In-Situ Synchrotron X-Ray Studies of Early-Stage Oxidation Processes

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Despite decades of study, little is still known about the atomic-level and mesoscopic processes that take place between the initial adsorption of oxygen on a clean metal surface and the formation by oxidation of a continuous, macroscopically-thick oxide layer. Early-stage oxidation theories such as that of Cabrera and Mott [1] are commonly cited and employed; however, they suffer serious deficiencies. For example, Yang *et al.* [2] recently pointed out that, while the Cabrera-Mott theory assumes uniform layer-by-layer growth starting with the initial monolayer, many recent studies have indicated that oxidation of many metals actually occurs by nucleation, growth, and coalescence of islands. Our approach to providing the needed missing information on early stage oxidation behavior is to use in-situ synchrotron x-ray scattering techniques. Using moderately high-energy x-rays (24 keV) to penetrate the reactive environment in our chamber, we are focusing on the oxidation and reduction behavior of single crystal Cu and Cu-alloys. Exposure of the metal surface to a controlled low partial pressure of oxygen (pO_2) over a wide range of temperatures initially results in formation of a reversible ordered surface structure with c(2x2) symmetry. As pO_2 is increased, Cu_2O islands nucleate and co-exist with the ordered surface structure. By measuring oxide island stability as a function of oxygen partial pressure, the thermodynamic limit between oxide growth and reduction has been determined over a wide range of temperatures. We find the Cu/Cu_2O phase boundary at several orders-of-magnitude larger pO_2 than predicted by bulk phase equilibria, and also find that the temperature dependence of this phase boundary is smaller than expected [3]. The observed phase boundary is at remarkably similar pO_2 as the narrow single-phase stability range observed recently by Lyubinetsky *et al.* in a study of MBE growth of Cu_2O nanoparticles (*Jn. Appl. Phys.*, **94**, no. 12, 7926, 2003); thus our observations provide insight into the general stability of oxide nanoclusters grown by various techniques. Preliminary results on the effects of water vapor on the oxidation behavior of Cu (001) will also be discussed. This work is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract W-31-109-Eng-38.

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1) N. Cabrera and N.F. Mott, *Rept. Prog. Phys.*, **12**, 163 (1948).
2) J.C. Yang, M. Yeadon, B. Kolasa, and J.M. Gibson, *Appl. Phys. Lett.*, **70**, no. 26, 3522 (1997).
3) J.A. Eastman, P.H. Fuoss, L.E. Rehn, P.M. Baldo, G.-W. Zhou, D.D. Fong, and L.J. Thompson, *Appl. Phys. Lett*. **87**, 051914, (2005).