Final Technical Report

Name of Recipient: Judith C Yang

Project Title: "Multiscale atomistic simulation of metal-oxygen surface interactions: methodological development, theoretical investigation, and correlation with experiment"

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Co-PIs: Alan McGaughey, Dept of Mechanical Engineering, Carnegie Mellon University; Susan Sinnott and Simon Philpot, Materials Science and Engineering, University of Florida, Gainesville.

1. Executive Summary

The purpose of this grant is to develop the multi-scale theoretical methods to describe the nanoscale oxidation of metal thin films, as the PI (Yang) extensive previous experience in the experimental elucidation of the initial stages of Cu oxidation by primarily in situ transmission electron microscopy methods. Through the use and development of computational tools at varying length (and time) scales, from atomistic quantum mechanical calculation, force field mesoscale simulations, to large scale Kinetic Monte Carlo (KMC) modeling, the fundamental underpinings of the initial stages of Cu oxidation have been elucidated. The development of computational modeling tools allows for accelerated materials discovery. The theoretical tools developed from this program impact a wide range of technologies that depend on surface reactions, including corrosion, catalysis, and nanomaterials fabrication.

2. Comparison of Original Goals & Objectives to the Actual Accomplishments Achieved.

The original goal of this program was to develop a multiscale modeling tool to correlate with the in situ TEM oxidation experimental data of the initial stages of Cu oxidation. More specifically, the proposed objectives were:

a. Development of a charge transfer interatomic potential for Cu-O systems.
b. Creation of TFOx-3D, an atomistic Monte Carlo simulation program that models island nucleation and growth into and above a substrate, and comparison of the simulation results to experimental observations obtained by in situ XRD and TEM
c. Determination of the energetic landscape that controls adatom transport, surface reconstructions, nucleation and growth.
d. Development of methodologies to determine the realistic input parameters (such as diffusion, sticking coefficients, binding energies, desorption) needed for TFOx-3D from first principles.
e. Identification of the critical physical processes and environmental parameters that control nano-island morphologies and coalescence.

This research team has successfully accomplished the development of the theoretical tools and extended the project to a broader scope by introducing the reactive force field ReaxFF. Specifically, this team has accomplished:

a. Investigation of the kinetics and thermodynamics at the early state of the Cu(100) surface oxidation under the framework of Density Functional Theorem (DFT), especially focus on the role of sub layer oxygen atoms in the phase transition of Cu oxidation (McGaughey) [1, 3-5].
b. Development of the charge optimized many-body (COMB) potentials for metallic copper and copper oxide systems, and apply the COMB potential in the modeling of the Cu(111)||Cu$_2$O(100) interface and the oxidation of the Cu (100) surface (Sinnot, Philpot) [2].

c. Development of thin film oxidation TFOx, a general atomistic Monte Carlo simulation program that models island nucleation and growth into and above a substrate, and comparison of the simulation results to previous experimental observations obtained by in situ TEM (Yang) [6-8].

d. Applying ReaxFF potential to the study of the dynamics of the oxidation on stepped Cu(100) surface and identify the effect of the step edge on the oxidation behavior (Yang) [9].

3. Project Activities

During the year 2009-2013, the collaborative team has developed the necessary multi-scale theory and simulation tools to correlate directly with in situ experiments, which provide critical structural and chemical information, for fundamental knowledge of nano-oxidation processes of Cu which can be extended to other metal surfaces (Figure 1). 9 peer reviewed journal articles have been published [1-9] and 8 conference presentations have been given. This team effort has slightly diverged from the original hypothesis, where the multiscale simulation scheme is connected by DFT, COMB force field and TFOx (Figure 1).
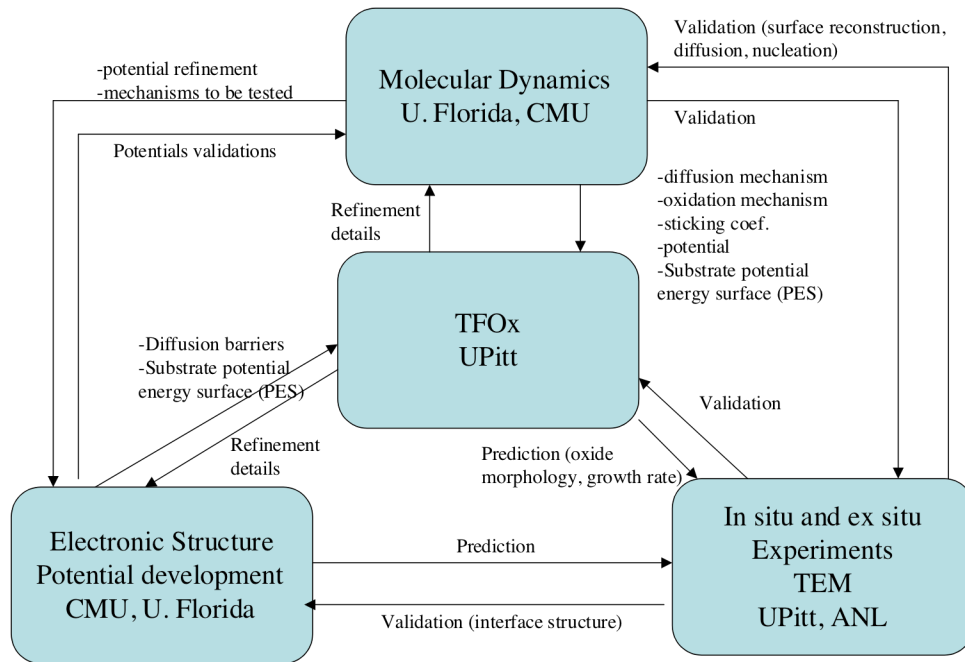

Figure 1: Schematic diagram of the inter-relationships between the various theoretical efforts (Molecular Dynamics, Electronic Structure Calculations, Kinetic Monte Carlo) and in situ and ex situ experiments on oxidation.

The COMB force field developed is reasonable in describing the interaction for a predefined Cu/Cu_2O interface, yet the ReaxFF potential produces better structure and thermodynamic agreement for dynamic oxidation process. We have also included ReaxFF potential in the MD simulation of Cu surface oxidation at the later stage of the project. The following paragraphs gives more details for each major theoretical method used to model the early to initial stages of Cu oxidation.

4a. Early state oxidation of Cu(100) surface from DFT calculations

McGaughey's group has conducted extensive density functional theory (DFT) calculations on the early stage of the Cu(100) surface oxidation. The atomic oxygen embedment into a Cu(100) surface is studied under the framework of DFT by calculation and the nudged elastic band method [3]. The oxygen coverage increases on the unreconstructed surface from 0.25 monolayer (ML) to 0.75 ML, the energy barrier for oxygen embedment decreases and an energetically favorable sub-surface site is found at 0.75 ML coverage. At a fixed oxygen coverage of 0.5 ML, the oxygen embedment energetics vary with the surface morphology and the embedment is found to be more probable for reconstructed structures compared to the bare surface. On the missing-row reconstructed surface, the energy barrier for atomic oxygen embedment is smaller through the missing-row compared to other paths, suggesting a mechanism for the formation of sub-surface oxygen structures that are consistent with recent in situ TEM experiments [10].
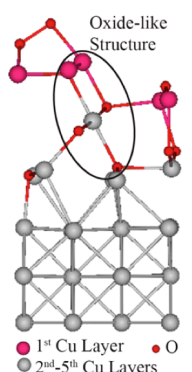

Figure 2: DFT-predicted formation of an oxide-like structure on the missing row reconstructed Cu(100) surface with sub-surface oxygen [1].

DFT calculations are also used to investigate the role of sub-surface oxygen in Cu(100) oxidation [1]. McGaughey's group has found that the presence of sub-surface oxygen atoms can cause the top copper layer of the missing-row reconstructed surface to rise by 1.7 Å compared to the bare metal surface. This prediction compares well to an earlier scanning tunneling microscopy measurement of 1.8 Å [11]. When the missing-row reconstructed surface is exposed to an additional oxygen molecule, surface restructuring that leads to oxide like structures is only observed when sub-surface oxygen is present. The oxide like nature of these structures is confirmed through structural, Bader charge, and electron density of states analyses. These findings, combined with the above discussed DFT results that predicted low energy barriers for the embedment of oxygen atoms into the sub-surface [3], demonstrate the key role played by sub-surface oxygen in Cu(100) oxidation.

The energetics and kinetics of the $c(2 \times 2)$ to $(2\sqrt{2} \times \sqrt{2})R45°$ missing-row reconstruction transition on the Cu(100) surface have also been investigated DFT calculations [4]. Oxygen-molecule-induced surface restructuring on the unreconstructed Cu(100) surface is compared to that on the missing-row reconstructed surface. They have found that the surface-oxide energy decrease on the missing-row reconstruction (−0.149 eV/ Å^2) is larger than that on the unreconstructed surface (−0.080 eV/ Å^2). Cu$_2$O-like structures, which are found on the reconstructed surface, are not found on the unreconstructed surface. These results indicate that the missing-row reconstruction is necessary for the formation of Cu$_2$O on the Cu(100) surface. Then, they have also investigated copper ejection from the $c(2 \times 2)$ phase using the nudged elastic band method. A series of ejections onto the nearest-neighbor copper atom is found to be the

most probable mechanism for the formation of the missing row. The barriers for the subsequent copper diffusion events are comparable to those on the perfect $c(2 \times 2)$ phase and the clean copper surface, suggesting that the $c(2 \times 2)$ phase acts as a copper diffusion channel during surface oxidation.
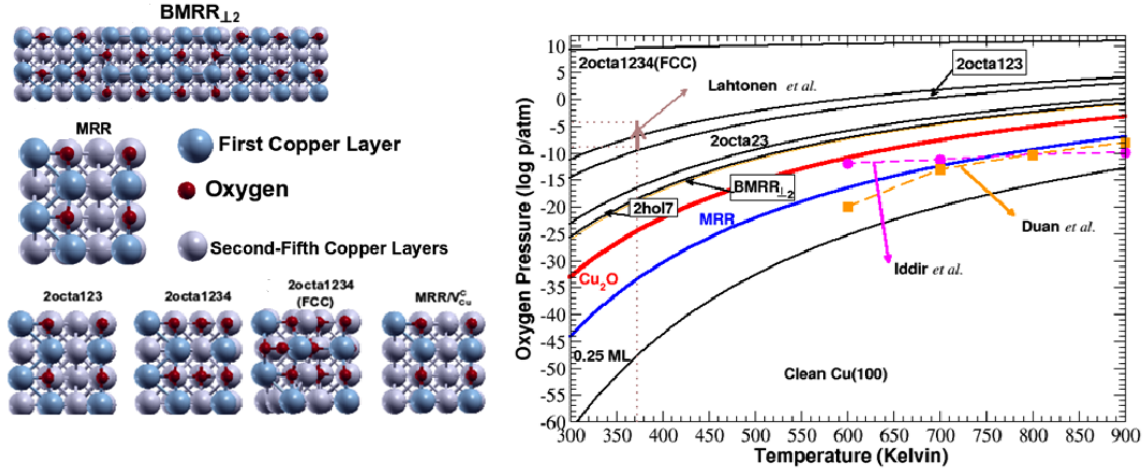

Figure 3: Top view of few potential surface structures during the early stages of Cu(100) oxidation. The phase diagram shows the stable phases as a function of temperature and oxygen partial pressure. The phase boundaries between 0.25 ML and MRR from experiment (Iddir et al.[12]) and a previous ab initio thermodynamic calculations (Duan et al.[13]) are shown for comparison. Additionally, we show the experimental range of oxygen partial pressures (solid brown line) at T = 373 K where Lahtonen et al.[10] previously reported on sub-surface oxidation as a result of penetration of the MRR phase.

Finally, under DFT framework, in collaboration with Wissam Saidi at University of Pittsburgh, the stable surface structures during the early stages of Cu(100) oxidation have been identified as function of the temperature and pressure conditions [5]. The clean surface, the 0.25 ML oxygen-covered surface, and the missing-row reconstruction is thermodynamically stable in the temperature and pressure range of 100–1000 K and 10^{-15}–10^5 atm, respectively. This result is consistent with previous experimental and theoretical results [11, 14, 15]. The thermodynamic stabilities of Cu-O precursors to Cu_2O formation including missing-row reconstruction structures that include extra on- or subsurface oxygen atoms as well as boundary phases formed from two missing-row nanodomains have been studied by DFT. While these structures are not predicted to be thermodynamically stable for oxygen chemical potentials below the nucleation limit of Cu_2O, they are likely to exist due to kinetic hindrance.

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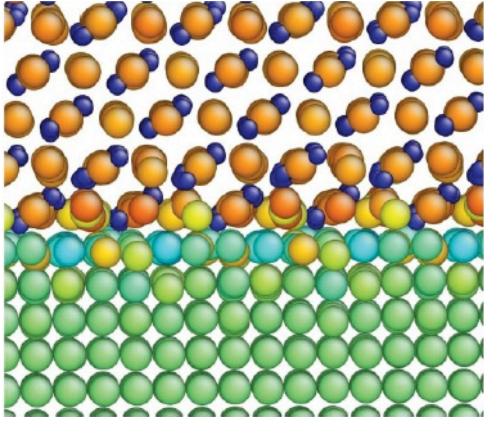## 4b. Development and application of Cu/O COMB force field potential

Figure 4: The Cu2O(111)‖Cu (100) interface viewed along the Cu[100] direction after annealing at 200 K for 10 ps. Color corresponds to charge with red=-1.3 e and blue = 1.3 e. The larger spheres are Cu. The smaller spheres are O [2].

The Florida group of Susan Sinnott and Simon Phillpot have developed a charge-optimized many-body potential (COMB) for metallic copper and copper oxide systems based on an extended Tersoff formalism coupled with variable charge electrostatics [2]. To faithfully reproduce interactions between molecular oxygen and the metal surface, the potential includes atomic polarizabilities via both a point dipole model and dynamic partial charges, both of which are equilibrated through an extended Lagrangian scheme. The potential is fit to a training set composed of both experimental and *ab initio* computational data for cohesive energies, formation enthalpies, elastic properties, and surface energies of several metallic and oxide phases as well as bond dissociation energies for molecular oxygen and several of its anions. The potential is also used in molecular dynamics simulations to model the Cu(111)‖Cu_2O(100) interface and the oxidation of the Cu (100) surface (Figure 4).

4c. Development and application of 3-dimensional Kinetic Monte Carlo Simulation: <u>T</u>hin <u>F</u>ilm <u>Ox</u>idation (TFOx)

At the University of Pittsburgh, Judith C. Yang and Wissam A. Saidi work together in the development of Kinetic Monte Carlo (KMC) program for thin film oxidation: TFOx.
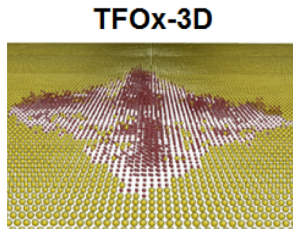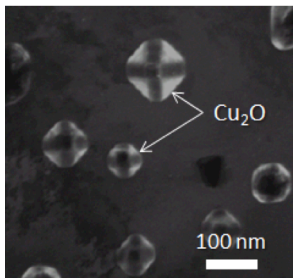

Figure 5: TFOx-3D simulation result comparing to in situ TEM result.

Thin film development and nanoscale oxidation studies have been of great interest recent years. Nucleation rate theory [16-18] has been successfully used to describe metal heteroepitaxy [19] and qualitatively explained the initial stage of oxidation behavior [20]. To further quantitative understanding of these nano-scale processes and the morphology evolution in general gas-metal reactions and thin film development, a powerful simulation tool is urgently needed. The Thin Film Oxidation (TFOx) model is an atomistic Kinetic Monte Carlo model, which has been developed of this purpose. The TFOx model includes all of the relevant microscopic processes in thin film growth. It simulates various steps and phenomenon during thin film development, which includes deposition, decomposition, adatom diffusion, nucleation, adatom desorption, island growth and et.al. TFOx has a large amount of input parameters compared to other KMC models to assure the

realistic and accuracy, which also makes itself a versatile tool of studying the thin film development. As motivated by the dramatic variations of Cu_2O island morphologies observed during in Yang's situ oxidation of Cu(001) thin films [21], the effects of simulation parameters on the morphological evolution of an isolated island were systematically studied utilizing TFOx. It is found that the most dramatic effects on the morphology were due to the strength of the potential gradient and the values of the attachment probabilities along orthogonal <10> and diagonal <11> directions. The potential gradients reflect the effects of strain and other intermediate range interactions on diffusion. Anisotropic attachment probabilities of adatoms model the effects of surface energy and interface energies during epitaxial thin film growth. Simulation parameters in TFOx were systematically adjusted to obtain a range of morphologies, such as dendritic, round, rod, and square that resemble the experimental observations of oxide morphologies due to in situ of copper thin films.

Recently, TFOx has been extended to the simulation film growth in 3D space [8]. This new version of TFOx-3D is composed of a C++ console program and Python graphical user interface (GUI), such that parameterized simulation, parallel execution. The effects of the potential gradient and the Ehrlich–Schwobel barrier are examined and it is found that the 3D island morphology is significantly influenced by the incorporation of these two factors. TFOx-3D promises a great improvement towards the correct description of 3D oxide island growth.
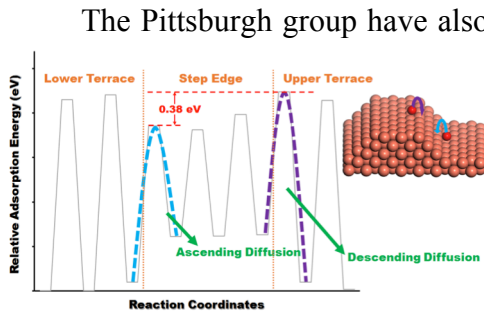
The Pittsburgh group have also probed the dynamics of the oxidation on stepped Cu(100) using molecular dynamic simulations in conjunction with reactive forcefield, and have elucidated the mechanisms and energy barriers affecting the oxidation process [9]. The molecular dynamic simulations show that the adsorbed oxygen adatoms are unevenly distributed on the stepped surface favoring the top terrace. It is shown that this behavior is due to Ehrlich-Schwöbel (ES) barrier effect. However, differently from the reduced interlayer self-diffusion in descending a step as in conventional ES barrier effect, they find instead that the ES barrier reduces the ascending diffusion barrier for oxygen promoting its transport across the step edge and enhances the oxidation of the upper terrace. Additionally, it is found that the ES barrier is step-height dependent where higher step-edges reduce more the oxygen ascending diffusion barrier and favor more oxidation of the stepped surfaces.

Figure 6: Reactive force field simulation shows that the oxygen adatom on Cu(100) stepped surface encounters smaller barrier when ascending the step edge comparing to descending diffusion, results in faster oxidation at the upper terrace of the surface step.

4d. Project Summary

The goal for the proposal is to create a multiscale modeling method for the metal oxidation process. The research team has chosen Cu as the example metal and tacked the

problem at multiple levels. At the smallest scale, McGaughey and Saidi have performed intensive DFT calculations to find the various intermediate and transition states of Cu-O configurations during the oxidation process. These results not only provided great insights in the understanding of the oxidation dynamics themselves, but also served as a data base and benchmark for Sinnott and Phillpot's work in the development of the Cu-O COMB force field, which is one of the most critical information needed in the force field development.

The major challenge for a successful KMC simulator is the access to an accurate rate table for the elementary steps that serve as the input parameters for TFOx, such as the adatom diffusion and nucleation probability (and sites). In order to obtain such information, the DFT results for the oxygen diffusion on the Cu surface along different surface directions are incorporated to distinguish the different diffusion probabilities, yet this is an extremely time-consuming task to determine all possible routes of Cu and O adatoms before the onset of Cu oxide nucleation and growth. The Ehrlich-Schwoebel barrier that controls the interlayer mass transport on 3D island has to be first calculated from an atomistic level and is currently being investigated [9].

The three collaborative groups have invested the oxidation on Cu surface and developed effective tools to describe the oxide film growth through theoretical approaches of multiple scales. Outcome from this research project provides great insight towards the understanding the early stage phase transition during the Cu surface oxidation, and the COMB force field and TFOx simulator developed from this project provides critical initial steps for the meso-scale simulation that allows direct comparison to experimental data. Results from this project also enhance the emergent field of predictive materials design for a critical surface reaction, oxidation.

5. Products
a. Publications

There are 9 peer reviewed journal articles published among these three research groups:

X. Han, R. McAfee, and J.C. Yang, *Development of a Versatile Kinetic Monte Carlo Code to Simulate Physical Processes in Thin Film Nucleation and Growth.* Multidiscipline Modeling in Materials and Structures, 2007. **3**(1): p. 12.

X.T. Han, R. McAfee, and 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.* Journal of Computational and Theoretical Nanoscience, 2008. **5**(1): p. 117-128.

M. Lee and A.J.H. McGaughey, *Energetics of oxygen embedment into unreconstructed and reconstructed Cu(100) surfaces: Density functional theory calculations.* Surface Science, 2009. **603**(24): p. 3404-3409.

M. Lee and A.J.H. McGaughey, *Role of sub-surface oxygen in Cu(100) oxidation.* Surface Science, 2010. **604**(17-18): p. 1425-1431.

M. Lee and A.J.H. McGaughey, *Energetics and kinetics of the c(2 x 2) to (2 √2 × √2)R45 degrees transition during the early stages of Cu(100) oxidation.* Physical Review B, 2011. **83**(16): p. 165447-1-8.

B. Devine, T.R. Shan, Y.T. Cheng, A.J.H. McGaughey, M. Lee, S.R. Phillpot, and S.B. Sinnott, *Atomistic simulations of copper oxidation and Cu/Cu2O interfaces using charge-optimized many-body potentials.* Physical Review B, 2011. **84**(12): p. 125308-1-17.

W.A. Saidi, M. Lee, L. Li, G.W. Zhou, and A.J.H. McGaughey, *Ab initio atomistic thermodynamics study of the early stages of Cu(100) oxidation.* Physical Review B, 2012. **86**(24): p. 245429-1-8.

Q. Zhu, C. Fleck, W.A. Saidi, A. McGaughey, and J.C. Yang, *TFOx: A versatile kinetic Monte Carlo program for simulations of island growth in three dimensions.* Computational Materials Science, 2014. **91**: p. 292-302.

Q. Zhu, W.A. Saidi, and J.C. Yang, *Step-Induced Oxygen Upward Diffusion on Stepped Cu(100) Surface.* Journal of Physical Chemistry C, 2014, Accepted.

b. Software Products

There are two computer resource developed in this project, including one COMB force field for the Cu-O interactions, and one KMC simulator named TFOx.

6. Computer Modeling
a. COMB Cu/O Force Field

The COMB potential aims to provide the flexibility to model dissimilar materials and with the transferability to describe varying bonding environments simultaneously. The physics in the empirical potentials contain two aspects: the bond order concept in the short-range interactions and the self-consistent. Since the electrostatic energy terms for an uncharged system are zero in COMB potential series, the bond order short-range interactions are attributed to the major component for the nonelectrostatic energy of a system. The selection of the bond order formalism in the COMB potential series originates from the Abell potential [22] derived from chemical pseudopotential theory. Later, the bond-order term was formulated by Tersoff to model covalent bonds in silicon [23].

The total potential energy ($U^{tot}[\{q\},\{r\}]$) of a system in the COMB potential series is composed of the electrostatic energies ($U^{es}[\{q\},\{r\}]$), short-range interactions ($U^{short}[\{q\},\{r\}]$), van der Waals interactions ($U^{vdW}[\{r\}]$), and correction terms

($U^{corr}[\{r\}]$), where $\{q\}$ and $\{r\}$ represent the charge array and coordinate array of the system, respectively:

$$U^{tot}[\{q\},\{r\}] = U^{es}[\{q\},\{r\}] + U^{short}[\{q\},\{r\}] + U^{vdw}[\{r\}] + U^{corr}[\{r\}]$$

In order to train a satisfactory COMB force filed for the Cu/O system, parameterization of atomic and metallic copper, molecular oxygen, copper oxide are carried out to achieve best agreement to high level *a,b* initio calculated results.

Since the original development of COMB potential, there has been three generations of COMB potential released. The original and the last generation, COMB and COMB3 potentials have been implemented in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [24], and is available as a pair style "pair_style comb". The Cu/O COMB force field has been distributed to users from more than 10 research groups and have resulted in a good influence to the MD simulation community. Documentation and user manual for COMB and COMB3 potentials can be found at:

http://lammps.sandia.gov/doc/pair_comb.html

b. TFOx KMC Simulator

TFOx simulator was originally written in Virtual Basic (VB), and is now powered by fast C++ console and glued by python user friendly interface. The simulation console is also enabled for parallel execution; thus large-scale calculations are feasible. The most recent TFOx-3D program allows the simulation of oxide growth in 3D space and provides significant improvement towards the originally 2D TFOx program.

TFOx simulator is constructed using the rejection free lattice-gas model on top of a Diffusion Limited Aggregation (DLA) model to solve the master equation of a dynamic process:

$$d\sigma_i = \sum_p \Gamma^+_{ip}(\sigma)dt - \sum_p \Gamma^-_{ip}(\sigma)dt$$

Atoms deposited on the film surface are subject to a random walk due to Brownian motion and can aggregate to form nuclei. In TFOx, the nucleation reaction is irreversible and is only limited by the diffusion. Through the inclusion of potential energy gradients, the elastic strain effect during oxide growth is accounted. Previous 2D TFOx implementation was limited to the study of adatom motion and island growth in a 2D lattice. For the most recent TFOx-3D program, we have extended TFOx to 3D growth where oxidation in the direction perpendicular to the interface can be simulated. This feature is a step forward towards a complete film growth simulation. Our results have shown that TFOx-3D can successfully reproduce the 3D oxide island structures observed in *in situ* experiments.

TFOx is now distributed through University of Pittsburgh Department of Chemical and Petroleum Engineering. The website for TFOx download is at:

http://www.engr2.pitt.edu/tfox/

The most recent version of TFOx is v 9.6.2, binaries for both Windows and Mac users are provided. Source code is also provided for advanced users. A user manual and tutorial are provided at the TFOx website as well.

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