Factors Mediating Smoothness in Epitaxial Thin-Film Growth

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Factors Mediating Smoothness in Epitaxial Thin-Film Growth

Abstract
Surface-sensitive diffraction techniques are often used to monitor the smoothness of epitaxial thin films during growth, i.e., the propensity for layer-by-layer growth. Interpretation of such data requires an understanding of the relative importance of various factors that mediate smoothness. These include the adsorption-site geometry, the dynamics of atoms during deposition, and possible transient mobility following deposition, as well as thermal diffusion. Here we present a systematic study of the first three factors, emphasizing the interplay between geometry and dynamics. This is achieved by a comparison of several “low-temperature” far-from-equilibrium growth models where adsorption occurs at on-top sites, bridge sites, or threefold or fourfold hollow sites. Film structure is elucidated through determination of the interface width, density of steps and adsorption sites, the kinematic Bragg intensity, and short-range-order parameters. Exact analysis of nonasymptotic properties of these statistical-mechanical models is in general impossible, and so most results presented are from Monte Carlo simulation.

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Factors mediating smoothness in epitaxial thin-film growth

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Surface-sensitive diffraction techniques are often used to monitor the smoothness of epitaxial thin films during growth, i.e., the propensity for layer-by-layer growth. Interpretation of such data requires an understanding of the relative importance of various factors that mediate smoothness. These include the adsorption-site geometry, the dynamics of atoms during deposition, and possible transient mobility following deposition, as well as thermal diffusion. Here we present a systematic study of the first three factors, emphasizing the interplay between geometry and dynamics. This is achieved by a comparison of several “low-temperature” far-from-equilibrium growth models where adsorption occurs on top sites, bridge sites, or threefold or fourfold hollow sites. Film structure is elucidated through determination of the interface width, density of steps and adsorption sites, the kinematic Bragg intensity, and short-range-order parameters. Exact analysis of nonasymptotic properties of these statistical-mechanical models is in general impossible, and so most results presented are from Monte Carlo simulation.

I. INTRODUCTION

Nearly layer-by-layer growth of “smooth” films is commonly perceived to occur via cyclical, growth, and coalescence of (two-dimensional) islands in successive layers.\(^1\) In this picture, significant mobility is required for atoms deposited on top of islands to migrate to the edges and be incorporated in the layer beneath. Such mobility is usually attributed to thermally activated diffusion.\(^2\,3\) Although it has recently been suggested that there could also be a contribution from transient diffusion—mobility possibly resulting from the inability of an adatom to immediately dissipate the energy released upon formation of the atom-surface bond.\(^2\) The occurrence of such transient mobility is currently disputed.\(^4\) In any case it should be clear that smoothness of thin films, especially in the early stages of growth, will be determined by a number of factors, including adsorption-site geometry, the dynamics of atoms during deposition, and possible transient mobility following deposition, as well as thermal diffusion. It is also possible that concerted (multiatom) dynamics,\(^4\) in addition to single-atom dynamics, could play a significant role in influencing structure.

Our study systematically elucidates the significant influence and interplay among the first three factors. This is done through consideration of several far-from-equilibrium growth models, excluding thermal diffusion, which can isolate the various aspects of growth. Such models are of interest in their own right as they provide insight into low-temperature thin-film growth, which is the subject of several recent studies.\(^2,3,5,6\) The key components of these models, and also some previous results, are now outlined in more detail.

(i) Adsorption-site geometry. The most appropriate classification of adsorption sites here is according to the number \(s\) of supporting atoms in the layer beneath. Thus \(s = 1, 2, 3, \) and 4 for on-top, bridge, threefold hollow (3fh), and fourfold hollow (4fh) sites, respectively. These could be associated with sc (100), one-dimensional, fcc (111), and fcc (100) substrates, respectively. To isolate the influence of adsorption-site geometry, it is convenient to consider random-deposition models, wherein atoms are added with equal probability to all adsorption sites. The \(s = 1\) on-top site adsorption model can readily be shown to generate a “broad” Poisson distribution of column heights.\(^7\) Exact but nontrivial analysis of other random-deposition models is possible,\(^7\) allowing detailed analysis of the relationship between film structure and adsorption-site geometry.

(ii) Dynamics during deposition. Here we assume that atoms initially impinge perpendicular to the clean substrate. The above random-deposition model assumes that all adsorption sites have equal “capture areas” and implies that if an atom does not impinge within one of these capture zones then it desorbs. However, it is more likely that atoms impinging anywhere are funneled downwards until reaching an adsorption site, as such motion, of course, has a significant component in the direction of initial impingement. This picture is generally supported by some recent molecular-dynamics studies.\(^3\) Here capture areas of various adsorption sites differ and are greater at the “bottom of valleys.” Note that for a substrate temperature of \(T = 0\) K, the deposition dynamics is a deterministic process, and so capture zones are uniquely defined. For \(T > 0\) K, capture zones should be thought of as “fuzzy sets.”\(^11,13\) In such funneling models, where all impinging atoms adsorb, sticking coefficient is constant (in contrast to random-deposition models).

(iii) Transient mobility of “hot” atoms immediately following deposition.\(^2\) Here we define transient mobility as motion between adsorption sites, as distinct from, e.g., downward funneling. Thus transient mobility has a major component perpendicular to the impingement direction. There have been studies for on-top site deposition models of the influence of transient diffusion to a column of minimum height within a finite distance of the depo-
tion site. The smoothing effect is dramatic even allowing diffusion to neighboring columns, as described further below. Studies of the on-top site model on a two-dimensional substrate indicate that the introduction of transient diffusion (even of limited range) will produce oscillations in step densities which correlate with those in certain diffracted intensities. In this contribution we will explore the role of transient mobility for different (more realistic) adsorption-site geometries with \( s > 1 \). Another possibility, for \( s > 1 \) adsorption-site models, is that the impinging atom may “knock out” one of the \( s \) supporting atoms, taking its place. It is also conceivable that “hot” atoms could dislodge previously deposited atoms and that various more complicated concerted atom rearrangement pathways are operative. The latter possibilities are not examined here.

Figure 1 provides a comparative schematic of deposition models incorporating the various features described above. In the following sections we shall consider in detail these different types of models for various adsorption-site geometries: bridge sites in Sec. III, three-fold hollow sites in Sec. IV, and fourfold hollow sites in Sec. V. Within each section we compare the relative influence on film structure of random deposition, downward funneling, transient mobility, and knock-out mechanisms. We summarize our findings in Sec. V. However, before embarking on this endeavor, it is appropriate to make some further remarks relating this work to the diverse array of research currently focused on far-from-equilibrium film growth.

The motivation for our work is provided by extensive ultrahigh-vacuum experimental studies of epitaxial thin-film growth using surface-sensitive diffraction techniques to monitor the evolution of structure. Nearly layer-by-layer growth produces oscillations in certain diffracted intensity amplitudes with the period of monolayer incorporation. The amplitude and persistence of the oscillations provide detailed information about the growth. In such experiments films are sometimes only grown to several layers, and typically to less than a few dozen layers thick. Thus our focus here is on the corresponding initial or nonasymptotic structure. Of necessity, discrete or lattice-type models are invoked since incorporation of the appropriate adsorption-site geometry is essential. Quantities calculated, which are described in detail in Sec. II, include the layer coverage distribution, the width of the film interface, step densities, spatial pair correlations, and kinematic diffracted intensities.

Another active but distinct body of theoretical investigation is directed toward analysis of the long-time asymptotic behavior in various far-from-equilibrium film-growth processes. Here the asymptotic scaling of the interface width \( W \), defined precisely in Sec. II, is of primary interest. Discrete microscopic models, similar to those described above, are often analyzed directly by computer simulation. A powerful alternative strategy proceeds via the assumption that the asymptotic interface evolution in these models can be described by a continuum Kardar-Parisi-Zhang-- (KPZ-) type equation. Analysis of this equation elucidates the distinction between the following classes of behavior at large coverage \( \theta \) for various substrate dimensions \( d = 1 \): (a) rough growth for random deposition at on-top sites, where \( W \sim \theta^{1/3} \); (b) smoother KPZ growth for models where \( d \theta /d t \) varies quadratically with the introduction of a small macroscopic surface slope; here \( W \sim \theta^{1/3} (\theta^{1/4}, \text{perhaps}) \) for \( d = 2 \) (or 3); (c) the smoothest Edwards-Wilkinson (EW) growth, where \( d \theta /d t \) does not depend quadratically on a macroscopic slope, but does at least depend on the macroscopic curvature, unlike (a); here \( W \sim \theta^{1/4} (\log \theta) \) for \( d = 2 \) (or 3).

Thus, although these two types of investigations often deal with the same sort of far-from-equilibrium film-growth models, and even calculate the same quantities, they focus on different (initial versus asymptotic) growth regimes. Detailed information on thin-film structure determining the short-time diffracted intensity oscillations is, of course, absent in the asymptotic scaling laws. On the other hand, clearly spreading of the film interface does degrade the diffracted intensity oscillations, and the relationship between the two has been considered in recent work. The key question is whether asymptotic behavior is reflected in the evolution over the experimentally relevant coverage regime. Results for our models suggest that this is true, and therefore that application of scaling ideas is instructive. These, for example, can explain the significant difference between the KPZ behavior of the random-deposition model for adsorption at bridge sites or fourfold hollow sites (which is equivalent to the so-called “single-step model”), and the EW behavior of the corresponding downward funneling models. A detailed discussion of these ideas is deferred to a separate communication.

II. QUANTITATIVE MEASURES OF FILM STRUCTURE

Our quantitative analysis of epitaxial growth models will focus on several measures of film structure. The most basic specification of structure and growth is given by the layer coverage distribution. We let \( \theta_j \) denote the coverage (in monolayers) of layer \( j \). Here \( j = 0 \) corre-

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**FIG. 1.** Schematic illustration of several models described in the text.
sponds to the top substrate layer so \( \theta_0 = 1 \). Clearly, \( N_j = \theta_j - \theta_{j+1} \) (\( \geq 0 \), for our models) reflects the net number of exposed atoms in layer \( j \). We consider the following.

(a) The interface width \( W \) (Refs. 3, 7, 8, 12, and 15-17), satisfying
\[
W^2 = \sum_{j=0}^{\infty} (j - \bar{j})^2 N_j ,
\]
where
\[
\bar{j} = \sum_{j=1}^{\infty} j N_j = \sum_{j=1}^{\infty} \theta_j = 0
\]
(the total coverage).

(b) The Lent-Cohen kinematic expression for the Bragg intensity \( I_{\text{Bragg}} \) (Ref. 19) at the out-of-phase condition where scattering from consecutive layers interferes destructively. Thus, when normalized to unity for a clean substrate,
\[
I_{\text{Bragg}} = (N_0 - N_1 + N_2 - \cdots)^2 ,
\]
assuming equal scattering factors from substrate and film atoms, and that each atom shields a net of one atom in the layer beneath.\(^7\)

The \( \theta_j \) contain no information on the intralayer ordering. Consequently, we also consider the nearest-neighbor (NN) correlations \( C_j = \theta_{j+1} - \theta_j^2 \), where \( \theta_{j+1} \) denotes the probability that a NN pair of layer \( j \) sites is occupied. Thus \( -\theta_j^2 \leq C_j \leq \theta_j (1 - \theta_j) \), and \( C_j > 0 \) (\( C_j < 0 \)) reflects clustering (anticlustering). From these quantities one can determine the following.

(c) The step density \( D \) (Refs. 3 and 13). Let \( \bar{\theta}_{j+} \) denote the probability that a NN pair of layer \( j \) sites has one filled and one empty site. Then we define
\[
D = \sum_{j=1}^{\infty} \bar{\theta}_{j+} = 2 \sum_{j=1}^{\infty} \left[ \theta_j (1 - \theta_j) - C_j \right] .
\]

It has been argued that the behavior of \( D \) correlates strongly with that of the reflection-high-energy-electron-diffraction intensities.\(^{13} \) Another somewhat related quantity of interest is the following.

(d) The adsorption-site density \( S \) normalized to unity for a perfect substrate. \( S \) will determine the adsorption rate, and thus the sticking probability, in some models considered below. We note that for steady-state film growth which is sufficiently layer-by-layer like, all the above quantities will oscillate periodically for the epitaxial geometries of interest here.

### III. DEPOSITION AT BRIDGE SITES

We first describe in detail the various models considered here for deposition at the bridge sites of a one-dimensional substrate (cf. Fig. 1). We then close this section with some comparative analysis of these models.

Random deposition (RD), i.e., addition with equal probability at all bridge sites. Here exact analysis is possible noting that the occupancy of any configuration of sites is determined by a finite number of supporting atoms.\(^7\) There are no correlations in the first layer. However, nearest-neighbor (NN) correlations \( C_j \) in higher layers, \( j > 1 \), are positive and increase monotonically with \( j \) to a maximum possible \( C_j \sim \theta_j (1 - \theta_j) \), as \( j \to \infty \). This reflects the occurrence of increasing by long strings of occupied sites (in partially filled layers), which is a direct consequence of the diverging interface width and bound of \( \pi/3 \) on the surface slope.\(^3\) This geometry-induced clustering effect will be present in all models considered here.

**Downward funneling (DF).** For any film configuration, every adsorption site constitutes the base of a "valley" formed by possibly higher-layer atoms. In our \( T = 0 \) K downward funneling model, that adsorption-site captures any atom impinging within its valley. It thus has a capture area of \( A = 1 + (l + r)/2 \), where \( l/r \geq 0 \) is the height of the left (right) wall of the valley (see Fig. 2). Specification of these capture areas completely determines growth. It should be clear that downward funneling will enhance the positive NN correlations (clustering) during growth relative to random deposition. This actually has the effect of creating more adsorption sites for higher layers (relative to random deposition) which alone would make the film rougher. However, this effect is somewhat overcompensated for by the enhanced rates for filling lower layers, whose adsorption sites typically have larger capture areas.

Fig. 2. Determination of the capture areas, \( A = 1 + (l + r)/2 \), for downward funneling to bridge sites on one-dimensional substrate.
Thus, in this restricted model, funneling generates positive NN correlations, $C_1 = P_2 - P_1^2$, with maximum value of 0.0363 at $\theta_1 = 0.57$. Longer-range correlations can also be determined exactly, and are positive.\(^{21}\)

One-hop transient mobility (1H). Here the random-deposition model is modified to allow atoms to make one hop immediately following deposition to a randomly chosen empty neighboring site, if one exists. If the atom hops right (left), it either finds another bridge site where it remains permanently, or it tumbles down the left-hand side (right-hand side) of valley until reaching a bridge site at the bottom (see Fig. 3). We show below that the effect of hopping within a layer is to produce negative NN correlations (anticlustering) and thus less adsorption sites for the next layer. This effect makes growth more layer-by-layer like. Tumbling from higher layers tends to produce positive NN correlations (clustering), but the associated enhanced rates for filling lower layers is the dominant film smoothing effect. The first layer NN correlations $C_1$ show a transition from negative values (minimum of $-0.017$ at $\theta_1 = 0.39$) to small positive values (maximum of 0.003 at $\theta_1 = 0.84$). Geometric clustering effects, observed in the random-deposition model, dominate the $C_j$, for $j > 1$.

Exact analysis of this model is not possible, as for (ii). However, to elucidate the correlations associated with intralayer transient hopping, it is instructive to consider the solvable restricted one-hop model with no occupied second or higher layer sites. Here atoms randomly fill empty first layer sites at rate $k$ and then hop to a randomly chosen empty NN site (if possible). Analysis of the $P_n$-hierarchy reveals that empty pairs of sites shield and that $P_n + 1/P_n = e^{-kt}$ for $n \geq 2$ (cf. Refs. 21 and 22). Subsequent solution of these equations shows that

$$P_1 = \exp(-kt),$$

$$P_2 = P_1^2 \exp[-(1-P_1)^2/2] \leq P_1^2. \tag{5}$$

Thus, in this restricted model, hopping generates negative (anticlustering) $C_1 = P_2 - P_1^2$, with minimum value of $-0.029$ at $\theta_1 = 0.49$.

Two-hop transient mobility (2H). Here the one-hop model is further modified so that if an atom reaches a bridge site (and thus remains in the same layer) after one hop, it then makes a second hop to a neighboring empty site. This hop is made in the same direction as the first if possible (which could then result in tumbling downhill as in the one-hop model), or back to the original deposition site if not. The observations on structure and correlations made for the one-hop model still apply. Of course, here the greater mobility range produces smoother films and modifies the correlations (e.g., $C_1$ now achieves a minimum of $-0.012$ at $\theta_1 = 0.27$ followed by a maximum of 0.014 at $\theta_1 = 0.76$).

Since this model is not amenable to exact analysis, we consider the solvable restricted two-hop model with no occupied second or higher layer sites. Analysis of the $P_n$ hierarchy reveals that empty quartets of sites shield, and that $P_{n+1}/P_n = e^{-kt}$ for $n \geq 4$ (cf. Ref. 21). Subsequent solution shows that

$$P_1 = \exp(-kt),$$

$$P_2 = P_1^2 \left[1 - \int_0^1 dx (1-x)^k \right] \leq P_1^2 \tag{6}.$$

Thus here hopping generates negative $C_1 = P_2 - P_1^2$ with a minimum value of $-0.020$ at $\theta_1 = 0.43$.

Knockout mechanism (KM). Here the random-deposition model is modified such that atoms adsorbing at a bridge site knock out one of the two supporting atoms to a randomly chosen NN empty site (if one exists). Then the deposited atom takes the place of the dislodged atom. If the latter is knocked out to a bridge site, it stays there. Otherwise, it tumbles downhill as in the one-hop model. The knockout mechanism will clearly enhance the positive NN correlations relative to the random-deposition model. However, this roughening effect is dominated by the smoothing associated with enhanced filling rates for lower layers.

The interface width increases monotonically and quite quickly for all these models (see Table I). Not surprisingly, the increase is fastest for random deposition, then for downward funneling, then for the one-hop model, and slowest for the two-hop and knockout models. This relative behavior is also reflected in the values of

$$\theta_1 = 0.744 \text{(RD)}, \quad 0.755 \text{(DF)}, \quad 0.801 \text{(1H)}, \quad 0.825 \text{(2H)}, \quad 0.824 \text{(KM)}. \tag{7}$$

at $\theta = 1$. Corresponding behavior of the short-lived oscillations in the Bragg intensity is revealed in Table II. Maximum values of NN correlations $C_j$ are shown in

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**FIG. 3.** Dynamics of the one-hop transient mobility model for deposition at bridge sites on a one-dimensional substrate.
Table II. Values at the /th local maximum (with coverage increasing) of the normalized Bragg intensity, \( I_{Bragg} / I_{Bragg} / I_{Bragg} / I_{Bragg} \), for bridge site deposition models.

<table>
<thead>
<tr>
<th></th>
<th>( I_{Bragg} )</th>
<th>( I_{Bragg} / I_{Bragg} )</th>
<th>( I_{Bragg} )</th>
<th>( I_{Bragg} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random</td>
<td>2.96[-3]</td>
<td>1.8[-4]</td>
<td>1.9[-5]</td>
<td>1.9[-5]</td>
</tr>
<tr>
<td>One hop</td>
<td>5.2[-2]</td>
<td>1.2[-2]</td>
<td>4.1[-3]</td>
<td>1.6[-3]</td>
</tr>
<tr>
<td>Two hop</td>
<td>9.8[-2]</td>
<td>3.4[-2]</td>
<td>1.4[-2]</td>
<td>6.8[-3]</td>
</tr>
<tr>
<td>Knockout</td>
<td>9.7[-2]</td>
<td>2.9[-2]</td>
<td>1.1[-2]</td>
<td>5.0[-3]</td>
</tr>
</tbody>
</table>

Table III. These are dominated by the geometrical clustering effect for \( j \geq 2 \), although the occurrence of additional dynamics-induced clustering is apparent in the funneling and knockout models.

Although exact analysis is possible only for the random-deposition model, one can to some extent elucidate the initial behavior of the \( \theta_j \) and \( C_j \) through an analysis of their exact Taylor expansions with respect to time or coverage.\(^{1,2}\) If \( k \) is the initial deposition rate for all models, then \( \theta_j \sim a_j (k t)^{K_j} \), as \( t \rightarrow 0 \), where \( a_j = 1 \) and \( K_j \) is the minimum number of atoms required to support a layer \( j \) atom (counting the atom itself). Thus \( K_j = (j^2 + j)/2 \) for random deposition and funneling, \( K_j = (j^2 + 3j + 2)/2 \) for the one-hop model, and \( K_j = (j^2 + 4j - 3)/2 \) for the two-hop and knockout models. A more detailed analysis shows that \( \theta_i \) increases initially like

\[
\theta_i \sim \frac{1}{2} \theta_i^1 (RD), \quad \frac{1}{2} \theta_i^1 (DF), \quad \frac{5}{4} \theta_i^1 (1H), \quad \frac{7}{49} \theta_i^1 (KM). \tag{8}
\]

The initial increase in \( \theta_i \) is faster in the DF than the RD model due to clustering, as reflected by the results

\[
C_i \sim 0 \ (RD), \quad \frac{1}{2} \theta_i^1 (DF), \quad - \frac{1}{2} \theta_i^1 (1H/2H), \quad \frac{1}{2} \theta_i^1 (KM). \tag{9}
\]

Finally we consider the behavior of the step density \( D \) and adsorption-site density \( S \). For the bridge-site deposition geometry, the film is entirely composed of stretches of steps and adsorption sites (Fig. 4). Thus, for the specific definitions of Sec. II, \( S \) and \( D \) are trivially related by

\[
2S + D = 2. \tag{10}
\]

We find that \( D \) (and thus \( S \)) exhibits one to two extremely weak oscillations in the two-hop and knockout models only, and is otherwise monotonic. \( D \) effectively saturates quickly to values (measured for \( \theta \sim 5 \)) of

\[
D \sim \begin{cases} 1.00 \ (RD) (Ref. 18), & 0.72 \ (DF), & 0.64 \ (1H), \\ 0.54 \ (2H), & 0.48 \ (KM). \end{cases} \tag{11}
\]

IV. DEPOSITION AT THREEFOLD HOLLOW (3FH) SITES

We next consider deposition at 3fh sites on an fcc (111) substrate. Unlike the bridge-site model of Sec. III, and the 4fh site model of Sec. V, here there are two types of adsorption sites: bulk (fcc) sites [which continue the abc packing of the fcc lattice (111) planes] and surface (hcp) sites. These can have differing adsorption rates and binding energies.\(^{24}\) However, a more basic complication here is that adsorption into any site blocks adsorption into the three NN sites of the opposite type. Thus, for example, first-layer atoms reside in one of two domains, associated with either surface or bulk sites. Adsorption saturates below a full monolayer (which would correspond to complete filling of one type of site). At this point, \( \theta_1 = \theta_1^1 \), say, and domains are separated only by domain boundaries (see Fig. 5).

For random deposition, exact analysis of kinetics and structure is no longer possible, even for the first layer. However, exact expansions are available,\(^{23}\) and for equal adsorption rates (\( k \)) at all 3fh sites, they show that

\[
\frac{d}{dt} \theta_1 = k (1 - 2 \theta_1 + \frac{1}{2} \theta_1^2 + \frac{1}{3} \theta_1^3 + \frac{1}{4} \theta_1^4 + \frac{1}{6} \theta_1^5 + \cdots). \tag{12}
\]

Resummation of (12) exploiting the near-saturation

TABLE III. Maximum values of layer \( j \) NN correlations, \( C_j \), for bridge site deposition models. See text for a discussion of \( C_j \) for the one-hop and two-hop models.

<table>
<thead>
<tr>
<th></th>
<th>( C_1 )</th>
<th>( C_2 )</th>
<th>( C_3 )</th>
<th>( C_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random</td>
<td>0</td>
<td>0.047</td>
<td>0.072</td>
<td>0.088</td>
</tr>
<tr>
<td>Funneling</td>
<td>0.033</td>
<td>0.069</td>
<td>0.089</td>
<td>0.102</td>
</tr>
<tr>
<td>One hop</td>
<td>0.049</td>
<td>0.074</td>
<td>0.089</td>
<td></td>
</tr>
<tr>
<td>Two hop</td>
<td>0.057</td>
<td>0.081</td>
<td>0.095</td>
<td></td>
</tr>
<tr>
<td>Knockout</td>
<td>0.024</td>
<td>0.080</td>
<td>0.103</td>
<td>0.116</td>
</tr>
</tbody>
</table>

FIG. 4. Decomposition of a growing film, for deposition at bridge sites, into contiguous stretches of steps (s) and adsorption sites (a).
asymptotic behavior\textsuperscript{23} $d \theta_1 / dt = -k (\theta_1^2 - \theta_1)$ produces uniformly accurate estimates of the kinetics, and an estimate of $\theta_1^2$ very close to our “exact” simulation value of 0.759 (cf. Refs. 25 and 26). Basing the filling of one type of adsorption site relative to the other increases $\theta_1^2$ towards unity. For an elucidation of the associated domain-percolation transition, and the behavior of the (effective) fractal dimension and ramification of large domains in the first layer, the reader is referred to Ref. 27.

Film growth obviously continues by deposition into higher-layer 3fh sites. Also possible are deposition at 3fh sites on the sides of growing “pyramids,”\textsuperscript{28} or nonepitaxial deposition at the base of domain boundaries, which eventually leads to randomly packed structures (in the absence of rearrangement).\textsuperscript{25} For simplicity here we ignore the latter two possibilities. Thus, in our model, each layer $j$ domain can support two disordered layer $j+1$ domains. Clearly, this multilayer growth process will also quickly saturate. From simulations with equal deposition rates at all 3fh sites, we find saturation coverages of $\theta_1^2 = 0.759$, $\theta_2^2 = 0.284$, $\theta_3^2 = 0.042$, $\theta_4^2 = 0.002$, \ldots, so $\theta^2 = 1.087$. For this process, $\theta_3 < \frac{1}{8} \theta_1^2$ for small $\theta_1$, the value of $I_{\text{Bragg}}$ at the first local maximum ($I_{\text{Bragg}}^1$) equals 0.019, and $\theta_3 \approx 0.747$ (near saturated) when $\theta = 1$.

For comparison with random-deposition models for bridge and 4fh adsorption sites, it is instructive to consider a modified 3fh site model where deposition occurs randomly into only one type of adsorption site in each layer. Here each layer can fill completely, and an exact analysis of the kinetics follows from the techniques of Ref. 7. Specifically, one finds that $d \theta_1^2 / dt = k (1 - \theta_1^2)$, $d \theta_2^2 / dt = k (\theta_1^2 - \theta_2^2)$, $\theta_3$ is determined by three additional equations, etc. From their solution, we find that $\theta_3 < \frac{1}{8} \theta_1^2$ for small $\theta_1$, the value of $I_{\text{Bragg}}$ at the first (second) local maximum equals 0.037 (0.012) [cf. 0.0030 (0.0002) for the bridge site model], and $\theta_3 \approx 0.791$ when $\theta = 1$. The lower value of $I_{\text{Bragg}}$ in the above model, where both domains are populated, reflects the enhanced ratio of second to first layer adsorption sites (as $\theta_1$ approaches $\theta_1^2$) in that model. Clearly, introduction of downward funneling, transient mobility, or knockout mechanisms into the 3fh-site-deposition models will make growth more layer-by-layer like. However, here we restrict our comparative study of these effects to bridge-site- and 4fh-site-deposition models.

V. DEPOSITION AT FOURFOLD HOLLOW (4fh) SITES

The models considered here for deposition at 4fh sites on a fcc (100) substrate precisely parallel those described in Sec. II. Brief reports of some of the following results have appeared previously.\textsuperscript{3, 8} Again the section is closed with some comparative analysis.

Random deposition (RD). The comments made for the bridge-site model on exact solvability, and growth of positive NN correlations $C_j$ associated with geometric clustering, still apply.\textsuperscript{7} In fact, $C_j$ behavior is quantitatively similar for both models (see Table IV).

Downward funneling (DF). For deposition at bridge sites on a one-dimensional substrate, there was a unique natural prescription of $T=0$ K downward-funneling and adsorption-site capture areas. For a real three-dimensional system, the $T=0$ K capture areas for various 4fh sites depend to some extent on the details of the interaction potentials determining the deposition dynamics. We have indicated elsewhere how this dependence can sometimes be parametrized by exploiting geometric constraints.\textsuperscript{3} Here, however, we are content with providing a relatively easily implementable prescription, which naturally generalizes that of Sec. II and incorporates the essential physics.

Let $x_i$ denote the lateral coordinates of a vertically impinging atom when far from the substrate. We now describe a stochastic algorithm for assigning each $x_i$ to a 4fh adsorption site in a way that mimics downward funneling. It is convenient to introduce the concept of incomplete adsorption sites, as opposed to (implicitly complete) 4fh adsorption sites. The former are empty sites of the fcc epitaxial lattice which have $1 \leq k \leq 3$ supporting atoms in the layer beneath, rather than $k=4$ as for complete adsorption sites.

One starts by partitioning the $x_i$ space as shown in Fig. 6. An atom impinging on a large square region, or single small square region, is assigned permanently to the corresponding $k = 4$ complete adsorption site. An atom impinging on an $L$-shaped region, rectangular or double small square region, or single small square region, is assigned initially to the corresponding $k = 3$, 2, or 1 incomplete adsorption site, respectively. (These assignments are simply achieved by filling adsorption sites at rate $k/4$.) Then immediately this atom is moved progressive-

\begin{table}[h]
\centering
\caption{Maximum deviation from zero of layer $j$ NN correlations $C_j$ for 4fh site deposition models. $C_j$ for one- and two-hop models has smaller positive values for high $\theta_i$.}
\begin{tabular}{|c|c|c|c|c|}
\hline
 & $C_1$ & $C_2$ & $C_3$ & $C_4$
\hline
Random & 0 & 0.050 & 0.073 & 0.087
\hline
Funneling & 0.024 & 0.054 & 0.066 & 0.073
\hline
One hop & -0.035 & 0.008 & 0.017 & 0.024
\hline
Two hop & -0.024 & 0.008 & 0.011 & 0.015
\hline
Knockout & 0.012 & 0.026 & 0.034 & 0.039
\hline
\end{tabular}
\end{table}
ly downward to (adjacent) lower adsorption sites until a complete one is found. More specifically, if \( k = 3 \) the downward move is uniquely prescribed. If \( k = 2 \), there are two adjacent lower adsorption sites and one is chosen randomly. If \( k = 1 \), the atom moves to the diagonally adjacent lower site with probability \( \delta \), or to one of the two laterally adjacent lower sites with probability \( (1-\delta)/2 \) (see Fig. 6).

Here we present results mainly for \( \delta = \frac{1}{3} \). This choice reproduces the (relative) capture rates of substrate 4fh sites for hard-sphere atoms "sliding downhill" once having made contact with immobile first layer atoms. We note, however, that the resulting film structure is fairly insensitive to \( \delta \). For example, \( \theta_1 = 0.845, 0.847, 0.848 \) when \( \theta = 1 \), and the first local maximum of \( I_{\text{Bragg}} \) equals \( 0.149, 0.153, 0.156 \) for \( \delta = 0, \frac{1}{3}, \frac{2}{3} \), respectively.

Again downward funneling enhances NN correlations, creating more adsorption sites, relative to random deposition, as seen in the first layer statistics (Table IV). However, this roughening effect is overwhelmed by the enhanced filling rates for lower layers, in contrast to bridge-site deposition.

One-hop transient mobility (1H). Here the random-deposition model is modified to allow atoms to make one hop immediately following deposition to a randomly chosen empty NN site, if one exists (cf. Sec. II). If the NN empty site is a 4fh site, the hopping atom remains there permanently. If not, that site is an incomplete adsorption site with \( k = 2 \) or 3, and the atom tumbles downhill until reaching a complete 4fh adsorption site.

We use the same prescription of the dynamics as for downward funneling except that here only sites with \( 2 \leq k \leq 4 \) are involved. Comments made for the bridge-site model on the influence of transient hopping on spatial correlations and layer filling rates still apply. For example, the restricted one-hop model with no occupied second or higher layer sites produces negative NN correlations \( C_1 \), with a minimum value of \(-0.039\) at \( \theta_1 = 0.56 \).

Two-hop transient mobility (2H). Here the one-hop model is further modified so that if an atom reaches a 4fh site (and thus remains in the same layer) after one hop, it then makes a second hop to an empty NN site. This hop is made in the same direction as the first hop if possible, at right angles as a second preference (either of which could result in tumbling downhill), and back to the original deposition site otherwise. We use the same prescription for downward tumbling dynamics as above. Observations on structure and correlations for the one-hop model still apply. For example, the restricted two-hop model with no occupied second or higher layer sites produces negative NN correlations \( C_1 \), with a minimum value of \(-0.026\) at \( \theta_1 = 0.52 \).

Knockout mechanism (KM). Here the random-deposition model is modified such that atoms adsorbing at a 4fh site knock out one of the four supporting atoms to a randomly chosen NN empty site (if one exists). Then the deposited atom takes the place of the dislodged atom. If the latter is knocked out to a 4fh site, it stays there. Otherwise it tumbles downhill as in the one-hop model.

Comments made on the influence of the knockout mechanism for the bridge-site model still apply.

Film growth for these 4fh-site-deposition models is much more layer-by-layer like than for the corresponding bridge-site models, although their relative behavior is the same. This is clearly reflected in both the interface width and Bragg intensity behavior (Fig. 7). The relative behavior of these 4fh site models is also reflected in the values of

\[
\theta_1 = 0.819 \text{ (RD)}, 0.847 \text{ (DF)}, 0.869 \text{ (1H)},
\]

\[
0.892 \text{ (2H)}, 0.911 \text{ (KM)}, \tag{13}
\]

at \( \theta = 1 \). Maximum amplitudes of the NN correlations \( C_j \) are shown in Table IV. Again geometric clustering effects drive the increase in the \( C_j \) maxima; however, the increase is much slower than in the bridge-site deposition models (except for random deposition), because of the much slower roughening of the film. Again, exact expansions give additional but somewhat limited insight into the relative behavior of these models; e.g., \( \theta_2 \) increases initially like\(^29\)

\[
\theta_2 \sim \frac{1}{2} \theta_1^4 \text{ (RD)}, \frac{8\delta}{18} \theta_1^4 \text{ (DF)}, \frac{1361}{80440} \theta_1^4 \text{ (1H)}, \frac{4}{960} \theta_1^4 \text{ (DF)}, \frac{1}{(1H/2H)}, \tag{14}
\]

The initial increase in \( \theta_2 \) is faster in the DF than the RD model due to clustering, as reflected by the results

\[
C_1 \sim 0 \text{ (RD)}, \left| \frac{1-\delta}{4} \theta_1^3 \text{ (DF)} \right|, \left| \frac{1}{2} \theta_1^4 \text{ (1H/2H)} \right|, \tag{15}
\]

Finally we consider the behavior of the step density \( D \) and adsorption-site density \( S \), where the latter corresponds to a sticking probability. \( S \) and \( D \) are no longer trivially related and display dramatic oscillations for the 1H, 2H, and KM models, unlike the bridge-site deposition models. \( D \) oscillations for the 1H and 2H models are also much stronger than corresponding on-top model results\(^1\) (see Fig. 7).

VI. CONCLUSIONS

The influence of adsorption-site geometry on the structure of epitaxial thin films during the early stages of
growth is clearly shown by comparison of Secs. III–V. Growth becomes dramatically more layer-by-layer like as the number $s$ of supporting atoms associated with the adsorption site increases. The influence on film structure of atomic dynamics during and immediately after deposition is also studied systematically. The dramatic smoothing effect of downward funneling, transient mobility, and knockout mechanisms is quantified. As noted previously, KPZ-scaling-type ideas\(^{16}\) can provide some insight into this behavior and will be discussed in detail for our models elsewhere.\(^{18}\) However, the detailed simulations provided here are necessary for quantitative comparison with experimental data and to ascertain whether asymptotic behavior is indeed reflected in the experimentally relevant regime. Asymptotic analyses cannot elucidate certain important aspects of the interplay between adsorption-site geometry and deposition dynamics. For example, we find that “conversion” from random deposition to downward funneling dynamics makes little difference in the kinematic Bragg intensity oscillations for deposition at bridge sites, but converts short-lived to long-lived oscillations for fourfold hollow sites. This is significant as we argue elsewhere\(^{3}\) that downward funneling is the predominant dynamics in low-temperature epitaxial growth of several thin metal films on fcc (100) substrates.

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24The ratio of bulk to surface site adsorption rates is probably much closer to unity than the ratio of the surface to bulk and bulk to surface site hopping rates. The latter reflects the difference in binding energies. See S. C. Wang and G. Ehrlich, Phys. Rev. Lett. 62, 2297 (1989).
29Note that $\partial_{i}V \partial_{j}^{0}$, where $K = 9$ ($K = 13$) for the 2H (KM) model.
FIG. 6. Partitioning of $x_i$ space for stochastic modeling of downward funneling to 4th sites. Some "trajectories" of downward funneling atoms are shown.