DOE-BES 401018

PI: Judith C Yang, Mechanical Eng. & Materials Science, University of Pittsburgh

Co-PI: Alan McGaughey, Mechanical Eng., Carnegie Mellon University

Susan Sinnott and Simon Phillpot, Materials Science & Eng., University of Florida

MULTISCALE ATOMISTIC SIMULATION OF METAL-OXYGEN SURFACE INTERACTIONS: METHODOLOGICAL DEVELOPMENT, THEORETICAL INVESTIGATION, AND CORRELATION WITH EXPERIMENT

FINAL REPORT

Our long-term vision is for a comprehensive and fundamental understanding of a critical gas-surface reaction, nano-oxidation—from the adsorption of oxygen atoms on the metal surface to the coalescence of the bulk oxide—via coordinated multi-scale theoretical and *in situ* experimental efforts. Reaching this goal necessitates close collaborations between theorists and experimentalists, and the development and utilization of unique and substantial theoretical and experimental tools. Achievement of this goal will be a major breakthrough in dynamic surface/interface reactions that will dramatically impact several scientific fields. Many of these are of interest to DOE, such as thin films and nanostructures that use oxidation for processing, heteroepitaxy, oxidation and corrosion, environmental stability of nano-devices, catalysis, fuel cells and sensors.

The purpose of this specific DOE program was the support for the theoretical effort. Our focus for the first round of funding has been the development of a Kinetic Monte Carlo (KMC) code to simulate the complexities of oxygen interactions with a metal surface. Our primary deliverable is a user-friendly, general and quite versatile KMC program, called Thin Film Oxidation (TFOx). TFOx-2D presently simulates the general behavior of irreversible 2-dimensional nucleation and growth of epitaxial islands on a square or rectangular lattice. The TFOx model explicitly considers a very large range of elementary steps, including deposition, adsorption, dissociation of gas molecules (such as O₂), surface diffusion, aggregation, desorption and substrate-mediated indirect interactions between static adatoms. This capability allows for the description of the numerous physical processes involved in nucleation and growth. The large number of possible input parameters used in this program provides a rich environment for the simulation of epitaxial growth or oxidation of thin films.

As a first demonstration of the power of TFOx-2D, the input parameters were systematically altered to observe how various physical processes impact morphologies. It was noted that potential gradients, developed to simulate medium-range substrate mediated interactions such as strain, and the probability of an adatom attaching to an island, have the largest effect on island morphologies. Nanorods, and round, square and dendritic shapes have all been observed (see section 2E) which correlate well with experimental observations of the wide range of oxide morphologies produced during *in situ* oxidation of Cu thin films. The people involved in the development and utilization of TFOx included a post-doc, Dr. Rich McAfee, and a graduate student, Ms. Xuetian Han. Both joined this program in August 2002. Dr. McAfee has been at Brashear Co., in Pittsburgh, PA since June 2004. To allow TFOx to be accessible to the rest of the scientific community, a web-site describing TFOx has been developed: www.tfox.org. No unexpended funds are expected at the completion of the current funding cycle.

For in-depth development of the theoretical effort, the Principle Investigator (PI) proposed in the initial grant to collaborate with Dr. Maria Bartelt at Lawrence Livermore National Lab (LLNL). A graduate student, Dr. Guangwen Zhou, was supported within this DOE program for several months, where he was to collaborate with Dr. Bartelt. Unfortunately, Dr.

Bartelt became very ill during this time and passed away in 2003. The focus of Dr. Zhou's thesis work (completed in December, 2003) was the wide variety of oxide nanostructures (e.g., nano-rods, domes, and pyramids) that form during oxidation of Cu thin films *in situ*. His primary contribution while supported on this DOE grant was the demonstration that the elastic strain relief model, as developed by Tersoff and Tromp to explain nanorod formation in Ge/Si system, explains Cu₂O nano-rod formation when Cu(100) is oxidized around 600°C. Validation of this model requires surface and interface energies, and calculations of these values are part of the ongoing effort with University of Florida (UF) and proposed activity with Carnegie Mellon University (CMU).

History and Relationship between Present Team and Proposed Expansion

Figure 1: Schematic diagram of the expanded and synergistic activities between theory and experiment, researchers involved and management, where the “red” is the theoretical effort proposed and the “blue” is the experimental effort funded through other sources.

Brief highlights of our progress to date are summarized below:

- Development of TFOx-2D, a versatile kinetic Monte Carlo code that can simulate atomistic transport, nucleation and growth, and includes potential gradients to simulate medium-range substrate mediated effects (e.g., strain).
- Systematic study of TFOx-2D input parameters to reveal a variety of nano-structures that resemble those seen experimentally.
- Parallelization of the Streitz-Mintmire potential and Rappe-Goddard approach for determining dynamic charge transfer at a metal-oxide interface, which is the critical step required for molecular dynamic simulations of oxygen-metal interactions.
- Benchmark calculations of Cu and Cu₂O physical properties to determine the most accurate electronic structure approach.
- Demonstration of the greater universality of the Tersoff-Tromp elastic strain relief model of nano-rod formation to a gas-surface reaction.

Hence, we have established the ground work for a truly comprehensive and multi-scale theoretical tool that can simulate any gas-surface reaction, including oxidation, from the atomic level to the mesoscale, from first principles. The direct comparison between these simulations and *in situ* experiments of metal nano-oxidation will lead to new knowledge of this important surface reaction.

Dissemination of Results:

Web-site for TFOx: www.tfox.org

Publications:

- G. Zhou and J. C. Yang, "Formation of Quasi One-dimensional Cu₂O Structures by *in situ* Cu(100) oxidation", (2002), Phys. Rev. Let., 89 (10), p.106101-4
- X. Han, R. McAfee, J. C. Yang, "Kinetic Monte Carlo Simulations of the Dramatic Effects of Attachment Probability and Potential Gradients on Island Morphology Variations under Heteroepitaxial Growth Conditions", *J. Computational and Theoretical Nanoscience*, 5, 117–128 (2008).
- X. Han, R. McAfee, J. C. Yang, "Kinetic Monte Carlo Simulations of the Dramatic Effects of Attachment Probability and Potential Gradients on Island Morphology Variations under Heteroepitaxial Growth Conditions", *J. Computational and Theoretical Nanoscience*, 5, 117–128 (2008).

Conference Proceedings

- Xuetian Han, Richard McAfee, and Judith C. Yang, "Kinetic Monte Carlo Model Simulating Nanoscale Oxidation Behavior", JJ9.4 MRS 2004 Fall Boston, Online Proceeding <http://www.mrs.org/members/proceedings/fall2004/jj/JJ9_4.pdf>

Conference Presentations

- Xuetian Han, Richard McAfee, and Judith C. Yang, "Simulation of the Nanoscale Oxidation Behavior of Cu (100)", MRS, Poster Presentation, 2003 Fall Boston (nominee for best poster).
- R. McAfee, X. Han and J. C. Yang., "Correlation of Atomic-scale Simulation to Experimental Results of the Formation and Growth of Oxide Nanostructures on Copper Thin Films", MRS, Poster Presentation, Boston, MA, December 2003.
- Xuetian Han, Richard McAfee, and Judith C. Yang, "Kinetic Monte Carlo Model Simulating Nanoscale Oxidation Behavior", Oral Presentation, MRS 2004 Fall Boston.
- Xuetian Han, Richard McAfee, and Judith C. Yang., "Simulation of the Nanoscale Oxidation Behavior of Cu (100)", Poster Presentation, 2004 AMS. 2nd Place for "Best Poster by a Graduate Student".
- A. J. H. McGaughey, S. R. Phillpot, S. B. Sinnott, and J. Yang, "Multiscale simulation of copper oxidation," to be presented at Materials Science & Technology 2005, September 2005, Pittsburgh, PA.
- B. Devine, A. J. H. McGaughey, S. R. Phillpot, and S. B. Sinnott, "Molecular dynamics study of the aluminum/ α -alumina interface using an efficient charge-transfer potential," to be presented at AVS International Symposium and Exhibition, November 2005, Boston, MA.

Budget:

University of Pittsburgh: The funding was used to support a post-doc, Dr. Alan McGaughey (for one year prior to his joining the faculty at Carnegie Mellon University) as well as another post-doc and graduate student during this time period. The remaining budget is zero.

Carnegie Mellon University: The funding was used to support a graduate student this time period. The remaining budget is zero.

University of Florida, Gainesville: The funding was used to support 50% of a graduate student, where the other 50% was a graduate student fellowship. The remaining budget is zero.