Abstract

Deep submicron interconnects and giant magnetoresistive multilayers require precision control of thin films atomic scale structures. The deposition strategies that achieve these structures exploit kinetically limited growth. This is complicated by the many mechanisms that contribute to the atomic assembly process. Interest has thus grown in the use of atomistic simulations to understand the atom-by-atom process.

A modeling procedure has been developed that enables simulation of the effects of substrate temperature, deposition rate, kinetic energy and deposition geometry. An extension to include two different atom fluxes has also been developed. The approach is based on a 2D kinetic Monte Carlo (kMC) method which simulates the many thermally activated pathways. The principal effects of the atoms impact energy (atom reflection, resputtering, bias diffusion, and the effect of thermal spike) are all incorporated utilizing results from recent molecular dynamics calculations of energetic atom impacts. The activation barriers have been obtained using molecular statics with an embedded atom method potential. An efficient algorithm is developed to compute key kMC steps.

The approach is first applied to the low energy deposition of nickel on a flat substrate. In simulating the effects of deposition rate and substrate temperature, the transition from a porous columnar structure to a fully dense structure was found to agree well with an empirical structure zone model. The low energy deposition of Ni/Cu multilayers is then investigated using local, composition dependent activation barriers and it was found that an optimal growth window exists. Next, the energy dependent kMC method is first used to examine the deposition of nickel films on a flat substrate. The simulations predict the existence of a minimum surface roughness at an incident angle that increases with increasing atom kinetic energy and substrate temperature and decreasing deposition rate. In simulating trench filling and liner coating of interconnect metallization, the results reveal good agreement with experimental observations, such as the critical role of resputtering on surface morphology at trench corners, the existence of optimal kinetic energy and incidence
angle distributions for complete trench filling and the prediction of the effect of trench width scale. Finally, prospects for the future role of kMC models in vapor deposition have been discussed and the extension of the approach to 3D explored by analyzing the growth of nanocrystals, investigating island mobility on planes, and evaluating the significance of growth kinetics manipulation in promoting step flow growth modes.
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<td>a</td>
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<td>β</td>
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<td>B_v</td>
<td>bulk modulus</td>
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<td>C, C^e</td>
<td>concentration, equilibrium concentration</td>
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<td>chemical vapor deposition</td>
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<td>ΔE</td>
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<td>EAM</td>
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<tr>
<td>φ_{ab}</td>
<td>two-body cross potential between two different species</td>
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<td>fcc</td>
<td>face-centered cubic</td>
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<tr>
<td>F_c</td>
<td>model parameter in the embedding function</td>
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<td>φ_e</td>
<td>model parameter in two-body potential</td>
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<td>FM</td>
<td>Frank-van der Merwe</td>
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<td>φ(r)</td>
<td>two-body potential as a function of the distance between two atoms</td>
</tr>
<tr>
<td>F(ρ)</td>
<td>energy to embed an atom into the electron density ρ</td>
</tr>
<tr>
<td>f(rij)</td>
<td>electron density at atom i due to atom j</td>
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<td>γ_{FV}</td>
<td>surface energy of the film-vapor interface</td>
</tr>
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<td>γ_{FS}</td>
<td>interfacial energy between the film and the substrate</td>
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<td>γ_{SV}</td>
<td>surface energy of the substrate-vapor interface</td>
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<tr>
<td>G_v</td>
<td>Voigt average shear modulus</td>
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<td>GMR</td>
<td>giant magnetoresistance</td>
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<td>HBC</td>
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<td>I, J, K</td>
<td>lattice site coordinates</td>
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<td>I-PVD</td>
<td>ionized physical vapor deposition</td>
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<td>k</td>
<td>Boltzmann’s constant</td>
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<td>kMC</td>
<td>kinetic Monte Carlo</td>
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<td>l_1, l_2, l_3, l_4</td>
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<td>molecular dynamics</td>
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List of Symbols

MS  molecular statics
ν, ν₀  vibration frequencies
NPOS  position number of a mesh point
pᵢ  jump rate
PVD  physical vapor deposition
θ  incident angle
r  interatomic separation distance
R  deposition rate
ρ  electron density at an atom due to the rest of the atoms in a system
r_c  cut-off distance
r_e  equilibrium interatomic separation distance
ρ_e  equilibrium electron density
r_ij  distance between atom i and atom j
SEM  scanning electron microscopy
SIMBAD  simulation ballistic deposition
SK  Stranski-Krastanov
STM  scanning tunneling microscopy
SZM  structure zone model
T  temperature
T_m  melting point
T/T_m  homologous temperature
t_n  system residence time
VW  Volmer-Weber
Ω  atomic volume
ξ, ξ₁, ξ₂, ξ₃  random numbers
Y_rf  reflection probability
Y_rs  resputtering yield
Chapter 1

Introduction

Physical vapor deposition (PVD) is a rapidly growing technology that increasingly underpins many products and components critical to numerous industry sectors [1]. For example, PVD is used to synthesize multilayered giant magnetoresistive (GMR) materials that are beginning to be used for highly sensitive magnetic field sensors in the read heads of hard disk drives [2], and for magnetic random access memories [3] characterized by non-volatility, radiation hardness, low power consumption and high read/write speed [4]. The semiconductor industry is actively pursuing and refining various vapor deposition technologies to manufacture semiconductor devices with deep sub-micron features [1]. Thermal barriers [5 - 7], photovoltaics thin films [8, 9], and many photonic components [10], all utilize PVD for their synthesis. However, in the past vapor phase manufacturing has relied heavily on trial and error approaches for process design. Growth has long been considered an art [11]. This situation can be well illustrated by metallization in the micro-electronics industry [12].

The commercial production of semiconductor integrated circuits requires hundreds of steps from production of the silicon substrates through final testing of a packaged component [1]. The formation of metal conducting circuits (interconnections) by a damascene approach is a key aspect of this integrated circuit production, Fig. 1.1(a) [1]. In the past, the chip component density was not high and the trench (or via) aspect ratio was small. Conventional sputtering processes were sufficient to fill these features with AlCu alloys. As circuit dimensions have shrunk, and the aspect ratio of the resulting features has
increased, the conventional sputter technology used to fill the trenches with the conducting material is no longer suitable. The basic problem encountered with large aspect ratio trenches is that vapor is preferentially accumulated at the trench opening leading to the formation of a void, Fig. 1.1(b). As a result, many efforts have been made to modify the sputter process for the trench and via filling (trench filling) [1].

Since the problem appears to result from the component of the flux that makes non-normal incidence with the wafer surface, one idea sought to insert a collimator between the substrate and the cathode in order to filter out non-normal incident atoms [14, 15]. While the enhanced incidence directionality helps fill a moderately deep trench, the penalty is significant. It included a considerably reduced deposition efficiency (and therefore deposition rate), a more complicated deposition tool design process, higher tool maintenance and greater process cost [16]. Another approach to directionality control increased
the distance between the substrate and the cathode (so-called long throw) to naturally filter out the high incidence angle component of the flux and overcome some of the collimators’ problems [17, 18]. The long throw design, although it dispensed with the collimator, resulted in low deposition efficiency as well. Moreover the asymmetric deposition caused additional uniformity problems. The directionality problem associated with the magnetron sputter deposition has also been addressed with a thermal reflow approach [19]. In this approach, an annealing step was used to provide sufficient migration of atoms on the film surface so that the adatoms migrated into deep features, resulting in enhanced filling. The main concern of thermal reflow processes is that it requires high levels of cleanliness because surface contamination of the wafer (from gas phase impurities such as water or oxygen) significantly impede the mobility of the surface atoms. In addition, reflow requires that the hole or trench remain open during the reflow process. This limits both the sputter deposition rate as well as the smallest feature size.

Recently, interest has shifted to an ionized physical vapor deposition (I-PVD) approach [20 - 23]. In I-PVD, metal atoms created either by sputtering or evaporation are intentionally introduced into a high density plasma. Once in the plasma, these metal atoms are easily ionized and directed (at normal incidence) toward the substrate by a negative bias voltage applied to the substrate. In a large diameter, fairly small throw distance geometry, the utilization of the sputtered species can approach 100% from a combination of direct deposition or recycling via cathode resputtering. This is a significant improvement over collimation or long-throw deposition, which typically have material utilization efficiencies of a few percent. Today, the I-PVD approach appears capable of extending PVD technology into the next chip generation (defined by feature size of 0.18 µm) [1]. It has also been proposed for diffusion barrier layer coating and for the deposition of copper seed layers that are necessary for subsequent electrochemical deposition of copper [1, 16].
The transition from the conventional PVD process to the I-PVD concept took more than a decade in part because of the trial and error search in laboratory and the subsequent lengthy transition to the production line. Many of the intermediate explorations, consuming a significant amount of research and development time, are short lived either because of complexity or because of low throughput and poor efficiency. Similar issues have arisen in perfecting the growth of metal multilayers for GMR materials [24, 25]. In today’s highly competitive industry environment, processes for metallization and GMR multilayers synthesis need to be explored and optimized with a minimum of experiments. This naturally leads to the question: whether or not many of those intermediate steps can be waived by using some type of predictive modeling, such as atomistic simulations; and whether or not the best route can be rapidly predicted by a more judicious combination of experiment and simulation.

This thesis develops a comprehensive kinetic Monte Carlo model which is capable of simulating the atom by atom assembly of thin films deposited on flat and featured surfaces. It addresses major process parameters including substrate temperature, deposition rate, adatom kinetic energy, the flux distribution and the substrate feature geometry. The model is then used to explore the relationships between process conditions and the film’s microstructure including its surface and interface morphology. The thesis begins with a review of modeling methods. It proceeds with the development of a model for low kinetic energy deposition where only thermal activation mediates atomic assembly. This model is used to explore deposition on flat substrate for both pure metal and metal multilayer growth. Next, recent molecular dynamics results are used to construct a Monte Carlo method for energetic (hyperthermal) deposition where non thermal processes contribute to atomic assembly. Using the energy-dependent Monte Carlo model, trench filling and liner coating simulations are conducted at various situations. Finally, the approach is extended to 3D and preliminary analyses of nanocrystal growth and the mobility of atoms on steps/ledges are conducted.
Chapter 2

Historical Perspective

Physical vapor deposition generally refers to the growth of materials by the condensation of their vapor [26]. The vapor can be created by either thermal evaporation or one of the many variants of sputtering [26]. In thermal evaporation, evaporated films result from heating (by resistance or electron beam methods) a material in a high vacuum enclosure to such a temperature that large number of atoms or molecules leave the surface of the material. Provided the background pressure is sufficiently low in the vacuum system, most of the evaporated atoms or molecules suffer no collisions with residual gas molecules and travel in straight lines to a cold substrate where they condense. The earliest record of a thin film deposition by this approach was a report by Faraday who in 1857 obtained metal films by rapidly evaporating a current-carrying metal wire [27]. Further experimentation in the 19th century was stimulated by interest in the optical phenomena associated with thin layers of materials and by investigations of the kinetic theory of gases and diffusion within them [26]. Thermal evaporation required sophisticated vacuum and heating equipment. Thus large-scale applications and abilities to control film properties had to await advances in vacuum technology which occurred in the 1920s [28]. Because the emitted atoms are thermally equilibrated with the region of the sample from which they were emitted, the atoms that condense have low impact energies (of order $kT/2$ which is $< 0.1$ eV). For decades, evaporated thin films have remained a focus of academic interest and commercial interest [11, 26].
Historical Perspective

High quality films require significant atom mobility during deposition. This is supplied thermally (by heating the film) in thermal evaporation processes. The rapid development of electronic applications in 1970s awakened interest in sputtering. Sputtering entails the bombardment of a target with energetic ions (usually positive gas ions) which cause some surface atoms to be ejected from the target. These ejected atoms deposit onto any solid which may be close to the target. The atoms and reflected (neutralized) ions that strike the substrate may do so with considerable energy and promote atom mobility. Although application of the sputtering process to the deposition of thin films has been known and practiced for well over a century, it was not until the 1970s that this method become a serious competitor to vacuum evaporation. Much of the early work on sputtering was prompted by the difficulties encountered in cathode erosion in electron tubes, and was conducted to learn the mechanisms of the interaction between the bombarding ions and the target, rather than to study the properties of the deposited material \textit{per se}. The delayed interest in sputtering and its slow maturation as a method for depositing films resulted from the greater tendency of sputtered films to be contaminated together with the large number of process parameters involved. The latter made process control difficult to achieve. In the last two decades, the demands of the electronics industry for films with qualities difficult or even impossible to attain by any other means have stimulated a good deal of fruitful effort directed toward solving these problems. Today sputtering as a deposition technique is receiving an increasing level of acceptance not only for electronic applications but for all areas where thin films are needed [26, 29].

Here efforts to model the atomic assembly process are briefly reviewed from a historical perspective. The next two chapters investigate in some detail the status of the kinetic Monte Carlo method, the associated interatomic forces needed to implement it, and a method for improved simulations of physical vapor deposition.
Vapor deposition of metal crystals is one of many methods of crystal growth. Any theoretical or modeling work regarding crystalline thin film growth is thus naturally associated with the whole crystal growth history. The earliest contribution toward understanding crystal growth can probably be attributed to Kepler [30]. In 1611, he postulated the existence of a correlation between surface morphology and crystal structure. In his work *De nive sexangula* [30], he supposed the regular shape of snow flakes derived from a hexagonal dense packing (Fig. 2.1(a), structure B), rather than cubic dense packing of Fig. 2.1(a), structure A, and explained growth by successive attachment of particles as shown in Fig. 2.1(b). The simple diagrams of Fig. 2.1(a) represents the first model of a crystal structure, and Fig. 2.1(b) is the first representation of a crystal growth process!

![Fig. 2.1. (a) Packing models of spheres and (b) the successive attachment of particles to achieve the hexagonal dense arrangement of snow crystals, from [30].](image)

Another early postulated principle of structural arrangement in crystals is based on the packing of tiny cubes, rhombohedra and other geometrical shapes which correspond to the idealized habit of the crystal, or to the shape of cleaved crystal fractions. This was done by Haüy [11]. Haüy was one of many with the idea during the period around 1784 who explained the formation of (mineral) octahedral faces by removal of cubic units, from a large cube, Fig. 2.2.
These early “atomic” approaches to understand the crystal structure were directed at natural crystals since high-purity chemicals and well-controlled thermal conditions need for artificial crystal growth were not available. Although the 19th century saw a large number of works on the crystallization of salts from solutions and of minerals from high-temperature solutions, the major breakthrough in the understanding of crystal structures occurred in the 20th century and was marked by the discovery of X-ray diffraction from crystal lattices by Von Laue in 1912 together with the structure determinations by W.L. Bragg from 1913 onwards.

It was recognized as early as the end of the nineteenth century that there are two distinct aspects in crystal growth, the equilibrium between the crystal and the surrounding medium, and the kinetics of growth. Even in 1878 Gibbs had developed a phenomenological (thermodynamical) treatment of the equilibrium form of the crystal which is defined by the minimum surface energy. In 1901 Wulff considered the specific surface energies of the individual crystal faces. The minima in the polar diagram of the specific surface

Fig. 2.2. Development of non-(100) faces from a cube by removal of cubic subunits: octahedral faces [11].
energy (Wulff plot) define the equilibrium shape. Growth experiments on crystal spheres showed that the final crystal was surrounded by the faces with the lowest growth rates. In general these are the equilibrium faces. However, this equilibrium treatment does not consider the atomic structure of the growing surface which is needed to understand the kinetics of crystallization.

The development of a kinetic theory of crystal was begun by several different groups. The first step towards growth kinetics was provided by Volmer in 1922, who postulated adsorption and surface diffusion in the “Volmer layer” and suggested two-dimensional nucleation. Kossel in 1927 postulated an inhomogeneity of the growing surface by the introduction of steps and kinks, Fig. 2.3, and formulated the “repeatable step” for the attachment of units at kinks and steps [31]. A similar approach was then introduced by Stranski in 1928 and the work of separating growth units calculated [32]. The steps were provided by two-dimensional nucleation on the perfect surface. However, there was a problem. Most crystals grew with a significantly smaller supersaturation than that required

Fig. 2.3. (a) The inhomogenous growing crystal surface postulated by Kossel [31] with repeatable steps and kinks for attachment of growth units; (b) A more detailed growing crystal interface with surface vacancies and adatoms present [41].
by the theory of two-dimensional nucleation. This was resolved by the breakthrough of Frank in 1949, who introduced screw dislocations as a continuous source of steps (see Fig. 2.4) and who, together with Burton and Cabrera developed the terrace, step and kink (TSK) theory [33], a general treatment of spiral growth taking into account interacting dislocations and diffusion problems.

![Fig. 2.4. Growth hillocks caused by growth at emerging screw dislocations. (a) Single screw source, (b) dipole source [33].](image-url)

The TSK theory addressed three aspects of growth. First, when all surfaces of high index (stepped surfaces) had disappeared, the crystal continued to grow by two-dimensional nucleation of new molecular layers on the surfaces of low index (saturated surfaces). Even a pure, perfect crystal of a single element has surfaces that are covered by steps with terraces in-between. These steps possess kinks or jogs. The different sites, terrances, steps and kinks hold adatoms for different lengths of time. Secondly, the crystals which grow are not perfect and their lattice imperfections (dislocations terminating in the surface with a screw component) provide steps on the crystal surface making the two-dimensional nucleation unnecessary. The origin of the surface steps is not produced by
thermal fluctuations. Thirdly, there is a transition temperature at which the surface roughness increases very rapidly (‘surface melting’).

Another important step leading to an atomic understanding of vapor growth came in 1928 from Roger’s extensive studies of a wide variety of overgrowths based on the reviews on natural phenomena and on structural data that had just become available from the first X-ray diffraction studies [34]. He established the conditions for oriented overgrowth and also defined the term epitaxy. On the basis of his observations, Roger put forward three rules of epitaxy, the most important of which is that oriented growth occurs only when it involves the parallelism of two lattice planes that have networks of identical or quasi-identical form and closely similar spacings. A misfit strain was defined as \[ \frac{100(b - a)}{a} \], where \( a \) and \( b \) are the corresponding network spacings in the substrate and overgrowth respectively. Experiments indicated that epitaxy occurs only if the misfit strain is no more than about 15%. The following years saw numerous studies of experimental epitaxial overgrowth and theoretical model for epitaxial monolayers including Frank and van der Merwe’s works introducing the concept of misfit dislocations at the interface between the substrate and deposit in 1949 [35]. The misfit dislocations were first observed by Jesser and Matthews in 1967 using transmission electron microscopy (TEM) [36].

While “atomic” approaches have been widely used in explaining crystal phenomena ever since, the classical description of vapor deposition was revisited by Bauer in 1958 [37]. The arguments were based on experimental observations of three different growth modes at near equilibrium conditions. They were called (a) the layer-by-layer or Frank-van der Merwe (FM) [35], (b) the island or Volmer-Weber (VW) [38], or (c) the layer-plus-island or Stranski-Krastanov (SK) [39] growth modes, Fig. 2.5.

It was conceived that in VW growth, nucleation is followed by three dimensional growth of the nuclei, which eventually coalesce leading to a continuous film. The topogra-
phy of such films is therefore initially quite rough on an atomic scale. When FM growth occurs, atoms or molecules impinging on a substrate surface diffuse, usually to a step, a kink, or a defect site in such a way as to extend the stepped layer. Thus ideally the crystal grows one layer at a time. SK growth typically means that growth is initiated in the FM mode; but then after one or more layers is formed, island growth nucleates on top of the initial layers.

Bauer showed that the three major thin film growth modes can be predicted from a consideration of the surface, interfacial and elastic energies involved [37]. He identified a parameter $\Delta \gamma_n = \gamma_{FV} + \gamma_{FS} + \gamma_{SV}$, where $\gamma_{FV}$ is the surface energy of the film-vapor interface, $\gamma_{FS}$ is the interfacial energy between the film and the substrate, and $\gamma_{SV}$ is the substrate surface energy. The subscript $n$ refers to the situation after $n$ equivalent layers have been deposited. VW occurs when $\Delta \gamma_n > 0$. FM, and SK growth are predicted when $\Delta \gamma_n \leq 0$. The difference between FM and SK growth lies mainly in the elastic strain energy associated with the film which is incorporated in the $\gamma_{FS}$ term [40]. Qualitatively, these thermodynamic results can be seen in terms of what happens during nucleation and growth: namely surface and interfacial energies ($\gamma_{FV} + \gamma_{FS}$) replace the surface energy $\gamma_{SV}$ of the substrate.
If the difference between these two quantities $\Delta \gamma_n$ is positive, an increase in energy occurs. In order to reduce this increase as much as possible, the film will tend to “ball up”, so as to decrease the surface atom to volume atom ratio. On the other hand if $\Delta \gamma_n$ is negative, the net energy can be reduced by increasing the surface atom to volume atom ratio. In this case the film would tend to grow by layers.

While both theoretical works and experimental observations were put on a solid foundation, the emergence from early 1970s on of fast computing machines further expanded the understanding on interface growth kinetics, initially by using such popular technique as kinetic Ising model (see Appendix A for the original Ising model) [41].

In the kinetic Ising model, the dynamics of crystal growth from the vapor are simulated by two basic events: impingement and evaporation [41]. The event and the site where it is to occur are chosen by computer-generated random numbers using a standard Monte Carlo procedure (Appendix B) [42]. Impingement is the addition of an atom at a site on the surface, and its probability is assumed to be proportional to the supersaturation in the vapor. In terms of the chemical potential, $\mu$, the deposition rate, $k^+ = \nu \exp(\mu/kT)$, where $\nu$ is a frequency factor, $T$ is the absolute temperature, and $k$ is Boltzmann’s constant [43]. The impingement rate is independent of the local surface structure, as expected for a crystal surface in contact with a vapor.

Evaporation is the removal of an atom from the surface region, and it proceeds with a frequency $k_n^-$ that is highly sensitive to the structure: $k_n^- = \nu \exp(-n\phi/kT)$, where $n$ is the number of bonds to other atoms of the crystal, and $\phi$ is the energy required to break one bond. The evaporation is treated as a simple activated process. Fig. 2.6 shows examples using the kinetic Ising model to simulate the effect of substrate temperature [41].

This popular model has provided much information about the nature of the surface roughening transition for crystal faces in equilibrium with the vapor and the influence
of defects and impurities on crystal growth are treated. The Ising model does not include information on the exact locations of atoms at a crystal surface and does not allow the formation of voids, vacancies or other lattice defects. Since the positions are usually represented by a coarse grid corresponding to the bulk crystal lattice sites, atomic vibrations and surface melting are also excluded. The important adatom self diffusion on the surface is excluded as well. Nevertheless, in most cases representative configurations can usually be obtained which provide data of sufficient accuracy for comparison with experiments and for the identification of trends.

At about the same time (1969), a phenomenological classification of thin film growth morphology called structure zone model (SZM) was developed by Movchan and Demchishin [44]. The model appears to be the culmination of ten years of work in the Soviet Union in which thin and thick films covering a variety of metals and oxides were deposited on substrates over which temperature gradients were maintained. While it is not a direct modeling of the interface or thin film evolution process, it has had extensive influence in the thin film community as a whole and in the simulation community in particular.

Fig. 2.6. Typical kinetic Ising model interface configurations after deposition of 25% of a monolayer on a flat (100) face of the crystal. The temperatures were identical for the two cases, but in case (a) $\beta \Delta \mu = 2$, (b) $\beta \Delta \mu = 10$, where $\beta = 1/kT$, $\Delta \mu = kT \ln (C/C^e)$, $C$ is the concentration in vapor and the superscript $e$ denotes an equilibrium quantity.
The basic conclusion of the SZM is that the coating could be represented as a function of $T/T_m$ in terms of the three zones shown in Fig. 2.7, each with its own characteristic structure and physical properties.

Zone 1 structure (formed when $T/T_m < 0.3$) consists of tapered crystals with domed tops which are separated by voided boundaries. The internal structure of the crystals is poorly defined, with a high dislocation density. The crystal diameter increases with $T/T_m$, and that dependence indicates a very low activation energy and implies very little surface diffusion. Metallic deposits with this structure have great hardness but little strength when tested in tension lateral to the growth direction.

Zone 2 ($0.3 < T/T_m < 0.5$) consists of columnar grains separated by distinct, dense, intercrystalline boundaries; the surface has a smooth, mat appearance. Dislocations are primarily in boundary regions. Grain sizes increase with $T/T_m$ and may extend through the coating thickness at high $T/T_m$. The grain width dependence on $T/T_m$ yields an activation energy about equal to that for surface diffusion. Metallic deposits have properties similar to cast metals.

Fig. 2.7. Structural zone models for coating growth. (a) Model proposed by Movchan and Demchishin [44]; (b) Model modified by Thornton for sputtered metal coatings [45].
Zone 3 ($0.5 < T/T_m < 1$) consists of equiaxed grains with a bright surface. The grain diameters increase with $T/T_m$ and yield an activation energy corresponding to that for bulk self-diffusion. The structure and properties correspond to a fully annealed metal.

Thornton later modified this “model” with the addition of a pressure axis and the basic conclusions were similar [45]. This is because the condensation step generally features shadowing (limited mobility), surface diffusion, bulk diffusion and desorption. These processes can be quantified in terms of the characteristic roughness of the coating surface, the activation energies for surface and bulk diffusion, and the sublimation energy. For many pure metals these energies are related and proportional to the melting point. Thus a number of basic processes can be expected to dominate over distinct ranges of $T/T_m$, and to manifest themselves as differences in the resultant coating structures and morphology. Such is the basis of all the structure zone models [44].

Various modeling approaches to such thin film evolution have since appeared with results either coincidently reflecting the SZM phenomena or aiming to confirm the SZM. The first work indirectly associated with the SZM classification was conducted by Henderson, Brodsky and Chaudhari (HBC) in 1974 in which they simulated an amorphous array with a morphology that exhibited anisotropy and void formation, Fig. 2.8 [46]. The simulation provides the key to an understanding of the physical origin of columnar structure in zone 1.

The HBC method proceeded by first assuming the incident atoms or molecules to be hard spheres. A horizontal surface upon which the hard spheres were deposited was assumed to be a square substrate. In order to simulate an infinite system, periodic boundary conditions were applied to this square unit cell. An initial random layer was placed upon the surface such that they prevented any other hard spheres from reaching the surface. Incident hard spheres were then assumed to travel on a straight line which was inclined at an angle $\theta$ from the normal to the plane, Fig. 2.8. The values of the coordinates
at which this line intersected the plane were chosen randomly. Each hard sphere was assumed to travel on the straight line until it came in contact with one of the already deposited hard spheres. A sticking coefficient of unity was assumed. Furthermore, the incident hard sphere was assumed always to remain in contact with the hard sphere in the film with which it first made contact. However, the incident hard sphere was allowed to relax to the extent that it moved to the nearest “pocket” where it made contact with two additional hard spheres which had been deposited previously. After this relaxation process was completed, the next incident hard sphere was considered. This process was continued until an appreciable thickness were built up for analysis. Although only qualitatively useful in predicting the general pattern of the thin film microstructure under low substrate

Fig. 2.8. HBC computer simulation of amorphous hard-sphere films deposited with flux angle $\theta = 45^\circ$. The figure shows slice in five atom thick through three-dimensional arrays [46].
temperature conditions, this model ushered in a thin film modeling fever in the following years.

The HBC idea was quickly picked up by Dirks and Leamy in 1977 [47]. Their simplified 2D hard disk simulation with and without relaxation more clearly demonstrated the shadowing origin of the columnar formation, Fig. 2.9. The treatment was essentially identical to HBC idea, yet the 2D model’s simplicity and its equal usefulness has made it a benchmark for many of the works to come.

Brett, in 1987, introduced simulation of ballistic deposition (SIMBAD) model that attempted to approximate the effect of substrate temperature on surface diffusion using a diffusion parameter defined as the range of a one-time diffusion event for an incident atom relaxation upon landing [48]. Higher substrate temperature resulted in a larger value of the parameter. Because of the automatic inclusion of the self-shadowing effect, the model simulated the columnar growth and the effect of the deposition geometry and substrate temperature, although the diffusion was oversimplified and no other process parameter was considered.

Fig. 2.9. The structure of an amorphous hard disk alloy deposited at $\theta = 0^\circ$. (a) Atomic relaxation was not allowed, and a chain-like structure resulted. (b) Relaxations were included, and the chain-like morphology was transformed into a columnar structure [47].
The first work that attempted to realistically simulate thin film growth was due to Müller in 1987 [49]. Instead of using a diffusion parameter, Müller introduced a multiple jump scheme for diffusion based on substrate temperature, deposition rate and jumping atom’s coordination. This well simulated low temperature morphology and the zone 1 and 2 transition for the first time. Fig. 2.10 is the simulated zone 1 and 2 transition. However,

Fig. 2-10. Monte Carlo simulation two-dimensional microstructure of nickel films deposited with an incident flux angle $\theta = 45^\circ$, deposition rate $R = 3.6 \ \mu\text{m h}^{-1}$. $t$ is the deposition time [49].
Historical Perspective

it suffered from a number of deficiencies. For example, the bond counting method used to assess the jump’s activation energy was too simple and could not correctly take the Schwoebel barrier [50] into account. The atomic jump decisions were made by comparing the thermal energy with the bond counting activation barrier and always making a possible jump into the site with the highest coordination. A proper link between the real deposition time and the diffusive process time was not made. Most importantly, the competing thermally activated process of diffusion is not correctly simulated.

A more physically realistic Monte Carlo simulation of thin film growth did not appear until the mid-1990s when a number of groups began to employ a new kinetic Monte Carlo (kMC) method for simulating vapor deposition [51 - 55]. The kMC method (described fully in next chapter) for the first time faithfully executed the various competing thermally activated diffusion processes and correctly simulated the thin film surface morphology evolution. For example, kMC was used to study the mechanism of monolayer epitaxial growth and the results compared well with scanning tunneling microscopy (STM) [51]. The kMC method was first used to study the thin film structure zone model and the effects of process parameters on the microstructure evolution [52]. A number of other areas included trench filling [53, 54], CVD diamond vapor growth [55].

As this work specifically aims to extend the kMC method, the various related aspects will be treated separately in the following two chapters including the algorithm, its strengths, shortcomings, proposed improvements and the needed energy parameters and an efficient implementation.

Molecular dynamics methods have also been widely used to model vapor deposition. The first efforts to simulate thin film growth were due to Gilmer in 1980 [56]. Motivation for the more realistic simulation was provided by the early days’ MC simulation [46, 47] which mostly rendered configurations with low density because of the artificially limited relaxation scheme. The MD simulation successfully simulated the effect of the
incident atoms energy and improved the resulting configuration density. Schneider, Rahman and Schuller used MD methods to simulate epitaxial growth [57]. Müller investigated thermalized nickel deposition with an assisting energetic argon ions and was among the first to demonstrate the potential of a relatively rigorous modeling means [58]. Many more have followed suit since then, devoting attentions on various defects formation, kinetic energy effects and multilayer growth simulation, etc. [59 - 63].

Because the MD method uses interatomic force laws to solve for the lattice dynamics, the computation of atomic positions and forces must performed at the lattice intervals comparable to the period of these vibrations (of order 10^{-12}s). Thus, problems that involve enough atoms to study vapor deposition processes can only analyze 1-10 nanoseconds of real-time behavior. Consequently only problems with unrealistically high deposition rates can be studied. Diffusional processes with longer time constants than this are not included in the analysis. Also, because of the intensive interatomic force calculations required, only a few thousand atoms can be normally simulated. Nevertheless, the MD approach provides a viable means to simulate the initial interaction of an incident atom with a growing film since these processes have time constants in the picosecond (ps) regime and require analysis of only a few thousand atoms. This thesis later explores the incorporation of MD results in kMC approaches. The principles of both approaches are next explored.
Chapter 3

Kinetic Monte Carlo Modeling

3.1 Introduction

The “Monte Carlo method” has its name from the use of “random numbers” to simulate statistical fluctuations in order to numerically generate probability distributions [64]. It is generally believed that the widespread use of Monte Carlo concept began with the Metropolis algorithm in the calculation for a rigid-sphere system [42]. This technique can be readily used to study equilibrium properties of a system of atoms. Since the kinetic path of evolution is physically meaningless in this scheme, it is not suitable for treating atomic assembly process in vapor deposition.

This chapter gives a detailed account of the kinetic Monte Carlo method which is suitable for simulating kinetic evolution process. The $n$-fold way algorithm [65] is first introduced which is believed to be the earliest form of the current kMC concept. A formal kMC procedure specifically formulated for simulating thin film growth in this thesis is next described. As a critical part of the kMC method, the activation barrier calculation through interatomic force law derived from the embedded atom method (EAM) is then followed. Finally, the basic principles of molecular dynamics method is explained. Molecular dynamics calculations provide a viable means to simulate the initial interactions of an incident atom with a growing film and enable the kMC to approximate the effects of kinetic energy through a kMC-MD coupling procedure introduced in chapter seven.
3.2 \textit{n-fold way algorithm}

The term “kinetic Monte Carlo” was initiated by Horia Metiu, Yan-Ten Lu and Zhenyu Zhang in a 1992 \textit{Science} paper titled “Epitaxial Growth and the Art of Computer Simulations” \cite{metiu1992}. The paper first pointed out the demands on atomic level control of modern electronic and photonic devices and the importance of \textit{in situ} STM observations of small atomic “clusters” to a theorist who wants to understand growth and segregation; it then elaborated upon the usefulness of kMC simulations in reproducing these experimental observations. The basic feature of their model was to move atoms site-to-site on a square lattice terrace. They postulated rates for all of the elementary processes involved, such as the site-to-site jumps, the jumps to leave or join a step or an existing adsorbate cluster, and so forth. The atoms were deposited on the surface and moved from site to site with a frequency proportional to the rate of the respective move: if the rate constant of the \textit{i}-th kinetic process was $k_i$, the largest rate was chosen as a reference and denoted $k_r$. The probability $P_i = k_i/k_r$ was then used in a Monte Carlo program as the probability that the atom performed a jump $i$. The work used Voter’s transition state theory \cite{voter1975} to monitor the simulation time. The overall scheme was close to what is used now and the essence through the references can be traced to Bortz, Kalow, and Lebowitz’s \textit{n-fold way} algorithm \cite{bortz1975, kalow1975, lebowitz1975} which appeared in 1975.

The \textit{n-fold way} idea was created to replace the standard Monte Carlo algorithm in generating new configurations in simulating Ising spin systems. In or near the equilibrium state, the standard MC scheme using a Boltzmann kinetic factor, $\exp(-\Delta E/kT)$, (where $\Delta E$ is the system energy change, $k$ is the Boltzmann constant and $T$ the absolute temperature) becomes very inefficient since the Boltzmann factor is usually very small in comparison with a random number over the interval $[0, 1]$ \cite{bortz1975}. On the other hand, the \textit{n-fold way} chooses a spin site from the entire ensemble based upon its probability of flipping. Once a site was selected, the flipping was guaranteed and could be immediately performed. The \textit{n-fold way} also provided a new simulation time concept. At each flip, the time was incre-
mented by a stochastic variable, $\Delta t$, whose expectation value is proportional to $Q_{10}^{-1}$ (where $Q_{10}$ is the number of spins times the average probability that an attempt will produce a flip for a given configuration). Mathematically, $\Delta t = -(\tau/Q_{10}) \ln R$, where $R$ is a random fraction and $\tau$ a system dependent time. This choice reflects properly the distribution of time intervals between flips for a reasonable physical model. The cumulative time thus summed is approximately proportional to real time. The $n$-fold way reduced computation time by an order of magnitude or more for many applications [65]. A similar concept was used in Voter’s 1987 transition state theory [66].

### 3.3 Kinetic Monte Carlo Method

The vapor deposition process consists of several distinct steps, creation of the vapor, the transport of species to the substrate, interaction of the incident atoms with the growing film, assembly of the adatoms on the substrate through diffusion process leading to either the incorporation of the adatom or its evaporation. To simulate the vapor growth process, all of the process should be incorporated. The most important step, however, is to correctly simulate the diffusion. Although diffusion may not be important at low temperature or very high deposition rate and can be approximated accordingly using the HBC model [46], in most practical situations deposition is conducted under conditions where atomic diffusion occurs simultaneously with deposition. This thermal diffusion must therefore be taken into account. The methodology should also address the many diffusional pathways available. It should also connect with the temperature and deposition rate since these control the available time for surface diffusional processes before the surface becomes covered by a new atom layer.

If Boltzmann statistics are assumed to govern the diffusional processes, the probability per unit time for a possible jump, $i$, to take place is given by:
where $v_0$ is the effective vibration frequency (taken to be $5 \times 10^{12}$/s for all the cases in this work), $E_i$ is the activation energy for the $i$-th type of jump, $k$ is Boltzmann’s constant and $T$ is the absolute temperature.

The reciprocal of an atomic jump probability per unit time is a residence time for an atom that moves by that specific type of jump. Since the jump probabilities of all the different types of jumps are independent, the overall probability per unit time for the system to change its state by any type of jump step is just the sum of all the possible specific jump type probabilities, and so the residence time for the system in a specific configuration is the reciprocal of this overall jump probability. The next diffusional step is determined by randomly choosing from among all the possible jumps weighted by their relative probability of occurrence. By following the ensuing discrete jump path for the system, accumulating the residence time of the system along the path, and linking this history to the adatom arrival interval (or the deposition rate), the diffusion process can be realistically simulated.

The calculation begins by determining a time interval between adatom arrivals based on the deposition rate. The average time interval between the arrival of two atoms in a 2D lattice model is

$$\Delta t = \frac{\sqrt{3}a}{2nR} \quad 3-2$$

where $R$ is the deposition rate, $a$ is the nearest neighbor distance and $n$ is the number of atoms comprising a monolayer in a close-packed 2D lattice. Clearly, the higher the deposition rate, the smaller the time interval between two consecutive deposition events in the
model. Time periods are then related to the diffusion process through a net (system) residence time, $t_n$, given by:

$$
 t_n = \left( \sum_{i=1}^{N} p_i \right)^{-1}
$$

where $N$ is the number of different types of jumps (i.e. different diffusion pathways). In this model, a single jump is allowed only to vacant nearest-neighbor sites or over a ledge at the surface, i.e. a Schwoebel jump [50]. The two time definitions (Eqns. 3-2 and 3-3) are then linked for the simulation.

An atom can then be dropped from a random position above the surface. It travels to the surface in a straight line and impacts the substrate at an angle $\theta$ to the normal. It is then instantly relaxed to the closest available lattice site. The set of atoms in the simulation system can then be monitored for diffusional modification prior to the arrival of the next atom, i.e. in the time $\Delta t$. If the system has a net jump probability greater than 1 in the $\Delta t$ time period, a jump is made and a time equal to the net residence time (calculated using Eqn. 3-3) is subtracted from $\Delta t$ so that there is less time remaining for further jumps in the allotted time period. This process is iterated until the probability of making any jump in the remaining time is less than one. Whether or not any jump is made in this time period can then be determined by random choice based on the remaining time and the net time for that particular state of the system. Whenever a jump is to be made, the specific one is determined by random choice based on the relative probabilities of all potential jumps. When the remaining time reaches zero, the clock is turned ahead by $\Delta t$ and another atom is then deposited. An implementation algorithm of this thermal diffusion simulation is described in next chapter.
3.4 Interatomic potentials

The concept of kMC simulation provides a powerful tool in the study of atom by atom assembly process of vapor deposition which is not accessible in experiment except for only a few techniques such as STM [69]. As a result, physical properties for most of the individual surface motions are extremely difficult to obtain under real observations. For example, the probability for an atomic jump occurrence depends upon a jump attempt rate (here assumed to be the maximum lattice vibration frequency) and the activation barrier for the jump. Very little experimental data about the magnitude of the barrier height exists. Thus alternatives must be sought to quantify them. The \textit{ab-initio} methods solving the many-electron Schrödinger equation would be desirable [70], but they are computationally expensive. Even with approximations to this scheme, such as the local-density approximation (LDA), and with recent impressive advances in computers and algorithms, these traditional band-structure calculations are impractical for systems with very low symmetry, such as grain boundaries [71].

An alternative approach is through the analysis of interatomic force laws which are often empirically derived by fitting coefficients in physical expressions to experimental quantities. The traditional two-body potentials such as Lennard-Jones potential, while yielding the total energy directly, require the use of an accompanying volume-dependent energy to correctly describe the elastic properties of a metal [72]. However, this volume becomes ambiguous to define in calculations involving surfaces [72], which would inevitably lead to inaccurate estimates of the activation barriers for atom migration on a surface.

A major development in addressing multi-body effect came in 1983 when Daw and Baskes proposed the embedded atom method (EAM) [73, 74]. The key assumption in the EAM procedure is that all atoms are viewed as being embedded in the host consisting of all other atoms. The embedding energy is electron-density dependent. Because the elec-
tron density is always definable, the problem of the ambiguity of defining the volume is circumvented. With these advantages, the EAM has attained a considerable success in problems, often intractable with pair potentials alone, covering a broad range of metals, impurities, alloys and surface properties.

In the following sections, Johnson’s format of the EAM potential [76, 77, 80] is introduced, followed by the fitting procedure needed to develop a specific nickel and copper EAM potential for use in this thesis along with the molecular statics method needed to deduce the activation energy parameters.

3.4.1 Embedded atom method potentials

In EAM, the energy of the metal is viewed as the energy obtained by embedding an atom into the local electron density provided by the remaining atoms of the system. In addition, there is a two-body central interaction. The basic equations are of the form:

\[ E_{tot} = \sum_i E_i \quad i = 1, 2, ..., N. \]  

where \( E_i = F_i(\rho_i) + \frac{1}{2} \sum_{i \neq j} \phi_{ij}(r_{ij}) \quad i, j = 1, 2, ..., N \)

and \( \rho_i = \sum_{i \neq j} f_j(r_{ij}) \quad i, j = 1, 2, ..., N \)

\( E_{tot} \) is the total internal energy of an assembly of atoms, \( E_i \) is the internal energy associated with atom \( i \), \( \rho_i \) is the total electron density at atom \( i \) due to the rest of the atoms in the system, \( F_i(\rho_i) \) is the energy to embed atom \( i \) into the electron density \( \rho_i \), \( \phi_{ij}(r_{ij}) \) is the two-body central potential between atom \( i \) and atom \( j \) separated by a distance \( r_{ij} \), and \( f_j(r_{ij}) \) is the contribution to the electron density at atom \( i \) due to atom \( j \) at a distance \( r_{ij} \) from atom \( i \).
Generally, the first term in Eqn. 3-5, the embedding energy, is dominant in providing atomic cohesion. Because the electron density comes from all of the neighboring atoms, the atom-host interaction is described in a way that is inherently more complex than the two-bond model. In this way, the embedding function incorporates some important many-atom interactions and demonstrates how bonding is affected by coordination. This naturally leads to an understanding of the difference between bulk and surface bonds, an essential feature in thin film growth process. However, it was found [74] that, for the special case when $F(\rho)$ is a linear function, the entire scheme is equivalent to the use of a different pair potential. In other words, $F''$ must be a non-zero number to ensure the multi-body interaction in the EAM scheme.

Actually, the first-principles calculations by Daw [75] did reveal that the embedding function should have a positive curvature for the background electron densities found in metals, that is $\frac{d^2F}{d\rho^2} > 0$. On the other hand, the EAM model’s invariance to the linear transformation (i.e. adding a linear contribution to the embedding function can be exactly compensated by a change in the pair interaction) makes it possible to construct an effective two-body potential. For example, one can have an embedding function with zero slope at the equilibrium electron density for a perfect lattice configuration: $\left. \frac{dF}{d\rho} \right|_e = 0$. The change from the perfect crystal energy is then dominated by the effective two-body potential for any atomic configuration in which the electron density at atom sites is not significantly altered. Since the electron density at an atom site is a superposition of the contribution from all neighboring atoms, its change is commonly small in defect configurations in tight-packed metals. Any EAM model can be so transformed and such a transformed model is called the normalized form of EAM [76, 77]. However, the present EAM form will not work as well for systems where directional bonding is important, such as semiconductors and elements from the middle of the transition series [78].
3.4.2 EAM potential fitting

To apply this method, the embedding energies, pair interaction, and electron densities expressed in Eqns. 3-4, 3-5 and 3-6 must be given. Daw has taken electron densities from Hartree-Fock calculations and calculated approximate values of the embedding energies and pair interactions from the formal definitions of these quantities in the density-functional framework [75]. Since these values only gave qualitatively correct predictions of the material properties, it is necessary to determine these functions empirically to obtain an accurate description.

Since the purpose behind two-dimensional atomistic calculations for vapor deposition (most of work in this thesis) is to obtain guidance in understanding the mechanisms and critical factors involved in the process and to seek trends and gain insight, there is little need to fit the atomistic model precisely to a specific material and the model should be as computationally efficient as possible [81]. However, for comparative studies a consistent model which gives a sense of the scaling between materials and the effect of alloying should be used. A nearest-neighbor embedded-atom method model fits these qualifications for metals [81].

A common practice in applying the normalized EAM is to first choose the specific functional form for $\phi(r)$ and $f(r)$, fit the model parameters in $\phi(r)$ and $f(r)$ to experimental data of lattice parameter $a$ or the atomic volume $\Omega$ ($\Omega = a^3/4$ for fcc metals), the cohesive energy $E_c$, the approximate vacancy formation energy $E_f$, the bulk modulus $B_v$ and Voigt average shear modulus $G_v$. The bulk modulus represents the resistance to volume change, while the Voigt average shear modulus represents the resistance to shear deformation.

For the embedding function, Foiles’ scheme via the equation of state of the pure metals [79] was often used to obtain $F(\rho)$ in the early days. Now an analytic form proposed by Johnson and Oh [76] is frequently applied for the embedded function:
where $\rho_e$ is the equilibrium electron density for a perfect lattice, and $F_1$, $F_0$, $m$ and $n$ are model parameters. EAM models are independent of the choice of $F_1$ [76]. For the universal form, the limit

$$\lim_{m \to n} \left[ \frac{n}{n-m} \left( \frac{\rho}{\rho_e} \right)^m - \frac{m}{n-m} \left( \frac{\rho}{\rho_e} \right)^n \right] = \left[ 1 - \ln \left( \frac{\rho}{\rho_e} \right)^m \right] \left( \frac{\rho}{\rho_e} \right)^n$$ 3-8

is required. With $F_1 = 0$, the embedding function becomes:

$$F(\rho) = F_0 \left[ 1 - \ln \left( \frac{\rho}{\rho_e} \right)^m \right] \left( \frac{\rho}{\rho_e} \right)^n$$ 3-9

Model parameters are then obtained from the following relations:

$$F_e(\rho) = -(E_c - E_f)$$ 3-10

$$F'_e(\rho) = 0$$ 3-11

$$F''_e(\rho) = \frac{9\Omega B_v - 15\Omega G_v}{\left( \sum_i r_i^{'2} \right)^2}$$ 3-12

Eqn. 3-10 implies that $F_e$ in the embedding function is determined by the cohesive energy and the single vacancy formation energy. From the original equation 3-5, $E_c = -(F_e + \Phi_e)$, where $\Phi_e$ is the contribution to the cohesive energy from the pair interaction. With the normalized embedding function that we are using, $F'(\rho_e) = 0$, and $F''(\rho_e)$ is small, so that the contribution to the vacancy formation energy $E_f$ is very small. As a result, $\Phi_e = -E_f$, and $F_e = -(E_c - E_f)$.
Eqn. 3-11 results from the normalized embedding energies. Eqn. 3-12 is due to the fitting conditions of relating the linear elastic constants to the EAM parameters by applying an infinitesimal homogeneous strain to a perfect pure crystal at equilibrium [76, 80].

Combining Eqns. 3-10 through 3-12 then gives the model parameters as follows:

\[ F_0 = -(E_c - E_f) \]  
\[ F_1 = 0 \]

\[ n^2 = \left( \frac{\sum f_{ie}}{\sum r_{ie} f_{ie}} \right)^2 \frac{9 \Omega B_v - 15 \Omega G_v}{E_c - E_f} \]

where \( E_c \) is the cohesive energy, subscript \( i \) denotes equilibrium value of the \( i \)th nearest neighbor in a perfect lattice, and \( \Omega \) is the atomic volume.

Next, we choose the electron density function \( f(r) \) and the two-body potential \( \phi(r) \) [81] as:

\[ f(r) = \frac{r_c}{r} \left( \frac{r - r_c}{r - r_c} \right)^2 \]

\[ \phi(r) = -\Phi_e \left[ 2 \left( \frac{r - r_c}{r - r_c} \right)^3 - 3 \left( \frac{r - r_c}{r - r_c} \right)^2 \right] \]

Where \( r_c \) is the equilibrium interatomic separation distance, \( r_c \) is a cut-off distance.

As was explained earlier, with the normalized model we are using, the contribution to the vacancy formation energy from the embedding function is small and we can assume \( \Phi_v \approx -E_f \). Therefore for the nearest-neighbor model we have:

\[ 6\phi(r_c) = -E_f \]
The normalization condition requires equilibrium at the perfect lattice setting:

\[ 6r_e \phi'(r_e) = 0 \] 3-19

The Voigt average shear moduli has to satisfy:

\[ 6r_e^2 \phi''(r_e) = 15 \Omega G_v \] 3-20

Also \( f(r) \) has to be continuous and smooth at the cutoff distance:

\[ \phi(r_c) = 0 \] 3-21
\[ \phi'(r_c) = 0 \] 3-22

Equations 3-18 through 3-22 are the conditions we used to fit for the two-body potential. The model parameters are finally determined by the following relations:

\[ \phi_e = \frac{1}{6} E_f \] 3-23
\[ r_e = \frac{1}{\sqrt{2}} a \] 3-24
\[ r_c = r_e \left[ 1 + \left( \frac{2E_f}{5\Omega G_v} \right)^{1/2} \right] \] 3-25
\[ F_e = -E_c + E_f \] 3-26
\[ n = \frac{r_c - r_e}{r_c - r_e} \left( \frac{9\Omega B_v - 15\Omega G_v}{E_c - E_f} \right)^{1/2} \] 3-27

The EAM fitting parameters for two fcc metals (copper and nickel) are listed in Table 3-1 [81].
Table 3-1 EAM physical and model parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Copper</th>
<th>Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Omega (\text{Å}^3)$</td>
<td>11.81</td>
<td>10.90</td>
</tr>
<tr>
<td>$E_c (\text{eV})$</td>
<td>3.54</td>
<td>4.45</td>
</tr>
<tr>
<td>$E_f (\text{eV})$</td>
<td>1.30</td>
<td>1.70</td>
</tr>
<tr>
<td>$\Omega B_v (\text{eV})$</td>
<td>10.17</td>
<td>12.28</td>
</tr>
<tr>
<td>$\Omega G_v (\text{eV})$</td>
<td>4.05</td>
<td>6.45</td>
</tr>
<tr>
<td>$\phi_e (\text{eV})$</td>
<td>-0.216667</td>
<td>-0.283333</td>
</tr>
<tr>
<td>$r_e (\text{Å})$</td>
<td>2.556162</td>
<td>2.489506</td>
</tr>
<tr>
<td>$r_c (\text{Å})$</td>
<td>3.472092</td>
<td>3.296827</td>
</tr>
<tr>
<td>$F_e (\text{eV})$</td>
<td>-2.24</td>
<td>-2.75</td>
</tr>
<tr>
<td>$n$</td>
<td>0.563224</td>
<td>0.312208</td>
</tr>
<tr>
<td>$\rho_e$</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>$r_e (\text{Å}), 2D$</td>
<td>2.44790</td>
<td>2.44567</td>
</tr>
<tr>
<td>$E_e (\text{eV}), 2D$</td>
<td>2.80547</td>
<td>3.55350</td>
</tr>
</tbody>
</table>

The last two rows in the table show that when this model is applied to a close-packed two-dimensional sheet, the equilibrium lattice constant is slightly reduced (2% for nickel, 4% for copper) and the cohesive energy is reduced by about 20%. Figs. 3-1 to 3-3 show examples of the functional forms of $f(r)$, $F(\rho)$ and $\phi(r)$ for nickel.
Molecular statics (MS) calculations can be used to estimate activation energies for diffusion for various possible configurations [72]. In MS calculations the total energy of a system of atoms is minimized as a function of all atoms’ coordinates. This is carried out iteratively. In each iteration step the forces on all atoms are calculated, and the atoms are moved in certain direction of the force over a distance proportional to the force. The pro-
cess is repeated until the system energy difference between two consecutive moves is smaller than a preset small number. The number of iterations needed for the system to converge depends strongly on the choices of the direction and the proportionality constant in the direction. If not chosen properly, convergence may be reached either only very slowly (because the atoms hardly move) or the system may start to oscillate because the adjustments overshoot. Thus speeding up convergence was the focus in the past. Use of the conjugate gradient method has simplified evaluation of the direction and proportionality constants at each iteration step [82, 83].

The activation energy for an atom to jump to a neighboring site can then be calculated as follows. First the total energy of the system is minimized, allowing all atoms to relax freely. Then the jumping atom is moved in small step along a line connecting its initial and final position. After each movement, the total energy of the system is calculated, allowing the jumping atom to relax freely in the plane perpendicular to the jump direction, and allowing all other atoms to relax freely. The diffusion path is then given by the successive positions of the jumping atom after relaxation. Note that the procedure described above does not force the diffusion path to be a straight line. The height of the diffusion barrier is given by the difference between the highest energy (after relaxation) between the initial and final state, and the energy in the initial situation. Since thermal vibration of atoms is not taken into account in MS calculations, the activation energies are calculated for the case of $T = 0 \text{ K}$.

Fig. 3.4 shows a sample energy barrier calculated by Johnson in this way for surface migration in two-dimensional copper [81]. The configuration at the left is for a ledge in a “surface” of tight-packed rows and at the right for a single atom one site away from the ledge. From left to right the number of bonds changes from 3 to 2, and vice versa. This corresponds to run 2 in the table of activation energies, Table 3-2. It can be seen that diffusion away from the ledge must overcome a barrier of 0.617 eV while diffusion toward the
ledge has only 0.227 eV. As a result, the jumping atom will sit at the ledge for most of the time. Table 3-2 lists activation energies for all possible nearest neighbor jumping paths encountered in 2D lattice model for both copper and nickel [81].

![Image of MS calculation for 2D jumping of copper atom from/to a ledge](image_url)

**Fig. 3.4.** Example of a MS calculation for the 2D jumping of a copper atom from/to a ledge [81].
<table>
<thead>
<tr>
<th>No.</th>
<th>Configurational transition</th>
<th>Jump</th>
<th>Nickel (eV)</th>
<th>Copper (eV)</th>
<th>Residence time (nickel at 350K) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>2 - 2</td>
<td>0.472</td>
<td>0.246</td>
<td>1.25e-6</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>2 - 3</td>
<td>0.447</td>
<td>0.227</td>
<td>5.47e-7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 - 2</td>
<td>0.848</td>
<td>0.617</td>
<td>3.25e-1</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>3 - 3</td>
<td>0.822</td>
<td>0.598</td>
<td>1.37e-1</td>
</tr>
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<td>0.217</td>
<td>1.33e-8</td>
</tr>
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<td>0.979</td>
<td>2.78e+3</td>
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<td>4 - 4</td>
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<td>0.815</td>
<td>1.33e-1</td>
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<tr>
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<td>3 - 4</td>
<td>0.819</td>
<td>0.596</td>
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<td></td>
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<td>0.965</td>
<td>4.35e+4</td>
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<td>4 - 5</td>
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<td>0.363</td>
<td>1.32e-5</td>
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<td>5 - 4</td>
<td>0.920</td>
<td>0.730</td>
<td>3.54e+0</td>
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<td>3 - 5</td>
<td>0.408</td>
<td>0.213</td>
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<td>0.538</td>
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<td>2 - 5</td>
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<td>0.037</td>
<td>3.51e-13</td>
</tr>
<tr>
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<td></td>
<td>5 - 2</td>
<td>1.089</td>
<td>1.029</td>
<td>9.61e+2</td>
</tr>
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<td></td>
<td>vacancy</td>
<td>1.142</td>
<td>0.768</td>
<td>5.57e+3</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>S2 - 3*</td>
<td>0.706</td>
<td>0.371</td>
<td>2.93e-3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S3 - 2*</td>
<td>1.090</td>
<td>0.720</td>
<td>9.93e+2</td>
</tr>
</tbody>
</table>

* Schwoebel jump
3.6 Molecular dynamics calculations

Molecular dynamics, in its most straightforward realization, is an old idea. Given the interaction potential and an initial configuration of $N$ particles at time $t$, the resulting forces acting on each atom are calculated. Newton equations of motion are then numerically solved for a small time interval $\Delta t$ under the assumption of constant force, obtaining the system configuration at time $t+\Delta t$. In the limit $\Delta t \to 0$ the solution is exact. The procedure can be iterated infinitely, and the evolution of the system can therefore be followed.

Suppose that a set of $N$ classical particles have coordinates, $r_i$, and masses $m_i$, $i = 1,..., N$. The particles interact through a potential $V_N$ which, in most investigations is taken to be:

$$V_N = \frac{1}{2} \sum_{i,j} \phi(r_{ij}), \quad i,j = 1, 2, ..., N,$$

where $r_{ij} = |r_i - r_j|$. Newton’s equations are then:

$$m_i \ddot{r}_i = \sum_{j \neq i} \frac{1}{r_{ij}} \frac{d\phi}{dr_{ij}} r_{ij}, \quad i = 1,..., N,$$

and are solved numerically. As the system evolves in time it eventually reaches equilibrium conditions in its dynamical and structural properties. For practical reasons $N$ is often restricted to a few thousand and for small systems surface effects are obviously very important. However, to simulate a bulk system the common practice is to use periodic boundary conditions. These are obtained by periodically repeating a unit cell of volume $W$ containing the $N$ particles by suitable translations. However the restriction that the MD cell be kept constant in volume and in shape severely restricts the applicability of the method to problems involving such factor as crystal structure transformations. In transformations changes in the shape of the cell most obviously play an essential role.
In order to overcome this difficulty, Andersen [84] has shown how MD calculations can be modified to study systems under constant pressure by introducing the volume of the system as an additional dynamical variable. Parrinello and Rahman [85] have modified the method so as to allow for changes in volume and shape of the MD cell containing a system of particles under constant external hydrostatic pressure, whereas Andersen’s method only allowed changes in the volume of the MD cell but not in its shape.

The implementation of MD is often based on the equations of motion derived by the classical Lagrangian. Thus the three cases described above in Lagrangian forms can be listed below.

1) The traditional Lagrangian:

\[
L_1 = \frac{1}{2} \sum_{i} m_i \dot{r}_i^2 - V_N
\]

Periodic boundary conditions are applied, most often, in the form of a repeating cubic cell of volume $L^3$. The point to note is that $L$ is a constant and can be used as the unit of length.

2) The introduction of a time-dependent volume $W(t)$ by Andersen who used

\[
L_2 = \frac{\Omega^{2/3}}{2} \sum_{i} m_i \dot{s}_i^2 - V_N + \frac{1}{2} C \dot{\Omega}^2 - p \Omega
\]

where $s_i = \frac{r_i}{\Omega}^{1/3}$. Periodic boundary conditions of the usual kind give a pulsating cubic box which changes in time according to a Lagrangian equation of motion [84]. The constant $C$, a coupling parameter, can be thought as the mass of a piston [84]. The mass determines the relaxation time for recovery from an imbalance between the external pressure and the internal stress. An appropriate choice for the value of $W$ can make this relaxation time of the same order of magnitude as that of the relaxation of a small portion of a much
larger sample. However, if one is interested only in static averages, \( W \) can be chosen on
the basis of computational convenience. In fact, in classical statistical mechanics, the equi-
librium properties of a system are independent of the masses of its constituent parts.

3) The introduction of a time-dependent shape by Parrinello and Rahman [85] who
used vectors \( a(t), b(t), \) and \( c(t) \) to define the molecular dynamics cell and used (a prime
indicating the transpose)

\[
L_3 = \frac{1}{2} \sum_{i}^N m_i \dot{s}_i \cdot G \dot{s}_i - V_N + \frac{1}{2} W Tr \dot{h}' h - p \Omega, \quad \text{(3-32)}
\]

where \( r_i = h s_i, h(t) = \{a,b,c\}, G = h' h, \Omega = \|h\| \) and \( W \) is a mass associated with the coor-
dinates \( h_{\lambda \mu} \). Periodic boundary conditions of the usual kind give a pulsating molecular
dynamics cell of arbitrary shape which changes according to Lagrangian equations of
motion. This is when only hydrostatic pressure \( p \) is applied. The introduction of an aniso-
tropic stress tensor \( S \) in place of \( p \) has been given by Parrinello and Rahman as well [85].

Since the earliest days’ work by Vineyard and coworkers [86] on dynamics of radi-
ation damage and Verlet [87] on computer “experiments” on classical fluids, the MD sim-
ulation has seen widespread use in materials science community. It has been used to
simulate melting of silicon, crystal growth, crack propagation, ion bombardment, multi-
layer deposition, to name just a few areas.

However, a full MD atomistic simulation of vapor-phase crystal growth is actually
extremely difficult. Two factors that enter into this are the large number of vapor atoms
that must be added to the substrate to grow a new layer, and the length of time that must
pass between introduction of new vapor atoms. This latter factor is the primary difficulty,
as the enormous disparity in time scales between experimental and simulated time scales
(perhaps 8-10 orders of magnitude) makes such simulations potentially misleading.
In this work, the purpose employing MD technique is to use its strength of physical dynamics to extract energetic interaction data for kMC simulation. We modified the DYNAMO MD program [88] in which the Lagrangian derived equations of motion were integrated to simulate the energetic atom’s interaction with the substrate. More details on the energy data extraction are given in chapter seven.
Chapter 4

Implementation of kMC Algorithm and Verification

4.1 Introduction

In the previous chapter a new kMC scheme was proposed. It does not simulate atomic vibration and is intrinsically faster than the molecular dynamics method. MC originally refers to Metropolis equilibrium sampling in which the Boltzmann factor is used to select an exchange event [42]. Since in or near the equilibrium state the Boltzmann factor becomes excessively small, the chance to select an event becomes small and the efficiency is reduced dramatically. Because of this, the \( n \)-fold way (the predecessor of kMC) was designed in which an exchange is guaranteed and the computing efficiency can be increased up to ten fold in many applications. As described in chapter three, the kMC method is a powerful concept and it naturally treats such phenomena as thermally activated competing process where numerous events with different occurring probabilities can happen nearly simultaneously at any given moment. The key to the success is to quantify the system residence time, as given by Eqn. 3-3, and then link the system residence time with the process parameter to realistically follow the whole thin film evolution. It is obvious that the magnitude of \( t_n \) largely depends on the system size (number of atoms) and other process parameters like substrate temperature. In the event of large system size and high temperature, the system residence time becomes extremely small (say \( 10^{-12} \) second [89]), which makes kMC very inefficient especially if the program is not optimized [90]. Although modifications (approximations) may be made to the kMC concept itself to speed up the simulation process [91, 92], code optimization should take priority before effort on
such approximations is made. In this chapter, the key steps in kMC simulation and traditional kMC implementations are first reviewed. A very efficient scheme is then developed.

### 4.2 The key steps in kMC algorithm

The implementation can be demonstrated in detail through a vapor deposition flowchart shown in Fig. 4.1. With the initiation of flux distribution, deposition rate and substrate temperature as well as the initial calculation and summation of atomic jump rates, the key steps lie in the execution of the thermal diffusion loop and can be described as follows:

1. Select a jump path at random weighting by individual rate;
2. Make the jump;
3. Update and sum up jump rates;
4. Turn ahead simulation clock;
5. Iterate step 1 through 4 until designated number of atoms is deposited.

The above seemingly simple procedure may be readily programmed and executed for small systems (say, several thousand atoms) without much concern for computation time. For bigger systems, say a million atoms, the step of selecting a jump path from millions of jump paths can be a daunting task and very careful programming is needed to obtain efficient execution. Otherwise, intrinsically fast MC method (compared to MD) can be unreasonably slow [90]. A comparison is made at the end of this chapter.

The essence of the first step for a diffusion problem can be illustrated by a pie chart, Fig. 4.2. Consider a system with numerous potential jump paths. Allow the big sectors to represent high probability jump paths and the small sectors to represent low probability paths. To faithfully execute the kMC process, any one of them, be it a high or low
Inputs: flux distribution, deposition rate & substrate temperature (T/Tm)

Fig. 4.1. Kinetic MC Implementation of the thermally activated diffusional processes.
Fig. 4.2. Schematic representation of various competing thermally activated diffusional processes. The large sectors represent jump paths with large jump rates and vice versa.

Circumference = \sum p_i

where

p_i = v_0 \exp\left(\frac{E_i}{kT}\right)
probability jump, should have a chance to be selected. This can be accomplished by allowing every point on the perimeter of the pie-chart to have an equal chance to be selected. This automatically takes into account the weighting process. Several approaches have been reported in the literature for implementing such a strategy and they are assessed below [54, 93].

4.3 Linear search

Selection of the jump path by linear search is represented by a cumulative and conditional probability process, Fig. 4.3. Suppose that there are three jumping atoms, the first has two jump paths and the second and third each have three. The eight available jump paths have probabilities \( p_{11}, p_{12}, p_{21}, p_{22}, p_{23}, p_{31}, p_{32}, \) and \( p_{33} \) respectively.

Suppose that the jump path, \( p_{31} \), has been randomly selected. This is equivalent to:

\[
\xi \leq \frac{p_{11} + p_{12} + p_{21} + p_{22} + p_{23} + p_{31}}{P},
\]

where \( P \) is the total length of the segment and \( \xi \) is a random number over the interval \([0, 1]\). For a small system, this algorithm should have no problem to execute. But for a large system, it would be unrealistically inefficient. In that case, the relationship for selecting the process can be written as
where $p_{ij}$ is the jump rate for the $i$-th atom at the $j$-th jump path, $n(i)$ is the total number of jump paths for the $i$-th atom, $N$ is the total number of atoms. Eqn. 4-1 indicates the $K$-th atom is selected with $K \leq N$. In a system with millions of atoms, selection of a jump path would require multi-million computational steps, which is very time consuming. Therefore, the linear search is intrinsically slow for any large system [53].

4.4 Class grouping algorithm

One approach to increase the search efficiency was introduced by Maksym [93]. The basic idea is to group sites so that each group contains $g$ sites. After each event, cumulative sums for the groups are updated. For the jump rates, this gives the sums

$$
\sum_{i=1}^{g} p_i, \quad \sum_{i=g+1}^{2g} p_i, \ldots, \quad \sum_{i=g\lceil N/g \rceil + 1}^{N} p_i \quad 4-2
$$

where $\lceil N/g \rceil$ is the largest integer and $\lceil N/g \rceil \leq N/g$. The group containing the site of the next event can be located very quickly using binary chopping. Once the group has been found, an exhaustive search is done to find the site within the group.

This method is more efficient because the binary chopping process enables a quick identification of the event-containing group. But the exhaustive search in the group, which is in the efficiency of the linear search, ultimately compromises the end result. Moreover, there is no clear standard to decide what the optimal group size is. This becomes worse in vapor deposition because the total number of sites increase with simulation time and the increase complicates the grouping process and the time cost increases accordingly.

This type of grouping technique was used by Huang, Gilmer and Diaz de la Rubia in their recent large scale simulation of trench filling [54]. They grouped the atoms into
different classes based on their surface diffusion jump rates and potential energies. Equivalently, these classes were determined by each atom’s number of nearest neighbors.

### 4.5 B-tree algorithm

The most efficient search method developed to date is the binary tree ($B$-tree) process [94, 95]. The implementation of a tree structure search is illustrated in Fig. 4.4. The lowest level consists of an array containing all of the jump rates for the entire system. These are called the leaf nodes. Each leaf node summates jump rates for each individual jump-capable atom. Then the jump rates in every two side-by-side leaf nodes are added and entered into another array at level two. These are called the intermediate nodes. This process is repeated until the root node is reached. The root node contains the summation of the total jump rate of the system. According to the kMC algorithm, the inverse of the root node jump rate is the residence time of the system at the moment.

The binary tree structure facilitates very significantly the identification of a jump event for any large system. Take the hypothetical system in Fig. 4.4 as an example. First spin a random number $\xi_1$ to decide the intermediate node below the root $l_4$. The decision is simply taken by $\xi_1 \leq l_3 / (l_4 - l_3)$. Suppose the selection is $l_3$. Similarly $l_2$ can be determined by $\xi_2 \leq l_2 / (l_3 - l_2)$, where $\xi_2$ is another random number. Ultimately, the process reaches $p_6$, the jump rate sum for some jump capable atom. Then a final random number can be used to determine the specific jump path of the atom.

The binary tree is efficient in updating the entire tree data as well. Generally, after each jump event, only a limited number of adjacent atoms have changed their jump rates. Thus only the affected tree branches need renewal. For example, if $p_6$ is changed, the only nodes needing change are $l_1$, $l_2$, $l_3$, and $l_4$, highlighted in Fig. 4.4 and the rest remains the same. The root always has different value each time a jump occurs. Therefore, each new jump results in a different residence time, that is $1/l_4$. 
Fig. 4.4 Sample binary tree structure for efficient selection of a jump path in a kinetic Monte Carlo simulation system. Leaf nodes $p_1$, $p_2$, etc. are individual jump rates. Root node $l_4$, the sum of all jump rates, together with intermediate nodes such as $l_1$, $l_2$ and $l_3$ build up the tree structure on the base of leaf nodes. Nodes $p_6$, $l_1$, $l_2$, $l_3$ and $l_4$ highlight one possible selection route.
The seemingly symmetric tree structure in Fig. 4.4 is not at all symmetric in reality. Some of the jump rates are considerably larger than others. For reasons discussed below it is desirable to allow many of the nodes to have zero values.

### 4.6 Implementation of kMC in vapor deposition

Selecting the jump path efficiently is just one part of the problem for the seemingly simple vapor deposition simulation; we also need to index the jump paths and efficiently make them available for selection in a continuous growth process.

As the thin film grows, new surface atoms continue to be added and other previously deposited atoms continued to be buried as bulk atoms. Thus, efficient mechanisms are needed to remove inactive atoms (i.e. when they turn into bulk atoms) and add new arriving adatoms. Otherwise, the array for the binary tree structure will be becoming too large to handle in a large system simulation. Secondly, the removing-and-adding process should not affect other parts of the tree structure.

A method is needed that can both index a lattice site uniquely and enable the index to be quickly deciphered into the lattice site (i.e. its cartesian coordinates). The method needs to recognize only movable atoms that are involved in diffusion. Because once an atom becomes a bulk atom (no place to move), it no longer participates in the diffusion and reassembly process. It should be allowed to disappear smoothly without affecting the $B$-tree structure and more importantly release the leaf node in the $B$-tree to be used by other newly arrived atoms in order to maintain a reasonable size of the $B$-tree leaf node.

One way to solve this is through the use of the hashing function technique [96]. But first we need a mesh point indexing system. The box method for locating an atom is appropriate here [96].

Suppose the mesh point has coordinate $(I, J, K)$. Then the position number $NPOS$ for a mesh point in a system is defined as:
NPOS = I + (J - 1)*NBD + (K - 1)*(NBD**2). 4-3

Given NPOS, we can obtain the relative mesh point indices using the following recipe:

\[ K = \frac{NPOS - 1}{NBD^2} + 1 \] 4-4

\[ NT = NPOS - (K - 1)*(NBD^2) \] 4-5

\[ J = \frac{NT - 1}{NBD} + 1 \] 4-6

\[ I = NT - (J - 1)*NBD \] 4-7

The number NBD can be arbitrarily determined according to the size of the simulation system; NT is an intermediate parameter. Therefore, given a lattice site index (I, J, K) we can immediately determine its position index NPOS from Eqn. 4-3. Suppose we identify some vacant site with index NPOS into which a jumping atom is able to enter. We can immediately calculate its coordinate (I, J, K) according to Eqns. 4-4, 4-5, 4-6 and 4-7. In here each NPOS has a unique corresponding coordinate (I, J, K) and vice versa.

For a two-dimensional case, the recipe above becomes:

\[ NPOS = I + (J - 1)*NBD \] 4-8

\[ J = \frac{NPOS - 1}{NBD} + 1 \] 4-9

\[ I = NPOS - (J - 1)*NBD \] 4-10

Given the NPOS index array, what we need to do now is to search a specific NPOS index as a jump path. The straightforward, linear search procedure is obviously prohibitively expensive if the entries are many. A hashing technique can be used to search for a specific entry in a table at a tiny fraction of the cost of a linear search. A hashing technique uses some property of the meshing position number NPOS to define its probable index N in the NPOS array. The recipe used to specify the probable index is called a hashing function. The probable index also is called the “home index”. The following is the modular
hashing function. To complete a hashing technique, there are two processes for both entering and determining a hashing number.

To enter a site into a hashing array:

\[ N_{POS} = I + (J - 1)\times NBD + (K - 1)\times (NBD\times 2) \] 4-11

\[ N = \text{MOD}(N_{POS}, N_{MAX}) + 1 \] 4-12

\[ *N = N + 1 \] 4-13

if \((N .gt. N_{MAX}) N = 1\) 4-14

if \((\text{nbox}(N) .gt. 0) \) goto * 4-15

\text{nbox}(N) = N_{POS} 4-16

where \(N_{MAX}\) is the maximum number of entries for \(N_{POS}\). This function is used to obtain the probable index \(N\). If another box number already is stored in \(N_{POS}(N)\), a linear method is then used to find an unused location in the table. Usually the value of \(N_{MAX}\) is large enough that the table is never more than half full so that little searching is necessary to enter (or determine) whether a site is empty or in the table.

To determine if a site is in the array

\[ N_{POS} = I + (J - 1)\times NBD + (K - 1)\times (NBD\times 2) \] 4-17

\[ N = \text{MOD}(N_{POS}, N_{MAX}) + 1 \] 4-18

\[ *N = N + 1 \] 4-19

if \((N .gt. N_{MAX}) N = 1\) 4-20

if \((\text{nbox}(N) .ne. N_{POS}) \) goto * 4-21
4.7 Comparison of CPU times

Table 4-1 and Fig. 4.5 show a CPU time comparison for 2D trench filling simulation using both the basic linear search and the B-tree search processes (The class grouping technique was not programmed for the comparison purpose). Three simulations for each method have been used, with each subsequent trench being scaled up one time over the previous one. That is, with a fixed aspect ratio of 2, when the small trench has a width of 200 atoms deposited with 100,000 atoms, then the medium one must have a doubled width of 400 atoms deposited with quadrupled number of atoms of 400,000 and the large one accordingly with 800 and 1,600,000 atoms respectively. The number of hours in the table are averages of three runs (on IBM RS/6000 workstation) rounding up to their close integers for comparison.

It can be seen that the brutal linear approach is indeed very inefficient. It takes 15 hours of CPU time to simulate the small trench while the B-tree search only needs one third of it with 5 hours. The medium trench takes the linear search 5.3 times as much of CPU hours (80 hours) to simulate the quadrupled number of atoms and 38.7 times as much (580 hours) to simulate the large one. In comparison, the B-tree method has only linear increase of CPU time, the times being 20 and 80 hours respectively and 4 and 16 folds accordingly.

In conclusion, an efficient algorithm was developed to handle the key kMC simulation steps. It was based on the B-tree search combined with a hashing function and the box indexing method. It has been shown that this method is in particular useful in simulating large system and the increase of CPU time increases linearly with increasing the number of atoms.
Table 4-1 CPU time comparison (hrs)

<table>
<thead>
<tr>
<th>number of atoms (width of system)</th>
<th>100000 (200)</th>
<th>400000 (400)</th>
<th>1600000 (800)</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>15</td>
<td>80</td>
<td>580</td>
</tr>
<tr>
<td>B-tree</td>
<td>5</td>
<td>20</td>
<td>80</td>
</tr>
</tbody>
</table>

Fig. 4.5. CPU time comparison between linear and binary tree search. In binary tree search, the CPU time increases linearly with increasing the number of atoms while the linear search results in much steeper increase of CPU time with increasing the number of simulated atoms.

4.8 Model verification

To verify if the critical diffusion step is correctly executed, random walk theory in one dimension problem has been used for examination [171]. Suppose that a particle suffers displacements along a straight line in the form of a series of steps of equal length, each step being taken, either in the forward, or in backward direction with equal probabil-
ity $\frac{1}{2}$. After taking $N$ such steps the particle could be at any of the points, $-N, -N+1, ..., -1, 0, +1, ..., N-1$ and $N$. The question is: What is the probability $W(m, N)$ that the particle arrives at the point $m$ after suffering $N$ displacements?

It has been shown that the probability has a Bernoullian distribution [171]:

$$W(m, N) = C_{N+m}/2 \left(\frac{1}{2}\right)^2,$$

where $C$’s in Eqn. 4-22 are the binomial coefficients. Accordingly, the expectation and the mean square deviation of $(N+m)/2$ are [171]

$$\frac{1}{2} \left< \frac{N+m}{2} \right>_\text{Av} = \frac{1}{2}N,$$

$$\left< \left( \frac{1}{2} \left( N+m \right) - \frac{1}{2}N \right)^2 \right>_\text{Av} = \frac{1}{4}N.$$

Hence,

$$\left<m\right>_\text{Av} = 0; \quad \left<m^2\right>_\text{Av} = N.$$

The root mean square displacement is therefore $\sqrt{N}$.

Simulations using 2D kMC model to track a single atom’s displacement from the starting point with $N$ ranging from 10 to 100,000 steps have been carried out and the results were agreed well with Eqn. 4-25, Fig. 4.6.
Fig. 4.6. Random walk theory vs. kinetic Monte Carlo implementation. An average over twenty runs was used for each simulation point. The dashed line is the prediction from the random walk theory.
Chapter 5

Low Energy Physical Vapor Deposition

5.1 Introduction

Physical vapor deposition (PVD) via either electron beam [97], resistive evaporation [98], or by a variant of sputtering [99] is widely used for depositing metal films at low to intermediate rates (<1 µm/min). Interest is growing in the development of potentially very high rate (1 - 100 µm/min) physical vapor deposition processes such as jet and directed vapor deposition (JVD™/DVD) [100 - 106] for synthesizing metal multilayers with minimal interlayer diffusion. In all these processes, the atomic flux (or equivalently the deposition rate), the flux incidence angle, the incident atom kinetic energy and the substrate temperature can all be independently varied. Since these parameters govern the kinetic phenomena involved in the atomic assembly and reconstruction of surfaces during film growth, many options are available for controlling the morphology/microstructure of a deposit during vapor phase manufacturing. The many variables of the processes make it difficult to identify the conditions that result in acceptable morphologies/microstructure.

The prediction of these morphologies/microstructures, and their dependence on material system properties and process parameters, has proven to be very difficult. The structures predicted by classical arguments [37] (e.g. layer-by-layer or Frank-van der Merwe [35], island or Volmer-Weber [38], and the layer-plus-island or Stranski-Krastanov [39] growth modes) are normally applicable only to the early stages of the nucleation and growth of epitaxy. The empirical Structure Zone Model (SZM) of Movchan, Demchishin [44] and Thornton [45] serves only as a rough guidance if a resulted thin film has a columnar structure
Low Energy Physical Vapor Deposition

with void or dense boundary at a given normalized substrate temperature. Many computer simulations, including the HBS [46], SIMBAD [48] and Müller’s Monte Carlo model [49], have been used to predict the thin film evolution and the process dependence, but none of these models correctly linked major process parameters, such as substrate temperature, deposition rate, and the atom kinetic energy.

Two phenomena must be incorporated in a kMC simulation of a physical vapor deposition. It is necessary to characterize the outcome of the adatom-substrate collision process that results in an initial adatom configuration. And it must properly simulate the diffusion of atoms both on the growing surface and within the previously deposited (interior region) film. The kMC described in chapter three can be used for the purpose. As for the adatom-substrate interaction, the low incident energy deposition associated with processes such as evaporation (where incident atoms have only thermal energy, $kT < 0.1$ eV) is first examined. In this case, the atoms (remote from the growth surface) kinetic energy is small compared with the surface diffusion barrier heights and can be ignored. A two-dimensional (2D) model is used for simplicity. The results of this work will be shown to provide a deeper insight into many of the different physical processes involved in physical vapor deposition and enables a systematic exploration of the effects of process conditions upon morphology and microstructure.

5.2 Adatom Incorporation

Energetic incident atom-substrate collision can result in many athermal interactions such as reflection and thermal spike [60, 61]. Adatoms deposited even in a low energy process can still carry considerable energy when they arrive at the substrate. For example, Zhou, Johnson and Wadley [59] using MD simulations found that a nickel atom with thermal energy of 0.1 eV can be accelerated to an kinetic energy as high as 1.0 eV in the attractive force field of the surface atoms before being incorporated in the lattice. Kinetic energy of
this magnitude can cause enough momentum to influence the initial adatom integration on the substrate. In particular, this can cause the HBC treatment for the initial integration model to be improper. To take this into account and at the same time to avoid a complex MD calculation for the low energy cases, the interaction at the moment of adatom incidence has been modified from the HBC model. As shown in Fig. 5.1, an incident atom $O$ travelling along the $cd$ direction inclined at an angle $\theta$ from the normal to the substrate will first touch atom $F$ located at position $f$. With HBC model's nearest cradle criterion, the atom was assumed to go to the nearest stable site which is $B$. This method results in a very low packing density which is not observed in experimental work. Thus, in considering the conservation of momentum it is proposed here that the atom $O$ will more likely move towards the cradle site $A$ when the landing point is to the left side of line $ef$ (for a head-on collision), even though the distance of path $oA$ is larger than that of $oB$. This is clearly an approximation to the complicated binary collision processes with a rough surface at low energy situations [107].

Fig. 5.1. Schematic illustration and comparison of the HBC model and the momentum scheme for the initial relaxation in the low energy Monte Carlo simulation. The shadowed disk represents an atom in flight and the dashed disk an atom hitting a previously deposited atom. Path $B$ stands for the HBC model and path $A$ the momentum scheme. $\theta$ is the incidence angle.
This simple modification, which we term the momentum scheme, generates configurations having significant differences with those of the HBC model. Two sample configurations are shown in Fig. 5.2, both with an incidence angle $\theta$ of 45°. In the momentum scheme, $\beta$ is the resultant column orientation angle.

Fig. 5.2. Representative configurations simulated using (a) the HBC model and (b) the momentum scheme. A flux incidence angle $\theta$ of 45° was used for both cases and $\beta$ is the resultant column orientation angle.
scheme, the column orientation angle with respect to the normal to the substrate, $\beta$, is significantly less than that with the HBC model. This trend continues for a range of $\theta$ as shown by Fig. 5.3(a). From a plot of packing density (defined as the fraction of atoms occupying the lattice sites in the deposited region) as a function of incidence angle, Fig. 5.3(b), it is seen that structures generated by the momentum scheme have considerable higher densities than those generated by the HBC model when $\theta$ is less than about 30°. When $\theta$ approaches 50°, the density tends to be similar for both models. Thus the momentum scheme provides a better initial relaxation model for prediction of density [46, 108 - 110].

![Graph](image)

**Fig. 5.3.** Comparison of the difference between the HBC model and the momentum scheme in terms of (a) the relationship between column orientation angle $\beta$ and incidence angle $\theta$ and (b) the relationship between packing density and incidence angle, $\theta$. The lack of measurement points on the left side in (a) was due to difficulty in precisely identifying the column orientation.
The decrease of the column orientation angle has also been evaluated by experiments. Using an evaporation process, Nakhodkin and Shaldervan conducted an extensive study on the effect of condensation condition on the profile of condensed films [110]. One of their results was that the column orientation angle decreased with an increase of the substrate temperature, which is in essence related to the increase of the surface mobility of adatoms. This is one of many reasons why thermally activated processes must be included in simulation of low energy deposition processes.

5.3 Thermally activated assembly results

In this low energy kMC model, the momentum scheme was used for the initial adsorption of the impinging atom and the diffusion model is used for simultaneous annealing during the deposition. Desorption was ignored because simulations are carried out at relatively low temperatures. All calculations are based on the parameters for the 2D nickel model and lateral periodic boundary conditions are employed to account for the limited system size. The substrate consisted of a perfect array of 200 close-packed atoms. A representative incidence angle, $\theta = 38^\circ$, was used for all the calculations, and 8000 atoms were deposited during each run. Five runs were carried out for each data point to determine the statistical spread in the data. Since this is a 2D model, the actual temperatures used for deposition are not directly related to those of a 3D system. To compensate, we note that the 2D vacancy formation energy is about 2/3 of the corresponding 3D value [111]. Thus, a homologous temperature is also given, based on a melting temperature, $T_m$, of 1150 K, which is 2/3 of the 3D nickel melting temperature of 1726 K.

Two series of computer experiments are reported. In one, the deposition rate was held fixed and the substrate temperature was varied. In the other, the substrate temperature was held fixed and the deposition rate was varied. Since this model incorporates a fixed lattice of sites which are either occupied or not, dislocations and grain boundaries cannot
occur. However, mounding of the surface profile yields a characteristic width that is used as a measure of the column size. The column width was approximated by dividing the width of the system by the number of mounds. In actual growth, the mounds often correspond to individual grains. The surface roughness is defined as the standard deviation of the surface height [112, 113] and is described in detail in Appendix C. Finally, the packing density is measured in the same way as that used in section two.

5.3.1 Effect of temperature on microstructure/morphology

The effect of the substrate temperature on the thin film structure has been simulated using a deposition rate of 10 µm/min and angle of incidence of 38°, Fig. 5.4. For some simulations, tracer atoms (shown as filled circles) were used to reveal the evolution of the internal structure of the deposit and to indicate possible mechanisms by which the evolution occurs. The tracer atoms corresponded to a set of marked adatoms deposited during a specific time period. Their position is observed throughout the remainder of the simulation run. When an adatom arrives at the growing surface, it is first adsorbed and then diffuses to some extent depending upon its local configuration and the deposition conditions.

At a fairly low temperature of 250 K \((T/T_m = 0.22)\), Fig. 5.4(a), a low density structure (packing density = 0.79) with voided growth boundaries, typical of zone I in the SZM model, is found. This structure forms because of self-shadowing [45]. With an increase of temperature to 300 K \((T/T_m = 0.26)\), Fig. 5.4(b), the voided growth boundaries are found to have almost disappeared (packing density = 0.97) and the internal columnar boundaries have become better defined, as demonstrated by the surface contour in relation to the tracer atom contour, although the surface is still quite rough. With a further increase of temperature to 400 K \((T/T_m = 0.35)\), a fully dense columnar structure (packing density = 1.0) and a facet-like surface typical of zone II in the SZM model was observed, Fig. 5.4(c). The column boundaries within the bulk can be seen with the aid of the tracer atoms: the columns nucleate at the beginning of deposition, are tilted toward the flux, and retain their
Fig. 5.4. Representative 2D configurations of nickel growth at various substrate temperatures at a deposition rate of 10 µm/min and an incidence angle $\theta$ of 38°. The momentum scheme was used to treat a low kinetic energy deposition process. Atoms, tagged as tracers to show sample atom movements, are shown as solid circles.
approximate width throughout the run. At a still higher temperature of 550 K \((T/T_m = 0.48)\), Fig. 5.4(d), the surface becomes fairly flat and the tracer atoms show a rapid increase of the column width. Tracer atoms show that little bulk diffusion occurs at this temperature.

The packing density as a function of temperature at this deposition rate (10 µm/min) is represented by the filled circles in Fig. 5.5. The fitted curve exhibits three regions. When the temperature is below about 150 K, the porous structure has a fairly constant density of about 0.68, whereas a fully dense structure is obtained when the temperature is above about 350 K. A transition occurs in the region between these two temperatures and marks the change from a porous columnar structure to a fully dense columnar structure. The transition temperature, \(T_r\), is defined as the onset of full structural densification, in conformity with the characteristic columnar boundary difference of zone I and zone II [45]. Using this definition, \(T_r = 350 \text{ K} \ (T/T_m = 0.3)\) for a deposition rate of 10 µm/min.

![Fig. 5.5. Packing density vs. substrate temperature at various deposition rates for \(\theta = 38^\circ\).](image)
This temperature is defined by both the mobility of the adatoms and the deposition rate. It delineates a temperature where adatom mobility is sufficient to fill shadowed regions. The shadowed regions grow at a rate proportional to $R$ and so $T_r$ corresponds to the temperature at which a balance between mobility and deposition rate is achieved, and so it must be deposition rate-dependent.

The results of simulations conducted for both a much higher (250 µm/min) and a much lower deposition rate (0.05 µm/min) are also plotted in Fig. 5.5. The faster deposition is seen to shift the transition region to a higher temperature ($T_r/T_m = 0.35$) while the slower deposition shifts it to a lower temperature ($T_r/T_m = 0.24$). The transition also occurs over a greater temperature spread as the deposition rate increases. This zone I - II transition was seen by Müller [114] as well from an analysis of packing density in his 2D calculations, although at a significantly higher temperature partly because of his use of the HBC model and the bond counting activation barrier energy.

The surface morphology (or roughness) also varied with the processing parameters and is well known to exhibit transition phenomena [45]. The effect of temperature on surface roughness predicted using the kMC model is shown in Fig. 5.6. It can be seen that in each case the roughness is approximately constant at low temperature, decreases with an increase of temperature and approaches a final saturation value of about 6 Å. The roughness transition is coincident with the transition in the density plot: for a deposition rate of 10 µm/min, the roughness is greatest below about 150 K (where densification starts) and becomes lowest at and above 350 K when densification is complete. Surface roughness thus provides an alternative way to measure the zone I - II transition.

Since a comprehensive experimental study of the relationship between the grain size of nickel thin films and processing parameters has been carried out [111], simulations were run at the same deposition rate of 0.06 µm/min used in the experiments. The relationship between average column width and substrate temperature is plotted in Fig. 5.7. The column
Fig. 5.6. Surface roughness vs. substrate temperature at various deposition rates for \( \theta = 38^\circ \).

Fig. 5.7. Average column width vs. substrate temperature at the same deposition rate of 0.06 \( \mu \)m/min as that used in the experiments [111].
width does not experience any significant change when the temperature is at or below about 200 K, but increases rapidly above about 250 K.

These results are compared with the experimental results from the literature [111], Fig. 5.8. Fig. 5.8(a) shows that at all substrate temperatures a range of grain sizes was observed and the difference between the maximum and the minimum observed grain sizes increased with the temperature. A reasonable agreement between the calculation and the minimum observed grain sizes can be seen. This suggests that a simulation approach that uses the activated processes of atomic diffusion and a relatively large system size can predict the trends in microstructure/morphology surprisingly well. Fig. 5.8(b) suggests that when the deposition temperature is scaled by the melting temperature, the grain size of many metals collapse onto a master curve and all can be fitted by a nickel model prediction.

![Fig. 5.8](image.png)

Fig. 5.8. (a) Plot of measured grain size variation with substrate temperature for nickel films deposited at a deposition rate of 0.06 µm/min using an e-beam evaporation process (ref. [111] with permission) compared with the simulated column width plotted in Fig. 5.7; (b) Comparisons with other metals.
Grovenor et al. [111] suggested that the universal nature of their graph of grain size vs. homologous temperature is due to the scaling of the activation energy for bulk diffusion with $T_m$. Since there is little bulk diffusion in the present calculations, the agreement of these results with their data indicates that surface diffusion activation energies, which also scale with $T_m$ [110], are controlling the microstructure development at lower temperatures.

5.3.2 Effect of deposition rate on microstructure

Some insight into the effect of the deposition rate on thin film structures has already been given. A more detailed view has been obtained by using a range of deposition rates and fixing the substrate temperature and the system size. Examples of representative structural configurations for deposition at 350 K are given in Fig. 5.9. As shown in Fig. 5.9(a), a fairly porous columnar structure (packing density = 0.96) results when a rapid deposition rate of 250 µm/min is used. The rate of 10 µm/min, typical of the high rate JVD$^\text{TM}$/DVD processes, results in a fully dense columnar structure with a facet-like surface morphology, Fig. 5.9(b). As indicated in Fig. 5.9(c), further decreasing the rate to 0.5 µm/min yields a structure with an increased column width and a facet-like surface. At a still lower rate of 0.05 µm/min (typical deposition rate for a sputtering process), a structure with a further enlarged column width is generated, Fig. 5.9(d).

The corresponding variations of the packing density, the surface roughness and the column width with deposition rate are plotted in Fig. 5.10. A transition from a porous columnar structure to a fully dense columnar structure occurs at a deposition rate of about 50 µm/min, Fig. 5.10(a). This is similar to the transition due to the change of substrate temperature observed earlier.
Fig. 5.9 2D nickel film configurations for growth at various deposition rates. Substrate temperature = 350 K, incidence angle $\theta = 38^\circ$. 
The roughness values show a plateau over a considerable range of deposition rates, as illustrated in Fig. 5.10(b). This plateau can be ascribed to the presence of a facet-like surface morphology, Fig. 5.9. That is, although the column width changes with the rate, the standard deviation of the surface height, which is used as a measure of surface roughness in this work, remains fairly constant. The variation of the column width with deposition rate
is illustrated in Fig. 5.10(c). It increases approximately as the logarithm of the deposition rate at rates less than about 200 µm/min, and is fairly constant at higher rates.

5.4 Discussion

The computer experiments above describe the atomistic evolution processes during low energy deposition over a wide range of substrate temperatures and deposition rates. A dependence of the density and roughness with deposition rate, flux angle or substrate temperature, a coarsening phenomenon at relatively high temperatures and low deposition rates as well as structural transitions are all exhibited by this model. These observations can be explained physically as the effect of the initial impact followed by thermal activation leading to atomistic surface diffusion. Bulk diffusional contributions to the microstructure evolution are relatively insignificant for the range of deposition rates and temperatures investigated here.

Although the activation energy parameters used in the present work are for nickel and the model results strictly apply only to this metal, the study indicates the observed patterns of behavior for physical vapor deposition are applicable to a broad range of metals. Experimental results for vapor deposition demonstrate such a general pattern regardless of the material and the crystal structure used [111]. As shown in Fig. 5.8(b), the variation of grain size as a function of $T_m/T_s$ (where $T_m$ is melting point and $T_s$ substrate temperature) is very similar for ten elements including a variety of b.c.c., hexagonal and f.c.c. metal films and motivated the development of the SZM model. The results of the present calculation are also plotted on this graph as the solid squares and show the same pattern.

Thin film growth is generally considered to occur in a series of steps [115]: transport of coating atoms to the substrate, adsorption of these atoms on the growing surface, their diffusion over the surface, eventual incorporation into the coating or release from the surface.
by thermal desorption or sputtering, and finally movement of atoms to lower energy positions within the lattice by bulk diffusion and solid state reactions. In an actual process, however, the simulations show that the surface morphology of a film and its internal structure may be dominated by just one of these steps.

The simulation confirms that in the SZM model, the zone I structure represents the result of limited atomic rearrangement in the vapor deposition process. When the deposition temperature is sufficiently low, relative to the deposition rate, the residence times for the adatoms are relatively large compared to the adatom arrival interval so that there is limited relaxation/diffusion on the surface before it is covered with additional atoms. Since every adatom essentially sticks close to where it arrives, the growth is dominated by the transport of the depositing atoms to the substrate and in particular by the set of directions from which these atoms arrive at the substrate. As a result, the self-shadowing effect is very important and void networks develop. Thus, the structure in zone I is generally characterized by low density poorly aligned crystals, a very rough domed top surface, and small column sizes. In each column, there are essentially several smaller sub-columns aligned in a similar direction, as reflected both in the experimental observations [111, 115 - 117] and the computer simulations. We find that this type of porosity (due to the limited rearrangement of adatoms) is difficult to eliminate [118]. Even when the films are subjected to post-deposition annealing, these voids tend only to change shape since the overall structural framework has been previously established.

The residence times of adatoms at a surface site decrease with an increase in temperature. When the temperature is increased to the point where the residence is comparable to the adatom arrival interval, $\Delta t$, the porous columnar structure begins to change to a fully dense columnar structure separated by distinct, dense and intercrystalline boundaries. This is the transition reflected in the density plot of Fig. 5.5 and in the roughness
The Zone II structure is controlled by surface diffusion, as indicated by the smooth contour of the tracer atoms in Fig. 5.4(c). Activation energies for surface diffusion are significantly less than those for bulk diffusion [115]. Accordingly, at a specific deposition rate, a temperature range normally exists which is high enough so that surface diffusion dominates over arrival rates, and the coating atoms lose memory of their arrival directions. This temperature is still low enough ($T_s/T_m < 0.5$) that bulk diffusion rates remain orders of magnitude less than surface diffusion rates and are consequently negligible. The direct effect is that the columns grow bigger with increasing temperature, Figs. 5.4(b) ~ 5.4(d), and facet-like faces are usually present in this zone. Alternatively, a zone II structure can be obtained by fixing the temperature and increasing the arrival interval, as shown in Fig. 5.9. The roughness is nearly constant in zone II, Fig. 5.10(b), and can therefore be used as a delimiter of this range.

It is found that the formation of facet-like mounds in zone II structures is quite universal and was present in every simulation carried out in this work. Experimentally, this also appears to be a fairly general phenomenon, occurring in a number of different systems [10, 116, 119 - 124]. We attribute this phenomenon to both self-shadowing and the presence of Schwoebel [50] (or step edge) barriers in the material. They make it more difficult for adatoms to move from one terrace to a lower one.

Zone III conditions occur at higher temperatures where bulk diffusion dominates over all other processes so that atoms lose all memory of the initial events associated with their condensation. Zone III conditions are not modeled in this work, in part because the activated character of the diffusion rate intrinsically demands a high computational cost. Zone III conditions are less likely in many advanced applications due to concerns about thermal stress and the stability of the substrate [10, 16, 116].
5.5 Summary

A low energy Monte Carlo method has been proposed and shown to generate reasonably realistic low energy deposition simulations over a wide range of deposition conditions. The model incorporates a momentum scheme in which the effect of low atomic kinetic energy at the instant of adatom impact with the substrate is approximated. This yields initial packing densities and column orientation angles that are closer to experimentally reported values than those yielded from the HBC model used in prior calculations. Using basic kinetic considerations of solid-state diffusion, a multipath diffusion model has been developed to provide a fundamental link between the deposition rate and atomic diffusive process on, and within, the sample. An embedded atom method is employed to calculate the activation energies for diffusion of a variety of atomic configurations.

This approach makes possible the simulation of low energy deposition over a broad range of physically realistic deposition parameters. The approach provides a practical method to simulate several aspects of the vapor deposition processes. In particular, it enables determination of the effect of vapor processing variables such as deposition flux density (deposition rate), flux angle and substrate temperature upon deposit microstructure/morphology parameters such as packing density, surface roughness and column width.

Although a 2-D model is used in this work, the simulation results demonstrate the transition from a porous columnar structure to a fully dense columnar structure in a way that agrees well with the SZM model. The transition is found to occur at a higher temperature as the deposition rate increases. The width of the columns in the simulated microstructure appears to correlate well with grain size, and the temperature dependence of the width correlates closely with experimental grain size data for many metals. This suggests that a Monte Carlo simulation that uses the activated processes of atomic surface diffusion can predict well the trends in microstructure/morphology evolution.
Chapter 6

Multilayer Deposition

6.1 Introduction

Metal multilayer structures have become an important topic because of the need in such areas as metal diffusion inhibitors in interconnects and the emergence of novel magnetic devices. For example, giant magnetoresistive sensors consisting of repeating [Ni$_{80}$Fe$_{20}$/Cu/Ni$_{80}$Fe$_{20}$] units have been developed for sensing magnetic fields and the nonvolatile storage of data [125 - 127]. For both applications a smooth NiFe/Cu interface free of interdiffusion is required. However, during growth at temperature where interdiffusion is unlikely, the roughness of a metal film can be significant and increases with film thickness. To date, only molecular dynamics simulations has been used to evaluate the surface morphology evolution [62]. The role of the substrate temperature and deposition rate are difficult to evaluate by this approach because of the short time step required. Here the extension of the kinetic Monte Carlo method is explored.

The key to applying the kMC technique to multilayer deposition is knowledge of the activation barriers. These depend both on the local atom configuration and composition. Therefore, unlike a pure metal simulation, the activation energy in a multi-component system must consider both the jumping atom’s coordination and its neighboring atomic species. This is likely to be particularly daunting for a full 3D kMC model. Here, the 2D kMC model used to simulate the deposition of nickel is extended to analyze Ni/Cu/Ni multilayer deposition. The interest is to identify the basic trends by such a simulation rather than attempt an exact simulation of the real system. The effect of deposition rate
and temperature upon the morphology of Ni/Cu/Ni multilayers grown from low energy atomic fluxes is explored and compared with the dependence of the surface morphology for pure nickel and copper films grown under identical conditions.

6.2 Methodology

Johnson has calculated the important activation barriers for a 2D Ni-Cu system using a molecular statics method and EAM potentials [81]. For an alloy model, an embedding function $F(r)$ and an atomic electron-density function $f(r)$ must be specified for each atomic species, and a two-body potential $\phi(r)$ specified for each possible combination of atomic species [170]. Since the electron density at any location is taken as a linear superposition of atomic electron densities, and since the embedding energy is assumed to be independent of the source of the electron density, these two functions can be taken directly from monatomic models. For a binary alloy with $a$- and $b$-type atoms, $\phi_{aa}$ and $\phi_{bb}$ are given by the monatomic models, and $\phi_{ab}$ and $\phi_{ba}$ are assumed to be equal. The alloy potential could be determined independent of the monatomic potentials if sufficient data were available, but the assumption is commonly made that it is a function of the monatomic potentials, like geometric and arithmetic averages [75].

It has been suggested that all models with the EAM format be transformed to a normalized form in which the slope of the embedding function is zero at the equilibrium electron density [77]. In this case, the two-body potential becomes the effective two-body potential that controls the energy change for any atomic configuration in which the electron density at the atom sites is not significantly altered. The effective two-body potentials are negative in some range of distances, and so a geometric average cannot be used.

According to Johnson [170], if the form

$$\phi_{ab} = \frac{1}{2} \left( \frac{f_b(r)}{f_a(r)} \phi_{aa}(r) + \frac{f_a(r)}{f_b(r)} \phi_{bb}(r) \right)$$  

(6-1)
is used for all alloy potentials, then alloy models are also invariant to transformations in
the monatomic models from which they are derived, and this invariance holds for any
number of different elements in an alloy.

To calculate the activation energies for the 2D Ni-Cu alloy model, three-dimen-
sional EAM models were obtained by Johnson for pure copper and nickel. These were fit-
ted to their respective equilibrium spacing, cohesive energy, vacancy formation energy,
bulk modulus and average shear modulus, and a two-body cross potential is defined. The
EAM parameters were then applied to a two-dimensional tight-packed plane of atoms.
Relaxation was permitted only in the plane, and a two-dimensional equilibrium distance
was obtained for the pure metals. The fitting procedure used for nickel and copper and the
relevant parameters are the same as those used earlier in chapter three with the two-body
cross-potential given by

\[
\phi_{cuni} = \frac{1}{2} \left( \frac{f_{ni}(r)}{f_{cu}(r)} \phi_{cu}(r) + \frac{f_{cu}(r)}{f_{ni}(r)} \phi_{ni}(r) \right)
\]

(6-2)

with subscripts \(cu\) and \(ni\) indicating copper and nickel, respectively. The resulting parame-
ters are summarized earlier in Table 3-1. Each pure-metal model was then applied to a
close-packed monolayer of atoms with full relaxation in the plane but no relaxation nor-
mal to the plane and a two-dimensional equilibrium spacing obtained. The relaxation of
copper was 4.4% and of nickel just 1.8%, yielding 2.448 Å and 2.446 Å for the lattice
parameters. Thus the two-dimensional equilibrium spacings were very similar.

The 2D potential was then used in a molecular statics method (as described in
chapter three) to determine the kinetic parameters for various configurations including
both copper and nickel species at each position. For a pure metal, 14 different configura-
tions could be summarized to represent the nearest neighboring model occurred in a 2D
assumptions. With just one more element, however, the configurations amount to be tens
of thousand of variations. It is unrealistic to obtain all such barrier energies using MS cal-
calculations. Therefore, an approximation is necessary to simplify the process while ensuring that the role of the second element is not lost.

Based on the observation that the activation energies are dominated by the nearest-neighbor configuration of the jumping atom, Johnson introduced a notation system to describe their relationship, Fig. 6.1. For example, the nearest neighboring atoms can be appropriately called saddle or bond (alternatively dog-leg) and the jumping atom itself called the jumper. The various bonds are further divided as broken bond dog-leg if the bond to be broken is not in line with the jumper, created bond dog-leg if the bond to be created is not in line with the jumper and broken bond inline if the breaking bond is in line with the jumper. Each site can be occupied by either nickel or copper atom, which would result in different activation energies. This type of differences are represented as the corrections given an identical environment as shown in Table 6-1. For example, for 2 - 2 jump path, Fig. 6.1(a), nickel jumper results in a positive correction of 0.06 eV and copper jumper a negative correction of 0.06 eV. The atom by which the jumper is about to jump over is called saddle. For a 2 - 2 jump, a nickel saddle has a positive correction of 0.02 eV and a copper saddle a negative correction of 0.02 eV. For atoms positioned as broken bond dog-leg, created bond dog-leg and broken bond inline positions, they all have different energy corrections depending on if they are nickel or copper. The Schwoebel jump needs special consideration, Fig. 6.1(c). In this process, two jumpers simultaneously jump to different places, thus giving two sets of saddle and bond atoms; in each set, different energies have been assigned. In determining all such energy corrections, Johnson conducted hundreds of molecular statics calculations. The activation barrier results are listed in Table 6.1.

The same kMC scheme used for the pure metal above was used for the binary alloy model. A programing modification was made to add a species index to each atom. A substrate consisting of three layers of nickel atoms was used for all the simulations. Copper
Fig. 6.1. A notation system created to facilitate the activation energy calculation of the two-component deposition. The jumping atom is called jumper and its nearest neighboring atoms are called saddle, dog-leg and/or bond depending on their relative position with respect to the jumper. Three most important jump paths in the 2D kMC simulation are illustrated: (a) adatom diffusion; (b) atom attachment/detachment at ledge; and (c) the Schwoebel jump. The labels show the position notation.
<table>
<thead>
<tr>
<th>No</th>
<th>Jumps (from - to)</th>
<th>Energy (basic value)</th>
<th>Corrections</th>
<th>Position identity</th>
<th>Nickel</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 - 2</td>
<td>E(2-2) = 0.34</td>
<td>Jumper</td>
<td>+ 0.06</td>
<td>- 0.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Saddle</td>
<td>- 0.02</td>
<td>+ 0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Broken bond (dog leg)</td>
<td>+ 0.04</td>
<td>- 0.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Created bond (dog leg)</td>
<td>+ 0.02</td>
<td>- 0.02</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2 - 3</td>
<td>E(2-3) = E(2-2) - 0.02</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 - 2</td>
<td>E(3-2) = E(2-2) + 0.37</td>
<td>Additional broken bond (in line)</td>
<td>+ 0.01</td>
<td>- 0.01</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3 - 3</td>
<td>E(3-3) = E(3-2) - 0.02</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2 - 4</td>
<td>E(2-4) = E(2-3) - 0.02</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 - 2</td>
<td>E(4-2) = E(3-2) + 0.37</td>
<td>Additional broken bond (dog leg)</td>
<td>+ 0.01</td>
<td>- 0.01</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3 - 4</td>
<td>E(3-4) = E(3-3)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 - 3</td>
<td>E(4-3) = E(3-3) + 0.37</td>
<td>Additional broken bond (dog leg)</td>
<td>+ 0.01</td>
<td>- 0.01</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2 - 5</td>
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<td>Jumper</td>
<td>- 0.015</td>
<td>+ 0.015</td>
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</tr>
<tr>
<td></td>
<td>5 - 2</td>
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<td>Jumper</td>
<td>+ 0.02</td>
<td>- 0.02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>4 - 4</td>
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<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>3 - 5</td>
<td>E(3-5) = E(2-4) + 0.01</td>
<td>Additional Saddle</td>
<td>- 0.01</td>
<td>+ 0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 - 3</td>
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<td></td>
<td></td>
<td></td>
</tr>
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<td>9</td>
<td>4 - 5</td>
<td>E(4-5) = E(3-5) + 0.14</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 - 4</td>
<td>E(5-4) = E(5-3) - 0.15</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>10</td>
<td>5 - 5</td>
<td>E(5-5) = E(5-4) - 0.18 (Surface)</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>5 - 5</td>
<td>E(5-5) = E(5-5)* + 0.31 (Bulk)</td>
<td>None</td>
<td></td>
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</table>

* Surface
and nickel atom fluxes were then sequentially introduced to deposit ten layers a time under normal incidence. The substrate temperature and deposition rate were kept constant for both metals during each simulation.

To explore the effect of process conditions upon surface roughness, seven substrate temperatures and equal number of deposition rates were used for the Ni/Cu/Ni multilayer depositions. Simulations with the same conditions were conducted for pure nickel and pure copper in order to compare the multilayer behavior with that of the pure metals. Ten runs were conducted for each process condition to obtain a necessary statistical estimate.
Unless otherwise indicated, the surface roughness is defined in the same way as in chapter five as the standard deviation of the surface height.

### 6.3 Simulation results

Fig. 6.2 shows the effect of deposition rate on the multilayer structure at two different substrate temperatures. At 250 K, the copper layers generally have a smooth surface and big columns. On the contrary, the nickel layers tend to evolve in island growth mode with a rugged surface and small columns. At a deposition rate of 6.0 µm/min, a porous columnar structure developed in the nickel layer and internal voids formed upon the ensuing copper layer. With decreasing the deposition rate from 6.0 µm/min to 0.006 µm/min, the nickel porosity disappeared, the number of columns on the nickel layer decreased and the average column width increased. The copper layers have also improved surface morphology. It is worthy of notice that the second copper layer has smoothed the intermediate nickel layer significantly and did not duplicate the rugged nickel layer’s morphology.

At 350 K, the overall surface morphology evolved very differently with decreasing deposition rate. The surface morphology did not appear much different at \( R = 6.0 \) and 0.6 µm/min from those at 250 K, but a surface instability in the first copper layer can be seen starting at \( R = 0.06 \) µm/min. A severe instability at \( R = 0.006 \) µm/min (corresponding to about 1 ML/s) changed the surface morphology dramatically. Both the usual smooth copper and rugged nickel layers were replaced by domed mounds. A copper layer breakdown (or nickel layer cross-talk) developed. This would be highly undesirable in the event that occurred in practice.

Fig. 6.3 shows the effect of substrate temperature on the multilayer surface morphology under two deposition rates. Configurations at the left side were done with \( R = 6.0 \) µm/min. At 200 K, columnar structure with domed top developed at the first copper layer. A completely porous columnar structure developed in the ensuing nickel layer. And the second copper layer extends the porous nickel layer with increased column size. With
Fig. 6.2. Surface morphology evolution with decreasing the deposition rate at substrate temperature of 250 K and 350 K respectively. The incidence angles ($\theta$) were the same at 0°. The substrate has 100 atoms in width and three nickel layers in thickness direction. In each case, simulation started with ten copper layers, followed by ten nickel layers and another ten copper layers.
Fig. 6.3. Surface morphology evolution with increasing the substrate temperature at deposition rate of 6.0 µm/min and 1.0 µm/min respectively. The incidence angles (θ) were the same at 0°. The substrate has 100 atoms in width and three nickel layers in thickness direction. In each case, simulation started with ten copper layers, followed by ten nickel layers and another ten copper layers.
increased mobility at 250 K, the first copper layer now had the familiar smooth surface feature. The nickel layer at the middle condensed considerably and had only a few internal voids left. The second copper layer at the top significantly smoothed the rugged nickel surface. With further increasing the temperature, voids no longer appeared, the copper layers become smoother and the nickel layer’s roughness magnitude seems decreased. Similar trends can be seen on the right at $R = 1.0 \, \mu m/min$ except for the configuration at 400 K where a surface instability similar to the earlier one again occurred.

Fig. 6.4 quantitatively plots the dependence of simulated surface roughness upon the deposition rate under different substrate temperatures. At 200 K, the roughness increased with increasing deposition rate with moderate slope. At 250 K, the roughness increased with increasing deposition rate but with smaller slope, reflecting the effect of more atomic mobility. At 300 K, the trend reversed and the roughness decreased slightly.

![Fig. 6.4. Surface roughness vs. deposition rate at different substrate temperatures under normal incidence. The roughness was measured at the second copper layer above the substrate.](image-url)
with increasing deposition rate. This abnormal behavior was strongly evident at 350 K where a very large surface roughness developed at low deposition rate. Obviously, this abnormal behavior is caused by the occurrence of the surface instability shown in Fig. 6.2.

Fig. 6.5 plots the surface roughness vs. the substrate temperature under various deposition rates. At high rates (6.0 and 0.6 µm/min), the roughness decreases monotonically with increasing the temperature. This is expected because of the increased thermal diffusion. At low rates of 0.06 and 0.006 µm/min, the roughness initially decreased moderately with increasing the temperature and it then abnormally increased rapidly with increasing the temperature. As above, this is caused by the surface instability, Fig. 6.3.

The data in Figs. 6.4 and 6.5 can be combined to create a 3D process map, Fig. 6.6. A valley-like zone can be identified in the middle of the map where the surface roughness has low values. Fig. 6.7 is a two-dimensional version showing the same trend and having

![Figure 6.5](image-url)
Fig. 6.6. Surface roughness vs. substrate temperature and deposition rate. A low roughness region in the middle can be identified for the Ni/Cu/Ni multilayer growth. The data corresponds to the third interface above the substrate.

Fig. 6.7. Surface roughness vs. substrate temperature and deposition rate in two-dimensional view of Fig. 6.6. The data corresponds to the third interface above the substrate.
clearer view of parameter magnitudes. In order to associate this phenomenon to pure metal behavior, simulations under identical conditions have been conducted for both nickel and copper metal and the two-dimensional roughness contour maps are shown in Figs. 6.8(a) and (b) respectively. Clearly, the plateau on the pure copper plot of Fig. 6.8(a) corresponds to the right lower-corner plateau on the multilayer plot in Fig. 6.7 and the plateau on the pure nickel plot corresponds to the left upper-corner plateau in Fig. 6.7. In copper, the high substrate temperature combined with low deposition rate result in a surface instability, while in nickel, the low substrate temperature combined with high deposition rate result in porous columnar structure. Away from the two corners with extreme conditions toward the diagonal line lies the low roughness region, Fig. 6.7.

Fig. 6.9 shows deposition on nickel substrate with ten copper and nine nickel layers alternatively using conditions selected for the low roughness region. The surface roughness from each copper and nickel layer is plotted in both Figs. 6.10 (a) and (b). (The roughness ratio concept [29, 128] used in Fig. 6.10(b) is explained in Appendix C). Evidently, the surface roughness scales almost linearly with the thin film thickness (layer). Whenever nickel is deposited on copper, the ensuing roughness measurements always go up, Figs. 6.10 (a) and (b). But when copper is deposited on a nickel layer, the ensuing roughness measurements are usually reduced; the only exception is that deviation roughness begins to increase from the fifth copper layer. Therefore, copper serves to smooth the rugged nickel surface. This can be seen from the configuration in Fig. 6.9 that copper layers always tend to form columns with flat tops. This also demonstrates that the ratio roughness measurement has better capability to reveal the difference between a surface with flat facets and one with only rugged columns. In other words, the ratio measurement better reflects roughness on the micro-scale while the deviation measurement better exposes roughness at the macro-scale. This difference is best demonstrated in Appendix C. Therefore, microscopically copper always tends to smooth a nickel surface while mac-
roscopically copper tends to smooth a nickel surface initially but tends to follow the nickel pattern eventually.

Fig. 6.8. The effect of process conditions on surface roughness for pure copper and nickel films under identical thickness and deposition conditions to those of the Ni/Cu/Ni multilayers. (a) Cu films; (b) Ni films.
Fig. 6.9. The surface roughness evolution of Ni/Cu/Ni multilayer thin films at a fixed substrate temperature of 325 K and a deposition rate of 6.0 µm/min. The incidence flux was normal to the substrate. The substrate has 100 atoms in width and three nickel layers in thickness direction.
Fig. 6.10. The surface roughness from each layer vs. the layer position. The copper and nickel layers were alternated with copper taking the first and the rest odd layers and nickel the second and the rest even layers. The solid lines indicate that new nickel always increases the surface roughness while the dash lines indicate that new copper mostly tends to smooth the rough surface caused by nickel. Substrate temperature was 325 K, deposition rate 6.0 µm/min and incidence normal. (a) roughness measured in standard deviation; (b) roughness in area ratio.
6.4 Discussion

The observation of surface instability (roughness transition or agglomeration) of copper at high temperature is a common phenomenon seen in thin film growth when the substrate temperature is higher than a threshold value [33, 129 - 132]. It is believed to be caused by the formation of facets resulting from thermally activated surface diffusion [123, 133]. An explanation based upon an atomic mechanism, however, has been elusive. Here, we provide an analysis based on a detailed atomistic configuration and conclude that such surface instability has its roots in the activation of certain atomic jump paths.

Fig. 6.11 represents a typical configuration seen on a thin film surface. Fig. 6.11(a) shows that atom A at the edge has two possible jumps represented by path 1 and 2. A close examination indicates that path 1 and 2 are microscopically equivalent in terms of the initial and ending site of the path. Examination of Table 3-2 shows that they are reverse Schwoebel jumps which occur by a “crumbling” mechanism. As both jumps have identical activation barriers, either jump can occur with equal probability at a given time. But the choice of jump direction has a significant consequence upon the resulting surface roughness. The process represented by path 1 leads to a smoother surface, Fig. 6.11(b), while the process represented by path 2 leads to a rougher surface, Fig. 6.11(c). Located at the edge, these two paths along with the Schwoebel jump either increase or decrease an edge height (at the same time shrink or extend an edge) and thus are most important jumps in determining surface roughness. The more frequent ledge attachment/detachment and adatom diffusion on flat surface (represented by jumps 2 and 1 in Table 3-2) serve only to create the configurations like that of Fig. 6.11(a) and have no direct effect on surface roughness.

When ledge atom detachment occurs, the next immediate diffusion step is most likely an attachment because of its low activation energy (see Table 3-2). Therefore during a simulation we monitor the jump frequencies of the jump path 1 and 2 along with the
Schwoebel jump, we can search for correlations between the instability and these jumps. Suppose that the pure Schwoebel jump is called type I jump; the equivalent paths 1 and 2 (in view of barrier energy) are collectively called type II jump. We have found that when type II jumps outnumbered type I jump, an instability started to appear. As long as the number of type II jumps remains less than that of the type I jumps or about the same, the instability never occurred. In reality, at low temperature, such as 200 K in Fig. 6.3, there are no type II jumps at all. Obviously, type II jumps have high activation energy and thus are intrinsically associated with relatively high temperature and increase rapidly with increasing the temperature. When instability has already occurred beyond a certain temperature, the film surface is then dominated by sloped surfaces where type II jump paths become abundant and flat surfaces shrink, as illustrated by the case of 400 K in Fig. 6.3.

Fig. 6.11. Atom A at the edge has two jump paths (a). The upward jump roughens the surface while the downward jump smooths the surface. The way that atoms A, B and C arrange after both jumps results from a concerted Schwoebel-type crumbling process as described in chapter five and the crumbling is energetically favored over a jump-over process.

An important message conveyed in the simulations is that atom mobility discrepancy between the two metals has a deciding effect on multilayer deposition. The mobility discrepancy comes from the large activation energy differences as shown in Table 3-2. The selection of a substrate temperature/deposition rate that produces a smooth copper surface results in a rugged nickel surface while the use of a temperature that smooths the nickel can lead to an unstable copper layer. In order to obtain a smooth interface, the consequences of such differences in activation barrier need to be minimized in real deposition
through process parameter manipulations. In addition to select an optimized combination of the substrate temperature and the deposition rate from the low roughness region, Fig. 6.6 or 6.7, other factors may be considered such as selectively varying adatom energy or using ion assistance (to enhance surface diffusion) to compensate for the diffusion difference from different metals. For example, nickel clearly tends to develop a rough surface featured by small islands. This suggests that a high nickel adatom energy or ion beam assistance might be used to smooth the surface. When depositing the next copper layer, such special arrangement can be switched off to avoid induce detrimental effects such as intermixing [62].

6.5 Concluding remarks

Kinetic Monte Carlo method has been used to explore Ni/Cu/Ni multilayer growth under low atom energy conditions where thermal diffusion is the only mechanism of atomic assembly. An embedded atom method potential with a two-body cross-potential enabled calculation of the activation energies. It takes into account both the atomic configuration of neighboring atoms and their species. Using this extended set of activation barriers simulations reveal that the surface roughness increases almost linearly with increasing growth thickness during the growth of Ni/Cu/Ni multilayers deposition, and is more pronounced when depositing a nickel layer than when depositing a copper layer. Depositing copper helps to smooth nickel layer. Simulation has shown that there is an optimal growth window for Ni/Cu/Ni multilayer deposition. The window lies in a region between two extreme corners on a substrate temperature vs. deposition rate process map. While one corner with high deposition rate and low temperature is characteristic of a porous columnar (nickel) structure, the other corner with low deposition rate and high substrate temperature is characteristic of a (copper) surface instability. Finally, an analysis of the atomic jumps reveals the cause of the surface instability to be the activation and rapid increase of reverse Schwoebel jumps above a temperature threshold.
Chapter 7

Energy-dependent Mechanisms

7.1 Introduction

To this point, the kinetic Monte Carlo approach has been used only to address low impact energy (i.e. thermal) deposition in which the incident kinetic energy of the adatom during impact can be ignored. In reality, many vapor deposition processes exploit high incident energy fluxes. For example, in ion beam or low pressure sputter deposition, incident atoms have an average incident kinetic energies of 1 ~ 5 eV while some possess an energies of 20 eV or more [12, 26, 134]. Even in evaporation process, kinetic energy has been incorporated as a process control option by using high speed gas jet [105], pulsed high current vacuum arc [135] or high density plasma [20]. As a result, any effort to realistically simulate these energetic PVD growth processes by a Monte Carlo approach should consider the effect of the adatoms kinetic energy. The incorporation of an adatom in the growth surface also releases the potential energy of the interacting species. This is several electron volts per atom and can induce atomic jumping before it is dissipated in the crystal [60, 61]. This also should be included in kinetic Monte Carlo simulation.

The impingement of energetic atoms with a growth surface can induce numerous physical and chemical phenomena [60, 61, 136]. Depending upon the energy and the surface condition, an incident atom can be trapped on the surface, implanted beneath it, reflected, and/or undergo long range biased diffusion in the impact direction on the surface. These, together with the release of the latent heat of condensation, can also cause localized heating which may induce atomic rearrangements that would normally not have
occurred at the average temperature of the film (we call this athermal diffusion). For high energy impacts, they may even cause resputtering of the already deposited film. Chemical reactions can occur with other chemisorbed species or a gas-phase atom or a physisorbed molecule. Electronic scale processes resulting from inelastic scattering can also occur but are less likely to influence the final structure of the film [136].

While various hyperthermal atom impact phenomena have been experimentally identified as a significant cause of thin film microstructure [45, 134], it has been difficult to quantify their individual contribution. It is even more difficult to quantify how each depends upon the incident energy and angle, the deposition rate and the films temperature. Considerable interest has therefore emerged in simulation approaches which seek to model the various effects and assess their likely relevance.

One approach to analyze the effects utilizes molecular dynamics (MD) techniques to simulate energetic impact processes. As described in chapter three, the MD method solves for the trajectories of each atom in a crystal by integrating Newton’s equations of motion using an interatomic force law [58, 59, 63, 137 - 139]. Since the MD method evolves atomic configurations by explicitly analyzing interatomic forces, it rigorously incorporates the atomic assembly mechanisms initiated by the high kinetic energy atom impacts, many of which are completed within five picoseconds.

Since the MD method is well suited to the analyses of single atom interaction with a film and the kMC is able to accommodate a wide spectrum of slower thermal relaxation processes, it is natural to ask if the two can be combined to simulate a complete process of energetic vapor deposition. Here it is shown that the answer is certainly yes, although the effectiveness depends upon how the two methods are joined together. It has been shown that any direct combination of MD and kMC is computationally impractical because of massive MD calculations [140]. Even for a relatively small surface area, thousands of MD simulations are needed per monolayer. In order for the method to be feasible, it is essential
that the island density not be too low. Big islands require a larger surface area and hence a larger number of MD simulations per monolayer, which requires simulations that run weeks to months on today’s high performance workstations [140]. For practically significant problems such as the trench filling process, direct combination is computationally prohibitive. As a result, alternative approximate approaches are needed.

The recent observation that the atomic assembly primary events associated with the impacting atoms kinetic and potential energy occur within 1 - 2 ps is exploited in a new method [60, 61]. This rapid process contrasts with the specific thermally activated atomic jumps which have residence times ranging from microsecond to hours [141]. Therefore the kMC is used as the foundation for a description of the basic growth evolution under the ever-present thermal diffusion. Superimposed upon this are the effects of fast interactions using empirical equations derived through MD calculations. The empirical equations covering all of the major interaction events are formulated from data obtained on sufficient sample surfaces. To use such equations, a computer program first sizes up the interaction locality in the system and next plugs process parameters and local information in the equations and finally turns them into corresponding actions in the simulation. To ensure an appropriate treatment, either experimental observations or other calculations such as MD are used to calibrate relevant model parameters. Compared with the direct accommodation [140], this approach is more realistic and easier to execute.

In the following sections, MD simulations of key processes are reviewed. This is followed by the incorporation of these energy dependent phenomena into the kMC scheme. In chapter eight, application of the treatment has been used on hyperthermal deposition on flat substrate. Application to deposition on a featured substrate will be described in chapter nine.
7.2 MD calculation of energetic impact effects

Zhou et al have recently conducted analyses of the interactions of energetic adatom with crystal surfaces [60, 61]. The EAM was used to calculate the interatomic forces in copper and nickel. Compared with the universal pair potential [142] that is fitted to the experimental data for high energy bombardment, the free parameters of the EAM potential were calibrated with measured material properties. Because the sublimation energy is exactly reproduced [75], EAM correctly accounts for the energy transfer during vapor atom collision on a surface. On the other hand, high energy impacts cause atoms to closely approach each other and short range interaction dominates. If the impact energy is not too high (< 100 eV), EAM potential can reasonably capture the impact phenomena and accurately reveal the subsequent atomic relaxation processes as its environment-dependent potential form realistically describe the energetics of local nonequilibrium atomic configurations. The EAM functions of copper and nickel determined by Foiles, Baskes, and Daw [75] was used by Zhou et al for the present calculations.

In collaboration with Zhou these potentials have been used to further study atomic impacts on the low index \{100\}, \{110\} and \{111\} surfaces of a copper and nickel crystals. Three computational substrate crystals corresponding to the three surfaces were created by assigning copper atoms to their bulk equilibrium f.c.c. lattice sites as shown in Fig. 7.1.

The dimensions of the crystals are notated as $n_x(ijk)_x \times n_y(ijk)_y \times n_z(ijk)_z$, where $n_{a(ijk)}$ refers to the number of the corresponding (ijk) planes in the a direction. $10(200) \times 10(020) \times 10(002)$, $10(002) \times 15(220) \times 14(220)$ and $24(224) \times 9(111) \times 14(220)$ size crystals were used. Periodic boundary conditions were used for both lateral ($x$ and $z$) directions, and a free surface boundary condition was used for the top ($y$) surface. The periodic boundary condition was implemented in a way that allowed the periodic lengths to change in order to fully relax the computational crystal and release internal stresses [85]. To avoid a crystal drift during impact, atoms within a $d_0$ thick region at the bottom of the crystal
Fig. 7.1. Schematic crystal substrate geometry for molecular dynamics simulation. The incident atom is fixed on $x$-$y$ plane with $\theta$ as incident angle and two angles of $\theta_1$ and $\theta_2$ are needed to define either reflected or resputtered atoms’ direction. The bottom layers with $d_0$ thickness are fixed to avoid crystal drift and the layers with $d_T$ thickness are used for temperature control.
Energy-dependent Mechanisms

were fixed, Fig. 7.1. The \( d_0 \) thick region was chosen to include either two (200) or (111) planes, or three (220) planes. Under this fixed boundary, atoms above the region were beyond the cut-off interaction range with atoms below the region. The crystals could then be viewed as extending to infinity in the thickness direction. A temperature control algorithm [59] was used to keep a two atomic plane \((d_T)\) thick region at the bottom of the crystal at a substrate temperature of 300 K. No constraint was applied to the region above, allowing a natural evolution of the surface during impact. The crystal temperature was initially created by assigning to each of the atoms above \( d_0 \) a velocity based on a Boltzmann distribution [59]. This velocity distribution was equilibrated by running the MD calculation for 50 fs with the temperature controller applied to the entire crystal above \( d_0 \), and for another 50 fs with the temperature controller applied only to the \( d_T \) region.

Atom impacts were initiated by introducing one copper (or nickel) atom at a random location above the interatomic potential cut-off distance (~ 5 Å) of the crystal surface. The atom was assigned an initial kinetic energy, and an initial direction of motion. To uniquely define a direction in a 3D space by a single incident angle (measured from the surface normal), the initial moving direction of the adatom was constrained to the \( x-y \) plane. The positions and velocities of all the atoms were then calculated for the entire impact process (usually this lasted about 2 - 5 ps of real time) and the positions and kinetic energies of atoms were recorded as a function of time. Because of periodic oscillation of the kinetic energy (due to lattice vibrations), the recorded kinetic energy was time averaged for 0.1 ps. To reduce statistical variations, all the results presented are the average of five separate MD simulations using a different random number seed for each.

Fig. 7.2 schematically shows four types of impact phenomena that were found to be important for the atomic assembly of a metal film: a) atomic reflection, b) resputtering, c) biased diffusion and d) thermal transient induced local atomic rearrangements. The MD simulations identified both the detailed atomic scale mechanism responsible for each
Fig. 7-2. Schematic drawings of four interaction events when an energetic atom impinges upon substrate. The black disks stand for incident atoms at transitional positions. The dashed lines point to and connect with all involved atoms and their eventual locations.
Energy-dependent Mechanisms

rearrangement process and have established their dependence upon the impact atoms incident energy and angle [60, 61].

7.2.1 Reflection

Under oblique incidence conditions energetic adatoms are readily reflected. When an energetic atom is reflected at a film surface, its normal velocity component must reverse direction rapidly during impact. This requires the activation of short range repulsive interactions between the incoming atom and those already deposited. The reflecting atom must also retain sufficient kinetic energy to enable its escape from the long-range attractive field of the surface. Reflection is therefore most probable when the atom’s incident energy exceeds a threshold (related to the latent heat of evaporation and the efficiency of the hot atoms energy transfer to the lattice) and when the atom has a small normal velocity component (i.e. when making an oblique impact with the surface). Fig. 7.3 shows the MD calculated reflection probability versus the incidence angle for copper metal (that for nickel was similarly conducted and is attached in Appendix D along other atom-substrate interaction events) [60, 61]. It is noteworthy that crystal planes have no clear effect on reflection probability. As a result, only data for (111) plane would be used for the 2D kMC simulation. In case that crystal plane dependence is observed, data for (111) plane would still be used for consistence.

Fig. 7.3 shows that the threshold angle for reflection is about 25°, and the incident angle for maximum reflection probability is somewhere between 65° and 80°. While the reflection probability increases with increasing incident angle up to 65°, it decreases rapidly as the incident angle is increased beyond 80°. This occurs because as an incident “hot” atom moves nearly parallel to the surface, it more effectively transfers its kinetic energy to the surface atoms. An expression for the reflection probability, \( Y_{rf} \), as a function of incident angle, \( \theta \), at a fixed energy of 50 eV \( (Y_{rf}(\theta)) \) has been fitted to the MD simulations of Fig. 7.3 and is given as Eqn. 7-1 in Table 7-1. In the equation, \( \theta_c \) is a threshold
angle for the onset of reflection (at 50 eV) and $\theta_m$ is the incident angle that corresponds to the maximum reflection probability (at 50 eV).

Fig. 7.4 shows the MD calculated reflection probability as a function of incident energy for an oblique angle of deposition (80°) [60, 61].

The reflection probability as a function of incident energy ($Y_{rf}(E_i)$) for an incident angle of 80° is given by Eqn. 7-2. $E_{ic}$ is a critical energy for reflection (give value for 80°). The reflection probabilities combined dependence upon both the incidence energy and incidence angle ($Y_{rf}(E_i, \theta)$) is given by Eqn. 7-3.

Since significant energy transfer to the substrate often occurs, the reflection angle is usually different to the incident angle, and the reflected energy less than the incident
energy. The angular and energy distributions for reflected atoms were also calculated from MD simulations [60, 61] and are summarized by Eqns. 7-4 and 7-6. The azimuthal angular distribution in Eqn. 7-5 would only be useful in a 3D simulation.

7.2.2 Resputtering

Resputtering (or atomic etching) occurs when an impacting atom imparts sufficient energy to surface or near surface atoms so that they can overcome their binding forces with the substrate and be ejected into the vapor. The probability that this energy is directly or indirectly (through multi-collisions sequences) transferred to an atom increases with the incident atoms kinetic energy. Only a single, or in some cases several atoms can be ejected. In general, the sputter yield (number of resputtered/incident atoms) increases with incident energy. The resputtering yield is also maximized when the incidence angle

Fig. 7.4. Reflection probability vs. incidence energy for copper under fixed incident angle. The symbols are used to show the effect of crystal planes on the reflection probability.
Table 7-1 Fitted Equations to MD copper reflection calculations

<table>
<thead>
<tr>
<th>Eqn. No.</th>
<th>Equations</th>
<th>Parameters</th>
</tr>
</thead>
</table>
| (7-1)   | Reflection probability as a function of $\theta$ at $E_i = 50.0$ eV:  
$$ Y_{rf}(\theta) = \min \left\{ 1, p + p \cdot \sin \left[ -90.0 + 180.0 \frac{\theta - \theta_c}{\theta_m - \theta_c} \right] \right\} $$  
$\theta \geq \theta_c$ | $\theta_c = 22.0^\circ$, $\theta_m = 72.0^\circ$, $p = 0.59$ and $\lambda = 1.70$ |
| (7-2)   | Reflection probability as a function of $E_i$ at $\theta = 80^\circ$:  
$$ Y_{rf}(E_i) = 1.0 - \exp \left[ \left( \frac{E_i - E_{ic}}{p} \right)^\lambda \right] \quad E_i \geq E_{ic} $$ | $E_{ic} = 10.0$ eV, $p = 25.4$, and $\lambda = 2.42$ |
| (7-3)   | Reflection probability as a function of incident angle and incident energy:  
$$ Y_{rf}(E_i, \theta) = Y_{rf}(\theta) \frac{Y_{rf}(E_i)}{Y_{rf}(E_i = 50.0\text{eV})} $$ | $p_n = \text{normalization factor},$  
(integral of $\rho$ equals 1)  
and $\beta = 1.62$ |
| (7-4)   | $\theta_1$ distribution of reflected atoms as a function of incident angle and energy:  
$$ \rho(\theta_1) = p_n (\theta_1 - \theta_{1L})^\alpha (90.0 - \theta_1)^\beta $$  
where  
$$ \alpha = \frac{\beta(\theta_{1p} - \theta_{1L})}{90.0 - \theta_{1p}} $$  
$$ \theta_{1L} = \max \left\{ 0.0, \theta + 5.0 - \frac{6.0 \times 10^4}{E_i^2} \right\} $$  
$$ \theta_{1p} = \min \left\{ 90.0, \theta + \frac{3.2(E_i - 40.0 + |E_i - 40.0|)}{E_i - 40.0 + |E_i - 40.0| + 2.0} \right\} $$ | $c = -1.9 \times 10^{-10}$ |
| (7-5)   | $\theta_2$ distribution of reflected atoms as a function of incident angle:  
$$ \rho(\theta_2) = p_n \exp \left( -c \cdot \theta_2^2 \right) $$ | $c = 1.10$, $E_0 = -13.06$ ,  
$\theta_0 = 47.0$, $\beta = 1.65$  
for the \{100\} and \{111\}  
surfaces; and $c = 1.04$,  
$E_0 = -12.76$, $\theta_0 = 47.5$,  
$\beta = 1.5$ for the \{110\} surface |
| (7-6)   | Energy distribution of reflected atoms as a function of incident angle and energy:  
$$ \rho(E) = p_n E^\alpha (E_i - E)^\beta $$  
where  
$$ \alpha = \frac{\beta E_p}{E_i - E_p} $$  
$$ E_p = \max \left\{ 5, (c \cdot E_i + E_0) \sin \left[ \frac{90.0(\theta - \theta_0)}{90.0 - \theta_0} \right] \right\} $$ | $c = 1.10$, $E_0 = -13.06$ ,  
$\theta_0 = 47.0$, $\beta = 1.65$  
for the \{100\} and \{111\}  
surfaces; and $c = 1.04$,  
$E_0 = -12.76$, $\theta_0 = 47.5$,  
$\beta = 1.5$ for the \{110\} surface |
of the impacting atom or ion transfers the maximum fraction of its energy to the lattice. This lies in the range of incident angle of 30° ~ 60°. Resputtering tends to be weaker for near normal (< 20°) incident angles because the transferred momentum is mainly directed into the film. This promotes collision cascades rather than sputtering. At very oblique incidence angles resputtering is low because the atom tends to skip over the surface (see biased diffusion later). Detailed molecular dynamics simulations have analyzed resputtering of nickel (and copper) deposits by nickel (and copper) adatoms [60, 61]. Figs. 7.5 and 7.6 shows that resputtering yield vs. incidence angle and incidence energy for copper.

![Resputtering Yield vs. Incidence Angle for Copper](image)

**Fig. 7.5.** Resputtering yield vs. incidence angle for copper under fixed incident kinetic energy. The symbols are used to show the effect of crystal planes on the resputtering yield.
In Table 7-2, the resputtering yield as a function of incident angle \( Y_{rs}(\theta) \) at an incident energy of 50 eV is given as Eqn.7-7, where \( \theta_m \) represents the incident angle for maximum resputtering yield. The yield as a function of incident energy \( Y_{rs}(E_i) \) at an incident angle of 40° is given by Eqn.7-8. The functional dependence of resputtering yield upon both incident angle and incident energy \( Y_{rs}(E_i, \theta) \) is then approximated by Eqn.7-9. Similar to high energy inert ion sputtering phenomena, the angular and energy distributions of the resputtered atoms are broadly distributed and are given as Eqns. 7-10 and 7-12. Eqn. 7-11 is the azimuthal distribution.
Table 7-2 Fitted Equations to MD copper respattering calculations

<table>
<thead>
<tr>
<th>Eqn. No.</th>
<th>Equations</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7-7)</td>
<td>$Y_{rs}(\theta) = p + p \cdot \sin\left[\theta_0 + (90.0 - \theta_0)\left(\frac{\theta}{\theta_m}\right)^{\lambda}\right]$, $\theta \leq \theta_m\left(\frac{270.0 - \theta_0}{90.0 - \theta_0}\right)^{\frac{1}{\lambda}}$</td>
<td>$\theta_m = 40.0^\circ$, $\theta_0 = -57.5^\circ$, $p = 0.31$, and $\lambda = 1.61$ for the {100} and {110} surfaces; and $\theta_m = 35.0^\circ$, $\theta_0 = -54.1^\circ$, $p = 0.17$, and $\lambda = 1.18$ for the {111} surface</td>
</tr>
<tr>
<td>(7-8)</td>
<td>$Y_{rs}(E_i) = p \cdot \exp\left[-\left(\frac{E_f}{E_i}\right)^{\lambda}\right]$</td>
<td>$p = 1.02$, $E_f = 36.0$ and $\lambda = 2.08$ for the {100} and {110} surfaces; and $p = 0.58$, $E_f = 39.86$ and $\lambda = 2.35$ for the {111} surface</td>
</tr>
<tr>
<td>(7-9)</td>
<td>$Y_{rs}(E_i, \theta) = Y_{rs}(\theta)\frac{Y_{rs}(E_i)}{Y_{rs}(E_i = 50\text{eV})}$</td>
<td></td>
</tr>
<tr>
<td>(7-10)</td>
<td>$\rho(\theta_1) = c \cdot \exp\left[-\lambda(\theta_1 - 45.0)^2\right]$</td>
<td>$c = 3.0 \times 10^{-2}$ and $\lambda = 3.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>(7-11)</td>
<td>$\rho(\theta_2) = \rho_0 + c \cdot \exp\left[-\lambda \cdot \theta_2^2\right]$</td>
<td>$\rho_0 = 7.0 \times 10^{-4}$, $c = 4.3 \times 10^{-3}$ and $\lambda = 1.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>(7-12)</td>
<td>$\rho(E) = p_n E^\alpha \exp\left(-\frac{\alpha}{E_m}\right)$, where $\alpha = \alpha_0 + c \cdot \exp(-\lambda E_i)$</td>
<td>$E_m = 4.92$ eV, $\alpha_0 = 1.68$, $c = 207.7$, $\lambda = 1.236 \times 10^{-1}$ for the {100} surface; $E_m = 6.88$ eV, $\alpha_0 = 2.05$, $c = 68.5$, $\lambda = 9.03 \times 10^{-2}$ for the {110} surface; and $E_m = 4.28$ eV, $\alpha_0 = 1.41$, $c = 8.83$, $\lambda = 4.06 \times 10^{-2}$ for the {111} surface</td>
</tr>
</tbody>
</table>
### 7.2.3 Biased diffusion

When adatoms make oblique impacts with atomically flat surfaces they are sometimes trapped by the attractive forces near the surfaces but cannot transfer their kinetic energy to the lattice fast enough to become attached to the surface. Instead, the component of momentum in the plane of the surface causes the atoms to skip across the surface in the impact direction for a significant distance from the point of first impingement before enough energy is transferred for the atom become arrested. The distance and duration of this kinetic energy induced skipping (so called biased diffusion) depends on the rate at which energy is transferred to the surface which in turn is governed by the angle of impact, the binding energy of the atom with the surface and the atom’s kinetic energy. Again detailed molecular dynamics simulation of biased diffusion indicate that the adatom is arrested within a few picoseconds of impact [60, 61]. Fig. 7.7 shows the dependence of biased diffusion distance on incidence angle under different incidence energies.

These simulations have allowed the biased diffusion distance to be parameterized as a function of the impact angle and energy \(d(\theta, E)\). An expression for this is listed as Eqn.7-13 in Table 7-3. Adatom biased diffusion distances are often many times those that would occur if normal thermal activation were the only mechanism of transport. It is thought to be responsible for significant step flow growth during the deposition of metal films at cryogenic temperature (77 K) where thermally driven diffusion is normally negligible [63, 138].

#### Table 7-3 Expressions for Copper Adatom Biased Diffusion \(d_s\)

<table>
<thead>
<tr>
<th>Eqn No.</th>
<th>Equations</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7-13)</td>
<td>(d_s(\theta, E_i) = zE_i^{\lambda \theta^V} \left[1 - \frac{1}{2}(\frac{\theta}{\theta_m})^{\nu V}\right])</td>
<td>Parameters (z = 1.03 \times 10^{10}, 4.03 \times 10^{-12}, 4.11 \times 10^{-7}, \lambda = 1.2, 1.37, 1.09,) and (\nu = 5.54, 6.08, 3.77) for the {100}, {110} and {111} surfaces respectively, (\theta_m = 81.0-30.0\exp(-0.18E_i))</td>
</tr>
</tbody>
</table>
Fig. 7.7. Biased diffusion distance vs. incidence angle for copper under (a) $E = 2$ eV; (b) 10 eV; and (c) 20 eV. The symbols are used to show the effect of crystal plane on biased diffusion distance. When energy is low, (a), slow incident atom is bent toward substrate by the attractive force from the substrate and resulted in a negative value.
7.2.4 Thermal transient induced diffusion

The impact of an energetic (or even a thermalized) atom with a surface results in a temporary increase in local surface temperature. It results from the combined contributions of the latent heat of condensation release and dissipation of the incident kinetic energy which are both partitioned amongst the vibrational modes of near surface atoms near the impact site [60, 61]. To quantify the phenomenon, a position \( s \) and a time \( t \) dependent equivalent surface temperature \( T(s,t) \) can be defined in terms of the average vibrational energy of the surface atoms, \( \bar{E}(t, s) \), 

\[
T(t, s) = \frac{2 \bar{E}(t, s)}{3k},
\]

where \( k \) is Boltzmann’s constant. This transient thermal spike is able to induce thermally activated atomic jumps near the impact site. Incorporation of the effect is of particular importance for low temperature deposition where this diffusion is often much more extensive than that associated with the thermal diffusion activation from the background temperature contribution. Molecular dynamics has been used to compute the thermal spike as a function of incident energy, \( E_i \) (Eqn.7-15 in Table 7-4; Eqn. 7-14 separates out the latent heat contribution) [60, 61]. Fig. 7.8 shows that dependence of the acquired energy in the neighborhood of the impact point upon elapsed time.

Fig. 7.8 indicates that this impact acquired energy perish near the impact site for only a few picoseconds at best. The significant (compared with that of the equilibrium Boltzmann distributed energy set by the background temperature) vibrational energy imparted to the atoms at the impact also therefore only exists for a few picoseconds. However, the energies are high compared with those required for atomic jumping and MD simulations of energetic deposition have shown that extensive atomic reconstruction can occur [60, 61].
Table 7-4 Expressions for Copper Local Effective Temperature ($T$)

<table>
<thead>
<tr>
<th>Eqn No.</th>
<th>Equations</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7-14)</td>
<td>$T(t, S) = T_{sub} + 29.76(t + 0.05) - \frac{3}{2} S^2 e^{-\frac{0.009 S^2}{t + 0.05}}$</td>
<td>$t =$ time, $S =$ distance from adatom, and $T_{sub} =$ substrate temperature</td>
</tr>
<tr>
<td>(7-15)</td>
<td>$T(t, S) = T_{sub} + 51.0 + 3.0E_i - 21.24e^{\frac{-3.21E_i}{t + 0.05}} - \frac{3}{2} S^2 e^{-\frac{0.009 S^2}{t + 0.05}}$</td>
<td>$E_i =$ incident energy</td>
</tr>
</tbody>
</table>
7.3 Energy-dependent kMC implementation

During the low rate deposition of metal atoms with either small incident energies or with a high substrate temperature, thermally activated atomic jumping on (and below) the growth surface allows a thin film to reduce its overall surface energy and defect content. This thermally activated process of atomic assembly has been modeled with a kMC method, as described in chapter five. In this approach, all of the diffusion paths (with different activation energies) were included in a 2D model of close-packed metal film growth. Fig. 4.1 schematically showed the simulation procedure for this kMC model. Incident atoms were introduced into the system at random positions above the substrate and were assigned an incident angle by random sampling of a pre-defined distribution (e.g. truncated cosine distribution). In the interval between atom impacts with the surface, the main loop of a Monte Carlo algorithm selects and implements diffusion steps. It does this by: (1) calculating the jump rates \( p_i \) for all possible jump paths; (2) selecting and executing a jump according to relative jump rates; (3) summing up the rates of all possible jumps \( P = \sum_i p_i \) and marching the system clock forward by a time interval \( t_n = 1/P \) [89].

The new atomic configuration was then used to compute new jump rate and the algorithm is repeated until the time between atom arrivals is exhausted. This algorithm was able to account for the effects of deposition rate, temperature and incident flux distribution in simulating thin metal film growth. Using the energy data summarized in Tables 7-1 to 7-4, the kMC model can be extended to include the effects of incident energy because the energetic interactions are completed with time in the order of magnitude of picoseconds, which is generally much smaller than the atom residence times at the substrates temperatures of typical interest. Thus, fast energetic reassembly events and thermal diffusion can to a reasonable approximation be treated as occurring sequentially.
7.3.1 Incorporation of reflection and resputtering

Three steps were used to incorporate both reflection and resputtering events. In step I, an event is identified. Suppose that an atom with kinetic energy, \( E \), approaches a surface at an incident angle, \( \theta \) (where \( \theta \) defined as the angle between the local surface normal and the incident direction). Its probability for reflection or resputtering can be calculated using Eqn. 7-3 in Table 7-1 or Eqn. 7-9 in Table 7-2 respectively. A random number (between 0 and 1) is then generated and compared with the probability. If the random number is less than the probability, the corresponding reflection or resputtering event is executed. Otherwise the program proceeds to simulate biased diffusion and atomic reconstructions associated with the thermal spike. Cases exist where both reflection and resputtering events can occur. In that case, the kinetic energy and emitting direction are saved for the resputtered atoms and the reflection is first executed. The data for the resputtered atom is then retrieved and the atom is treated as a new incident atom. In step 2, the reflected or the resputtered atom is ballistically moved until it impinges upon new surface, or is removed from the system when no new surface is encountered. A third step is used to determine the possibility of further reflection and/or resputtering events if an atom retains sufficient kinetic energy. The same procedure is repeated until no further reflection and resputtering events are possible.

The local incident angle, \( \theta \), used for the above calculations depends on the local surface normal at the impact site. This can be defined for a small surface area near the impact. In the case of a flat plane, its value remains the same regardless the size of the sample area, but for a rough surface, the sample area needs to be large enough to fully cover the local information, yet small enough to avoid inaccuracy caused by features such as sharp corners and other roughness features. Various test calculations were performed to determine an appropriate size for defining the local normal. It was found that five surface atoms generally give rise to reasonable surface normal and were hence used for all the simulations.
7.3.2 Biased diffusion

To execute biased diffusion, the incident atom’s skipping distance $d_s$ is first calculated using Eqn. 7-13 in Table 7-3. The execution of biased diffusion on a smooth surface simply moves the incident atom in the direction of its momentum by the skipping distance. To biased diffuse an atom on a rough surface, the skipping distance was first compared with the unit move distance (taken to be nearest neighbor distance). If the skipping distance is larger, the atom is moved by the unit distance. Then the remaining skipping distance is reduced by a predetermined value to account for the effects of the rough surface. The procedure continues until the skipping distance is completely consumed. Mathematically, this can be described by:

$$S_{i+1} = S_i - C_i \cdot a$$

where $S_i$ is the remaining skipping distance at $ith$ jump, $a$ the unit move distance, $C_i$ is a coefficient and $S_{i+1}$ the remaining skipping distance at $(i+1)th$ jump. As long as $S_{i+1}$ is positive and larger than $a$, we continue to move the atom.

The parameter $C_i$ was obtained based on the statistical analysis of MD simulations for skipping on rough surfaces [143]. The values of $C_i$ are usually different at each jump site $i$. For example, $C_i = 1$ for a perfect smooth plane, $C_i$ is larger when the atom moves down or against a ledge, and $C_i = S_i/a$ (i.e. stop after the jump) when the atom encounters a sharp valley or a higher ledge and so on. Fig. 7.9 illustrates the flow chart for the implementation of reflection, resputtering and biased diffusion.
Fig. 7.9. Implementation of athermal interaction of incident atom and growing surface (biased diffusion, reflection and resputtering).
7.3.3 Transient thermal diffusion

When an energetic atom impinges upon a growing film, rearrangement among atoms in the thermal spike zone near the impact site takes place. The extent of this local rearrangement depends upon both the atoms’s acquired energy (or equivalently the temporary rise of temperature) for each atom in the neighborhood of the impact and its neighborhood restraint. The atom with highest energy yet least neighborhood restraint is assumed to have the highest probability to jump to a lower energy site. The criterion for a jump along the $i$-th pathway to occur then can be expressed by:

$$P_i > P, \quad P_i = \left(\frac{E}{Q}\right)^n,$$

where $E$ is the energy (can be converted to temperature increase) of an atom in the thermal spike zone calculated using Eqn. 7-15 in Table 7-4, and $Q$ the neighborhood restraint taken to be the activation energy for a jump pathway. $n$ and $P$ are adjustable parameters. Suppose that an atom has a pathway meeting the condition of Eqn. 7-17. It then is said to have a probability to jump to a new place through that path. When many atoms have the probability to jump in different paths, the jump simulation is conducted in such a way that probability for the jump in the $i$-th pathway scales with $P_i$. Once the jump is made, $P_i$ is updated for all the paths. This procedure was repeated until no atoms have a probability to move.

The parameters $n$ (energy sensitivity index) and $P$ (a cut-off number) are related to the number of times that an atom could move and the number of atoms which could make such a move in the impact area. These two parameters were determined by matching the configurations obtained using MD simulations at short time/length scale to those obtained from the kMC calculations at the same conditions. Using the values of $P$ and $n$ determined this way, both MD and kMC simulations results in similar configurations at various kinetic energies ranging from 0.1 to 2.0 eV and normal incident angle. Fig. 7.10 shows a
flow chart for implementation of the thermal spike induced “athermal diffusion” process.

7.4 Concluding remarks

A new method has been proposed to simulate energy-dependent (i.e. hyperthermal) vapor deposition. It is based on kMC’s capacity to accommodate a spectrum of rate processes of thermal diffusion and superimposes it with energy effects represented by empirical equations derived from MD calculations on sample surfaces. A flow chart for the complete energy-dependent kMC algorithm incorporating the effects of reflection, resputtering, biased diffusion and transient athermal diffusion is summarized in Fig. 7.11. First, an incident atom is randomly introduced just above the substrate. Its incident angle and kinetic energy are next selected according to user defined distributions. Non-thermal interactions (reflection, resputtering and biased diffusion) of incident atom with the substrate (growing film) are then simulated, followed by the athermal diffusion caused by the thermal spike. Finally, a conventional kinetic Monte Carlo procedure is employed to treat the thermal diffusion between adatom arrivals. The whole process iterates until the designated number of atoms is deposited.
Incidence angle and energy

Calculate incoming atom impact site

Use previous MD results to assign energy \((E_k)\) to atom in the neighborhood of the impact \((t = 0)\).

For each jump path with barrier energy \(E_i\), calculate \((E_k / E_i)^n\) as jump condition.

Enable atom possibility of a jump only if \((E_k / E_i)^n > \text{constant}\).

Compute summation:

\[
\sum_{i=1}^{N} \left( \frac{E_k}{E_i} \right)^n
\]

Does any atom have a jump probability?

Yes: Randomly select a jump path weighted by \((E_k / E_i)^n\)

No: Next step

Randomly select a jump path weighted by \((E_k / E_i)^n\)

Execute the jump

Update \(t\) by jump time

Update acquired energy according to MD results

Update \((E_k / E_i)^n\) for each path

Next step

Fig. 7.10. Athermal diffusion implementation due to energetic spike.
Fig. 7.11. The energy-dependent kinetic Monte Carlo simulation steps.
Chapter 8

Hyperthermal Physical Vapor Deposition

8.1 Introduction

Smaller, brighter, faster, these modern trends in electronic and photonic devices impose strict demands on crystal growth via the vapor phase [51]. Extremely small structures must be fabricated with high material uniformity and interface smoothness. This requirement demands control at an atomic level. For example, thin film devices based upon the giant magnetoresistance (GMR) effect require the growth of Ni$_{88}$Fe$_{17}$/Cu/ Ni$_{83}$Fe$_{17}$ planar multilayers in which the interfacial roughness is less than a few angstroms and intermixing of the dissimilar metal layers is negligible [125, 126]. Vapor deposition strategies that achieve this microstructure exploit kinetically limited growth mechanisms. Designing deposition processes that can achieve atomic scale perfection by controlling the kinetics of film growth is complicated because of the many mechanisms that contribute to the atomic assembly process. The atomic assembly events that occur in vapor deposition processes are “enabled” by thermally activated atomic diffusion, the sudden local heating associated with the latent heat of condensation release and the incident energy effects associated with hyperthermal atoms impacts. In spite of their dramatic influences on film morphology, structure, defect populations and residual stress, little atomistic modeling has incorporated the transient thermal spike due to latent heat nor impact energy induced effects. To realistically simulate the growth of films under energetic deposition conditions, modeling must address both conventional thermally activated processes and the other energetic effects responsible for additional atomic rearrangement mecha-
nisms.

8.2 Methodology

The method developed in chapter seven was used here to simulate deposition on a flat substrate. Each time after introducing an incident atom, the major incident energy induced effects (including reflection, resputtering, biased diffusion and athermal diffusion) were first incorporated in sequence one after another. Thermally activated atomic diffusion was then simulated using the kMC method. The steps were iterated until a designated number of atoms had been deposited.

Simulations were based on a 2D approximation of nickel deposition. Periodic boundary conditions were employed laterally to minimize the effect of relatively small system size. The nickel substrate was constructed to contain eight rows of 200 close-packed nickel atoms. A total of 8000 nickel atoms were deposited for each condition. Incident atoms were added from above the substrate based upon a flux with either a cosine or unidirectional distribution with a fixed incident angle. To quantify the surface morphology, a surface area ratio (length ratio in 2D case) concept [29, 128] was used to better quantify thin film’s microscopical roughness, as described in Appendix C. To minimize statistical variations, ten separate simulations (each with different random number seed) were conducted and the average was used for a surface roughness data point. To simulate nickel atoms’ interaction with growing film, same MD calculations as those done in chapter seven have been carried out and very similar empirical equations (Appendix D) were obtained for the implementation.

8.3 Simulation results and discussion

8.3.1 Relative contributions of mechanisms

When latent heat and incident energy induced effects are separately treated, it is important to know the individual contribution from various energy mechanisms. This is to
ensure that, on one hand, the most important mechanism is identified under different conditions and on the other, each treatment individually looks reasonable. Here, an incident energy of 40 eV was used to emphasize the energy effects (This would therefore mimic the conditions when a metal flux was fully ionized and a bias voltage of about 40 V used to accelerate the metal atoms towards the substrate). The deposition rate was initially fixed at 0.1 µm/min, and a (non-truncated) cosine angular distribution for the incident atomic flux was assumed. First, a ballistic deposition model was used to show the configuration of deposited film with very limited atomic relaxation. This was done by simply placing the depositing atom at the lattice site nearest to the location of impingement and then freezing it. The configurations are shown in Fig. 8.1(a). Obviously, the configurations that this methodology results in are process temperature independent and are thus indistinguishable for the two temperatures. The very rough and highly porous structure results from self shadowing. This is likely to represent the porous configuration under extremely low temperature conditions. The traditional kMC model was then used to illustrate the effects of thermal diffusion of both surface and bulk atoms. Fig. 8.1(b). It should represent thermal deposition excluding only latent heat. By successively turning on the mechanisms of athermal diffusion due to latent heat release (i.e., thermal spike at zero incident energy), atom reflection, resputtering, biased diffusion, and athermal diffusion due to impact energy (i.e., thermal spike at non-zero incident energy), the kMC simulations described earlier were carried out to reveal the effects of individual mechanisms. The results are shown as Figs. 8.1(c) - (g).

First examine the configurations in the left column, i.e. for lower temperature ($T/T_m = 0.17$). Fig. 8.1(a) shows that the exclusion of thermal diffusion of atoms results in a very porous columnar structure. Fig. 8.1(b) shows that thermal diffusion significantly increases the column size. As for the effects of the various energy mechanisms, Fig. 8.1(c) indicates that the latent heat release induces considerable atomic rearrangements which lead to larger column size and less inter-column voids. High energy reflection and
Fig. 8.1. Contributions of various growth mechanisms in hyperthermal physical vapor deposition. The substrate temperature was $T = 200 \text{ K} \ (T/T_m = 0.17)$ and $500 \text{ K} \ (T/T_m = 0.43)$ respectively. The deposition rate was $0.1 \text{ µm/min}$, and the kinetic energy was $40 \text{ eV}$. Incident flux with a full cosine distribution was used for the simulation. The deposition of 8000 nickel atoms was simulated.
resputtering are not seen to have noticeable effects on the film structures, Figs. 8.1(d) and (e). In fact, although reflection and resputtering events occur under the simulated conditions, these events only result in re-deposition of atoms at different locations and do not cause a local atomic rearrangement. Fig. 8.1(f) shows that the inclusion of biased diffusion resulted in fully densified structure and much smaller roughness. This occurs because the biased diffusion enables atoms to move in both a short and long range and preferentially come to rest at lattice ledges. However, the biased diffusion only treats the adatom itself, not those adjacent to the impinging site during high energy deposition. By including thermal spike induced rearrangement from neighboring atoms, a fully dense and rather flat configuration is generated, Fig. 8.1(g).

At higher temperature of $T/T_m = 0.43$, effects associated with various energy mechanisms mostly disappear. The much more intensive thermal diffusion overwhelms the energy induced atomic rearrangement.

8.3.2 Effect of kinetic energy on surface morphology

It has been shown that the contribution of energy mechanisms to the atomic assembly process depends on temperature and is especially significant when thermal diffusion is low. To systematically explore the energy effects, the full hyperthermal kMC model was used to simulate vapor deposition at various incident energies from 0 to 20 eV at fixed substrate temperature of $T/T_m = 0.17$, a deposition rate of 0.1 µm/min, and a standard cosine flux angular distribution. Four representative configurations are shown in Fig. 8.2.

It is evident that higher incident energy helps decrease surface roughness and promote a denser film. At zero incident energy (thermal energy only), Fig. 8.2(a), the configuration is a porous columnar structure with a roughness ratio of 3.22 (see Appendix C for definition). It results from limited atomic mobilities and self-shadowing. At zero incident energy, there are no biased diffusion, reflection and resputtering and only the latent heat release enables the local reconstruction of atoms. The microstructure represents zone I
Fig. 8.2. Effect of kinetic energy on surface morphology at substrate temperature of 200 K ($T/T_m = 0.17$), deposition rate of 0.1 µm/min and incident flux angle with cosine probability distribution. The deposition of 8000 nickel atoms was simulated.
structure in the structure zone model \[45\]. At 5 eV, Fig. 8.2(b), the porosity significantly decreases and the roughness ratio reduces to 1.67. Since reflection and resputtering are not activated at this energy, the observed change should be a result of a stronger thermal spike induced athermal diffusion and biased diffusion. As the incident energy increases to 10 eV, Fig. 8.2(c), the roughness ratio drops to 1.55, and voids are completely eliminated. Finally, at 20 eV, Fig. 8.2(d), the surface becomes much smoother and the roughness ratios reduces to 1.29. When the kinetic energy is at 20 eV or higher, several new mechanism are activated. First, reflection becomes possible. A reflected atom generally tends to move in the forward direction and is less likely to attach to an existing mound. When it jumps onto the edge of the mound, it enables the mound to grow in the horizontal rather than in the thickness direction. Secondly, resputtering can occur at 20 eV. Resputtering occurs most likely at surface asperities as these places are exposed to more incoming flux. The preferential etching of these sites promotes smoothness as well.

More detailed simulations on the effect of incident energy have been conducted at various substrate temperatures. Representative results are shown in Fig. 8.3. It can be seen that at a low temperature of \(T/T_m = 0.17\), the surface roughness initially decreases very rapidly as the incident kinetic energy increases up to 15 eV. Further increases of energy then cause only a small change in the roughness. Increasing the substrate temperature causes a roughness decrease over the whole energy range. In addition the effects of incident energy on reducing the surface roughness become progressively less significant with increasing the temperature. For temperature above \(T/T_m = 0.26\), the effect of energy becomes negligible. As a result, energy modification is more effective at low temperature than at high temperature.

The functional relationship of surface roughness and incident energy at different deposition rates was also simulated at a fixed \(T/T_m\) of 0.22 and a cosine angular flux probability distribution, Fig. 8.4. It shows that at the highest attempted deposition rate of 10
Hyperthermal Physical Vapor Deposition

130

µm/min, increasing the incident energy from 0 to 15 eV very significantly reduced the surface roughness. The roughness appeared to saturate when the energy was increased above 15 eV. Similar to the effect of temperature increase, decreasing the deposition rate reduced the roughness over the whole energy range, and resulted in a progressively less energy effect on roughness. Evidently, the roughness becomes almost independent on incident energy when deposition rate decreased below 0.01 µm/min at $T/T_m = 0.22$.

The simulations demonstrate the interplay between thermal diffusion and various energy related mechanisms on surface roughness. At either low substrate temperatures or high deposition rates, thermal diffusion is not significant and the flattening of the surface is then mainly achieved by energy related mechanisms such as athermal diffusion, biased
Hyperthermal Physical Vapor Deposition

diffusion, reflection and resputtering. At high temperature or low deposition rate, thermally activated diffusion often suffices to evolve a flat surface and the energy mechanisms are overwhelmed.

There are abundant experimental results showing that the use of energetic atoms during thin films deposition promote layer-by-layer growth and that energetic atoms activate surface processes [134, 144 - 149]. Most of them were on semiconductors and it is difficult to find systematic investigations on metal films at relevant conditions that can be used for direct comparison with the simulation results. In almost all cases, the experimental results were attributed to the dissociation of small clusters by energetic bombardment and subsequent mobility enhancement. The dissociated atoms are then able to reach step

![Image of a graph showing the effect of incident energy on surface roughness of nickel films under different deposition rates. The substrate temperature (T/T_m) was 0.22 and the incident angle was in a cosine distribution.](image_url)
edges and facilitate layer-by-layer epitaxial growth. However, these desirable results are often compromised by deleterious effects introduced by the energetic particles themselves. As energy increases above a threshold, permanent damage to the lattice increases more rapidly than the annealing processes are capable of healing, resulting in a sharp increase on the number of defects [146, 149]. Thus there is an optimum energy window for achieving layer-by-layer epitaxial growth and high crystalline quality films which are relatively defect free [146].

8.3.3 Effect of incidence angle on surface morphology

Thin films grown under low substrate temperature/low impact energy conditions are generally known for their characteristic (and often detrimental) columnar structure caused by self-shadowing. Self-shadowing is particularly strong when incident atoms are away from the substrate normal. To explore the interplay of incident energy and incident angle on surface morphology, the energy-dependent kMC model has been used to simulate deposition when all incident atoms were assumed to have the same direction and kinetic energy.

Fig. 8.5 shows a series of configurations for different incident directions under otherwise identical conditions. At normal incidence of \( \theta = 0^\circ \), clear mounds on a rough surface can be identified. They grow broader and the number is decreased accordingly with increasing the incidence angle to \( 20^\circ \). The surface becomes considerably smooth at \( \theta = 40^\circ \) and the mounds can be barely identified. Further increasing the incidence angle to \( 60^\circ \), the surface reverses the smoothing trend and becomes rougher.

More simulations on the effect of manipulating the incident angle were carried out and the results are shown in Figs. 8.6 and 8.7. The first plot compares the effect of incident angle on surface roughness for four incident energies at fixed \( T/T_m = 0.22 \) and deposition rate of \( 0.1 \) \( \mu \)m/min. The second is a similar result for four substrate temperatures. Fig. 8.6 shows that at zero incident energy, the surface roughness initially increases slowly with
Fig. 8.5. Effect of incident angle on surface morphology of nickel films at substrate temperature of 300 K \((T/T_m = 0.26)\), deposition rate of 0.1 \(\mu\)m/min and kinetic energy of 20 eV. The deposition of 8000 nickel atoms was simulated.
increasing incident angle, then very rapidly when the incident angle is beyond about 40°. This implies a strong self-shadowing that can not be healed by latent heat induced atomic relaxation alone. The rapid increase of roughness at 40° signals the formation of voided columnar structure. With the incident energy at 5 eV, a dramatic change takes place on the surface roughness vs. the incident angle functional relationship. The surface roughness now initially decreases with increasing incident angle up to about 30°, then increases with increasing the incident angle, at first slowly and then rapidly. The overall roughness has also been greatly reduced. This trend gives the curve a roughness minimum. For more energetic depositions at 10 and 20 eV, similar trend can be seen and the roughness is further reduced, especially for large incident angle end. In addition, the minimum roughness position moves towards right side with increasing the energy. Alternately, the higher the
incident energy, the larger the angle that has the minimum roughness. This occurs because high energy activates more surface processes which help smooth out rough surface and in turn neutralize self-shadowing that leads to inter-column voids. Nevertheless, it is noteworthy that the effect of kinetic energy on reducing the surface roughness is strongest when the energy is initially applied at 5 eV, suggesting the significance of athermal and short-range biased diffusion on smoothing the surface.

The effect of substrate temperature on the roughness-incident angle relationship is similar to that of incident energy, Fig. 8.7. Increasing the temperature generally reduces the roughness, especially at high incident angle. For an incident energy of 10 eV, the angle for the minimum roughness increases from about 35° to about 42° as the temperature
increases from $T/T_m = 0.17$ to 0.30. This arises because thermal diffusion promotes surface reconstruction that flattens a rough surface and eliminates voided columnar structure.

At the energy levels treated above, reflection and resputtering are not significant. Spike-induced athermal diffusion and biased diffusion mostly shape the observed microstructure, with the biased diffusion having special effect during oblique angle deposition. An oblique deposition is able to turn the otherwise randomly distributed biased diffusion into a directional biased diffusion. This effect increases with increasing the incident angle. Such unidirectional diffusion promotes local layer-by-layer growth and results in a smooth surface. On the other hand, the large incident angle causes self-shadowing at rough surface. As a result, there is a compromise between the benefit and the disadvantage and the magnitude of an optimal angle depends on process conditions including especially the incident energy.

### 8.4 Conclusions

The energy-dependent kinetic Monte Carlo method developed in chapter seven has been used to simulate physical vapor deposition on a flat substrate. The method allows a realistic study of incident energy effects during deposition, as well as their interplay with other conditions, such as substrate temperature, deposition rate, and incident angle. Application of the method to the deposition of nickel films demonstrates:

1. In addition to thermal diffusion, the primary energy-induced contributions to the thin film’s densification and smoothing come from short-range atomic rearrangement mechanisms including biased and thermal spike-induced athermal diffusion, while those from reflection and resputtering are secondary and cause only material redistribution;

2. Surface roughness decreases with increasing kinetic energy, which becomes stronger as the substrate temperature is lowered and/or the rate of deposition increases;

3. For directional hyperthermal deposition, a minimum surface roughness is
observed. The incident angle corresponding to the minimum value increases with increasing kinetic energy, substrate temperature and with decreasing deposition rate.
Chapter 9

Trench Filling by Physical Vapor Deposition

9.1 Introduction

The manufacture of semiconductor integrated circuits requires hundreds of steps from production of the silicon wafers through final testing of a packaged component [1]. The formation of metal interconnections is a key aspect in the process. The general trend in the area is away from blanket coatings and subsequent reactive ion etching patterning towards damascene processes, which utilize the filling of embedded trenches and vias and subsequent planarization by chemical-mechanical polishing. The width dimension (less than half micron) and aspect ratios (i.e. depth:width > 1) of these trenches and vias are generally incompatible with conventional sputter deposition due to the broad angular distribution of the sputtered atoms [16]. Sputter deposition into these features results in overhang and eventual void formation, which causes increased resistance and reliability concerns. Three solutions to this problem established over the years have been ionized PVD [1], CVD [150] and electroplating [151]. CVD by surface reaction kinetics is advantageous for deposition in high aspect ratio cases, but it has problems such as low deposition rate, poor reproducibility, poor polycrystalline texture control, and contamination, etc. [152]. The emerging electroplating process has better filling capability for high aspect ratio features than sputtering or CVD and is projecting to play major role in future microelectronics industry, although it needs a seed layer to guide film growth and a barrier layer to prevent conducting metal from reaching and destroying active devices. The seed and barrier layer (collectively called liner layer) are both prepared by ionized PVD. Alterna-
tively, ionized PVD in combination with reflow is considered to be a key technology in ULSI manufacturing especially for via holes of higher level interconnects whose aspect ratio is not very large [152].

This chapter addresses the important PVD process. The evolution of PVD technology in metallization and previous simulations in the area are first described, followed by modeling work.

9.2 PVD metallization

9.2.1 Metallization experiments

PVD in the microelectronics industry generally refers to sputter deposition. There are a number of reasons why PVD sputter has been so successful in the field [12]. First, sputtering can be used to deposit all of the conducting films used in interconnect metallization schemes, including metals with vastly different melting points such as aluminum ($T_m = 660^\circ$C) and titanium ($T_m = 1670^\circ$C). Second, deposition of alloys can be accomplished from a single alloy target with the film retaining the stoichiometry. This is problematic with evaporation due to different individual vapor pressures. Third, the deposition rate can reach 1 µm/min for thick films, sufficient for economical wafer fabrication [12]. Fourth, sputter films have superior purity, microstructure and surface roughness for physical and process requirements. Finally, the use of an extended target area minimizes spatial variations of film thickness and shadowing which results in good step coverage over features provided aspect ratio < 1 [12]. As a result, ever since PVD emerged in the 1970s as a production-worthy technology for microelectronic fabrication, its major application has continued to be metallization and interconnection [12].

The isotropic nature of the sputtered atoms, valuable for coherently coating over steps, edges and other low aspect ratio surface features, creates a problem for deposition into high aspect ratio features such as those used in a damascene process. The majority of
the depositing atoms are moving at angles far from normal incidence, which results in significant lateral deposition on the upper sidewalls. Such lateral build-up quickly results in a narrowing and eventual closure of the trench or via. Since sputtered atoms are primarily neutral, their trajectory cannot be controlled by electric fields.

A variety of approaches have emerged to improve its usability for high aspect ratio features in the course of microelectronics applications. They can be divided into two groups: those based on the deposition of neutral species, and those based on the deposition of ions. The former includes the geometrical filtering of the sputtered flux [16] and increase of the surface mobility of the deposited atoms on the wafer surface [16]. The latter controls incidence directionality by using in-flight ionization of a sputtered or evaporated flux together with acceleration of the metal ions to the sample using a bias voltage. In such case, resputtering and grazing angle ion bombardment can then be induced.

Flux collimation belongs to the directional filtering [14, 15]. Often using spot welded sheetmetal arrays of hexagonal holes, the efficiency of the collimator depends on the aspect ratio of the collimators holes. Larger collimator aspect ratio results in more filtering, but an accompanying lower deposition rate, more frequent clogging, particle formation and costly maintenance. Because of the low efficiency and handling inconvenience, collimation is often limited to the deposition of the thin (diffusion inhibiting) liner coating. It is rarely used for filling a trench or via. [1].

Long-throw deposition is another geometrical filtering. By moving the sample farther away from the target, an increasing fraction of the sputtered atoms which are moving mostly laterally are lost to the chamber walls. This practice requires low chamber pressure to reduce in-flight gas scattering. It also introduces a fundamental geometrical asymmetry because the incidence angle distribution at the substrate edge is intrinsically different from that at the center. Because of the long distance, the deposition rate is also low.
On the other hand, the thermal reflow attempts to make use of the conducting metal’s temperature-dependent surface property [19]. The argument is that if surface atoms have sufficient mobility, they may migrate down into deep features, resulting in enhanced filling. Thus the initial incidence directionality becomes unimportant. There are a number of requirements for any successful reflow process. First, the feature must remain open in the course such that there is a continuous surface from the field region to the bottom of the feature. Secondly, an adhesion layer must be first deposited to prevent agglomeration. Third, reflow requires high levels of cleanliness as contamination significantly impede the mobility of the surface atoms [1]. Although reflow have been successfully applied to the AlCu and copper interconnect systems, those requirements especially the open throat limits both the sputter deposition rate as well as the smallest feature size. A related technique is force-fill, which is more complicated [153].

The methods that have the potential to extend the PVD technology several chip generations are typified by ionized PVD (I-PVD) which is based on in-flight ionization of a sputtered or evaporated flux and the subsequent acceleration of the metal ions to the sample by means of an electrical potential [1]. This technique was first applied to the deposition of copper on semiconductor features by Holber et al. [154] who evaporated copper into an electron cyclotron resonance (ECR) plasma, and then condensed films from copper ions on a nearby, negatively biased wafer. More recently, deposition with metal ions has been extended to a related technology using magnetron sputtering as the metal source and inductively coupled RF plasmas as the means of ionization [1]. This latter technique has the advantage of compatibility with existing manufacturing hardware and processes as well as the capability to deposit alloys.

In I-PVD, metal atoms are sputtered from a conventional magnetron source using an inert gas and a conventional magnetron power supply. A second plasma, nominally different from the magnetron source plasma, is produced in the region between the sputtering
source and the sample using the same background gas. Some fraction of the sputtered metal atoms are ionized as they transit this second plasma. Finally, just above the sample surface, the metal ions are accelerated to the sample by the difference between the plasma potential (usually slightly positive) and the sample potential, which can be controlled externally to be either a zero or a negative voltage.

The transition from a conventional PVD process to the I-PVD concept took more than a decade of trial and error search in the laboratory and then the scaled up for the production line. Many of the intermediate explorations, consuming significant amount of research and development time, are short lived either because of complexity or because of low throughput and poor efficiency.

Today, the microelectronics industry is faced with the economic and technical challenge of making ultralarge scale integrated devices having minimum feature size 0.18 µm [16, 155]. Additional challenges are posed by the increase in silicon wafer size from 200 mm to 300 mm, the replacement of Al alloy interconnects with copper interconnects, and the related requirements for high quality copper diffusion barrier films and damascene processing. In order to meet the metallization challenge of ULSI devices, processes for metallization need to be explored and optimized with a minimum of experiments. This naturally leads to the question: whether or not many of those intermediate steps can be waived by using some type of predictive modeling, such as atomistic simulations; and whether or not the most rewarding route can be indicated by modeling. This chapter attempts to simulate the atom by atom assembly of trench metallization processes using the energy-dependent kMC method developed earlier. It addresses major process parameters including substrate temperature, deposition rate, adatom kinetic energy, the flux distribution and the trench geometry.

9.2.2 Metallization simulations

Various tools simulating PVD deposition have been developed by the microelec-
tronics community. They can be roughly divided into two categories; continuum-based methods and those based on atomistic models. The continuum approach seeks to represent the surface by a sequence of nodes and strings such as in the SHADE method [156], the SAMPLE method [157], and the SPEEDIE method [158] or described by an equation with mesh points (or cells) embedded in the system such as in the emerging level set method of Sethian [159]. The basic idea is to first numerically calculate the speed with which the material is to be added to or removed from a node (or a cell) which depends on the net effect of deposition, etching and other processes. An algorithm (e.g. shock wave [156]) is then used for incremental surface advancement. To approximate the effects of the impacting atoms kinetic energy, a sticking coefficient approximation is sometimes made. The angular distribution of the incident flux can also be incorporated. Important factors such as self-flux shadowing by protuberances on the surface have sometimes been included [156], enabling the topography of the growth surface to be evolved in a metallization process. However, the often considerable effect of temperature and deposition rate can not be sensibly simulated by these methods yet because of the difficulty of incorporating diffusion both on and beneath the growth surface. Although a continuum method is likely to be the eventual approach for a large wafer scale assessment, it is currently unsuited to the analysis of individual device features that have entered the deep sub-micron (<0.2 µm) region where diffusion distances can be compared to the dimensions of the feature.

Current atomistic approaches for simulating metallization usually are based on the SIMBAD method, a Monte Carlo model [160]. In this approach, the effect of temperature or deposition rate, surface diffusion is usually approximated by a “mobility” factor. A landed adatom or a disk is allowed to move a specified distance once before stopping for good. A higher temperature is modeled by a longer distance. The effects of adatom kinetic energy (reflection and resputtering) were treated using data from experimental measurements. Often the data for a specific metal under certain conditions are rarely available and approximations have to be made to fit needed conditions. This type of model then is sup-
posed to be able to simulate process conditions. However, since diffusion of any one of the atoms in the system is once allowed, the constant rearrangement of the whole atomic configuration can not be simulated, and since time is also not explicitly included, the role of the deposition rate can not be quantitatively analyzed nor its trade-off against temperature.

The latest attempt in simulating interconnect metallization was conducted by Huang, Gilmer and de la Rubia [54]. Their kMC approach was able to simulate the effect of substrate temperature and deposition rate but did not included the role of kinetic energy. Therefore, the model can only address low energy deposition; processes such as I-PVD are not appropriate.

9.3 Methodology

To simulate the I-PVD metallization processes, two major steps need to be addressed. The primary one is to properly treat the atomic diffusion. When deposition takes place in zone I and/or zone II of the structure zone model [45], it is the surface diffusion that dominates the evolution of surface profile while the bulk diffusion is negligible. An appropriate diffusion model thus is the critical element to simulate the growth process. It should reflect the dynamic nature of constant rearrangement of the entire simulation system, i.e. any one of the atoms in the system should be allowed to move at any time in the whole simulation process as long as it has the probability to do so. In this regard, the kMC method presented in chapter three is the best solution so far. The second step is to incorporate the interactions of energetic incident atoms with the growing film. This includes the reflection, resputtering, biased diffusion and athermal rearrangement caused by thermal spike. A schematic drawing for such effects is shown in Fig. 9.1. In this respect, the treatment used in chapter eight is equally suitable for a featured substrate. The methodology described in chapter eight was therefore employed here.
Different PVD processes often have different metal flux distributions at the substrate. The introduction of incident fluxes in a PVD process simulation is therefore worthy explanation. The angular distribution of sputtered atoms is generally described as a cosine distribution, Fig. 9.2(a) [26]. That is, the relative fluxes in each direction can be represented by the fluxes at the normal direction times the cosine of the angle from the surface normal. The angular distributions of collimated incidence and long-throw deposition can be represented by Fig. 9.2(b) [16]. The magnitude of $\theta$ is determined either by aspect ratio in case of collimator or by the distance between the cathode and the substrate in case of long-throw. The bigger the aspect ratio or the longer the distance, the smaller the $\theta$. In I-

Fig. 9.1. Schematic geometry of interactions of an energetic incident atom with a trench. The incidence angle of the atoms are assumed to be represented by a cosine probability distribution. All major interaction events are indicated including reflection, resputtering, biased diffusion and athermal diffusion.
PVD, the ions are concentrated near $\theta = 0^\circ$, whereas the neutral species follow a cosine-like distribution. Thus the overall distribution can be viewed as a superposition of a cosine and directional distribution, Fig. 9.2(c). The relative magnitude of the two components depends on the ionization ratio. High levels of ionization of the metal species are possible (e.g. > 75%), and in this case the majority of the depositing species arrive at normal incidence to the sample surface when a bias voltage is applied.

Experience has shown that filling larger aspect ratio features needs very directional flux so that it reaches the bottom of the feature without shadowing from the sidewalls. Such directionality can only be achieved by applying a pull upon incident atoms using bias voltage (about 20 eV at least [156]) on substrate. However, to deposit a liner layer, a more divergent incidence is desired to cover both the bottom and the sidewalls.

![Fig. 9.2. Representative incidence distributions in PVD deposition. (a) conventional cosine distribution, (b) collimated distribution, and (c) distribution in I-PVD process where the circle represents neutral atoms’ and the sector the ions’ distribution.](image)

### 9.4 Trench filling Results

The simulation methodology developed in chapter seven has been used to investigate the filling of trenches under various conditions. To quantify filling performance a filling factor has been calculated. It was defined as the ratio of the number of occupied lattice sites in a trench to the total number of available sites. The advantage over more traditional definitions of step coverage (e.g. the ratio of film thickness inside the feature to that out-
side the feature) is that the filling factor is a direct measurement of the status of the filling performance and is simple to calculate after (or during) a simulation. Periodic boundary conditions were used to avoid the effects of a limited system size. A total of 80,000 nickel atoms were used for each simulation. A typical run took about four hours of CPU time on a RS/6000 workstation. To minimize the statistical data spread, five runs were conducted and the average was used for each data point.

9.4.1 Effect of incident collimation

Fig. 9.3 shows the effect of incident collimation on the surface morphology. The deposition was conducted at a substrate temperature of $T/T_m = 0.48$ K, a deposition rate of 1.0 µm/min, a kinetic energy of 50 eV and trench aspect ratio of 2. It shows that best filling was achieved with a cut-off of ±3° (or less). However, complete filling was still achievable for a cut-off of ±11°. Increasing the angle of incidence to ±16° resulted in void formation. Apparently, complete filling prefers more a restrict cut-off.

To fully explore the collimation effect, more simulations at similar conditions have been conducted and the results are shown in Fig. 9.4. Here, 13 cut-off angles were used and the filling factor was calculated four times at different filling stages. The results surprisingly indicate the existence of a maximum filling efficiency at about 5°. The peak is initially unclear and becomes evident with the process. Intuitively, this means that the sum of atoms directly getting into the inside of the trench and those reflected and/or resputtered into the inside of the trench reach a maximum at certain collimation angle. The fraction that directly reach the trench bottom decreases with increasing the angle, while the reflected/resputtered fraction increases with increasing the angle. The two components work against each other and reach a maximum at a nonzero cut-off. At larger cut-off angles, more reflected and resputtered atoms redeposit at the trench throat area and result in a pinch-off.
Fig. 9.3. Effect of incidence collimation angle on trench filling. The substrate temperature was 550 K ($T/T_m = 0.48$), the kinetic energy 50 eV, the deposition rate 1.0 µm/min and the aspect ratio of 2. Nickel atoms of 80000 were used in the simulations.
The curves also expose big differences for the filling efficiency at various stages. At \( n = 20,000 \), the filling factor decreases slightly with increasing \( \theta \). At 40,000 and more, it decreases much faster. When fixing \( \theta \), the filling efficiency depends greatly on the number of deposited atoms. At 10°, for example, it takes 20,000 atoms to achieve a filling factor of 40%, 40,000 to about 72%, 60,000 to 89% and 80,000 to 97%. These dependences result from both a changing aspect ratio in the deposition and the formation of overhangs.

9.4.2 Effect of incident energy

Fig. 9.5 shows the effect of incident energy on trench filling. A cut-off angle of 11° and conditions otherwise identical to Fig. 9.3 were used. At a low energy of 10 eV, a
Fig. 9.5. Effect of incidence energy on trench filling. The substrate temperature was 550 K ($T/T_m = 0.48$), the incident collision angle $11^\circ$, the deposition rate 1.0 µm/min and the aspect ratio of 2. Nickel atoms of 80000 were used in the simulations.
complete fill is seen. The wide opening at the top indicates no immediate risk of pinch-off. At 20 eV, the filling becomes worse and the opening at the top is reduced. When the energy is increased to 30 eV, filling deteriorated to point where a pinch-off had formed. However, the trend was reversed at 50 eV with the pinch-off gone and the filling improved. The new trend continued to an energy of 70 eV where a complete fill was reached. With further increase of energy, the filling decreased again. The detailed trend of energy dependence of trench filling can be best seen in Fig. 9.6. Fig. 9.6 indicates a minimum fill energy of about 10 eV and a second full trench filling energy at about 70 eV. At other range, the filling efficiency becomes worse. In I-PVD a minimum bias voltage must be applied to the ions before their directions can be controlled. According to experiments [156], the necessary bias voltage was about 20 eV. Thus the trench filling simulated at 10 eV should be viewed as an idealistic situation unlikely to be encountered in practice. Similarly, the energy trend at an early stage of filling is less obvious and stands out only when shadowing effects start to become a factor as a deposit builds up at the trench opening.

The reason behind these trends lies in the various effects of the incident energy. At low energy, the incident atoms did not activate reflection or resputtering. Only biased diffusion and athermal rearrangement mechanisms occur. The athermal rearrangement did not play a significant role at the high temperature deposition. The biased diffusion’s role was two-fold. It enabled the adatom to diffuse further down inside the trench, it also enabled atoms to relatively easily accumulate at the trench throat area, thus blocking incident atoms from entering the trench inside. This process is responsible for the observed worsening as the energy increased to 20 and then 30 eV. The improvement seen at 50 and 70 eV resulted from the significant activation of both reflection and resputtering. The threshold energies for both processes are about 20 eV. Thus from 20 eV onwards, there are two forces that works against each other. The constructive force on trench filling prevails about 30 eV and maximizes at about 70 eV. With further increasing kinetic energy, the disadvantage of the interactions take over. That is, the reflection and resputtering tends
The filling efficiency decreases again.

9.4.3 Effect of substrate temperature and deposition rate

Fig. 9.7 shows the effect of substrate temperature on trench filling under conditions similar to Fig. 9.3. It can be seen that thermal activated diffusion is a must for trench filling process. The intense surface diffusion at high temperature can be seen from the change of mound shape at the trench bottom. At low temperature, Figs. 9.7(a) and (b), the mounds are large. At the complete filling case, Fig. 9.7(d), the mound almost disappears. Intense diffusion helps spread incident atoms to the whole trench bottom. Such intensity also exists on the sidewalls, which ensures an opening trench throat to let flux pass. High
Fig. 9.7. Effect of substrate temperature on trench filling. The incident energy was 50 eV, the incident collimation angle 11°, the deposition rate 1.0 µm/min and the aspect ratio of 2. Nickel atoms of 80000 were used in the simulations.
surface diffusivity at elevated substrate temperature is the basis of the so-called thermal reflow process.

Increasing deposition rate functions similarly to lowering the temperature, Fig. 9.8. Both reduce the chance for adatom relaxation or rearrangement upon arrival at the substrate. The former realizes this by restricting atoms’ jumping capability while the latter by reducing available time for atomic jumps. Both conditions prevent the morphology from evolving towards equilibrium.

9.4.4 Effect of feature width

To simulate the effect of feature width on trench filling, three considerably different trench widths, 0.05 µm, 0.1 µm and 0.2 µm, have been used. Substrate temperature, deposition rate, incident energy and trench aspect ratio are all kept unchanged at 550 K, 1.0 µm/min, 50 eV and 2.0 respectively. Two sets of collimation angles were used to emphasize the importance of directionality. The number of deposited atoms for the three widths were 80,000, 320,000 and 1,280,000 respectively to ensure the correct square scaling factor for similarity requirement. To better visualize the filling evolution, the surface morphology at three different stages are plotted for each feature. Results for the two arrangements are shown in Figs. 9.9 and 9.10.

Fig. 9.9 is result at θ of 15°. It is evident that the trench filling is more difficult for smaller trench. Fig. 9.10 shows a result at a reduced θ of 11°. It confirms the trend but demonstrates improved coverage. The improvement is seen to result from the enlarged opening at the upper sidewalls.

The reason for the different filling performance at different trench sizes might be tentatively derived from the shape of the inner top surface inside the trench. The difference is best illustrated at 15°. In Fig. 9.9(c), the large trench has developed a convex mound in the centre. The mound becomes very small at the medium trench, Fig. 9.10(b). And it totally disappears in the small one and the inner surface even turns concave.
Fig. 9.8. Effect of deposition rate on trench filling. The incident energy was 50 eV, the substrate temperature 550 K ($T/T_m = 0.48$), the incident collimation angle 11°, the deposition rate 1.0 µm/min and the aspect ratio of 2. Nickel atoms of 80000 were used in the simulations.
Fig. 9.9. Effect of trench width on filling. The kinetic energy was 50 eV, the deposition rate 1.0 µm/min, the substrate temperature 550 K \((T/T_m = 0.48)\) and the aspect ratio of 2. The incidence collimation angle was fixed at 15°. The number of deposited nickel atoms for the three widths were 80,000, 320,000 and 1,280,000 respectively. Three stages of filling are shown.
Fig. 9.10. Effect of trench width on filling. The kinetic energy was 50 eV, the deposition rate 1.0 µm/min, the substrate temperature 550 K ($T/T_m = 0.48$) and the aspect ratio of 2. The incidence collimation angle was fixed at 11°. The number of deposited nickel atoms for the three widths were 80,000, 320,000 and 1,280,000 respectively. Three stages of filling are shown.
Because the process conditions and the geometry are identical, this should be explained as the effect of the length scale on diffusive activities. In the large trench, the incident atoms land mostly in the center (because of the sidewalls’ protuberance) and are unable to diffuse away to the distant corners. In contrast, the atoms landing inside the small trench have relatively short distance (small space) and be able to reach the corners. That is, the relative magnitude of distance for mass redistribution decides the end result. In other words, there is an interplay between diffusivity and diffusion space. Mound formation and its relation to diffusion is clearly seen in Fig. 9.7.

The same logic applies to the sidewall because it is the sidewall shape that largely determine the passing of the flux into the inside of the trench. When the trench is small and the distance to the protuberance is short, atoms landing on the sidewalls relatively easily migrate towards the center of the sidewall and block incidence from reaching the inside of the trench.

9.5 Step coverage results

A critical requirement for a liner layer in metallization is continuity. No void should exist on the film, otherwise the metals used to fill the trench can diffuse (during latter high temperature process steps) to reach and destroy active devices. Continuity becomes difficult when deposition is on a large aspect ratio trench because of shadowing from the sidewalls which makes lower sidewall areas difficult to access. One way to overcome the problem is to use directional energetic incident atoms. In this section, the emphasis is on the effect of incident energy on the uniformity of the liner coating. Related effects of trench aspect ratio and collimation extent are also simulated. Again nickel was used for demonstration.

9.5.1 Effect of incident energy

Fig. 9.11 shows a sketch of a commonly observed thin liner coating morphology inside a trench using I-PVD process [1]. The coating on the sidewalls is rather uniform.
Fig. 9.11. Typical trench liner layer contour using I-PVD process [1, 152]. The lower corner areas have extraordinary thickness because of effect of kinetic energy. This feature can serve as a test if a simulation is correct. The trench has an aspect ratio of 5.
The thickness at the trench throat and the lower corner areas are slightly higher, which makes the coating on the sidewall a concave shape. This concave curve can only be possible when the thickness at the lower corners are bigger than that on the middle section. Since the lower corners are expected to receive the least amount of materials, energy induced material redistribution must account for the unusual thickness.

Fig. 9.12 compares three simulated configurations using different incident energies. When the energy is low (20 eV), Fig. 9.12(a), the lower parts of the sidewalls have insufficient coverage. At higher energy (40 eV), the coverage is evidently improved. When the energy is increased to 70 eV, Fig. 9.12(c), the concave shape seen in Fig. 9.11 can be found. Such energy induced redistribution is caused by the same processes active in trench filling with one caveat. At very high levels of sputtering, the thin liner coating at the trench throat can be completely etched away [12].

9.5.2 Effect of incidence collimation

Fig. 9.13 shows the effect of collimation angle on liner coating process. At 5°, Fig. 9.13(a), most of the sidewalls are sparingly coated because of the narrow incident distribution. But an extraordinary amount of material is seen at the lower corners. Since incident atoms can rarely hit the sidewalls and diffusion would not have a major effect at the low $T/T_m$ of 0.3, the extra deposit must come from the bottom through reflection and resputtering. From the geometry viewpoint, reflection from the bottom should be ruled out, the resputtering thus becomes the only source.

At 25°, Fig. 9.13(b), better sidewall coverage can be seen because of the broader incident distribution. At the same time, the thickness at the bottom is significantly reduced. The reduction in turn decreases the fraction of resputtered atoms that can reach the sidewalls. At 45°, the even broader distribution delivers more atoms onto the upper half of the sidewalls and less onto the lower half and the bottom. The resputtering induced redistribution is even less. An undesired wedge-shape coating thus develops along the
Fig. 9.12. Effect of incident energy on step coverage. The substrate temperature was 350 K ($T/T_m = 0.3$), the deposition rate 1.0 µm/min, the incidence collimation angle 25° and the aspect ratio of 5. 15,000 nickel atoms were used in the simulations. [Note: The tiny voids seen at the lighter substrate and the darker coating interfaces were artifacts caused by graphics because the substrates were drawn in order to reduce processing time. When the substrates are represented by individual atoms from the simulations, the voids would be filled with atoms from the substrates, a result of interdiffusion].
Fig. 9.13. Effect of collimation angle on step coverage. The substrate temperature was 350 K \((T/T_m = 0.3)\), the deposition rate 1.0 \(\mu\)m/min, the incident kinetic energy 70 eV and the aspect ratio of 5. 15, 000 nickel atoms were used in the simulations [see note in Fig. 9.12].
sidewalls. As a result, there exists an optimal incident collimation angle for the liner coating process.

9.5.3 Effect of aspect ratio

Fig. 9.14 shows the aspect ratio effect on liner coating for a fixed set of process conditions. At aspect ratio of 3, the coating thickness along the sidewalls is fairly uniform. At aspect ratio of 5, the coating at the lower half is evidently thinner except for the areas near the corners because of the energy effect. When aspect ratio is increased to 7, undesirable discontinuity can be observed at the lower half in comparison to the configurations seen at aspect ratio of 3 and 5 under the identical conditions. As the resputtering induced redistribution becomes negligible, the corner effect now becomes limited. In such situation, more directional flux is needed to deliver more atoms to the lower half and the bottom on which more redistribution can be induced through resputtering.

9.6 Discussion

In trench metallization, the critical point is to keep the trench throat open as wide as possible during the whole process. Since the throat areas are closer to the source material than the inside, the throat is always the first to receive incident atoms. Since a growing accumulation (of deposit) naturally tends to expand into free space, the trench throat provides an ideal extra space (in addition to the open space above the substrate) for such expansion for deposit adjacent to the throat. These two factors make the deposit at the throat bulge into the space above the trench. The bulging, or protuberance, block subsequent incidence into the inside and further promote the growth of the protuberance. When this process is out of control, a pinch-off (and an internal void) quickly forms. Thus the primary requirement of keeping the throat open is to either avoid its accumulation at the throat or to use some method to rapidly remove it.

There are two ways to aid removal of deposit from the throat area. One is to utilize surface diffusion by increasing substrate temperature. At higher temperature, atoms have
Fig. 9.14. Effect of aspect ratio on step coverage. The substrate temperature was 350 K \((T/T_m = 0.3)\), the deposition rate 1.0 µm/min, the incidence collimation angle 25° and the incident kinetic energy 70 eV. 15,000 nickel atoms were used in the simulations [see note in Fig. 9.12].
more chance to find stable sites to lower overall system free energy. In other word, when thermal fluctuation is sufficient, surface cusps with small curvature always tends to disappear. This is what the reflow’s mechanism comes from. Fig. 9.7 shows only when the substrate temperature reaches certain value that a filling can be completed. However, such a strategy is inappropriate for liner deposition. These materials have very high melting points and to induce surface diffusion requires the use of excessively high temperature.

The second approach is to use energetic bombardment. Energetic atoms can trigger either reflection or resputtering at the impingement site, as described in chapter seven. Either helps redistribute material that otherwise would accumulate at the throat areas. The effect can be seen in Fig. 9.5 where an optimal kinetic energy is needed to achieve the desired effect. When the energy is low, it would not trigger the desired interactions, instead it would induce sometimes harmful athermal biased diffusion that facilitate accumulation at the throat. As is shown in Figs. 9.5(b), (c) and (d), detrimental void tends to form. When the energy is overly supplied, Fig. 9.5(f), energy induced redistributed atoms tend to land and accumulate at the throat areas and make the situation worse. Thus the optimal case is that shown in Fig. 9.5(e). The energetic atoms are able to etch away previous deposited atoms or reflect into the inside of the trench.

Fig. 9.15 shows the experimentally observed effect of kinetic energy [16]. According to the authors, 20 V was about the minimum voltage to effectively pull the ions into the trenches. At that level, the energy induced effects seem to be minimum. Higher voltages induced more resputtering, etc., eventually closing off the feature. The experiments and the simulation were conducted with somewhat different conditions, but the phenomena and the intrinsic mechanisms appear to be similar.

The two discussed above to maintain trench throat openness depend on the process geometry. This establishes the appropriate directional incidence distribution. As shown in Fig. 9.3, a very focused incidence is needed for a complete trench filling. Fig. 9.14 shows
a liner deposition under identical process conditions except for aspect ratio. The uniformity of the coating at aspect ratio of 3 is much better than that for aspect ratio of 7. Obviously, adjustments to the flux must be made to achieve the same uniformity as the aspect ratio is varied. Fig. 9.16 shows the observed effect of incidence geometry [16]. Since ionized atoms generally go straight down onto the substrate and neutrals have broad cosine type of distribution, the directionality of the incidence is increased from the left to the right. The low directionality at Fig. 9.16(a) results in an early feature closure while the high directionality leads to a complete fill.

Fig. 9.15. Effect of kinetic energy on trench filling. The AlCu films were deposited into trenches using ionized magnetron sputter deposition as a function of ion energy: (a) 20 eV; (b) 70 eV; (c) 120 eV. The relative ionization in these cases was approximately 50% [16].

Overall, the two key factors in achieving desired metallization are process geometry and diffusion. Manipulating incident distribution belongs to the geometry domain. Using ionized atoms aim to obtain better directionality. It hence can be said that PVD deposition in metallization is equivalent to a process of interplay of geometry and thermal diffusion. As diffusion generally does not have much room for change under normal process conditions, geometry manipulation becomes more important in reality. This explains all the efforts on using collimator, increasing throw distance and obtaining directionality.
It is interesting to ask how important the post impact atomic assembly processes are to liner deposition. A line-of-sight model can be developed to quantitatively predict the flux illumination of the interior trench. The energy-dependent kMC simulation can then be used to evaluate the role of thermal diffusion and kinetic energy upon coverage.

The basic idea of the illumination model is to obtain a criterion that can be used to characterize the easiness of any point in the trench to access the incident atoms under a given process. The criterion is thus a pure geometry factor and free of any influence of process conditions. In other word, it can be used to identify the intrinsic difficulty of metallization for a feature under the given process geometry.

As is shown in Fig. 9.17, any point on the top surface of the trench is open to the source incidence, thus it has the maximum incidence reach. We define this maximum incidence reach as unity. It is evident that incidence reach for any point inside the trench is less than unity most of the time (except for small aspect ratio feature and normal incidence deposition). A general expression that describes the incidence reach on all of the inside

Fig. 9.16. Effect of incidence distribution on trench filling [16]. The AlCu films were deposited into trenches using ionized magnetron sputter deposition as a function of relative ionization at ambient temperature: (a) approx. 30%; (b) approx. 50%; and (c) approx. 68% ionized. The trenches are 4,000 Å in width with aspect ratio of 1.5.
surfaces of the trench, Fig. 9.17, is what we need here. With such expression, we can compare with what we obtain from a real process. We can then identify where are those extra reach (or shortage) come from and what kind of measures we need take to make adjustment. The result is derived in Appendix E.

The curves in Figs. 9.18 and 9.19 are examples of using the expressions derived in Appendix E. Results are plotted by inserting trench size parameters $H$ and $L$, an incidence distribution and the various monitoring sites as shown in Fig. 9.17. In order to compare the effect of kinetic energy described presently, the curves in the two figures have the same conditions.

The curves show that flux illumination at the bottom of the trench decreases with increasing cut-off angle. The rate of decrease is particularly steep from 10 to 30°. Illumination of the upper sidewalls increases linearly with increasing the cut-off angle. The
level-off at the end is due to the monitor size. But the reach at the middle and the lower sidewalls have different trends. Both initially increase and then decrease after reaching a maximum. It is interesting to notice that the maximum from the lower sidewall curve identifies a range of cut-off angle (about $0^\circ \sim 12^\circ$) that enables a homogeneous flux illumination on the whole sidewalls. Likewise, the maximum from the middle sidewall curve identifies a range of cut-off angle (about $0^\circ \sim 22^\circ$) that enables a homogeneous incidence reach on the upper half of the sidewalls. Clearly, with increasing the cut-off angle, the segment with uniform reach would keep shrinking until it completely disappeared at a cut-off angle of $90^\circ$. It can be inferred that changing the trench aspect ratio would effect the special segment length as well. It is this type of changing flux illumination along the sidewall.

Fig. 9.18. Effect of incident cut-off angle on step coverage. The curve was predicted from the line of sight analysis. The symbols represent simulated data on various positions inside the trench. The simulations were done with temperature of 350 K ($T/T_m = 0.3$), deposition rate of 1.0 µm/min, aspect ratio of 5 and 15000 nickel atoms.
that makes a deposition process for any featured substrate intrinsically difficult. Thus unless very carefully controlled, the upper sidewalls always tend to receive more incident atoms.

To reveal the effect of kinetic energy in mitigating the intrinsic geometry limitation, one simulation with incident energy of 70 eV was compared to another with 0 eV using a trench with aspect ratio of 5. In both cases, nickel was the incidence species, relatively low temperature of 350 K was used to emphasize the effect of energy and the deposition rate was 1.0 µm/min. Both had incidence as a collimated cosine distribution and the same monitoring procedure was set up as in the analysis, Fig. 9.17. Finally, the simulation results were plotted along with the curves in Figs. 9.18 and 9.19 respectively.

Fig. 9.18 shows the points with 0 eV. The data for the simulated bottom coverage follow the curve fairly well. The deviation is rather small for $\theta < 40^\circ$ and becomes appreciable since then. This is caused by the formation of overhang at the upper corners which reduce incidence toward inside. The data for the upper sidewall has agreement only in the medium angle range. The maximum deviation for $\theta > 60^\circ$ comes from pinch-off formation. Significant deviation also occurs at small $\theta$ end. This is caused by shadowing, similar to Fig. 9.12(a). The coverage at the middle sidewall follows the analysis fairly well except that the data are consistently lower than the curve. This is due to a general effect of shadowing and the ever-increasing trench aspect ratio because of the constant increase of trench height and decrease of trench width with the deposition. On the contrary, the lower sidewall sees the points mostly above the corresponding curve. This should be an indication of surface diffusion from both the bottom and the wall. Overall, without the effect of kinetic energy, the analysis predicts fairly well the liner thickness inside a trench.

Fig. 9.19 shows the data with 70 eV. Significant differences can be found in comparison to Fig. 9.18. The coverage at the bottom has a similar trend, but points are now mostly above the curve. This is an indication of reflection and resputtering from the side
walls. At the upper walls, a significant difference is seen at the small angle range. The simulated data now are significantly higher than the predicted curve. The reason can be best seen from Fig. 9.12. Severe shadowing seen at low energy, Fig. 9.12(a), is greatly reduced at higher energy because of energetic interactions as in Fig. 9.12(c). The same great difference is also seen at the lower walls. This time, the extra material is due to the resputtering at the bottom, as shown in Fig. 9.13(a). At the middle walls, only overall coverage increase can be seen. Because of its long distance, it neither suffers great loss resulting from shadowing nor it can benefit from the resputtering from the bottom. Therefore, the coverage trends at the three locations under the influence of kinetic energy demonstrate why a concave shape is usually observed for liner coating. Also, the simulated
points in Fig. 9.19 are mostly above the curves, an indication that more than allotted mate-
rial (by the geometry) has entered the trench [161]. Evidently, the extra material comes
from the neighborhood space of the trench and can be discerned in Fig. 9.12.

In summary, the above analysis combined with atomistic simulation can be used to
reveal the interplay of process geometry and parameters in achieving a desired metalliza-
tion performance.

9.7 Conclusions

The energy-dependent kMC simulation was used to explore semiconductor metal-
lization process. The diffusion model, replacing previous diffusion parameter method, was
able to realistically simulate the effect of substrate temperature and deposition rate. The
impingement incorporating MD derived energy data, replacing practice of sticking coeffi-
cient assumption, was able to take into account the constant change of incident kinetic
energy and feature locality. The comprehensive approach indicates:

1) There exists an optimal incident kinetic energy for trench filling process. While
low kinetic energy induces little resputtering and reflection to redistribute incident atoms
into trench inside, high energy causes incident atoms redistribution mostly at the throat
areas. At an optimal energy, energy induced athermal diffusion and redistribution are com-
promised;

2) There is an optimal incidence distribution for metallization process. A pure nor-
mal incidence gives the best coverage at the bottom but not enough coverage at the upper
sidewall because of shadowing from the throat protuberances. An overly broad distribu-
tion tends to concentrate incidence at the trench throat. Only at certain distribution that the
coverage at the bottom and the sidewalls can be compromised;

3) The substrate temperature must be high enough to induce surface diffusion for
trench filling. Insufficient diffusion tends to accumulate incident atoms at the trench
throat. There is a correlation between temperature and deposition rate. Higher deposition rate reduces available time for atomic relaxation and thus requires higher temperature for compensation;

4) It has been shown that a good process conditions for a big trench may not suitable for a smaller trench with the same aspect ratio;

5) The typical concave shape on sidewalls in liner coating process results form resputtering from the trench bottom. The compensation effect decreases with increasing trench aspect ratio;

6) Combination of a line-of-sight geometrical analysis and an energy kMC simulation can be used to identify a proper process condition.
Chapter 10

Discussion

10.1 Introduction

This thesis has sought to use atomistic modeling methods to better understand the mechanisms of atomic assembly during physical vapor deposition processes. This chapter pulls these results together and examines their relevance for vapor phase processing. It discusses potential improvements to the modeling approach and points out future potentially rewarding researches.

10.2 Relevance for physical vapor deposition

Vapor deposition is an atom-by-atom assembly process. It can generally be envisioned as proceeding in four steps [115]. The first step involves the transport of the depositing species to the substrate. The second step involves the interaction (impact) of the incident atoms with the substrate. The third step involves the atomic surface diffusion over the substrate or growing film. Finally, it involves the atom’s eventual integration into the film configuration. The most important step among them is the atomic surface diffusion and has been the central modeling topic of the present work. For example, under low energy impact conditions and limited thermal diffusion, thin films formed from fluxes with a range of incident angles develop an often (but not always) undesired porous columnar structure, Fig. 5.4(a). Changes made to process conditions often aim at promoting desired diffusion. Changes of diffusion paths at the same time affect the integration process. As a result, efforts to design processes to achieve specific microstructural outcomes must involve a detailed analysis of diffusion and the means for its control.
The single most important parameter that affects atomic diffusion is substrate temperature. The substrate temperature provides atoms with constant thermal fluctuation that enables them to overcome activation barrier to reach stable sites and minimize system free energy. Since the atomic jump rate is exponentially dependent upon temperature (through Eqn. 3-1), the use of a low homologous temperature enormously restraints atomic mobility and results in porous columnar structure due to self shadowing. The kinetic Monte Carlo developed here enables a simulation of the experimental observation that increasing the temperature can very effectively transform a thin films structure from porous to a dense columnar structure, Fig. 5.4. The kMC model also reveals that in trench filling processes, the flux is more easily shadowed than on a flat surface that is perpendicular to the flux. As a result, a higher homologous temperature must be used for a complete trench filling, Fig. 9.7.

However, excessive surface diffusion can be harmful. Simulations of multilayered deposition reveal the formation of a surface instability for copper, Figs. 6.2 and 6.4. The kMC model allowed the mechanisms responsible for this to be effectively analyzed and an optimum growth condition window in process parameter space to be identified. The effectiveness of thermal diffusion also depends on deposition rate. A high deposition rate reduces the time available for atoms to assembly into a more equilibrium structure. The limited mobility attendant with high rate depositions results in a reduced column width for deposition on flat substrates, Fig. 5.9, and the formation of overhangs, and eventually internal void formation during trench filling, Fig. 9.8. Process geometry is another factor having very significant effect on thermal diffusion. As shown in Fig. 9.3, a very broad incidence distribution tends to facilitate deposit build-up at the throat of a trench. When a pinch-off forms, it then becomes impossible for any material to migrate down into the trench.
Low homologous temperature deposition is often necessary to avoid interdiffusion with substrates or other layers (e.g. the growth of GMR multilayer). In such situations, the atoms kinetic energy can be employed as a means to provide atoms with extra mobility (over that associated with thermal diffusion). The hyperthermal kMC model developed here enabled many of these mechanisms to be addressed. By minimizing thermal diffusion and controlling adatom energy, flat films with kinetically limited structures can be achieved, Fig. 8.2. This concept, when combined with flux directionality control can be used to directional induce mobility. Fig. 8.5 predicts the surface roughness under different incidence directions and the optimal angle can be identified. During the filling of trenches such concepts provide an opportunity to create new deposition processes for filling features whose widths can be reduced to 25 nm.

Atomic assembly is clearly a critical phenomenon to control. Because so many factors contribute, it is very costly and slow to rely only on experiments to map out the best process route in laboratory. It is logical and convenient to make increasing use of the kMC models developed here. However, simulation should not be treated as a substitute for all experiments, its primary value is prediction of structure trends with process design variables. For example, it can be difficult to intuitively account for the dual role of kinetic energy in trench filling processes. Simulations help to identify the existence of an optimal process for best filling performance, Fig. 9.8. It has been shown that the process parameters that work best for a large trench width may not work as well for a small trench under identical process conditions and aspect ratio. As trench widths continue to decrease, atomistic simulations may be the best means to identify candidate processes, Fig. 9.12 and 9.13. In long-throw deposition, kMC simulation can readily predict the geometry related incidence illumination and mobility asymmetry and the impact of process parameters upon them. Such prediction can help eliminate much experimental trial and error and speed the discovery of an optimal set of process parameters.
Other examples of the beneficial use of kinetic Monte Carlo simulation were found during the analysis of continuous liner layer deposition. This is a key step in the creation of copper interconnects and can be difficult to achieve without over depositing the liner in some regions (which precludes these regions for subsequent conduction during use of a device). The kMC simulation methodology can be used to identify specific contributions from each assembly mechanism. For instance, the unexpected thickness at the lower corners resulted from atomic respattering at the bottom, Figs. 9.12 and 9.13. Other factors can be similarly analyzed. Therefore, an optimal process window can again be mapped out.

10.3 Growth kinetics manipulation

One of the benefits of doing computer simulation is that when a well developed model is available, numerous virtual vapor depositions with different arrangements of process parameters can be rapidly conducted on computer monitor so that new concepts can be generated or confirmed to guide real experimental explorations. For instance, as described earlier, low temperature condition tends to greatly restrain adatom mobility, and many small islands are nucleated which promotes a porous columnar structure. However, while the use of a high temperature can greatly increase the adatom mobility, this frequently leads to columnar structures with long wave length roughness. Both approaches can generate undesired structures for GMR devices. It has been suggested [169] that if a small atom fluency is used to seed a surface with many islands at low temperature, then completion of the layer at higher temperature may enhance mobility at high temperature and result in a smoother surface than could be obtained by a constant deposition temperature process. Such a proposal can be quickly confirmed by employing kMC simulations.

As an example, consider the nucleation of a thin film. The 2D kMC model can be generalized to 3D in a straightforward way. Instead of defining a 2D lattice plane of occupiable states, a 3D cube of lattice points can be defined. Local atom configuration dependent mobility barriers can be defined (see Appendix F). Figs. 10.1 and 10.2 show
configurations that are simulated using the technique. Fig. 10.1(a) is a configuration of low energy vapor deposition of 5000 nickel on (100) plane at 500 K. Fig. 10.1(b) differs from Fig. 10.1(a) in that 500 atom is first deposited as seeds at 350 K and 4500 atoms is subsequently deposited at 500 K.

It can be seen that the second configuration with seeding has significantly fewer atoms on the second layer and much improved surface coverage on the first layer because of more atoms on the layer and more initial nucleation centers formed at lower temperature. A systematic simulation result is shown in Fig. 10.2 in which seven different seeding temperatures have been used at otherwise identical condition as that used in Fig. 10.1(b). The plot reveals a convincing pattern on the relationship of the number of atoms at the second layer versus the seeding temperature. With seeding at identical temperature of 500 K (equivalent to no seeding), the number at the second layer has the maximum value at about 1000 atoms. With decreasing the seeding temperature from 500 K to at 350 K, the atoms at the second layer decrease rapidly and steadily. Continuing to decrease the temperature shows less significant effect and eventual saturation. As a result, computer
The idea behind the improvement can be explained as follows. There generally exist two types of diffusions, intralayer diffusions and interlayer jumps. Intralayer diffusion controls the uniformity in the horizontal direction; interlayer mass transport controls the uniformity in the vertical direction. A smooth growth front can only be maintained if sufficient interlayer mass transport occurs during growth. Sufficient interlayer mass transport depends on more atoms having more chance to jump off edges. Low temperature seeding creates more small islands in the first incomplete layer. High temperature deposition enables atoms on top of smaller islands to visit island edges more frequently, thereby increasing its downward jumping chance.
Chapter 11

Future Directions

11.1 Modeling issues

Generally speaking, simulation results presented in the thesis mimic reasonably well many of the observations of the real world. This indicates that key aspects of the process are well treated and useful to a certain extent. When the details are reexamined at each step, however, we must realize that major assumptions and simplifications have been made in conducting the simulations. It is important to take one more look at them in order to make improvements in the future.

First, the biggest simplification in this thesis has been the use of two dimensional model to represent three dimensional phenomena. The 2D model can in many cases well represent what is observed in reality. The simulation of transitions observed in the structure zone model in Fig. 5.4 is one example. The correct prediction of liner coating thickness profile in Fig. 9.13 is another. Generally, when the microstructure details are not important and only the general trend is of concern, a 2D model is well grounded.

However, in many other situations the detailed atomic process is important, and a 2D model is inappropriate. A frequently encountered phenomenon is the formation of crystal facets in which low surface energy planes tend to survive while high energy planes disappear. In this case, a 2D model is impossible to handle the three dimensional growth. As indicated in the previous chapter, the 2D multi-mobility path kMC methodology can be straightforwardly extended to 3D. Fig. 11.1 shows a 3D kMC simulation of the deposition of nickel atoms onto a small nickel sphere at two different substrate temperatures. The
incident atoms are added uniformly from all directions. The deposition rate is the same and only thermal diffusion is simulated. It can be seen that at 500 K the (111) and (100) planes are equally developed. At higher temperature of 550 K the (111) planes which has lower surface energy expands at the expense of (100) planes which has higher surface energy. Therefore a 3D simulation can be used to investigate the effect of process parameters on crystal external shape. This can be significant for present interconnect metallization at quarter micron scale because filling of trenches and vias may be limited by the \{111\} faceting among others [54]. Nevertheless, a 3D kMC simulation is much more complicated than a 2D counterpart in terms of activation barrier energy calculation and computation time consumption. Unless absolutely necessary, a 2D model is likely to be preferred for many phenomenological explorations.

The second major simplification in kMC model is its use of an Ising lattice. Up to date, lattice model is a rule rather than an exception in simulation community. It facilitates

Fig. 11.1. kMC simulation of effect of substrate temperature on facet formation. The simulation began with a nickel sphere and incident atoms were introduced from all directions in the space. The deposition rate was fixed at 1.0 µm/min. The substrate temperature was (a) 500 K and (b) 550 K. Low surface energy planes of (111) and (100) are indicated.
program implementation, reduces calculation, and more importantly makes critical activation energy calculation much simpler. When trend prediction rather than quantitative comparison with the real world is the criterion, it can often give quite satisfactory results. Using lattice model should be regarded as the first choice in this type of modeling practice: keep it simple and yet retain the essential elements of the thermally competing activated process in place. When it becomes affordable to use an off-lattice model in terms of model fundamentals and computation power, it is inevitable for off-lattice to develop in the future. An off-lattice model enable more complex phenomena to be explored, such as a true grain growth process and stacking fault formation. Ultimately, the real world is in off-lattice and simulation in off-lattice thus is one step closer to reality.

The third major simplification is the estimation of activation energy. Early days work on atomistic treatment often used break-bond model (or bond-counting), such as in the quasi-chemical model [162], SOS models [41] and kMC models [49]. When atoms are adjacent with each other in condensed matter, bond-counting is the most logical guess. The assumption is that bonds between atoms are independent of each other. Or, the strength of one bond is considered unaffected by the presence of other bonds. The bond-counting approach was often modified by adding a correction term [49, 114]. The molecular statics was next used to give more realistic account of the neighbor dependence nature, as used in this work. MS method maps out the jump activation energy along a route from the starting site to the ending site and identify the saddle point as the jump path activation barrier, Fig. 3.4. To use MS method, one has to have an empirical interatomic potential first such as pair potential or EAM. Cut-off distance at the nearest neighbor are often used in the calculation. MS calculation eliminates the oversimplification of bond-counting method and is relatively fast to execute. Today, density function theory (DFT) seems to be the choice [163, 164]. By definition, calculation at the electronic level should have the best fidelity. The fidelity comes at the expense of much more intensive computation.
Would more sophisticated activation energies be a guarantee for better kMC simulation? The answer depends if you compare one simulation with another or with direct observations. When the comparison is made with experiments, the question would be if the activation energy is the only determining factor. In reality, intensive island mobility can compromise the effect obtained from site-to-site atomic jump. Contamination is inevitable. And in most cases thin films have polycrystalline structure. Thus when a simulation is done even with the most sophisticated energy data, the result might be very different from a direct observation. For example, the STM measurements [51, 165, 166] showed that the islands formed after the deposition of a sub-monolayer of silicon on the Si(100) surface were thin, long, and parallel to each other and consisted mainly of one or two dimer rows. The preference for this shape was intriguing, especially because the thin islands were perpendicular to the direction of rapid migration. The kinetic stability of these islands is incomprehensible unless a mechanism is found by which the large number of particles reaching the island’s long shore is transported to its short side. Clearly, whether or not a barrier energy data is sophisticated is not the most critical factor. To get the mechanism correct actually takes priority. This will be further illustrated in the following point. Sophisticated barrier data is important, but not essential. What really matters is to use reasonably obtained barriers (such as model potential-based MS calculation) and direct observation together to produce models having desired predictive power.

The fourth critical simplification lies in the very heart of the kMC model. The basic kMC assumption is that atoms move only between nearest neighbor sites without considering correlated motion. Correlated motion such as island mobility can be significant at high substrate temperature [167]. Presumably, we need information on island activation energies and a set of island move rules to include them. Presently, there is no effective means to do such direct simulation. On the other hand, we need to know if current kMC simulations themselves have already inherently incorporated such island mobility.
Fig. 11.2 shows the simulation that was specifically set up to test island mobility. At the starting point, seven nickel atoms are simultaneously deposited onto a 100×100 Ni (111) substrate. The atoms then start to diffuse at a temperature of 500 K with diffusion time of each subsequent configuration being ten times longer than the previous one. It can be seen that two islands (three and four atoms in size respectively) are initially formed respectively and become coalescence very quickly. The island then migrate as a whole. This is a clear evidence that kMC is able to simulate island mobility. So far there is no report in literature in kind. A report by Raeker and DePristo [63] simulated the mobility of Fe island on Cu (111) at 300 K. In the simulation, the island mobility rates were first extracted from MD calculations beforehand. For example, the jump rate for a seven-atom cluster had a rate of 0.002 jumps/ps.

It is logical to assume that islands of different size have their characteristic activation energies. Thus at low temperature, big islands would not have noticeable mobility. To confirm this, simulation has been conducted at 400 K for the same seven-atom Ni cluster at the identical set-up and indeed no significant mobility was observed. However, is this type of island mobility realistic? Can island activation energies that may be extracted from such simulations be used in such process as reflow application? The answers are obviously difficult. In such situations, direct observation is critical to guide any credible simulation efforts. Also, while present simulations are either pure continuum or pure atomistic nature, it is conceivable that hybrid methods would be important in the near future to combine continuum methods that model macro-scale phenomena and atomistic methods that simulate micro-scale phenomena.

The fifth simplification is related to a method that is capable of joining MC and MD to include all controllable process parameters. It appears that no model can reliably cover every aspect of a deposition process such as ionized PVD. Neither MD nor kMC can handle it alone. The natural process then is to explore if these two methods can be joined
Fig. 11.2. Island mobility simulation. Seven nickel atoms were initially deposited onto nickel (111) substrate at the same time and diffused at 500 K. The diffusion time for each subsequent configuration was ten times longer than its previous one. By the time when step 1 started, the seven atoms have formed a 3-atom and a 4-atom cluster. The two clusters remained separately after the step, indicated by the arrows. They coalesced into a single cluster at step 2 and moved together since then at step 3 and step 4.
together in some type of approximation. Few efforts so far have appeared to address such possibility.

An ideal approach should be a direct combination of the strengths from both MD and kMC, as done by Jacobsen, Cooper and Sethna [140]. They used MD to introduce energetic incident atoms onto substrate and kMC to follow thermal diffusion. Although it looks ideal, major difficulty remains. First it is very computationally demanding. Most of the time is spent on MD runs for introducing new energetic atoms. Even for a relatively small surface areas, a thousand to a few thousands of MD simulations are needed per monolayer. In order for the method to be feasible, it is essential that the island density not be too low. Big islands require a larger surface area and hence a larger number of MD simulations per monolayer. The simulations ran for weeks to months on reasonable high end workstations per monolayer deposited. Another major concern is the lattice nature of the kMC. When relative large energy is used, the lattice cell would inevitably be disrupted. Atoms originally located at regular lattice sites would be displaced to off-lattice sites. Defects can be generated. It is very difficult for lattice model to handle them. Another work of the type was done by Coronell et al [168] which simulated interconnect metallization. Their approach was similar to what has been used in the current thesis except that they did not consider athermal diffusions caused by thermal spike and biased diffusion.

Exactly which approach would be used should be problem-dependent. In metallization processes involving possibly millions of atoms, a true kMC-MD combination may not be realistic for computational expense alone. If any possibility, it might be limited for calibration along with direct observations. As for the early stage simulation of thin film growth, a direct kMC-MD combination probably is the way to go. One more caveat is: energetic atom often induces very distant biased diffusion and MD simulation cell has to be cut-off to keep the CPU time reasonable [140].
In summary, five major simplifications often exist in Monte Carlo simulation in order to capture the essential features of vapor deposition. It is these simplifications that make the modeling possible and it is the same simplifications that need to be refined to make the model better.

11.2 Summary

Through five major simplifications as described above, this thesis has mapped out a possible route to simulate physical vapor deposition. The simulation results have given reasonably good qualitative-nature prediction on a number of fronts in thin film growth applications. As more powerful computers and more advanced microscopic instruments become available, quantitative simulations are inevitably desired in order to give more accurate prediction of microstructure evolution. Toward this end and based on what we have learned in the thesis, the following topics seem important to refine the kinetic Monte Carlo method.

First, it is necessary to obtain more accurate activation barrier energies. The barrier energy is the core of any quantitative kMC simulation. It is not a problem to use model potential-based molecular statics or any other coarser method like bond-counting to predict a qualitative trend, but it takes basic method such as density function theory to get more faithful numbers. More importantly, it is imperative that the results of the simulations are compared with direct observation using such tool as scanning tunneling microscope. If the simulation does not agree with the observation, appropriate corrections have to be made on barrier energies even if they are calculated from DFT method. Second, it is important to clarify some delicate atomic mechanisms. This is closely related to the first topic and it also takes careful direct observation for determination. This determination step may be the real core of any modeling approach. Because only when one knows how atoms naturally move, one knows how to calculate the related parameters. Third, a three-dimensional off-lattice model is an obvious requirement for accurate comparison with observa-
tion. Absolute off-lattice Monte Carlo model is unrealistic. Otherwise it becomes molecular dynamics method. The reasonable approach may be to identify some typical crystal defects and to define a limited off-lattice alternative according to such defects. Off-lattice simulation probably is best for the early stage nucleation and growth of vapor deposition. Finally, there is a need to couple the kMC and MD method for a complete thin film growth simulation. The essence of such coupling is that the outputs of MD automatically become the inputs of kMC. Therefore, care must be taken to guarantee that the two models must match at the “boundaries” at which they meet. Such boundaries may include the atomic positions and oscillation magnitudes.

In essence, the future generation model would mimic and predict the reality better than today. This entails more details, less simplifications and close interaction between modeling and observation.
Chapter 12

Conclusions

A kinetic Monte Carlo method has been developed to analyze multipath thermally activated diffusion. It evolves atomic configurations by identifying their thermally activated atomic jump paths and implements a probabilistic scheme for their subsequent execution. In applying the kMC method to the analysis of film growth, the likelihood that an atom jumps from one lattice site to another depends upon its local atomic configuration which can be characterized by an activation energy and a jump attempt frequency. The simulation first deduces the set of jump probabilities for every allowed jump path using precalculated activation energies and then executes jumps according to their relative probabilities. After a jump is executed, time is advanced by a computational time step determined by the residence time of the system, i.e. the reciprocal of the sum of the jump rates for all the allowed jump paths of the system. This process is then repeated until the time between atom arrivals is exhausted. A new atom is added and the algorithm iterated. By using this new approach to kMC, the time scale discrepancy among different rate processes that was once considered as major modeling difficulty has been resolved. The kMC enables a realistic simulation of the effects of substrate temperature and deposition rate.

The kMC model is used to simulate low energy vapor deposition on a flat substrate. The simulation results reveal a transition from a porous columnar structure to a fully dense columnar structure consistent with the structure zone model. The transition was found to occur at a higher temperature as the deposition rate increased. The width of the columns in the simulated microstructure appears to correlate well with grain size, and
the temperature dependence of the width correlates closely with experimental grain size data for many metals. This suggests that a Monte Carlo simulation that uses the activated processes of atomic surface diffusion can predict well the trends in microstructure/morphology evolution.

The kinetic Monte Carlo method has been extended to explore the growth of Ni/Cu/Ni multilayers under conditions where atomic assembly occurs only by thermal diffusion. The method exploits an EAM-based potential to calculate alloy activation energies which takes into account both coordination and chemistry of the neighboring atoms. The simulation has shown that surface roughness increases almost linearly with increasing growth thickness. The roughness is more a result of depositing a nickel layer than depositing a copper layer. Depositing copper helps to smooth nickel layer. Simulation has shown that there is an optimal growth window for Ni/Cu/Ni multilayer deposition. The window lies in a region between two extreme corners on a substrate temperature-deposition rate process map. While one corner with high deposition rate and low temperature is characteristic of porous columnar structure, the other corner with low deposition rate and high substrate temperature is characteristic of surface instability. An analysis showed that the surface instability results from a flow of upside reverse Schwoebel jumps that become active beyond certain temperature threshold.

The kMC model is extended to treat energetic atom impact effects upon atomic assembly by reducing recent MD results. The MD method solves for the trajectories of each atom in a crystal by integrating Newton’s equations of motion using an interatomic force law. The lattice atom vibration is explicitly obtained in this approach and the forces on atoms are calculated several times per lattice vibration period. As a result, it rigorously incorporates the atomic assembly mechanisms initiated by the high kinetic energy atom impacts, many of which are completed in less than a few picoseconds. By using MD method’s dynamic nature, the effect of incident kinetic energy was included and various
energy-dependent data was formulated as empirical equations. A special procedure was then used to incorporate the MD data into the kMC algorithm. This includes the incorporation of reflection, resputtering, biased diffusion and athermal diffusion induced by thermal spike.

The energy-dependent kMC model has been used to analyze deposition on a flat substrate. The contributions of the energy-dependent mechanisms to surface morphology were found to grow in importance as the substrate temperature is reduced and/or as the rate of deposition increased. The simulation methodology was used to establish functional relationships between surface roughness and the atom’s kinetic energy and direction of incidence during the hyperthermal deposition of nickel vapor. The simulations reveal the existence of a minimum surface roughness at an incident angle which increases as the impact atom kinetic energy and substrate temperature are increased and/or as the deposition rate decreased. Modification of the impact energy was shown to be a viable method for controlling surface morphology during hyperthermal PVD process under high deposition rate, low deposition temperature growth conditions.

Finally, the energy-dependent kMC simulation was used to explore the filling of trenches with metals. The use of kMC diffusion model instead of previous diffusion parameter treatment realistically links the effect of substrate temperature and deposition rate. The approach has been used to correctly predict trends in trench filling and liner coating. In particular it reveals that: (1) There exists an optimal incident kinetic energy for trench filling. While low kinetic energy induces little resputtering and reflection to redistribute incident atoms within the trench, high energy results in incident atoms redistribution only near the trench throat. The optimal energy occurs when energy induced athermal diffusion and redistribution are balanced; (2) There exists an optimal incidence atom angle distribution for metallization of trenches. A perfect normal incidence gives the best coverage on the trench bottom but insufficient coverage on the upper sidewalls because of shad-
owing by trench throat protuberances. An overly broad angular probability distribution tends to concentrate deposition at the trench throat. Best filling occurs for fluxes that contain atoms making impact within ±11° of the surface normal; (3) The substrate temperature must be high enough to induce surface diffusion for complete trench filling. Insufficient diffusion tends to accumulate incident atoms at the trench throat. There is a correlation between temperature and deposition rate. Higher deposition rate reduces available time for atomic relaxation and thus requires higher temperature for compensation; and (4) It has been shown that the best process conditions for a wide shallow trench may not be suitable for a smaller width trench, or one of different aspect ratio.

In looking forward, several improvements to the kMC method have been identified. It is important to obtain accurate experimentally validated activation barrier energies. The barrier energy is the core of any quantitative kMC simulation. It is imperative that the results of the simulations are compared with direct observations using such tools as scanning tunneling microscope. It is important that all important atomic assembly mechanisms are captured. Monte Carlo approaches can only be valid when they capture all of the ways in which atoms manage to move during vapor deposition. Extension to a three-dimensional model in most cases is an obvious requirement for accurate comparison with observations. There is also a need for an off-lattice model. Off-lattice simulation probably is best for the early stage nucleation and growth of vapor deposition. Finally, there is a need to couple the kMC and MD method for a complete thin film growth simulation. The essence of such coupling is that the outputs of MD calculations could automatically become the inputs of kMC simulations. Therefore, care must be taken to guarantee that the two models must match at the “boundaries” at which they meet. Such boundaries obviously include the atomic positions and oscillation magnitudes.
References

43. This is obtained using the dilute-solution approximation relating the chemical potential and the concentration $C$ in the vapor, $\mu - \mu^{(e)} = kT \ln C/C^{(e)}$, where the superscript denotes an equilibrium quantity.
References

81. R.A. Johnson, private communications.
83. R. Fletcher, and C.M. Reeves, Computer J., 7, 149 (1964).
89. The system residence time depends on the system size and process parameters and would obviously be infinitely small when a system is infinitely large. A system residence time of 10^{-12} second can be recorded when a deposition of 5000 nickel atoms is conducted on a trench substrate of 100\times100 atoms on (100) plane with aspect ratio of 1 at a temperature of 550 K. The system residence time is very different from the single jump path’s residence time. In any competing thermally activated diffusional processes, the single jump path can have order of magnitudes different path residence times for different jump paths, as shown in Table 3-2. However, the system residence time is relatively stable.
91. X.W. Zhou, private communications. Zhou is attempting to combine kinetic Monte Carlo method for thermal diffusion and SIMBAD model [48] that approximates initial placement of incident atom. In this way, the initial adatom diffusion may presumably be simulated with a reduced CPU time.
141. For example, the residence time for nickel adatom jump at 350 K is 1.25 micron seconds and that for bulk vacancy is 93 minutes, as shown in Table 3-2.
142. R. E. Johnson, in Energetic Charged-Particles Interactions with Atmospheres

143. To investigate the effect of rough surface on biased diffusion resulting from energetic interaction, molecular dynamics simulations using embedded atom method interatomic potential were conducted. Smooth surface was first used at different combinations of incidence angle and energy and the results were compared with those conducted on surfaces with various defects, which include simple ledge, double ledge in both the uphill and downhill set-ups, single line of surface atoms and vacancies. Simulations indicated that surface defects greatly affect the surface diffusion and biased diffusion distance data have very significant spreads depending upon the impingement sites.

161. Kwok Fai Lai (Novellus), private communications.
163. William Butler, private communications.
164. Hongmei Wen, private communications.
167. J.M. Howe, private communications.
Appendix A

The Ising Model

In metals like Fe and Ni, a finite fraction of the spins of the atoms becomes spontaneously polarized in the same direction, giving rise to a macroscopic magnetic field. This happens, however, only when the temperature is lower than a characteristic temperature known as the Curie temperature. Above the Curie temperature the spins are oriented at random, producing no net magnetic field. As the Curie temperature is approached from both sides the specific heat of the metal approaches infinity. The transition from the non-ferromagnetic state to the ferromagnetic state is a phase transition of a kind not included in the Ehrenfest classification of phase transitions.

The Ising model [A1] is a crude attempt to simulate the structure of a physical ferromagnetic substance. Its main virtue lies in the fact that a two-dimensional Ising model yields to an exact treatment in statistical mechanics. It is the only nontrivial example of a phase transition that can be worked out with mathematical rigor.

In the Ising model [A2] the system considered is an array of $N$ fixed points called lattice sites that form an $n$-dimensional periodic lattice ($n = 1, 2, 3$). The geometrical structure of the lattice may be cubic or hexagonal. Associated with each lattice site is a spin variable $s_i$ ($i = 1,..., N$) which is a number that is either +1 or -1. There are no other variables. If $s_i = +1$, the $i$th site is said to have spin up, and if $s_i = -1$, it is said to have spin down. A given set of numbers \( \{s_i\} \) specifies a configuration of the whole system. The energy of the system in the configuration specified by \( \{s_i\} \) is defined to be

\[
E_I\{s_i\} = -\sum_{ij} \epsilon_{ij} s_is_j - B \sum_{i=1}^{N} s_i
\]  

Aa-1
where the subscript $I$ stands for Ising and the symbol $<ij>$ denotes a nearest-neighbor pair of spins. There is no distinction between $<ij>$ and $<ji>$. Thus the sum over $<ij>$ contains $\gamma N/2$ terms, where $\gamma$ is the number of nearest neighbors of any given site. The interaction energy $\varepsilon_{ij}$ and the external magnetic field $B$ are given constants. The geometry of the lattice enters the problem through $\gamma$ and $\varepsilon_{ij}$. The ordering tendency of this interaction energy is of course opposed by the entropy, which favors a random disorder of the $s_i$ values.

Refinements of the basic Ising model can include the effects of interactions between more distant neighbors, as in the ANNNI model (axial next nearest neighbor Ising) [A3].
Appendix B

The Metropolis Algorithm

The Metropolis algorithm [A7] for generating a thermal equilibrium ensemble of configuration states, at a specified temperature, for an array of atoms is used frequently in materials science work. It can be best illustrated using a binary alloy which is depicted schematically in Fig. Ab.1 [A8]. The open circles represent one type of atom and the filled circles another type. It is traditional to call these two types $A$ and $B$ atoms. Here we assume that the atoms must occupy sites on a triangular lattice and that we know the interaction energies $\varepsilon_{aa}$, $\varepsilon_{bb}$, and $\varepsilon_{ab}$ for the interaction of two $A$ atoms, two $B$ atoms, and an $AB$ pair, respectively.

![Binary alloy](image)

Fig. Ab.1. A binary alloy, in which open circles represent type-A atoms and solid circles represent type-B atoms.

The algorithm proceeds as a series of repetitions of the following process:

1. Select two atoms $I$ and $J$ from the array at random;
2. Compute the interaction energy $E_b(I)$ for atom $I$ and the interaction energy $E_b(J)$ for atom $J$;
3. Interchange the positions of atoms $I$ and $J$;
4. Compute the interaction energy $E_a(I)$ for atom $I$ and interaction energy $E_a(J)$ in their new positions;
5. Determine \( \Delta E = (E_a(I) + E_a(J)) - (E_b(I) + E_b(J)) \).

6. If \( \Delta E \) is negative, retain the new configuration given by the interchange;

7. If \( \Delta E \) is positive, compute \( \pi = \exp(-\Delta E/kT) \) where \( k \) is Boltzmann’s constant and \( T \) is the absolute temperature;

8. Select a random number \( \xi \) from the unit interval \([0, 1]\);

9. If \( \xi \) is less than \( \pi \), retain the new configuration given by the interchange; otherwise reject the new configuration.

This process generates an ensemble of configuration states. The ensemble average energy provides an estimate of the average energy for the system at temperature \( T \).
Appendix C

Surface Roughness Definition

There are two types of surface roughness measurements, the standard deviation roughness [A5] and the roughness factor measured by the ratio of the real to geometric area [A6].

The surface roughness $W$ defined by standard deviation of the surface height is as follows: $W^2 = \sum N^{-1} (h_i - \bar{h})^2$, with $\bar{h}$ the average height of the surface layer, $h_i$ the height of $i$th site and $N$ the total number of surface sites. As for the roughness factor, the real surface area of a thin film is generally measured by the well-known BET (Braunner-Emmet-Teller) method in which the volume (which is proportional to the surface area) of a suitable gas adsorbed on the film is measured. This factor approaches unity for epitaxial film and films deposited at elevated temperatures. Values as high as 100 are obtained for films condensed at low temperatures or at oblique incidence [A6]. In kMC simulated films, the real area refers to the area covered by the surface atoms.

Introduction of two roughness concepts is based on the fact that each method measures a different aspect of the thin film surface property. This can be illustrated as follows.

Fig. Ad.1 is a two-dimensional hypothetical thin film surface with ten atoms as substrate and five atoms are deposited on top of it. Two modes of assembly are assumed. One puts the five deposited atoms in a layer-by-layer growth mode, Fig. Ad.1(a), and the other in hit-and-stick mode, Fig. Ad.1(b). Clearly, the first one should have the least surface roughness no matter how the roughness is measured and the second one should have higher roughness.
According to the definitions, we can readily calculate the roughness using the two different approaches. First take a look at the deviation approach. Assume the inter-layer distance is $d$ and the first layer has a height of 0; then the second layer has a height of $d$. Because the layer-by-layer mode has 11 atoms as surface atoms and the second one has all of the 15 atoms as surface atoms, the average height of the surface atoms is $(5d/11)$ for the first one and $(d/3)$ for the second. By using the deviation formulae listed above, it can be obtained that the deviation roughness for the layer-by-layer is $0.5d$ while that for the hit-and-stick growth mode is $0.47d$. It is surprised to notice that a perfect layer-by-layer growth mode has a “rougher” surface than a real rough surface.

It is evident that the layer-by-layer surface has a roughness factor of 1.1 (the perfect flat surface has 1.0) and the hit-and-stick growth has a roughness factor of 1.5. The roughness factor measurement clearly better reflect the reality while the deviation is not. Thus the roughness factor approach better reveals the micro-scale roughness. In other case, the deviation measurement is better to measure macro-scale roughness.

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*Fig. Ad.1. Two hypothetical thin film surfaces with (a) the deposited atoms and the substrate form a layer-by-layer growth mode; (b) the deposited atoms and the substrate form a hit-and-stick growth mode.*
Appendix D

Tables of Fitted Equations to MD Nickel Calculations

The following three tables are results of nickel atom-substrate interactions under similar conditions to those obtained for copper shown in chapter seven. The fitted equations also take similar formats.
### Table A-d1 Fitted Equations to MD nickel reflection calculations

<table>
<thead>
<tr>
<th>Eqn. No.</th>
<th>Equations</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>$Y_{rf}(\theta) = \min\left{1, p + p \cdot \sin\left[90.0 + 180.0 \left(\frac{\theta - \theta_c}{\theta_m - \theta_c}\right)\lambda\right]\right}$, $\theta \geq \theta_c$</td>
<td>$\theta_c = 22.0^\circ$, $\theta_m = 72^\circ$, $p = 0.55$, $\lambda = 1.43$</td>
</tr>
<tr>
<td>(2)</td>
<td>$Y_{rf}(E_i) = 1.0 - \exp\left[-\left(\frac{E_i - E_{ic}}{p}\right)\lambda\right]$, $E_i \geq E_{ic}$</td>
<td>$E_{ic} = 15$ eV, $p = 31.5$, $\lambda = 2.03$</td>
</tr>
<tr>
<td>(3)</td>
<td>$Y_{rf}(E, \theta) = \frac{Y_{rf}(E)}{Y(E_i = 70.0 eV)}$</td>
<td>$\beta = 1.38$, $G_i = E_i - 39.1 +</td>
</tr>
<tr>
<td>(4)</td>
<td>$\rho(\xi) = \rho_n(\xi - \theta_l)^\alpha (90.0 - \xi)^\beta$ where $\alpha = \frac{\beta(\theta - \theta_l)}{90.0 - \theta}$, $\theta_p = \min\left{90.0, \theta + \frac{90.0 - \theta}{90.0} \cdot \frac{18.6 G_i}{G_i + 2.0}\right}$, $\theta_l = \max\left{0.0, \theta - 15.1 - \frac{1.3 \times 10^4}{E_i^2}\right}$</td>
<td>$p_n = \text{normalization factor}$ (integral of $\rho$ equals 1).</td>
</tr>
<tr>
<td>(5)</td>
<td>$\rho(E) = \rho_n E^\alpha (E_i - E)^\beta$ where $\alpha = \frac{\beta E}{E_i - E}$, $E_p = (c \cdot E_i + E_\theta) \sin\left[\frac{90.0(\theta - \theta_\theta)}{90.0 - \theta_\theta}\right]$</td>
<td>$\beta = 2.1$, $c = 1.07$, $E_o = -13.39$, $\theta_o = 50.8^\circ$</td>
</tr>
</tbody>
</table>
### Table Ad-2 Fitted Equations to MD nickel resputtering calculations

<table>
<thead>
<tr>
<th>Eqn. No.</th>
<th>Equations</th>
<th>Parameters</th>
</tr>
</thead>
</table>
| (6) | Resputtering yield as a function of $\theta$ at $E_i = 70.0$ eV:  

$$Y_{rs}(\theta) = p + p \cdot \sin \left[ \theta \left( 90.0 - \theta \right) \left( \frac{\theta}{\theta_m} \right)^{\lambda} \right],$$  

$$\theta \leq \frac{270.0 - \theta}{90.0 - \theta} \left( \frac{1}{\lambda} \right)$$  

$p = 0.28, \lambda = 1.93, \theta = -40.9^\circ, \theta = 40^\circ$ |
| (7) | Resputtering yield as a function of $E_i$ at $\theta = 40^\circ$:  

$$Y_{rs}(E_i) = p \cdot \exp \left( -\frac{E_i}{E_i} \right)$$  

$p = 0.60, E_f = 44.7$ eV, $\lambda = 5.93$ |
| (8) | Resputtering yield as a function of incident angle and incident energy:  

$$Y_{rs}(E_i, \theta) = Y_{rs}(\theta) \frac{Y_{rs}(E_i)}{Y_{rs}(E_i = 70eV)}$$ |
| (9) | Angular distribution of resputtered atoms:  

$$\rho(\xi) = c \cdot \exp \left[ -\lambda(\xi - 45.0)^2 \right]$$  

$c = 0.031, \lambda = 0.003$ |
| (10) | Energy distribution of resputtered atoms as a function of incident energy:  

$$\rho(E) = p \cdot E^\alpha \exp \left( \frac{\alpha}{E_m} E \right),$$  

where $\alpha = \alpha_o + c \cdot \exp(\lambda((G_i + [G_i]) / 2))$,  

$$E_m = 3.8 + 6.2[1.0 - \exp(a((G_i + [G_i]) / 2))]$$  

$G_i = E_i - 38.0, \alpha = -0.027, c = 1.9, \alpha_o = 2.0, \lambda = 0.124$ |
### Table Ad-3 Fitted Eqns for Local Effective Temp. and Biased Diffusion Distance

<table>
<thead>
<tr>
<th>Eqn. No.</th>
<th>Equations</th>
<th>Parameters</th>
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</thead>
</table>
| (11) Biased diffusion distance: | \[ d(\theta, E_i) = z E_i^\lambda \theta^\nu \left[ 1 - \frac{1}{2} \left( \frac{\theta}{\theta_m} \right)^\nu \right] \]  
where \( \theta = 81.0 - 30.0 \exp(-0.18 E_i) \) | \( Z = 1.31 \times 10^{-7}, \lambda = 1.16 \)  
\( \nu = 3.83 \) |
| (12) Local effective temperature due to latent heat release and incident kinetic energy: | \[ T(t, s) = T_{sub} + \left( 66.0 + 3.6 E_i - 18.8 e^{-8 E_i} \right) (t + 0.05)^{3/2} \]  
\[ \times \exp \left( \frac{0.009 s^2}{t + 0.05} \right) \] | \( T_{sub} = \) substrate temperature, \( E_i = \) incident energy, \( t = \) elapsed time, \( s = \) distance from adatom |
Appendix E

Flux Arrival Distribution at Trench

To get the initial distributions of the incident material on various surfaces in the trench, we assume no kinetic energy induced reflection and resputtering. Every atom sticks to where they initially arrive, i.e., a sticking coefficient of 1.0. We further assume the incident flux to be the conventional cosine distribution (it can be any other type of continuous distribution) which may be truncated using such mechanism as collimator. Fig. 5.1 shows a sketch of a trench with an incidence distribution truncated by $\theta$. Arbitrary feature width and unit are used in the analysis. Flux at the top is normalized to be 100%; flux on all other surfaces would thus be correspondingly lower.

At positions with open space such as those at the trench top, the net flux can be expressed as

$$f(x) = \int_{-\theta}^{\theta} \cos \alpha d\alpha.$$  \hspace{1cm} (Ae-1)

Where $\cos(\alpha)$ is the assumed distribution function (can be replaced by any other type of function) and $\pm \theta$ the truncated incidence. For overall trench horizontal surfaces including the trench bottom, the expression becomes:

$$f(x) = \int_{\theta_l}^{\theta_u} \cos \alpha d\alpha,$$  \hspace{1cm} (Ae-2)

where $\theta_l = -\Omega_1 \cdot \theta - \Omega_2 \cdot \arctan \frac{x}{H}$ and $\theta_u = \Omega_3 \cdot \theta + \Omega_4 \cdot \arctan \frac{L-x}{H}$ have taken into account the effect of the sidewalls; $H$ is the height, $L$ the width of the trench and $x$ the position. The coefficients $\Omega_i$ ($i = 1 \sim 4$) in terms of either 1 or 0 are used to switch between positions upon which the sidewalls have or have no effect. Expressions for the
coefficients are as follows:

\[
\Omega_1 = \text{int}\left(\frac{x}{H \cdot \tan \theta}\right) - \left\lfloor \text{int}\left(\frac{x}{H \cdot \tan \theta}\right) \right\rfloor - \delta,
\]

\[
\Omega_2 = \text{int}\left(\frac{H \cdot \tan \theta}{x}\right) - \left\lfloor \text{int}\left(\frac{H \cdot \tan \theta}{x}\right) \right\rfloor - \delta,
\]

\[
\Omega_3 = \text{int}\left(\frac{L-x}{H \cdot \tan \theta}\right) - \left\lfloor \text{int}\left(\frac{L-x}{H \cdot \tan \theta}\right) \right\rfloor - \delta \quad \text{and}
\]

\[
\Omega_4 = \text{int}\left(\frac{H \cdot \tan \theta}{L-x}\right) - \left\lfloor \text{int}\left(\frac{H \cdot \tan \theta}{L-x}\right) \right\rfloor - \delta.
\]

The above actions of taking integer through intrinsic function \(\text{int}\) and the use of a small fraction \(\delta\) enable such switches possible. Finally the position-dependent incidence distribution at the top and the bottom of the trench upon integration of Eqn. Ae-2 becomes:

\[
f(x) = \sin\left(\Omega_1 \cdot \theta + \Omega_2 \cdot \arctan\left(\frac{x}{H}\right)\right) + \sin\left(\Omega_3 \cdot \theta + \Omega_4 \cdot \arctan\left(\frac{L-x}{H}\right)\right). \quad \text{(Ae-3)}
\]

Considering that the sidewalls are perpendicular to the bottom, a slightly different expression for \(y\)-dependent incidence distribution along the sidewalls can be similarly obtained:

\[
f(y) = 1.0 - \cos\left(\Omega_5 \cdot \theta + \Omega_6 \cdot \arctan\left(\frac{L}{y}\right)\right), \quad \text{(Ae-4)}
\]

where \(\Omega_5 = \text{int}\left(\frac{L}{y \cdot \tan \theta}\right) - \left\lfloor \text{int}\left(\frac{L}{y \cdot \tan \theta}\right) \right\rfloor - \delta\) and
Using Eqns. Ae-3 and Ae-4 the flux arrival distribution along the whole trench exterior surface can be obtained for the symmetric cosine distribution (and any other distribution with corresponding modifications as well).

As an example, the effect of incidence cut-off angle on flux arrival distribution calculated for a fixed aspect ratio of two is shown in Fig. Ae-1. The plots on the left column are distributions at the trench bottom which mostly is close to a horizontal uniform line whose y axis value (flux arrival) decreases with increasing $\theta$. At $\theta = 10^\circ$, the sidewalls have small effect and the central part of the bottom receives as much flux as those outside of the trench. The plots on the right column are the distribution along the sidewalls. As expected, the lower part of the trench walls generally is less likely to receive flux except for very small angle where there is a uniform distribution. The magnitude of the flux arrival at the uniform section increases with increasing $\theta$ and the length decreases at the same time.
Flux Arrival Distribution at Trench

Fig. Ae.1. Flux arrival distributions calculated for both the bottom and sidewalls of the trench under different incidence cut-off angle. The aspect ratio is fixed at 2. Arbitrary unit is used for trench dimension and the maximum flux arrival on the terraces is normalized to be 1.0.
3D KMC Barrier Energy Formulae

Since the 3D situation was so complex, a functional form for the energy barriers was derived by Johnson [A4] for copper and nickel. Data fitted was obtained from EAM, experimental and other data in the literature. Since more data exists for nickel in the literature, some copper data was inferred to be on the order of 60% the nickel values, based on the ratio of copper to nickel data available. The energy function was of the form:

\[
E_i = E_o \left(2N_{in} - N_f\right) \left(\frac{r}{r_{nn}}\right)^2 + B \quad [\text{eV}]
\]

where \(N_{in}\) is the initial number of nearest neighbors to the atom, \(N_f\) is the number of nearest neighbors to the atom after the prospective jump, \(r\) is the distance of the jump, and \(r_{nn}\) is the nearest neighbor distance. A cutoff distance for \(r\) was implemented in the model to reduce tracking of unlikely jumps. \(B\) is a modification parameter for the cases where an atom jumps from an fcc site to an hcp site, or the reverse, since the fcc site is more stable for these metals. \(B = +0.01\) eV for jumps from an fcc site to an hcp site, \(B = -0.01\) eV for jumps from an hcp site to an fcc site, and \(B = 0\) for all others.

\(E_o\) is a fitting constant for the element to be deposited. In order to determine \(E_o\), the available energy barriers were categorized in order to plot them. Examining above equation more carefully, one can see that the factors labelled as “jump index” are purely geometric and essentially unique for each jump. Therefore, the literature data could be
plotted as $E_i$ versus jump index and a linear least-squares fit applied to determine $E_o$. The resulting $E_o$ fits to these data are: 0.04944 for copper and 0.09061 for nickel.
References to Appendices