

Constructing a Predictive Model of Copper Oxidation from Experiment and Theory

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Corrosion costs the U.S.A. a few percent of its gross national product. Given the ubiquity of metals in modern materials and infrastructure, a comprehensive predictive model of oxidation is necessary for the tailored design of robust corrosion-resistant coatings. However, classical models of oxidation (e.g. Wagner or Cabrera-Mott theory) use the simplifying assumption of the uniform growth of metal oxides due to the lack of historical experimental tools to explore structural changes at the nanoscale. *In situ* environmental transmission electron microscopy (ETEM) experiments challenges these classical assumptions. Furthermore, *in situ* ETEM observations of metal oxidation allow for the continuous collection of data during a chemical process, in contrast to *ex situ* experiments, which can introduce ambiguity of results (e.g. exposure to ambient environment during specimen transfer or temporal gaps) and these ambiguous results can increase the overall costs of computational modeling. This work aims to establish a correlative investigation utilizing theory and *in situ* ETEM in tandem to bridge the spatial and temporal gaps between experimental and computational approaches. Initially focusing on the oxidation of copper (a well-studied model system for metal oxidation)[1], ultimately this work aspires to develop a continuous and precise predictive model of oxidation across all studied scales of measurement.

We investigated the Cu₂O island nucleation preference sites (edge or terrace) using both experiment and theory for three low index ((001), (011), and (111)) copper film surfaces (~70 nm thick) were grown via ultra-high vacuum electron-beam evaporation on a NaCl crystal of a specific orientation. These single crystalline Cu films were annealed *in situ* using a Hitachi H9500 ETEM equipped with a double-tilt heating holder ($T_{\max} = 1000$ °C) – to produce faceted holes of pristine Cu surfaces – using a hydrogen atmosphere (1×10^{-3} Torr H₂). Initiation of controlled oxidation (O₂) at 350 °C was achieved using a custom built gas delivery system with three gas input lines a variety of available gases (CH₄, CO₂, CO, H₂, H₂O, Methanol, and O₂). Computational methods, such as climbing image nudged elastic band within density functional theory (NEB-DFT) and molecular mechanics frameworks provided a quantitative and comprehensive assessment of the relative energetics of oxygen adsorption states, activation barriers, and surface reconstructions for different facets.[2,3] The most probable diffusion pathways of oxygen and adsorption sites predict whether nucleation of Cu₂O is preferred at edge or terrace sites for given surface orientations (Figure 1). Our initial results showed good agreement between the identified nucleation site preferences determined by our computational models and those observed with *in situ* ETEM (Figure 2). The Cu₂O island density (the number of islands/ total perimeter of holes) was determined from dark field TEM images and was found to increase from Cu (001) > (011) > (111) 4.9×10^{-3} , 1.5×10^{-2} , and 2.8×10^{-2} islands/nm, respectively. Whereas island density on the terrace (number of islands/ total terrace area) increases from Cu (001) > (011) > (111) 5.0×10^{-5} , 1.4×10^{-4} , and 1.7×10^{-4} islands/nm², respectively. Cu₂O island nucleation favors edge over terrace sites with increasing preference for Cu (001) compared to the Cu (011) and (111). Correlating these experimental data and simulations will reveal further relationships between reaction mechanisms and aid in developing a holistic understanding of how oxidation proceeds. This, in turn, will enhance the predictive power of computational models of oxidation onset [4,5], and ultimately direct future corrosion mitigation strategies, as well as the engineering of materials tuned for specific applications.[6]

References:

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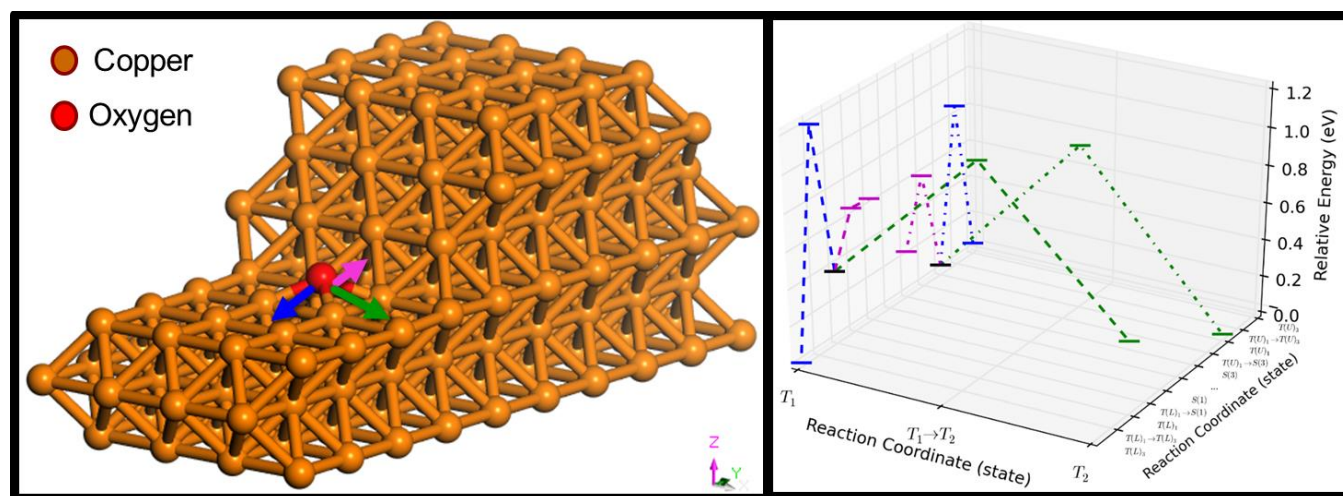


Figure 1. A visual depiction of the Cu(100){111} facet calculation with a three step height and an O atom placed at the lower step edge, indicating possible step (magenta), terrace (blue), and edge (green) diffusion paths pointed to the minimum energy endpoints of nearest neighbor hops (left). Oxygen diffusion energetic barriers and states calculated using DFT-NEB in a 3D plot results indicating possible energetically favorable barriers and sites (right).

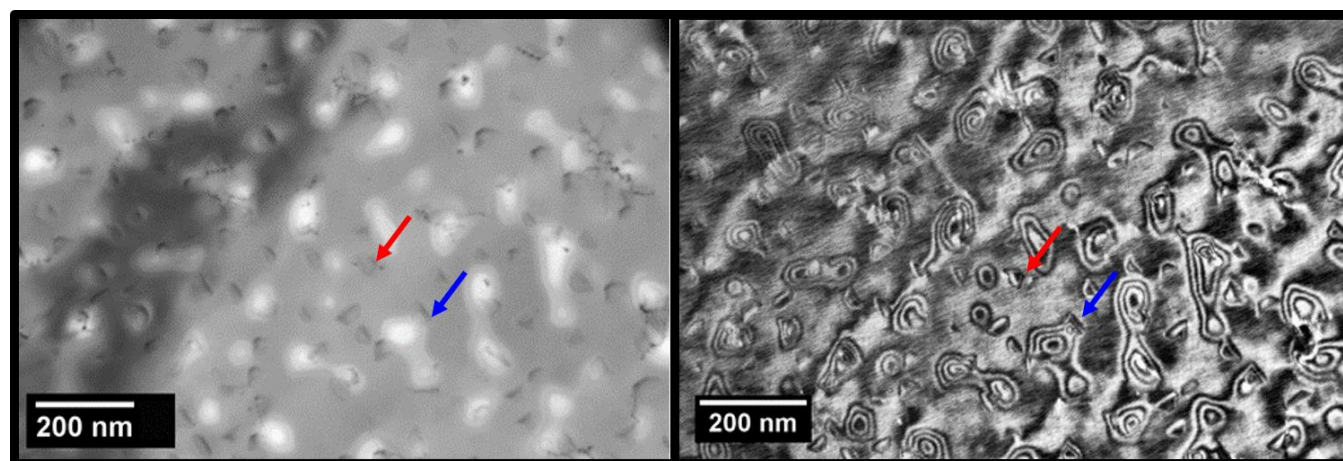


Figure 2. TEM micrographs show the location of Cu₂O island nucleation on a Cu(001) film after *in situ* oxidation at 350 °C and 7.4x10⁻⁴ Torr O₂. Bright field TEM (left) and dark field TEM (right) showing the location of oxide islands and Cu film favor edge (blue) to terrace (red) sites 82 to 21 islands, respectively.