

## Probing Dynamic Processes of the Initial Stages of Cu(100) Surface Oxidation by *in situ* Environmental TEM and Multiscale Simulations

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Corrosion is one of the biggest challenges facing the safe and reliable use of metals and alloys, especially under elevated temperatures. Understanding the microscopic mechanisms for surface oxidation is critical to unveil the mysteries of corrosion, and will also facilitate research in fields such as environmental stability, high-temperature corrosion, and catalytic reactions. The process of surface oxidation can be divided into three stages, namely oxygen chemisorption, oxide nucleation and growth, and bulk oxide growth. Despite numerous studies focusing on the initial stage of oxidation that commences with oxygen chemisorption on clean metal surfaces and ends with oxide nucleation and growth, this stage remains poorly understood due to the lack of experimental methods available for studying this stage. For example, surface science techniques such as Scanning Tunneling Microscopy (STM) and atomistic simulations have shown that after oxygen chemisorption, clean Cu(100) surfaces will undergo several surface reconstructions, demonstrating  $c(2\times 2)$  reconstruction and missing row reconstruction (MRR) structures [1]. However, characterization of the atomic mechanisms forming reconstructions, as well as determination of whether reconstruction is necessary for oxide nucleation, have not been conclusively investigated, given the lack of direct experimental observation.

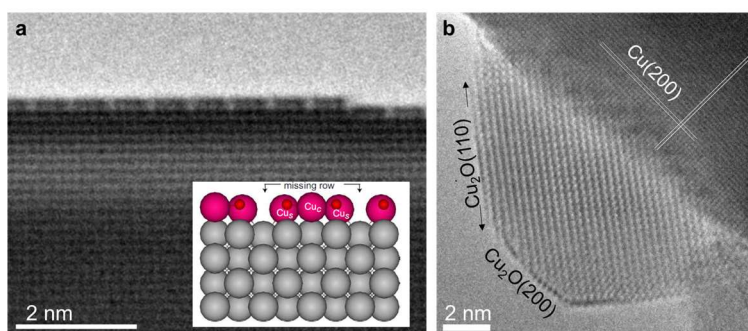
In this work, using state-of-the-art Environmental TEM (ETEM) (Hitachi H-9500 operating at 300 keV) and multiscale atomistic simulation, we explore the dynamic processes of the initial stages of Cu(100) oxidation. By *in situ* annealing and reducing Cu(100) thin films inside the ETEM with flowing H<sub>2</sub> gas injection, pristine Cu films with faceted holes were created, enabling observation of surface reconstructions as well as oxide nucleation and growth processes on the facets from the cross-sectional view. Oxidation experiments were carried out at various temperatures with flowing O<sub>2</sub> gas to study the initial stages of oxidation. As is shown in Figure 1, surface reconstruction was observed prior to oxide nucleation and the dynamic process of oxide growth was observed, delimiting the initial oxidation stage threshold at which ETEM can effectively discern dynamic processes. Over various Cu surface and facet orientations, oxide nucleation patterns differ with respect to facet edge preference, potentially leading to known differences in observed reconstructions on differently oriented surfaces [2].

In order to understand what contributes to these differences in oxidation behavior, computational study was carried out to investigate the initial stage of oxidation up to the experimental threshold between surface reconstruction and oxide nucleation [3-5]. Initially, single O diffusion events were modeled using the Climbing Image Nudged Elastic Band (CI-NEB) method in Density Functional Theory (DFT). Subsequently, DFT structures and energetics were applied to optimize Reactive Force Fields (RFFs) describing these and related diffusion events following our previous work [6]. After validating these single O diffusion events via a Molecular Mechanics (MM) implementation of CI-NEB, the oxidation

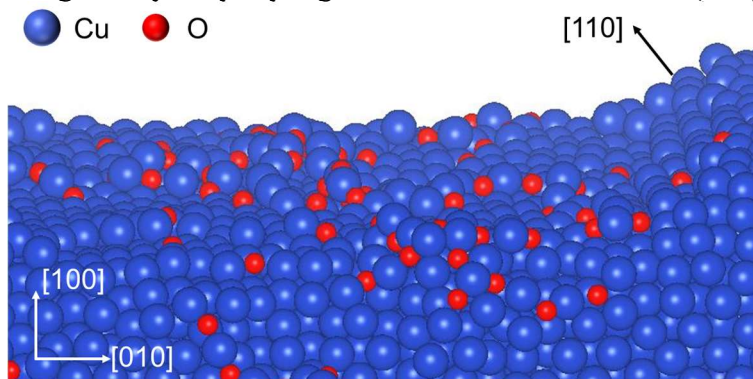
behaviors of single diffusing O were generalized (Figure 2) to O densities, O surface coverages, and ultimately reconstructed surfaces modeled using Molecular Dynamics (MD). Upon establishing this link between O diffusion events and reconstructed surfaces, all previously studied Cu-O interfacial systems will be applied to generate rate tables for adaptive Kinetic Monte Carlo (aKMC) simulations, which will be applied to determine whether the experimentally observed reconstructions for each surface orientation are capable of and necessary for oxide nucleation over testable time scales. Ultimately, these results can be used to improve current understanding of how surface structure impacts the initial stage of oxidation on an atomistic scale, as well as how surface reconstruction enables oxide nucleation to conclude initial stage oxidation [7].

#### References:

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 [7] The authors acknowledge funding from National Science Foundation (NSF) grants DMR-1410055, NSF DMR-1508417, and DMR-1410335, as well as support from Hitachi-High-Tech and technical assistance from the Nanoscale Fabrication and Characterization Facility (NFCF) in the Petersen Institute of Nano Science and Engineering (PINSE) at the University of Pittsburgh.



**Figure 1.** (a) HRTEM image of the MRR Cu(100) surface, the inset shows the atomic model for MRR; (b) HRTEM image showing the layer-by-layer growth of Cu<sub>2</sub>O island on Cu(100) surface.



**Figure 2.** MD simulation depicting widespread Cu ejection, O subsurface diffusion, and surface reconstruction adjacent to the Cu(001){110} facet.