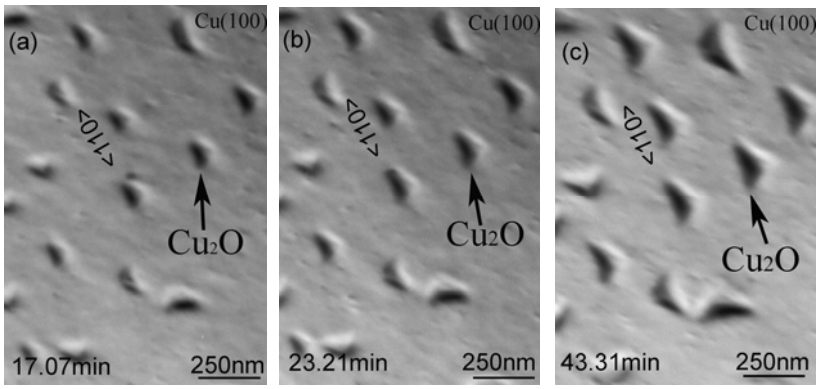

Figure 1 *In situ* bright field TEM images of Cu_2O island growth on Cu(100) taken as a function of oxidation time, (a) 17.07 min,(b) 23.21 min (c) 43.31 min at constant oxygen partial pressure of 5×10^{-4} torr and temperature of 250°C.

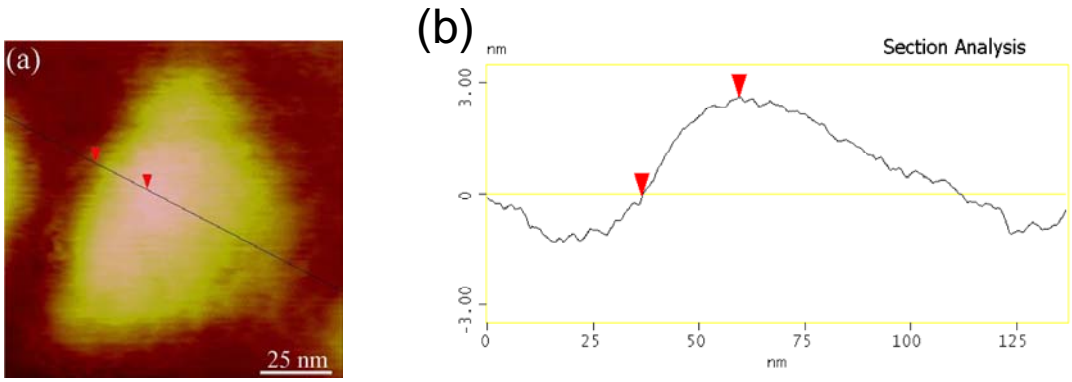

Figure 2 (a) AFM image of typical Cu_2O islands formed on Cu(100) at 200°C, and constant oxygen pressure of 5×10^{-4} torr (b) cross-sectional profile drawn along the marked lines indicated in (a).

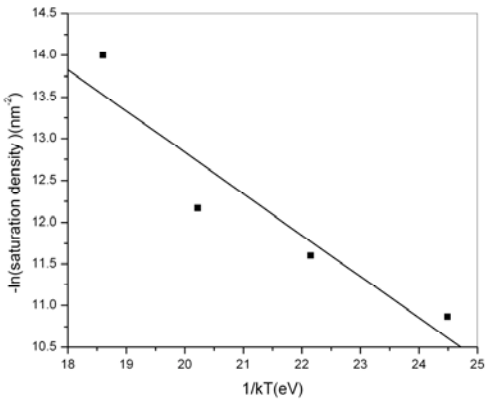

Figure 3 Cu_2O saturation island density versus inverse temperature. The absolute value of slope is the E_a for the surface-limited process. E_a= 0.5eV±0.13eV

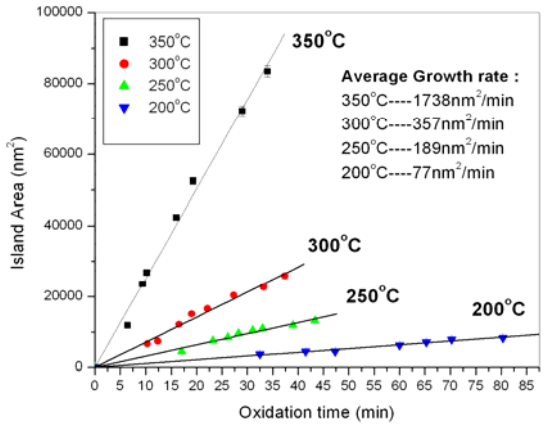

Figure 4 Comparison of the experimental data at the temperature ■350°C , ●300 °C , ▲250 °C ,▼200 °C and the theoretical function for the surface diffusion for the 3-D growth of Cu_2O islands.

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