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Kinetic Monte Carlo simulations of nanocrystalline film deposition

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A full diffusion kinetic Monte Carlo algorithm is used to model nanocrystalline film deposition, and study the mechanisms of grain nucleation and microstructure formation in such films. The major finding of this work is that new grain nucleation occurs predominantly on surface peaks. Consequently, development of a nanocrystalline structure is promoted by a growth surface with nanoscale roughness, on which new grains can nucleate and grow separately from one another. The grain minor dimension (in the plane of the film) is primarily dictated by surface peak spacing, which in turn is reduced at low temperatures and high deposition rates. The grain major dimension (in the growth direction) is related to the probability of nucleating new grains on top of pre-existing ones, with finer grains being formed at low temperatures and low grain boundary energies. Because vacancies kinetically pin grain boundaries, high vacancy content, which is obtained at high deposition rate, also favors nanograins. Consistent with empirical observations common in the experimental literature, it is found that as grains shrink, they transition from elongated to equiaxed.


I. INTRODUCTION

Nanocrystalline films often exhibit superior properties, such as increased corrosion resistance, wear resistance, and improved hardness, as compared to their microcrystalline counterparts.1–9 Thus, they enjoy wide interest for applications in microelectronic, optical, and magnetic devices, as well as for coatings applied to surfaces of structural materials. Various deposition techniques, such as chemical and physical vapor deposition, molecular beam epitaxy, electrochemical deposition, and reactive sputtering, have been successfully employed to produce nanostructured films. While extensive experimental works1–5,9 have been carried out to investigate the effects of processing conditions on such properties as film porosity, surface roughness and grain size, the growth mechanisms of nanostructured films are, as yet, incompletely understood on a microscopic level.

A variety of computer simulations have also been used to study polycrystalline film growth. Continuum models have been proposed for the evolution of grain microstructure, surface roughness, and texture during film growth,10,11 and involve evaluation of the equations of motion for grain boundaries. Such models can incorporate various driving forces, including grain boundary curvature and anisotropic grain boundary energy. However, these models do not explicitly consider other defects formed during film growth, such as vacancies and voids,12,13 and it is not straightforward to incorporate nucleation of new grains—a process that must occur during nanostructured film growth.4 On the other hand, discrete models based on molecular dynamics have not only been employed to simulate kinetic processes such as diffusion and grain boundary migration,14 but also to simulate vacancy entrapment and void formation during the film growth process.15,16 For example, Smith and co-workers15 explored the mechanism of void formation during film growth, as well as interactions between voids and grain boundaries in bicrystals.16 The major drawback of molecular dynamics pertains to the small length and time scales it can access, which, in the above studies limited the deposited film thickness to at most 100 monolayers. Kinetic roughening and subsequent grain nucleation during film growth thus cannot be adequately captured via molecular dynamics methods.

By excluding details of atomic vibrations and using a rigid lattice, discrete models that are based on the kinetic Monte Carlo (kMC) algorithm17 are less computationally expensive and have been used to simulate film growth up to 10⁴ monolayers thick and beyond.18–22 Various kMC models have been employed to study how the growth interface roughens during film deposition.18–27 Among these models, the most realistic ones incorporate vacancy and void formation but only consider the growth of a single crystal.19–22 One approach to extend this method to the growth of polycrystalline films is to use multiple lattices to represent different grain orientations. However, this approach is computationally expensive and has not been successful at simulating film growth over a reasonable time scale.28–31 Bruschi and co-workers32 used a quasicontinuous coordinate system, such that the simulated film was represented by a two-dimensional array of square cells with the exact positions of the atoms within each cell represented by a continuous x-y coordinate system. While this method allowed different grain orientations to be represented, the simulated films were at most one monolayer thick. Using similar concepts as Bruschi et al., Rubio et al.30 restricted the positions within each cell to those commensurate with ten possible sublattices. However, their simulated films were less than 50 monolayers thick. Huang and Zhou29 proposed a memory-efficient method to map multiple lattices onto a single lattice, but even so, their simulated films were less than 100 monolayers thick. Thus,
these methods also pose problems for the simulation of nanocrystalline film growth, during which the frequent nucleation of new grains must occur.

A more viable approach to simulate polycrystalline film growth over longer time scales is to incorporate some features of the Q-state Potts model proposed by Srolovitz and co-workers.\textsuperscript{32,33} This method essentially involves prescribing a spin number to each atom that is added to a fixed lattice during deposition. This spin number represents which grain the atom belongs to; nearest neighbor atoms that possess the same spin number belong to the same grain. Using this approach, the kMC algorithm has been employed by several authors to study polycrystalline film growth; they explored the effects of substrate temperature, deposition rate and incident angle of deposition flux, on grain morphology and crystallographic orientation of deposited films.\textsuperscript{34–40} However, these models suffer from several limitations, such as the unrealistic imposition of an infinite energy barrier for diffusion across grain boundaries,\textsuperscript{36,37,39} deposition times that span less than 100 monolayers\textsuperscript{34–40} and restrictions on the number of grains by forbidding new grains to nucleate during the film growth process.\textsuperscript{34–40} Additionally, these works either qualitatively treat or completely ignore kinetic roughening and void formation. Even though kinetic roughening, vacancy entrapment, grain nucleation and grain evolution all occur during nanostructured film growth, to our knowledge, there is no model that incorporates all these phenomena over an appreciable thickness.

The purpose of this paper is to take some steps toward addressing the issues outlined above in a kMC model of nanocrystalline film growth. We do not aim to simulate any specific deposition process, nor a specific material; our main objective here is to develop a reasonable schematic model that permits study of the basic mechanisms that lead to nanostructure formation during film growth. It is hoped that with improved understanding of the factors that control grain size in nanocrystalline deposits in general, future modeling efforts may focus more effectively on details specific to a given material and process. The model used here includes diffusion, permits voids and vacancies to form, and also allows new grains to nucleate and grow during the film growth process; it can access film thicknesses that comprise many nanoscale grains through the thickness. Thus, the interplay between kinetic roughening, void formation and grain evolution can be analyzed.

II. MODEL

kMC simulations are performed in (1+1) dimension using a close-packed (hexagonal) lattice as the simulation grid. Each lattice site can either be unoccupied, or occupied by a single atom that is also assigned a grain number corresponding to its grain identity. In the initial configuration, the substrate comprises a row of \( L \) atoms of the same grain number, which are locked into position and unable to change their grain numbers. Figure 1 shows a schematic of a growing film, where growth occurs in the \( y \)-direction. Periodic boundary conditions are imposed in the \( x \)-direction, which is parallel to the substrate.

FIG. 1. A schematic diagram of the close-packed lattice and coordinate system used to simulate film growth. Deposition occurs in \( -y \)-direction. Light gray atoms belong to the process zone; dark gray atoms belong to the bulk. Atoms in the lowest columns are outlined in bold. The atom labeled “\( g_1 \)” is allowed to hop in directions indicated by solid arrows; dashed arrows represent forbidden hops. Atom \( g_2 \) can also switch its grain number to \( g_3 \); Interlayer transport of atom \( g_4 \) occurs if it carries out two successive jumps, as indicated by the solid arrows. The first jump results in a net loss of one bond and brings the atom to an activated state.

The simulation involves three basic types of events:

(i) Deposition: a new atom is added onto the lattice,
(ii) Diffusion: a single atom hops to an adjacent vacant lattice site while retaining its grain number, and
(iii) Grain boundary switching: a grain boundary atom switches its grain number without changing its location.

Atoms are deposited onto the surface of the growing film along the close-packed direction denoted “\( y \)” in Fig. 1, using a random solid-on-solid deposition rule.\textsuperscript{41} Each new atom is assigned a unique grain number, so that every atom can in principle form the nucleus of a new grain. These deposition events occur at a fixed interval of real time, so as to simulate a constant deposition rate. By defining the height of each column, \( h \), as the \( y \)-value of its topmost occupied site, each deposition event causes the height of the chosen lattice column to increase by one unit. Therefore, \( h(x,t) \) is a discrete function that describes the growing surface at time, \( t \).

Between deposition events, the kMC algorithm is used to implement diffusion and grain boundary switching events.\textsuperscript{42,43} During diffusion, each atom can hop to a vacant nearest neighbor lattice site while retaining its grain number. However, hops that lead to desorption are not allowed, i.e., an atom must retain at least one nearest neighbor atom after the jump. As an illustration, in Fig. 1, the atom with grain number \( g_1 \) can only hop to two of the four vacant sites, because if it were to perform the hops indicated by dashed arrows, it would not have any nearest neighbor atoms around it after the hop. The rate of a diffusion event, where an atom changes from state \( i \) to state \( f \), is given by \( r_{i\rightarrow f}=k_0 \times \exp(-\Delta E_{\text{diff}}/k_B T) \), where \( k_B \) is Boltzmann’s constant, \( T \) is absolute temperature, \( k_0=k_BT/h' \) is the vibration frequency of an atom, \( h' \) is Planck’s constant and \( \Delta E_{\text{diff}} \) is the activation energy for the corresponding change in state of the atom during diffusion. The activation energy is assigned as \( \Delta E_{\text{diff}}=E_{\text{barrier}}+(E_f-E_i)/2 \), where \( E_{\text{barrier}} \) is the energy barrier for diffusion (defined to be positive), \( E_i \) and \( E_f \) are the bind-
ing energies at the initial and final states respectively (defined to be negative). The binding energy of an atom is a function of its local environment and is assumed pair-wise additive and limited to nearest neighbor interactions. For an atom that is surrounded by \( n_s \) nearest neighbors with the same grain number as itself, and \( n_d \) nearest neighbors with different grain numbers, the binding energy, \( E \), of that atom is given by \( E = n_s E_s + n_d E_d \), where \( E_s \) and \( E_d \) represent the bond energies between two atoms that have the same and different grain numbers respectively. We define the difference between \( E_s \) and \( E_d \) as the grain boundary energy per bond, i.e., \( E_{gb} = E_d - E_s \). Thus, an atom that traverses a grain boundary experiences an additional energy penalty that is proportional to \( E_{gb} \).

Grain boundary switching involves a grain boundary atom changing its grain number to that of one of its nearest neighbors, while remaining in the same location on the lattice. For example, atom \( g_1 \) in Fig. 1 may change its grain number to \( g_2 \) or \( g_3 \). The rate of a grain boundary switching event is given by \( r_{gb} = k_0 \exp(-\Delta E_{\text{switch}}/k_BT) \), where \( \Delta E_{\text{switch}} \) is the activation energy for the corresponding change in state of the grain boundary atom. The activation energy is assigned \( \Delta E_{\text{switch}} = E_{\text{switch}}^{\text{barrier}} + (E_f - E_i)/2 \), where \( E_{\text{switch}}^{\text{barrier}} \) is the energy barrier for grain boundary switching (defined to be positive). In our model, we assign the same value to \( E_{\text{diff}}^{\text{barrier}} \) and \( E_{\text{switch}}^{\text{barrier}} \). Herein, we will use \( \Delta E \) and \( E_{\text{barrier}} \) to denote the activation energy and energy barrier for both diffusion and grain boundary switching.

In experimental film growth settings, there is often an orders-of-magnitude difference in surface versus bulk atomic kinetic rates, especially for energetic deposition processes, such as those involving pulsed lasers, plasmas, or ion beams, as well as in sputter deposition and electrochemical deposition. In these cases there is enhanced kinetic activity in the upper layers of the film (perhaps spanning some dozens of monolayers), the enhanced kinetics are sometimes due to the naturally lower activation barriers for surface processes, sometimes due to higher local temperatures at the interface, or sometimes due to extrinsic effects, such as from the film/electrolyte interface during electrodeposition. In any case, an important aspect of the present model is the ability to roughly model such situations through the inclusion of a “process zone,” in which the kinetics are allowed to be different from the bulk of the growing film. In this zone, the site-independent energy barrier for diffusion is defined as \( E_{\text{barrier}}^{\text{ps}} \) whereas the corresponding parameter in the bulk is represented by \( E_{\text{barrier}}^{\text{bulk}} \), where \( E_{\text{barrier}}^{\text{bulk}} > E_{\text{barrier}}^{\text{ps}} \). The process zone is assigned to lie above a prescribed height, which is \( \Delta h \) units below the topmost atom of the lowest lattice column, \( h_{\text{min}} \). In Fig. 1, we show an example to illustrate; the atoms in the lowest lattice columns are circled in bold and all the atoms that lie in the process zone are shaded light gray. Bulk atoms that lie below the process zone are represented by the dark gray atoms. In Fig. 1, \( \Delta h = 1 \). However, in all of the simulations described below, \( \Delta h \) is set at a fixed value of 20.

The kMC algorithm computes a list of all possible diffusion and grain boundary switch events in the process zone and the bulk, and their corresponding rates. For atoms that are surrounded by multiple vacant sites and/or nearest neighbors with different grain numbers, each possible diffusion and/or grain boundary switch is considered as a distinct and separate event; for instance, atom \( g_1 \) in Fig. 1 contributes two diffusion and two grain boundary switching events to the list of all possible events. An event is then chosen based on its relative rate. Since all the individual event rates are independent, the residence time for the system is related to the reciprocal of the product of the rates of all possible events, and the system time is advanced by this amount after each event. This process of event selection and execution is repeated until the prescribed time interval between deposition events is exhausted, at which point a new atom is deposited and the algorithm continues.

To avoid strong finite-size effects, the system size must be much larger than the effective diffusion length of an atom; we find that for \( L = 500 \), this condition is fulfilled for the conditions employed in this study. For all simulations, the bond energy between atoms with the same grain number is kept at \( E_s = -0.4000 \) eV, and the diffusion barrier for surface diffusion in the process zone is \( E_{\text{diff}}^{\text{barrier}} = 0.5000 \) eV. Using the relationship between melting temperature and cohesive energy, \( T_m = E_{\text{coh}}/6 \), where \( E_{\text{coh}} = 3E_s \), we define the normalized temperature as \( T^* = T/T_m \) and the normalized grain boundary energy as \( E_{gb}^* = E_{gb}/E_s \). The normalized deposition rate, \( D_{gb}^* \), is given by the ratio of the rate of monolayer coverage, \( D_s \), and the rate of a characteristic surface diffusion event at \( T^* = 1 \), i.e., \( D_{gb}^* = D_s/[k_B T_m/(h' \exp(-E_{\text{barrier}}^{\text{ps}}/k_B T_m))] \).

Simulations are carried out over a range of \( T^* \) between 0.35 and 0.91 and \( D_{gb}^* \) spanning more than two orders of magnitude between 2.10 \times 10^{-3} and 0.84, for a fixed grain boundary energy of \( E_{gb}^* = 0.48 \). The effects of grain boundary energy are studied at \( T^* = 0.43 \) and 0.78 with three different values of \( E_{gb}^* = 0.48, 0.24 \) and 0.12.

We have conducted two different sets of simulations in this paper. In the first set, which may more closely represent thermal deposition techniques, \( E_{\text{barrier}}^{\text{bulk}} \) is assigned a conservative value of 1.0000 eV; while this is twice the activation barrier for diffusion in the process zone, it still permits activity in the bulk. In the second set, which may more closely relate to energetic deposition processes, we take \( E_{\text{barrier}}^{\text{barrier}} \to \infty \), that is, bulk diffusion is suppressed, and all atomic activity is relegated to the process zone.

### III. Steady-State Microstructure

All our simulated films exhibit microstructural defects: rough surfaces, bulk vacancies, and grain boundaries. In this section, we investigate the time evolution of these defects and confirm the existence of a steady-state film microstructure.

Figure 2 shows typical time evolution plots of (a) surface step height, (b) surface peak spacing, and (c) vacancy content, expressed in units of average monolayer coverage time (ML). The surface step height is defined as \( G(1, t) = \langle |h(x+1, t) - h(x, t)| \rangle \), where the average is taken over all \( L \) lattice columns, and the peak spacing refers to the average distance along the \( x \)-axis between local height maxima. For each layer of the simulated film, we also calculated its grain dimensions along the \( x \)- and \( y \)-axes, herein referred to as the
The structures of our simulated films are shown in Figs. 3 and 4. Features of the microstructure. Typical steady-state micro-size model was used and the simulated films also exhibited the work of Schimschak and Krug,21 where a surface diffusion zone near the surface. We shall see in later sections that this is indeed true, and that the surface structure plays a determinant role in governing the bulk film microstructure.

Interestingly, the above observations are found to be true whether or not bulk diffusion processes are permitted (i.e., with an activation barrier $E_{\text{bulk}} = 1.000$ eV or with $E_{\text{bulk}} \to \infty$). Figure 2(d) shows the cumulative distribution of the steady-state grain size (circular-equivalent diameter) for both sets of conditions; the results are essentially identical at low to moderate temperatures and only exhibit small differences that are still within measurement scatter at high temperatures. The surface features and vacancy contents are also found to be statistically similar for both sets of simulations. From these results we conclude that nanostructure formation in deposited films (at least under the conditions studied here) is principally controlled by activity in the rapid-kinetic process zone near the surface. We shall see in later sections that this is indeed true, and that the surface structure plays a determinant role in governing the bulk film microstructure. These results also suggest that the effects of bulk diffusion are relatively insignificant for the conditions of the present simulations; in what follows, then, we do not differentiate between the two sets of simulations (with $E_{\text{bulk}} = 1.000$ eV versus $E_{\text{bulk}} \to \infty$), which give the same results.

The results in Figs. 2(a)–2(c) are in good agreement with the work of Schimschak and Krug,21 where a surface diffusion model was used and the simulated films also exhibited steady-state step heights and vacancy contents; the present results further confirm that the grain structure reaches a steady-state on roughly the same timescale as these other features of the microstructure. Typical steady-state microstructures of our simulated films are shown in Figs. 3 and 4.

Approximately 1000 monolayers are shown in these figures, where the lattice sites are color-coded according to their grain numbers and vacancies that are trapped in the bulk are colored black. Figures 3(a)–3(c) show films deposited at different deposition rates at a constant temperature of 0.65. While the effect of surface morphology, Figs. 3(d)–3(f) illustrate the effects of deposition rate, and Figs. 4(a) and 4(b) highlight the effects of boundary energies. From Figs. 2–4 it is clear that deposition conditions dramatically impact the steady-state film microstructure; a more quantitative treatment is presented in what follows. Because of the complex intertwined relationships among the different types of defects (surface morphology, vacancies and grain boundaries), we begin by systematically investigating factors controlling surface morphology and vacancy content. As we shall see later, both of these factors in turn affect the grain structure.

**IV. SURFACE MORPHOLOGY**

Figure 5 summarizes the effects of deposition conditions on the steady-state step height, $G(1, t)$. While the effect of deposition rate is quite minimal (a decade change in rate...
yields a change in step height on the order of one atom, temperature has a determinant role on the steady-state step height (doubling temperature yields an order of magnitude decrease in step height). Figure 5 also suggests that under most deposition conditions, grain boundary energy does not significantly affect step height, except at high deposition rates and low temperatures, where lower grain boundary energy results in a higher step height.

The above results can be rationalized through comparison with the work of Schimschak and Krug,\(^2\) who developed a model to investigate surface roughening during epitaxial growth. They employed a square lattice and their model incorporated random deposition and isotropic surface diffusion. Surface diffusion was restricted to singly-bonded surface atoms, and the number of diffusion trials per surface atom was explicitly fixed for each simulation. If a selected singly-bonded surface atom had a vacant nearest neighbor, the atom would hop to that empty site with probability \(\exp(-E_{\text{step}})\), where \(E_{\text{step}}\) denotes the Schwoebel-type step-edge energy barrier. The authors observed that as they increased the number of diffusion trials per surface atom from 200 to 800, which translates into a fourfold decrease in deposition rate, the steady-state step height decreased from about 0.90 to 0.56. This observation is broadly in line with ours, where decreasing the deposition rate by an order of magnitude causes the step height to decrease by about one.

Even though our model does not explicitly incorporate the Schwoebel-type step-edge barrier, the effects of decreasing \(E_{\text{step}}\) on step height in Schimschak and Krug’s study are qualitatively and quantitatively similar to those of increasing temperature in our study. Figures 2 and 3(a)–3(c) show that as temperature increases, the surface morphologies of our films transition from tall pointed peaks to shorter, more rounded ones; quantitatively, this translates into a decrease in steady-state step height from \(\sim 16\) to \(\sim 2\). In Schimschak and Krug’s study, as \(E_{\text{step}}\) decreased from 3 to 0, a similar morphological transition was observed and the step heights decreased from \(\sim 10\) to \(\sim 1\). Schimschak and Krug suggested that such differences in surface morphologies could be attributed to the effects of the step-edge barrier in restricting interlayer diffusion and preventing the formation of overhangs, thus causing pointed peaks to dominate the surface morphology as \(E_{\text{step}}\) increased.

In the present model, the basic process of interlayer transport is illustrated by the atom labeled \(g_4\) in Fig. 1. Unlike the square-lattice model of Schimschak and Krug,\(^2\) on our hexagonal lattice interlayer transport does not require a next-nearest neighbor hop. Rather, atom \(g_4\) traverses a step through two successive jumps, where the first involves a net loss of one bond and results in an overhang formation. To a good approximation, the entire two-step process of interlayer transport may be considered as an activated event with a barrier corresponding to the lost energy of the broken bond. Thus, relative to an average diffusion event that involves no energy bias, its probability is \(\exp(-E_{\text{bond}}/2k_BT)\), where \(E_{\text{bond}}\) is the average bond energy; we may thus approximate \(E_{\text{eff}} = E_{\text{bond}}/2k_BT\) as the effective Schwoebel-type step-edge barrier in our model.

Using \(E_{\text{bond}} = -0.4000\) eV, the bulk bond energy used in our simulations, we computed \(E_{\text{eff}}\) at different temperatures. These results, together with the range of steady-state step height values obtained at each temperature, are presented in Fig. 6. Also shown in Fig. 6 are the results obtained by Schimschak and Krug,\(^2\) which are consistent with ours; this supports our interpretation that a Schwoebel-type step-edge barrier implicitly operates in our model. Therefore, the trend observed in Fig. 5 where step height increases as temperature decreases, can be attributed to the corresponding increase in \(E_{\text{eff}}\), which restricts overhang formation and interlayer transport. The relatively weak dependence of surface step height upon deposition rate (Fig. 5) also then follows, since its effect on the rate of interlayer transport is through the linear pre-exponential attempt frequency, as compared to the exponential effect of temperature. Grain boundary energy affects
step height by altering $E_{\text{bond}}$, where lower grain boundary energy results in higher $E_{\text{bond}}$; this effect becomes dominant at low temperature and when the fraction of grain boundary bonds is high (i.e., high deposition rates).

Figure 7 summarizes the effects of deposition conditions on peak spacing: peak spacing increases when deposition rate decreases, temperature increases and grain boundary energy decreases. Across the range of temperatures and grain boundary energies examined, decreasing deposition rate by an order of magnitude causes the peak spacing to approximately double. At a constant normalized deposition rate of 0.252, increasing the temperature from 0.35 to 0.91 causes the peak spacing to double from ~10 to ~20. Since decreasing deposition rate and increasing temperature allow more diffusion events to occur, Fig. 7 suggests that peak spacing is primarily diffusion-controlled, and may be indicative of the characteristic diffusion length of the atoms during the initial stages of film growth, as postulated by Schimschak and Krug.21 Figure 7 also presents an interesting relationship between grain boundary energy and peak spacing, where decreasing $E_{\text{gb}}$ from 0.48 to 0.12 causes the peak spacing to increase subtly but consistently; this effect is stronger at low temperatures, where the maximum increase in peak spacing is about 30%.

V. BULK NANOSTRUCTURE OF THE DEPOSITS

The bulk features of the deposited films, well below the process zone, involve vacancies (and agglomerations thereof) and grain structures. We discuss these features, their original genesis in the process zone, as well as their interrelations, in the following.

A. Vacancy incorporation

Figure 8 summarizes the effects of deposition conditions on the steady-state vacancy content. Except at $T^* = 0.35$, vacancy content increases predictably and quickly as deposition rate increases. Diffusion has a dual role in vacancy generation and annihilation. In the limiting case where there is negligible diffusion (i.e., high deposition rate), the film is expected to exhibit zero vacancy content since deposition does not create vacancies. In the other extreme scenario, infinite diffusion also results in extremely low bulk porosity, because excess (nonequilibrium) vacancies would tend to be healed by diffusion. In the present simulations, the situation is intermediate; with limited diffusion, overhang and void formation occurs via non-volume-conserving diffusion events, and only a fraction of these vacancies are healed by volume-conserving diffusion events.21 Thus, the resulting vacancy content depends on the competing effects between these two types of diffusion events. For most of the conditions employed in this study, increasing deposition rate decreases the ratio of volume-conserving to non-volume-conserving diffusion events, and only a fraction of these vacancies are healed by volume-conserving diffusion events.21 Thus, the resulting vacancy content depends on the competing effects between these two types of diffusion events. For most of the conditions employed in this study, increasing deposition rate decreases the ratio of volume-conserving to non-volume-conserving diffusion events, thus causing the vacancy content to increase. The anomalous inflection observed at $T^* = 0.35$ is attributed to the relatively low rate of defect-forming diffusion events at very high deposition rate.

That non-volume-conserving diffusion events lead to formation of overhangs and voids implies that void morphology is intimately related to the surface profile of the growing film. Figures 3 and 4 qualitatively show that films that exhibit steep step heights also exhibit elongated voids [cf. Figs. 3(a) and 4], whereas films with smoother surfaces contain voids that are more equiaxed [cf. Fig. 3(c)]. Despite the close relationship between surface morphology and void struct-
nucleus continues to grow in the vertical direction. A typical example showing the birth and growth of a grain; this nucleus forms a triple point with nearby grains in (d). The dashed ellipse in (b) shows a nucleus that is eventually eliminated in (f). Regions enclosed in blue boxes in (g)–(h) illustrate grain boundary migration until the grain boundaries are pinned by voids.

B. Grain nucleation mechanism

The above analyses on surface morphology and vacancy content are broadly in line with prior surface diffusion deposition models that do not incorporate grain structure. Of more interest in this study is the fact that the grain structure that evolves in deposited films is directly related to the surface morphology and vacancy content, since new grains form on the surface and their growth in the bulk is affected by vacancies. This can be quickly appreciated by examining supplementary movies 1–2 (Ref. 51) and Figs. 9 and 10. These figures highlight a principal finding of our work: the nucleation of new grains during deposition occurs essentially exclusively atop surface peaks.

A typical example showing the birth and growth of a new grain is denoted by a blue ellipse in Fig. 9(a); this nucleus continues to grow in the vertical direction [cf. Figs. 9(b)–9(e)] until its further growth is inhibited by the nucleation of a new grain above it [cf. Fig. 9(f)]. The red ellipses at the right of Figs. 9(c)–9(e) illustrate another example of vertical grain growth being interrupted by subsequent grain nucleation events on a surface peak [cf. Fig. 9(e)]. Additionally, the red ellipses in Figs. 9(f)–9(h) illustrate a typical example of grain growth in the lateral direction, which appears limited by peak separation. In other words, grains typically develop independently of one another on separate peaks, and become lateral neighbors by growing into mutual contact.

Within the bulk, grains continue to change their size and shape in more subtle ways. Generally, we observe some grain boundary motion shortly after grains impinge, but grain boundary migration is usually arrested soon after, once the grain boundaries encounter voids and become pinned; an example of this is illustrated by the regions enclosed in the blue boxes in Figs. 9(a)–9(h)]. This stagnation of grain boundary migration happens very early in the life of a grain, usually when it is still located within the process zone (as for the example in Fig. 9). Of course, once the grains enter the bulk region, the kinetics of structure evolution is further slowed.

The images in Fig. 9 are also complemented by those in Fig. 10, which show many of the same features, but for a higher deposition temperature with a correspondingly smoother surface. The same basic mechanisms are observed here: grains nucleate on surface peaks; their height (grain major) is principally governed by the likelihood that a new grain forms atop them, while their width (grain minor) is governed by the spacing of peaks and lateral pinning by strings of vacancies and voids. In what follows, we present a quantitative analysis of the factors governing grain evolution, separately examining the minor and major axes of the grain structure.

C. Factors controlling grain dimensions

Figures 11(a) and 11(b) show that increasing temperature and decreasing deposition rate cause both grain minor and major to increase; such trends are generally consistent with experimental observations.\(^\text{52-62}\) One plausible explanation for these trends is that increasing temperature and decreasing deposition rate correspond to more time-at-temperature, promoting more grain boundary migration. However, Figs. 11(a) and 11(b) also show that decreasing grain boundary energy has an opposite effect on grain major and minor dimensions,
Despite the fact that this change lowers the driving force for grain growth, reduces grain boundary migration, and should simultaneously reduce both grain dimensions. Thus, consistent with the qualitative results shown in Fig. 9, Fig. 11 presents quantitative evidence that grain minor and major are principally governed by different factors, and that grain minor is not primarily controlled by the rate of grain boundary migration, which is the case for conventional grain growth.

Instead, the trends on grain minor may be understood by revisiting the implications of supplementary movies 1–2 and Figs. 9 and 10: because new grains nucleate principally on top of surface peaks, there is a consistent correspondence between valley positions and grain boundary regions, as can also be appreciated from Figs. 3 and 4. That grain minor is intimately related to surface morphology is borne out in Fig. 12, which shows grain minor plotted against mean peak spacing for the simulated films. An approximate linear relationship is consistently observed for each series of simulations (although the slope is a function of temperature). Figure 12 also helps to explain why grain minor increases as grain boundary energy decreases (as this causes an increase in the peak spacing).

Grain major, on the other hand, appears to be primarily dictated by the rate of grain nucleation atop the surface grains. Because each freshly-deposited atom is randomly assigned a grain number, each deposition event constitutes an opportunity to nucleate a new grain. That new grains tend to nucleate on peaks is intuitively reasonable, since freshly-deposited atoms are less likely to switch their grain numbers and join a pre-existing grain if they are poorly coordinated by atoms of the pre-existing grain. Such atoms can then form nuclei for new grain formation. Consider the case where an existing grain with grain number \( g_1 \) is located at a surface peak. When a freshly-deposited atom of grain number \( g_2 \) lands on top of the peak, a \( g_1 - g_2 \) grain boundary bond is formed. The driving force for the new atom to switch its grain number from \( g_2 \) to \( g_1 \) depends on the grain boundary energy, and the activation energy for such a switch event is given by \( \Delta E = E_{\text{barrier}}^{g_2} - E_{\text{barrier}}^{g_1} / 2 \). If this switch event occurs, the new atom is assimilated into grain \( g_1 \) and no grain nucleation occurs. Even though such a switch event is always thermodynamically favorable, it can be kinetically avoided depending upon the deposition rate. More specifically, if another new atom of grain number \( g_3 \) is added on top of the atom of grain number \( g_2 \), the topmost atom may join grain \( g_2 \). When this happens, the \( g_2 \) atom that is in contact with grain \( g_1 \) has a \( g_2 - g_2 \) bond, in addition to the \( g_1 - g_2 \) grain boundary bond. Because a switch event that converts the \( g_1 - g_2 \) grain boundary bond to a \( g_1 - g_1 \) bond would occur at the expense of converting the \( g_2 - g_2 \) bond into a \( g_1 - g_2 \) grain boundary bond, there is no net change in the number of grain boundary bonds for such a switch event. Thus, the activation energy for grain boundary switching of the two-atom grain nucleus is \( \Delta E = E_{\text{barrier}}^{g_2} \), which is higher than that of the one-atom grain nucleus. Therefore, a grain nucleus of two atoms is significantly less likely to be assimilated into pre-existing grains than a one-atom nucleus.

Thus, we view the nucleation of new grains as a kinetic competition between switching events that assimilate freshly-deposited atoms into the existing grain structure (with a rate proportional to \( k_{0p} \exp[-(E_{\text{barrier}}^{g_2} - E_{\text{barrier}}^{g_1} / 2)/k_{B}T]\), and the local clustering of new atoms into incipient grain nuclei (with a rate governed by the addition of new atoms, and thus proportional to \( D_{p} \), the rate of monolayer coverage). Assuming that the grain major is primarily governed by the rate at which new grains nucleate on top of pre-existing grains and neglecting the effects of subsequent grain bound-
ARY migration on the grain major, this grain nucleation model suggests that the grain major is related to the normalized switch rate, which we define as \( \frac{k_0 \exp[-(E_{\text{barrier}} - E_{gb}/2)/k_BT]}{D_p} \). Figure 13 shows the average grain major as a function of the normalized switch rate for our simulations. The data collapse reasonably well onto a single curve supports our view of grain major being limited by the nucleation rate for new grains on the top of surface peaks.

The data collapse in Fig. 13 is especially good at lower normalized temperatures, between 0.35 and 0.52, where we also observe that the relationship between grain minor and peak spacing is close to a 1:1 correspondence (cf. Fig. 12). In this low temperature regime, each surface grain is clearly defined by a peak (cf. Figs. 3(a) and 4). Recall from Fig. 5 that this is also the temperature range where films exhibit steep step heights greater than ~4–5 atomic distances. Because the peaks are tall and separated, grains on each peak are isolated from those on neighboring peaks and thus, they evolve independently and peak spacing corresponds to the grain width. It is likely also significant that in this case, the grains within each peak form into a bamboo structure with grain boundaries normal to the growth direction. Such a structure is stable against coarsening (low boundary curvature), and therefore promotes the retention of a nanoscale structure.

At higher normalized temperatures above 0.52, the grain minor often exceeds the peak spacing (cf. Fig. 12) and the data collapse in Fig. 13 is less convincing, with a temperature dependence appearing to spread the data points. This is because at these temperatures, the surface exhibits a smoother and more nodular structure, instead of tall pointed peaks (cf. Figs. 3 and 10). Because of the gentler step height and peak slope, the peaks communicate more readily with one another and do not evolve independently as they do at lower temperatures. Consequently, some grain widths span multiple peaks, as seen in Figs. 3(e), 3(f), and 10. Despite the different surface morphology, grains are still found to nucleate in the same basic way, i.e., nucleation events still occur preferentially on surface peaks. However, supplementary movie 2 and Fig. 10 show that in these cases there is an additional factor that affects the stability of these grain nuclei. Specifically, nuclei located on peaks nearer the lateral edge of a grain, i.e., in close proximity to adjacent grains, are more stable against elimination than those that form in the center of a pre-existing grain. Compare, for example, the nucleus enclosed in the solid red ellipse with the one enclosed in dashed blue in Fig. 10(b). This additional stability of such edge-nuclei arises because shortly after they form atop a first grain, film growth brings them into lateral contact with a second grain, forming a triple junction. This stabilizes the nucleus by setting up a local kinetic competition; a nucleus connected to only one grain experiences switch events at a higher rate than when it is abutted by two. Therefore, as temperature increases and the surface becomes composed of smaller and gentler peaks that are spanned by individual grains, more nuclei survive through this additional mechanism, and the grain minor decreases for the same normalized switch rates, as shown in Fig. 13.

**D. Vacancy-grain boundary interactions**

Upon closer inspection, supplementary movies 1–2 and Figs. 9 and 10 [see for example regions enclosed in blue boxes in Figs. 9(a)–9(h) and Figs. 10(g) and 10(h)] also show that vacancies and voids retard grain boundary migration; grain boundaries that are not decorated with voids migrate freely until they encounter some, after which their motion becomes impeded. These observations suggest that because of grain boundary pinning, high vacancy and void contents (i.e., high deposition rates) favor small grains. They also suggest that the state of vacancy incorporation in grain boundaries (or the grain boundary free volume) is principally a dynamical feature of the microstructure. We may verify this by examining the segregation state of the vacancies to grain boundaries.

Defining the vacancy segregation energy as the difference in formation energy of the vacancy at the grain boundary and in the bulk, we obtain positive segregation energies for all grain boundary energies employed in this study. From an energetic standpoint, we thus expect vacancy segregation to be favored in all of our simulations, with higher segregation tendencies as grain boundary energy increases; of course temperature would tend to randomize the vacancy distribution and therefore decrease the segregation tendency. To assess such trends, we use the Gibbsian interfacial excess, defined as \([N_{gb}/N_{bulk} - (N_{gb}/N_{bulk})/N_{bulk}]\), where \(N_{gb}\) and \(N_{bulk}\) are the number of vacancies in the grain boundary and grain interior regions, and \(N_{gb}\) and \(N_{bulk}\) are the total number of sites in the grain boundary and grain interior regions, respectively. Although we do not plot the results here, we find that in general the interfacial vacancy excess is a weak function of deposition rate, and increases as temperature and grain boundary energy increase. That interfacial excess increases as grain boundary energy increases is in line with the energetic arguments laid out above. However, the effects of temperature on interfacial excess defy energetic predictions. Such a discrepancy must be attributed to kinetics, and is
likely related to the more rapid grain boundary migration at higher temperatures which leads to more interceptions of voids by boundaries.

**E. Grain size versus shape**

As a final point, Fig. 14 summarizes an overarching finding of our work, which concurs with experimental findings: as the average grain size (i.e., average circular-equivalent grain diameter) decreases, so does its aspect ratio. All other things being equal, we find that promoting finer grains through, e.g., more rapid deposition or lower deposition temperature, also promotes more equiaxed structures. Our analysis provides a straightforward explanation of this common observation. The grain minor is largely governed by the surface structure and specifically the separation of the peaks, both of which are only slightly affected by deposition conditions [e.g., increasing the deposition rate by an order of magnitude reduces the peak spacing by only ~5 atomic units (cf. Fig. 7)]. On the other hand, the grain major exhibits a much stronger dependence on deposition variables since they directly affect the grain nucleation rate [an order of magnitude increase in deposition rate increases the grain major by almost two orders of magnitude (cf. Fig. 13)]. Therefore, changes in the deposition condition that promote finer grains are more strongly manifested in the grain major; grain size and aspect ratio are thus dynamically linked, and nanoscale grains tend to be more equiaxed.

**VI. CONCLUSIONS**

We employ a full diffusion kMC model to simulate nanocrystalline film deposition. We find, in line with prior simulation works of film deposition, that the surface structure (step height and peak spacing), as well as the vacancy content, achieve a steady-state condition after an initial growth transient. What is more, these features of the film change with temperature and deposition rate in ways consistent with prior models. However, the present work also evaluates the evolution of the grain structure and its dependence on deposition conditions, by associating individual atoms with specific grains and permitting atoms to switch their allegiance based on a kinetic law that incorporates a grain boundary energy penalty. Broadly, our conclusions in regard to the grain structure of deposited nanocrystalline films are as follows:

- Like the surface structure and vacancy content, the grain structure of the growing film exhibits a steady-state condition, in which the grain dimensions and aspect ratio remain approximately constant.
- The grain structure of the film is essentially governed by the steady-state surface morphology because new grain nucleation occurs exclusively on surface peaks. Thus, bulk nanocrystalline deposits are favored by the presence of nanoscale roughness at the growth surface.
- Nucleation of new grains is viewed as a kinetic competition between the clustering of a few atoms into a new grain at the surface peaks on the one hand, and their incorporation into the grain beneath on the other. When freshly-deposited atoms cluster with one another rather than join the pre-existing grains of the film below, a new grain can nucleate and form; this condition is facilitated by the low coordination of atoms at surface peaks. At higher temperatures, the surface peaks are small and closely spaced; in this case grain nucleation is facilitated when a nucleus comes into contact with another adjacent grain, forming a triple junction.
- As a result of the nucleation mechanism being relegated to surface peaks, the grain minor dimension (in the plane of the film) is primarily dictated by surface peak spacing, which in turn is reduced at low temperatures and high deposition rates. The grain major dimension (in the growth direction) is related to the probability of nucleating new grains on top of pre-existing ones, with finer grains being formed at low temperatures, high deposition rates and low grain boundary energies. Because vacancies and voids kinetically pin grain boundaries, high vacancy (or free volume) content, which is obtained at high deposition rate, also favors nanograins.
- Because surface roughening and tighter peak spacing are less easily induced by deposition conditions than grain nucleation events, as grains shrink, they transition from columnar, to elongated, and eventually to equiaxed.

These results provide some initial insight on the kinetic mechanisms by which the grain structure of deposited films may be tuned, and generally support empirical observations common in the experimental literature.

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