Effects of surface step on Cu_2O thin film growth and Cu_2O surface reactivity

Liang Li[1,2], M. K. Y. Chan[1], Langli Luo[2], Jim Ciston[3, 4], Wissam A. Saidi[5], Eric A. Stach[4], Judith C. Yang[5], Guangwen Zhou[2],

[1]Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL

[2]Department of Mechanical Engineering, State University of New York at Binghamton, NY

[3]National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA

[4]Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY

[5]Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA

Fundamental understanding of metal oxidation has received extensive interest due to its significant importance in many fields including high temperature corrosion, catalytic reactions and thin film processing. However, many questions still remain unresolved concerning the early stages of oxidation, which is inaccessible by the traditional surface science and ‘‘bulk’’ materials science techniques. The nucleation and growth of surface oxide is often complicated by surface inhomogeneities caused by the presence of surface defects such as steps. In this work, through the use of in-situ transmission electron microscopy (TEM) we observe that the presence of surface steps leads to the decomposition of the Cu_2O overlayer at the growth front of the Cu substrate, thereby resulting in oscillatory Cu_2O film growth. Using density-functional theory (DFT) total energy calculations and *ab initio* molecular dynamics (AIMD) simulations, we show that oxygen adsorption on the lower terrace destabilizes the Cu_2O thin film formed on the upper terrace that leads to oxide decomposition. Our results reveal the unique role of surface defects in oxide film growth and may have broader implications for understanding the fundamental process governing gas-surface reaction kinetics as modulated by atomic defects on a solid surface [1]. We will also discuss the effects of step edge on the surface reactivity of Cu_2O, revealed via DFT calculations of gas species adsorption on the terrace and step edges of Cu_2O surfaces.

[1] L. Li, L. Luo, J. Ciston, W. A. Saidi, E. A. Stach, J. C. Yang, and G. Zhou, Phys. Rev. Lett. **113**, 136104 (2014).