A MOLECULAR DYNAMICS STUDY OF NICKEL VAPOR DEPOSITION: TEMPERATURE, INCIDENT ANGLE, AND ADATOM ENERGY EFFECTS

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Abstract—The morphology and microstructure of metallic thin films synthesized by physical vapor deposition are known to be sensitive functions of the incident flux, its angular distribution and kinetic energy as well as the substrate temperature. Using an embedded atom method to represent the interatomic interactions, two-dimensional molecular dynamics simulations have been conducted to identify the role of these variables upon vacancy formation and surface morphology evolution during nickel deposition. The results reveal the existence of a critical incident angle above which mono-vacancies and vacancy clusters/voids are created by atomic shadowing. Increasing the substrate temperature and the adatom kinetic energy in the 0.1-2.0 eV range significantly reduces vacancy formation. Time lapse analyses have been used to identify the atomic mechanisms for this. They indicate that low defect concentration films can be synthesized at low temperatures by increasing the adatom kinetic energy to a few eV. A simple empirical model is proposed to relate the vacancy concentration to the controllable process conditions.

1. INTRODUCTION

The emergence of sputtering, thermal evaporation and molecular beam epitaxy techniques permits the atomic assembly of thin films at low growth rates (<1 μm/min) [1]. These vapor deposition methods are being increasingly used to synthesize metal electronic interconnects [2], magnetic [3], ferroelectric [4], and superconducting [5] thin films as well as many coatings for structural applications [6]. Newer Directed/Jet Vapor Deposition™ (DVD/JVD™) processes are also being developed for the much higher rate vapor deposition of a wide range of materials [7-9]. These newer processes use inexpensive, high rate evaporation methods to create concentrated evaporant entrained in a trans/supersonic He or other inert gas jet flow. If the jet velocity is high (say Mach 1–2) and the evaporant has an atomic mass significantly greater than that of the inert gas, the atomically dispersed evaporant impinges directly onto the substrate with an incident angle defined by the jet axis and the local substrate normal, and with a kinetic energy proportional to the square of the jet velocity [8]. For jet velocities in the Mach 1–5 range and elements of intermediate atomic mass, this kinetic energy lies approximately between 0.1 and 2.0 eV. The energy distribution of the neutral atom flux in many sputter deposition and thermal evaporation processes also peaks in this energy range [10]. Although these adatom energies are much smaller than the ~100 eV ion energies used to modify structure in ion assisted deposition processes [11, 12], they can still exceed that available thermally, and so might assist adatom motion and promote surface reconstruction during a deposition event. This could reduce the incidence of defects (such as vacancies, voids, and dislocations) that are often formed in films, especially when the deposition rate is high, the flux is oblique, or the substrate temperature is low [13].

The defects formed during high rate/low temperature/oblique incidence deposition are important to control. For example, the resistivity and electromigration resistance of the metal alloy interconnects used in microelectronic devices are both adversely affected by the vacancies and voids formed during vapor deposition. In metallic multilayer applications (e.g. Cu–Ni multilayers that exhibit giant magnetoresistance), surface roughness is undesirable. Experiments have shown that, in general, vacancy and void concentrations in the deposition layer and the layer roughness all increase when the substrate temperature decreases, or when the incident angle increases [13]. Thus, relationships exist between film properties, defect concentrations, and the process conditions that define the incident flux. To optimize the process conditions, a detailed knowledge of defect formation mechanisms as a function of the process variables is needed. While experimental studies have been helpful for this, the availability of predictive models would provide the opportunity to use recently developed process optimization techniques to identify process trajectories that result in desired microstructures [14].
One approach to the modeling of thin film structure development involves energy minimization concepts to a cluster of atoms [15–19]. These approaches are able to predict the preferential growth mode [15] and structure [16–19] but are unable to explore the time related kinetic phenomena that control defect formation. To investigate kinetic phenomena, several studies have sought to calculate the activation energies and the corresponding pre-exponential factors for the different diffusion paths on the surfaces of metals [20–26].

Studies of deposition kinetics reveal that a variety of surface morphologies can develop during a vapor deposition process. Depending on the deposition temperature, incident angle, adatom energy, deposition species, and the time available for adatom diffusion, a film can grow by the Frank–van der Merwe (FM) mode which involves repetitive layer-by-layer growth on surfaces that are wetted by the vapor [27], by the Volmer–Weber (VW) mode where new atomic layers are nucleated before complete coverage of the first layer, or by the Stranski–Krastanov (SK) mode which involves a mixture of the former two. Because completion of the coverage of atomic layers is essential for reducing the surface roughness and defect concentration, an epitaxial atomically flat film with a low defect concentration can be produced in an FM growth mode. The surface roughness and defect concentration are intermediate for the SK growth mode and will be highest in the VW growth mode. Low substrate temperature and low adatom kinetic energy or high deposition rate and oblique flux are all likely to promote the transition of the growth mode from FM to VW and thus to increase defect concentrations and surface roughness.

An energetic adatom arriving at a surface may relocate by ballistic displacement or cause the collapse of metastable atomic configurations [28] and could thus significantly affect surface reconstruction kinetics, particularly when the growth is by the VW mode. The surface morphology can also reconstruct by surface diffusion. Since diffusion rates on different crystal planes vary [21, 22, 25], the diffusion behavior is likely to depend on the local surface orientation [21–25]. Even for a macroscopically flat surface, diffusion is affected by atomistic terraces, ledges, or kinks on the surface [22, 23]. Because the surface morphology is growth path dependent and many different diffusion routes are available for an adatom, the deposition problem is very difficult to treat by classical approaches. The alternative is to pursue an atomistic approach to simulate the adsorption of atoms by a solid surface, follow their subsequent diffusion over the surface, and observe the resulting film morphology and microstructure [28–49].

Two distinctively different atomistic modeling approaches can be used for the simulation of vapor deposition. Monte Carlo (MC) methods use estimates for the probabilities of atom jumps (or MC moves) without considering the lattice dynamics directly. These methods are computationally fast and have been extensively employed to study surface segregation [29], surface morphology [30–32], and growth mode [33–34]. The recently developed kinetic Monte Carlo methods [31, 32] are able to incorporate the multiplicity of diffusion paths and successfully reproduce the development of surface morphology as a function of substrate temperature, flux incidence angle, and deposition rate [32]. The primary limitation of the MC approach is that it ignores the force between atoms and therefore cannot provide insight into film stress, the adatom collision with the surface, and the effect of the adatom kinetic energy upon the atomic assembling mechanisms active during thin film growth. In addition, since MC methods [31, 32] are based upon a predetermined discrete set of lattice sites, they cannot model lattice strain, heteroepitaxy, dislocations and twins, different grain orientations and textures, surface reconstruction, etc. Although an MC simulation without a single Ising lattice restriction might be possible [33], its application to the three-dimensional (3D) modeling of vapor deposition may well be computationally inefficient. Another problem with traditional MC simulation is its reliance on artificially defined MC moves. New MC methods developed by Voter [35, 36] use multistate Transition-State Theory (TST) and provide a stricter definition of allowable MC moves. While they yield more realistic results, they are computationally more demanding, and their current application is restricted to a monolayer of atoms [35, 36].

In contrast to the MC methods, a Molecular Dynamics (MD) simulation determines the positions and velocities of atoms on the time scale of the lattice vibrations. It is based upon the analysis of interatomic forces and therefore incorporates more of the relevant phenomena in a model of vapor deposition. However, since the lattice vibration frequencies are in the $10^3$ Hz range, the time between calculations of a set of atomic coordinates/velocities must be very short (a few fs). Since knowledge of the force acting on each of the atoms owing to its neighboring atoms is required, an MD calculation spends a major part of its computational time finding the atomic neighbors. In the simplest algorithm, the neighbors of the first atom can be determined by calculating the distances between this atom and all the other $N - 1$ atoms, where $N$ is the total number of atoms in the system. Likewise, the neighbors of the second atom can be decided by calculating the distances between the second atom and all the other $N - 2$ atoms, since at this point the relationship between the first and the second atoms is known. The neighbors of all atoms can be obtained by calculating a total of $N - 1 + N - 2 + \cdots + 1 = 0.5N(N - 1)$ distances. Thus, the computational time of an MD calculation scales with $N^2$ when it is dominated by such a neighbor finding algorithm. The
computational time of MD simulations can be improved to scale with $N$ [37]. However, the calculation is still expensive for the large number of atoms needed to observe the microstructure evolution. Usually, MD simulations of vapor deposition are applied to small systems (up to a few thousand atoms) and for short periods of deposition (for up to a few nanoseconds). The consequence of this is that MD can only simulate an extremely high deposition rate procedure. If, for example, a hundred atomic planes are deposited in 10 ns, the deposition rate is around 2 m/s, which is many orders of magnitude above that used in practice. However, provided it is recognized that the simulated deposition is a high rate bound, the MD method can still be used to reveal the variational trend in microstructure with deposition conditions [39].

The interatomic forces used in an MD simulation are obtained from the spatial derivatives of an interatomic potential. In the past, the interatomic potential has been approximated by various pair potentials that incorporated long range interatomic attractions and short range Coulombic repulsions associated with inner electron shell forces [50–53]. Since the force can be expressed as an explicit summation term for the pairwise potential, the pair potential model is very easy to implement in a computationally efficient MD calculation. Unfortunately, the pair potential approach cannot handle the influence of the local environment on the (pairwise) atomic interactions, and this can introduce serious problems in atomistic calculations. For example, pair potential models incorrectly predict that the vacancy formation energy is approximately equal to the cohesive energy, and that the elastic stiffness constants satisfy the relation $C_{12} = C_{44}$ [54]. Furthermore, since the local atomic environment on the surface of a body is different from the bulk, a classical pair potential model usually cannot treat surface problems correctly [55].

Ab initio methods, based upon direct solutions of the Schrödinger equation by density functional theory [56] or the tight binding model [57], can eliminate the problems associated with pair potentials. However, these approaches involve repeated matrix diagonalization [56, 57], and when applied to an MD calculation, the approach is quite computationally extensive. Usually, only a few (10–50) atoms can be included in such a calculation [56, 57]. Empirical Embedded-Atom Methods (EAM) appear to be a good compromise for many f.c.c. metal deposition problems [54]. The EAM approach accounts for the influence of the local atomic environment on the potential through a many-body term and is both sufficiently accurate and computationally efficient for MD calculations.

Two-dimensional (2D) MD [39–41] has been used to study the effects of the incident energy [39], the ion energy of ion assisted deposition (up to 100 eV) [40], and the substrate temperature [41] on film structure. The results of these calculations indicated that increasing the incident adatom energy or ion energy could reduce both the surface roughness and defect concentration [39, 40] and that increasing the substrate temperature might cause the misfit dislocations at the boundary between the substrate and the deposited materials to be transported into the films [41]. It should be pointed out that the films deposited in Ref. [41] were not thick enough to reveal the substrate temperature effect on the formation of defects such as vacancies. Because of the computational expense, most 3D MD calculations have been confined to the examination of monolayer or submonolayer deposition of adatoms [42–45] or very small systems [28, 46–49]. These studies, while able to reveal the structure and energetics of the atomic clusters as well as the growth mode at an early stage in the deposition, have given little insight into the formation of defects such as vacancies.

The calculation of vacancy formation during vapor deposition is an important first step in the development of relationships between defect concentrations and the way in which vapor deposition is conducted. The intent of the present work is to obtain a fundamental mechanistic insight into vacancy formation. Ni on Ni vapor deposition has been chosen for study because of the availability of a well tested embedded atom force law for Ni that gives realistic point defect formation and surface energies [55, 58]. To run the calculations within a practical computational time, the present work was confined to a 2D model. The 2D approximation constraints the possible crystal orientations and changes the atomic environment of defects. Thus, the activation energies for vacancy formation and migration will not be the same as in a 3D crystal. This is manifested as a shift in temperature for those processes that involve thermally activated diffusion. Nevertheless, the results obtained reveal the basic phenomena involved in vacancy formation and allow a simple relationship between structure and processing variables to be proposed. To explore the relationship between vacancy concentration and deposition conditions, extensive molecular dynamics calculations were carried out to determine the vacancy concentration as a function of the substrate temperature, the incident adatom angle, and the incident adatom energy. The work focuses on adatom energies in the 0.1–2.0 eV range, processing energies obtained using the new directed vapor deposition process [7, 8].

2. EMBEDDED ATOM POTENTIALS

The EAM originally developed by Daw and Baskes [54] provides a practical method to account for the effect of the local environment on the interaction between atoms and has been successfully applied to the study of a variety of point defect and surface problems in many f.c.c. metals, including Ni, Cu, Al, Ag, Au, Pd, and Pt [21, 22, 54, 55]. The EAM
potentials are obtained by empirically fitting the predictions of the potential to measured material properties, such as the lattice constant, the bulk modulus, other elastic constants, the sublimation energy, heat of solution, surface energy, stacking fault energy, activation energy for diffusion, etc. [59]. Explicit EAM functional forms need not necessarily be assumed, and EAM potentials are usually tabulated in numerical form [55, 59]. Johnson proposed that EAM potentials could also be given in a simple analytic form that is well suited to MD simulations [58]. In the present work, Johnson’s analytic nearest neighbor EAM functions were used, and since no stacking fault is involved in a 2D calculation, neglect of interactions beyond nearest neighbors does not significantly affect results.

In the notation used by Johnson, the basic equations of the EAM are

\[ E_i = \sum_j F(\rho_j) + \frac{1}{2} \sum_{ij} \phi(r_{ij}) \quad (1) \]

\[ \rho_i = \sum_j f(r_{ij}) \quad (2) \]

where \( E_i \) is the total internal energy, \( \rho \) is the electron density at atom \( i \) due to all other atoms, \( f(r_{ij}) \) is the energy to embed atom \( i \) in an electron density \( \rho_i \), and \( \phi(r_{ij}) \) is a two-body potential between atoms \( i \) and \( j \). The electron density and two-body potential can be written as:

\[ f(r) = f_c \exp\left[-\beta\left(\frac{r}{r_e} - 1\right)\right] \quad (3) \]

\[ \phi(r) = \phi_c \exp\left[-\gamma\left(\frac{r}{r_e} - 1\right)\right] \quad (4) \]

where \( f_c \), \( \phi_c \), \( \beta \), and \( \gamma \) are the model parameters, and \( r_e \) is the equilibrium spacing between nearest neighbor atoms (in the 3D crystal [58]). The embedding function is determined by equating the total energy to the universal equation of state [58, 60], which leads to

\[ F(\rho) = E_0 (1 - \ln \rho) + 6 \phi_c \rho \quad (5) \]

where \( E_0 \) is the cohesive energy, \( x = (\rho/\rho_0)^{\alpha} \), \( y = (\rho/\rho_0)^{\beta} \), \( \alpha = 3\Omega R/E_0 \), \( \Omega \) is the atomic volume, \( B \) is the bulk modulus, and \( \rho_0 \) is the equilibrium electron density at the lattice site (in the 3D crystal).

Since the values of \( E_0 \), \( \Omega \), and \( B \) are exactly reproduced by EAM, their experimental data can be directly used. For Ni, \( E_0 = 4.45 \text{ eV} \), \( \Omega = 10.9 \text{ Å}^3 \), and \( B = 1.13 \text{ eV/Å}^3 \). The corresponding lattice constant, \( a = (4\Omega)^{1/3} = (4 \times 10.9)^{1/3} = 3.52 \text{ Å} \).

By fitting the experimental atomic volume, the cohesive energy, the unrelaxed vacancy formation energy, the bulk modulus, and the Voigt-average shear modulus \( G \), and considering only the nearest neighbor interactions between atoms, Johnson determined all the model parameters used in equations (1) and (2) [58]. These are listed in Table 1. Since only nearest neighbor interactions are considered, a truncation cut-off distance midway between the nearest and next nearest neighbor spacings was used in the present work.

### 3. MOLECULAR DYNAMICS SIMULATION

In an MD atomistic simulation, a computational crystal is created by defining the positions of an assembly of atoms in terms of the lattice sites. To reduce or eliminate effects associated with the small system size, periodic boundary conditions can be used. Since the MD simulations are always conducted at a user defined temperature, the meaning of temperature in a 2D system is important to understand. The temperature within a given region of the computational crystal is related to the average velocity of the atoms in that region. For a 3D crystal, the relationship between temperature \( T_0 \) and the average kinetic energy per atom \( E_{kin} \) is given by \( T_0 = (2E_{kin})/(3k) \), where \( k \) is the Boltzmann constant. Equipartition of energy among the three degrees of freedom implies that for a 2D crystal, the temperature \( T_2 = E_{kin}/k \), where \( E_{kin} \) is the average kinetic energy per atom in a 2D crystal. To achieve the initial temperature, the initial values of the two velocity components of the atoms in a 2D system are assigned according to a Boltzmann distribution. The velocities are then scaled so that the average kinetic energy gives rise to the correct temperature. Before the simulation, a short period MD run is often necessary to equilibrate this velocity distribution.

During an MD calculation for an isolated system, the temperature is constant due to the conservation of total internal energy and equipartition between kinetic and potential energies. However, if the system is not isolated, the temperature need not be constant. For example, the internal energy of a crystal can change when the crystal is subject to an external stress or when a new atom is added. To maintain a fixed temperature within a given region, the temperature within the region is first calculated from the current average kinetic energy. If the corresponding temperature is higher than desired, drag forces are applied to all the atoms in that region to reduce their kinetic energies to the set-point of the calculation. These forces are usually proportional to the product of the temperature deviation and the atomic velocity of an individual atom. If the temperature is lower than desired, similar forces, but with an opposite sign, are applied to the atoms to increase their kinetic energies.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( f_c ) (eV)</th>
<th>( \phi_c ) (eV)</th>
<th>( \beta )</th>
<th>( \gamma )</th>
</tr>
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<tbody>
<tr>
<td>Value</td>
<td>0.41</td>
<td>0.74</td>
<td>4.98</td>
<td>6.41</td>
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Based upon the calculation of interatomic forces, the evolution of the atomic configuration for the crystal at a given temperature is determined by integrating Newton’s equations of motion using a numerical method such as Nordsieck’s integration scheme [62, 63]. It should be pointed out that the Lagrangian form of Newton’s equations of motion must be used [50] to account for the crystal deformation under periodic boundary conditions. In the present work, this procedure allows a change in the periodic length in the horizontal coordinate direction.

For the 2D calculations performed here, a single close-packed (111) plane of atoms was studied. This affects the calculated lattice constant due to the change in atomic environment. To determine this effect, a separate molecular dynamics calculation was performed. A 2D crystal on a (111) plane was constructed to contain 20 atomic rows stacked along the [112] direction, each with 20 atoms along the [110] direction. The “crystal” was then equilibrated at different temperatures between 0 and 1000 K by running a molecular dynamics calculation for 1 ps (with a 1 fs time step) under the periodic boundary conditions. To fully relax the 2D lattice, displacement of atoms normal to the crystal plane was not permitted but the atoms were allowed to adjust their in-plane spacings. The lattice constant, $a$, was then calculated using $a = 2r/n$, where $r$ is the equilibrium spacing between nearest neighbor atoms. The lattice constant as a function of temperature, calculated from the average nearest neighbor spacing, was determined as $a = 3.41991(1 + 3.842645 \times 10^{-7}T)$ Å. The 2D approximation caused the lattice constant at zero K to be reduced from 3.52 to 3.42 Å and the thermal expansion coefficient to be reduced from $1.34 \times 10^{-5}$ K$^{-1}$ to $3.84 \times 10^{-7}$ K$^{-1}$.

The basic geometry of the Computational crystals used in our MD simulation of vapor deposition is shown in Fig. 1. The black circles indicate the original substrate atoms and the grey circles indicate the vapor or deposited atoms. A close-packed (111) plane composed of six atomic rows, each containing 40 atoms, was first created at the 2D equilibrium atomic spacing to represent the Ni substrate. The horizontal atomic rows are in the [110] direction and are vertically stacked in the [112] direction. Initially, a vapor region was introduced by simultaneously placing 100 Ni atoms at random positions above the substrate with the condition that there are no interactions between vapor atoms or vapor and substrate atoms (i.e. the atomic spacing is larger than the cut-off distance of the EAM potential). This allowed the study of monoatomic deposition and not the deposition of clusters. The incident angle and the incident energy were controlled by the velocity assigned to each of the vapor atoms. For an incident angle, $\theta$, and an incident energy, $E_i$, the velocity $v$ in the $\theta$ direction has a magnitude $(2E/m)^{1/2}$, where $m$ is the atomic mass (for Ni, $m = 58.71$ amu = 0.6085 $\times 10^{-2}$ eV $\text{ps}^2/\text{Å}^2$). The desired deposition rate, $\dot{D}$, was obtained by controlling the density of the vapor. If the atomic density of the substrate is $\rho_s = 4/(3a^3)^{1/2}$, where $a$ is the lattice constant, the necessary density of the vapor, $\rho_v$, to achieve a given $\dot{D}$ is $\rho_v = -\dot{D}p_v/v_y$, where $v_y$ is the $y$ component of the velocity of the vapor atoms.

An atom’s transition from the vapor to the solid is associated with a decrease in interatomic potential energy and a latent heat release. In addition, the adatom kinetic energy is merged with the thermal energy of the solid during deposition. Both effects lead to a local increase in surface temperature. Since vapor deposition usually occurs under isothermal conditions, it is necessary to control the temperature during deposition. In the present work, the temperature control method described above was
applied to keep a region below the surface at a fixed substrate temperature and act as a sink for the latent heat and the adatom kinetic energy. Between the temperature controlled region and the surface, a heat thermal gradient was naturally created. To minimize the change of this region, we allowed the thermostated region maintained at the substrate temperature to propagate upward during vapor deposition. Because surface roughness develops during the deposition, the temperature controlled region was propagated at 0.75 Å to prevent it from passing beyond the deposited surface boundary. In the simulation, the periodic boundary condition was used along the horizontal direction, and the free boundary condition was used along the vertical direction. The time step was taken to be 1 fs, and the lattice constant was allowed to relax. Once 50 of the 100 vapor atoms had deposited on the substrate, another 50 vapor atoms were added so that the deposition proceeded continuously. In the present work, ~40 Å thick thin films were grown under systematically varied process conditions. A typical computation required about 24 h on a Sparc20 workstation.

4. RESULTS AND DISCUSSION

4.1. Effects of substrate temperature

Numerous simulations were carried out at different substrate temperatures between 100 and 1100 K at a constant incident energy of 0.5 eV, an incident angle of 0°, and a deposition rate of 10 nm/ns. Two examples of the atomic configurations resulting from 400 ps of deposition at T = 100 K and T = 650 K are shown in Fig. 1(a) and (b), respectively. At the low temperatures, numerous mono- and di-vacancies were formed. Their concentration was reduced by increasing the substrate temperature. To quantify the simulation results, the vacancy concentration in the deposited film was calculated as the number of vacant sites divided by the total number of lattice sites in the film. To prevent the surface roughness from being counted as vacancies, incomplete atomic layers near the surface were excluded from the calculation. The data are summarized in Fig. 2, where the line is the prediction of a simple empirical model fit as described later. Figure 2 indicates that the vacancy concentration rapidly decreases with increasing substrate temperature. Using the vacancy formation energy for the 2D model, the equilibrium vacancy concentration is less than 10⁻⁷% [64] even at the high temperature of 650 K. In fact, no vacancies were observed in the MC simulation of Ni deposition using a system consisting of 6000 atoms for deposition at 350 K and at a much lower rate ~10⁻⁸ nm/ns [32]. This is expected since an equilibrium 10⁻⁷% vacancy concentration corresponds to one vacancy per 100 000 atoms. The observation of a vacancy concentration far above the predicted "equilibrium" or low growth rate value indicates that the vacancy concentration is controlled by kinetic trapping.

Increasing the temperature reduces this effect because the thermal activation after deposition enables adatoms to overcome energy barriers during migration to the lowest energy vacant lattice sites. However, for the deposition conditions encountered here, there is insufficient time to reach the equilibrium state even at 1100 K.

To examine the vacancy formation mechanism, the positions of adatoms at different times are shown in Fig. 3 for a low (100 K) deposition temperature. In Fig. 3, the open circles signify atom locations at the first time indicated in the figures [e.g. 250 ps after the start of deposition in Fig. 3(a)], each arrow represents the displacement of the corresponding atom during the next 10 ps period, and the solid circles indicate atom positions after the displacement. Figure 3(a) shows a common mechanism for the formation of a mono-vacancy (at site A) due to the deposition of an atom at site B. Type A site configurations are frequently observed at low temperatures due to self shadowing. They are called potential vacancy sites since they can form real vacancies if an atom moves to site B before another atom diffuses over the surface to fill site A. Figure 3(b) shows a mechanism for the formation of a di-vacancy. At 100 K, metastable configurations consisting of tall base-narrow islands frequently develop because of self shadowing and limited adatom mobility at low temperatures. When these islands are high enough, impingement of an adatom causes their collapse as in Fig. 3(b). This collapse embeds a di- or even tri-vacancy in the film. Similar stop-action analyses conducted for the higher temperature (650 K) deposition reveal that since there is significantly more surface diffusion, the configurations conducive to vacancy creation are less likely to form. The film then grows more like the FM mode. Thus, the shown temperature dependence of the vacancy concentration observed in these high rate deposition simulations is governed mostly by the
4.2. Effects of incident angle

It is well known from MC results that the self-shadowing mechanism responsible for the island growth seen in Figs 1 and 3 is enhanced at high flux incidence angles [32]. Thus, an increase in flux incidence angle should lead to an increase in the vacancy concentration. To investigate this, vapor deposition was simulated at various incident angles between 0° and 60°, at a constant incident energy of 0.5 eV, a constant substrate temperature of 600 K, and a constant deposition rate of 10 nm/ns. Examples of two of the resulting atomic configurations are shown in Fig. 4 for low (5°) and relatively high (35°) incident angles. The overall vacancy concentration as a function of incident angle is drawn in Fig. 5 (upper curve). Figure 5 shows that at an incident energy of 0.5 eV, there exists a critical angle (~30°) below which the vacancy concentration does not depend significantly on θ. However, when the incident angle is larger than the critical value, the vacancy concentration increases abruptly.

Examination of Fig. 4(b) indicates that this abrupt increase in vacancy concentration is associated with the formation of large vacancy clusters or voids. Detailed analysis of the as-deposited structures reveals that multi-vacancy clusters abruptly begin to form as the incident angle increases beyond ~30°. Stop-action analyses indicate that the large vacancy clusters/voids are again caused by the shadowing effect. During deposition, some local atomic clusters randomly grow out on the film surface. At large
incident angles, these clusters can block the flux of arriving adatoms, leaving a deep unreachable space (shadowing) behind them, which enhances the VW growth mode. Abrupt relaxations of these metastable configurations can cap the shadowed region and embed a vacancy cluster or void deep within the film. The kinetics of the bulk diffusion are insufficient to annihilate these defects at high deposition rates.

4.3. Effects of incident energy

Point defect trapping during deposition has been shown to be closely connected with the formation of metastable nonplanar features on a surface. Higher substrate temperatures provide an opportunity for surface diffusional reconstruction at a high enough rate to avoid the formation of these features, and thus the formation of vacancies is avoided. This process is also aided by the latent heat released (4.45 eV/atom) when a vapor atom is entrained in the surface of the deposit. In directed/jet deposition processes, additional energy for surface relaxation can be added by the kinetic energy (i.e. the velocity) of the adatoms. Kinetic energies in the range 0.1–2.0 eV are comparable to the typical activation energies of surface diffusion (0.2–1.3 eV for Ni [32, 64, 65]). To explore the significance of this adatom kinetic energy, computational experiments were conducted for incident atom energies between 0.1 and 2.0 eV at substrate temperatures of either 100 K or 600 K and an incident angle of 0° using a deposition rate of 10 nm/ns. Examples of the resulting atomic configurations for vapor deposited films at 100 K are shown in Fig. 6, and the vacancy concentration as a function of incident energy is plotted in Fig. 7. As indicated in Fig. 6(a), a very high vacancy concentration is formed in films deposited at the lower incident energy $E_i = 0.1$ eV. The vacancy concentration is reduced at $E_i = 1.0$ eV in Fig. 6(b) and is not measurable at $E_i = 2.0$ eV in Fig. 6(c). Figure 5 also indicates a much less sensitive dependence of the vacancy concentration upon the incident angle for a 2.0 eV incident energy. The size of vacancy clusters at large incident angles was also significantly smaller at a 2.0 eV as opposed to a 0.1 eV incident energy. It can be seen from these figures that increasing the incident energy has an effect similar to increasing the substrate temperature. Since the incident energy can help adatoms overcome the energy barrier of diffusion during the initial impact, it will provide them with a greater chance of moving to energetically stable sites, such as vacant lattice sites, resulting in a lower vacancy concentration.

For low adatom energies, Fig. 6(a) shows that at low temperature, the majority of the vacancies are either mono- or di-vacancies, but a few tri- and even larger vacancy clusters are also present. The positions of adatoms at various time steps during deposition at
100 K and incident energies of either 0.1 eV or 2.0 eV are displayed in Fig. 8(a) and (b), respectively. In Fig. 8(a) and (b), each arrow represents the displacement of the atoms during 1 ps, and the trace of each of the atoms is recorded by five arrows for a total of 5 ps. Figure 8(a) shows the formation of a vacancy from a potential vacancy site at the low incident energy of $E_i = 0.1$ eV. Extensive potential vacancy sites were observed in deposition at this energy level due to the low mobility of the adatoms on the high terrace. Also, these potential vacancy sites were found to develop into vacancies easily, since the nearby adatom has little chance of overcoming the energy barrier to fill them before the formation of the vacancies. These findings account for the high defect production rates of low incident energies. In contrast, Fig. 8(b) shows that the impingement of adatoms of high incident energy levels can cause the surface atoms to adjust their positions actively to achieve relatively low energy configurations. As a result, not only the potential vacancy sites are less likely to form, but when they do form, they are more likely to be filled before the formation of vacancies. Figure 8(b) also indicates that the impact effect of high incident energy can cause the vacancy near the surface to diffuse back to, and be eliminated at, the surface. Incident energy can also reduce the shadowing effect of the angular flux which causes metastable atomic clusters. The accumulation of these processes leaves a low vacancy concentration in the film.

It is seen in Fig. 8(a) that, instead of row-by-row growth, the atoms tend to form a metastable 2D configuration, as indicated by the movement of the two atoms during 50-51 ps. In other words, the film tends to grow by the VW mode at the low incident energy of $E_i = 0.1$ eV. In the $E_i = 2.0$ eV deposition, we did not observe the 2D nucleation growth as seen in Fig. 8(a). The surface roughness revealed in Fig. 8(b) is caused by the randomly landing adatoms not having enough time to diffuse out of the high terrace at a high deposition rate. It is expected that at low deposition rate, the film will tend to grow via the layer-by-layer (FM) mode. The effect of incident energy at 600 K is similar and hence will not be repeated here. However, it is seen in Fig. 9 that atoms can diffuse as a ring leading to a rotation of the configuration, similar to results reported from experiments [66].

4.4. Empirical model

The MD simulations demonstrate the effect of the adatom kinetic energy $E_i$, the substrate temperature $T$ and the incident angle $\theta$ on the resultant vacancy concentration $C_v$. The variation of the vacancy concentration with these three processing parameters is sufficiently regular that its functional dependence can be captured by simple empirical formulas.

The effect of the impact from adatom kinetic energy $E_i$ is found to vary inversely with the incident energy at all temperatures for normal incidence. Then the concentration of these vacancies is decreased as the temperature is raised by a thermally activated term with an effective activation energy $Q$. Thus, the vacancy concentration at normal incidence can be approximated by the form

$$C_v(E, T) = C_{v0} \frac{E_i}{E} \left[1 - \exp\left(-\frac{Q}{kT}\right)\right]$$

with $C_{v0} = 0.86$ (%), $E_{0} = 1$ eV and $Q = 0.0273$ eV. The effective activation energy $Q$ clearly has no relation to the activation energies for vacancy and bulk diffusion (0.583 eV and 0.908 eV, respectively [64]).

The effect of adatom incident angle $\theta$ (measured from the normal) is dominated by an angle $\theta_i$ which acts roughly as a threshold for strong shadowing. Although it has no temperature dependence, increasing the impact energy mitigates this effect. These variations are satisfactorily approximated by the form

$$K(\theta, E_i) = \frac{1 + \left(\frac{\theta}{\theta_i}\right)^4}{1 + \left(\frac{\theta}{\theta_i \left(1 + \frac{E_i}{E_0}\right)}\right)^4}$$

with $\theta_i = 0.0273$ eV.
Fig. 8. Trace map for deposition at 100 K, 0°, and 10 nm/ns. Each arrow represents the displacement within 1 ps. (a) Energy 0.1 eV: (1) 46-47 ps; (2) 47-48 ps; (3) 48-49 ps; (4) 49-50 ps; (5) 50-51 ps. (b) Energy 2.0 eV: (1) 263-264 ps; (2) 264-265 ps; (3) 265-266 ps; (4) 266-267 ps; (5) 267-268 ps.
which can be used as a multiplicative factor for equation (6). The threshold \( \theta_0 \) is taken as 30° and \( \theta_1 \) as the trends are all seen to be satisfactorily matched from equations (6) and (7). The magnitudes as well as the critical incident angle \( \theta_0 \) above which large vacancy clusters and voids form are calculated by these empirical formulas.

5. CONCLUSIONS

Molecular dynamics simulation of the 2D vapor deposition of Ni on Ni has revealed that:

(1) The vacancy concentration decreases with substrate temperature and incident energy and increases with incident angle. Vacancies formed during low angle vapor deposition are mainly mono- or occasionally di-vacancies. For fixed substrate temperature and incident energy, there exists a critical incident angle \( \theta_0 \) above which large vacancy clusters and voids start to form due to a shadowing effect.

(2) Increasing the substrate temperature and incident adatom energy, or decreasing the incident adatom angle, promotes the FM growth mode, while the reverse promotes the VW growth mode. The collapse of large metastable configurations encountered in the VW growth mode results in the formation of large vacancy clusters and voids.

(3) The vacancy/void content of films deposited at high rates is formation rate controlled. The kinetics of bulk diffusion are insufficient to significantly reduce the defect concentration at any of the temperatures studied.

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