Evolution of Nanoscale Film Morphology

(NSF Nanoscale Modeling and Simulation Grant EEC-0083604)

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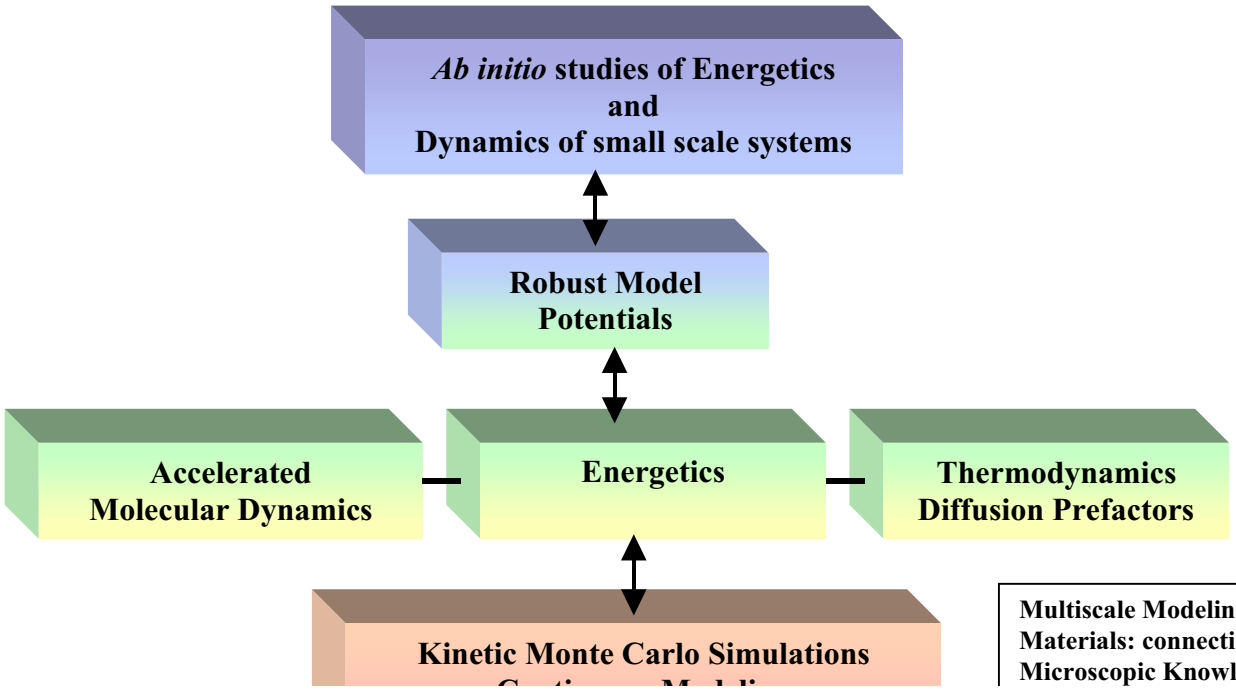
1. Research Objectives

The goal of the proposed research is to conduct a multi-scale computational and theoretical investigation of the evolution of thin film morphology on metal and semi-conductor surfaces. This topic has been chosen for several reasons. First, the ability to create interfaces with well-defined structures is technologically important in synthesizing interfacial materials with unique optical, electronic, catalytic, magnetic, and mechanical properties. Second, the understanding of growth processes at surfaces is important for scientific reasons. In particular, many of the kinetic processes that conspire to determine thin-film structure, such as cluster diffusion, are poorly understood. Similarly, full ramifications of predicted electronic effects in determining growth morphologies and the properties of the resulting films, are not well understood. Finally, a complete theoretical description of thin-film growth involves the application of a wide range of theoretical techniques ranging from *ab initio* electronic structure calculations and solid-state theory, to techniques of statistical mechanics, such as transition-state theory (TST), molecular-dynamics (MD), and kinetic Monte Carlo (KMC), to continuum modeling. Together, this collection of techniques addresses aspects of thin-film structure, dynamics, and properties ranging from the atomic level (Å lengths and ps times) to the laboratory scale (_s-s times and ~ nm - _m lengths). The seamless integration of these techniques will allow for unprecedented insight into the interactions and kinetics which ultimately determine the structure and properties of thin films. Further, the methods that we plan to develop and implement can be applied to a varietyof other applications in materials science, such as catalysis, chemical vapor deposition, diffusion and structural evolution of polymers, separations with molecular sieves, and microstructural design of solids. As prototype systems we are examining the evolution of the morphology of thin Ag films on Ag(111) and on strained Ag(111). We will also study the evolution of Ag films on Si(100) and Si(111). For Ag on unstrained and strained Ag(111) experimental data indicate large changes in activation barriers and diffusion prefactors with the introduction of surface strain. In the case Ag deposition on Si(111), the observation of isolated islands with strongly preferred heights and flat tops, rather than the expected pyramids, has led to the speculation that the growth mode maybe electronically driven.



Multiscale Modeling of Materials: connecting Microscopic Knowledge to

2. Methodology

The research will involve several nanoscale modeling strategies:

(1) *ab initio* electronic structure calculations for small-scale systems using density functional theory and quantum chemistry approaches for energetics, electronic effects, diffusion paths, and selected adsorbate vibrational modes;
(2) development of robust model potentials from parameterization of results from the proposed *ab initio* calculations and experimental data;
(3) application of recently developed accelerated MD code to examine novel cluster diffusion processes which may appear when simulations are performed for micro-milli seconds;
(4) determination, successively, of the vibrational dynamics, thermodynamics, diffusion prefactors and rates for small Ag clusters on the proposed substrates;
(5) calculation of energy barriers and diffusion paths for Ag clusters on proposed substrates using the model potentials;
(6) modeling of epitaxial growth for realistic system sizes (microns) using the calculated diffusion rates an energetics in kinetic Monte Carlo technique;
(7) continuum modeling of nanostructure relaxations using information from all of the above. An added strategy is to work in tandem with on-going experiments to provide constant feedback.

3. Proposed Projects

(a) Modeling at the Atomistic Level

Adatom Energetics, Vibrations, Pair Interactions, and Electronic Effects :

We propose to carry out a comprehensive study of the energetics of adatoms and dimers on Ag(111), on strained Ag(111), and on Si surfaces, using the *ab initio* electronic structure methods. For the metal on metal substrate systems DFT calculations will be performed using codes we have developed. The examination of Ag adatoms, and dimers on Si surfaces will be carried out by both DFT and quantum chemistry methods. Both sets of results will be used to develop the robust model potentials discussed below. Examination of vibrational dynamics of adatoms, and dimers on the four substrates will be valuable in determining the nature of the bonding between the adsorbed atoms and the substrate. They will also provide essential input for the calculation of the diffusion prefactors. The study of interactions between Ag atoms on Ag films on Si should provide insights into the electronic indirect interaction on metals: on the bare Si surface, the interaction between pairs of Ag atoms is expected to be purely repulsively and relatively isotropic (since Si is elastically relatively isotropic), decaying monotonically with separation. For thick Ag films, one should find indirect electronic interactions, as studied recently by Fichthorn. For thin films, the effects of strain may modify these indirect interactions.

Construction of Robust Interaction Potentials :

The goal of constructing a realistic and robust model interaction potential is many-fold: i) to calculate the activation barriers and diffusion paths of Ag clusters of different sizes and shapes (compact and irregular) on Ag and Si surfaces; ii) to calculate reliably the vibrational dynamics and hence the activation free energies and activation entropies for cluster diffusion on Ag and Si surfaces; iii) as input to the proposed accelerated molecular dynamics simulations; and iv) to perform large-scale simulations of epitaxial growth. We propose to develop environment sensitive interatomic potentials for Ag and for Ag/Si system for application to the extensive studies proposed here. These potentials will be constructed following the procedures already developed for monoatomic systems using information from ab initio calculations and experimental data.

Adatom and Small Cluster Diffusion :

Diffusion paths for a single atom on a flat, periodic surface can be determined accurately by *ab initio* methods supplemented by simple symmetry arguments. The situation becomes already difficult when it comes to the diffusion of a dimer as several mechanisms, involving the substrate atoms may compete. An *a priori* assumption of the diffusion paths may lead to overlooking some relevant and important ones. In a preliminary study of a Ag adatom descending from a small Ag island on Ag(111), we find that the identification of the minimum energy path and the diffusion mechanism required sophisticated techniques for mapping out the full potential energy surface. We are using a combination of techniques like eigenvector-following method and the Nudged Elastic Band method.

Accelerated MD Simulations for Long Time Simulations :

In an effort to extend the time scales that can be probed in MD simulations we are pursuing the recently proposed Step-Bias Method to accelerate MD simulations of systems for which dynamical evolution occurs via rare-event dynamics. In implementing this method, an N-body bias potential is used to raise the potential energy in regions other than the transition states. In doing this, we reduce the number of time steps spent in simulating motion in the potential-energy minima without violating the detailed balance criterion (because transition states are unaltered). Correct equilibrium and dynamical properties are achieved by using a time increment based on the principles of importance sampling.

(b) Beyond Atomistic Simulations: Modeling of Epitaxial Growth

Submonolayer Nucleation :

For growth of Ag films on Ag(111), a fundamental goal is to bridge the gap between atomistic KMC simulation of nucleation and growth, and continuum models of island evolution. The key step will be provided by solving continuum equations for the diffusion, and capture of deposited atoms by the complex distribution of islands on the surface. Detailed atomistic information on the relevant energetics and dynamics obtained in related studies will be crucial to developing effective KMC models for growth. We will also develop coarse-grained or continuum models for multilayer growth. Additionally we will treat the edges of islands in each layer with a continuum theory, but retain discrete vertical atomic layers. We will further coarse-grain to obtain a stochastic evolution equation for a continuous film height versus continuous lateral coordinate. The key challenge here is to determine the lateral mass currents (both the destabilizing uphill currents due to step-edge barriers, and any stabilizing downhill currents, e.g., due to downward funneling). This can be done exploiting atomistic information on energetics and deposition dynamics, which is input into specially tailored KMC simulations.

(c) Modeling at the Continuum Level

Descriptions of Nanostructure Relaxations :

Work on complex interfaces has concentrated on application of the continuum step model in which steps on surfaces are characterized by three macroscopic parameters: their stiffness (resistance to bending, so dependent on the energy of kinks and the temperature), the strength of the elastic (and entropic) repulsion between steps, and an appropriate measure of the ability of steps to move, such as kinetic coefficient/mobility or diffusion constant, depending on the atomistic process dominating step motion. The test of the valid has been whether the same set of parameters can describe a broad range of physical phenomena, e.g. phase diagrams, characteristic times of step fluctuations, size-dependent diffusion constants of single-layer clusters, unbunching rates of step bunches, electromigration of steps, electromigration of single-layer clusters, decay rates of mounds. We propose to look for similar behavior on various model nanostructures, working at the continuum limit. We also propose to look at barriers and prefactors near step edges, to see whether we can understand the microscopic processes which produce the observable macroscopic behavior. A goal is to zoom in on the small barriers leading to avalanches. We will investigate possible systematic differences between the metals we can consider. If possible, we would also like to tackle the harder analogous calculation for Si to try to understand why its decay is so different.

Some Relevant References:

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