A Dissertation
entitled
Multi-scale Simulations of Thin-Film Metal Epitaxial Growth

by
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Submitted as partial fulfillment of the requirements for the
Doctor of Philosophy Degree in Physics

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College of Graduate Studies

The University of Toledo
August 2008
An Abstract of

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The main objective of the work presented in this thesis is to contribute to the understanding of how the growth conditions may affect the surface morphology during deposition. In thin film growth physical processes in a very wide range of time and length scales are relevant. A set of quite different methods of modelling is required when aiming at a more or less complete realistic picture of the growth process. Accordingly, both computer simulations/modelling and analytic calculations were employed in our studies of thin film growth. In particular, a hybrid multi-scale model, which combines a kinetic Monte Carlo simulation for the thermal surface diffusion with a Molecular Dynamics simulation of deposition events, was developed and successfully employed to study Cu/Cu(100) growth at a range of substrate temperatures and deposition angles. Predictive capabilities of this model allowed us to explain a number of puzzling experimental observations. Another accomplishment presented in this thesis is an analytic calculation of the surface current and selected mound angle for the case of epitaxial growth on fcc(111) surface. The results of this calculation help to understand the morphologies observed experimentally for a wide range of systems.
and deposition conditions.
Acknowledgments

Many thanks to my research advisor, Prof. Jacques G. Amar, for his guidance during my stay at UT, for the interesting projects I had an opportunity to work on, and for his open-mindedness in allowing me to explore on my own. Thanks as well to Dr. Yunsic Shim for his help and many stimulating discussions.

I would also like to thank all faculty and staff members of the Department of Physics and Astronomy for their various forms of support during my graduate study. Special thanks to my committee members - Prof. Robert W. Collins, Prof. Sanjay V. Khare, Prof. Nancy D. Morrison and Prof. Arunan Nadarajah.
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Chapter 1

Introduction

1.1 Thin film growth

Thin films can be grown in numerous different ways. Depending on the particular application, one may wish to produce either atomically flat or nano-structured surface. A wide variety of vapor deposition methods has been introduced for synthesizing the crystals which can be used in commercial applications. They include sputtering, chemical vapor deposition (CVD), and molecular beam epitaxy (MBE). These deposition routes provide access to a wide range of deposition rates, incident atom energies, angles of deposition, and substrate temperatures.

Among the different realizations of epitaxial growth, MBE is a particularly clear-cut one. Crystals grown by MBE form the basis for today’s most advanced device structures in solid-state physics, electronics and optoelectronics. In this technique, an adsorbate material is heated in an oven, which is contained in an ultra-high vacuum chamber. The evaporating particles form an atomic beam which is directed onto a
substrate crystal. As they arrive at the surface particles are incorporated and contribute to the growing film upon the substrate. MBE has become a well-established technique for the production of high-quality crystals, as it allows for a very precise control of the growth conditions. It is, for instance, possible to control the amount of deposited matter with an accuracy of a single monolayer. MBE is applied, for example, in the growth of layered semiconductor heterostructures for electronic devices, or in the development of thin magnetic films for novel storage media. MBE plays also a significant role as a tool in the design of nano-structures, such as Quantum Wires or Dots. The range of materials used in MBE includes conventional semiconductors, elementary metals, metal-oxides, and organic molecules.

Growth in an MBE environment is clearly far from equilibrium, as the system is constantly driven by the deposition flux and an extremely low pressure is maintained in the vacuum chamber. The rich variety of complex far-from-equilibrium morphologies which can form during deposition contrasts with simple equilibrium structure of epitaxial films. These complex morphologies result from the inhibition on the time-scale of deposition of various equilibrating surface diffusion processes, and their formation can be influenced dramatically by the deposition geometry. All these features make MBE very attractive from a theoretical point of view, as it provides a workshop in which to put forward analytical approaches and develop tools for the simulation of more general non-equilibrium systems.

In MBE, physical processes in a very wide range of time and length scales are relevant. Accordingly, a set of quite different methods of modelling is required when aiming at a more or less complete realistic picture of the growth process.
Figure 1-1: Characteristic time and length scales for various materials simulation methods

1.2 Introduction to multi-scale modelling

Multi-scale computational modelling of materials behavior is currently becoming a reliable tool to underpin scientific investigations and to complement traditional theoretical and experimental research. Multi-scale modelling usually consists in conveniently piecing together a hierarchy of numerical models operating at particular scales. The methods currently used in materials science simulations at various length and time scales (see Fig. 1-1) are (non-exhaustive list with characteristic time and length scales):

a) Density functional theory (DFT), quantum molecular dynamics (MD) (timescale \( \leq \) ns, length-scale \( \leq \) nm). \textit{Ab initio} methods are capable of describing electronic in-
interactions between a few hundreds of atoms over extremely short time scales (in case of quantum MD). They are used for calculating properties, such as band structures, cohesive energies and activation barriers (which can be used as an input for the next level methods, such us classical MD, and KMC simulation).

b) Classical Molecular Dynamics (timescale $\leq$ ms, length-scale $\leq$ 100 nm). Electronic interactions are represented by empirical potentials in classical MD models, thus enabling the simulation of the real atomic motion in systems up to $10^5$ atoms over up to $10^{-3}$ s.

c) Monte Carlo techniques (timescale $\leq$ $10^3$ s, length-scale $\leq$ 10$\mu$ m). Kinetic Monte Carlo (KMC) models, which are generally lattice based, are capable of simulating atomic motion in systems consisting of more than $10^6$ atoms over typically $10^3$ s. KMC models do not provide a description of atomic interactions as accurate as MD models, but they have a unique potential of bridging atomic scale and microscopic scale in a simulation.

d) Continuum methods (timescale $\leq$ $10^4$ s, length-scale $\leq$ 10 m). Continuum equations, typically in the form of deterministic or stochastic partial differential equations, are formulated from basic principles, such as the conservation of energy or momentum, etc. Such methods permit one to examine macroscopic regions in space over extended periods of time.

There are two basic multi-scale approaches:

1) Hierarchial methods

2) Hybrid or concurrent methods.

In hierarchial modelling first simulations at the higher resolution are performed
Figure 1-2: Example of successively implemented concurrent coupling of length scales: simulation of crack propagation in silicon [4]. A quantum-mechanical model of bonding, semi-empirical tight binding (TB), employed in the region of dynamical breaking bonds, surrounding the crack tip; TB region is embedded into the atomistic molecular dynamics (MD) region, which is, in turn, surrounded by the continuum region, where the finite elements (FE) method is applied. The acronym, MAAD, stands for “macro-atomistic ab initio dynamics”.
and properties that were extracted are used as an input in the next level method. Hybrid multi-scale simulation concept is based on the development of methods allowing for the consideration of multiple scales simultaneously. The approach of hierarchial modelling is the most developed one and is widely employed. The hybrid methods that permit concurrent simulations seem to be more interesting, since one would have to perform just one calculation to simulate the behavior of a material system, but for the time being such approach is much less employed. Some of the latest perspective approaches for coupling of length/time scales are described in Refs. [1, 2, 3, 4].

The scheme that is better suitable for solving a particular materials science problem would be the one that would facilitate the coupling of the methods briefly described above in one “product”. Further development of hybrid methods, wider use of DFT calculations and their integration into multi-scale simulations is, perhaps, the most important, but also the most difficult challenge for the next years.

1.3 Scope of this thesis

In this thesis the epitaxial metal thin-film growth is studied theoretically using both computer simulations/modelling and analytic calculations.

In chapter 2 the influence of the effects of deposition geometry on growth behavior in metal(100) epitaxy is studied in general, using a hybrid KMC-MD multi-scale simulation model. Somewhat simplified models for deposition and surface diffusion are employed to cover a wide range of possible deposition conditions. The dependence of the surface roughness and the anisotropy of the surface morphology on the
deposition geometry is elucidated and typical scenarios are discussed.

In chapter 3 the same hybrid multi-scale concept is employed to study Cu/Cu(100) growth at a range of substrate temperatures and deposition angles. The KMC model designed specifically to describe thermal Cu/Cu(100) diffusion is used now, along with more sophisticated deposition scheme to describe more accurately the atom-surface collision event during the deposition process. Strong influence of deposition angle on growth behavior at low deposition temperatures is demonstrated and a long-standing puzzle (disagreement of two different experimental results for the growth behavior of Cu/Cu(100) at 160K) is solved.

Chapter 4 presents the results of large-scale MD simulations of Cu/Cu(100) and Ag/Ag(100) growth at very low growth temperatures, such that the growth is not epitaxial and defects become important. The idea of small-scale MD simulation of deposition process (for each deposition a chunk of substrate atoms is carved out from the substrate to simulate the impact event) is implemented; this allows to reach large length-scales in the simulation of growth. Specifically, the dependence of compressive strain accumulation, vacancy (and other defects) density in the growing film, on the angle of deposition is studied. These results are used, along with simulated X-ray diffraction patterns, to explain a number of puzzling and intriguing experimental observations. In particular, it is demonstrated that the experimentally observed behavior could only be explained by taking the angle of deposition into account.

In chapter 5 an analytic calculation of the surface current and selected mound angle for the case of irreversible epitaxial growth on an fcc(111) surface is presented. The dependence of the surface current and selected mound slope on the Ehrlich-
Schwoebel step barrier, the degree of uphill funneling, due to short-range attraction, and other growth parameters is discussed for the two different kinds of steps on fcc(111) surface (so called, A and B steps).

Chapter 6 summarizes the results of the preceding chapters and formulates the main conclusions.

In the next sections of this chapter we describe in more detail KMC and MD simulation techniques, as well as a hybrid KMC-MD multi-scale model, used to obtain the most of the results described in this thesis.

1.4 Kinetic Monte Carlo simulation technique

KMC has become one of the most widely used tools in the modelling of epitaxial growth. The success of the approach is due to the fact that it is extremely flexible and versatile. Conceptually very simple models can be used in the investigation of basic, perhaps universal properties. It is quite straightforward to set up, for instance, a simple cubic model with only a few distinct surface diffusion rates. Such a system can be implemented very efficiently and already allows for the study of various essential phenomena.

For the most of the time during MBE crystal growth there is no non-thermal atomic mobility on the surface. Only the thermal diffusion of atoms is active. KMC is a very efficient way to evolve the surface for this time in between the deposition events, given a model for the thermal diffusion. The key step in designing a KMC model for the thermally activated diffusion events on the surface of the growing crystal
is the setting up of the catalogue of possible events. Closely related and equally important is the assignment of rates to the considered processes. For each type of diffusion process we evaluate its rate as \( R_i = \nu \exp(-E_i/k_BT) \), where \( \nu \) is an attempt frequency \((\sim 10^{12} \text{ s}^{-1})\), \( E_i \) is the energy barrier which characterizes the corresponding thermally activated move, and \( k_BT \) is a typical thermal energy in the system, i.e. the higher the temperature, the more frequent becomes the event.

The faithful representation of all relevant events in a KMC simulation can be quite involved. The potential extension to island mobility and other concerted processes would make the catalogue of events even more complex. For practical reasons, or because the required detailed information about the rates is simply not available, one frequently resorts to simplifying schemes. The aim is to capture the essential features of a material system. In some cases it is possible to find efficient parameterizations of the relevant barriers in terms of a small number of independent quantities. Bond counting schemes have been particularly successful in this context. The idea is to consider only a few distinct barriers, but to take into account the energies of the involved binding states explicitly. In particularly simple schemes only the energy of the initial state determines the rate, whereas, in general, initial and final configurations are considered. One of the parameterizations for diffusion barriers which we have used in our simulations will be described in Chapter 3.

After the catalogue of possible events with the corresponding energy barriers has been set up, the simulation is completely defined. For every atom on the surface we examine if it can potentially make a lattice jump in any of the processes described in the catalogue of events, and if so, we add these specific atomic moves and their rates
to a list of all possible diffusion processes the given surface configuration can evolve by. Also included into the list is the deposition rate, given by the deposition flux times the substrate area. In every loop of the program, with a probability proportional to its rate, one particular atomic move is chosen from the list of potentially possible diffusion processes. After the execution of the move, the surface configuration and the list of potential processes is updated accordingly, taking advantage of the fact that there will be only local changes.

Given a certain configuration of the system, the next process, say event number \( i \), has to be selected with the correct probability \( R_i / \sum_{i=1}^{N} R_i \). The simplest realization of the correct selection requires only one random number \( \psi \in [0, 1] \): the event \( i \) which satisfies the condition:

\[
\sum_{k=1}^{i-1} R_k < \psi \sum_{k=1}^{N} R_k \leq \sum_{k=1}^{i} R_k \tag{1.1}
\]

is chosen and performed. The costly linear search, which requires \( \sim N \) operations can be replaced by more sophisticated tree-like representations of the catalogue of events (see Fig. 1-3). The following algorithm can be used to perform the MBE growth simulation:

1. Set the start time \( t = 0 \).

2. Update the list of all possible event types that can occur and rates for each type in the system.

3. Construct a binary tree where each node contains the sum of the rates below the node (see Fig. 1-3) and the lowest level nodes contain the sums of the rates for
Figure 1-3: A binary tree including the sums of transition rates for events of the same type at the lowest level, and the cumulative rate at higher levels. The arrows indicate the direction of descend when choosing the type of event to be executed. The highest node contains the total activity rate of the system $S_{total}$.

the events of the same type: $S^0[i] = n[i]R[i]$. The top of the tree $S_{total} = S^k[0]$ is a total activity rate of the system, where $k$ is the number of levels.

4. Generate a random number $\psi \in [0, S_{total}]$ and start from the top of the tree ($n = k$, $i = 0$).

5. Compare the number $\psi$ with the left branch $S^{n-1}[2i]$.

6a. If $\psi \leq S^{n-1}[2i]$, descend to the left branch $n \rightarrow n - 1$, $i \rightarrow 2i$ (see Fig. 1-3) and continue from 5.

6b. If $\psi > S^{n-1}[2i]$, update the random number $\psi \rightarrow \psi - S^{n-1}[2i]$ and descend to the right branch $n \rightarrow n - 1$, $i \rightarrow 2i + 1$ (see Fig. 1-3). Continue from 5.

6c. If the lowest level $n = 0$ has been reached, generate another random number $u \in [0, n[i]]$ and perform the event $j$ for which $n^{j-1}[i] < u \leq n^j[i]$.

7. Update the tree.

8. Update the time $t = t - \ln(r)/S_{total}$, where $r \in (0, 1]$ is a random number.
Because there is a thermally activated diffusion move or a deposition event in every loop of the program, KMC is a very efficient method, and can bridge the gap of time scales: between relatively fast thermal diffusion processes and rare deposition events. One of the major disadvantages of the KMC simulation is that all event rates have to be known in advance. The method itself can do nothing to predict them, and they can only be obtained from the fits to growth experiments, or, using other simulation techniques, such as, MD simulations, or \textit{ab initio} calculations.

\subsection{1.5 Molecular Dynamics simulation technique}

In MD simulation the trajectories of each atom are followed through time by integrating Newton’s classical equations of motion. The integration is performed in a stepwise manner over finite time steps. The forces driving the motion of the atoms are computed from the gradient of the potential energy of the system with respect to the positions of each particle: 

\[ F_i = -\nabla_i V = m_i \frac{d^2 \mathbf{r}_i}{dt^2} , \]

where \( V \) is the potential energy of the system.

We can consider, as an example, one of the most popular integrators, the velocity-Verlet method, which we use in our MD simulations. The following algorithm is iterated:

\[ \dot{\mathbf{r}}_i(t + \frac{\Delta t}{2}) = \dot{\mathbf{r}}_i(t) + \frac{\Delta t}{2m} \mathbf{F}_i(t) , \]
\[ \mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta t \, \mathbf{\dot{r}}_i(t + \frac{\Delta t}{2}), \]
\[ \mathbf{F}_i(t + \Delta t) = -\frac{\partial V}{\partial \mathbf{r}_i(t + \Delta t)}, \]
\[ \mathbf{\ddot{r}}_i(t + \Delta t) = \mathbf{\dot{r}}_i(t + \frac{\Delta t}{2}) + \frac{\Delta t}{2m} \mathbf{F}_i(t + \Delta t). \] (1.2)

At each iteration, each of the four steps is performed sequentially for every atom \( i \) in the system. After exiting the last step, the simulation time is incremented by \( \Delta t \).

However, since the lattice vibration frequencies are in the \( 10^{12} \) Hz range, the time \( \Delta t \) between calculations of a set of atomic coordinates/velocities must be very short.

Since knowledge of the force acting on each of the atoms owing to its neighbors is required, an MD calculation spends a major part of its computational time finding the atomic neighbors and evaluating the forces, and this large numerical calculation must be repeated every femtosecond or so, and this technique is extremely computationally expensive. As a result, serial MD simulations usually applied to small systems (up to a few thousand atoms) and 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) Exact dynamics for the chosen interatomic potential (no assumptions of on-lattice behavior, known mechanisms of thermal behavior)

c) Very accurate, compared to experiment, if potential is accurate
d) Can probe the behavior that is unavailable from experiment

1.5.1 Embedded atom method (EAM) potentials

We note again that the results of MD or KMC simulations are only as accurate as the underlying interatomic potential. In the past, interatomic potential has been approximated by various pair potentials that incorporated long range interatomic interactions and short range Coulomb repulsion associated with inner electron shell forces. Since the force can be expressed as an explicit summation term for pairwise potential, the pair potential model is very easy to implement in MD simulation. Unfortunately, the pair potential approach can not handle the influence of the local environment on the atomic interactions. Systems such as metals and semiconductors can not be modelled with pairwise potentials. 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.

The EAM is based on density functional theory (DFT) and provides a practical model to account for the effect of the local environment on the interaction between the atoms due to inclusion of the many-body terms necessary to describe a variety of atomic environments, such as the perfect fcc metal, free surfaces, vacancies, interstitials. 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.

Within the framework of DFT, the electronic energy for an arbitrary arrangement of nuclei can be written as a unique functional of the total-electron density. The starting point of EAM is the observation that the total-electron density in a metal is reasonably approximated by 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 the metal system has the following form:

$$ E_{tot} = \sum_i F_i(\rho_{h,i}) + \frac{1}{2} \sum_i \sum_{j(\neq i)} \phi_{ij}(R_{ij}) $$

(1.3)

In this expression, $\rho_{h,i}$ is the host electron density at atom $i$ due to the remaining
atoms of the system, $F_i(\rho)$ is the energy to embed atom $i$ into the background electron density $\rho$, and $\phi_{ij}(R_{ij})$ 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,

$$\rho_{h,i} = \sum_{j(\neq i)} \rho_j(R_{ij}) \quad (1.4)$$

where $\rho_j(R_{ij})$ is the electron density contributed by atom $j$.

To apply this method, the embedding functions, pair repulsions, and atomic densities must be known.

### 1.6 Hybrid KMC-MD method

Hybrid KMC-MD method is a multi-scale model that combines a kinetic Monte Carlo simulation for the thermal surface diffusion with a small scale molecular dynamics simulation of every single deposition event. In MBE growth deposition rate is typically very slow ($\sim 1$ monolayer/min). The idea behind the KMC-MD method is precisely that the depositions are rare events. For the most of the time during the crystal growth there is no non-thermal atomic mobility on the surface. Only the thermal diffusion of atoms is active. KMC is a very efficient way to evolve the surface for this time in between the depositions. Once in a great while (on the time scale of diffusion) a deposition event occurs. We depart from the standard way of simulating crystal growth with KMC in the way we handle the deposition events. Usually in
KMC simulation when a deposition event is chosen to happen, a new atom is simply introduced at the random surface lattice site. Instead, we carry out a MD simulation of deposition process. This serves several purposes.

First of all, the atom-surface collision is described correctly, which includes the transient mobility of freshly deposited adatom, as well as possible rearrangements of the surface atoms induced by the impact. A deposited atom arrives with a certain momentum at the surface. Some additional kinetic energy may be gained while travelling to the surface via the attractive interaction with the atoms of substrate. For homo-epitaxial metal systems the energy transfer is very efficient, and the incoming atom generally slows down quickly. Also, in the crystalline environment the excess energy dissipates away very quickly due to phonons. Consequently, non-thermal mobility is limited to a very short period of time after the collision. Furthermore, for not-too-high incoming energies, the collision-induced mobility is fairly short ranged. For these reasons, it is enough to run a single deposition event simulation for only a few pico-seconds, and include only the local region in the vicinity of the landing point into MD simulation.

Secondly, the mentioned above interaction of depositing atom with the atoms of substrate may have a significant effect on the particle’s trajectory and may lead to a deviation of the actual landing point from the deposition site expected in case of ballistic trajectory for depositing atom. Such steering effects have been observed explicitly in, e.g., metal epitaxy. The strength of the steering effect increases for off-normal angles of deposition.

Finally, it is worth mentioning, that traditional KMC simulation does not allow
studies of growth processes in which the incoming atoms are deposited under the angle with respect to substrate normal. Such an off-normal deposition geometry may have a significant impact on the surface morphology of the growing crystal due to non-local shadowing effects and the effects of long range attraction between a depositing atom and the atoms of substrate. These effects could be naturally taken into account if deposition process is represented by MD simulation.

More detailed description for an MD simulation of a deposition process will be given in the next chapters. Here we briefly describe the process in the most general form. During an initial stage of a deposition the depositing atom trajectory is determined using the pair-interactions with the atoms of the substrate, which are held fixed at this stage. The type of this interaction is a long-range (LR) Van der Waals attraction. As soon as the depositing atom has reached a specified cutoff distance to the nearest substrate atom, we switch to the multi-atom MD for simulation of the impact event. For this purpose we carve out the chunk of substrate atoms surrounding the expected landing point, using the KMC site-occupancy information. Then follows the MD simulation of the atom-surface collision. After having done the MD simulation, we feed KMC simulation with the final position of the depositing atom, and take into account possible atomic rearrangements on the surface, induced by the impact event. After that all atomic mobility is once again thermal and we continue with KMC simulation of diffusion moves until the next deposition event.

A major advantage of the method described above is that it allows one to evolve the surface of the growing thin film without making any simplifying assumptions about the deposition related processes - they are modelled accurately by molecular
dynamics (∼1\text{ps}, ∼1\text{nm}), whereas the thermally activated diffusion processes which take place in between the deposition events are modelled very efficiently by KMC (∼\text{hours}, ∼100\text{nm}). The incorporation of KMC and MD into the on-going simulation, capable of overcoming this huge gap in time scales (and an apparent gap in length scales), seems to be a particularly promising route to more complete description of epitaxial growth processes.
Chapter 2

Effects of shadowing and steering in oblique-incidence metal(100) epitaxial growth

2.1 Introduction

Recently there has been a great deal of interest in understanding the detailed mechanisms controlling the surface morphology in epitaxial growth.[5, 6] While much of the theoretical effort has focused on understanding the effects of various surface relaxation processes, such as the Ehrlich-Schwoebel barrier to interlayer diffusion[7] and edge- and corner diffusion,[8, 9, 10] recently attention has also focused on the deposition process. For example, in recent glancing angle deposition experiments on Cu/Cu(100) growth by van Dijken et al.[11, 12] which were carried out at constant deposition rate, a dramatic dependence of the surface morphology on deposition angle
was observed. In these experiments a series of transitions was observed from symmetric mound structures for deposition angles up to $\theta = 55^\circ$ (where $\theta$ is the angle between the beam and the substrate normal), to asymmetric mounds with increasing slopes for deposition angles up to $70^\circ$, to asymmetric ripples oriented perpendicular to the beam with (113)/(111) facets on the shadow/illuminated sides at $\theta = 80^\circ$, and finally to symmetric pyramidal structures with (111) facets at $\theta = 85^\circ$. In addition, it was found that grazing incidence Co/Cu(001) growth [13] and Co/SiGe templates on Si(100) growth [14] generates a strong uniaxial magnetic anisotropy due to the surface anisotropy produced by oblique deposition.

Motivated in part by these experiments, as well as by earlier experiments on Cu/Cu(100) growth of Ernst et al, [15] recent theoretical studies[16, 17, 18] have shown that even in the case of normal incidence deposition, the effects of steering due to the short-range (SR) attraction of depositing atoms to step-edges can significantly enhance the surface roughness. In addition, recent multiscale simulations of the early stages of Cu/Cu(100) and Cu(100) vicinal growth[19, 20] have demonstrated that at large deposition angles, the long-range (LR) van der Waals attraction of depositing atoms to the surface can also play an important role. However, because of the extremely time-consuming nature of these simulations, only very recently has it become possible to extend these simulations to multilayer growth.[21, 22]

Recently, a simplified model with ballistic deposition was used[23], in order to show that many of the qualitative and semi-quantitative features observed in high-angle oblique incidence growth by van Dijken et al,[11, 12] can be explained by geometrical (shadowing) effects. The results presented in Ref. [23] also indicated that the for-
formation of (111) facets is crucial to the formation of ripple structures at large angles of incidence. A second transition from ripples to rods oriented parallel to the beam was also observed at high incident angles and large film thickness. However, these results do not take into account the effects of SR and LR attraction. Therefore it is of interest to determine to what extent these effects might alter the surface morphology, as well as the picture previously presented in Ref. [23]. In addition, we note that while it is of interest to carry out detailed simulations of a specific system, such as Cu/Cu(100) growth[19, 22] it is also interesting to carry out simulations in which the deposition parameters and conditions such as attraction, azimuthal angle, growth temperature etc. can be easily varied in order to obtain a general understanding of the contributions of different effects to the surface morphology.

In this chapter we present the results of extensive simulations of a model of metal(100) growth which is similar to that studied in Ref. [23], but in which the additional modifying effects of SR and LR attraction have been included. Our results indicate that the qualitative picture presented in earlier ballistic deposition simulations,[23] including the existence of a transition from mounds to asymmetric ripples oriented perpendicular to the beam at large deposition angles, as well as a second transition to rods with (111) facets oriented parallel to the beam at larger deposition angles and film thicknesses, is not fundamentally altered by the inclusion of SR and LR attraction. However, the results presented here also demonstrate that attraction can have several important effects. The first effect, due primarily to LR attraction, is a reduction in shadowing in the submonolayer regime which leads to decreased anisotropy in this regime. The second effect which occurs primarily in the
multilayer regime is “flux-focusing” due to SR and LR attraction.[11, 12] This effect tends to increase the surface roughness and feature size and reduce the critical thickness for ripple and rod formation, and can also enhance the anisotropy in the early stages of multilayer growth. In the later stages of growth it also leads to “sideways attraction” which tends to limit the anisotropy in the “rod” phase. Along with the existence of a competition between ripples and rods at high deposition angles, this second effect may explain the experimental observation of symmetric pyramids for deposition angles beyond the critical angle for ripple formation.

The organization of this chapter is as follows. In section II, we describe the model used in our simulations along with a summary of the simulation parameters and measured quantities. We then present our results in section III. In particular, we first present results for the effects of SR and LR attraction on shadowing and steering, and then more detailed description is given to the effects of attraction on the surface morphology. Finally, in section IV, we summarize and discuss our results. The quantities we use to characterize the surface morphology are briefly introduced in the Appendix A.

2.2 Simulation Details

In order to take into account the effects of shadowing as well as the attraction of depositing atoms to the substrate, we have carried out simulations using a hybrid model which combines a one-atom molecular dynamics (MD) simulation to describe the deposition process, with kinetic Monte Carlo (KMC) simulations to describe
surface relaxation. We first describe the KMC model used in our simulations, and then describe the deposition process in more detail.

2.2.1 Kinetic Monte Carlo Model

Since our goal is to compare with previous results without attraction,[23] and also to determine the general qualitative effects of attraction on the surface morphology in oblique incidence growth, we have used the same KMC model as was previously used in Ref. [23] for the case of ballistic deposition. We note that this model is similar to previous models[24, 25] used to study metal (100) growth at normal incidence in which the fcc crystal geometry has been taken into account. In particular, atoms are deposited with a (per site) deposition rate $F$, while adatoms (monomers) on a flat terrace are assumed to diffuse with hopping rate $D$. Since the Ehrlich-Schwoebel (ES) barrier typically plays an important role in metal epitaxial growth, the rate for an adatom at a descending step-edge to diffuse over the step is given by $D_{ES} = D_e^{-E_{ES}/k_B T}$ where $E_{ES}$ is the Ehrlich-Schwoebel barrier and $k_B$ is the Boltzmann’s constant. Compact islands are also assumed and accordingly a moderate amount of edge- and corner-diffusion ($D_e = D_c = 0.01 D$) was included in our simulations, while the attachment of atoms to existing islands was assumed to be irreversible. Thus the key parameters in our KMC model are the ratio $D/F$ of the monomer diffusion rate to the deposition rate, and the magnitude of the ES barrier. In most of our simulations, a deposition rate corresponding to $D/F = 10^5$ was used, and a moderate ES barrier corresponding to $E_{ES} = 0.07$ eV.
In order to examine the dependence of the surface morphology on deposition conditions we have calculated a variety of different quantities as a function of average film thickness $t$ in units of monolayer (ML) and deposition angle $\theta$. These include the r.m.s. surface height or “width” $w$, the lateral correlation lengths $\xi_\parallel$ and $\xi_\perp$ determined from the zero-crossing of the height-height correlation functions parallel and perpendicular to the beam respectively, and the anisotropy $\alpha' = \xi_\perp / \xi_\parallel$.

To minimize finite-size effects our simulations were typically carried out using relatively large system sizes ranging from $L = 512$ to $L = 2048$. For the case of ballistic deposition our results were averaged over $30 - 100$ runs. For the more time-consuming case of deposition with attraction, a more moderate system size ($L = 512$) was used along with averages over 10 runs.

\section*{2.2.2 Deposition}

In order to distinguish between the geometrical effects of shadowing and the effects of steering due to attraction, we have carried out simulations both with SR and LR attraction as well as without attraction (ballistic deposition). In both cases, the depositing atom is launched from a random position above the substrate and at a height equal to the height of the highest point of the film plus the cutoff distance $r_{\text{cut}}$, and with a selected deposition angle $\theta$ with respect to the substrate normal. In most cases the azimuthal angle $\phi$ was chosen such that the deposition direction was parallel to the close-packed step-edge, i.e. along the $[1\bar{1}0]$ direction, as in the experiments of Ref. [11] and Ref. [12]. However, we have also carried out some simulations with
deposition along the [100] direction in order to determine the effects of azimuthal angle on the surface morphology and roughness. The initial kinetic energy of the deposited atom corresponded to the average value \( \bar{K}_i = 2k_B T_m \) (where \( T_m \) is the melting temperature of the depositing material). Since our goal is to determine the general effects of attraction on the surface morphology in metal(100) growth, for simplicity we have chosen deposition parameters corresponding to Cu/Cu(100) growth, i.e. \( T_m = 1356 \text{ K} \) and \( \bar{K}_i \approx 0.20 \text{ eV} \).

Since a full molecular dynamics (MD) simulation of each deposition event is prohibitive for the system sizes (\( L = 512 \) and larger), film-thicknesses (up to 50 ML) and number of runs (\( 10 - 100 \) runs) considered here, in our simulations 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 particular, the depositing atom undergoes a one-atom MD simulation until its distance to the closest substrate atom is equal to the nearest-neighbor distance \( a_1 = a/\sqrt{2} \) (where \( a \) is the crystal lattice constant). At that point, the particle is then assumed to “cascade” randomly via downward funneling (DF)[26] from a site corresponding to this atom, until it reaches a four-fold hollow site. Thus, in our model atoms deposited on (111) microfacets are assumed to diffuse essentially instantaneously via DF to the terrace below. When considering the extremely low barriers for diffusion on metal (111) surfaces (approximately 0.05 eV for Cu(111)[27]) this is a very reasonable approximation except at extremely low temperatures.

While a relatively efficient ‘restricted’ four-neighbor search was used in our previous ballistic deposition simulations[23] to identify the nearest lattice-site to the
depositing atom at each point of the deposition process, in most of the results presented here a more accurate ‘extended’ nine-neighbor search was used. While there is very little difference in the qualitative behavior, the surface roughness obtained from simulations using the extended search is slightly larger than when using the restricted search. This suggests that the extended search method leads to enhanced uphill funneling (or equivalently reduced downhill funneling) near step-edges, in good agreement with MD simulations, [18, 28] thus resulting in a larger surface roughness. It is also interesting to note that in the case of ballistic deposition at normal incidence ($\theta = 0$), the surface roughness obtained using the restricted search is in perfect agreement with the results of ordinary KMC simulations with DF in which the deposition site is selected randomly rather than via molecular dynamics.

As in several previous simulations of steering effects in Cu/Cu(100) growth,[19, 20, 18] in our simulations with attraction, we have used a Lennard-Jones (LJ) copper potential[29] of the form,

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

(2.1)

(where $\epsilon = 0.4093$ eV and $\sigma = 2.3377$ Å) to represent the SR interaction. We note that in previous MD simulations of adatom deposition near Cu(100) close-packed steps,[18] it was found that the results obtained using this potential with a cutoff distance $r_{cut}^{SR} = 2\sigma$ which is close to that of a more sophisticated embedded-atom-method (EAM) Cu potential,[30] were essentially identical to those obtained using the EAM potential.
In order to include the effects of long-range (LR) interactions, we have also included a LR van der Waals attraction\cite{11, 31} for atoms which are farther than the cutoff distance for the short-range interaction. To speed up our simulations, the LR interaction was divided into two parts. The first part corresponds to the LR attraction between the depositing atom and the semi-infinite slab below the last completely filled layer of the substrate, and has the form $U_{LR}(z) = -C_3/z^3$ (where $z$ is the height of the depositing atom above this layer). The main effect of this interaction is to bend the path of the depositing atom as it approaches the substrate. The second part corresponds to pair-interactions with the atoms above the last completely filled layer of the substrate and has the form $V_{LR}(r) = -C_6/r^6$, where $r$ is the distance between the depositing atom and the substrate atom. At high angles, this interaction can lead to flux-focusing towards protruding structures which can significantly enhance the surface roughness.\cite{11}

As for the SR interaction, the values of the constants describing the long-range interaction ($C_3 = 2.1 \, eV\cdot\AA^3$ and $C_6 = (3a^3C_3/2\pi) \simeq 47.2 \, eV\cdot\AA^6$ where $a$ is the lattice constant of Cu) were chosen to correspond to Cu/Cu(100). We note that these values were obtained in a previous calculation\cite{31} and are significantly weaker than predicted by the LR ($1/r^6$) portion of the LJ Cu potential. Therefore, to avoid a discontinuity we have used the following expression for the pair-potential in our simulations,

$$V_T(r) = (1 - f(r))V_{LJ}(r) + f(r)V_{LR}(r) \quad (2.2)$$

where $f(r) = 1/[1 + e^{-(r-2\sigma)/R}]$ is the sigmoid function centered on $r = 2\sigma$ with width
$R = 0.125\sigma$. To save computation time in our calculations of the pair-interaction, a long-range cutoff $r_{\text{cut}} = 7\sigma$ was used, since the results were found not to depend on the cutoff for larger values.

2.3 Results

2.3.1 Effects of steering and shadowing

In order to understand the effects of SR and LR attraction on shadowing and steering during deposition, we have first compared the flux distribution for atoms deposited near a large $50 \times 50$ single-layer-high island with the corresponding results obtained using ballistic deposition. We note that similar calculations have been carried out by van Dijken et al[11, 12] although in this case a much stronger LR interaction (corresponding to the LR portion of the LJ Cu interaction in Eq. 2.1) was used. Fig. 2-1 shows the normalized flux distribution profile (averaged over the width of the island) for two deposition angles $\theta = 55^\circ$ and $\theta = 80^\circ$. As can be seen, for both the case of ballistic deposition and deposition with attraction, the flux near the front edge of the island ($40 < x/a_1 < 50$) is enhanced due to shadowing and/or steering effects, which increase with deposition angle. However, in the case of ballistic deposition, this enhancement only occurs at the bottom and top of the front step-edge, while in the case of attraction it is “smeared” out over a significantly larger region beyond the step. Similarly, while the size of the shadowed region beyond the back edge of the island also increases with deposition angle (see Fig. 2-1(b)) it is again
Figure 2-1: Normalized deposition flux near a one-layer-high square island (corresponding to $0 \leq x/a_1 \leq 49$) for deposition angles $\theta = 55^\circ$ and $80^\circ$ with attraction (filled symbols) and without attraction (open symbols). (a) Front side and (b) back side. Inset shows orientation of island with respect to particle beam. Error-bars (not shown) are smaller than symbol size.

...significantly larger in the case of attraction than in the case of ballistic deposition. However, due to steering effects, in the case of attraction the amount of shadowing immediately behind the island, is less than in the case of ballistic deposition. As discussed in the next subsection, this leads to decreased submonolayer anisotropy in the case of deposition with attraction when compared to ballistic deposition.

In order to quantify the effects of steering due to LR attraction in the early stages of growth, we have calculated the impact angle $\theta_i(z)$ of atoms approaching a flat substrate as a function of the vertical distance $z$ from the substrate for various deposition angles. Here the angle $\theta_i(z)$ is calculated using $\theta_i = \tan^{-1}(v_z/v_{\parallel})$ where
Figure 2-2: (a) Incidence angle $\theta_{I}(z)$ of depositing atoms as a function of distance $z/\sigma$ above a flat substrate in the case of LR attraction. (b) Average impact angle at a distance $r = 2\sigma$ above a growing film as a function of film thickness. All results are for $D/F = 10^5$ and moderate ES barrier. Error-bars (not shown) are comparable to line-thickness.

$v_{||} = (v_x^2 + v_y^2)^{1/2}$ and $v_i$ is the $i$ component of velocity of a deposited atom. As can be seen in Fig. 2-2(a), due to LR attraction, there is a significant difference between the initial deposition angle $\theta$ and the impact angle near the substrate, especially for large deposition angles. It is this steering effect which reduces the effects of shadowing in the submonolayer growth regime, when compared to ballistic deposition for large deposition angles.

To quantify the effects of steering due to LR attraction in the later stages of
growth, we have also measured the average “impact” angle at a distance $r = 2\sigma$ from the surface, for the case of slow deposition with $D/F = 10^5$ and $E_{ES} = 0.07$ eV, as a function of film-thickness as shown in Fig. 2-2(b). As can be seen, with increasing film thickness the effects of steering due to LR attraction become weaker and as a result the effects of shadowing become more important. This reduction in the degree of “downwards steering” due to attraction, is due to the increase in the film roughness with increasing thickness, which implies that the depositing atom remains farther from most of the substrate before being “focused” on a local peak or protuberance. Thus, while steering due to attraction can substantially alter the time evolution of the surface morphology, at large film thicknesses, the effects of shadowing become dominant as characteristic structures such as mounds and ripples are developed on the surface of growing films. We now consider the effects of SR and LR attraction on the surface morphology.

2.3.2 Effects of attraction on surface morphology

In order to distinguish the effects of attraction from those of shadowing, we have carried out simulations both with and without attraction for the case of $D/F = 10^5$ and $E_{ES} = 0.07$ eV. Fig. 2-3 shows the corresponding results for the surface width as a function of film thickness for deposition angles ranging from $0^\circ$ to $85^\circ$. As can be seen, both with and without attraction the surface roughness and effective growth exponent $\beta$ (where $w \sim t^{\beta}$) increase with deposition angle. In particular, the effective exponent $\beta$ at large film thicknesses increases from a value close to $1/4$ at
small angles to a value close to 1 at large angles. However, in the case of attraction both the roughness and effective exponent $\beta$ are larger at large film thicknesses than in the case of ballistic deposition due to the effects of flux-focusing.

The behavior for large deposition angles ($\theta \geq 70^\circ$) is particularly interesting. For example, while the “enhancement” of the surface roughness due to attraction tends to increase with deposition angle, for very large deposition angles ($\theta = 85^\circ$) the relative enhancement of the surface roughness due to attraction, is actually lower than at a somewhat lower angle ($\theta = 80^\circ$). In addition, for $\theta = 85^\circ$, the roughness at small film-thicknesses ($t < 6$ ML) is actually lower in the case of attraction than in the case of ballistic deposition. This is due to the fact that at very high deposition angles and small thicknesses, the effects of shadowing are significantly reduced by the LR attraction which decreases the effective deposition angle, as discussed in previous

Figure 2-3: Surface roughness as a function of film thickness for $\theta = 0^\circ - 85^\circ$ with and without attraction (ballistic deposition).
Figure 2-4: Gray-scale pictures of surface morphology for $\theta = 70^\circ - 88^\circ$ with $L = 512$ at $t = 50$ ML. Here, (a)−(d) are for ballistic deposition while (e)−(h) correspond to case of deposition with attraction. Arrow in (a) indicates deposition direction.

section. However, at higher thicknesses, the LR steering effect is reduced (see Fig. 2-2(b)), since the depositing atom remains farther from the substrate before impacting the surface, as discussed in Sec. II. As a result, the surface is again rougher in the case of attraction due to flux-focusing.

We now examine the general effects of SR and LR attraction on the surface morphology. Fig. 2-4 shows typical pictures of the surface at a film thickness of 50 ML for the case of ballistic deposition ((a)−(d)) as well as for the case of deposition with attraction ((e)−(h)) for the same set of parameters used in Fig. 2-3. In all cases, the resulting structures move towards the beam as they grow and coarsen. As in the simulations carried out in Ref. [23], for the case of ballistic deposition there is a series of morphological transitions with increasing deposition angle, from asymmetric mounds at $\theta = 70^\circ$, to asymmetric ripples with (111) facets on the illuminated side at
\( \theta = 80^\circ \), to larger, more well-defined ripples with some evidence of (111) side-facets at \( \theta = 85^\circ \), and finally to rods with well-defined (111) front- and side-facets at \( \theta = 88^\circ \). On the other hand, in the case of attraction, at a thickness of 50 ML, ripples are already formed at a deposition angle \( \theta = 70^\circ \) (see Fig. 2-4(e)), while at \( \theta = 80^\circ \) (see Fig. 2-4(f)), there is an indication of competition between ripples and rods, and at \( \theta = 85^\circ \), rods are clearly visible with (111) facets. These results indicate that one of the main effects of attraction is to cause the transitions from asymmetric mounds to ripples and from ripples to rods to occur at lower thicknesses and/or mound angles than in the case of ballistic deposition. In addition, the corresponding feature sizes are larger in the case of attraction than in the case of ballistic deposition, due to flux-focusing. A second important effect of attraction is to reduce the magnitude of the anisotropy in both the ripple and rod phases. For example, at \( \theta = 80^\circ \) the ripples are less pronounced and anisotropic in the case of attraction than in the case of ballistic deposition, while at \( \theta = 88^\circ \) the rods are also less anisotropic due to sideways attraction. Similarly, at \( \theta = 85^\circ \), sideways attraction tends to favor the formation of pyramidal structures as is observed experimentally.[11, 12]

These results can be understood more quantitatively by measuring the anisotropy \( \alpha' = \xi_{||}/\xi_{\perp} \) as a function of film thickness, as shown in Fig. 2-5. As can be seen, for deposition angles \( \theta \geq 70^\circ \), there is an abrupt increase in the anisotropy at a critical thickness \( t_c \) which decreases with increasing deposition angle. This abrupt increase coincides with the onset of the formation of (111) facets on the illuminated sides of mounds. Since (111) facets can efficiently capture and transport depositing atoms to the sides, this leads to a strong enhancement of mound coalescence in the direction
Figure 2-5: Anisotropy as a function of film thickness in the case of deposition with attraction (solid lines) and without attraction (dashed lines) for case of $D/F = 10^5$ and $E_{ES} = 0.07$ eV in multilayer regime.
perpendicular to the beam, followed by the formation and growth of ripples with extended (111) facets on the front side. As growth continues, the (111) facets become larger while the mounds coalesce and tend to form ripples, while the anisotropy remains relatively constant. For large enough angles and thicknesses, this is followed by a decrease in the anisotropy which coincides with the formation of the rod phase.

Fig. 2-5 also indicates that for large angles ($\theta \geq 80^\circ$) the anisotropy tends to be smaller in the case of attraction than in the case of ballistic deposition. However, for smaller angles ($\theta \leq 70^\circ$) and large thicknesses, the reverse is true since the effects of steering due to LR attraction are relatively weak. We note that in the submonolayer regime (Fig. 2-6) there is relatively little difference in the anisotropy with and without attraction, except for very large angles ($\theta \geq 80^\circ$) for which the effects of steering due to LR attraction tend to reduce the effects of shadowing as already discussed, and
thus significantly reduce the anisotropy.

2.3.3 Dependence on azimuthal angle

While the results presented so far correspond to deposition along the [110] direction (corresponding to an azimuthal angle $\phi = 0^\circ$ with respect to the principal lattice directions, as in the experiments of Ref. [11]) for comparison we have also carried out simulations for the case of deposition along the [100] direction corresponding to $\phi = 45^\circ$. As can be seen in Fig. 2-7, for large deposition angles the azimuthal angle has a significant effect on the surface morphology. In particular, for the case of deposition along the [100] direction and $\theta = 80^\circ$, the ripples are effectively “rotated” so that they remain perpendicular to the beam, but consist of “zig-zag” facets oriented
Figure 2-8: Surface roughness as function of film thickness for the case of deposition along the [110] direction (solid lines) and along the [100] direction (dashed lines) for different deposition angles $\theta$ with $D/F = 10^5$ and $E_{ES} = 0.07$ eV.

along the principal crystal directions. Similarly, for higher angles ($\theta = 85^\circ$), the rod formation observed for deposition along the [110] direction is replaced by the formation of “zig-zag” ripples and rods in the case of deposition along the [100] direction. However, as shown in Fig. 2-8, despite these dramatic effects on the surface morphology, the surface roughness exhibits only a very weak dependence on the azimuthal angle.

2.4 Discussion

We have carried out extensive simulations of a model of oblique incidence metal(100) growth in order to understand to what extent the effects of steering and flux-focusing due to SR and LR attraction as well as shadowing may affect the surface morphology.
For comparison, we have presented the results of simulations both with and without attraction. In both cases, due to computational constraints, we have used a simplified model of deposition, in which a one-atom MD simulation is carried out until the depositing atom is one nearest-neighbor distance away from the nearest film atom, and then “cascades” via DF until it reaches a four-fold hollow site.

In general, our results indicate that the qualitative picture of oblique incidence metal(100) growth obtained from earlier ballistic deposition simulations[23] is not fundamentally altered by the inclusion of attraction. In particular, we find that for the case of deposition along the [110] direction there is a series of transitions with increasing deposition angle and film thickness, from asymmetric mounds at moderate deposition angles, to asymmetric ripples oriented perpendicular to the beam at larger deposition angles, and finally to “rods” with (111) facets oriented parallel to the beam at larger deposition angles and/or film thicknesses. However, our results also indicate that the attraction of depositing atoms to the substrate can have several important modifying effects on the surface morphology.

The first effect, due primarily to LR attraction, is a reduction in the anisotropy in the submonolayer regime when compared to ballistic deposition. As indicated by our results for the normalized flux near an island, this is due to the effect of steering which reduces the angle of incidence for large deposition angles and thus tends to reduce the amount of shadowing directly behind submonolayer islands and thus inhibit island-coalescence in the beam direction. For very large angles, this effect can also lead to reduced surface roughness in the early stages of multilayer growth.

The second effect is due to “flux-focusing”[11, 12] and tends to occur in the multi-
layer regime. This effect tends to increase the surface roughness and feature size and also reduce the critical thickness for ripple and rod formation. It can also affect the anisotropy in the early stages of multilayer growth. For large deposition angles and film thicknesses this effect also leads to sideways attraction which tends to limit the anisotropy in the “rod” phase. Our simulation results also indicate that the effects of flux-focusing and sideways attraction may explain the experimental observation of symmetric pyramids in Cu/Cu(100) growth for deposition angles and film thicknesses near the transition from ripple to rod formation.

While we have primarily focused on the case of deposition along the [110] direction, as in the experiments of Ref. [11], we have also carried out simulations corresponding to deposition along the [100] direction in order to examine the dependence on azimuthal angle. This leads to dramatic changes in the surface morphology, including the formation of “zig-zag” ripples perpendicular to the beam at large angles of incidence, as well a “mixed” rod and ripple phase at larger deposition angles. However, despite these effects on the surface morphology we find that the azimuthal angle has very little effect on the surface roughness.

Finally, we note that while the results presented here are based on a generic model of metal(100) oblique incidence growth, it is interesting to consider the possible differences between our model and a model more specific to Cu/Cu(100) growth.[22] One of the main differences is the existence of an extremely low barrier for the diffusion of adatoms along Cu [110] island edges.[32, 33, 34, 35] The resulting fast edge-diffusion enhances the mound instability at normal incidence[8] and also leads to very regular islands and ripples.[25, 21, 22] It also leads to relatively large feature sizes and length
scales which makes simulations at high deposition angles extremely computationally demanding.[25, 21]

In summary, we have carried out extensive simulations of a model of oblique incidence metal(100) growth in order to understand the effects of steering and flux-focusing due to attraction as well as shadowing on the surface morphology. We have also studied the dependence of the surface morphology on a variety of deposition parameters including the azimuthal angle, growth temperature, and flux as well as deposition angle and film thickness. While our results indicate that much of the qualitative behavior previously observed in experiments[11, 12] can be explained primarily by geometric effects which dominate at large deposition angles, we find that the effects of flux-focusing and steering due to attraction also play an important role.
Chapter 3

Effects of deposition angle in low temperature metal(100) epitaxial growth

3.1 Introduction

Recently, there has been a great deal of progress in understanding the morphological evolution in epitaxial thin film growth (for a recent review see Ref. [6]), and a variety of effects and processes have been shown to play an important role. In addition to growth temperature and flux, these include the effects of crystal geometry,[39, 24] as well as such effects as the Ehrlich-Schwoebel (ES) barrier to interlayer diffusion,[7] edge- and corner-diffusion,[8, 25] and the attraction of depositing atoms to the substrate.[17, 18] More recently, it has been found that in the case of glancing incidence, the deposition angle can also play an important
While such effects have traditionally been assumed to be negligible for moderate deposition angles, they have not yet been fully investigated, especially at low temperatures. Understanding these effects is important, since they can have a strong effect on a variety of important properties including the surface morphology.

One case which turns out to be relevant and of particular interest is that of Cu/Cu(100) growth at low and intermediate temperatures, which was first studied by Ernst et al.[15] and, more recently, by Botez et al.[40] In both of these experiments, the growth of the surface roughness $w$ corresponding to the r.m.s. height-fluctuation was studied as a function of film thickness $t$ along with the corresponding growth exponent $\beta (w \sim t^\beta)$. In particular, as the growth temperature was increased from 160 K to 200 K, Ernst et al observed a significant increase in the surface roughness. The corresponding growth exponent $\beta$ was also observed to increase dramatically from a value of approximately 0.26 at 160 K to approximately 0.56 at 200 K. In contrast, Botez et al found very little difference between their results for the surface roughness at $T = 200$ K ($\beta = 0.54$) and $T = 160$ K ($\beta = 0.52$). Thus, while the results of Botez et al and Ernst et al are in agreement at 200 K, at $T = 160$ K they disagree not only quantitatively but also qualitatively. This discrepancy between the experimental results for Cu/Cu(100) at 160 K has so far not been explained.[6] This puzzle is made more intriguing by the existence of good agreement between the experimental results of Ernst et al and Botez et al at $T = 200$ K.

In this Chapter we demonstrate that, by taking into account the effects of deposition angle on the surface roughness, this puzzle can be resolved. In particular,
we find that good agreement between our simulations and both experiments can be obtained if we assume that the experiments of Ernst et al (Ref. [15]) correspond to normal or close-to-normal deposition, while the experiments of Botez et al (Ref. [40]) correspond to off-normal deposition. Our results also demonstrate that, in general, the effects of deposition angle must be considered in low-temperature growth even for moderate deposition angles.

3.2 Simulation Model

In order to simulate the effects of shadowing and attraction during deposition, as well as surface relaxation processes after deposition, we have carried out simulations using a hybrid model which combines molecular dynamics (MD) simulations to describe the deposition process, with kinetic Monte Carlo (KMC) simulations to describe surface relaxation.

3.2.1 Kinetic Monte Carlo Model

The activation barriers in our KMC model are based on a parametrization of the effective medium theory (EMT) barriers for Cu(100) calculated by Jacobsen.[32] We note that these barriers were originally used, along with the inclusion of “uphill funneling” due to short-range (SR) attraction of depositing atoms, to obtain good quantitative agreement with the observed roughening behavior in Cu/Cu(100) growth obtained by Ernst et al at 160 K.[18] More recently, by slightly enhancing the rate of corner diffusion, it was shown[25] that this model can also explain the large roughening
Figure 3-1: Schematic diagram showing neighboring atoms affecting the energy barrier of a diffusing atom (filled circle) in EMT model.

exponent ($\beta \simeq 0.5$) obtained by the same group at 200 K.

As shown in Fig. 3-1, in this model the energy barriers for hopping of an adatom on a flat terrace are determined by interactions with five of the eight neighboring atoms. In particular, if an adatom (filled circle) has a lateral bond with neighboring site $i$ (where $i = A, B_1, B_2, C_1$ and $C_2$), then the occupation number $N_i$ for that site is 1 and otherwise it is zero. The energy barrier $E_{\text{barr}}$ for hopping may then be calculated using the expression,[32]

$$E_{\text{barr}} = E_a + \frac{E_a}{2} [\delta(N_A, 1) - 1 + \delta(N_{C_1}, 0)\delta(N_{C_2}, 0) (1 + \delta(N_{B_1}, 1)\delta(N_{B_2}, 1))]$$ (3.1)

where $E_a = 0.425$ eV is the activation energy for monomer diffusion. Once the activation barrier is obtained, the rate for a given move is given by $D = D_0 e^{-E_{\text{barr}}/k_B T}$. Prefactor $D_0 = 3 \times 10^{11}$ sec$^{-1}$, was obtained from the fits to experimentally observed island densities[37, 38]. As indicated by Eq. 3.1, in this model the barrier for edge-diffusion ($E_e \simeq 0.21$ eV) is much lower than that for monomer diffusion ($E_a = 0.425$ eV).
Figure 3-2: Schematic diagram showing edge and corner diffusion with activation barriers $E_e$ and $E_c$ respectively, along with corner detachment barrier $E_d$.

eV) while the effective rate for dimer-diffusion is essentially the same as for monomer diffusion. The barrier for detachment from a corner site in a direction parallel to the edge ($E_d \simeq 0.425$ eV, see Fig. 3-2 is the same as for monomer diffusion. We note that once an atom has detached from a corner site, the barrier to re-attach (either to the same corner site or to the other corner site) is significantly lower e.g. $E_{att} \simeq 0.21$ eV. Thus the effective barrier for corner diffusion in this model is $E_c \simeq 0.425$ eV.

We also note that this model leads to parameters which are very similar to those recently obtained by Furman et al[35] using an EAM potential, and which lead to excellent agreement with submonolayer experiments[37] over the temperature range $T = 180 - 300$ K.

### 3.2.2 Deposition

As in several previous simulations of steering effects in Cu/Cu(100) growth,[19, 20, 18] a Lennard-Jones (LJ) copper potential[29] of the form $V_{LJ}(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]$ (where $\epsilon = 0.4093$ eV and $\sigma = 2.3377$ Å) was used to take into account the SR interac-
tion in our MD simulations of the deposition process. We note that in simulations of
adatom deposition near Cu(100) close-packed steps,[18] it was found that the results
obtained using this potential (with cutoff distance $2\sigma$) were essentially identical to
those obtained using a more sophisticated EAM Cu potential.[30] However, in order
to include the effects of long-range (LR) interactions, we have also included a van der
Waals attraction[11, 31] for atoms which are farther than the cutoff distance for the
short-range interaction.

For convenience, the LR interaction may be divided into two parts. The first
part corresponds to the LR attraction between the depositing atom and the semi-
infinite slab below the last completely filled layer of the substrate, and has the form
$U_{LR}(z) = -C_3/z^3$ (where $z$ is the height of the depositing atom above this layer).
The main effect of this interaction is to bend the path of the depositing atom as it
approaches the substrate. The second part corresponds to pair-interactions with
the atoms above the last completely filled layer of the substrate and has the form
$V_{LR}(r) = -C_6/r^6$, where $r$ is the distance between the depositing atom and the
substrate atom. At high angles, this interaction can lead to flux-focusing towards
protruding structures which can significantly enhance the surface roughness.[11] We
note that the values of the constants $C_3$ and $C_6$ describing the long-range interaction
are related ($C_3 = 2.1 \text{ eV}\cdot\text{Å}^3$ and $C_6 = (3a^3C_3/2\pi) \simeq 47.2 \text{ eV}\cdot\text{Å}^6$ where $a$ is the lattice
constant of Cu), and were obtained in a previous calculation.[31] We also note that
these values are significantly weaker than predicted by the $1/r^6$ "tail" of the LJ Cu
potential. Therefore, to avoid a discontinuity we have used the following expression
for the pair-potential in our simulations,

\[ V_T(r) = (1 - f(r))V_{LJ}(r) + f(r)V_{LR}(r) \]  

(3.2)

where \( f(r) = 1/[1 + e^{-(r-2\sigma)/R}] \) is the sigmoid function centered on \( r = 2\sigma \) with width \( R = 0.125\sigma \). We note that for comparison we have also carried out calculations using the less-accurate LJ Cu potential \( V_{LJ}(r) \) (corresponding to \( f(r) = 0 \) in Eq. 3.2 in which the LR interaction with atoms below the last completely filled layer was represented by the corresponding \( 1/z^3 \) potential \( (U_{LJ}(z) = \frac{8\pi\sigma^6}{3\sigma^3z^3}) \). As expected, this leads to an enhancement of the effects reported here, i.e. to results which are equivalent to those obtained with the more accurate interaction for a deposition angle which is \( 2^\circ - 3^\circ \) smaller.

In order to accurately simulate the entire interaction of the depositing atom with the substrate as well as the effects of shadowing and steering in oblique angle deposition, multiscale simulations[41] (in which both the depositing atom and the surrounding substrate atoms undergo molecular dynamics during each deposition) are required. Since a full MD simulation of each deposition event is prohibitive for the system sizes \( (L = 512) \) and film-thicknesses considered here, in most of our simulations a simplified method was used in which 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 its interaction with the substrate until its distance to the closest substrate atom is equal to the nearest-neighbor distance. As in previous work,
[39, 24] it then “cascades” randomly via downward funneling (DF) [26, 42] from a site corresponding to this atom, until it reaches a four-fold hollow site. We note that this approach takes into account the bulk of the steering effects due to LR and SR attraction. However, for comparison we have also carried out fully multiscale simulations in which a full MD simulation was carried out for each deposition event for smaller system sizes ($L = 256$) for a few specific cases. In these simulations, velocity rescaling of atoms below the surface was used to maintain constant temperature. We note that in a few percent of deposition events, the deposited atom does not find a four-fold hollow site on molecular dynamics time-scales, and in this case DF was assumed. We believe that this is a reasonable approximation since the substrate temperature is relatively high (for comparison, see for example, Ref. [43]) while the relevant barriers are typically quite small, i.e. less than 0.2 eV.[42]

Since the results were found not to depend on the cutoff for larger values, to save computation time in our calculations of the pair-interaction, a long-range cutoff $r_{\text{cut}} = 7\sigma$ was used. As in previous work,[18] in our MD simulations the initial kinetic energy of the deposited atom corresponded to the average value $\bar{K}_i = 2k_B T_m \simeq 0.20$ eV (where $T_m = 1356$ K is the melting temperature of copper), while the starting point was randomly chosen a distance $r_{\text{cut}}$ above the maximum film-height. In order to maximize the speed and accuracy of our one-atom MD simulations, a variable time-step was used, such that the depositing atom moves a fixed distance $\delta$ in every time-step. A larger value ($\delta = 0.1\AA$) was used at distances $r > 2\sigma$ such that the SR attraction is not yet effective, while a somewhat smaller value ($\delta = 0.05\AA$) was used at shorter distances. In the simulation results shown here the azimuthal angle was
Figure 3-3: Comparison of experimental results of Ernst et al[15] (filled circles) and Botez et al[40] (open circles) for Cu/Cu(100) growth at $T = 160$ K, along with full MD (dashed lines) and one-atom MD (solid lines) simulation results for different angles of deposition.

chosen such that the deposition direction was parallel to the close-packed step-edge, i.e. along the [110] direction. However, we have also carried out simulations with other azimuthal angles, and while the surface morphology was found to depend on the azimuthal angle, only a negligible effect on the surface roughness was observed.

### 3.3 Simulation Results and Discussion

Fig. 3-3 shows the experimental results of Ernst et al (filled circles) and Botez et al (open circles) for the surface roughness obtained in Cu/Cu(100) growth at 160 K. Also shown are our one-atom MD simulation results (solid lines) as well as our fully multiscale results (dashed lines) for different deposition angles $\theta$ with respect...
to the substrate normal. As can be seen, at normal incidence our simulation results are in relatively good agreement with the experimental results obtained by Ernst et al in Ref. [15], and are essentially the same as obtained in previous simulations of normal incidence growth at this temperature.[18, 25] In addition, we find that for deposition angles up to 30° (not shown) there is a negligible dependence on the deposition angle, in agreement with the experimental results of Ref. [15]. However, for deposition angles larger than 45°, both the growth exponent $\beta$ and the surface roughness increase dramatically. In particular, for deposition angles close to 60° our simulation results are in good quantitative agreement with the experimental results of Botez et al. As discussed in more detail below, these results suggest that in these experiments the deposition angles were not negligible.

They also indicate that at low temperatures, the deposition angle can have a strong effect on the growth behavior even for moderate values, i.e. away from glancing incidence. We also note that our one-atom MD simulations slightly underestimate the effects of the SR interaction after collision with the substrate. In particular, the roughness obtained in our fully multiscale simulations is somewhat larger than in the case of one-atom MD, and the difference appears to increase with deposition angle.

Fig. 3-4 shows the corresponding experimental results of Ernst et al[15] and Botez et al[40] at 200 K, along with our simulation results for the same range of deposition angles as in Fig. 1. As can be seen, at this temperature the differences between the experimental results are relatively small, although the roughness is slightly higher in the experiments of Botez et al. Similarly, our simulation results exhibit a relatively weak dependence on the deposition angle, although the roughness is somewhat higher
Figure 3-4: Comparison of experimental results of Ernst et al[15] (filled circles) and Botez et al[40] (open circles) for Cu/Cu(100) growth at $T = 200$ K along with one-atom MD simulation results (solid lines) corresponding to normal and off-normal deposition.
for the case of off-normal deposition than at normal incidence. Thus, again there is reasonable agreement between our simulation results and the experimental results.

These results indicate that at the lower temperature ($T = 160$ K) there is a strong dependence of the surface roughness on the deposition angle, while at higher temperature ($T = 200$ K), the dependence is relatively weak. The significantly weaker dependence on deposition angle at 200 K may be explained by the fact that at this temperature, both the mound slope and mound-density (and, correspondingly, step-density) are significantly smaller than at 160 K (See Pics. 3-6 - 3-9). This is consistent with the observation by Ernst et al of (115) facets at 200 K and (113) facets at 160 K as well as with previous simulation results at normal incidence.[25] The decreased mound slope at 200 K reduces the effects of shadowing, while the lower step-density minimizes the effects of steering due to SR attraction during deposition. We have also carried out simulations at temperatures higher than 200 K and slightly lower than 160 K. As expected, we find that, at higher temperatures the effects of deposition angle are weaker while at lower temperatures they become increasingly significant.

In order to determine the relative importance of the effects of shadowing and SR and LR attraction, we have also carried out additional simulations. Fig. 3-5 shows a comparison of our results for the surface roughness at 160 K ($\theta = 64^\circ$) with the SR and LR interaction included, with the corresponding results obtained with SR but no LR attraction (long dashes), as well as in the absence of both SR and LR attraction corresponding to ballistic deposition (short dashes). As can be seen, the LR attraction has a relatively weak effect on the surface roughness at this angle. This is consistent with the experimental results of van Dijken et al at higher temperature,[11] and can
Figure 3-5: Comparison of one-atom MD simulation results for the surface roughness at 160 K at normal and off-normal incidence (solid lines), with off-normal incidence simulation results ($\theta = 64^\circ$) obtained without LR attraction (long dashes), as well as in the absence of both SR and LR attraction (short dashes). Experimental results from Refs. [15] and [40] are included for reference.
Figure 3-6: Simulated surface morphology (thickness 50 ML). Normal incidence deposition at T = 160 K. 192 × 192 portion of 512 × 512 system is shown.
Figure 3-7: Simulated surface morphology (thickness 50 ML). Normal incidence deposition at $T = 200$ K. $192 \times 192$ portion of $512 \times 512$ system is shown.
Figure 3-8: Simulated surface morphology (thickness 50 ML). Deposition angle 64°, T = 160 K. Deposition direction is along the [110] direction (from the lower right to the upper left corner). 192 × 192 portion of 512 × 512 system is shown.
Figure 3-9: Simulated surface morphology (thickness 50 ML). Deposition angle 64°, T = 200 K. Deposition direction is along the [110] direction (from the lower right to the upper left corner). 192 × 192 portion of 512 × 512 system is shown.
be explained by the fact that, since the LR attraction is relatively weak, only for large glancing angles is the normal component of the depositing particle’s velocity small enough to allow sufficient time for it to have an effect. In contrast, Fig. 3-5 indicates that for moderate deposition angles both shadowing and SR attraction play important roles in enhancing the surface roughness at low temperature. These effects reinforce each other, i.e. increased roughness due to shadowing leads to a higher step density which enhances the effects of SR attraction. The combination of both effects leads to the dramatic increase in the surface roughness and growth exponent observed in our simulations as the deposition angle is increased.

We now compare the deposition angles used in the experiments with those in our simulations. In Ref. [15] the deposition geometry was described and indicates normal incidence, as assumed in previous simulations[25] as well as here. In Ref. [15] it was also found that the surface roughness was independent of deposition angle for $\theta < 30^\circ$, in agreement with our simulation results. After the results presented here were obtained, an estimate of the deposition angle in the experiment of Ref. [40] was also carried out,[44] and is in good quantitative agreement with the values used here. Thus, the available evidence strongly supports our conclusion that the results of both experiments can be explained once the deposition angle is taken into account.

### 3.4 Conclusions

In conclusion, by taking into account the deposition angle along with the effects of shadowing and SR attraction, we have obtained good qualitative and semi-
quantitative agreement with the experimental results of Ernst et al[15] and Botez et al[40] at both 160 K and 200 K. Our simulation results resolve the long standing puzzle of a discrepancy between these experimental results at 160 K. Our results also demonstrate that the deposition angle can have a significant effect on the surface morphology at low-temperatures, even for moderate deposition angles. In this connection, we note that low-temperature growth has recently been studied in a variety of other systems.[45, 46, 47, 48, 49, 50] Our results indicate that, in general, the deposition angle should be considered along with the growth temperature in analyzing and/or interpreting these and similar experiments.
Chapter 4

Molecular dynamics simulations of very low temperature metal(100) growth

4.1 Introduction

Metal epitaxial growth has been a field of active experimental and theoretical research for the last three decades. Considerable progress has been made in understanding of how the deposition conditions can affect the evolving surface morphology of the growing thin film. Commercial applications typically require defect-free films. For this reason understanding of the processes which lead to formation of defects under particular growth conditions is crucial if one aims to control the quality of the growing crystal. Development and application of modern experimental techniques, such as scanning tunnelling microscopy (STM) and X-ray diffraction (XRD) has recently
provided a great deal of information on atomic and nano-scale structure of thin films. While this information is extremely helpful, each experimental technique has its own limitations. For instance, in case of metal epitaxial growth at low temperatures, STM tip can not fully probe the deep valleys and X-ray diffraction analysis provides only indirect information about vacancies, voids and other subsurface defects incorporated into the film. Another issue is a high cost of state of the art experimental techniques and deposition methods such as MBE. For these reasons the development of predictive theoretical models for description of crystal growth processes has received significant attention recently (for a recent review see Ref. [6]).

In this Chapter we study Cu/Cu(100) epitaxial growth at very low temperature employing molecular dynamics (MD) simulation, with embedded atom method (EAM) for description of interatomic interactions. While the process of atomic deposition on the surface has been extensively studied with MD simulations in the past [51, 52, 53], there are still many interesting problems which remain unresolved. Besides, the ongoing experimental investigations provide new, sometimes rather surprising, information about the processes which had been considered well-understood. One of the most recent surprises serves as a motivation for this work - synchrotron X-ray scattering studies [47, 48, 49] of Cu/Cu(100), Ag/Ag(100) and Ag/Ag(111) thin films grown at very low temperatures have recently provided evidence for surprisingly high vacancy concentration (2%) incorporated in the deposited thin films.

What was actually observed in the experiments is a strong effect that the growth temperature has on the reflectivity line shape. When the growth temperature was lowered to 100K reflectivity profiles measured around the Bragg reflection exhibited
a well-pronounced asymmetry and interference fringes. These changes in diffraction pattern were observed to increase with decreasing growth temperature. The lowest temperature reached in the experiments was 50K. The interpretation of observed phenomena was the following - development of interference fringes suggests that there are structural differences between the deposited film and underlying substrate, while the asymmetry towards higher surface-normal scattering vectors $Q_z$ around Bragg reflection is an indication of a compressive surface-normal strain which developed in the film during the growth process. The existence of the strain in the deposited overlayers was explained [47, 48, 49] by the assumption of incorporation of a large vacancy concentration in the films grown at low temperature.

Even though, a deposition rate in an MD simulation is much higher than those used in the experiments, meaning that thermally activated processes are effectively inoperative, which makes effective temperature of the simulation extremely low, we keep in mind that the effect observed experimentally was most pronounced at the lowest temperatures, where most of the atomic rearrangements on the surface are deposition activated events. For this reason we are confident, that in this case, MD simulation is a perfect technique to study the observed phenomena. It can provide meaningful description of far-from-equilibrium growth process, and reveal the trends in development of nanostructures on the surface, and defect incorporation into the film, during the growth under particular deposition conditions.

In a recent paper [22] we demonstrated that in the experiments of the same group on Cu/Cu(100) growth [40] at intermediate temperatures, where the surface roughness $w$ of the thin films grown at different temperatures was studied as a function of film
thickness, the actual deposition angles were far-off-normal ($\approx 60^\circ$). We note that, the existence of accidental off-normal deposition conditions was confirmed later by the experimental group [44]. Moreover, accidental off-normal deposition conditions with angles of deposition of the same order ($\approx 60^\circ$) may be expected in the experiments which serve as a motivation for this work [47, 48, 49]. For this reason, in our MD simulations a range of deposition angles was used to elucidate a possible effect of deposition geometry, combined with very low growth temperature, on accumulation of compressive strain in the growing thin film and development of the distinctive features in the diffraction patterns.

4.2 Simulation Model

A model we have used for simulation of the deposition process includes a one-atom MD simulation to describe the deposition process while the depositing atom is travelling towards the substrate and the distance to the nearest substrate atom is greater than the cutoff distance of EAM potential (4.961 Å), and a multi-atom MD simulation of an impact event, in which both the depositing atom and the surrounding substrate atoms undergo molecular dynamics.

The scheme of one-atom MD simulation has been described in detail in our previous work [22] (See Chapter 3). Here we briefly note that before simulation of impact event the depositing atom trajectory is determined using the pair-interactions with the atoms of the substrate. The type of this interaction is a long-range (LR) Van der Waals attraction, the form of potential is $U(r) = -C_6/r^6$, where $r$ is the distance
between the depositing atom and the substrate atom and the value for the Van der Waals constant [31] is \( C_6 = 47.2 \, eV \cdot Å^6 \).

As soon as a depositing atom has reached the EAM cutoff distance to the nearest substrate atom, we switch to the multi-atom MD for simulation of the impact event. For this purpose we carve out the chunk of substrate atoms (see Figs. 4-1 - 4-3) surrounding the expected landing point. The idea of small scale MD simulation of impact event [41] helps to extend the length scale of the simulated system (system size \( L = 192 \, (\approx 347 \, Å) \) was used in our simulations), and avoid the finite system size effects in simulated surface morphology associated with deposition under the angle with respect to surface-normal at low temperatures. The outer shell of the chunk consists of immobile (frozen) atoms (see Figs. 4-1 - 4-3). The trajectories of the rest of the atoms are calculated integrating Newton’s equations of motion, with EAM potential [30] for calculation of interatomic forces. There is a thermostated shell of atoms adjacent to the frozen shell, to mimic the isothermal deposition condition. Once the chunk of substrate atoms is carved out, the system is equilibrated for 1.5 ps at desired temperature. Then follows the simulation of impact event of depositing atom with substrate (3 ps). The velocity Verlet algorithm with variable time step is used for integration of the equations of motion. The time step is defined in such a way, that maximum atomic displacement in the system does not exceed 0.006 Å in one integration step.

Serial MD simulation of growth, for the system sizes and coverages (20 ml.), considered here, is extremely time consuming. For this reason we implemented a parallel version of described above deposition process. This modification allows a
Figure 4-1: Chunk of substrate atoms for MD simulation of impact event (top view).

Figure 4-2: Chunk of substrate atoms for MD simulation of impact event (rotated view).

Figure 4-3: Chunk of substrate atoms for MD simulation of impact event (side view).
simultaneous deposition of a number of atoms in different areas of the surface, each of them being handled by a single processor. To avoid possible conflicts, which occur if two or more of deposited in one cycle atoms land close to each other (closer then the diameter of the thermostated region of the chunk, carved out to simulate the impact event), we decompose the simulated system into $N_p$ processor regions, each of them, in turn, decomposed into 4 sublattice regions (so called, square decomposition of the system). The depositing in one cycle atoms are, then, allocated to the same sublattice of different processor regions (starting positions are picked randomly above the sublattice regions and the choice of sublattice region for the particular cycle of deposition is random, as well). We note, that this method has been tested with kinetic Monte Carlo simulations of growth at higher temperatures [22], and proved to be accurate, as long as the diffusion length of the atoms on the surface does not exceed the sublattice size. Since the thermally activated processes are effectively inoperative in MD simulations, as well as in the experiments on growth at very low temperatures, our model for parallelization is valid, and the maximum number of simultaneous depositions, which can be used without conflicts, is proportional to the ratio of the system area to the square of the diameter of the moving region of the deposition chunk. Since in our parallel MD simulations each chunk carved out for simulation of impact event includes the outer shell of immobile atoms, it is possible that the system may build up some unrelaxed strain [54]. To avoid this artificial strain accumulation, we perform a global relaxation of the whole system relatively frequently (8 times per monolayer of atoms deposited).

During the simulation of growth the roughness of the surface, defect’s densities
and strain (local and average) were recorded as the functions of coverage. More importantly, the diffraction patterns from simulated atomic configurations were numerically calculated at a range of coverages. The detailed description of how the structure of thin films can be solved using X-ray diffraction methods can be found in Refs. [55], [56] (See Appendix B). Here we note that two contributions to the scattered intensity need to be taken into account: from the substrate and the deposited thin film. The presence of compressive surface-normal strain in the film corresponds to a decrease in inter-layer spacing $d_{\text{film}}$, compared to the inter-layer spacing of substrate $d$. The intensity distribution can be calculated (See Appendix B) using the following expression [56]:

$$I(Q_z) \propto \frac{1}{Q_z} \left| \frac{N_{\text{substr}}}{1 - e^{i Q_z d}} \right| + \sum_{j=1}^{N_{\text{film}}} e^{-i Q_z z_j} |^2$$

(4.1)

Here $Q_z$ is the wave-vector transfer along the substrate normal, $N_{\text{substr}}$ is a number of atoms in one layer of substrate, $N_{\text{film}}$ is a number of adatoms in the deposited film, $z_j$ is the $z$-coordinate of atom $j$, and $d$ is the (100) plane spacing in the bulk (substrate).

### 4.3 Simulation Results and Discussion

Fig. 4-4 shows our numerically calculated diffraction patterns for different coverages and deposition angles $\theta$ with respect to the substrate normal. As can be seen, there is relatively little asymmetry in the diffraction patterns up to 20 ML, and only minimal reflectance oscillations, for the lower angles of deposition $\theta = 0, 30^\circ$. In contrast, in diffraction patterns, which correspond to MD simulations carried out for
Figure 4-4: Evolution of reflectivity line shape as a function of deposition angle and coverage. Experimental results (open symbols) from Ref. [48] are shown on top of our simulated XRD patterns for $\theta = 55^\circ$.

higher deposition angles ($\theta = 45^\circ - 60^\circ$), strong reflectance oscillations can be seen. In particular, as shown in Fig. 4-4 there is a good qualitative agreement between the calculated XRD pattern obtained from our MD simulations for deposition angle $\theta = 55^\circ$ and the experimentally determined diffraction pattern from Ref. [48] for the case of deposition at $T = 110$ K (open symbols).

The strong dependence of the reflectivity line shape evolution with coverage on the angle of deposition and good agreement of our result for $\theta = 55^\circ$ with experimentally observed one [48] confirms our assumption about off-normal deposition conditions in the experiments. In Fig. 4-5 the average surface-normal compressive strain in the simulated atomic configurations is shown as a function of coverage for a range of deposition angles. We note that the strain was defined, following Refs. [47, 48, 49], as $\frac{d_{\text{film}} - d}{d}$, where $d_{\text{film}}$ is an average height difference between the atom and its
Figure 4-5: Compressive strain in the growing thin film as a function of deposition angle and coverage.

nearest neighbors in the plain below, and \( d \) is the corresponding bulk value. Only the deposited atoms of the film were included into the average strain calculation. In the beginning of the deposition process major part of the deposited particles are the surface atoms, which, having reduced coordination, tend to have a shorter bond length, compared to the bulk atoms. This explains the large values of strain at low coverages. Later on, as the film gets thicker, the average strain decreases due to the contribution from the increased number of bulk atoms in the film. On the other hand, at some critical coverage, which is angle dependent, the strain in the film begins to increase. The nature of this phenomena is explained later in the text. Here, again, a strong dependence on the deposition angle is present: at a given coverage the strain is larger for the higher deposition angles. In order to determine, if the
observed in our simulations strain in deposited overlayers is due to the vacancies incorporated into the films, as proposed by the experimentalists [47, 48, 49], we compare the results for the vacancy density $C_v$ as a function of coverage for the same as in Fig. 4-4 range of deposition angles (see Fig. 4-6). We first note, that the vacancy density in the growing film is almost an order of magnitude smaller than the inferred experimental value of 2%. In addition, it is only very weakly dependent on the deposition angle, and so cannot explain the strong dependence of the XRD pattern on deposition angle. In order to understand better how the presence/absence of vacancies in the simulated films may affect the shape of the reflectivity line, we filled all the vacancies found in the films, which diffraction patterns exhibited the distinctive features, and relaxed the atomic configurations. In all cases, there was no significant change in either the average compressive strain or the calculated XRD
pattern. Thus, while vacancy formation does occur in our simulations, it is not the cause of the compressive strain, or the experimentally observed asymmetry of XRD patterns and the reflectance oscillations.

If not the vacancies, than what is the reason for compressive strain accumulation during the low temperature growth? To answer this question we consider the surface morphologies obtained in our MD simulations at a range of deposition angles. Fig. 4-7 demonstrates the growth of the surface roughness as a function of film thickness for the range of deposition angles used in our simulations (from 0° to 60°). It is clear that the differences for the values of roughness at a given coverage are much more pronounced for different angles of deposition then the differences in the vacancy densities (see Fig. 4-6). The increase of roughness is associated with an increase in the number of surface atoms, which, having reduced coordination, tend to have a shorter bond
Figure 4-8: Surface-morphology of the simulated film (side view - slice along [100] direction; slice thickness is 3 atomic planes) for the angle of incidence $\theta = 0^\circ$ (thickness 10 ML, simulated system size is $192 \times 192$).

Figure 4-9: Surface-morphology of the simulated film (side view - slice along [100] direction; slice thickness is 3 atomic planes) for the angle of incidence $\theta = 60^\circ$ (thickness 10 ML, simulated system size is $192 \times 192$).
Figure 4-10: Surface of the simulated film for the angle of incidence $\theta = 0^\circ$ (thickness 10 ML, simulated system size is $192 \times 192$).

$\theta = 0^\circ$

Figure 4-11: Surface of the simulated film for the angle of incidence $\theta = 60^\circ$ (thickness 10 ML, simulated system size is $192 \times 192$).

$\theta = 60^\circ$
length, compared to the bulk atoms. Due to the suppression of thermally activated processes at low growth temperatures, the meta-stable “nanostructures” with large number of “overhangs”, induced by off-normal deposition, develop on the surface (see Fig. 4-9, 4-11). The formation of such “nanostructures” strongly enhances the surface atom density, while the relaxation of the corresponding surface atoms, which have a reduced bond length [57] due to their reduced coordination, leads to the large compressive strain. We note, that the presence of a rough surface with overhangs can lead to oscillations in the simulated XRD pattern, even without taking into account the effect of strain (see Appendix B, Figs. B-3, B-4 ). However, the accompanying compressive strain significantly enhances the diffraction oscillations for $Q_z d/2\pi < 1$ and shifts them to larger $Q_z$. Thus, the observed asymmetry and oscillations in the XRD patterns are due to the existence of a rough surface with overhangs and the resulting development of compressive strain in the films.

Due to the well-established similarity in growth behavior for (100) orientations of Copper and Silver [6], one would expect similar behavior for the evolution of reflectivity line shape with coverage for both systems. On the other hand, the experimentally obtained results [47, 48] suggested some differences, i.e. at low values of $Q_z$ interference fringes were observed in case of $Cu/Cu(100)$ growth [48], but were absent in case of $Ag/Ag(100)$ growth [47]. The presence of fringes at low-$Q_z$ was attributed to the extended [47, 48] distribution of exposed terraces, which results in significant population of lower terraces.

We argue, that the presence or absence of interference fringes at low-$Q_z$ can be also explained by taking into account the angle of deposition. We observe interference
fringes at low-$Q_z$ in diffraction patterns, taken from our simulated atomic configurations, for the higher angles of deposition, while they are absent at lower angles (see Fig. 4-12). This suggests possible differences in the deposition geometries which were used in the experiments on $Cu/Cu(100)$ [48] and $Ag/Ag(100)$ [47] low temperature growth, i.e. higher angles of deposition for Copper, compared to those for Silver. We note that an increase in deposition angle, indeed, leads to extended distribution of exposed terraces with significant population of lower terraces, as a result of formation of ridge-like structures [53] and deep valleys between them (see Fig. 4-9, 4-11).

Another observation one can make, comparing specular reflectivity measurements experimentally taken at different coverages for the two systems, is a pronounced de-
lay in formation of thin-film interference fringes around the (002) Bragg reflection for Ag/Ag(100) [47] growth, compared with the observed behavior for Cu/Cu(100) [48] growth at the temperatures of growth 100K and 110K correspondingly. This observation supports our previous argument about accidental differences in deposition angles used in the experiments on Copper and Silver - the delay in formation of interference fringes is well-pronounced in case of our simulation results for Cu/Cu(100) growth at \( \theta = 30, 45^\circ \), compared to the results for \( \theta = 55^\circ \) (see Fig. 4-4). While the simulation of Ag/Ag(100) growth under the same deposition conditions (\( T = 110, \theta = 60^\circ \)), as were used for Cu/Cu(100), yields very similar results, in terms of evolution of reflectivity line with coverage (see Fig. 4-12).

### 4.4 Conclusions

In conclusion, we have demonstrated that the observed experimentally reflectivity profiles, were influenced by off-normal deposition conditions, which, in combination with low growth temperature, lead to a rapid increase of the surface roughness, density of surface atoms, and increased number of the “overhangs”. These factors explain the experimentally observed large strain in the films deposited at very low temperatures. Our results also indicate that while there also exists a relatively small vacancy density at low temperature, this vacancy density is not necessary to explain the large compressive strain. We expect, that more sophisticated models of growth, such as, temperature accelerated dynamics [58], would give better quantitative agreement with experiment.
Finally, we note that low-temperature growth has recently been studied in a variety of other systems. [45, 46] It is quite possible, that some of the intriguing discoveries, made in low temperature experiments and remain unresolved yet, could be explained by consideration of accidental off-normal growth conditions.
Chapter 5

Mound formation and slope selection in irreversible $fcc(111)$ growth

5.1 Introduction

Recently, there has been a great deal of interest in understanding the evolution of the surface morphology in epitaxial growth [59]. In particular, the appearance and the dynamics of asymmetric three-dimensional mound structures [60], which grow and coarsen with increasing film thickness during homoepitaxial growth on singular (low-miscut) surfaces, are not well-understood in terms of the underlying microscopic processes. While in some cases mounds have been observed to form with a slowly increasing mound angle, in many cases, especially in metals, mounds have been observed to form with a clearly selected mound angle. Once formed, the typical
mound size increases with increasing film thickness as mounds coalesce and coarsen to form new larger mound structures.

The selection of a stable mound slope [61] has been related to the interplay of different microscopic processes leading to the balance between uphill and downhill currents. In particular, while diffusion bias may be due to a variety of different mechanisms, such as step-adatom attraction [62],[63], or step-edge diffusion [8], in many cases the primary cause is the existence of a barrier to diffusion over descending steps, often called an Ehrlich-Schwoebel (ES) barrier [7].

There have been a number of theoretical efforts to understand the interplay between mound evolution behavior and surface currents, taking into account surface symmetry and microscopic processes [64],[9],[65]. In addition, it has recently been shown [18],[28] that the existence of short-range attraction of depositing atoms to step-edges can lead to significant deviations from the standard downward funneling (DF) [26] picture in epitaxial growth on metal (100) and (111) surfaces. However while a general calculation of the surface current and selected mound slope has been recently presented [28] for the case of an arbitrary crystal geometry with an infinite Ehrlich-Schwoebel barrier, and earlier calculations were presented for the case of a (100) surface with a finite ES barrier [63], there has been no calculation of the surface current and selected mound slopes for finite ES barrier for (111) surfaces.

In order to gain further insight into the dependence of the surface morphology on growth parameters, we have carried out an analytic calculation of the surface current and selected mound slope as a function of the ES step barrier for a model of homoepitaxial growth on fcc(111) surfaces. There are two types of close-packed step
edges on an \textit{fcc}(111) surface: \textit{A} steps corresponding to (100) microfacets and \textit{B} steps corresponding to (111) microfacets. Due to the asymmetry between these two types of step edges, surface current and selected mound slope are significantly different for \textit{A} and \textit{B} steps.

Wee have found out that various scenarios are possible, depending on the values of the ES barrier, substrate temperature, uphill funneling probabilities $P_{up}$, $P'_{up}$ \cite{28} for atoms deposited near step-edges, \textit{etc}. In particular, for some combinations of the parameters, critical value of the probability of diffusion down the step exist, above which mound formation is not possible.

This Chapter is organized as follows. In Sec.II we describe our model. In Sec.III, we describe the calculation of the surface current and selected mound slope of \textit{B} steps and present expressions for the surface current and selected mound slope of \textit{A} steps. The cases of short terrace lengths and mixture of terraces with different lengths are discussed separately. In Sec.IV we analyze and discuss our results. Finally, in Sec.V we summarize our results.

\section{5.2 Model}

To calculate the surface current, we consider a regular stepped \textit{fcc}(111) surface with infinitely long straight steps (either \textit{A} or \textit{B} steps, see Fig.5-1). As shown in Fig.5-1, the total surface current per particle $J/F$, where $J$ is the surface current and $F$ is the deposition flux, may be divided into four contributions due to deposition in four different regions. Region I corresponds to atoms deposited just beyond the step-
Figure 5-1: Schematic diagram (top view) of A and B steps on fcc (111) surface. Site labelled * corresponds to last 3-fold hollow site on upper terrace (see text).
edge but close enough to feel the effects of short-range attraction to the step. Region II corresponds to particles slightly farther away from the step-edge and is needed to connect to the terrace region. Region III corresponds to atoms deposited on a terrace away from a step. Finally region IV corresponds to atoms deposited near a step-edge on the upper side. In region III we apply a discrete approach, while in regions I, II and IV we apply a continuous approach.

For a given terrace length \( L \), the surface current per particle \( J/F \) may be calculated by multiplying the probability that an atom will be deposited at a given site by the average (signed) distance travelled before absorption at an ascending or descending step [66]. For simplicity, we assume irreversible attachment at ascending steps (site 0 or \( c \) in Fig.5-1) which is appropriate for a variety of systems over a range of temperatures, although at high temperatures detachment from step edges may need to be taken into account. Atoms which are deposited on a flat terrace away from a step-edge are assumed to first “cascade” to the nearest \( fcc \) or \( hcp \) site and then diffuse alternately between \( fcc \) and \( hcp \) sites until reaching \( fcc \) attachment site at an ascending step-edge (see Fig. 5-1. We note that recent work [71] indicates that for some systems, long jumps may also occur above a critical system-dependent temperature. Here, we assume that we are at low enough temperatures that such correlated jumps do not occur. For convenience, we define \( \Delta = \sqrt{3}a_1/6 \) as the unit of length, where \( a_1 \) is the nearest neighbor distance.

While typically there exists a difference between the binding energies of adatoms at \( fcc \) and \( hcp \) sites [72], this difference turns out not to be important for our calculations. For example, if an atom is at a \( fcc(hcp) \) hollow site away from a step, it
can hop with equal probability to each one of the three nearest hcp(fcc) sites (see Fig. 5-1). Accordingly, the probability of an atom to hop away (towards) the ascending step alternates between the values of 1/3 and 2/3 depending on whether or not the adatom is at an fcc or an hcp site on the terrace (see Fig. 5-1). As a result, the diffusion process can be mapped to a one-dimensional random walk with alternating probabilities $p$ and $q$ between two absorbing barriers, one at site 0 corresponding to the ascending step-edge and the other at site $c$ corresponding to the descending step (see Fig. 5-2). For example, if an atom is at site $k$, and $k$ is odd, the probability of going to the lower site $k-1$ is given by $p$, where $p = 1/3$ for $A$-steps and $p = 2/3$ for $B$-steps, while the probability of going to a higher site $k+1$ is given by $q = 1 - p$. Similarly, using the same definition of $p$ as given above, if $k$ is even, the probability of going to the lower site $k-1$ is given by $q = 1 - p$ and to a higher site $k+1$ is given by $p$.

Due to the existence of an Ehrlich-Schwoebel step-barrier [7], the rate for an atom at the edge of a step to diffuse to the terrace below is typically different from the rate for hopping on a flat terrace. For generality we assume that adatoms may diffuse to the terrace below from both the fcc and hcp sites nearest to the step-edge with different probabilities. In particular, we assume that the process of interlayer diffusion may be described as follows: for an atom in the last fcc site at the edge of a terrace near an $A$-step, the probability to go over the step (either via hopping or exchange) to the absorption site $c$ is given by $\epsilon_A$ where $\epsilon_A \leq 1$, while the probability to go over the step from the last hcp site is given by $\epsilon'_A$ where $\epsilon'_A \leq 1$. The corresponding probabilities for interlayer diffusion near a $B$ step are given by $\epsilon_B$ and $\epsilon'_B$ (see Fig. 5-3).
A steps  \[ p = \frac{2}{3}, \quad q = \frac{1}{3} \]

\[ 0 \xrightarrow{2/3} 1 \xrightarrow{1/3} c \]

B steps  \[ p = \frac{1}{3}, \quad q = \frac{2}{3} \]

\[ 0 \xrightarrow{1/3} 1 \xrightarrow{2/3} c \]

Figure 5-2: Diagram showing random walk between absorbing sites at 0 and \( c \). \( \gamma \) corresponds to overall probability that at an atom at site \( c - 1 \) will diffuse to the layer below (see text).

![Diagram showing random walk between absorbing sites at 0 and \( c \). \( \gamma \) corresponds to overall probability that at an atom at site \( c - 1 \) will diffuse to the layer below (see text).](image)

Figure 5-3: Diagram showing details of interlayer diffusion at A and B steps.

In order to calculate the surface current \( J \), the effects of terrace diffusion as well as of the short-range attraction \([63],[18],[28]\) of atoms deposited near step-edges must be taken into account, as we discuss in more detail below. The selected terrace width \( L_0 \) and corresponding selected slope \( m_0 = h/L_0 \) (where the layer- height \( h = \sqrt{6}a_1/3 \) and \( a_1 \) is the nearest-neighbor distance) then correspond to those values for which the surface current per particle \( J/F \) is equal to zero. Taking into account that the unit of length was defined as \( \Delta = \frac{\sqrt{3}a_1}{6} \), the selected slope \( m_0 \) may be written, \( m_0 = \frac{2\sqrt{2}}{L_0} \)
5.3 Surface current and selected mound slope

5.3.1 General expression for attachment probabilities $P_i$

Before calculating the surface current, we first obtain general expressions for the probability $P_i$ that a diffusing adatom at site $i$ on a terrace of width $L$ will attach to the upper (ascending) step, i.e. be absorbed at site 0. For simplicity we first consider the following set of difference equations [69], corresponding to the case in which adatoms can only diffuse to the layer below from the last site on the terrace which we denote here as $c - 1$ (see Fig. 5-2(a)).

\[
P_{2k-1} = pP_{2k-2} + qP_{2k} \quad (1 \leq k \leq \frac{c-1}{2}) \tag{5.1}
\]

\[
P_{2k} = qP_{2k-1} + pP_{2k+1} \quad (1 \leq k \leq \frac{c-3}{2}) \tag{5.2}
\]

\[
P_{c-1} = (1 - \gamma)P_{c-2} + \gamma P_c \tag{5.3}
\]

with boundary conditions: $P_0 = 1$ and $P_c = 0$. For odd $c$, which is the case for $A$-steps the probability $P_i$ that a particle deposited at site $i$ (either an fcc or hcp site) will be absorbed at site 0 is given by:

\[
P_{2k} = 1 - \frac{k}{K + q + \frac{\bar{\gamma}}{\gamma}} \quad 0 \leq k \leq K \tag{5.4}
\]

\[
P_{2k+1} = 1 - \frac{k + q}{K + q + \frac{\bar{\gamma}}{\gamma}} \quad 0 \leq k \leq K \tag{5.5}
\]

\[
P_{c-1} = 1 - \frac{K + 1}{K + q + \frac{\bar{\gamma}}{\gamma}} \tag{5.6}
\]
For even \(c\), which is the case for \(B\)-steps the solution is given by:

\[
P_{2k} = 1 - \frac{k}{K + \frac{q}{\gamma}} \quad 0 \leq k \leq K
\]

(5.7)

\[
P_{2k+1} = 1 - \frac{k + q}{K + \frac{q}{\gamma}} \quad 0 \leq k \leq K
\]

(5.8)

\[
P_{c-1} = 1 - \frac{K + q}{K + \frac{q}{\gamma}}
\]

(5.9)

We note that in the real problem the set of difference equations is more complicated, since we allow interlayer diffusion from both the last and the next-to-last sites on the top terrace. However, as discussed in the Appendix C this problem may be mapped to the problem discussed above, by relabelling sites such that site \(c - 1\) corresponds to the next-to-last site on the top terrace, and renormalizing the value of \(\gamma\) so that it may be written in terms of the probabilities \(\epsilon\) and \(\epsilon'\) of interlayer diffusion from both sites. This is discussed in full detail in the Appendix C, along with the dependence of \(\gamma\) on \(\epsilon\) and \(\epsilon'\).

5.3.2 Surface Current for \(B\) Steps \((L \geq 7)\)

We first consider the case of \(B\) steps. In this case the relationship between the absorption site \(c\) in the 1D random-walk picture (Fig. 2) and the terrace width \(L\) in our units is \(L = (3c + 8)/2\) where \(c\) is an integer which satisfies \(c = 2K + 2\) where \(K = 0, 1, 2, 3, \ldots\). We note that the case \(c = 0\) \((K = -1)\) corresponds to a short terrace length \(L = 4\), when there is no diffusion on the terrace due to the fact that the only site available for deposition is an attachment site and will be discussed separately.
As shown in Fig. 5-1, the total surface current per particle \( J/F \), may be divided into four contributions due to deposition in four different regions. We first consider the contribution \( J_3/F \) due to atoms deposited in region III away from the step-edges. Since this region is far away from the steps, an atom deposited in this region will first arrive at either the nearest \( fcc \) or \( hcp \) site. If an atom is deposited at an even \( (fcc) \) site \( 2k \), the probability of absorption at site \( 0 \) is given by \( P_{2k} \) while the distance between the deposition site \( 2k \) and the attachment site \( 0 \) is \( d_{2k} = 3k \). However, if an atom is deposited at an odd \( (hcp) \) site \( 2k+1 \), the probability of absorption at site \( 0 \) is given by \( P_{2k+1} \) while the distance between the deposition site \( 2k+1 \) and the attachment site \( 0 \) is given by \( d_{2k+1} = 3k + 2 \). This leads to the following expression for the surface current per particle,

\[
\frac{J_3}{F} = \frac{3}{2L} \left\{ \sum_{k=1}^{K} [3kP_{2k} - (L - 3k)(1 - P_{2k})] + \sum_{k=0}^{K-1} [(3k+2)P_{2k+1} - (L - 3k - 2)(1 - P_{2k+1})] \right\}
\]  

(5.10)

where each term in the summations corresponds to the product of the distance a particle must travel from the initial landing position to the absorption site at an ascending (descending) step times the probability \( P(1 - P) \) of arriving at that site. The factor of \( 1/L \) corresponds to the deposition probability per unit interval \( \Delta \) while the factor of \( \frac{3}{2} \) in front of the expression is there to take into account the fact that in the sum we have included \( two \) sites per \( three \) units of length \( \Delta \) in discrete region III.

Taking into account that \( L = \frac{3c+8}{2} \) and \( c = 2K + 2 \) for \( B \) steps, we obtain for \( K \):

\[
K = \frac{L - 7}{3}
\]  

(5.11)
Substituting Eqs. (5.7), (5.8), (5.9) for $P_i$ along with Eq. (5.11) for $K$ into Eq. (5.10) along with the well-known formula for arithmetic series, we obtain for the surface current in region III:

$$\frac{J_3}{F} = \frac{(2 - 7 \gamma) (35 - 12 L + L^2)}{2L (2 + \gamma (L - 7))} \quad (5.12)$$

The second contribution to the surface current corresponds to atoms deposited within a distance $\delta = \pm 3\Delta$ from the step edge (regions I and IV, see Fig. 5-1). We first discuss region I corresponding to atoms deposited beyond the step-edge. To take into account the effects of short-range attraction during deposition, we consider the local uphill funneling probability $P_B(x)dx$ that an atom deposited above the lower terrace at an initial distance between $x$ and $x + dx$ beyond the step edge lands on the upper terrace (see Fig. 5-1). We assume that upon landing such an atom “cascades” to the last fcc (hcp) site with probability $\alpha(x) (\beta(x))$ where $\alpha(x) + \beta(x) = 1$. This leads to the following expression for the corresponding surface current,

$$\frac{J_1}{F} = \frac{1}{L} \int_L^{L+3} [\alpha(x)(1 - \epsilon) + \beta(x)]P_B(x)P_{c-1}(x - 3)dx$$

$$- \frac{1}{L} \int_L^{L+3} \alpha(x)\epsilon P_B(x) (L + 3 - x)dx$$

$$- \frac{1}{L} \int_L^{L+3} \beta(x) P_{c-1} P_B(x) (L + 3 - x)dx$$

$$- \frac{1}{L} \int_L^{L+3} (1 - P_B(x))(L + 3 - x)dx \quad (5.13)$$

The first and second integrals correspond to atoms which land on the upper terrace and then diffuse to the ascending step and descending steps respectively. The third integral corresponds to atoms which attach immediately (without diffusing) to the
descending step after being deposited. As before, the factor of $1/L$ arises from
the fact that the probability that the particle lands in a particular interval $dx$ is given by
$dx/L$.

Similarly, in region IV, we consider the local uphill funneling probability $P^B(x)dx$
that an atom deposited above the upper terrace at an initial distance between $x$ and
$x + dx$ from a step edge lands on the upper terrace (see Fig.5-1). We assume that
upon landing such an atom “cascades” to the last $fcc(hcp)$ site with probability
$\alpha'(x)$ ($\beta'(x)$) where $\alpha'(x) + \beta'(x) = 1$. This leads to the following expression for the
corresponding surface current,

$$\frac{J_4}{F} = \frac{1}{L} \int_{L-3}^{L} \left( \alpha'(x)(1 - \epsilon)P_{c-1} + \beta'(x)P_{c-1} \right) P^B(x)(x-3)dx$$
$$- \frac{1}{L} \int_{L-3}^{L} \alpha'(x)(1 - (1 - \epsilon)P_{c-1}) P^B(x)(L - x + 3) dx$$
$$- \frac{1}{L} \int_{L-3}^{L} \beta'(x)(1 - P_{c-1}) P^B(x)(L - x + 3) dx$$
$$- \frac{1}{L} \int_{L-3}^{L} (1 - P^B(x))(L - x + 3)dx \quad (5.14)$$

Combining both contributions, we obtain an expression for the contribution from
regions I and IV,

$$\frac{J_1 + J_4}{F} = \frac{6(P_\alpha^B + P_\beta^B + P_{c-1}^B + P_{c-1}^B - \epsilon(P_\alpha^B + P_\alpha^B))(1 - \gamma)}{2 + \gamma(L - 7)} - \frac{18}{L} \quad (5.15)$$
where we have introduced the quantities,

$$P'^B_\alpha = \frac{1}{3} \int_{L-3}^{L} \alpha'(x)P'^B(x)dx$$  (5.16)

$$P^B_\alpha = \frac{1}{3} \int_{L}^{L+3} \alpha(x)P^B(x)dx$$  (5.17)

$$P'^B_\beta = \frac{1}{3} \int_{L-3}^{L} \beta'(x)P'^B(x)dx$$  (5.18)

$$P^B_\beta = \frac{1}{3} \int_{L}^{L+3} \beta(x)P^B(x)dx$$  (5.19)

corresponding to the overall probabilities \((P'^B_\alpha, P^B_\alpha)\) \([(P'^B_\beta, P^B_\beta)]\) that an atom uniformly deposited in regions I or IV remains on the upper terrace at the last \((fcc)\) \([(hcp)]\) site immediately after deposition.

Finally, we consider the contribution from region II which can be simply expressed as:

$$J_2 = \frac{1}{L} \int_{3}^{4} (x - 3)dx = \frac{1}{2L}$$  (5.20)

Here we have taken into account that the diffusion distance is \(x - 3\) and the probability of immediate absorption of the particles, deposited within the region II at site 0 is equal to one.

Combining all four contributions, we obtain the following general expression for the total surface current of \(B\) steps:

$$\frac{J^B}{F} = \frac{(2 - 10\epsilon - 7\epsilon' + 10\epsilon\epsilon')L}{4 - 20\epsilon - 34\epsilon' + 20\epsilon\epsilon' + (4\epsilon + 6\epsilon' - 4\epsilon\epsilon')L}$$
\[
- \frac{12(2 - (P'_a B + P_a B + P'_b B + P_b B))}{4 - 20\epsilon - 34\epsilon' + 20\epsilon\epsilon' + (4\epsilon + 6\epsilon' - 4\epsilon\epsilon')L} \\
+ \frac{\epsilon (50 - 12(P'_a B + P_a B))}{4 - 20\epsilon - 34\epsilon' + 20\epsilon\epsilon' + (4\epsilon + 6\epsilon' - 4\epsilon\epsilon')L} \\
+ \frac{\epsilon' (99 - 12(P'_a B + P_a B + P'_b B + P_b B))}{4 - 20\epsilon - 34\epsilon' + 20\epsilon\epsilon' + (4\epsilon + 6\epsilon' - 4\epsilon\epsilon')L} \\
- \frac{(4\epsilon + 6\epsilon' - 4\epsilon\epsilon')L}{4 - 20\epsilon - 34\epsilon' + 20\epsilon\epsilon' + (4\epsilon + 6\epsilon' - 4\epsilon\epsilon')L}
\]

(5.21)

Where \((L \geq 7)\). Taking into account that for \(B\)-steps \(\epsilon = \frac{\rho}{2+\rho}\) and \(\epsilon' = \frac{\rho}{3+\rho}\), where
\[
\rho = \frac{\nu_B}{v_0} \exp(-E_{ES}/(k_B T))
\]
(see Appendix C), we obtain,

\[
\frac{J^B}{F} = \frac{(4 - 18\rho - 5\rho^2)L - 48 + 24(P'_a B + P_a B + P'_b B + P_b B)}{2(4 + 2(2L - 9)\rho + (L - 5)\rho^2)} \\
+ \frac{2(38 + 6(P'_b B + P_b B)\rho + 25\rho^2)}{2(4 + 2(2L - 9)\rho + (L - 5)\rho^2)}
\]

(5.22)

From Eq.(5.22) we may obtain the selected slope \(m_0^B = h/L_0 = 2\sqrt{2}/L_0\), corresponding to the value of the terrace length for which the surface current \(J/F\) is zero [61]:

\[
m_0^B = \frac{2\sqrt{2}(4 - 18\rho - 5\rho^2)}{48 - 24(P'_a B + P_a B + P'_b B + P_b B) - 2(38 + 6(P'_b B + P_b B)\rho - 25\rho^2)}
\]

(5.23)

We note that expressions (5.22) and (5.23) are only correct for terrace width \(L \geq 7\) which corresponds to selected slopes \(m_0 \leq 1/7\), since for higher slopes (smaller terrace widths) there is an overlap between the regions II and IV.

The quantities \(P'_a B, P_a B, [P'_b B, P_b B]\) were defined as the overall probabilities that an atom uniformly deposited in region I or in region IV remains on the upper terrace at
the last $fcc[hcp]$ site immediately after deposition where $P'_{\alpha} + P'_{\beta} = P'_{up}$ and $P^B + P^B_{\beta} = P^B_{up}$. However, these expressions can be simplified by making two reasonable assumptions. The first assumption is that $P'_{\alpha} = P'_{\beta} = \frac{1}{2}P'_{up}$. This assumption is consistent with the fact that deposition in region IV is equally likely to be above the last $fcc$ site as above the last $hcp$ site and is also consistent with the results of recent molecular dynamics simulations carried out for deposition near B-steps on Cu(111) [28]. In addition, it is reasonable to assume that atoms deposited beyond a $B$-step edge will end up on the nearest three-fold hollow site. Using these assumptions, Eqs.(5.22) and (5.23) become,

$$
\frac{J^B}{F} = \frac{(4 - 18\rho - 5\rho^2)\rho}{2} \left(4 - 2(2L - 9)\rho + (L - 5)\rho^2\right) \quad (L \geq 7) \quad (5.24)
$$

$$
m^B_0 = \frac{2\sqrt{2}(4 - 18\rho - 5\rho^2)}{48(1 - P^B_{av}) - 2(38 + 3P'_{up})\rho - 25\rho^2} \quad (m^B_0 \leq \frac{2\sqrt{2}}{7}) \quad (5.25)
$$

5.3.3 Surface Current for B Steps ($L = 4$)

We now consider the special case of shorter terrace lengths e.g. $L < 7$. Since the possible terrace widths for B-steps are $L = 1, 4, 7$ etc., the two possible special cases correspond to $L = 1$ and $L = 4$. The case $L = 1$ corresponds to a $(111)$microfacet and in terms of our model the surface current is negative (downhill) anyway, due to the fact that there are no $(111)fcc/hcp$ attachment sites available. So we only have to consider the special case $L = 4$.

When $L = 4$, the only site on the terrace (see Fig.5-4), where deposited atoms can land corresponds to the absorption $fcc$ site $(0)$. Assuming irreversible attachment,
Figure 5-4: Schematic diagram (top view) of A and B steps on fcc(111) surface for the case of short terrace length.
diffusion over the step is not allowed from this site. In this case, we consider the contributions to the surface current from two regions: region I \((4 \leq x < 6)\) and region IV \((2 \leq x < 4)\), which are similar to but slightly different from the regions I and IV considered in the general case. The resulting expressions for the surface current have the following forms:

\[
\tilde{J}_1 \frac{F}{L} = \frac{1}{L} \int_{L}^{L+2} \{P^B(x)(x-3) - (1 - P^B(x))(L + 3 - x)\} \, dx \quad (5.26)
\]

\[
\tilde{J}_4 \frac{F}{L} = \frac{1}{L} \int_{L-2}^{L} \{P'(x)(x-3) - (1 - P'(x))(L + 3 - x)\} \, dx \quad (5.27)
\]

Simplifying, summing Eq.(5.27),(5.26) and substituting \(L = 4\) we obtain an expression for the surface current per particle \(\tilde{J}^B / F\) for the case of short terrace length \(L = 4\),

\[
\tilde{J}^B \frac{F}{L} = 4 \tilde{P}_{av} - 3 \quad (5.28)
\]

Here \(\tilde{P}_{av} = \frac{\tilde{P}_{up} + \tilde{P}_{up}'}{2}\) where

\[
\tilde{P}_{up} = \frac{1}{2} \int_{4}^{6} P^B(x) \, dx \quad (5.29)
\]

\[
\tilde{P}_{up}' = \frac{1}{2} \int_{2}^{4} P'(x) \, dx \quad (5.30)
\]

correspond to the overall probabilities that an atom uniformly deposited in region I \((\tilde{P}_{up})\) or in region IV \((\tilde{P}_{up}')\) remains on the upper terrace immediately after deposition.

From Eq. 5.28 we can see that \(L_0 = 4\) is possible only if \(\tilde{P}_{av} = 0.75\). For \(\tilde{P}_{av} < 0.75\), the surface current is negative and the corresponding selected terrace length will be longer than \(L = 4\). However, for \(\tilde{P}_{av} > 0.75\), the surface current is positive
for $L = 4$ and the corresponding selected terrace length will in between the value $(L = 1)$ corresponding to a $\{111\}$ microfacet and $L = 4$. We note that geometric DF corresponds to $\tilde{P}_{av}^B = 1/2$ and thus implies a selected terrace length $L_0 > 4$.

### 5.3.4 Surface Current for A Steps ($L \geq 8$)

The calculation for $A$ steps is similar to that for $B$ steps except that, as already noted, in this case, one has $q = \frac{1}{3}$ and $p = \frac{2}{3}$. The relationship between the absorption site $c$ in the 1D random-walk picture (Fig. 2) and the terrace width $L$ in our units is $L = (3c + 7)/2$ where $c$ is an integer which satisfies $c = 2K + 3$ where $K = 0, 1, 2, 3, \ldots$.

In addition, the last fcc site is not the site closest to the step-edge. In this case, the probability for inter-layer diffusion from the fcc-site is again given by $\epsilon$ and the probability of diffusion down the step from the last hcp site on the terrace is given by $\epsilon'$.

Taking into account all these differences, we obtain the general expression for the total surface current of $A$ steps:

$$\frac{J^A}{F} = \frac{(6 - 51\epsilon - 30\epsilon' + 30\epsilon\epsilon')L}{12 - 102\epsilon - 60\epsilon' + 60\epsilon\epsilon' + (18\epsilon + 12\epsilon' - 12\epsilon\epsilon')L}$$

$$- \frac{72 - 36(P'_A + P_A + P'_{\beta} + P_{\beta})}{12 - 102\epsilon - 60\epsilon' + 60\epsilon\epsilon' + (18\epsilon + 12\epsilon' - 12\epsilon\epsilon')L}$$

$$+ \frac{\epsilon(300 - 36(P'_A + P_A + P'_{\beta} + P_{\beta}))}{12 - 102\epsilon - 60\epsilon' + 60\epsilon\epsilon' + (18\epsilon + 12\epsilon' - 12\epsilon\epsilon')L}$$

$$+ \frac{\epsilon'(152 - 36(P'_A + P_A))}{12 - 102\epsilon - 60\epsilon' + 60\epsilon\epsilon' + (18\epsilon + 12\epsilon' - 12\epsilon\epsilon')L}$$

(5.31)
Where \((L \geq 8)\). Taking into account that \(\epsilon = \frac{\rho}{3+\rho}\) and \(\epsilon' = \frac{\rho}{2+\rho}\), where

\[
\rho = \frac{\nu_B}{\nu_0} \exp\left(-\frac{E_A}{k_B T}\right) \quad \text{(see Appendix C)},
\]

we obtain,

\[
\frac{J^A}{F} = \frac{3 (4 - 18\rho - 5\rho^2) L - 144(1 - P_{av}^A) + 2(116 + 9P_{up}^A)\rho + 76\rho^2}{6(4 + (4L - 18)\rho + (L - 5)\rho^2)} \quad (L \geq 8)
\]

\[
(m_0^A = \frac{3 (4 - 18\rho - 5\rho^2)}{144(1 - P_{av}^A) - 2(116 + 9P_{up}^A)\rho - 76\rho^2} \quad (m_0^A \leq \frac{2\sqrt{2}}{8})
\]

### 5.3.5 Surface Current for A Steps \((L = 5)\)

We may also consider the surface current for the special case of shorter terrace lengths \(L < 8\) for which there is an overlap between regions II and IV and Eq.(5.32),(5.33) may break down. Since the possible terrace widths for A-steps are \(L = 2, 5, 8\ etc.,\) the two possible special cases correspond to \(L = 2\) and \(L = 5\). The case \(L = 2\) corresponds to a \((100)\ microfacet\) and in terms of our model the surface current is negative (downhill) anyway, due to the fact that there are no \((111)fcc/hcp\) attachment sites available. For the special case \(L = 5\) we obtain:

\[
\frac{\dot{J}^A}{F} = 5\dot{P}_{av}^A - 3
\]
where
\[ \tilde{P}_{av}^A = \frac{\tilde{P}_{up}^{A'} + \tilde{P}_{up}^A}{2} \] (5.35)

and
\[ \tilde{P}_{up}^{A'} = \frac{1}{2.5} \int_{2.5}^{5} P^{A'}(x) dx \] (5.36)
\[ \tilde{P}_{up}^A = \frac{1}{2.5} \int_{5}^{7.5} P^A(x) dx \] (5.37)

We can see that \( L_0 = 5 \) is possible only if \( \tilde{P}_{av}^A = 0.6 \); for all \( 0 < \tilde{P}_{av}^A < 0.6 \), the surface current is negative and corresponding selected terrace length will be longer than \( L_0 = 5 \). Here we note again that geometric DF corresponds to \( \tilde{P}_{av}^B = 1/2 \) and thus implies a selected terrace length \( L_0 > 5 \). For all \( \tilde{P}_{av}^A > 0.6 \), the surface current is positive and the corresponding selected terrace length will be shorter than \( L_0 = 5 \): in between the \( L = 5 \) and the value corresponding to (100) microfacet \( (L = 2) \), depending on the particular value of \( \tilde{P}_{av}^A \).

5.3.6 Calculation of selected slopes for intermediate cases

Intermediate case 1: mixture of short terraces and longer terraces

We note that for certain values of \( P_{av} \), the selected terrace width \( L_0 \) will be intermediate between that for a short terrace \( (L = 4(5) \text{ for B (A) steps}) \) and that for the shortest “general” terrace case \( (L = 7(8) \text{ for B (A) steps}) \). In this case, the selected slope will be determined by combining our results for a short terrace as described in the previous section. We first consider the case of \( B \)-steps. We suppose that \( \tilde{P}_{av}^B < 0.75 \) (see Sec. 5.3.3) and the surface current per particle \( J_4^B/F \)
corresponding to the short terrace \( L = 4 \) is negative. We also assume that the surface current per particle \( J^B_i/F \) corresponding to \( L = 7 \) is positive. We are looking for values of \( N_4 \) and \( N_7 \) such that the total surface current over \( N_4 \) terraces of length \( L = 4 \) and \( N_7 \) terraces of length \( L = 7 \) is equal to zero:

\[
7 \frac{J^B_i}{F} N_7 + 4 \frac{J^B_i}{F} N_4 = 0 \quad (5.38)
\]

Here we have taken into account the fact that the total number of atoms which land on a terrace of width \( L \) is proportional to \( L \). The intermediate value of selected slope, corresponding to a mixture of \( N_4 \) terraces of length \( L = 4 \) and \( N_7 \) terraces of length \( L = 7 \) can then be expressed as:

\[
m^B_0 = \frac{(N_7 + N_4)h}{7N_7 + 4N_4} \quad (5.39)
\]

Taking into account Eq. 5.38, we obtain,

\[
m^B_0 = \frac{(4 - 7 \frac{J^B_i}{F})h}{28(1 - \frac{J^B_i}{F})} \quad (5.40)
\]

Using Eq. 5.24 (with \( L = 7 \)) and Eq. 5.28, we obtain finally,

\[
m^B_0 = \frac{-(22 - 168 \tilde{P}^B_{av} + 55\rho - 21 \tilde{P}^B_{up} \rho + 11\rho^2 + 32 \tilde{P}^B_{av}(2 + 5\rho + \rho^2))}{28(2 + 24 \tilde{P}^B_{av} + 5\rho + 3 \tilde{P}^B_{up} \rho + \rho^2 - 8 \tilde{P}^B_{av}(2 + 5\rho + \rho^2))}h \quad (5.41)
\]

Using the same approach, we can obtain the intermediate value of selected slope corresponding to a mixture of terraces with terrace lengths \( L = 5 \) and \( L = 8 \) for \( A \).
steps:

\[ m_0^A = \frac{-(12 - 576P_{av}^A + 170\rho - 72P_{av}'^A\rho + 41\rho^2 + 75\tilde{P}_{av}^A(4 + 14\rho + 3\rho^2))}{40(12 + 72P_{av}^A + 26\rho + 9P_{av}'^A\rho + 5\rho^2 - 15\tilde{P}_{av}^A(4 + 14\rho + 3\rho^2))} \hbar \] (5.42)

Intermediate case 2: mixture of short terraces and facets

For higher values of \( P_{av} \) such that the surface current is positive for a short terrace, the selected terrace width will be intermediate between that for a microfacet (\( L = 1 \) for B steps and \( L = 2 \) for A steps) and a short terrace (\( L = 4 \) for B steps and \( L = 5 \) for A steps). We first consider the case of B-steps (\( \tilde{P}_{av}^B > 0.75 \), see Sec. 5.3.3). We assume that there are \( n_f \) regions with \( N_f^i \) microfacets in each region, with \( i = 1 \) to \( n_f \) and, similarly, there are \( n_t \) regions with \( N_t^i \) terraces in each region with \( i = 1 \) to \( n_t \). The total number of facets is \( N_f = \sum_{i=1}^{n_f} N_f^i \) and the total number of terraces is \( N_t = \sum_{i=1}^{n_t} N_t^i \). Once the values of \( N_f \) and \( N_t \) are determined, the mound slope may be expressed as,

\[ <m^B> = \frac{N_t + N_f}{4N_t + N_f}\hbar \]
(5.43)

Without loss of generality we can assume that \( n_f = n_t = n \). The surface current per particle corresponding to a region composed of a sequence of \( N_f^i \) microfacets can be expressed as,

\[ \frac{J_f^i}{F} = \frac{1}{L} \int_0^2 [P^B(x)(1+x) - (1-P^B(x))(N_f^i + 3-x)]dx - \frac{1}{L} \int_2^{N_f^i} [N_f^i + 3-x)]dx \]
(5.44)

where \( L = N_f + 4N_t \) where we assume that any particle deposited on a facet diffuses
to attachment site at the lower terrace. This may be rewritten as,

\[ \frac{J_f^i}{F} = \frac{1}{L} \left[ 4(2\tilde{P}_{up}^B - 1) + 2(\tilde{P}_{up}^B - 1)N_f^i - \frac{(N_f^i)^2}{2} - N_f^i + 4 \right] \tag{5.45} \]

where

\[ \tilde{P}_{up}^B = \frac{1}{2} \int_4^6 P^B(x)dx \tag{5.46} \]

The total contribution to the surface current per particle due to the faceted regions can be expressed as:

\[ \frac{J_f}{F} = \sum_{i=1}^{n} \frac{J_f^i}{F} = \frac{1}{L} \left[ 2\tilde{P}_{up}^B(4n + N_f^i) - 3N_f^i - \frac{1}{2} \sum_{i=1}^{n} (N_f^i)^2 \right] \tag{5.47} \]

We now consider the surface current due to the regions comprised of short terraces, which contain 3 contributions: \( J_1 \) due to the topmost terrace in each region, \( J_2 \) due to the bottom terrace in each region, and \( J_3 \) due to the interior terraces in each region. The surface current \( J_3 \) may be calculated by using the general expression for the
Figure 5-6: Details of deposition over topmost terrace in a sequence of short terraces. However, to calculate $J_1$ and $J_2$ one must take into account the effect of the neighboring facet.

The current $J_1$ may be written,

$$
\frac{J_1^t}{F} = \frac{n}{L} \int_0^2 (x - 3) dx
+ \frac{n}{L} \int_2^4 (P^B(x)(x - 3) - (1 - P^B(x))(7 - x)) dx
= \frac{n}{L} [8 \tilde{P}'_{up} - 12] \tag{5.48}
$$

where

$$\tilde{P}'_{up} \equiv \frac{1}{2} \int_2^4 P^B(x) dx \tag{5.49}$$

The current $J_2$ may be written,

$$
\frac{J_2^t}{F} = \frac{1}{L} \sum_{i=1}^n \left[ \int_0^2 (P^B(x)(1 + x) - (1 - P^B(x))(3 - x)) dx
+ \int_2^4 (P^B(x)(x - 3) - (1 - P^B(x))(N_i^f + 7 - x)) dx \right] \tag{5.50}
$$

$$\frac{J_2^t}{F} = \frac{1}{L} [16 \tilde{P}_av n - 12n - 2(1 - \tilde{P}'_{up})N^f] \tag{5.51}$$
Figure 5-7: Details of deposition over bottom terrace in a sequence of short terraces.

where the factor $N_i^f$ takes into account the probability that an atom deposited near the step-edge lands on the facet and diffuses to the bottom of the faceted region.

Using Eq. 5.28 for the surface current per particle due to a single terrace, the contribution from all the other terraces can be expressed as:

$$
\frac{J_i^2}{F} = \frac{\tilde{J}^B 4(N^i - 2n)}{L} = \frac{4}{L} (4\tilde{P}_{av}^B - 3)(N^i - 2n)
$$

(5.52)

where the factor of $N^i - 2n$ corresponds to the total number of short-terraces in this intermediate region. Combining all three contributions and using the simplifying assumption that $N_i^f = N_f$ and $N_i^t = N_t$ for all $i$, along with the requirement that the total surface current is zero yields,

$$
N_f^2 + 2(5 - 4\tilde{P}_{av}^B)N_f - 8(4\tilde{P}_{av}^B - 3)N_t = 0
$$

(5.53)
Solving for $N_f$, we obtain:

$$N_f^B = \frac{-2(5 - 4\tilde{P}_B^{av}) + \sqrt{4(5 - 4\tilde{P}_B^{av})^2 + 32(4\tilde{P}_B^{av} - 3)N_t}}{2} \quad (0.75 < \tilde{P}_B^{av} \leq 1) \quad (5.54)$$

For simplicity we have made the reasonable assumption that the uphill funneling probability for atoms deposited above the facetted region adjacent to the upper terrace within a distance $\delta = 2$ from the step edge has the same distribution $P^B(x)$ ($P'^B(x)$) as in the case of the deposition near step-edge between two short terraces (see Sec. Sec. 5.3.3).

Using the same approach, we can obtain the intermediate value of the selected slope corresponding to a mixture of short terraces ($L = 5$) and (100) microfacets ($L = 2$) for $A$ steps:

$$< m^A > = \frac{N^t + N_f}{5N^t + 2N_f} h \quad (5.55)$$

$$N_f^A = \frac{-(11 - 10\tilde{P}_B^{av}) + \sqrt{(11 - 10\tilde{P}_B^{av})^2 - 40(3 - 5\tilde{P}_B^{av})N_t^A}}{4} \quad (0.6 < \tilde{P}_B^{av} \leq 1) \quad (5.56)$$

We note that Eqs. (5.43),(5.54) and (5.55),(5.56) indicate that the selected slope depends on the values of $N_f$ and $N_t$. However, for realistic values of uphill funneling probabilities, we find that, except for small $N_f$, the selected slope depends relatively weakly on the value of $N_f$. 
5.4 Discussion

As already noted, for both $A$ and $B$-steps the parameter $\rho$ used in our calculations is connected to the Ehrlich-Schwoebel barrier $E_{ES}$ as,

$$\rho = \frac{\nu_B}{\nu_0} \exp(-E_{ES}/(k_B T))$$  \hspace{1cm} (5.57)

where, in general, the values of $E_{ES}$ are different for $A$ and $B$ steps.

We note that for the case of an infinite ES barrier, one has $\rho = 0$ and the expressions for the selected slope (Eq.(5.25),(5.33)) reproduce the expressions derived previously for this case [28]:

$$m_0 = \frac{h}{12(1 - P_{av})} = \frac{\sqrt{2}}{6(1 - P_{av})}$$  \hspace{1cm} (5.58)

We now discuss in more detail the consequences of our results for the predicted mound slopes as a function of the corresponding uphill funneling probabilities as well as $\rho$.

We note that Eqs. ((5.24), (5.32)) for the surface current and Eqs. ((5.25), (5.33)) for the selected mound slope can be written in the following general forms:

$$\frac{J}{F} = \frac{(A - B\rho - C\rho^2)L - (D - E\rho - F\rho^2)}{X}$$  \hspace{1cm} (5.59)

$$m_0 = \frac{A - B\rho - C\rho^2}{D - E\rho - F\rho^2}$$  \hspace{1cm} (5.60)

where $A, B, C, D, E, F, X > 0$ for all terrace widths $L$ for which Eqs. ((5.24), (5.32))
and (5.33), (5.33)) are valid.

Since the criterion for a mound instability is that the surface current is positive for small slopes, while the selected slope is determined by the zero of the surface current, this implies that there exists a critical value of \( \rho, \rho_c \), equal to the positive root of the equation \( A - B\rho - C\rho^2 = 0 \) such that for \( \rho < \rho_c \) there will be an instability with a non-zero selected mound slope, while for \( \rho > \rho_c \) no instability will exist. We also define \( \rho_0 \) as the positive root of the equation \( D - E\rho - F\rho^2 = 0 \).

Depending on the system parameters and the values of \( A, B, C, D, E \), and \( F \), there are two different possible scenarios.

**Scenario 1:** \( \rho_c \leq \rho_0 \) As discussed in more detail below, this case applies when the uphill funneling probabilities \( P_{up} \) and \( P'_{up} \) are not too high. For example (see Eq. 5.25) the usual downward funneling assumption [26] \((P_{up} = 0, P'_{up} = 1)\) falls into this case. In this case, with increasing \( \rho \), the numerator in expression (5.60) for the selected mound slope goes to zero before the denominator. This implies that as \( \rho \) approaches the critical value \( \rho_c \) from below, the selected mound slope decreases to zero (see Fig. 5-8). Conversely, for \( \rho > \rho_c \), the surface current is negative for all slopes so there is no instability.

**Scenario 2:** \( \rho_c > \rho_0 \)

As discussed in more detail below, this case applies when the uphill funneling probabilities \( P_{up} \) and \( P'_{up} \) are relatively high. In this case, with increasing \( \rho \), the denominator of expression (5.60) goes to zero at \( \rho = \rho_0 \), i.e. before the numerator which goes to zero at \( \rho = \rho_c \) (see Fig. 5-8). As a result, for \( 0 < \rho < \rho_c \) the values of the selected slope predicted by Eq. (5.25) are much higher than the limits of their
validity, which correspond to the minimum terrace lengths that may be considered in our general calculations of the surface current and selected mound slope. Accordingly, the selected slopes need to be calculated by considering the special cases corresponding to either a mixture of a short-terrace and the shortest general terrace, or of a facet and a short-terrace discussed in Sec. 5.3.6.

On the other hand, for $\rho > \rho_c$ the surface current, is negative for small slopes, although it becomes positive for larger slopes due to the high values of $P_{up}$ and $P_{up}'$. So that, in the presence of inevitable fluctuations and shot noise in the growth, a particular “critical” value of the slope can be reached, for which the surface current is zero. Once the local slope has gone beyond this critical value, it will continue to increase due to the positive surface current until the surface current again becomes zero due to the existence of facets (see Sec. 5.3.6).
As already noted, scenario 1 holds when the uphill funneling is not too large, while scenario 2 corresponds to enhanced uphill funneling.

For $B$-steps, scenario 1 holds when

\[
\frac{-9 + \sqrt{101}}{5} \leq \frac{1}{50}[-2(38 + 3P_{\text{up}}^B) + \sqrt{4800(1 - P_{\text{av}}^B) + 4(38 + 3P_{\text{up}}^B)^2}] \quad (5.61)
\]

while scenario 2 holds when

\[
\frac{-9 + \sqrt{101}}{5} > \frac{1}{50}[-2(38 + 3P_{\text{up}}^B) + \sqrt{4800(1 - P_{\text{av}}^B) + 4(38 + 3P_{\text{up}}^B)^2}] \quad (5.62)
\]

For $A$-steps, scenario 1 holds when

\[
\frac{-9 + \sqrt{101}}{5} \leq \frac{1}{76}[-116 - 9P_{\text{up}}^A] + \sqrt{24400 - 10944P_{\text{av}}^A + 2088P_{\text{up}}^A + 81(P_{\text{up}}^A)^2] \quad (5.63)
\]

while scenario 2 holds when

\[
\frac{-9 + \sqrt{101}}{5} > \frac{1}{76}[-116 - 9P_{\text{up}}^A] + \sqrt{24400 - 10944P_{\text{av}}^A + 2088P_{\text{up}}^A + 81(P_{\text{up}}^A)^2] \quad (5.64)
\]

Since the numerators in Eqs. ((5.25), (5.33)) are independent of the uphill funneling probabilities, the critical value of $\rho$ is also independent, i.e. one has,

\[
\rho_c = \frac{-9 + \sqrt{101}}{5} \approx 0.21 \quad (5.65)
\]

for both $A$ and $B$ steps.
Figure 5-9: Selected mound slope of A steps as function of $\rho$ (scenario 1) for several different values of $P_{av}$ and $\tilde{P}_{av}$. (a) $P_{av}$ and $\tilde{P}_{av}$ both not too large ($\tilde{P}_{av} < 0.6$). Case 1 corresponds to $P_{av} = 0$, case 2 to $P_{av} = 1/2$ (DF), case 3 to $P_{av} = 0.57$, $\tilde{P}_{av} = 0.59$. (b) Discontinuity in slope ($P_{av} = 0.57$, $P'_{up} = 1, \tilde{P}_{av} = 0.65$). Dashed curve indicates critical slope for fluctuation-induced mound formation.

We note that for some combinations of $P_{up}$, $P'_{up}$ and $\rho$, Eqs.(5.25) and (5.33) can give values of the selected slope which are greater than $m_{max}^B = \frac{h}{7} \simeq 0.4$ and $m_{max}^A = \frac{h}{8} \simeq 0.354$. In this case, depending on the particular values of uphill funneling probabilities, the results of Sec. 5.3.6 (Eqs.(5.42), (5.41)) or (Eqs.(5.54), (5.55), (5.56)) are applicable.

Figures 5-9 - 5-12 show the range of possible behaviors for the selected slope as a function of $\rho$ for both scenario 1 and scenario 2 for A and B steps. In particular, results are shown with $P_{av}$ ranging from zero (maximum downhill funneling) to very strong uphill funneling. Also shown are results for geometric downhill funneling (DF).

We note that recent molecular dynamics simulations of deposition near the steps on $fcc(111)$ metal surfaces [28] indicate a significant asymmetry between the interaction of depositing atoms at A and B steps. In particular, it was found that for A-steps,
Figure 5-10: Selected mound slope of $A$ steps as function of $\rho$ for scenario 2 (enhanced uphill funneling). Parameters here are: $P_{av} = 0.72$, $\tilde{P}_{av} = 0.76$, $P'_{up} = 1$. Dashed curve indicates critical slope for fluctuation-induced mound formation.

Figure 5-11: Selected mound slope of $B$ steps as function of $\rho$ (scenario 1) for several different values of $P_{av}$ and $\tilde{P}_{av}$. (a) $P_{av}$ and $\tilde{P}_{av}$ both not too large ($\tilde{P}_{av} < 0.75$). Case 1 corresponds to $P_{av} = 0$, case 2 to $P_{av} = 1/2$ (DF), case 3 to $P_{av} = 0.53$, $P'_{up} = 0.71$, $\tilde{P}_{av} = 0.62$. (b) Discontinuity in slope ($P_{av} = 0.57$, $P'_{up} = 0.9$, $\tilde{P}_{av} = 0.77$). Dashed curve indicates critical slope for fluctuation-induced mound formation.
due to the short-range attraction of depositing atoms to the step-edge, the overall uphill funneling probability $P_{av}^A$ is significantly larger than predicted by downward funneling. This corresponds to the second scenario discussed above (see Fig. 5-10). In contrast, due to high probability of “knockout” or exchange at $B$-steps, the overall uphill funneling probability $P_{av}^B$ is significantly lower, and appear to be close to the downward funneling prediction. This corresponds to the first scenario discussed above (see Fig. 5-11). Consequently, the behavior of the selected slope with respect to $\rho$ is significantly different for $A$ and $B$ steps, and for the fixed $\rho$ the selected mound slopes corresponding to $A$ and $B$ steps are different in most cases. These results imply a significant asymmetry in the mound shape for the case of unstable irreversible growth on metal $fcc(111)$ surfaces and may play an important role in explaining the observed mound morphology.
5.5 Conclusions

We have obtained general expressions for the surface current and selected mound slope for irreversible growth on a regular stepped $fcc(111)$ surface with two types of close-packed step edges, $A$ steps and $B$ steps, for the case of finite step barrier. We took into account the effects of interaction of depositing atoms with the steps, that reflect the differences in underlying geometry as well as the corresponding activation barriers of $A$ and $B$ steps. The obtained expressions for the surface current and selected mound slope depend sensitively on the values of the uphill funneling probabilities as well as on the value of $\rho = \frac{\nu_B}{\nu_0} \exp(-\frac{E_{ES}}{k_B T})$.

We discussed separately the case of the short terrace lengths ($L = 4$ for $B$ steps and $L = 5$ for $A$ steps), in which cases the general expressions for the surface current and selected mound slope may break down. It was shown that enhanced uphill funneling $\tilde{P}_B^{av} = 0.75$ ($\tilde{P}_A^{av} = 0.6$) is required, $L = 4$ ($L = 5$) to be selected terrace length for $B$ steps ($A$ steps).

We also corrected the general expressions for selected slope in the regions, where they give the values of slope greater than the ones corresponding to the minimum terrace lengths that may be considered in general expressions for the surface current ($m_{B_{\text{max}}} = \frac{h}{4} \approx 0.4$ and $m_{A_{\text{max}}} = \frac{h}{8} \approx 0.354$) and provided the expressions for the intermediate values of the selected slope that are in between the values corresponding to the short terrace lengths ($L_B = 4$ and $L_A = 5$) and the values corresponding to the minimum terrace lengths that may be considered in general expressions for the surface current ($I_{B_{\text{min}}} = 7$ and $L_{A_{\text{min}}} = 8$) for $\tilde{P}_B^{av} < 0.75$, $\tilde{P}_A^{av} < 0.6$ (See Sec. 5.3.6).
For the cases when the surface current is positive even for the short terrace lengths \((L^B = 4 \text{ and } L^A = 5)\) we suggested the way to calculate the intermediate value of selected slope that is in between the ones, corresponding to the short terraces and \((111)\) microfacet (for B steps) or \((100)\) microfacet (for A steps)(See Sec. 5.3.6).

We analyzed the expressions for the surface current and selected mound slope and discussed the scenarios corresponding to the various values of parameters \((\rho, P_{up}' \text{ and } P_{up})\).

For the case when the uphill funneling is not too large (for example, \(P_{up}'^A = P_{up}'^B = 1\) and \(P_{av}^A < 0.612, P_{av}^B < 0.618\)) we found the critical value of \(\rho (\rho_c^B = \rho_c^B = -\frac{9+\sqrt{101}}{5} \simeq 0.21)\) required for mound formation. For all \(P_{up}' \text{ and } P_{av}\) that correspond to enhanced uphill funneling (for example, \(P_{up}'^A = P_{up}'^B = 1 \text{ and } P_{av}^A > 0.62, P_{av}^B > 0.62\)), we predict the existence of the region \(\rho > \rho_c\), where the values of slope exist for which the surface current is zero, and this “critical” slope exhibit the “unnatural” behavior - it increases with the increasing \(\rho\). This implies, that in the presence of inevitable thermal fluctuations and shot noise in the growth, the mentioned above values of the “critical” slope can be reached and further increase of the slope (up to the values that are in between the ones corresponding to the short terraces \((L^B = 4 \text{ and } L^A = 5)\) and \((111)\) microfacet for B steps or \((100)\) microfacet for A steps) in this case produces an additional uphill surface current.

Our results suggest that the behavior of selected slope with respect to \(\rho\) is significantly different for A and B steps, which implies a significant asymmetry in the mound shape for the case of unstable irreversible growth on metal \(fcc(111)\) surfaces.

We note that the future work will be needed to include in our model new effects and
processes recently observed, such as long-range effect of the step boundary \cite{73},\cite{74}, which consists of non-uniformity of the surface potential near a step, including the existence of a so-called “empty zone” which separates the central region of the terrace from the step-edge by additional energy barrier. Such an effect may play a significant role in addition to the Ehrlich-Schwoebel barrier in determining surface morphology.

We expect that the results presented here can be useful in further understanding the mound morphology and selected mound angles observed in metal $fcc(111)$ epitaxial growth.
Chapter 6

Conclusions

In this thesis we have presented the results of simulations and analytic calculations carried out in order to understand the morphology and evolution of the surface in thin-film growth. A complete description of epitaxial growth requires the consideration of processes on many different time and length scales. We successfully applied the hybrid KMC-MD multi-scale simulation model to study the dependence of growth behavior on the variety of growth parameters, which include deposition geometry, growth temperature and flux. In particular the effects of attraction in oblique incidence metal(100) epitaxial growth were studied by comparing the results of simulations which include the effects of short-range (SR) and long-range (LR) attraction with results obtained in the absence of attraction. In general, we find that the qualitative dependence of the surface morphology on deposition angle and film thickness, including the existence of a transition from mounds to asymmetric ripples oriented perpendicular to the beam at large deposition angles, as well as a second transition from ripples to rods with (111) facets oriented parallel to the beam at larger deposi-
tion angles and film thicknesses, is not altered by the presence of attraction. However, we found that attraction could have two important effects. The first effect, which is a result of steering due to LR attraction and leads to decreased shadowing, leads to decreased anisotropy in the submonolayer regime and can also lead to decreased surface roughness for high deposition angles and intermediate film thicknesses. The second effect, due to flux-focusing, leads to an increase in the surface roughness and feature size and also reduces the critical thickness for ripple and rod formation. This effect also tends to limit the anisotropy in the rod phase for high deposition angles and film thicknesses.

While the effects of deposition angle have traditionally been assumed to be negligible in epitaxial growth for moderate deposition angles, they have not been fully investigated, especially at low temperatures of growth. The results of our simulations of Cu/Cu(100) epitaxy at a range of growth temperatures demonstrated strong temperature dependence for the effect of deposition angle on the surface roughness. Our results resolved a long standing puzzle regarding the growth behavior of Cu/Cu(100) over the temperature range from 160 K to 200 K. Our results also demonstrated that, in general, the effects of deposition angle must be considered in low-temperature growth even for moderate deposition angles.

At even lower growth temperatures, where the thermally activated diffusion processes are effectively inoperative and, correspondingly, KMC simulation of diffusion events is not crucial for correct description of growth processes, we employed MD simulation technique to study the development of compressive surface-normal strain and incorporation of vacancies in Cu/Cu(100), and Ag/Ag(100) thin films grown at
very low temperatures. The results obtained via MD, along with X-ray diffraction patterns, calculated numerically using simulated atomic configurations, suggested that the strain observed experimentally was not due to incorporation of vacancies into the films (as proposed by the experimental group), but due to increased surface roughness/area and peculiarities of shape/size of the surface features. Here, again, the experimentally observed behavior could only be explained by taking the angle of deposition into account.

The last part of the thesis presented an analytic calculation of the surface current and selected mound angle for the case of irreversible epitaxial growth on an $fcc(111)$ surface with a finite Ehrlich-Schwoebel (ES) barrier. The special cases of short terraces and combinations of short terraces with facets which lead to large mound slopes were also discussed. We find that for both $A$ and $B$ steps the surface current and selected mound slope are determined by two key parameters - the Ehrlich-Schwoebel (ES) barrier and the degree of uphill funneling due to short-range attraction. However, the presence or absence of a small-slope instability is exclusively determined by the value of the ES barrier. In particular there exists a critical value of the parameter $\rho$ (where $\rho = (\nu_0/\nu_{ES})e^{-E_{ES}/k_B T}$ and $E_{ES}$ is the ES barrier) such that for $\rho < \rho_c$, the flat surface is unstable to mound formation while for $\rho > \rho_c$ there is no such instability. The critical value $\rho_c \simeq 0.21$ is the same for both $A$ and $B$ steps and independent of the degree of uphill funneling due to short-range attraction. When the uphill funneling is not too large, the selected slope decreases continuously with increasing $\rho$, reaching zero at $\rho_c$. However, in the presence of sufficiently large uphill funneling, the selected slope is independent of $\rho$ for $\rho < \rho_c$. In this case a new phenomenon
which we refer to as fluctuation-induced instability also occurs. In particular, while the surface remains stable for $\rho > \rho_c$ for small slopes, for larger slopes the surface current may become positive due to uphill funneling. Thus, even in the presence of a small ES barrier, mound formation may still occur. Additionally, we present typical results for the dependence of the mound slope on $\rho$ for both $A$ and $B$ steps. These results can be used to estimate the selected mound angles for a variety of materials and growth conditions in case of growth on an $fcc(111)$ surface.

Finally, we note that thin film deposition is just one of the many problems in which the physics is inherently multi-scale. Single scale higher resolution methods, such as $ab$ initio quantum mechanical models or molecular dynamics, will have difficulty in analyzing the behavior of such systems due to the limitations in terms of the time and length scales that each method is confined to. At the same time, the important atomistic details can not be grasped with the methods operating on the coarse scales. Application of multi-scale approaches, in which the fine scale model is applied only in localized regions where the atomic scale resolution is crucial, to this class of problems seems to be the most promising route. The work presented in this thesis demonstrates the capability of the multi-scale concept in efficient resolution of the real, experimentally imposed puzzles.

Many of the multi-scale methods, introduced recently, are still at their embryonic stage of development. In general, there are several major issues to be challenged in future: the proper treatment of the interface between the coarse and fine scales, extension of the time/length range currently available in quantum and traditional molecular dynamics, wider use of $ab$ initio quantum mechanical models and their
integration into multi-scale simulations.
Appendix A

Characterization of surface morphology

The surface roughness during far-from-equilibrium thin film growth may be characterized by the fluctuations of the height $h_i(t)$ around its mean value $\bar{h}(t)$. One important quantity is the global interface width,

$$W(L, t) = \sqrt{\frac{1}{L^{d-1}} \sum_i [h_i(t) - \bar{h}(t)]^2}$$

(A.1)

where $L$ is the linear system size in $d$-dimensional space, $d$-1 dimensionality of the substrate, the single-valued function $h_i(t)$ describes the height of the film at the $i$-th location at time $t$, the index $i$ labels lattice sites, and $\bar{h}(t) = \frac{1}{L^{d-1}} \sum_i h_i(t)$ the mean height of the film at time $t$.

In many cases surface height fluctuations exhibit universal behavior leading to scaling in both time and space with three characteristic scaling exponents: roughness
exponent $\alpha$, roughening, or growth exponent $\beta$, and dynamic exponent $z$. In case of a self-affine surface, the profile of the growth interface and its properties are, generally, statistically invariant under anisotropic transformations, i.e. the length in a direction parallel to the surface is scaled by a factor and simultaneously the length in the perpendicular direction and time $t$ are scaled by factors related to the first one.

Assuming an initially flat surface, the interface width $W(L,t)$ typically scales as a power of time in the initial stages of growth,

$$W(L,t) \sim t^\beta \quad \text{for} \quad t \ll t_X$$  \hspace{1cm} (A.2)

where $\beta$ is a roughness exponent. Due to the lateral correlation in surface heights and the finite size of the system, the width eventually saturates. The saturation value of the interface width scales with a power of the system size $L$,

$$W(L,t) \sim L^\alpha \quad \text{for} \quad t \gg t_X$$  \hspace{1cm} (A.3)

where $\alpha$ is the roughness exponent. The crossover time, $t_X$, at which the interface crosses from the behavior described by the Eq. A.2 to that of Eq. A.3 depends on the system size,

$$t_X \sim L^z$$  \hspace{1cm} (A.4)

where $z$ is so called dynamic exponent.

It was pointed out by Family and Viscek [36] that these three exponents, $\beta$, $\alpha$, and $z$, are not independent and the scaling forms for the growth and saturation of
the width of the interface can be described by the following scaling relation:

$$W(L, t) \sim L^\alpha f\left(\frac{t}{L^z}\right)$$  \hspace{1cm} (A.5)

where \(f(x) \sim t^\beta\) for \(x \ll 1\) and \(f(x) = \text{const}\) for \(x \gg 1\). Thus

$$z = \frac{\alpha}{\beta}$$  \hspace{1cm} (A.6)

Another basic quantity is the lateral correlation length \(\xi_\parallel\), the typical distance over which the surface heights “know about” each other - the characteristic distance over which they are correlated. At the beginning of the growth, the sites are uncorrelated. During deposition \(\xi_\parallel\) growth with time. In the initial stages of growth,

$$\xi_\parallel \sim t^{1/z} \hspace{1cm} \text{for} \hspace{1cm} t \ll t_X$$  \hspace{1cm} (A.7)

while at saturation,

$$\xi_\parallel \sim L \hspace{1cm} \text{for} \hspace{1cm} t \gg t_X$$  \hspace{1cm} (A.8)

These results imply that the scaling behavior of the surface for a particular model may be characterized by two parameters, the growth exponent \(\beta\) and the roughness exponent \(\alpha\). Thus one may expect that different types of growth may fall into a small number of universality classes, each characterized by a given set of scaling exponents.

Alternatively, one may calculate other quantities related to correlations over a distance \(r\) from which the scaling behavior of the surface can be derived. One of
these quantities is the height-height correlation function $G(r, t)$:

$$
G(r, t) = \langle \bar{h}(0, t) \cdot \bar{h}(r, t) \rangle = \frac{1}{L^{d-1}} \sum_i (h_i(t) - \bar{h}(t))(h_{i+r}(t) - \bar{h}(t)) 
$$

(A.9)

The surface width can be related to the height-height correlation function $G(r, t)$ as,

$$
W^2(L, t) = G(0, t) 
$$

(A.10)

Typically, the lateral surface correlation length $\xi_\parallel$ is assumed to be the value of the distance $r_0$ at which the height-height correlation function $G(r, t)$ first crosses zero, i.e.

$$
\xi_\parallel \simeq r_0 
$$

(A.11)
Appendix B

Scattering from crystal lattice

The defining property of a crystalline material is that it is periodic in space. Bragg’s law gives the condition for the constructive interference of waves which have an angle of incidence $\theta$ to a set of lattice planes a distance $d$ apart:

$$m\lambda = 2d \sin \theta$$  \hspace{1cm} (B.1)

where $m$ is an integer. While this is a useful construction, it does have its limitations, principal among which is that it does not enable us to calculate the intensity of the scattering for which constructive interference occurs.

Laue condition for the observation of X-ray diffraction can be expressed as,

$$Q = G$$  \hspace{1cm} (B.2)

where $Q$ is a wave-vector transfer and $G$ is a reciprocal lattice vector. This condition
can be explained, if we consider scattering amplitude of a crystal, which factorizes into the product of two terms:

\[
F^{\text{crystal}}(Q) = \sum_{r_j} f_j(Q) \exp(iQ \cdot r_j) \sum_{R_n} \exp(iQ \cdot R_n)
\]  

(B.3)

where the first term is the unit cell structure factor, and the second term is a sum over lattice sites. All the terms in the lattice sum are phase factors located on the unit circle in the complex plane. The sum will therefore be of the order of unity unless the wave-vector transfer happens to fulfill,

\[
Q \cdot R_n = 2\pi \times \text{integer}
\]  

(B.4)

in which case it becomes of order N, the number of unit cells, which is a huge number. The lattice vectors \( R_n \) are of the form,

\[
R_n = n_1 a_1 + n_2 a_2 + n_3 a_3
\]  

(B.5)

where \( (a_1, a_2, a_3) \) are the basis vectors of the lattice and \( (n_1, n_2, n_3) \) are integers. A unique solution to Eq. B.4 can be found by introducing the important concept of the reciprocal lattice. This new lattice is spanned by the reciprocal lattice vectors which are defined by

\[
a_1^* = 2\pi \frac{a_2 \times a_3}{a_1 \cdot (a_2 \times a_3)}, \quad a_2^* = 2\pi \frac{a_3 \times a_1}{a_1 \cdot (a_2 \times a_3)}, \quad a_3^* = 2\pi \frac{a_1 \times a_2}{a_1 \cdot (a_2 \times a_3)}
\]  

(B.6)
so that the lattice in the reciprocal space is given by

\[ \mathbf{G} = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^* \]  

(B.7)

where \( h, k, l \) are all integers. We can see that the product of a lattice vector in the reciprocal \( \mathbf{G} \) and direct \( \mathbf{R}_n \) spaces is

\[ \mathbf{G} \cdot \mathbf{R}_n = 2\pi(hn_1 + kn_2 + ln_3) = 2\pi \times \text{integer} \]  

(B.8)

and hence the solution to Eq. B.4 that we are seeking is to require that

\[ \mathbf{Q} = \mathbf{G} \]  

(B.9)

which shows that \( F_{\text{crystal}}(\mathbf{Q}) \) is non-vanishing if and only if \( \mathbf{Q} \) coincides with a reciprocal lattice vector.

In case of an infinite three dimensional crystal the lattice sum produces a delta function; scattering is confined to distinct points in reciprocal space. For a finite size crystal Laue condition is relaxed and the scattering then extends over a volume in reciprocal space, inversely proportional to the size of the crystal. If we imagine that the crystal is cleaved, so as to produce a flat surface, the scattering will no longer be isotropic and streaks of scattering appear in the direction parallel to the surface normal. These are the \textit{crystal truncation rods} (CTR).

To develop an expression for the intensity distribution of the CTR we need only consider the lattice sum in the direction of the surface normal, for instance, \( \mathbf{a}_3 \). If
$A(Q)$ is a scattering amplitude from a layer of atoms (here for simplicity assumed to be the same for all layers), then the scattering amplitude from a semi-infinite stack of such layers is

$$F^{CTR} = A(Q) \sum_{j=0}^{\infty} e^{iQ_z a_3 j} = \frac{A(Q)}{1 - e^{iQ_z a_3}} = \frac{A(Q)}{1 - e^{2\pi l}}$$ (B.10)

where the wave-vector transfer along the surface normal is $Q_z = \frac{2\pi l}{a_3}$. The intensity distribution along the crystal truncation rod is

$$I^{CTR} = |F^{CTR}|^2 = \frac{|A(Q)|^2}{(1 - e^{i2\pi l})(1 - e^{-i2\pi l})} = \frac{|A(Q)|^2}{4 \sin^2(\pi l)}$$ (B.11)

This expression is clearly only valid away from the Bragg peaks when $l$ is not an integer, otherwise $\sin(\pi l)$ is zero and the intensity diverges.

The intensity distribution along the CTR depends on the exact way in which the surface is terminated, and measurements of CTR’s have become a very useful probe of the structure of the surface and near-surface region of single crystals. This can be illustrated by imagining that the top most layer, having $j = -1$ in Eq. B.10, of the crystal has a lattice spacing that is different from the bulk value. The total scattering amplitude is then

$$F^{total} = F^{CTR} + F^{top layer} = \frac{A(Q)}{1 - e^{i2\pi l}} + A(Q)e^{-i2\pi(1+z_0)l}$$ (B.12)

where $z_0$ is the relative displacement of the top layer away from the bulk lattice spacing of $a_3$. For $z_0 = 0$ the same intensity distribution along the rod is found. If $z_0$
Figure B-1: Crystal truncation rod from a flat surface with an overlayer. The relative displacement of the overlayer from the bulk lattice spacing is given by $z_0$. The effect of the displacement is seen to become more pronounced at higher wave-vector transfers.

If $z_0$ is non-zero then the interference between the scattering from the top layer and the rest of the crystal leads to characteristic features in the CTR, as shown in Fig. B-1. The expression for one overlayer on top of the semi-infinite substrate (See Eq. B.12) can be extended for the case of an arbitrary number of overlayers. The result, calculated for the case of ten uniformly strained overlayers on top of the semi-infinite substrate is shown in Fig. B-2. As can be seen, reflectivity curve exhibits oscillations, resulting from the interference effects between the reflections from the perfectly spaced bulk layers and strained overlayers.

Interestingly, the presence of a rough surface, itself, can lead to oscillations in the simulated XRD pattern (no strain in this case), (see Figs. B-3, B-4 ). We note that the appreciable separation between the levels is a crucial factor in this case for
Figure B-2: Crystal truncation rod from a flat surface with 10 overlayers. Inter-layer distance for overlayers is 5% smaller than the bulk (substrate) value.

the development of oscillations. As shown in Fig. B-4, the increase of the separation between the levels in a simple 2 level system (See Fig. B-3) we consider here, leads to the increased frequency of the oscillations. We note that the different models can yield qualitatively similar (in terms of the presence of the oscillations) reflectivity curves. This illustrates that reflectivity experiments can not uniquely reveal the true

Figure B-3: Stepped interface (side view - slice (slice thickness three atomic planes)).
Figure B-4: Reflectivity of a two level surface. Solid oscillating curve corresponds to the interface shown in Fig. B-3. Dashed oscillating curve corresponds to double-increased height of the structures shown in Fig. B-3. Dashed curve without oscillations corresponds to a flat surface.
nature of an interface. This is one of the reasons why the development of atomistic simulation models is so important for more complete understanding of crystal growth processes.
Appendix C

General expression for attachment probabilities for the atoms at a step-edge

Here we show how to obtain Eq. (5.3), expression for $\gamma$ in terms of $\epsilon$ and $\epsilon'$, as well as expressions for $\epsilon$ and $\epsilon'$ in terms of $\rho$, that we used as the variable in the general expressions for the surface current and selected mound slope. As already noted, $\epsilon$ and $\epsilon'$ are the probabilities of diffusion down the step from the nearest to the step edge $fcc$ and $hcp$ sites correspondingly. For $B$-steps (see Figs. ((5-2),(5-3) and (C-1))):

\begin{equation}
    P_{c-1} = \sigma' P_{c-2} + 2\sigma' P_\ast + \epsilon' P_c \tag{C.1}
\end{equation}

\begin{equation}
    P_\ast = 2\sigma P_{c-1} + \epsilon P_c \tag{C.2}
\end{equation}
where \( \sigma' \) is the probability of going from the last \( hcp \) site at the edge of the terrace to any of the nearby \( fcc \) sites and \( \sigma \) is the probability of going from the last \( fcc \) site at the edge of the terrace to any of the nearby \( hcp \) sites. We note that \( 3\sigma' + \epsilon' = 1 \), \( 2\sigma + \epsilon = 1 \) and \( P_c = 0 \). \( P_i \) is the probability that a particle deposited at site \( i \) will be absorbed at site \( 0 \). \( P_* \) corresponds to the last site on the terrace, which one is an \( fcc \) site in case of \( B \) steps.

Substituting Eq. (C.2) into Eq. (C.1) we obtain,

\[
P_{c-1} = \frac{\sigma'}{1 - 4\sigma'\sigma}P_{c-2}
\]

(C.3)

Taking into account that \( \sigma' = \frac{1-\epsilon'}{3} \), \( \sigma = \frac{1-\epsilon}{2} \) and comparing Eq. (C.3) with the Eq. (5.3), that defines \( \gamma \),

\[
P_{c-1} = (1 - \gamma)P_{c-2} + \epsilon'P_c
\]

where \( P_c = 0 \), we obtain:

\[
\gamma = \frac{2\epsilon + 3\epsilon' - 2\epsilon\epsilon'}{1 + 2\epsilon + 2\epsilon - 2\epsilon\epsilon'}
\]

(C.4)

Assuming that the rate for hopping from the last \( fcc \) site (*) to any of the nearby \( hcp \) sites \((c-1)\) is given by \( R = \nu_0 e^{-E_a/k_BT} \) (where \( E_a \) is the corresponding activation energy for diffusion from \( fcc \) to \( hcp \) site on the flat terrace) and the rate for interlayer diffusion from the last \( fcc \) site (*) is given by \( R_\epsilon = \nu_B e^{-(E_a+E_{ES})/k_BT} \) we obtain,

\[
\sigma = \frac{R}{2R + R_\epsilon}
\]

(C.5)
Figure C-1: Diagram showing details of diffusion down the step for B steps

Defining the difference between the binding energies of adatoms at fcc and hcp sites as $\Delta E$, we can see that the rate for hopping from the last hcp site ($c-1$) to any of the nearby fcc sites is given by $R' = \nu_0 e^{-E_a+\Delta E/k_BT} = e^{\Delta E/(k_BT)} R$

and the rate for interlayer diffusion from the last hcp site ($c-1$) is given by $R'_c = \nu_B e^{-(ES+E_a)+\Delta E/k_BT} = e^{\Delta E/(k_BT)} R_c$. Then we obtain for $\sigma'$,

$$\sigma' = \frac{R'}{3R' + R'_c} = \frac{R}{3R + R_c} \tag{C.6}$$

Defining $\rho$ as,

$$\rho = \frac{R_c}{R} = \frac{\nu_B}{\nu_0} e^{-(ES)/k_BT} \tag{C.7}$$

we obtain: $\sigma = \frac{1}{2+\rho}, \sigma' = \frac{1}{3+\rho}, \epsilon = \frac{\rho}{2+\rho}$ and $\epsilon' = \frac{\rho}{3+\rho}$

For A step we can use the same approach, except that the last site on the terrace
is an \textit{hcp} one in case of \textit{A} steps. Taking this difference into account, we obtain:

\[
\gamma = \frac{3\epsilon + 2\epsilon' - 2\epsilon\epsilon'}{1 + 2\epsilon + 2\epsilon' - 2\epsilon\epsilon'}
\]  \hspace{1cm} (C.8)

\[\sigma = \frac{1}{3+\rho}, \quad \sigma' = \frac{1}{2+\rho}, \quad \epsilon = \frac{\rho}{3+\rho} \quad \text{and} \quad \epsilon' = \frac{\rho}{2+\rho}\]

Where, as already noted, \(\epsilon\) and \(\epsilon'\) are the probabilities of diffusion down the step from the nearest to the step edge \textit{fcc} and \textit{hcp} sites correspondingly and \(\rho = \frac{v_B}{v_0} e^{-E_{ES}/k_B T}\). We note, that in general the values of \(E_{ES}\) are different for \textit{A} and \textit{B} steps.
Bibliography


[44] We note that in the experiments of Ref. [40], the experimental geometry was not precisely characterized. However, after the results presented in Ref. [22] were obtained, an analysis was carried out which leads to an estimate of $\theta = 56^\circ$ with an estimated uncertainty of $10^\circ$. (P. Miceli, private communication).


[66] Here we assume that the diffusion length $l_D$ is sufficiently large, compared to the terrace length $L$. However, when $l_D \leq L$, the surface current may be modified by the presence of the islands nucleating on the terrace.


