Spatiotemporal Distribution of Nucleation Events during Crystal Growth

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(Received 14 September 2000; published 12 July 2001)

We consider irreversible second-layer nucleation that occurs when two adatoms on a terrace meet. We solve the problem analytically in one dimension for zero and infinite step-edge barriers, and numerically for any value of the barriers in one and two dimensions. For large barriers, the spatial distribution of nucleation events strongly differs from ρ^2, where ρ is the stationary adatom density in the presence of a constant flux. Theories of the nucleation rate ω based on the assumption that it is proportional to ρ^2 are shown to overestimate ω by a factor proportional to the number of times an adatom diffusing on the terrace visits an already visited lattice site.

DOI: 10.1103/PhysRevLett.87.056102 PACS numbers: 68.55.–a, 05.40.–a, 81.10.Aj

Molecular beam epitaxy (MBE) is one of the most common techniques for growing nanoscale materials [1]: A controlled flux of particles arrives ballistically on a substrate whose temperature is generally high enough to activate surface diffusion of newly deposited adatoms. In the absence of preexisting steps, i.e., for high-symmetry surfaces, growth proceeds through the formation of stable dimers (or largest nuclei, depending upon the temperature, the flux, and the surface symmetry [2]) and the subsequent aggregation of diffusing particles.

Nucleation processes take place on a flat surface during the submonolayer regime [3] and afterwards on islands. In this Letter we are interested in the latter case, where the process of nucleation occurs as follows: adatoms are deposited at a rate F per unit time and lattice site and diffuse at a rate D. The typical time between two deposition events on a terrace of size L is $\tau_{\rm dep} = (FL^d)^{-1}$ and the typical residence time of an adatom on the terrace is [4] $\tau_{\rm res} \sim L(L + \alpha_d \ell_{\rm ES})/D$, where $\ell_{\rm ES}$ is the Ehrlich-Schwoebel (ES) length [5] that measures the strength of step-edge barriers [6] hindering the descent of adatoms; α_d is a numerical factor depending on dimension only. A nucleation event takes place when a newly deposited adatom finds the previous one still on the terrace *and* they meet before descending, forming a stable dimer. Once two adatoms are on the terrace at the same time a nucleation event takes place, if it does, in a time of order $\tau_{\rm tr} \sim L^2/D$, the typical time required for a traversal of the terrace [4]. Therefore the probability that a third atom influences the nucleation process is of order $p_3 \sim \tau_{\rm tr}/\tau_{\rm dep}$, which is very small in all physically relevant cases. More precisely, in $d = 2$, $p_3 \sim L^4/\ell_{\rm D}^6$, where $\ell_{\rm D} \sim (D/F)^{1/6}$—the so-called diffusion length [2]—is the typical size of a terrace when nucleation occurs. Since $L \leq \ell_{\rm D}$ and $\ell_{\rm D} \gg 1$ we conclude that $p_3 \ll 1$ and for irreversible nucleation only processes involving two adatoms must be taken into account.

The simplest theoretical treatment of nucleation phenomena in crystal growth is based on the assumption [7] that the nucleation rate ω is proportional to the square of the stationary adatom density ρ in the presence of a constant flux F. Such a mean-field treatment has been used to estimate physical parameters of materials [8,9] and as an ingredient in mesoscopic models of epitaxial growth [10]. However, recent papers [4,11] have shown (via Monte Carlo simulations and scaling arguments [11] or theoretically [4]) that the mean-field prediction $\omega \sim \rho^2$ for the nucleation rate is not correct in $d = 2$ for large ES barriers. This prompted us to reconsider the general validity of mean-field theory. It is *a priori* not clear to what extent two-particle properties as ω can be simply obtained from ρ, a quantity describing a single particle on a terrace. In this Letter we solve exactly the problem of irreversible nucleation on a terrace in one and two dimensions for all values of the ES barrier. We compute (analytically or numerically) the spatial and temporal distributions of nucleation events and the total nucleation rate. In this way we are able to assess when and why the mean-field approximation provides sufficiently accurate results and by how much it fails.

Let us start with the case $\ell_{\rm ES} = 0$. The discrete evolution equation for the probability $p_n(t)$ of finding a single adatom in site n at time t is

$$p_n(t + 1) = \frac{1}{2}[\, p_{n+1}(t) + p_{n-1}(t)]. \qquad (1)$$

The boundary conditions are $p_0(t) = p_{L+1}(t) = 0$.

By looking for solutions of Eq. (1) of the form $p_n(t) = N_n T(t)$ one finds the general solution

$$p_n(t) = \sum_{k=1}^{L} A_k \cos^t(k\Pi) \sin(nk\Pi), \qquad (2)$$

with coefficients $A_k = \frac{2}{L+1} \sum_{n=1}^{L} p_n(0) \sin(nk\Pi)$, where $\Pi = \pi/(L + 1)$.

Nucleation occurs when two adatoms wandering on the same terrace meet. The one-dimensional diffusion of two particles can be reformulated by taking the coordinates m, n of the two walkers as the coordinates of *one* walker in $d' = 2$ moving on a square lattice $(L \times L)$. The

generalization of (1) to two dimensions is $p_{m,n}(t+1) = \frac{1}{4}[p_{m+1,n}(t) + p_{m-1,n}(t) + p_{m,n+1}(t) + p_{m,n-1}(t)]$ with boundary conditions $p_{0,n} = p_{L+1,n} = p_{m,0} = p_{m,L+1} = 0$. Again, separating space and time variables one obtains the most general solution

$$p_{m,n}(t) = \sum_{k,j=1}^{L} \frac{B_{kj}}{2^t} [\cos(k\Pi) + \cos(j\Pi)]^t \times \sin(mk\Pi)\sin(nj\Pi), \quad (3)$$

where the coefficients B_{kj} are

$$B_{kj} = \left(\frac{2}{L+1}\right)^2 \sum_{m,n=1}^{L} p_{m,n}(0)\sin(mk\Pi)\sin(nj\Pi). \quad (4)$$

The initial condition $p_{m,n}(0) = \hat{p}_m \hat{p}_n$ encodes the information about the way particles are deposited. Notice that $t = 0$ indicates in Eqs. (3) and (4) the time when the second adatom arrives. We consider adatoms landing on the terrace with spatially uniform probability $p_n^U = 1/L$. However, since arrivals on the terrace are not simultaneous, the distribution of the first adatom has changed to $p_m(t')$ [Eq. (2)] when the second one lands on the terrace. The nucleation process depends therefore on the precise interarrival time t', which is a Poissonian random variable $P_{\mathrm{ARR}}(t') = (\tau_{\mathrm{dep}})^{-1}\exp(-t'/\tau_{\mathrm{dep}})$.

One must compute physical quantities O by averaging over t': $O = \sum_{t'=0}^{\infty} P_{\mathrm{ARR}}(t')O(t')$, where $O(t')$ is computed using as initial distributions $p_m(t')$ for the first particle and $p_n^U = 1/L$ for the second. If $O(t')$ is linear with respect to the initial distributions (as are all the quantities considered below), the sum can be replaced by a single computation of O with the initial distribution of the first adatom given by $\hat{p}_m = \sum_{t'=0}^{\infty} P_{\mathrm{ARR}}(t')p_m(t')$.

The general solution can be found [12], but in the limit $\tau_{\mathrm{res}} \ll \tau_{\mathrm{dep}}$, which is realistic for MBE, one can consider $P_{\mathrm{ARR}}(t')$ as a constant on the scale τ_{res} and then $\hat{p}_m = \sum_{t'=0}^{\infty} p_m(t')$. Therefore $\hat{p}_m$ is proportional to the normalized stationary solution p_m^S of (1) in the presence of a constant flux [13]: $p_m^S = 6/[L(L+1)(L+2)]m(L+1-m)$; p_m^S will be taken as the distribution for the first particle for computing $P(n)$ and $Q(t)$.

So far we have not considered the interaction between adatoms, i.e., the fact that when the two particles meet they stop diffusing. An irreversible nucleation event generally occurs when two adatoms are on nearest neighbor sites. To allow an analytic treatment we consider here a nucleation event to occur when the adatoms are on the *same* site. When this occurs the dynamics stops, implying $p_{m,m}(t) = 0$ for all $t > 0$. This boundary condition can be taken into account by the classical image method [14,15]: The initial condition is chosen to be antisymmetric with respect to particles exchange $p_{m,n}(0) = -p_{n,m}(0)$. This implies $B_{kj} = -B_{jk}$ and therefore $p_{m,n}(t) = -p_{n,m}(t)$. In this way the boundary condition $p_{m,m}(t) = 0$ is obeyed for all t because the two triangles $(m > n)$ and $(m < n)$ are dynamically disconnected.

When the antisymmetric initial condition is not imposed adatoms diffuse without interacting: They do not feel each other even if they are on the same site and they wander until they get off the terrace. In the following we will speak of nucleations for these noninteracting adatoms, intending that they "nucleate" when they are on the same site. Clearly two noninteracting adatoms may give rise to several "nucleation" events before leaving the terrace.

For noninteracting adatoms the coefficients B_{kj} are simply the product of the single adatom coefficients $A_k A_j$. In the case of interacting adatoms we obtain [12] $B_{kj} = [2/(L+1)]^2[B_{kj}^{<} - B_{jk}^{<}]$, where $B_{kj}^{<} = \sum_{m<n} \times p_{m,n}(0)\sin(mk\Pi)\sin(nj\Pi)$.

For interacting adatoms the probability of a nucleation event on site n at time $t+1$ is given by $(1/2) \times [p_{n,n+1}(t) + p_{n-1,n}(t)]$, while for $t = 0$ it is $p_{n,n}(0)$. For noninteracting adatoms it is simply $p_{n,n}(t)$ at any time. By summing over t one obtains the spatial distribution $P(n)$ of nucleation sites, which is reported in Fig. 1. It turns out immediately that the mean-field prediction ρ_n^2 is exact only if adatoms do not interact, i.e., nucleation events following the first one are taken into account. In the interacting case the distribution of nucleation sites differs from ρ_n^2, but the discrepancy is rather small.

We now discuss the distribution of nucleation times, i.e., the probability $Q(t)$ that adatoms meet at time t after the deposition of the second adatom.

For noninteracting adatoms,

$$Q(t) = \sum_{n=1}^{L} p_{n,n}(t) = \frac{L+1}{2} \sum_{k=1}^{L} B_{kk}\cos^t(k\Pi). \quad (5)$$

We can rewrite $\cos^t(\phi) = \exp[t\ln\cos(\phi)]$ and since the coefficients B_{kk} diverge for small k as k^{-4}, we expand the cosine for small ϕ and finally extract the dominant contribution coming from the mode $k = 1$: $Q(t) \sim \exp[-\Pi^2 t/2]$.

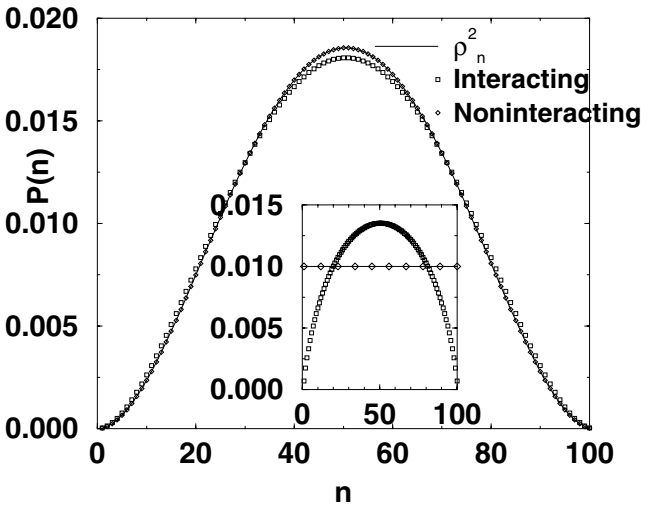

FIG. 1. Main: normalized distribution of the nucleation sites $P(n)$ in $d = 1$ for $\ell_{\mathrm{ES}} = 0$ and $L = 100$. $\rho_n \sim p_n^S$ is the (normalized) stationary solution of Eq. (1) in the presence of a constant flux. Inset: The same for $\ell_{\mathrm{ES}} = \infty$.

In the case of interacting adatoms $Q(t+1) = \sum_{n=1}^{L} \times \frac{1}{2}[p_{n,n+1}(t) + p_{n-1,n}(t)]$. By evaluating the summation, we obtain $Q(t+1) = \sum_{k,j=1}^{L} B_{kj} C_{kj} 2^{-t} [\cos(k\Pi) + \cos(j\Pi)]^t$, where the $C_{kj} = \sum_{n=1}^{L} \sin[k\Pi(n-1)] \times \sin(j\Pi n)$ can be evaluated explicitly. Approximations along the lines of the above treatment lead to [12]

$$Q(t) \simeq \frac{32}{\pi^2 L^2} \sum_{k=1}^{L} \exp\left\{-\frac{\Pi^2}{4}[k^2 + (k+1)^2]t\right\}. \quad (6)$$

The sum can be rewritten as the integral $\int_1^L \exp[\cdots]\,dk$ plus the boundary term for $k = 1$: $(1/2)\exp[-(5/4)\Pi^2 t]$ (the boundary term for $k = L$ is always negligible). It is easy to see that the integral prevails for $t \ll L^2/\pi$ and gives $Q(t) \approx 16\sqrt{2}/(L\pi^{5/2}\sqrt{t})$, while in the opposite limit we have an exponential decay. The existence of the two regimes is clearly shown in Fig. 2. The two behaviors can be interpreted physically. For short times, terrace edges can be neglected and one can focus on the relative coordinate $(n - m)$ of the two particles. Nucleation occurs when $(n - m)$ vanishes for the first time and $Q(t) \sim t^{-1/2}$ is simply the spatial integral of the first-passage distribution probability [16]. The exponential decay for long time is the effect of the decaying probability that the adatoms remain on the terrace times the vanishing probability that they have not yet met.

In two dimensions the two diffusing adatoms can be mapped into a four-dimensional problem for a single random walker: $p_{m_1,n_1,m_2,n_2}(t)$ is the probability of finding one atom on site (m_1, n_1) and the other in (m_2, n_2) at time t. The solution in the noninteracting case on the four-dimensional hypercube is easily found. However, the simple generalization of the interacting case to $d = 2$ is not possible because the plane corresponding to nucleation events does not divide the hypercube into two dynamically separated regions, reflecting the fact that in two dimensions two adatoms can exchange their positions without meeting. The results shown for the interacting case are obtained by numerically solving the evolution equation for the probability p.

The main part of Fig. 3 clearly shows how the results obtained in $d = 1$ for the spatial distribution of nucleation sites are also true in two dimensions: for noninteracting atoms $P(m,n) \equiv \rho_{m,n}^2$; in the interacting case a discrepancy exists but is practically negligible. The distribution of nucleation times $Q(t)$ decays exponentially for long time, as in $d = 1$. Again, at short time it can be derived [12] by using the first-passage probability arguments, yielding—for interacting adatoms—$Q(t) \sim 1/\ln(t/t_0)$ (Fig. 2, inset).

Let us now consider $\ell_{ES} = \infty$. In this case, the boundary conditions for a single adatom in $d = 1$ are $p_0(t) = p_1(t)$ and $p_{L+1}(t) = p_L(t)$. The general solution is now a superposition of the functions $X_k(n) = \tan[k\pi/(2L)]\sin(nk\pi/L) + \cos(nk\pi/L)$, with $k = 0, \ldots, L-1$ and the solution of the nucleation problem is found much in the same way as for zero barriers [12]. The initial condition is now with both adatoms uniformly distributed, because for $\ell_{ES} = \infty$ the stationary solution for the single adatom is $p_n^S = 1/L$.

The spatial distribution $P(n)$ of nucleation events is compared to the mean-field prediction $[P(n) = 1/L^d]$ in the insets of Fig. 1 ($d = 1$) and Fig. 3 ($d = 2$): they are in striking disagreement. We conclude that—concerning $P(n)$—mean-field theory is a good approximation for weak step-edge barriers, but the agreement is extremely poor for strong ones.

The temporal distribution $Q(t)$ of nucleation events does not change qualitatively when the value of ℓ_{ES} is varied (see Fig. 2). The power-law ($d = 1$) and logarithmic ($d = 2$) decays at short time do not depend on the

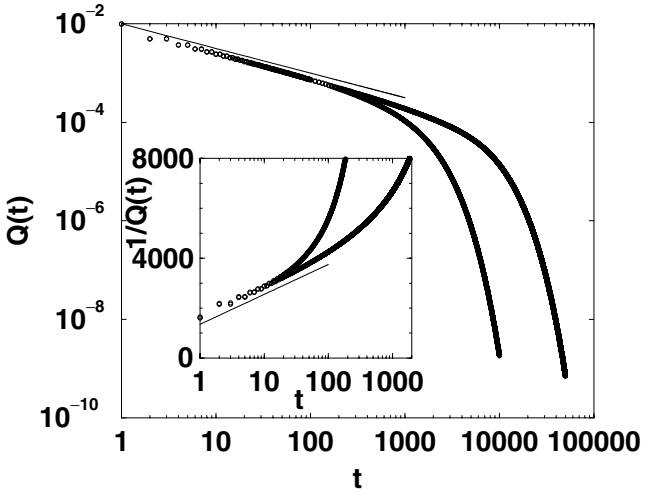

FIG. 2. Main: $Q(t)$ on a log-log scale for $L = 100$ in $d = 1$ for $\ell_{ES} = 0$ (bottom) and $\ell_{ES} = \infty$ (upper curve). The straight line shows a decay of $Q(t)$ as $t^{-1/2}$. Inset: $1/Q(t)$ on a log-lin scale for $L = 40$ in $d = 2$ for $\ell_{ES} = 0$ (top) and $\ell_{ES} = \infty$ (lower curve). The straight line shows a decay of $Q(t)$ as $1/\ln(t/t_0)$.

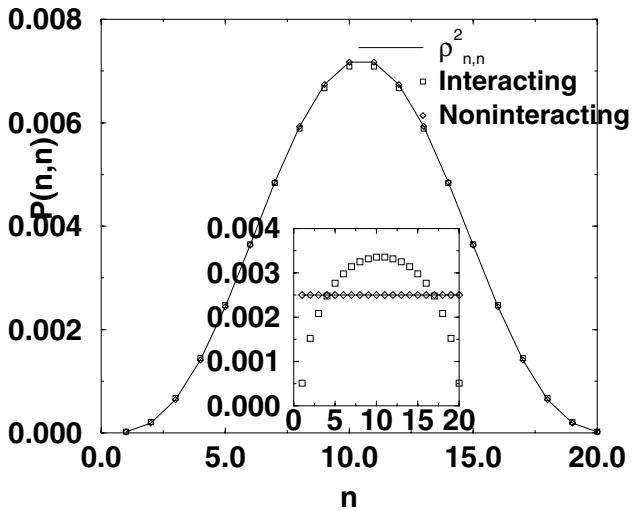

FIG. 3. Main: values of the normalized distribution of nucleation sites along the diagonal $P(n,n)$ for $\ell_{ES} = 0$, $d = 2$, and $L = 20$. Inset: the same for $\ell_{ES} = \infty$.

finite size of the terrace and therefore on $\ell_{\rm ES}$, which enters in boundary conditions only. The typical time necessary for the adatom to feel the presence of the boundaries corresponds to the time $\tau_{\rm tr} \sim L^2/D$. For longer times $Q(t)$ vanishes exponentially. In this case the probability for adatoms to remain on the terrace is clearly constant. Nonetheless $Q(t)$ *must* decay rapidly since its integral is the total probability of a nucleation event, which is 1 for infinite barriers: The exponential decay is due to the vanishing probability that the two adatoms have not yet met before.

From the experimental point of view, a relevant quantity is the nucleation rate ω, defined as the number of nucleation events per unit time on the whole terrace. Within our framework, we can rigorously show, in all dimensions and for all values of the barriers, that the mean-field value $\omega_{\rm MF} = DL^d\bar{\rho}^2$, with $\bar{\rho} = F\tau_{\rm res}$ the average density of occupied sites, must be corrected by a factor proportional to $\mathcal{N} \equiv \frac{N_{\rm all}}{N_{\rm dis}}$, where $N_{\rm dis,all}$ are, respectively, the number of *distinct* or *all* sites visited by a single atom on a terrace. For reasons of space we only sketch here the derivation of this result that will be presented in detail in a longer publication [12]. The nucleation rate ω is equal to the deposition rate of a single particle $1/\tau_{\rm dep}$ times the probability $p_{\rm nuc}$ that such a particle nucleates a dimer before leaving the terrace. $p_{\rm nuc}$ is the average over all interarrival times t' of the probability that two particles meet, when the second is deposited a time t' after the first. As discussed previously for the generic quantity O, $p_{\rm nuc}$ can be computed by considering the two particles deposited simultaneously, but with the first distributed spatially as $\hat{p}_m$. This last function is shown to be equal to $(\tau_{\rm res}/\tau_{\rm dep})p_m^S$, where p_m^S is the *normalized* solution of the stationary diffusion equation for a single particle. Hence we have $p_{\rm nuc} = (\tau_{\rm res}/\tau_{\rm dep})W$, where $W = \sum_{t=0}^{\infty} Q(t)$ is the probability that two adatoms, deposited at the same time with normalized distributions, meet before leaving the terrace; W can be shown to be proportional to $N_{\rm dis}/L^d$. Putting all together and using $\tau_{\rm dep} = 1/(FL^d)$ and $F\tau_{\rm res} = \bar{\rho}$, we obtain $\omega \sim FL^d\bar{\rho}N_{\rm dis}$. In a perfectly analogous way one can show, for noninteracting adatoms, $\omega_{\rm NI} \sim FL^d\bar{\rho}N_{\rm all}$. By considering that for noninteracting particles $\tau_{\rm res} = N_{\rm all}/D$ one sees that $\omega_{\rm NI}$ is proportional to $\omega_{\rm MF}$, so that finally

$$\frac{\omega_{\rm MF}}{\omega} \sim \frac{W_{\rm NI}}{W} \sim \frac{N_{\rm all}}{N_{\rm dis}} \equiv \mathcal{N}\,. \tag{7}$$

This result holds in all dimensions and for any barrier.

The value of the correction factor $\mathcal{N}$ depends of course on d, L, and $\ell_{\rm ES}$. The numerator $N_{\rm all}$ is just proportional to the average density of adatoms on the terrace: $N_{\rm all} \sim L(L + \alpha_d\ell_{\rm ES})$. The value of the denominator $N_{\rm dis}$ is well known [16] in absence of step-edge barriers, being of order L in $d = 1$ and of order $L^2/\ln L$ in $d = 2$, and it is trivial in the limit of infinite barriers, being exactly equal to L^d. Hence in $d = 1$ we obtain $\mathcal{N} \sim (L + \alpha_1\ell_{\rm ES})$. In $d = 2$ it is possible to find [17] an interpolation between the limits $\mathcal{N} \sim \ln L(\ell_{\rm ES} \ll L)$ and $\mathcal{N} \sim \ell_{\rm ES}/L$ $(\ell_{\rm ES} \gg L)$: $\mathcal{N} \sim (1 + \alpha_2\ell_{\rm ES}/L)/p_s$, where $p_s = 1 - [1 - 1/(\ln L)]^{\tau_{\rm res}/\tau_{\rm tr}}$. The previous interpolation is in reasonable agreement with Monte Carlo simulations [12] performed for intermediate barriers.

In conclusion we have provided exact results for the spatiotemporal distributions and total nucleation rates for irreversible nucleation on terraces during crystal growth. These results should be used wherever mean-field approximate results were so far commonly used. One example is the experimental determination of ES barriers from the rate of nucleation on terraces [8,9]. Another example is the modelization of epitaxial growth with mesoscopic models [5]: The location of new terraces must be chosen according to the correct spatial distribution of nucleation events, derived here.

We thank S. Redner for pointing out useful references and F. Colomo and E. Caglioti for interesting discussions.

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[17] The argument is as follows. The atom performs on average a number $N_{\rm tr} = \tau_{\rm res}/\tau_{\rm tr}$ of traversals of the island. During a single traversal each site has a probability $p_1 \sim (1/\ln L)$ to be visited. After all $N_{\rm tr}$ traversals the probability p_s that a generic site has been visited at least once is given by $1 - p_s = (1 - p_1)^{N_{\rm tr}}$.