doi:10.1017/S1431927618002003
Microsc. Microanal. 24 (Suppl 1), 2018

In situ Observation of Cu_2O Island Shrinking on Cu(100) Facet under Methanol Using Environmental Transmission Electron Microscopy

Hao Chi[1], Christopher M. Andolina[1], Matthew T. Curnan[1], Meng Li[1], Götz Veser[1,2] and Judith C. Yang[1,3]

[1.] Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA.
[2.] Center for Energy, University of Pittsburgh, Pittsburgh, PA.
[3.] Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA.

In situ Environmental Transmission Electron Microscopy (ETEM) has progressed dramatically in recent years, currently allowing for temperature, time, and pressure resolved imaging of oxidation at the atomic scale [1]. Recent *in situ* studies have provided a significant understanding of atomic scale Cu oxidation, especially during early stage oxidation [2, 3]. In contrast, the reduction of metal oxides, such as Cu_2O, has been studied much less extensively. However, such reductions play an important role in many technologies such as catalytic reaction design, environmental stability, and electrochemistry [4]. In this work, we investigate the structural dynamics of Cu_2O islands on Cu(100) under MeOH in ETEM, using oriented Cu thin film produced by *e*-beam evaporation. Cu_2O nano-islands on Cu facets were created *via* controlled *in situ* oxidation of copper films, followed by reduction in MeOH vapor.

Cu(100) thin films with a thickness of 600 Å were produced by *e*-beam evaporation of 99.999% pure Cu pellets on NaCl(100) substrates. The films were grown in a ultrahigh vacuum evaporator system with a base pressure of 1×10^{-9} Torr. The growth parameters for Cu films include a deposition rate of 1.2 Å/s and a substrate temperature of 300 °C. We used an ETEM (Hitachi H9500) equipped with a differential pumping system, as well as a specially designed double-tilt heating holder and gas injection system [5]. ETEM images and videos were evaluated using Fiji-imageJ software (NIH).[6]

Native oxides (Cu_2O) on Cu films were removed by injection of H_2 on those films at a H_2 partial pressure (p_{H2}) of 7.6×10^{-6} Torr and a temperature of 550 °C. Annealing at elevated temperature facilitates the formation of faceted holes on Cu films (figure 1a). In order to form Cu_2O nano-islands along Cu(100) facets, we performed controlled *in situ* oxidation of Cu films ($pO_2 = 1.5\text{x}10^{-4}$ Torr, 350 °C) after cleaning the native oxides inside the ETEM. During this process, Cu_2O islands are formed with the epitaxial relation $Cu_2O(200)//Cu(200)$ (figure 1b). These islands were then reduced in MeOH ($7.6\text{x}10^{-6}$ Torr, 250°C) and the process was imaged and recorded to evaluate Cu_2O nano-island shrinking dynamics. Figure 2 shows the shrinking of a Cu_2O island during reduction with MeOH. The Cu_2O nano-island sitting on the Cu(100) facet initially has a height of 2 nm and radius (i.e. half of the width) of 5.5 nm. During the first 15 s of reduction, the Cu_2O island shrinks anisotropically, i.e. the island radius decreases strongly from 5.5 to 2 nm while its height only decreases slightly to ~1.7 nm. Interestingly, once the island radius roughly matches its height (at t~17 s), the shrinking switches from anisotropic to isotropic as both island height and radius simultaneously shrink until the whole island is removed at around 25 s. This shrinking behavior was observed uniformly for all other Cu_2O islands studied on Cu(100) (a total of 8 islands), i.e. it appears to be representative of the shrinking dynamics of Cu_2O islands on Cu(100) in an MeOH atmosphere. We propose that this behavior is caused by a preferential reaction between MeOH and stepped surfaces on the sides of the Cu_2O islands (*e.g.* Cu(110) with atomic steps) which show substantially higher reactivity than the island top terrace (Cu(100)). We are currently collecting additional, atomically resolved data for Cu_2O reduction on Cu(100) to further support our hypothesis. In parallel, we are calculating MeOH adsorption

energies for Cu(110) and Cu(100) surfaces using DFT to further corroborate this hypothesis and explain the difference in reactivity between these surfaces. The combination of *in situ* observations and theoretical calculations in this work will hence serve to reveal insights into methanol reactivity on different crystallographic facets of Cu_2O surfaces. More broadly, this work aims to contribute to the understanding and manipulation of supported metal oxide systems including those that are widely used in heterogeneous catalysis [7].

References:

[1] Zhou, G. *et al,* Chem Commun (Camb) **49** (2013), p. 10862.
[2] Zhou, G. *et al,* Physical Review Letters **109** (2012), p. 235502.
[3] Andolina, C. *et al,* J. Microscopy and Microanalysis **23(S1)** (2017), p. 920.
[4] Zhou, G. and Yang, J.C., Phys Rev Lett **93** (2004), p. 226101.
[5] Chi, H. *et al,* Microscopy and Microanalysis **23(S1)** (2017), p. 2100.
[6] Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, https://imagej.nih.gov/ij/, 1997-2016
[7] Financial support of this work from National Science Foundation (NSF) through CBET #1264637 and technical assistance from Nanoscale Fabrication and Characterization Facility (NFCF) at University of Pittsburgh are gratefully acknowledged.

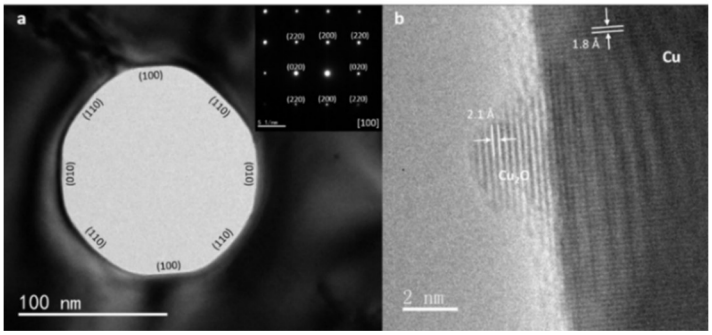

Figure 1. **a.** Representative TEM image and matching selected area electron diffraction pattern of a Cu film. *In situ* faceted hole formation and removal of the native copper oxide occurs at 550 °C and 7.6×10^{-4} Torr H_2. **b.** High-resolution ETEM image of a Cu_2O nano-island formed on a Cu(100) facet at pO_2 = 1.5×10^{-4} Torr and 350 °C.

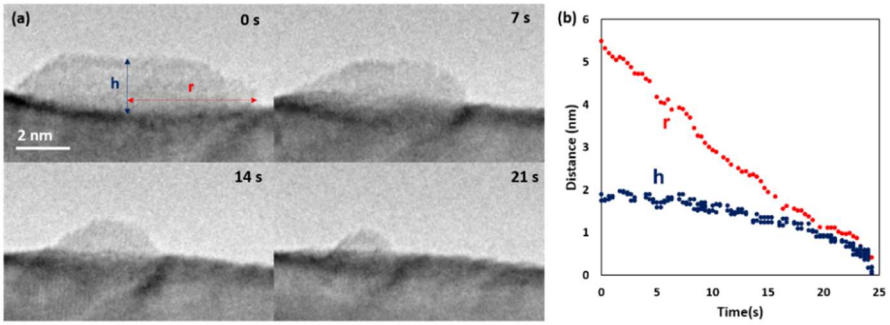

Figure 2. Morphological changes of Cu_2O nano-islands on Cu(100) facets under 7.6×10^{-6} Torr MeOH vapor and at 250°C. **a.** BF ETEM images depicting Cu_2O nano-island shrinking over time. **b.** Dimensions of the Cu_2O nano-island measured by Fiji-imageJ.

https://doi.org/10.1017/S1431927618002003 Published online by Cambridge University Press