

***In-situ* Atomic-Resolution Observations of Oxide-Reduction Induced Formation of Nano-Holes in Cu₂O Thin Films**

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Reduction is an important method used to modify the stoichiometry, phase, microstructure, defects and atomic termination of oxides, thereby tuning the physical and chemical properties of metal oxides for a large variety of applications ranging from heterogeneous catalysis to electronic devices. Oxide reduction becomes operative once the loss of lattice oxygen sets in. Therefore, the oxide reducibility depends on the ability of the oxide to release oxygen. Oxide reduction typically involves multiple length scales and proceeds generally with the surface adsorption of a reducing agent (e.g., H₂, CO), its reaction with the lattice oxygen to form gas molecules (e.g., H₂O, CO₂) that desorb from the surface and then the oxygen-loss induced phase and microstructure evolution. For reactions occurring on such multiple length and time scales, factors influencing the oxide reduction mechanisms are many, and are both macroscopic (geometry, support, etc.) and microscopic (defects, interfaces, atomic transport, etc.). Averaging tools have been widely used to study oxide reduction on the global scale, including temperature-programmed reduction (TPR) to monitor oxide reduction induced oxygen loss and X-ray diffraction to understand oxide reduction induced structural and phase evolution. However, significant challenges exist in controlling the oxide reduction processes, particularly at the atomic scale. Several reasons for this include the long-standing challenges in performing in-situ measurements on the oxide surfaces. This is because many surface-sensitive techniques are based on charged particles and cannot be applied to oxides which are usually insulating (or wide-gap) materials.

Transmission electron microscopy (TEM) has evolved dramatically in recent years to allow temperature- and pressure-resolved imaging/diffraction of gas-surface reactions at the atomic scale. This is accomplished by differentially pumped environmental TEM and the incorporation of aberration correction techniques. Environmental TEM thus provides an elegant solution to directly observe, at the atomic-scale, the dynamics of oxide reduction at elevated pressure and temperature. In this work, we employ environmental TEM (FEI Titan 80-300) to observe, at the atomic scale and in real time, the oxide reduction induced structural evolution of Cu₂O thin films and show how atomistic insight can be obtained by coupling these observations with density-functional theory (DFT) modeling. Our in-situ TEM experiment involves a two-step process. First, a 50-nm thick Cu film is annealed at ~ 600 °C in H₂ gas flow, which reduces the native Cu oxides to Cu and generated tears and holes with faceted edges. The annealed Cu film is then oxidized at 350 °C by introducing oxygen gas at pO₂ = 5×10⁻³ Torr to form free-standing Cu₂O films that grow into the empty space of the hole area [1]. The Cu₂O film is then reduced at 350 °C by flowing H₂ gas (pH₂ ~ 1.2×10⁻² Torr) and in-situ TEM observations of the Cu₂O reduction are made in the planar view with the H₂ gas flow. To ensure that we observe intrinsic behavior of the surface phenomena, an imaging protocol based on low-dose microscopy techniques was adopted to minimize the effects of electron beam irradiation, including performing focusing and crystal zone-axis orientation on an adjacent region of the specimen and then moving the specimen to the area of interest

for TEM imaging. In addition, the e-beam is on the sample only when taking the images to minimize any e-beam induced oxide reduction [2].

Fig. 1 shows in-situ high-resolution TEM images captured from the reduction of a $\text{Cu}_2\text{O}(100)$ film. As the reduction proceed, an area with brighter image contrast (marked by the black dashed circle in Fig. 1(a)) appears. This suggests that the oxide is reduced in the local area, which results in a thinned region. This trend in the inhomogeneous reduction of the oxide film is further confirmed from in-situ TEM observations that provide atomic detail of the nanoscale hole formation from the local oxide reduction of the oxide film. As shown in Fig. 1(b), the continued oxide reduction results in a tiny hole with multiple atomic steps along the (110) edge, as indicated by the red, yellow, and blue arrows at different atomic layers. The oxide reduction induced nucleation and lateral propagation of the (110)-type atomic steps results in expansion of the hole in the oxide film. Detailed tracing of the evolution of these atomic steps along the edge of the hole is shown in Fig. 1(h). The in-situ TEM observations demonstrate that surface defects (atomic steps and kinks) play a key role in controlling the oxide reduction process. Such defect limited oxide reduction is further confirmed using DFT modelling of the preferred surface adsorption of H_2 molecules at the atomic steps. Adsorbed H_2 molecules react with lattice oxygen to form H_2O molecules desorbing from the oxide surface and freed Cu atoms diffusing away (Fig. 1(i,j)) [3].

References:

[1] Zou, L. *et al.*, Nat. Commun. **8** (2017), p. 307.

[2] Zhou, G. and Yang J., Phys. Rev. Lett. **93** (2004), p. 226101.

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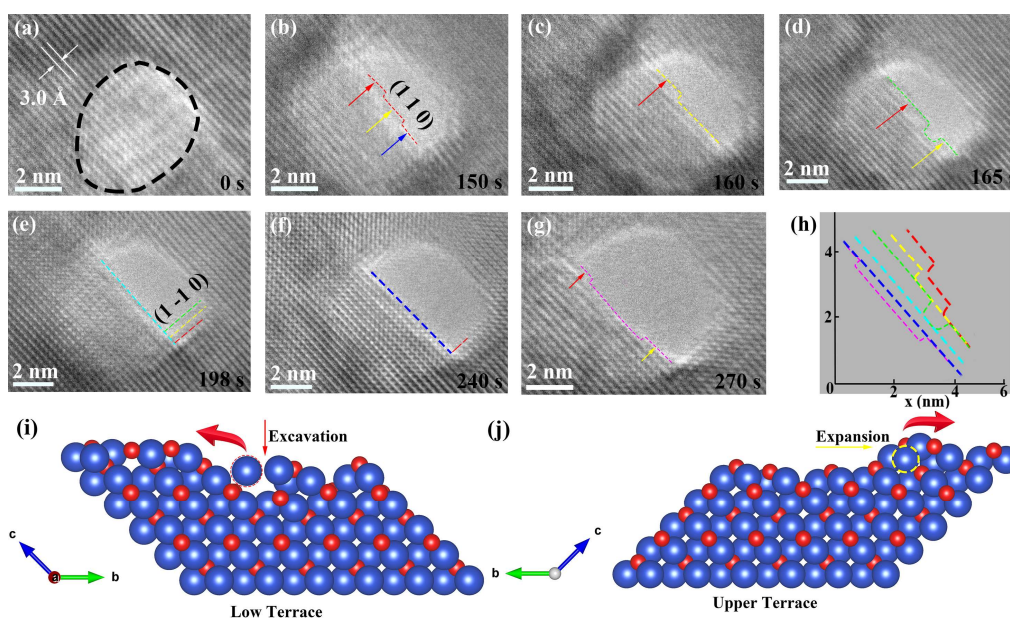


Figure 1. (a-g) Time-resolved HRTEM images showing the nano-hole formation induced by the localized reduction of $\text{Cu}_2\text{O}(100)$ at $T=350$ °C and $p_{\text{H}_2}=1.2 \times 10^{-2}$ Torr. (h) Traces of the evolution of the (110) steps along the nano-hole. (i, j) DFT modeling of the surface adsorption of H_2 molecules and migration of freed Cu atoms at the (110) step edges of the $\text{Cu}_2\text{O}(100)$ surface.