

Quantifying atomic scale oxidation dynamics of Cu using in situ ETEM and advanced data analysis

Meng Li¹, Matthew T. Curnan^{1,3}, Richard Burke Garza^{1,3}, Stephen D. House^{1,2}, Wissam A. Saidi^{3*}, Judith C. Yang^{1,2,4*}

¹Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA (USA)

²Environmental TEM Catalysis Consortium (ECC), University of Pittsburgh, Pittsburgh, PA (USA)

³Department of Mechanical Engineering & Materials Science, University of Pittsburgh, Pittsburgh, PA (USA)

⁴Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA (USA)

* Corresponding author: judyyang@pitt.edu; alsaidi@pitt.edu

Understanding surface oxidation processes at the atomic level is critical for fundamental understanding of corrosion and catalyst design, as well as the advanced manufacturing of oxide heterostructures. Despite numerous prior studies on metal oxidation focusing on the evolution of oxide scales, the microstructural evolution during early oxidation – especially before oxide scale formation – is poorly understood. Existing oxidation theories, such as Cabrera-Mott theory or Wagner theory, assume uniform oxide layer and did not consider the effect of microstructure on oxidation. Hence, although these theories are still widely used to guide oxide growth in bulk materials, they are less accurate in guiding the growth of nanostructured oxides. The development of Environmental Transmission Electron Microscopy (ETEM) has enabled real-time observation of gas-solid reactions at the atomic scale, and has shown many successful applications in catalysts. However, previous ETEM investigation on early-stage surface oxidation mainly focused on morphology evolution, while in-depth and quantitative analyses are lacking. In classical oxidation studies, kinetics measured from weight change curves during oxidation could be used to infer the microstructures of oxides, such as whether oxides are protective. Although the spatial resolution of ETEM has been improved to the atomic scale, its temporal resolution is still inadequate to accommodate the timespans of atomic level oxidation processes. Thus, extracting statistically meaningful quantitative atomic-scale growth kinetics from in-situ TEM movies could provide critical information to understand atomic scale reaction kinetics. However, quantifying atomic-level dynamics from in situ TEM movies is very challenging. This is due to sample drift during the long timespans of oxidation processes, poor image contrast caused by low-dose imaging to eliminate electron-beam effects, and the difficulty of identifying atomic positions in HRTEM images.

In this work, we will present two examples that use atomic-scale in situ ETEM, quantitative advanced data analysis, and correlated atomistic simulations to investigate how microstructures – characterized by particular interfacial orientations and defects – affect the initial oxidation processes of Cu(100) thin films. The first example is about the surface reconstruction process. Upon oxygen injection, the pristine Cu surface was observed to transform into a reconstructed surface. However, capturing comprehensive reconstruction formation dynamics is very challenging, since the sample drift caused by gas injection coincides with the fast dynamics of surface reconstruction formation. We developed software to get atomically aligned frames in HRTEM movies, outperforming existing alignment software via better accuracy and stronger performance on HRTEM movies with fast evolving features. Using in situ ETEM and this data processing method, we revealed atomic-scale surface reconstruction formation dynamics on stepped surfaces (Figure 1). The studied surface reconstruction was found to be uneven on stepped surfaces, namely due to step induced O diffusion barrier differences.[1] The second example concerns

the oxide growth process. As shown in Figure 2, epitaxial Cu_2O islands on $\text{Cu}(100)$ were observed to grow layer-by-layer along $\text{Cu}_2\text{O}(110)$ planes, instead of previously expected $\text{Cu}_2\text{O}(100)$ planes, using in situ ETEM. Using advanced data processing based on computer vision, atomic-scale quantitative oxide growth kinetics were extracted (Figure 2(g-h)). The growth of each $\text{Cu}_2\text{O}(110)$ monolayer showed similar trends that fit cubic relationships ($l^3 \sim t$). Advanced machine learning based statistical analysis was performed on the extracted data to identify changes in atomistic dynamics behind such observed phenomena. Sudden changes in measured growth rates are attributed to two sources: new layer nucleation (N) and interlayer atomic diffusion (P). These quantitative data suggest a diffusion-limited oxide growth dynamics substantiated by our atomistic simulations.[2] These results showed the importance of advanced data analysis to further unveil physics beyond the experimental visualization of in situ and in operando TEM.

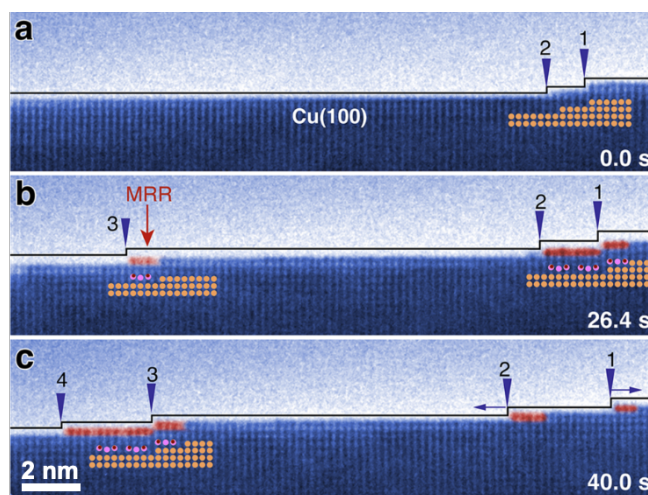


Figure 1. In situ ETEM observation of missing row reconstruction (MRR) formation dynamics on $\text{Cu}(100)$ surface. The movie frames are atomically aligned using the code we developed to compensate sample drift caused by gas-injection. The MRR formation showed clear preference on upper terrace sites of the step edges.

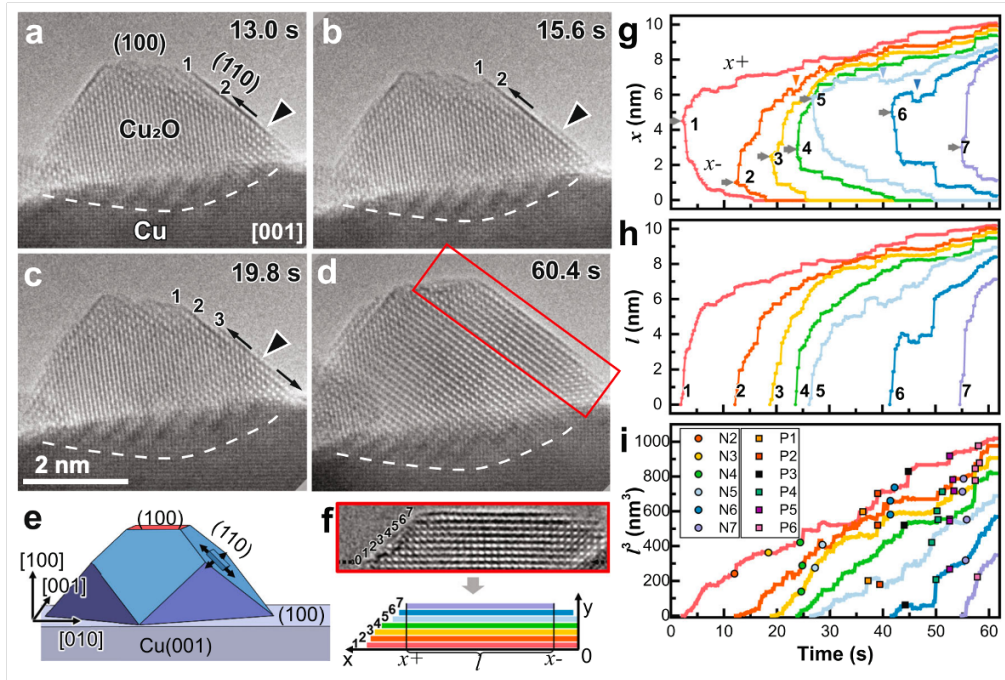


Figure 2. (a-d) In situ ETEM observation of layer-by-layer Cu₂O island growth along Cu₂O(110). **(e)** Corresponding schematic 3D model of the observed island. **(f)** Extracted area for automated detection of atomic level growth rate. **(g)** Measured growth trajectory of each atomic layer. **(h)** Projection length of each monolayer over time. **(i)** Statically defined breakpoints in growth rates indicate nucleation events (N) and interlayer atom diffusion events (P).

References:

- [1] Li, M., Curnan, M. T., Saidi, W. A. & Yang, J. C. Uneven Oxidation and Surface Reconstructions on Stepped Cu(100) and Cu(110). *Nano Lett.* **22**, 1075–1082 (2022).
- [2] Li, M. *et al.* Unusual layer-by-layer growth of epitaxial oxide islands during Cu oxidation. *Nat. Commun.* **12**, 2781 (2021).
- [3] The authors acknowledge funding from the National Science Foundation (NSF) grants DMR-1410055, DMR-1508417, DMR-1410335, and CMMI-1905647, as well as support from Hitachi High Technologies 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. The ECC is funded through the University of Pittsburgh and Hitachi High Technologies.