

Correlated *in situ* ETEM and Multiscale Computational Study of Dynamic Processes Characterizing the Initial Stage of Copper Oxidation

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Oxidation is one of the major mechanisms for corrosion of metals and alloys, especially under elevated temperatures. Fundamental understanding of the microscopic mechanisms for surface oxidation is crucial for unveiling the mysteries of corrosion, as well as for significantly improving catalyst performance, thin film processing, and designing oxidation resistant materials. The process of surface oxidation can be divided into three stages, namely oxygen chemisorption, oxide nucleation and growth, and bulk oxide growth. Among these three stages, the initial stage, which spans from the start of oxygen chemisorption to surface reconstruction and the onset of oxide nucleation, is the least understood regime of oxidation, as it is inaccessible to traditional surface science and bulk material science experimental methods. Current computational capabilities can and have characterized oxygen chemisorption and diffusion, metal-oxygen clustering, metal ejection, and surface reconstruction for a wide variety of metals, including Cu. However, computational capabilities and theoretical modeling have yet to encompass oxide nucleation due to the large computational expense required to simulate nucleation over sufficiently large time and size scales.

In this work, by combining Environmental TEM (ETEM) with multiscale atomistic simulation, we explore the dynamic processes of the initial stages of copper oxidation (Figure 1). By *in situ* oxidizing Cu thin films inside the Hitachi H-9500 ETEM (300 kV, LaB₆, with homebuilt gas delivery system with up to 3 lines of gas injection) at various temperatures with flowing O₂ gas, the initial stages of oxidation were investigated. Our results show that surface steps can change the mass transport of both Cu and O atoms during oxide growth, and lead to the formation of different oxide morphologies¹. In addition, over various Cu surface and facet orientations, oxide nucleation preferences differ over adjacent facet edges, potentially leading to known differences in observed reconstructions on differently oriented surfaces. With increasing temperature, a transition in the preferred oxidation facet was also observed in Cu(100) films beside morphology changes of the oxide islands. Using atomic scale *in situ* HRTEM imaging, several surface reconstruction modes on Cu(100) and Cu(110) facets were observed prior to oxide nucleation. Oxide islands were observed to nucleate and grow on these reconstructed surfaces in a layer-by-layer manner. To better understand the dynamic processes from reconstruction to the onset of oxide island nucleation, a multi-scale computational approach was applied. With the development of Reactive Force Field (RFF) potentials and corresponding use of the Nudged Elastic Band (NEB) method, single initial oxidation stage events ranging from oxygen chemisorption to surface reconstruction can be modeled. To further model oxide nucleation and growth at size and time scales consistent with ETEM results at feasible computational expense, structures and energetics produced by RFF NEB calculations are generalized to rate tables for adaptive kinetic Monte Carlo (akMC) simulations². This multiscale simulation method forms a feedback loop with ETEM results that allows computational and experimental results to validate and support one other, and helps to fundamentally explain oxide nucleation preference as function of orientation, defects (such as steps), temperature and pressure, and other environmental factors.

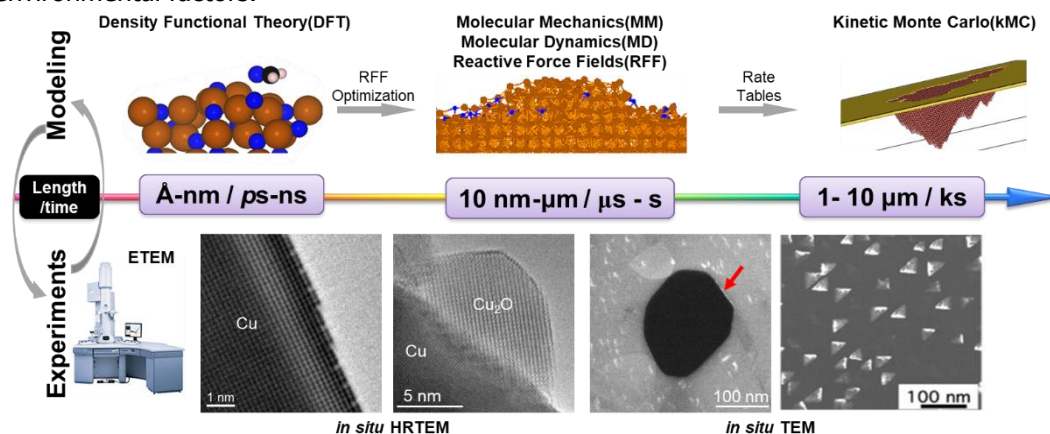


Figure 1. Illustration of the correlated *in situ* ETEM and multiscale simulation study on initial stages of Cu oxidation.

References:

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