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INITIAL OXIDATION KINETICS OF COPPER FILMS INVESTIGATED BY IN-SITU UHV-TEM

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In the study of metal oxidation, there is a wide gap between information provided by surface science methods and that provided by bulk oxidation studies. The former have mostly examined the adsorption of up to ~1 monolayer (ML) of oxygen on the metal surface, while as both low and high temperature bulk oxidation studies have mainly focused on the growth of an oxide layer at the later stages of oxidation. Hence, we are visualizing the initial oxidation stages of a model metal system by *in situ* ultra-high vacuum (UHV) transmission electron microscopy (TEM), where the surfaces are atomically clean, in order to gain new understanding of these ambiguous stages of oxidation. We have previously studied that the growth of Cu_2O islands during initial oxidation of Cu(100) film.[1,2] We are presently investigating the initial stages of Cu(110), and Cu(111) oxidation, from 10^{-4} Torr O_2 to atmospheric pressures and temperature range from room temperature to 700°C.

Single crystal 99.999% pure 1000Å Cu films were grown on (110) and (111)NaCl in an UHV e-beam evaporator system, where the base pressure was 10^{-10} torr. The Cu film was mounted on a specially prepared Si mount which along with the modified specimen holder, allows for the resistive heating of the specimen. The microscope was a modified JEOL200 CX with a spatial resolution of 2.5Å and permits introduction of gasses via a leak valve.[5] To remove the native oxide formed due to oxidation in air, the specimen was annealed at 350 ^{0}C and to remove the Cu_2O formed due to *in situ* oxidation, annealing was followed by exposure to methanol.[6]

Figures a-c are the bright field images when the Cu films were oxidized at 350°C but different with orientations. The oxidation rate of Cu(111) is ~20 times faster than the other two orientations. At a higher temperature of 500°C as shown in Figures (d), (e), (f), the morphologies of Cu2O islands formed on different orientations of Cu films are dramatically different from each other. The Cu2O islands on Cu(100) are square-based pyramids, with no sharp contrast within islands. The islands on Cu(110) are trapezoid in cross-section. Oxidation of Cu(111) revealed a continuous growth of oxide with cellular morphology, while the overall oxide layer shows 3-fold symmetry when it grows to very larger (>1μm), and side facets are formed.

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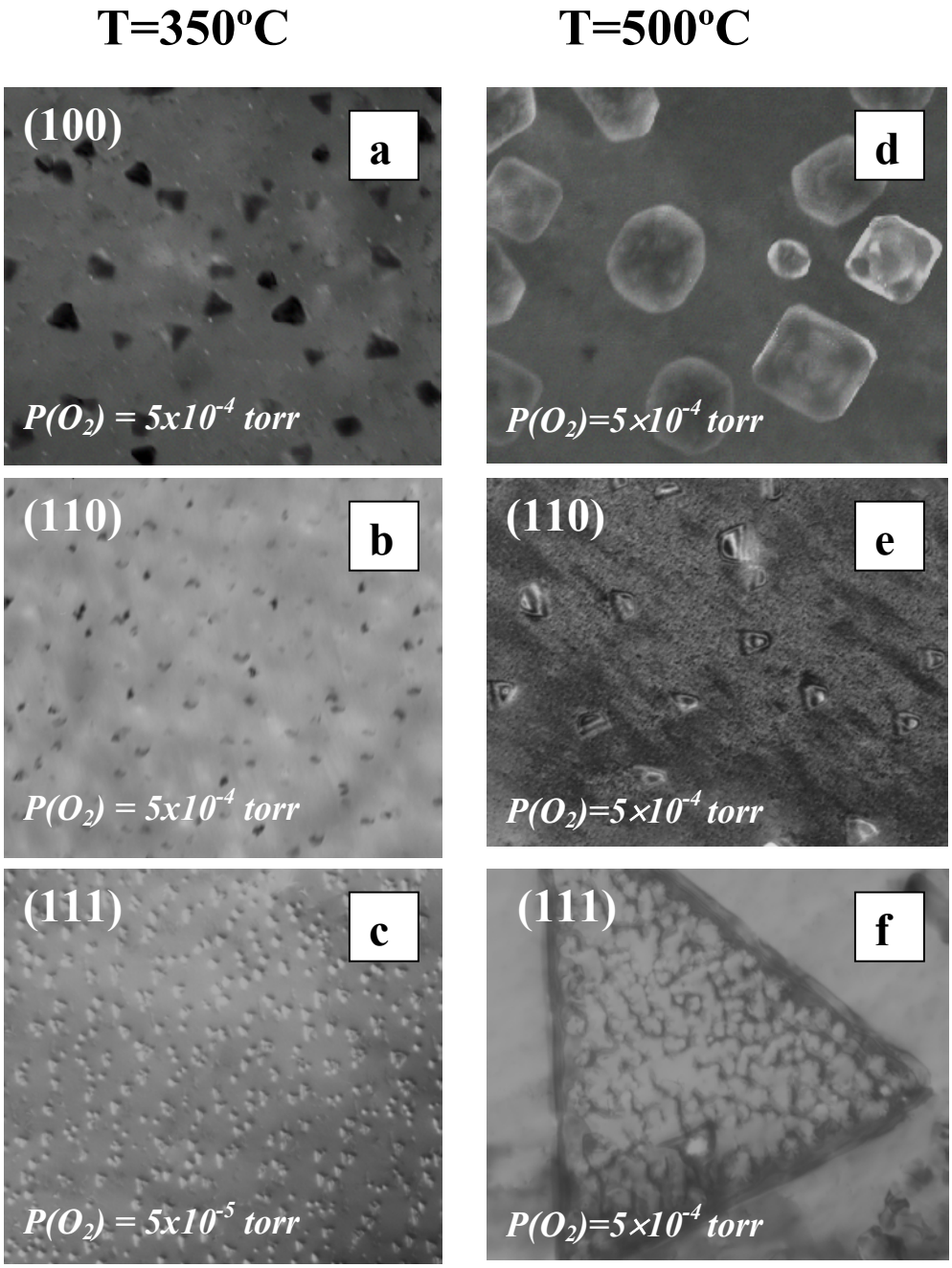

Figure: Oxidation of Cu films at 350ºC for (a) Cu(100) at $P(O_2)=5\times10^{-4}$Torr for 20 min; (b) Cu(110) at $P(O_2)=5\times10^{-4}$Torr for 10 min;(c) Cu(111) at $P(O_2)=5\times10^{-5}$ Torr for 5 min; and 500ºC for (d) Cu(100) at $P(O_2)=5\times10^{-4}$Torr for 20 min; (e) Cu(110) at $P(O_2)=5\times10^{-4}$ Torr for 10 min; and (f) Cu(111) at $P(O_2)=5\times10^{-5}$Torr for 10 min.

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