A Thesis

entitled

GPU Enhanced Simulations of Glancing Angle Deposition of Metal Thin-Films

By

Xuejing Liu

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the Master of Science Degree in Electrical Engineering

______________________________
Dr. Jacques G. Amar, Committee Chair

______________________________
Dr. Lingfeng Wang, Committee Member

______________________________
Dr. Mansoor Alam, Committee Member

______________________________
Dr. Patricia R. Komuniecki, Dean

College of Graduate Studies

The University of Toledo
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An Abstract of

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Thin-films grown via glancing-angle deposition (GLAD) have interesting structural, mechanical, and optical properties and may be used for a variety of applications including sensors, optical filters, antireflection coatings, fuel cells, and magnetic data storage. However, due in part to the complexity of the resulting thin-film structures as well as to the large range of time- and length- scales, realistic simulations of the thin-film growth process for large deposition angles have in the past been difficult. As a result, typically only simulations of effective models of GLAD, or of more realistic models for smaller deposition angles, have been carried out.

As a first step in understanding the dependence of the surface morphology and microstructure in GLAD on deposition parameters, here we present the results of large-scale MD simulations of Cu/Cu(100) growth for the case of large deposition angle. In particular, by taking advantage of the speed of recently developed graphical-processing-units (GPUs) we have carried out large-scale GPU-enhanced MD simulations of Cu/Cu(100) growth up to 20 monolayers (ML) for deposition angles (corresponding to the angle with respect to the substrate normal) ranging from 50° to 85° and for both
random and fixed azimuthal angles. In general, we find good agreement with experiment results for the dependence of thin-film porosity on deposition angle and film-thickness. Results for the dependence of the surface roughness, lateral correlation length and microstructure (e.g. defect density, vacancy density, surface sites, and strain) on the deposition angle and film thickness are also presented.
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1 Introduction

1.1 Glancing Angle Deposition

Glancing angle deposition (GLAD) is a physical vapor deposition technique [1, 2] that exploits atomic shadowing effects to engineer thin-films with a wide variety of interesting nanostructures. Unlike many other thin-film growth processes (such as molecular beam epitaxy) in which the deposited atoms are typically deposited normal to the substrate, or chemical vapor deposition and sputtering in which the deposition angle is random and is not carefully controlled, in glancing angle deposition (GLAD) the geometry of deposition is controlled so that the flux of depositing particles arrives at a large (glancing) but well-controlled angle with respect to the substrate normal. By dynamically adjusting the azimuthal angle along with the polar angle and deposition temperature T (in order to control the size-scale) GLAD may be used to deposit thin-films with a range of different nanostructures including vertical or tilted pillars, springs, spirals, tubes, and branched or multi-component nanorods with different structural,
mechanical, electrical and optical properties (see Fig. 1-1 and Fig. 1-2).

1-1 (a) Schematic picture of glancing-angle deposition with a fixed azimuthal angle [3]. (b) Experimental Scanning electron microscopy (SEM) image obtained for GLAD SiO$_2$ film [3].

1-2 SEM cross-section images [5] of some nanostructures obtained by oblique angle deposition. All nanostructures are made of silicon. Figure 2 (a) corresponds to columnar growth with a rotating substrate (equivalent to a random azimuthal angle).

As a result, this technique has become popular as a method to control the nanostructure of deposited thin-films for a variety of applications including sensors, optical filters, antireflecting coatings, fuel-cells, and magnetic data storage. As a particular example which is of relevance to photovoltaic devices, transparent conducting oxide (TCO) thin-films deposited at a glancing polar angle lead to columnar growth, optical anisotropy, and low ordinary indices of refraction [4]. Such graded-index films can act as broadband anti-reflectors and thus maximize optical absorption. Therefore, it is of interest to understand the dependence of key quantities such as surface roughness,
porosity, and anisotropy as well as microstructural quantities such as defect density on deposition parameters.

Figure 1-1 shows a schematic indicating the geometry used in GLAD along with some cross-section SEM pictures showing the nanostructures which may be created. As can be seen, if the substrate is held fixed (corresponding to fixed azimuthal angle) the columnar structures are tilted towards the incident beam. In contrast, if the flat substrates are rotated about the surface normal (corresponding to a random azimuthal angle \( \phi \)) then vertical columns or nanorods are observed that broaden with increasing film thickness \( t \). Therefore, in order to compare the surface morphology and microstructure for these two cases, we have carried out simulations for both fixed and random \( \phi \).

In this thesis, the results of simulations of glancing angle deposition of Cu thin-films (grown on a Cu(100) substrate) are presented. In particular, we have carried out molecular dynamics simulations in order to study the dependence of the thin-film porosity, surface roughness, thin-film surface area, scaling behavior, and vacancy and defect density on film-thickness \( t \), deposition angle \( \theta \) and azimuthal angle \( \phi \). In order to carry out these simulations, we have developed a method which combines the use of a “one-atom” molecular dynamics simulation of the initial stages of deposition (for each of several atoms which are deposited simultaneously in different parts of the thin-film), with fully atomistic molecular dynamics simulations of the rest of the deposition process including relaxation of the entire film.

We note that in previous molecular dynamics simulations of oblique-incidence Cu/Cu(100) growth at low-temperature [10], the deposition process has been modeled by carrying out independent parallel molecular dynamics simulations over different
“chunks” of atoms surrounding each depositing atom. While this method is computationally efficient, due to the large magnitude of the thin-film roughness for large deposition angles (which can lead to conflicts due to “overlap” between different chunks) as well as the fact that depositing atoms can leave a selected chunk, it was only possible to simulate low to moderate deposition angles using this method, and as a result glancing-angle deposition (GLAD) could not be studied. In addition, while combined one-atom molecular dynamics and kinetic Monte Carlo simulations have also been carried out for high-angle Cu/Cu(100) growth at high temperatures [7,8,9], due to the low deposition rate and the enforcement of the “no-overhang” condition, these simulations led to mound formation rather than the typical columnar growth structures found in GLAD. As a result, previous simulations of columnar growth via GLAD deposition [4,6] have typically used effective models, in which each “particle” represents a cluster or group of atoms, while the deposited particles are assumed for simplicity to grow on a cubic lattice. In addition, the effects of the short-range attraction of the depositing atoms to the thin-film are not included. As a result, these “effective models” do not properly take into account the crystal structure and geometry, and in some cases this can lead to unphysical effects [11]. In contrast, our large-scale GPU-enhanced molecular dynamics simulations are able to properly take into account the crystal structure as well as defects along with a variety of relaxation processes and the effects of short-range attraction.
1.2 Thesis Outline

This thesis is organized as follows. In Chapter 2 we first discuss the Molecular dynamics (MD) simulation method, including details of the velocity-Verlet integration algorithm, and the use of different ensembles including the constant temperature (Langevin) ensemble. We also discuss the two interatomic interaction potentials which are used in this thesis - the Embedded-Atom Method (EAM) many-body potential and the Lennard-Jones (LJ) pair potential. In Chapter 3 we then discuss the computational methods used in our simulations including the use of CPU-based MD simulations based on the public-domain LAMMPS (“Large-scale Atomic/Molecular Massively Parallel Simulator) software and the use of chunks. We also discuss the use of the GPU-enhanced public domain HOOMD (“Highly Optimized Object-oriented Molecular Dynamics”) software in our large-scale MD simulations of Cu/Cu(100) glancing-angle deposition (GLAD) along with the use of a variety of computer languages, such as C, Python, Unix SED commands to control the simulation process. The details of our simulation procedure are also discussed. In Chapter 4, we then discuss the simulation parameters used in our GLAD simulations along with a variety of physical quantities measured in our simulation. These include the surface roughness, correlation length scale, scaled correlation function and porosity, in addition to microstructural quantities such as the vacancy and defect density, effective surface area, and the strain between layers. We
then present our simulation results in Chapter 5. In Chapter 6, we summarize our results and discuss the future work concerning GLAD thin-film growth.
2 Molecular Dynamics (MD)

Molecular dynamics (MD) is a widely-used computational tool for elucidating complex properties of liquids and solids at atomistic level in research areas such as chemistry, thermodynamics and several other areas. The basic idea of molecular dynamics is to calculate the forces, potential energy, velocities etc. of the atoms and molecules of the system, in order to obtain the corresponding dynamical evolution. In the most common case, the trajectories of atoms and molecules are determined by numerically solving Newton’s equations of motion for a system of interacting particles, where the potential energy and forces between the particles are defined by molecular mechanics force fields.

2.1 Velocity-Verlet Integration Method

One of the most popular integration methods used in MD simulations is the velocity-Verlet algorithm [12]. One of the major advantages of this method is that it is relatively easy to implement efficiently and also provides good numerical precision and
stability. Using this algorithm, which is based on a 2nd order Taylor expansion of the position and velocity as a function of time, the evolution of the positions and velocities of the atoms in a system may be calculated as follows:

- **Step 0 (Initialization):** Based on the current positions, calculate the local forces and accelerations \( \overrightarrow{a_i}(t) \) on each particle (assume the current velocities \( \overrightarrow{v_i}(t) \) are known) \( \overrightarrow{v_i}(t + \Delta t) \). The acceleration is calculated by calculating the derivative of the potential energy, e.g.,
  
  Eq. (2.1) \[ F_i = -\nabla_i V = m_i a_i \]

  where \( V \) is the potential energy of the system, \( F_i \) is the force on the \( i \)th particle.

- **Step 1:** Use the current velocities and accelerations to calculate the new particle positions after a small time-interval \( \Delta t \):
  
  \[ \overrightarrow{x_i}(t + \Delta t) = \overrightarrow{x_i}(t) + \overrightarrow{v_i}(t)\Delta t + \frac{1}{2} \overrightarrow{a_i}(t)\Delta t^2 \]

- **Step 2:** Calculate the new accelerations \( \overrightarrow{a_i}(t + \Delta t) \) from the interaction potential based on the new particle positions \( \overrightarrow{x_i}(t + \Delta t) \).

- **Step 3:** Use the average of the new and old accelerations to calculate the new velocities: \( \overrightarrow{v_i}(t + \Delta t) \):
  
  \[ \overrightarrow{v_i}(t + \Delta t) = \overrightarrow{v_i}(t) + \frac{1}{2} (\overrightarrow{a_i}(t) + \overrightarrow{a_i}(t + \Delta t))\Delta t \]

- **Step 4:** Set \( \overrightarrow{a_i}(t) = \overrightarrow{a_i}(t + \Delta t), \overrightarrow{v_i}(t) = \overrightarrow{v_i}(t + \Delta t) \) and \( \overrightarrow{x_i}(t) = \overrightarrow{x_i}(t + \Delta t) \) and go back to step 1 and repeat. Note that this algorithm assumes that the acceleration \( \overrightarrow{a_i}(t + \Delta t) \) only depends on the position \( \overrightarrow{x_i}(t + \Delta t) \), and does not depend on the velocity \( \overrightarrow{v_i}(t + \Delta t) \).
During each iteration, every one of the four steps above is performed sequentially for each atom in the system. After finishing the last step, the simulation time \( t \) is incremented by \( \Delta t \). Nevertheless, since a typical vibration period is \( 10^{12} \) s or 1 picosecond (ps), and the time \( \Delta t \) between calculations of a set of atomic coordinates/velocities must be significantly shorter than the period, a typical time-step in MD simulations of solid materials is of the order of \( 10^{-15} \) (s) or 1 femtosecond (fs). Moreover, knowledge of the force acting on each of the particles owing to its neighbors is required, because an MD calculation spends the major part of its computational time finding the atomic neighbors in order to evaluate the forces, and this large numerical calculation must be repeated every time-step. This makes this technique extremely computationally expensive. As a result, serial MD simulations are usually applied to small systems (up to a few thousand atoms) as well as for short periods of real deposition time (up to a few nanoseconds).

In spite of its practical restrictions, Molecular Dynamics has been and continues to be extremely useful in context of epitaxial growth. There are several reasons for its wide-spread use and popularity:

a) the method can be easily implemented

b) it provides exact dynamics for the chosen interatomic potential (no assumptions of on lattice behavior, known mechanisms of thermal behavior)

c) can be very accurate, if the potential is accurate

d) can probe time- and length-scales which are difficult to observe experimentally
2.2 Molecular Dynamics Ensembles

2.2.1 Microcanonical or NVE Ensemble

The Verlet algorithm described above applies to a system which is isolated and thus conserves energy. This is sometimes referred to as the microcanonical or (NVE) ensemble since in this case the quantities N (corresponding to the number of atoms), V (corresponding to the volume of the system) and E (corresponding to the total energy) are all conserved. In the microcanonical, or NVE ensemble, the system is isolated from changes in moles (N), volume (V) and energy (E). It corresponds to an adiabatic process with no heat exchange. A microcanonical molecular dynamics trajectory may be seen as an exchange of potential and kinetic energy, with total energy being conserved.

However, a real system is not usually isolated and is typically at some finite temperature determined by its surroundings. In general, the temperature of a system may be calculated using the relation:

\[
\frac{1}{2} m \sum_i v_i^2 = \frac{3}{2} N k_B T
\]

where \( T \) is the temperature, \( v_i \) is the velocity of each particle, \( N \) is the number of particles, and \( k_B \) is Boltzmann’s constant. Therefore, each energy E in the NVE ensembles corresponds to a given temperature and so to calculate the dynamics of the
system at a given temperature one needs to set the energy correctly. In order to conveniently set the temperature, and take into account the interaction of a system with the outside world at some temperature T, a different dynamics, sometimes referred to as the (NVT) ensemble is used. One way to do this involves the use of a Langevin thermostat, while using HOOMD (GPU-based MD simulator) this thermostat is referred to as Brownian dynamics.

2.2.2 NVT Ensemble Using the Langevin (Brownian) Thermostat

The basic idea of Langevin thermostat is to take into account the interaction of atoms with a “heat-bath” by allowing them to exchange energy with a fictitious system at a given temperature T. This may be performed by adding two fictitious forces $F_r$ (corresponding to a random force) and $F_f$ (corresponding to a damping force) to the force on each atom due to the other atoms in the system, e.g.: $\mathbf{F} = \mathbf{F}_c + \mathbf{F}_r + \mathbf{F}_f$, where

$$F_f = -\frac{m}{\text{damp}} v,$$

where $m$ is the mass of the particle, $v$ is its velocity, and damp is the damping factor specified by the user. $F_r$ is proportional to

$$\frac{k_B T m}{\sqrt{d t \text{damp}}},$$

where $k_B$ is the Boltzmann constant, $T$ is the desired temperature, $m$ is the mass of the particle, $dt$ is the timestep size, and damp is the damping factor. Random numbers are used to randomize the direction and magnitude of this force, where a uniform random number is used (instead of a Gaussian random number) for speed. $F_c$ is the conservative force computed via the usual inter-particle interactions. As can be seen from the above expression $F_r$ is a frictional drag or viscous damping term proportional to the particle's velocity. This
integrator only modifies forces to effect thermostating. Thus a separate time integrator, like NVE must be used to actually update the velocities and positions of atoms using the modified forces. When employing this method the desired temperature at each timestep is a ramped value during the run from $T_{\text{start}}$ to $T_{\text{stop}}$. The damp parameter is specified in time units and determines how rapidly the temperature is relaxed. The damping factor can be thought of as inversely related to the viscosity of the solvent.

A variety of thermostat methods is available to add and remove energy from the boundaries of an MD system in a more or less realistic way, approximating the canonical ensemble. For poor initial conditions that include overlapping atoms, a limit $dt$ in Brownian can be specified to the movement a particle is allowed to make in one time step. After a few thousand time steps with the limit set, the system should be in a safe state to continue with unconstrained integration.

### 2.3 Embedded-Atom Method (EAM) Potential

In the past, interatomic potentials have often been approximated by various pair potentials that incorporate long-range interatomic interactions and short range repulsion associated with inner electron shell forces. Since the force can be expressed as an explicit summation term for a pairwise potential, the pair potential model is very easy to implement in MD simulation. Unfortunately, the pair potential approach cannot handle the influence of the local environment on the atomic interactions which plays an important role in metals and semiconductors. Furthermore, since the local atomic
environment on the surface is different from the bulk, a classical pair potential model usually can not treat surface problems correctly.

In order to resolve this problem and take into account many-body effects, the embedded atom method or EAM [14] potential has been developed. In this method, the energy is assumed to be a function of a sum of functions of the separation between an atom and its neighbors. EAM potentials have been found to be particularly appropriate for metallic systems and as a result are widely used in molecular dynamics simulations.

By fitting EAM potentials to *ab initio* density functional theory (DFT) calculations for a variety of atomic environments, such as the perfect fcc metal, free surfaces, vacancies, interstitials, as well as to experiments one may obtain a practical model to account for the effects of the local environment on the potential energy. As will be discussed below, in the EAM, the energy of each atom is computed from the energy needed to embed the atom in the local-electron density as provided by the other atoms of the metal. The electron density is approximated by the superposition of atomic-electron densities. Since this density is well defined, for instance, at surfaces, there are no ambiguities involved in this approach. Computationally, the EAM energy can be evaluated with about the same amount of work as simple pair potentials. Therefore, it is still feasible to perform relatively large-scale computer simulations of a wide variety of phenomena. Thus the EAM provides a powerful technique for atomistic calculations of metallic systems.

The starting point of EAM is the observation that the total-electron density in a metal is reasonably approximated by a linear superposition of contributions from the individual atoms. The electron density in the vicinity of each atom can then be expressed
as a sum of the density contributed by the atom in question, plus the electron density from all the surrounding atoms. The latter contribution is a slowly varying function of position. By making the simplification that this background electron density is a constant (local density approximation (LDA)), the energy of this atom is the energy associated with the electron density of the atom plus the constant background density. This defines an embedding energy as a function of the background electron density and the atomic species. In addition, there is an electrostatic energy contribution due to core-core overlap. Correspondingly, the approximation for the total energy of a metal system has the following form:

\[ E_{\text{tot}} = \sum_i E_i^{\text{f}}(\rho_{\text{h},i}) + \frac{1}{2} \sum_i \sum_j \rho_{ij}(R_{ij}) \]

where \( \rho_{\text{h},i} \) is the host electron density at atom \( i \) due to the remaining atoms of the system, \( E_i^{\text{f}}(\rho) \) is the energy to embed atom \( i \) into the background electron density \( \rho \), and \( \rho_{ij}(R_{ij}) \) is the core-core pair repulsion between atoms \( i \) and \( j \) separated by the distance \( R_{ij} \). The electron density is, as stated above, approximated by the superposition of atomic densities,

\[ \rho_{\text{h},i} = \sum_j \rho_j(R_{ij}) \]

Since the electron cloud density is a summation over many atoms, usually limited by a cutoff radius, the EAM potential is a multi-body potential. For a single element system of atoms, three scalar functions must be specified: the embedding function, a pair-wise interaction, and an electron cloud contribution function. For a binary alloy, the EAM potential requires seven functions: three pair-wise interactions (A-A, A-B, B-B), two embedding functions, and two electron cloud contribution functions. Generally these functions are provided in a tabularized format and interpolated by cubic splines.
2.4 Lennard-Jones (LJ) Pair Potential

While EAM potentials are useful to simulate the detailed interactions between atoms once they are close to the substrate, in order to efficiently calculate the trajectories of the atoms during deposition, it is convenient to use a somewhat simpler Lennard-Jones pair-interaction potential for the deposition procedure. In particular, in our simulations of Cu/Cu(100) glancing angle deposition (GLAD), we have carried out a one-atom MD (Molecular Dynamics) of the depositing atom by using a Lennard-Jones (LJ) pair potential [13] of the form,

\[
V_{LJ}(r) = 4\epsilon\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6
\]

where \( \epsilon = 0.4093 \text{ eV} \) and \( \sigma = 2.337\text{ Å} \) to represent the interaction of the depositing atom with the bulk atoms from the cutoff distance \( r_{cut} = 2.35 \sigma \) to \( d_{impact} \) (where \( d_{impact} \) corresponds to a distance ranging from 3.0 Å to 4 Å, depending on the deposition angle as well as the different stages of the simulation). It was found that the results obtained using this potential (with cutoff distance \( 2\sigma \)) were essentially close to those obtained using a more sophisticated EAM Cu potential. As can be seen from Figure 2-1, the cutoff distance of LJ potential is equal to \( 2\sigma \) \( (r_{cut} = 2\sigma) \). If the distance between particles is increasing from 0 to \( r_{cut} \), the interaction potential changed from positive to negative, i.e. the interactions between the particles are changing from repulsive to attractive, and the repulsion is much very significant. Nevertheless if the distance is larger than \( r_{cut} \), there is
only attraction between them, and it’s becoming weaker and weaker as the distance
takes.

![](image)

2-1 Schematic picture of Lennard-Jones pair potential as a function of distance $r$ between
two particles.
Using LAMMPS and HOOMD to Simulate Thin-Film Growth

3.1 Molecular Dynamics (MD) Using LAMMPS

In order to simulate GLAD of Cu/Cu(100) thin-films, we first carried out MD simulations using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) molecular dynamics package. This package has a wide variety of potentials including the EAM potential, and is also known to be an efficient tool for parallel MD. In particular, we have investigated the use of the LAMMPS package to carry out MD simulations of GLAD at $T = 300$ K for relatively large system sizes. However, since in these simulations we only deposited one atom at a time, while our system was relatively large, an MD simulation of the entire system during deposition is wasteful and time-consuming. Therefore to improve the computational efficiency, we have carried out a slightly different procedure in which a full MD simulation was only carried out for the
thin-film atoms in the region of the depositing atom. In particular, our simulations were carried out in 4 stages:

(i) place the depositing atom at a random position \((x, y)\) parallel to the substrate and at height \(z\) equals to the maximum height of the film plus the interaction cutoff distance

(ii) carry out a ballistic deposition [13] simulation until the deposited atom is within a distance equal to the cutoff distance from the film

(iii) carry out a one-atom Lennard-Jones [9] MD simulation until the depositing atom is within a distance (impact distance) approximately equal to the nearest-neighbor distance from the film

(iv) Use this location to define (“carve”) a chunk of atoms corresponding to the deposition region for a full MD simulation. Then place the atom at the cutoff distance from the film, and carry out the full MD simulation for the depositing atom and the selected “chunk” atoms

As can be seen in Figure 3-1~3-3 (which offers top view, rotated view and side view of the inner sphere and two outer shells) the chunk of atoms surrounding the deposition site includes both nearby moving atoms (red), constant-temperature atoms (yellow) needed to remove the kinetic energy of condensation from the deposition region, and fixed atoms (green). In our study, we set the radius of the three spheres to be 8 Å, 10 Å, and 13 Å, i.e., the medium shell length is 2 Å, and the outer shell length is 3 Å. In order to mimic the isothermal deposition condition, we set atoms of three regions within the chunk to three different thermostats. The outer shell of the chunk consists of fixed atoms. The
trajectories of the rest of the atoms within the chunk are calculated integrating Newton’s equations of motion, with EAM potential for calculation of interatomic forces. The atoms within the buffer shell adjacent to the fixed shell, are set to Langevin thermostat, (which in turn can distribute the deposition heat within this region), as well as the atoms within the inner sphere are set to NVE ensemble. The atoms within the inner sphere are supposed to interact with the depositing atoms, while the atoms within the buffer region are used to dissipate the heat cause by the deposition.

3-1 Chunk of substrate atoms for MD simulation using LAMMPS (Top view).

3-2 Chunk of substrate atoms for MD simulation using LAMMPS (Rotated view).
As outlined above, the following procedure was used. For a given deposition angle and azimuthal angle, we first choose a depositing position with random x and y coordinates, while z coordinates are set as the height of highest atom in the system plus the LJ cutoff 2.35σ (where σ = 2.3377Å from LJ interaction potential) plus 0.01 Å. We then carry out ballistic deposition until the atom is within the LJ cutoff-distance from the film. A one-atom MD simulation is then carried out using the LJ potential until the depositing atom is within a distance (dimpact ≈ 3.0 - 4.0 Å) from the nearest substrate atom. We then carve out a chunk of substrate atoms (see Figures 3-4 ~ 3-5) surrounding the expected landing point. Once the chunk of substrate atoms is carved out, the moving atoms within the chunk are equilibrated for 1.5 ps (picoseconds) at the desired temperature. We then used LAMMPS to carry out a full MD simulation of the depositing atom plus chunk atoms (including all the moving chunk atoms) using the EAM potential.

While this method is relatively efficient and has been used previously for low-to-moderate deposition angles θ ≤ 60° [8], for high deposition angles θ > 70° we have found that the use of a deposition chunk leads to problems. In particular, for high deposition angles, the depositing atom can flow across the chunk and encounter the fixed region. To avoid this problem we could make the chunk bigger, but this makes the simulations much
more time-consuming and defeats our goal of carrying out efficient simulations over large length-scales. Accordingly, we have used a different method in which multiple atoms are deposited simultaneously in different regions of the substrate, while the entire system is simulated using parallel MD. In particular, it has been shown that for systems containing more than 10,000 atoms, MD simulations using a graphical processing unit (GPU) can be at least 100 times faster than a serial processor. Therefore, by using this method, we can not only speed-up our simulations, but also avoid any problems associated with atoms deposited near the edge of a chunk, and at the same time we have the advantage that all parts of the system are allowed to “relax” during the entire deposition period.

3.2 GPU Based Parallel MD Using HOOMD

While a parallel MD simulation of multiple atom deposition could be carried out using LAMMPS, to do so requires access to a large number of processors (CPUs). Alternatively, the recent development of graphics-processing units (GPUs) [16] has led to the ability to perform a large-scale parallel MD simulation on a single card. CPUs have few (two to eight) large, complex cores, while GPUs can have up to several hundred small, simple cores. These high-performance “many-core” processors of GPUs are increasingly being used to accelerate parallel computation efficiency. Unlike CPUs, GPU cores are not general purpose, but are focused solely on computation, with little support for I/O devices, interrupts, and complex assembly instructions. GPUs still require CPUs
to access data from disk, to exchange data between compute nodes in a multi-node cluster, and other tasks. CPUs are very good at executing serial tasks and as more and more cores are combined on a single chip, CPUs are becoming parallel as well. Only applications that have a substantial amount of parallelism can benefit from GPUs. By carrying out MD simulations on GPU clusters the computation can be parallelized at two levels: particle or domain decomposition for the computation of a single trajectory and parallel run of the bunch of trajectories at different cluster nodes. Contemporary GPUs provide tremendous computational power but at the same time require specific highly parallelized codes.

Recently a specific GPU-based MD package called HOOMD (Highly Optimized Object-oriented Many-particle Dynamics) has been developed for specific parallel MD computation on GPUs. Moreover it is based on the NVIDIA CUDA (Compute Unified Device Architecture) environment and is highly optimized with respect to the specific NVIDIA GPU architecture. To reduce the host-device data transfer most MD algorithms such as building of the neighbor list, calculation of inter-particle forces and solution of the equation of motion are performed on GPU. The user interface, python scripting and XML format used in HOOMD also make it very extensible and adaptable. The details of our GPU-enhanced parallel MD simulations of GLAD deposition are discussed in Chapter 4. However, here we first discuss the use of scripting, data files, and C programs to integrate our ballistic deposition and one-atom MD simulations with our parallel MD simulations carried out with HOOMD.
3.3 Continuous Simulation Model

In order to integrate our HOOMD simulations with our ballistic deposition and one-atom MD simulations we have used a variety of computer languages including, Unix stream-editor (SED), shell scripting, Python and C. The UNIX SED command is one of very early UNIX commands built for command line processing of data files and allows powerful and interesting data processing to be done by shell scripts. The best-known function is in-place editing of files (e.g., update the files). In particular, we have used the file-editing functions of SED to replace the matching occurrences in the line with a dedicated expression phrase to automatically update the data files and scripting files. Also the flow control function, managed by the use of a label and the branch instruction, was used to set threshold for the simulation. In addition, the instruction command followed by a valid label name was used to move procedure to the block following that label. If the label does not exist then the branch will end the script.

Since HOOMD uses python scripting and XML format data files, HOOMD input and output configuration files are all in XML format which can be easily modified by python. Here we have used Python to write input script for HOOMD simulations and extract positions and velocities from HOOMD output files to offer read-in configuration files for deposition procedure. Also we have used Python to combine specific information from hundreds of files to make a movie file for visualization.
In order to set-up the initial configurations for MD simulations carried out by HOOMD we have written several C programs. In particular, we first wrote a C program to create the initial substrate of Cu atoms, consisting of 128,000 Cu atoms with an fcc (face-centered-crystal) structure corresponding to 80 x 80 x 5 unit cells (4 atoms per unit cell), with 3 bottom planes of fixed atoms, 4 planes of Brownian-dynamics atoms, and 3 (top) planes of moving atoms. HOOMD was then used to equilibrate this system at a temperature $T = 300$ K. We then wrote an extensive “grid” code to:

i. read-in the latest thin-film configuration

ii. perform ballistic deposition for each of $n_{grid} \times n_{grid}$ atoms (where $n_{grid} = 8$) on a 2-dimensional grid at a distance equals to the $2.35\sigma$ (where $\sigma = 2.3377$Å). Here an additional check routine of cubic grid of atom positions (with “grid” or cube size equal to the EAM cutoff distance) was used to speed-up the calculation of the distance between each depositing atom and the atoms in the film

iii. perform a one-atom Lennard-Jones (LJ) MD simulation for all $n_{grid} \times n_{grid}$ depositing atoms until they reach a distance $d_{impact}$ (apprimitely equal to 3 - 4Å) from the thin-film

iv. carry out a full MD simulation using HOOMD for 2 ps of the entire film including the depositing atoms

Again, in this case the atoms were mapped to a cubic grid (with “grid” or cube size equal to the EAM cutoff distance plus an additional “shell” of 1 Å or so in order to minimize the frequency of updating the nearest-neighbor table) so that at each point of the simulation, only the interaction between the depositing atom and the film atoms in the neighboring 27 “grids” needed to be included.
3.4 Details of Simulations

3.4.1 Substrate Structure

3-4 Substrate crystal structure based on FCC cubic unit cell (system size 20 x 20 x 5 unit cells).

Figure 3-4 shows a substrate structure with 20 unit cells in both x and y directions and 5 unit cells in z direction, respectively. The FCC lattice unit cell is represented in Figure 3-5, as can be seen, the face-centered cubic (FCC) crystal structure with atoms only occupying the corner sites and every center of the facet of the cube. In our simulation the substrate contains 80 lattice units in x and y directions and 5 in z direction, respectively.

The lattice units correspond to the distance between two adjacent atom sites along the parallel direction of x, y or z direction (as denoted in Figure 3-5)
3.4.2 Deposition Procedure

As already mentioned, the model that we have used for our deposition process included ballistic deposition and one-atom Molecular Dynamics (MD) [9] deposition which correspond to the deposition process while the depositing atom flowing towards the substrate from the height equals to the maximal height of the substrate plus a cutoff distance $r_{cut}$, $(r_{cut} = 2.35\sigma, \sigma = 2.3377\text{Å})$, and the one-atom MD deposition trajectory starts from the end of the ballistic deposition at $r_{cut}$ until the nearest substrate atom is within the distance $d_{\text{impact}}$ equals to 3.0-4.0 Å which depends on different incident angles as well as different stages of the simulation. Following this procedure a full MD simulation for the entire system including depositing atoms was carried out for 2 ps.

The ballistic depositing position was chosen randomly at both $x$ and $y$ dimensions (parallel to the substrate) while in $z$ dimension the position was chosen at a height which is equal to the maximal height of the substrate plus the cutoff distance $r_{cut}$. To take into
account the effects of shadowing and crystal geometry, each depositing atom is assumed to travel ballistically which means parallel to each other without any interaction among the deposit atoms and the substrate atoms until the nearest atom from the substrate is within a distance of \( r_{\text{cut}} \).

Since the deposition angles in glancing angle deposition can be very large, the depositing atom needs to travel a long distance before it impacts with the substrate. In order to speed-up this part of the simulation, we have used a simplified method, corresponding to a one-atom MD of the depositing atom, using a Lennard-Jones Cu pair potential, with the remaining atoms held fixed. In this method, the substrate atoms were all held fixed at their lattice positions while a one-atom MD simulation of the trajectory of the depositing atom was carried out. In this case, the depositing atom was assumed to follow the trajectory determined by LJ pair potential until it impacts with the substrate at a defined distance at \( d_{\text{impact}} = 3.0\sim4.0\text{Å} \), which varies as we want to improve our efficiency of the very high angle deposition.

### 3.4.3 Full MD Using Parallel Deposition

While the ballistic deposition and one-atom MD simulations were carried out using the procedure described above using codes that we have written, the final stages of deposition and relaxation in which the depositing atom(s) are incorporated into the thin-film, were simulated by carrying out a full MD simulation of the entire system on a single GPU using HOOMD. Because the many-body EAM [15] Cu potential can realistically
describe the short-range interactions of the depositing atom and the thin-film as well as the interactions between all other atoms in the film, this potential was used for our GPU-enhanced full MD simulations. In order to further speed up this part of our simulations, we have simultaneously deposited 64 atoms (starting at random positions within an 8 x 8 grid) during each HOOMD MD simulation. Since our system size is \( L = 80 \text{ a} \) (where \( a = 3.615 \text{ Å} \) is the lattice constant of Cu) the use of such a grid implies that on average each depositing atom is sufficiently far apart that the depositing atoms do not interact (see below). Figure 3-6 shows an example grid with \( n_{\text{grid}} = 3 \) rather than 8 for simplicity. As can be seen, each grid square (solid lines) has been further divided into four sublattices [17] A, B, C, and D in order to further minimize the interaction between depositing particles. In particular, at each deposition stage, atoms are only deposited within one sublattice. Thus, for example for \( n_{\text{grid}} = 8 \) (3) we first deposit 64 (9) atoms within the A sublattice, then within the B sublattice, then the C sublattice, then the D sublattice etc. However, within a given sublattice the starting x and y position of the deposited atom is selected randomly within the sublattice, thus guaranteeing that for the case \( n_{\text{grid}} = 8 \), the initial x and y separations of each deposited atom will be at least equal to \( L/(2*n_{\text{grid}}) = (80 \text{ a})/16 = 5 \text{ a} \approx 18 \text{ Å} \) where \( a = 3.615 \text{ Å} \) is the lattice constant of Cu.
Diagram illustrating square sublattice decomposition on the substrate (top view of the substrate).

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4 Simulation Parameters and Quantities Measured

4.1 Simulation Parameters

In oblique angle growth, one modifies the substrate holder of a typical deposition system to be able to rotate and tilt. Due to the shadowing effect, the incident particles of a material that come to the surface with an oblique angle are preferentially deposited on the top of surface features with larger values in height. This preferential growth dynamic gives rise to the formation of isolated nanostructures. Figures 5-1 and 5-7 show typical simulation pictures of tilted columns and columnar copper structure obtained at large oblique angles (θ=60°~85°) measured from the surface normal with substrate rotation. Many nanostructures of technological interest besides columns can be obtained by simply controlling the deposition angle, deposition rate, rotation speed, and material specific parameters such as surface diffusion and crystal plane effects.

In order to study the dependence of the Cu/Cu(100) thin-film morphology and microstructure on deposition parameters, we have carried out GLAD simulations for
values of the deposition angle $\theta$ equal to 50°, 60°, 70°, 80°, 85°. In addition, in order to determine the effects of the azimuthal angle on the morphology, we have carried out simulations for both random azimuthal angle $\phi$ as well as for fixed azimuthal angle ($\phi = 0^\circ$, aligned with the substrate). In all cases, we have deposited 20 MLs (monolayers) while sublattice deposition with $n_{\text{grid}} = 8$ (corresponding to 64 atoms or 0.005 ML per deposition step) was used. Since in the experiments, the Cu atoms are obtained by vapor deposition, in our simulations the initial speed $v_0$ of our depositing atoms was assumed to be equal to $v_0 = \sqrt{4k_B T_m/m} = 8.43$ Å/ps where $k_B$ is Boltzmann’s constant, $T_m = 1357$ K is the melting temperature of Cu and $m$ is the mass of a Cu atom. In addition, in our HOOMD simulations we have used a time-step, $\Delta t = 0.005 \tau_{\text{HOOMD}} = 0.050$ fs, where $\tau_{\text{HOOMD}} = \sqrt{m N \varepsilon^2/\sigma}$ = 0.010 ps (where $m_N$ = 1.67 x $10^{-27}$ kg is the mass of a nucleon, $\varepsilon$ = 1 eV is the HOOMD unit of energy, and $\sigma$ = 1Å is the HOOMD unit of length. In addition, in all of our simulations we have assumed a substrate temperature $T = 300$ K corresponding to room-temperature. Unfortunately, because of confusion about the time unit $\tau_{\text{HOOMD}}$ used in HOOMD, the actual value of $v_0$ used in our simulations was approximately $\sqrt{63}$ times bigger, e.g. $v_0 = 67$ Å/ps, which implies that the initial kinetic energy corresponded to approximately 12.6 eV rather than the expected value given by $2k_B T_m = 0.2$ eV. While this energy is significantly larger than typical energies used in physical vapor deposition via evaporation, it is of the order of magnitude of typical deposition energies used in sputter-deposited GLAD thin-films. Accordingly, our simulations may provide a useful model of sputter-deposited thin-films. In addition, we note that each MD simulation carried out using HOOMD was carried out for 20,000 – 40,000 timesteps $\Delta t$, which corresponds to a typical deposition time $t_{\text{dep}} = 1 – 2$ ps. Since
each deposition corresponds to $\Delta \theta = 64/(80^2 \times 2)$ ML = 0.005 ML, the deposition rate $F$ used in our simulations, was $F = \Delta \theta/t_{dep} = 2.5 \times 10^9$ ML/sec. While this deposition rate is significantly faster than typically used in experiments (e.g. 1 - 100 ML/sec) we expect that since the dominant effects on the surface morphology in GLAD are due to shadowing along with the short-time (e.g. ps) relaxation events as atoms are deposited on the surface, our simulation results will be similar to those obtained experimentally.

4.2 Quantities Measured

In order to determine the dependence of the surface morphology on deposition parameters we have calculated a variety of quantities as a function of deposition angle and thin-film thickness including, the surface roughness or “width” $w$ corresponding to the root-mean-square (r.m.s.) height-fluctuations of the film, the lateral length-scale $\xi$ corresponding to the width of the columnar structures formed, the height-height correlation $G(r)$, and the thin-film porosity. In addition, we have also calculated a number of quantities related to the thin-film microstructure including the interstitial defect density, the density of non-fcc sites or twin-sites, the vacancy density, effective surface sites, and the strain in the vertical ($z$) direction. A more detailed discussion of the calculation of the surface width $w$, lateral length-scale $\xi$, correlation function $G(r)$ and porosity $P$ is provided later in this section.

As can be seen in Figures 5-1 and 5-7, with increasing film-thickness and deposition angle, the film becomes rougher and more porous. In order to quantify this
dependence we have calculated the porosity $P$, corresponding to the fraction of empty space in the thin film as a function of thickness $t$ and incident angle $\theta$. Here $P$ may be calculated using the expression $P = 1 - \frac{N_v}{V}$, where $N$ is the number of atoms deposited, $v = a^3/4$ is the volume per atom in the fcc crystal structure and $a$ is the lattice constant of Cu, and $V = h_{\text{max}}L^2a^2$ is the total volume, and $h_{\text{max}}$ is the maximum height above the substrate.

In order to further quantify the dependence of the surface morphology on thickness and deposition angle we have also measured the surface roughness or “width”, $w$, corresponding to the r.m.s. height-fluctuation as a function of film thickness $t$ using the following expression,

\[ w^2 = \frac{1}{N} \sum_{i=1}^{N} (h_i - \bar{h})^2 \]

where the summation is over all substrate lattice sites $r_i$, $h_i$ is the maximum height of the film at site $i$, and $\bar{h}$ is the average height. In addition, we have also estimated the typical lateral length-scale $\xi$ by calculating the circularly-averaged height-height correlation function,

\[ G(r) = \langle \frac{1}{N} \sum_{i=1}^{N} (h(r_i + r) - \bar{h})(h(r_i) - \bar{h}) \rangle_c \]

where the brackets correspond to a circular average over all possible directions $r$ along the substrate. The average lateral correlation length or feature size $\xi$ is then defined as equal to the value of $r$ corresponding to the first minimum of $G(r/\xi)$ (see Figure 5-6).

In order to analyze the microstructural properties, we have also measured several other parameters including the number of interstitial defects, non-fcc sites, and vacancy sites by mapping all of the atoms into fcc crystal sites as well as non-fcc sites. The defect
density can be calculated as the ratio of the number of interstitials plus non-fcc sites to the number of depositing atoms. The interstitials are defined as the atoms occupying positions in between the fcc sites instead of belonging to any crystal structure sites. While the non-fcc density can be expressed as number of non-fcc sites divided by the number of depositing atoms, where non-fcc sites (twining atoms) corresponding to those atoms occupying the non-fcc sites instead of staying at the fcc sites. The vacancy density corresponds to the ratio of the number of vacant lattice sites to the number of depositing atoms. In order to understand the morphology of thin films by oblique deposition, we have also measured the effective surface area [6] since this may be significantly enhanced by oblique incident deposition owing to columnar formation and increasing with the deposit angles. Figure 5-17 shows a relative surface area of the simulated thin films, where the relative surface area is defined as the surface atoms over the number of atoms in one monolayer (ML). We also calculated the surface site density which, defined as the ratio of the number of surface site atoms to the number of substrate bulk atoms.

Since the thin-film growth is a nonequilibrium process, we can investigate whether the thin film is compressed or stretched by calculating the strains among those monolayers (ML). The strain can be defined in the following expression [10],

\[
\varepsilon = \frac{d_{\text{layer}} - a_{\text{half}}}{a_{\text{half}}}
\]

where \(d_{\text{layer}}\) measured as the distance between layers, and \(a_{\text{half}}\) corresponds to the bulk (100) plane spacing which is equal to half of the lattice constant \(a\) (where \(a = 3.615 \text{ Å}\)).
5 Results Analysis

5.1 Thin-Film Morphology

We now discuss our simulation results for the dependence of the thin-film morphology on deposition angle and azimuthal angle. Since the morphology for the case of fixed azimuthal angle is somewhat different from that for the case of random deposition angle, we first discuss this case.

5.1.1 Fixed Azimuthal Angle

Figure 5-1 shows the typical morphology obtained in our simulations for the case of a fixed azimuthal angle ($\phi = 0^\circ$) for different values of the deposition angle $\theta$ ($\theta = 50^\circ$, $60^\circ$, $70^\circ$, $80^\circ$, and $85^\circ$) at two different thicknesses corresponding to $t = 10$ ML and $t = 20$ ML. As can be seen, the surface roughness increases with deposition angle $\theta$ and film-thickness $t$, while at a critical angle corresponding to approximately $70^\circ$, there is a
transition from rippled growth, in which the ripples run perpendicular to the deposition direction, to columnar growth with well-defined columns oriented in the direction of the deposition flux. We note that the rippled growth behavior for small deposition angles is similar to that which has been observed previously [14] in both temperature-accelerated dynamics and molecular dynamics simulations of Cu/Cu(100) growth at $\theta = 60^\circ$. However, the columnar growth observed for $\theta \geq 70^\circ$ has not been previously observed in large-scale molecular dynamics simulations of thin-film growth since most previous simulations have focused either on deposition at small and/or moderate angles or on deposition rates corresponding to mound/ripple formation rather than columnar growth.
Thin-film pictures for fixed azimuthal angle $\phi = 0^\circ$ for different deposition angle $\theta = 50^\circ, 60^\circ, 70^\circ, 80^\circ, 85^\circ$, and two different thicknesses, 10 ML and 20 ML.
Porosity \( P \) as a function of deposition angle \( \theta \), and different thicknesses (6 ML, 10ML, and average of 12-20 ML) for the case of fixed azimuthal angle \( \phi = 0^\circ \).

Figure 5-2 shows our results for the porosity \( P \) as a function of deposition angle at both low coverage (corresponding to film thicknesses \( t = 6 \) ML and 10 ML) and at higher coverage (\( t = 12-20 \) ML). As can be seen, the porosity increases rapidly with increasing deposition angle. We note that for the case of fixed azimuthal angle, Poxson et al [18] have developed a theoretical expression of the form, \( P = \frac{\theta \tan \theta}{c + \theta \tan \theta} \), where the constant \( c \) is a fitting parameter related to the diffusion length and the volume of a typical nanocolumn, and \( \theta \) is depositing angle.

The solid curve in Figure 5-2 shows the best fit to our data obtained using this form the above porosity expression, corresponding to a value of \( c \) given by \( c = 3.5 \). As can be seen there is good agreement with this form for large deposition angles although
the agreement is not quite as good for smaller deposition angles. Interestingly, in oblique-angle deposition of ITO (indium-tin-oxide) nanoporous films, Poxson et al found that a similar value, e.g. $c = 3.55$ gave very good agreement with experiments, even though the scale of the nanopillars was significantly bigger.

We note that for $t \geq 10$ ML, Figure 5-2 indicates that the porosity is relatively independent of film-thickness for $\theta \geq 70^\circ$. Surprisingly, this result indicates that over this range of deposition angles the porosity saturates at relatively low film thicknesses. However, for smaller deposition angles, e.g. $\theta = 50^\circ$ and $60^\circ$, the porosity tends to decrease somewhat over this range. This can be seen more clearly in Figure 5-3.

5-3 Porosity ($P$) as a function of thickness (in ML) for deposition angle $\theta = 50^\circ$, $60^\circ$, $70^\circ$, $80^\circ$, and $85^\circ$, and fixed azimuthal angle $\phi = 0^\circ$. 

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Surface roughness, or width $w$, as a function of film thickness (in ML) and deposition angles, for fixed azimuthal angle $\phi = 0^\circ$.

Figure 5-4 shows a log-log plot of our results for the dependence of the surface roughness $w$ on film thickness $t$ for $\theta = 50^\circ - 85^\circ$. As can be seen, the surface width or roughness increases with increasing film thickness and deposition angle. While there is an initial “transient” behavior up to 8-10 ML, for larger thicknesses we find that the roughness grows as $w \sim t^\beta$ where the value of $\beta$ increases from $\beta \approx 0.30$ for $\theta = 50^\circ$ to $\beta \approx 0.80$ for $\theta = 85^\circ$. We note that a similar dependence of the roughness exponent $\beta$ on deposition angle has recently been observed in kinetic Monte Carlo simulations (in the absence of overhangs [9]) of a generic model of oblique-angle metal(100) deposition for which the deposition rate is significantly (e.g. 5-6 orders of magnitude) lower.
Correlation length $\xi$ as a function of film thickness and deposition angle $\theta$, for azimuthal angle $\phi = 0^\circ$.

The corresponding results for the dependence of the lateral correlation length $\xi$ on thickness and deposition angle are shown in Figure 5-5. As can be seen, the lateral correlation length increases rapidly with increasing film thickness and deposition angle. In particular, the exponent $n$ describing the dependence on film thickness (e.g. $\xi \sim t^n$) increases from a small value (e.g. $n \sim 0.2 - 0.3$) for $\theta = 50^\circ - 60^\circ$ (for which ripples are observed) to a somewhat higher value, e.g. $n \sim 0.5$ for $\theta = 70^\circ - 85^\circ$, corresponding to columnar growth. We note that this value of $n$ is close to that observed in low-temperature GLAD columnar-growth of Ta, Nb, and Cr [20].
5-6 Scaled correlation function $G(r/\xi)$ at different thicknesses, from $t = 2\text{ML}$ to $t = 14\text{ML}$, for deposition angle $\theta = 80^\circ$ and fixed azimuthal angle $\phi = 0^\circ$.

Figure 5-6 shows a typical plot of the scaled correlation function $G(r/\xi)$ for $\theta = 80^\circ$ and $\phi = 0^\circ$ for thicknesses ranging from $t = 2\text{ML}$ to $14\text{ML}$. As can be seen there is relatively good scaling up to $8\text{ML}$. However, at for large film thickness the scaling is not as good. This is most likely because we have averaged $G(r)$ over all lateral directions in order to obtain an average lateral correlation length, while for large film-thicknesses the anisotropy due to the fixed deposition angle becomes significant.
5.1.2 Random Azimuthal Angle

We now present results for the case of a random azimuthal angle $\phi$. Figure 5-7 shows pictures of the typical morphology obtained in this case for different values of the deposition angle $\theta = 50^\circ, 60^\circ, 70^\circ, 80^\circ, \text{and} 85^\circ$ at two different thicknesses corresponding to $t = 10 \text{ ML and} t = 20 \text{ ML}$. 
Thin-film pictures for random azimuthal angle $\phi$ for different deposition angles $\theta = 50^\circ, 60^\circ, 70^\circ, 80^\circ, 85^\circ$, as well as two different film thicknesses, 10 ML and 20 ML.

As for the case of fixed deposition angle, as can be seen in Fig. 5-7 for the case of random deposition angle the surface gets rougher with increasing deposition angle and film thickness, while a transition is again seen from rippled growth to columnar growth at
an angle of approximately 70°. However, in this case for small deposition angles there are ripples running both parallel and perpendicular to the x-axis (e.g. along both preferred crystalline orientations) while for large deposition angles columnar growth is again observed but with the columns growing in the vertical direction. Interestingly, while the tilted nanocolumns in the case of fixed azimuthal angle for θ = 80° and 85° are relatively narrow and uniform, in the case of random azimuthal angle, the nanocolumns are wider and significantly more irregular.

5-8 Porosity (P) as a function of deposition angle θ and different thicknesses (6 ML, 10ML, and average of 12-20 ML) for the case of random azimuthal angle φ.

Figure 5-8 shows the corresponding porosity P as a function of deposition angle at both low coverage (t = 6 ML and 10 ML) and at higher coverage (t = 12-20 ML). We note that in this case there is better scaling (e.g. the porosity depends less on film thickness) even for small deposition angle. In addition, the porosity is slightly lower than
for the case of fixed azimuthal angle. As a result, the best fit to the porosity of the form of Poxson et al’s expression with a somewhat higher value of $c$, e.g. $c = 4.0$ than obtained for the case of fixed azimuthal angle.

5-9 Porosity ($P$) as a function of film thickness (in ML) for deposition angle $\theta = 50^\circ$, $60^\circ$, $70^\circ$, $80^\circ$, and $85^\circ$, for random azimuthal angle $\phi$.

In order to investigate the correlation of porosity and coverage, we plot the corresponding dependence of the porosity on film thickness for different deposition angles. As can be seen from Figure 5-9, the dependence on film thickness is relatively even for high deposition angles. A comparison between our porosity results for fixed and random azimuthal angle $\phi$ is also shown in Figure 5-10. As can be seen, the porosity is only slightly lower for random azimuthal angle than for fixed azimuthal angle.
Porosity as a function of deposition angle $\theta$ for both fixed azimuthal angle $\phi = 0^\circ$ and random azimuthal angle, two lines corresponding to experimental results of SiO$_2$ and ITO.

We now consider the surface roughness and lateral coarsening behavior for this case. As can be seen in Figure 5-11, in this case we find that the surface roughness $w$ increases approximately linearly with film thickness for $t > 10$ ML for all deposition angles, although the roughness is much larger for large deposition angles. This behavior is completely different from that obtained for the case of fixed azimuthal angle (for which the growth exponent depended strongly on deposition angle) and may be explained by the approximately “vertical” growth of the nanocolumns in this case.
5-11 Surface roughness, or width $w$, as a function of film thickness (in ML) and deposition angle $\theta$, for random azimuthal angle $\phi$. 
5-12 Correlation length $\xi$ as a function of film thickness and deposition angle $\theta$ for random azimuthal angle $\phi$.

In contrast, the behavior of the lateral correlation length as can be seen from figure 5-12, is very similar to that already found for the case of fixed deposition angle, e.g. the coarsening exponent $n$ increases from a value of approximately $0.2 - 0.3$ for small $\theta$, to a value close to $\frac{1}{2}$ for large $\theta$. As shown in Figure 5-13, in this case the scaled correlation function $G(r/\xi)$ exhibits much better scaling as a function of film thickness than for the case of azimuthal deposition angle. This is perhaps not surprising, since in this case there is no preferred orientation, and as a result the circular average is appropriate.
5.2 Thin-Film Microstructure

We now consider the effects of glancing-angle deposition on the thin-film microstructure. Figure 5-14 shows the defect density due to interstitials and non-fcc sites as a function of film thickness at different deposition angles $\theta = 50^\circ$, $60^\circ$, $70^\circ$, $80^\circ$ and $85^\circ$ for both fixed $\phi$, and random $\phi$. While in all cases the defect density increases with film thickness, for small deposition angles ($\theta < 70^\circ$) the defect density is relatively small. However, for large deposition angles ($\theta \geq 70^\circ$) the defect density becomes quite large.
reaching more than 20% for $\theta = 85^\circ$ at thickness $t = 20$ ML. The large defect density for these angles is most likely due to grain-boundary twinning atoms which occur at large deposition angles due to the formation of (111) facets and the corresponding deposition of atoms on non-fcc (e.g. hcp) sites rather than fcc sites. Interestingly, the defect densities are a little bit higher for the case of random $\phi$ than for the case of fixed $\phi$ ($\phi = 0^\circ$). Figure 5-15 shows the density of non-fcc atoms, also known as twinning atoms as a function of film thickness and deposition and for both random and fixed azimuthal angle. The non-fcc density corresponds to the ratio of the number of non-fcc sites to the total number of deposited atoms. As for the higher incident angles like $\theta = 80^\circ$ and $85^\circ$, the depositing atoms are more likely to form the (111) facet, combine with the factor that there is no significantly energy difference for atoms to deposit either on fcc sites or non-fcc sites, accordingly the non-fcc sites account for the majority of the defect density.

5-14 Defect density, including interstitials and twinning atoms (non-fcc sites atoms) as a function of film thickness and deposition angle for (a) fixed azimuthal angle $\phi = 0^\circ$ and (b) random azimuthal angle.
5-15 Non-Fcc site density as a function of film thickness for different deposition incident angle $\theta = 50^\circ$ to $85^\circ$ for (a) fixed azimuthal angle $\phi = 0^\circ$ and (b) random azimuthal angle.

We now consider the thin-film vacancy density. Figure 5-16 shows our results for the vacancy density as a function of film thickness and deposition angle for both fixed and random azimuthal angles. In good agreement with previous MD and accelerated MD simulations [10] of Cu/Cu(100) growth with $\theta = 50^\circ$ and fixed deposition angle, as we can see from Figure 5-16 the vacancy density is relatively small (e.g. a few percent) but increases rapidly with film thickness. Similar behavior is found for the case of random deposition angle, although in this case the vacancy density is several times smaller. Thus, in general we find that the vacancy density for random azimuthal angle is smaller than for fixed deposition angle, perhaps because shadowing plays a weaker role due to the isotropic azimuthal angle. However, surprisingly our results indicate that for very large deposition angles $\theta = 70^\circ$ - $85^\circ$ the vacancy density is smaller than for $\theta = 50^\circ$ and $\theta = 60^\circ$. We believe that this large decrease in the vacancy density with increasing deposition angle may be related to the change in morphology over this range of angles from “ripple”
growth to columnar growth, since deposition-induced vacancy healing due to impact induced heating will be more effective for a columnar structure than for a ripple structure.

5-16 Vacancy density as a function of film thickness in ML at different incident angles from 50° to 85° for (a) fixed azimuthal angle $\phi = 0^\circ$ and (b) random azimuthal angle.

As can be seen from Figure 5-17, the surface site density increases with increasing film thickness and deposition angle for both the case of fixed azimuthal angle and random azimuthal angle. This can be explained as for much higher angle deposition the more nanocolumnar structures growing owing to shadowing effects, therefore the effective surface area can be enhanced by high glancing deposition angle [6]. The vacancies are much harder to exist if there are significant amount of surface atoms, where vacancy corresponds to a hollow position surrounded by four atoms. Consequently, there is likely a way to understand why we got more vacancy for lower angles like 50°, and 60°, and significantly lower vacancy for higher angle 80° and 85°, while 70° is a critical angle for vacancy. We also calculated surface sites density which corresponds to the ratio expression of surface/volume. As can be seen from Figure 5-17, the surface site density is
increases with deposition angle as well as film thickness and is much higher for random $\phi$ than for fixed $\phi$. Interestingly the surface sites density increases linearly with thickness for different incident angles, which can be explain as the followed discussion. Since for the GLAD with randomly rotated substrate, the columnar structure are roundly and preferentially formed that the size of columnar structure is responsible for the surface density increasing.

5-17 Surface site density $n_{\text{surf}}/(2L^2)$ as a function of film thickness and deposition angle for (a) fixed azimuthal angle $\phi = 0^\circ$ and (b) random azimuthal angle $\phi$.

Finally, we consider the dependence of the thin-film strain on deposition angle, azimuthal angle, and film-thickness. As can be seen in Figure 5-18, during the early stages of growth (corresponding to a few ML) there is significant compressive strain for both fixed and random azimuthal angles. This initial compressive strain may be understood simply as due to the relaxation of atoms near the surface which are missing bonds. In both cases, for low deposition angles the average compressive strain decreases with increasing film thickness, due to the fact that the average lattice constant now
includes a significant contribution from atoms which are far below the surface. However, for larger deposition angles, more atoms remain near the surface for large film-thicknesses, and as a result the average compressive strain does not decrease as rapidly. In particular, for $\theta = 80^\circ$ and $85^\circ$ and $t = 20$ ML there is still a net compressive (e.g. negative) strain due to the fact that a larger number of atoms are near the surface as a result of the columnar morphology.

5.18 Compressive strain as a function of film thickness and deposition angle and for (a) fixed azimuthal angle $\phi = 0^\circ$ and (b) random azimuthal angle $\phi$. 


6 Conclusion and Future Work

In this thesis we have carried out large-scale GPU-enhanced molecular dynamics simulations of glancing-angle deposition (GLAD) of Cu/Cu(100) growth. In particular, we have studied the effects of deposition angle and azimuthal angle on the thin-film morphology and microstructure. In contrast, to previous work which was limited to deposition angles less than 60°, by using GPUs to carry out a full-scale molecular dynamics (MD) simulation for each deposition event, we have been able to study the morphology for very large deposition angles, e.g. θ = 70° - 85°, for which columnar growth is observed.

Interestingly, despite the fact that our system is relatively simple, we have found very good agreement between our simulation results for the dependence of the porosity on deposition angle, and previous GLAD experiments of more complicated systems of interest in photovoltaics such as SiO₂ and indium-tin-oxide (ITO). The good agreement between our simulation results and experiments indicates that the dominant contribution to the porosity is the effect of shadowing, and that more detailed effects such as atomic relaxation and surface deposition have a relatively weak influence. However, because our
deposition rate is much higher than in the experiments, the length-scale of our nanostructures at high deposition angles (e.g. 10-60 nanometers) was found to be significantly smaller than the typical experimental length-scale (e.g. typically 50 – 200 nm).

Our results also indicate that while there are some significant differences in the surface morphology between the case of fixed azimuthal angle and random azimuthal angle (for example, the surface roughness increases linearly for random azimuthal angle even for moderate deposition angles, while for fixed azimuthal angle it increases much more weakly) the porosity depends only weakly on azimuthal angle. In addition, to the porosity, we have also studied the dependence of a variety of other quantities describing the surface morphology such as the surface roughness and lateral length-scale on deposition parameters. As for the case of porosity, we find that the surface roughness and lateral length-scale depend strongly on the deposition angle while the surface roughness also depends strongly on the deposition angle.

In addition to the surface morphology, we have also studied the dependence of the thin-film microstructure on deposition parameters. In particular, we have studied the dependence of the vacancy density, defect density, surface atom density, and strain on film thickness, deposition angle, and azimuthal angle. Surprisingly, we have found that for large deposition angles ($\theta \geq 70^\circ$) the defect density is much higher than was found in previous simulations for angles less than or equal to $60^\circ$. We believe that this enhancement in the defect density for large deposition angles, is due to the formation of (111) facets which leads to the formation of stacking faults, e.g. growth at non-fcc sites. Interestingly, our results also indicate that the defect density is higher for the case of
random azimuthal angle than for the case of fixed azimuthal angle. These results may also explain our observation that for large thicknesses (20 ML) the compressive strain in the thin-film grown with a random azimuthal angle is larger than for the case of fixed azimuthal angle.

We now consider some possible extensions of this work. While our simulations have demonstrated that it is possible to get a basic understanding of the dependence of the thin-film morphology and microstructure on deposition parameters by the use of molecular dynamics simulations, for the case of large deposition angles (corresponding to columnar growth) as well as moderate deposition angles, the deposition rate used in our simulations (e.g. $F = 2.5 \times 10^9$ ML/sec) is much higher than that used in experiments. Therefore, in the future it would be of interest to study the dependence of the thin-film morphology on deposition rate by varying the deposition rate in our simulations. With access to faster and more GPUs this may be possible in the near future. We note that recently, Mukherjee, Zhou, and Gall [21] have studied the experimental temperature-dependence of the lateral length scale in GLAD growth for the case of random deposition angle for a variety of different metal films and have found interesting scaling behavior for the dependence of the surface morphology on the homologous temperature $T/T_m$ where $T_m$ is the melting temperature. Therefore, it would also be of interest to carry out additional MD simulations at different temperatures in order to understand the temperature-dependence. Finally, we note that it may eventually be possible to carry out a fully realistic simulation on time-scales approaching experimental time-scales by carrying accelerated dynamics simulations. While such simulations are quite demanding,
they may also lead to a better understanding of the formation and healing of defects as well as of the evolution of grain boundaries which may occur during growth.
References


Appendix A

Source Code for UNIX SED Code

```bash
#PBS -l walltime=168:00:00
#PBS -l nodes=1:ppn=8,feature=gpu
#PBS -N cuda-cam
#PBS -j oe
module load cuda-4.0
cd $HOME/

$Npart $Tatoms $Igroup $tag_max
Igroup=1
Tatoms=384000
Npart=128000
tag_max=128063

while [[ $Npart -lt $Tatoms ]]
do
    python extract.py $Npart
    sed -e's/Npart=128000/Npart='$Npart'/g' <grid.c>gridtemp1.c
    sed -e's/Igroup=1/Igroup='$Igroup'/g' <gridtemp1.c>gridtemp11.c
    gcc gridtemp11.c -lm -o gridtemp11.out
    ./gridtemp11.out
```

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mv profile.txt profile$Npart.txt
cat configv.xml >> velocity.txt
cat velocity.txt >> config.xml

mv xue_slab.xml xue_slab$Npart.xml

hoomd input.hoomd $tag_max
until [ -f slab.xml ];
do
    echo 'other sleepy time'
sleep 5
done

Npart=`expr $Npart + 64`
Igroup=`expr $Igroup + 1`
tag_max=`expr $tag_max + 64`
done
from sys import argv

input=open("slab.xml","r")
everything=[]
positions=[]
velocities=[]
natoms=int(argv[1])
pos=0
vel=0
count=0
fake=384000-natoms
for guy in input.readlines():
    everything.append(guy.strip())
    if (guy.strip().split(" ")[0]=='<position>':
        pos=count
    if (guy.strip().split(" ")[0]=='<velocity>':
        vel=count
    count=count+1
output=open("profile.txt","w")
for i in range(pos+1,pos+1+natoms):
    print >> output, everything[i]
output.close()

output=open("velocity.txt","w")
print >> output, '<velocity>'
for i in range(vel+1,vel+1+natoms):
    print >> output, everything[i]
if (fake%12800==0):
    output=open("frame.xyz","w")
    print >> output, natoms
    print >> output, 'Atoms'

    for i in range(pos+1,pos+1+natoms):
        print >> output, 1, everything[i]

    output.close()
Appendix C

HOOMD Input Script

from hoomd_script import *
from sys import argv
max=int(argv[1])
init.read_xml(filename="config.xml")
eam=pair.eam(file='Cu01.eam.alloy', type='Alloy')
fixed=group.tags(name="fixed", tag_min=0, tag_max=38399)
constTemp=group.tags(name="constTemp", tag_min=38400, tag_max=102399)
moving=group.tags(name="moving", tag_min=102400, tag_max=max)

integrate.mode_standard(dt=.005)
integrate.bdnvt(group=constTemp, T=.025851, seed=100)
integrate.nve(group=moving)

compute.thermo(group=moving)
analyze.log(filename='mylog.log', quantities=['temperature'], period=100, header_prefix='#')

xml=dump.xml()
xml.set_params(position=True, velocity=True)

#dump.mol2(filename="atoms.dump", period=30)
#mol2=dump.mol2()

run(40000)
xml.write(filename="slab.xml")