

Rapid Communications

The Rapid Communications section is intended for the accelerated publication of important new results. Since manuscripts submitted to this section are given priority treatment both in the editorial office and in production, authors should explain in their submittal letter why the work justifies this special handling. A Rapid Communication should be no longer than 3½ printed pages and must be accompanied by an abstract. Page proofs are sent to authors, but, because of the accelerated schedule, publication is not delayed for receipt of corrections unless requested by the author or noted by the editor.

Low-temperature epitaxial growth of thin metal films

J. W. Evans, D. E. Sanders, P. A. Thiel, and Andrew E. DePristo

Departments of Physics and Chemistry, and Ames Laboratory, Iowa State University, Ames, Iowa 50011

(Received 5 October 1989)

We present a different mechanism to explain the occurrence of long-lived oscillations in diffraction spot intensities during epitaxial growth of metal films on fcc(100) substrates at low temperature. Rather than rely on the common picture of cyclical nucleation and growth to produce the oscillations, the model invokes "downward funneling" deposition dynamics to fourfold-hollow adsorption sites.

There have been many experimental observations of long-lived oscillations in reflection-high-energy electron diffraction (RHEED) during epitaxial growth of semiconductor and metal films.¹⁻³ Traditionally, such oscillations have been associated with layer-by-layer growth, involving cyclical nucleation, growth, and coalescence of islands in each layer, made possible by thermal diffusion.^{1,2} However, long-lived oscillations have been reported recently during epitaxial growth at temperatures so low that thermally activated surface diffusion is thought to be negligibly slow.^{2,3} This prompted the proposal² that the nucleation and growth picture essentially still applies with "transient diffusion" or ballistic motion of the adsorbate replacing thermal diffusion. This transient diffusion is envisioned to result from the need to dissipate the energy released upon formation of the atom-surface bond. This event is exothermic by up to 3 eV (69 kcal/mol) for metallic systems.^{2,3}

In this paper, we demonstrate that neither traditional nucleation and growth nor transient diffusion are *necessary* to obtain long-lived diffraction intensity oscillations in low-temperature epitaxial growth on fcc(100) substrates. The term transient diffusion is used here specifically to refer to motion from one fourfold-hollow adsorption site to another. Such motion necessarily involves a component perpendicular to the direction of vertical impingement on the (100) face. Instead we show that these oscillations can result primarily from a "downward funneling" prescription of the deposition dynamics incorporating the physically reasonable fourfold-hollow adsorption site requirement. Such downward funneling might correspond to channeling down the (111) faces of micro-pyramids which develop during film growth (after impingement at 45° in these faces). We conclude by presenting independent molecular-dynamics (MD) studies of the deposition dynamics of individual atoms using

corrected effective medium (CEM) based interaction potentials.⁴ These show conclusively that adsorption on clean fcc(100) metals leads irreversibly to binding at a fourfold-hollow site *without* transient mobility. These MD studies also generally support the downward funneling picture.

There are several previous studies pertinent to low-temperature film growth. One very simple and well-known model involves random, immobile deposition of particles onto the tops of columns growing from the (100) face of a simple-cubic crystal.⁵ Here the column heights satisfy a Poisson distribution with standard deviation (interface width) equal to $\Theta^{1/2}$, where Θ is the mean coverage in monolayers. Since diffraction from this growing film does *not* produce oscillations, the model fails to describe the above-mentioned experimental behavior. (This simple model probably spawned the widespread belief that some sort of mobility is essential to achieve oscillations.) In contrast to this model, MD studies of deposition on a fcc(111) substrate using simple Lennard-Jones potential⁶ indicated significant transient diffusion, at least, in the first layer at $T=0$ K. This facilitates ordering, as reflected by a first layer saturation coverage of $\sim 96\%$,⁶ compared with 76% for random immobile deposition.⁷ (Filling is incomplete due to domain boundaries, which cannot develop in the models we consider.) However, our MD simulations, described below, indicate that this behavior is due to having only one movable substrate layer. The degree of mobility is greatly reduced with three movable layers. Finally, we note that simple Monte Carlo (MC) modeling shows that transient diffusion leads to smooth films,⁸ and the appearance of RHEED oscillations at $T=0$ K.⁹

Our aim here is to develop models for fcc epitaxial growth via deposition at fourfold-hollow sites starting from a (100) substrate. We first categorize all fcc lattice

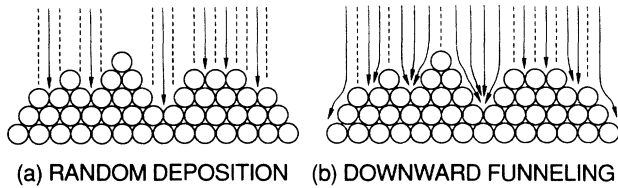


FIG. 1. Schematic of random immobile deposition (Ref. 7) vs downward funneling deposition dynamics.

sites where adsorption has or potentially can occur as either filled, empty complete, or empty incomplete adsorption sites. Complete adsorption sites have a cluster of $k=4$ supporting atoms in the layer beneath, whereas incomplete adsorption sites have $1 \leq k \leq 3$. Previously, an exact analytic solution was obtained for the model where the adsorption probabilities are nonzero (and equal) only at complete adsorption sites.⁷ This simplistic choice of adsorption probabilities produces nontrivial film growth which is initially quite layer-by-layer-like, but becomes less and less so as deposition progresses. Associated diffracted intensity oscillations effectively die out by $\Theta \approx 3$. This model mimics the experimental LEED oscillations, but not the sticking coefficient behavior observed for Pt/Pd(100) at 80 K.¹⁰ In contrast, RHEED oscillations in other metallic systems are long lived, which rules out the applicability of this simple model. However, we show that a slight modification of the deposition dynamics in this model produces surprisingly long-lived oscillations which are in qualitative agreement with the RHEED data.

This modified model incorporates *downward funneling to complete adsorption sites of all impinging atoms* at $T=0$ K (see Fig. 1). Here it is assumed that these atoms impinge vertically with a continuum of initial lateral coordinates, \mathbf{X}_{\parallel} . Since this $T=0$ K process is deterministic, there is a unique adsorption site associated with each \mathbf{X}_{\parallel} , i.e., for any film configuration the \mathbf{X}_{\parallel} space can be partitioned into “capture zones” for the various complete adsorption sites. Thus, we simulate the deposition process by allowing complete adsorption sites to fill at rates proportional to their associated capture areas (rather than with equal rates as above and in Ref. 7).

Consider first the funneling-off layer j atoms to complete adsorption sites supported by layer $j-1$ atoms (e.g., funneling off first layer atoms to adsorption sites on the substrate), and assume that the shape of the capture zone is influenced only by atoms diagonally or laterally adjacent to the adsorption site. If there are no such adjacent atoms, then by symmetry, the capture zone is the square shown in Fig. 2(a) with area $A_0 \equiv 1$. Figure 2(b) shows the capture zones for adsorption sites with one diagonal or one laterally adjacent atom. Clearly their areas A_D and A_L , respectively, must satisfy $4A_D + 4A_L = 9$. The capture zone area A_{DL} for an adsorption site with the diagonally and laterally adjacent atoms shown in Fig. 2(c) satisfies $4A_D + 2A_L + 4A_{DL} = 12$. Continuing in this way, one can express the capture zone area for an adsorption site with any number of diagonally and laterally adjacent atoms in terms of one free parameter, $A_D \equiv 1 + \delta_D$, say. We note

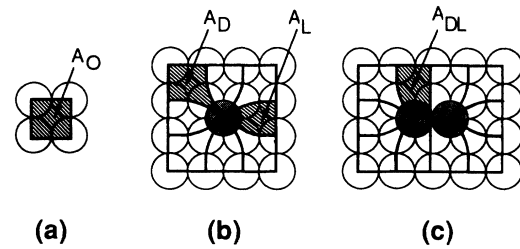


FIG. 2. Capture areas for continuous downward funneling.

that the need to catalog capture zone areas for funneling off higher layer atoms to lower layer adsorption sites constitutes a major complication in this model since so many configurations must be considered.

It is thus convenient to introduce a *discretized version of the downward funneling model* which is simpler to implement. We utilize the concept of complete ($k=4$) and incomplete ($1 \leq k \leq 3$) adsorption sites as described above. One starts by partitioning the \mathbf{X}_{\parallel} space as shown in Fig. 3. Any atom impinging on a large square region is assigned permanently to the corresponding $k=4$ complete adsorption site. Any atom impinging on an L shaped, rectangular or small square region is assigned initially to the corresponding $k=3, 2, 1$ incomplete adsorption site, respectively. (These assignments are simply achieved by filling adsorption sites at rate $k/4$.) Then immediately this atom is moved progressively 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 a diagonally adjacent lower site with probability 4δ , or to one of the two laterally adjacent lower sites with probability $(1-4\delta)/2$ (see Fig. 3).

For these models, let Θ_j denote the coverage (in monolayers) of layer j . Here $j=0$ corresponds to the top substrate layer, so $\Theta_0=1$. Then $N_j = \Theta_j - \Theta_{j+1}$ reflects the net number of exposed atoms in layer j . We consider the following quantities:

(i) The interface width W satisfying $W^2 = \sum_{j=0}^{\infty} (j-\bar{j})^2 N_j$, where $\bar{j} = \sum_{j=0}^{\infty} j N_j = \sum_{j=0}^{\infty} \Theta_j = \Theta$ (the total coverage).¹¹

(ii) The step density which is simply taken as the density of horizontal nearest-neighbor (NN) pairs of empty-filled sites in the [010] direction.⁹

(iii) The Lent-Cohen kinematic expression for the Bragg intensity I_{Br} at the out-of-phase condition where scattering from consecutive layers interferes destructively-

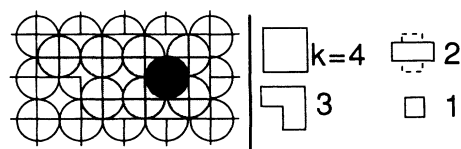


FIG. 3. Partition of \mathbf{X}_{\parallel} space for discretized downward funneling.

ly.¹² Here $I_{Br} = (N_0 - N_1 + N_2 - \dots)^2$ assuming equal scattering factors for substrate and film atoms.

Occurrence of RHEED intensity oscillations should be reflected in the behavior of I_{Br} and of the step density.⁹ Neglect of multiple scattering rules out quantitative agreement with I_{Br} , however. Results below are obtained from MC simulation. Since the models considered here generate only very short-range spatial correlations (for thin films), ca. 30 MC trials on a 100×100 substrate are sufficient to obtain essentially exact statistics.

Figure 4 contrasts the behavior of these quantities for random immobile deposition at fourfold-hollow sites (Ref. 7), the discretized funneling model with $\delta = \frac{1}{6}$, and a simplified form of the continuum funneling model. The latter considers only layer j atoms when calculating capture areas for adsorption sites supported by layer $j-1$ atoms, and sets $\delta_D = \frac{1}{6}$. This parameter choice corresponds to a hard-sphere potential where impinging atoms make contact with film atoms and then slide "downhill" to an adsorption site. Note that for layer-by-layer growth, $W^2 = \theta(1-\theta)$ and $I_{Br} = (1-2\theta)^2$, for $0 \leq \theta \leq 1$, and these functions repeat periodically for higher Θ . For random deposition on top of columns, $W^2 = \theta$ and $I_{Br} = e^{-4\theta}$.^{5,7}

One finds persistent long-lived I_{Br} oscillations in the funneling models, in marked contrast to the simple random immobile deposition model of Ref. 7. Oscillations for the full continuum model are undoubtedly larger than in the simplified version shown. Clearly these models include no propensity for island formation in the usual sense, their spatial pair correlations always remaining short ranged. However, the observed oscillations indicate the (rapid) development of quasi-steady-state growth, wherein the film structure roughly repeats itself with the period of monolayer incorporation, e.g., $\Theta_j(\Theta = x) \approx \Theta_{j+1}(\Theta = x+1)$. This behavior is clearly reflected in

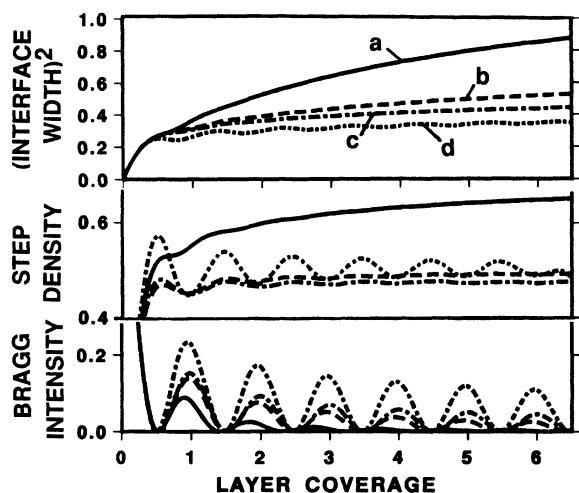


FIG. 4. Interface width, step density, and Bragg intensity behavior for (a) random immobile deposition (Ref. 7), (b) simplified continuous downward funneling, (c) discretized downward funneling, and (d) one-hop transient mobility models.

the slowly increasing surface width. Growth is not strictly layer-by-layer, but at most a couple of layers have significant partial coverage at any one time.

Closer examination of the funneling models reveals that the funneling dynamics enhance short-range clustering (i.e., increase the NN spatial pair correlations) relative to random deposition.¹³ Thus funneling produces more adsorption sites in the upper layer, which alone would make growth less layer-by-layer-like. However, funneling also boosts the filling rate for lower layers relative to random deposition. The latter effect dominates in this competition, producing quasi-steady-state growth. (In contrast, for an analogous 1D bridge-site deposition model, these competing effects roughly cancel.¹³)

We assert below that transient diffusion is absent at $T=0$ K in metal-on-metal systems. However, it is still instructive to compare the behavior of the above funneling models with that for models incorporating very short-range transient mobility. Thus we modify the model of Ref. 7 for random immobile deposition at fourfold-hollow sites by allowing atoms to make one hop to a randomly chosen empty neighboring site immediately after deposition. If that site is complete ($k=4$) the atom remains there. Otherwise it tumbles downhill, as in the discrete funneling model. The I_{Br} oscillations are even larger than for the funneling models, and oscillations are visible in the step density and interface width (see Fig. 4). In another modification of the model of Ref. 7, atoms adsorbing at complete fourfold-hollow sites "knock out" one of the four supporting atoms to an adjacent empty site (if one exists), and then take its place. The dislodged atom stays at the empty site if complete ($k=4$), or otherwise tumbles downhill to a complete adsorption site. Oscillations in measured quantities here are larger than in the above one-hop (or even an extended two-hop) transient mobility model. Clearly, transient mobility or knockout phenomena enhance the layer-by-layer character of growth. However, our main point in this paper is that these phenomena are not necessary to achieve the long-lived oscillations in I_{Br} which are usually taken as experimental confirmation of layer-by-layer growth.

Finally we performed MD studies of the deposition dynamics of individual atoms, designed to check the validity of the above ideas. Several systems were considered, including Cu/Cu(100), Pt/Pd(100), and Cu/Ag(100) using sophisticated interaction potentials obtained from the corrected effective medium theory. These should be quite reliable for metallic systems.⁴ In contrast, Lennard-Jones (12,6) potentials used previously⁶ cannot accurately describe the elastic constants, binding energy, and lattice constant, simultaneously. In our simulations, one atom impinges onto ≈ 250 "target" substrate atoms in three movable layers with Langevin coupling to the rest of the bulk.¹⁴ The analysis reveals that transient motion does not occur at 80 K. Rather, the atom always settles into the fourfold-hollow site on which it impinges (see Fig. 5). This result is insensitive to the initial kinetic energy of the impinging atom at least up to ~ 0.25 eV, since the near-surface kinetic energy is determined primarily by the attractive atom-substrate interaction. Additional MD studies of atoms impinging on small pyramids generally sup-

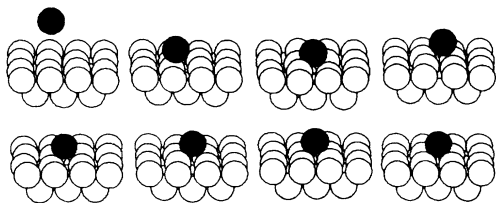


FIG. 5. Deposition dynamics for 0.25-eV Cu impinging vertically on a Cu(100) surface held at 80 K. Only a small subset of the moving substrate atoms is shown. The time increment (from left to right) is 0.20 ps.

port the funneling picture. Dynamics following impingement on larger inclines is more complicated, but these configurations are statistically rare. These studies also indicate that the knockout mechanisms, described above, are typically inoperative.

Our MD results agree, in fact, with earlier field-ion-microscopy (FIM) measurements,¹⁵ which showed that tungsten atoms evaporated on a W tip at 80 K do not mi-

grate even a single lattice constant away from the initial impingement site. Thus, the MD simulations using CEM potentials, and the earlier FIM measurements both serve to rule out the idea of transient mobility in metal-on-metal systems. Consequently, we conclude that the traditional picture of mobility-mediated island nucleation and growth does not describe low-temperature epitaxial growth of thin metal films. However, an alternative model incorporating downward funneling to physically reasonable fourfold-hollow adsorption sites is herein provided. This model can explain the long-lived oscillations observed in the diffracted intensities, and the associated quasi-steady-state growth.

This work was supported by National Science Foundation Grants No. CHE-8451317 and No. CHE-8609832, Cray Research Inc., Camille and Henry Dreyfus Foundation, IBM (D.E.S.), and the Ames Laboratory. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. This work was supported by the Office of Basic Energy Sciences.

¹*Reflection High-Energy Electron Diffraction and Reflection Imaging of Surfaces*, edited by P. K. Larson and P. J. Dobson (Plenum, New York, 1988).

²W. F. Egelhoff and I. Jacob, *Phys. Rev. Lett.* **62**, 921 (1989). Many references are given here which describe the traditional nucleation and growth picture.

³C. Koziol, G. Lilienkamp, and E. Bauer, *Appl. Phys. Lett.* **51**, 901 (1987).

⁴J. D. Kress, M. D. Stave, and A. E. DePristo, *J. Phys. Chem.* **93**, 1556 (1989); T. J. Raeker and A. E. DePristo, *Phys. Rev. B* **39**, 9967 (1989).

⁵F. Reif, *Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), p. 42.

⁶M. Schneider, A. Rahman, and I. K. Schuller, *Phys. Rev. Lett.*

55, 604 (1985).

⁷J. W. Evans, *Phys. Rev. B* **39**, 5655 (1989).

⁸F. Family, *J. Phys. A* **19**, L441 (1986).

⁹S. Clarke and D. D. Vvedensky, *Phys. Rev. B* **37**, 6559 (1988).

¹⁰D. K. Flynn, J. W. Evans, and P. A. Thiel, *J. Vac. Sci. Technol. A* **7**, 2162 (1989).

¹¹M. Thomsen and A. Madhukar, *J. Cryst. Growth* **80**, 275 (1987).

¹²C. S. Lent and P. I. Cohen, *Surf. Sci.* **139**, 121 (1984).

¹³J. W. Evans (unpublished).

¹⁴A. E. DePristo and H. Metiu, *J. Chem. Phys.* **90**, 1229 (1989).

¹⁵R. D. Young and D. C. Schubert, *J. Chem. Phys.* **42**, 3943 (1965).

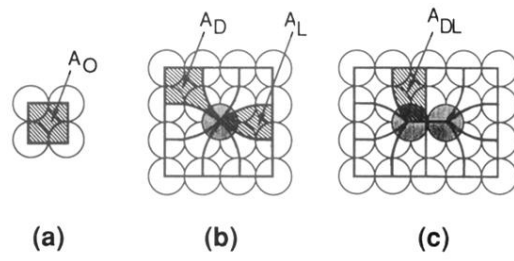


FIG. 2. Capture areas for continuous downward funneling.

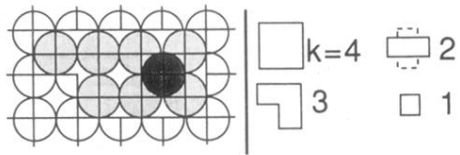


FIG. 3. Partition of \mathbf{X}_i space for discretized downward funneling.