In situ Early Stage Oxidation Observations of Copper (100), (110), and (111) Facets Using Environmental High-Resolution Transmission Electron Microscopy

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The engineering of metals and their alloys has played an important role in the advancement of civilizations for millennia. However, the prevention and mitigation of corrosion in these materials continue to be difficult and expensive endeavors, costing ~$276 billion/year.[1] Understanding the mechanisms and processes of corrosion is necessary for the rational improvement of mitigation strategies. The elucidating the mechanism(s) of metal oxidation is of particular importance, given the ubiquitous employment of metals in infrastructure. *Ex situ* observations do not allow for the continuous collection of data during a chemical process/reaction under relevant conditions. Additionally, the experimental logistics accompanying *ex situ* experiments – e.g., exposure to ambient environment during specimen transfer or temporal gaps – can introduce ambiguity into the observations. High-resolution environmental transmission electron microscopy (ETEM) enables the processes to be observed on micron-to-nano length scales during exposure to gaseous, liquid, and/or heating environments.

The oxidation of copper materials has been studied for over 80 year, and is considered a model oxidation system.[2,3] Previous studies have focused on bulk scale or nanoscale oxide formation. Only recently, have investigations with atomic detail been reported at the earliest stages of oxidation. In this work, we continue to investigate the early stages of oxidation in copper thin films[2,3] at (100), (110), and (111) facets which were studied in real time, at low temperatures (250 °C), and low oxygen pressure ($1x10^{-5}$ Torr) to compare and contrast the oxidative process among these facets. Detailed high-resolution transmission electron micrographs (HRTEM) and videos of the growing Cu/Cu_2O interface not only provide mechanistic insight with respect to structural changes but also reveal that the oxidation rate differs between the facets due to differences in the coordination environment of the surface atoms of these crystal planes. This work is the first report of HRTEM copper oxidation for these three facets under similar experimental conditions, allowing for direct comparison of the oxidation process. The ability to directly relate these results is necessary for developing a holistic understanding of how oxidation proceeds (at the atomic scale), improving the precision of computational models of oxidation onset [4,5], and ultimately directing future corrosion mitigation strategies. This work is also being paired with computational modeling efforts to help bridge the time-scale gap between computational (picoseconds) and experimental (millisecond+) efforts.

Copper thin films were prepared using an ultra-high vacuum electron-beam evaporator (Pascal Technologies, Inc.) with thicknesses of ~70 nm on a NaCl crystal with a specific crystal orientation, Figure 1A,B. Subsequent processing and observation was performed in a Hitachi H9500 ETEM using a double tilt heating holder. The films were annealed, Figure 1C,D, to produce faceted holes of pristine Cu surface, followed by the initiation of controlled oxidations, Figure 2.

References:
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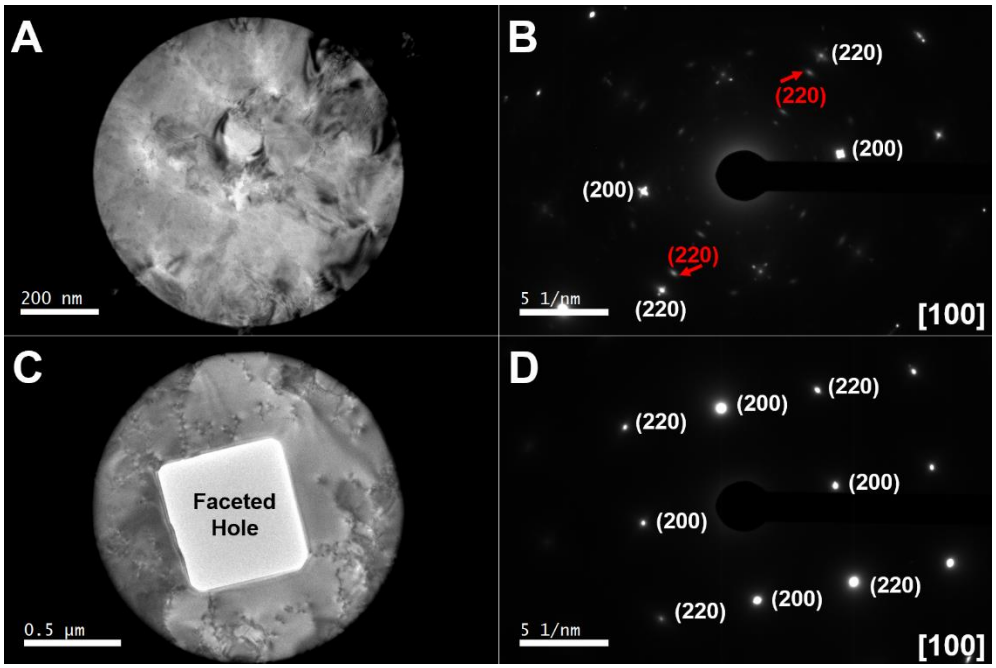

Figure 1. Representative bright-field TEM micrographs (A,C) and corresponding selected area electron diffraction patterns (B,D) of a copper film. The *in situ* faceted hole formation and removal of the native copper oxide at 550° C and $7.6x10^{-4}$ Torr H_2 is highlighted in panels C and D.

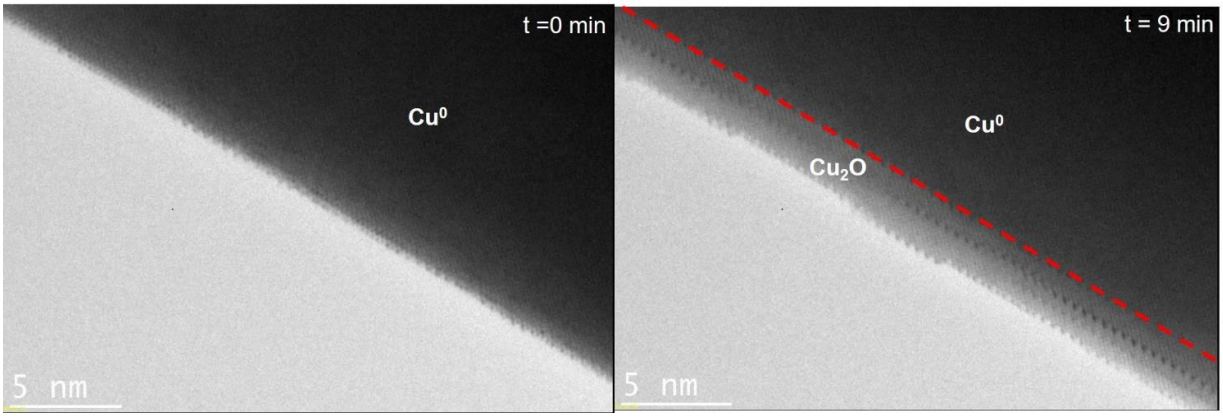

Figure 2. *In situ* oxidation of a copper film at a faceted hole. The initial Cu (110) surface prior to oxidation (left) and after 35 mins of oxidation at 250°C and $1x10^{-5}$ Torr O_2 (right). The red dashed line indicates approximate initial site of the metallic copper facet (right).