IRREVERSIBLE NUCLEATION IN MULTILAYER GROWTH

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Abstract. The epitaxial growth process of a high symmetry surface occurs because adatoms meet and nucleate new islands, that eventually coalesce and complete atomic layers. During multilayer growth, nucleation usually takes place on top of terraces where the geometry of the diffusion process is well defined; We have studied in detail the spatiotemporal distribution of nucleation events and the resulting nucleation rate, a quantity of primary importance to model experimental results and evaluate diffusion barriers at step-edges. We provide rigorous results for irreversible nucleation and we assess the limits of mean-field theory (MFT): we show that MFT overestimates the correct result by a factor proportional to the number of times an adatom diffusing on the terrace visits an already visited lattice site. In this report we aim at giving a simple physical account of our results.

1. Introduction

Crystal growth by Molecular Beam Epitaxy can be schematically depicted [1, 2] as a process of uniform deposition of particles, their surface diffusion, and their incorporation at the growing surface. Incorporation means attachment to another diffusing adatom or to a growing island or to a preexisting step: The two first cases are typical of a high symmetry surface where steps are
continuously created and destroyed by the growth process, while attachment to a preexisting train of steps is the growth mode of a vicinal surface.

Here we investigate the process of attachment between diffusing adatoms, called ‘nucleation’ because the so formed dimer may be the nucleus of a new terrace [3, 4]. On a high symmetry surface nucleation may be considered as the first step of the growth process, followed by the capture of other adatoms and by the coalescence of neighbouring islands. This is surely true for the very first stages of growth (the so called submonolayer regime) where it is possible to separate the three mentioned steps by monitoring the adatom and island densities [5]. In this regime nucleation takes place on the flat substrate and nucleation events are not independent processes: the formation of a nucleus reduces the adatom density in its surroundings and therefore disfavors further nucleations. In a sense, nucleation sites repel each other.

Beyond the submonolayer regime, nucleation mainly occurs on top terraces: in this case, therefore, the diffusion process and the possible nucleus formation take place in a confined region of well defined geometry. This makes the theoretical study of the nucleation process on top of a terrace easier than on a flat surface. However, the spatio-temporal distribution of nucleation events cannot directly be related to experiments; in order to obtain experimentally relevant information it is necessary to complement the results for a top terrace with the growth dynamics of such a terrace. Because of this the full study of ‘terrace nucleation’ is not a ‘single terrace’ problem (we will come back to this issue in the next Section).

We have not mentioned so far the possibility that adatom attachment may not be the end of the story. In fact, depending on the substrate temperature, the intensity of the incoming flux and the surface symmetry, dimer formation may be an irreversible process or not. Irreversible nucleation means that once two adatoms meet they stop diffusing and do not detach: in the following we are going to study this case. Furthermore islands will be supposed to be compact: this requires that attachment of adatoms to islands is followed by step-edge diffusion allowing the search of high coordination sites along the edge of the terrace [6].

A short report on the results that will be presented here has already appeared [7] and a paper with all the mathematical details of the calculations is being prepared [8]. Here we aim at giving a simple physical description of our approach, of the results and of the open questions. We will consider mainly two quantities: the nucleation rate \( \omega \) and the spatial distribution \( P(n) \) of nucleation events. \( \omega \) is defined as the number of nucleation events per unit time on the whole terrace (it is therefore proportional to the area \( L^d \) of the island); \( P(n) \) is a normalized quantity (\( \sum_n P(n) = 1 \)) that tells
how nucleations are spatially distributed on the sites $n$ of the terrace. A third quantity is of interest as well [7]: the probability $Q(t)$ that nucleation takes place at time $t$ after the deposition of the second adatom. It has less experimental relevance than $\omega$ and $P(n)$ and therefore it will not be discussed here.

2. Time scales and basic assumptions

The process of nucleation on a top terrace involves three typical time scales, whose detailed discussion can be found in Ref. [9]. If $F$ is the intensity of the incoming flux, $D$ the adatom surface diffusion constant, $L$ the linear size of the terrace and $d = 1, 2$ the dimension of the terrace, we define $\tau_{\text{dep}} = (FL^d)^{-1}$ as the average time interval between deposition events on the terrace, $\tau_{\text{tr}} \sim L^2/D$ as the typical time taken by the adatom to travel through the terrace, and $\tau_{\text{res}}$ as the typical time an adatom stays on the terrace before getting off. This last quantity depends on the boundary conditions at the terrace edge, i.e. on the possible existence of an Ehrlich-Schwoebel (ES) barrier pushing back adatoms [10]; by introducing the interlayer transport rate $D'$ we can define the so called ES length $\ell_{\text{ES}} = (D/D' - 1)$ [2] and in terms of it the regimes of weak and strong barriers correspond to $\ell_{\text{ES}} \ll L$ and $\ell_{\text{ES}} \gg L$, respectively. The time $\tau_{\text{res}}$ has to do with the average stationary adatom density $\bar{\rho}$ on the island [9]: $\tau_{\text{res}} = \bar{\rho}/F \simeq L(L + \alpha_d \ell_{\text{ES}})/D$ where $\alpha_d$ is a numerical factor depending on the dimension and the shape of the terrace. It is straightforward that $\tau_{\text{res}} \sim \tau_{\text{tr}}$ for absorbing boundaries ($\ell_{\text{ES}} = 0$).

The relation $\tau_{\text{tr}} \ll \tau_{\text{dep}}$ is always verified in realistic growth conditions and therefore, according to the value of the ratio $\ell_{\text{ES}}/L$ we can distinguish three different regimes: (i) $\tau_{\text{tr}} \sim \tau_{\text{res}} \ll \tau_{\text{dep}}$ (weak ES effect); (ii) $\tau_{\text{tr}} \ll \tau_{\text{res}} \ll \tau_{\text{dep}}$ (strong ES effect); (iii) $\tau_{\text{tr}} \ll \tau_{\text{dep}} \ll \tau_{\text{res}}$ (infinite ES effect).

The word ‘infinite’ for the third regime is to be intended in physical terms: it means that if an atom is on the terrace a second atom will surely arrive before the first one leaves the terrace, so that the nucleation rate is just the inverse of $\tau_{\text{dep}}$.

Since we study irreversible nucleation and $\tau_{\text{tr}} \ll \tau_{\text{dep}}$, we can limit ourselves to study nucleation as a “two adatoms” process disregarding processes involving three adatoms or more. We can show the validity of this assumption in the most unfavorable case of infinite ES barriers: a first atom is deposited at time $t = 0$ and stays on the terrace; after an average time $\tau_{\text{dep}}$ a second atom comes: they meet in a typical time $\tau_{\text{tr}}$ and the probability that a third atom arrives in the meanwhile is negligible just because $\tau_{\text{tr}}/\tau_{\text{dep}} \ll 1$.

\[1\] In $d = 2$ the index $n$ should be meant as a pair of integer indices $(n_x, n_y)$.
A further issue deserves to be discussed before the illustration of our approach. We study quantities concerning a terrace of fixed size $L$: it is obvious that a given island grows in time, but the nucleation rate $\omega(L)$ is evaluated keeping $L$ constant. The expressions for $\omega$ and $P(n)$ are general and do not depend on the details of the growth process that determine the actual time dependence of the terrace size $L(t)$. These details do enter in the problem if—for example—we want to compute the probability $f(t)$ that a nucleation event has occurred before time $t$ [12], because the evaluation of $f(t) = 1 - \exp\{-\int_0^t d\tau \omega(L(\tau))\}$ requires the knowledge of $L(\tau)$.

3. The nucleation rate: method and results

We have argued that it is sufficient to study two adatoms processes. This means that the following picture applies: Adatoms arrive on the terrace at a rate $FLd = \tau_{\text{dep}}^{-1}$ and stay there an average time $\tau_{\text{res}}$; a nucleation event takes place if an adatom is still on the terrace when the next one is coming and they meet before getting out. It is therefore possible to define a nucleation probability per atom $p_{\text{nuc}}$ such that $\omega = \tau_{\text{dep}}^{-1} p_{\text{nuc}}$. If $P_{\text{dep}}(t) = \tau_{\text{dep}}^{-1} \exp(-t/\tau_{\text{dep}})$ is the probability that a second atom is deposited a time $t$ after a first one, we have

$$p_{\text{nuc}} = \int_0^\infty dt P_{\text{dep}}(t) \tilde{p}_{\text{nuc}}(t) ,$$

where $\tilde{p}_{\text{nuc}}(t)$ is the probability that the first atom $A$ deposited at time zero and the second atom $B$ deposited a time $t$ later meet.

In the same manner, if we are looking for the spatial probability distribution $P(n)$ of nucleation sites we need to evaluate the integral

$$P(n) = \int_0^\infty dt P_{\text{dep}}(t) \tilde{P}(n; t) ,$$

where $\tilde{P}(n; t)$ is the distribution evaluated for the first atom $A$ deposited at time zero and the second atom $B$ deposited a time $t$ later.

Both $\tilde{p}_{\text{nuc}}(t)$ and $\tilde{P}(n; t)$ depend linearly on the initial ‘probability distributions’ for atoms $A$ and $B$. Therefore we only need to evaluate $\tilde{p}_{\text{nuc}}(t)$ and $\tilde{P}(n; t)$ for two particles deposited simultaneously with an effective initial distribution [7] for particle $A$:

$$p_{\text{eff}}^A(n) = \int_0^\infty dt P_{\text{dep}}(t) p_A(n, t) ,$$

where $p_A(n, t)$ is the distribution of a particle evolving alone on the terrace for time $t$: it is the dynamical evolution of the single particle probability
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\[ p_\Lambda(n,0) = \frac{1}{L^d} \]

via the discrete diffusion equation:

\[ p_\Lambda(n,t+1) = \frac{1}{2d} \sum_{\delta} p_\Lambda(n + \delta, t) \, , \quad (4) \]

where “\(n + \delta\)” labels the neighboring sites of “\(n\)”.

We can explain the meaning of Eq. (3) easily: atom \(A\) is deposited uniformly at time zero; atom \(B\) has a probability \(P_{\text{dep}}(t)\) to be deposited at time \(t\) and therefore it has probability \(P_{\text{dep}}(t)\) to find atom \(A\) on the terrace with distribution \(p_\Lambda(n,t)\). It is worth stressing that \(p_\Lambda(n,t)\) is not normalized: its sum on all sites, \(S(t)\), is the probability that atom \(A\) is still on the terrace when \(B\) comes in. In conclusion, we have to study the problem of two atoms diffusing on the terrace, whose starting distributions are \(p^\text{eff}_\Lambda(n)\) and \(p_B(n) = \frac{1}{L^d}\), respectively.

The effective distribution carries two pieces of information: its integral \((\mathcal{I} = \sum_n p^\text{eff}_\Lambda(n))\) determines the scaling of the nucleation rate \(\omega\) while its normalized version \((p_S(n))\) influences the shape of \(P(n)\).

Using the definition (3) and the explicit knowledge of \(P_{\text{dep}}(t)\) we can write down a differential equation for \(p^\text{eff}_\Lambda(n)\), whose solution is possible [8] for any \(\ell_{\text{ES}}\). We propose here a simpler argument: The normalization factor of \(p^\text{eff}_\Lambda(n)\) is given by \(\mathcal{I} = \tau_{\text{res}} / \tau_{\text{dep}} \int_0^\infty dt \exp(-t/\tau_{\text{dep}})S(t)\) where \(S(t)\) is exactly the probability that atom \(A\) is still on the terrace at time \(t\). For weak ES barriers the exponential can be taken as a constant on the time scale of the decay of \(S(t)\) and \(\mathcal{I} = \tau_{\text{res}} / (\tau_{\text{res}} + \tau_{\text{dep}})\). For strong ES barriers \(S(t)\) decays exponentially [13] and \(\mathcal{I} = \tau_{\text{res}} / (\tau_{\text{res}} + \tau_{\text{dep}})\). The solution of the differential equation mentioned above confirms [8] this result for any \(\ell_{\text{ES}}\).

It is therefore possible to write \(p^\text{eff}_\Lambda(n) = \frac{\tau_{\text{res}}}{\tau_{\text{res}} + \tau_{\text{dep}}} p_S(n)\): The question is now how \(p_S(n)\) looks like. In the limit of weak ES barriers we can repeat the above argument and find that \(p^\text{eff}_\Lambda(n) = \tau_{\text{dep}} \int_0^\infty dt p_\Lambda(n,t)\). The time integral of the single particle probability distribution is nothing but the solution of the stationary diffusion equation in the presence of a constant flux [7], which is known to have a parabolic form [14]. We can conclude that for any \(\ell_{\text{ES}}\):

\[ p^\text{eff}_\Lambda(n) = \frac{\tau_{\text{res}}}{\tau_{\text{res}} + \tau_{\text{dep}}} p_S(n) \, , \quad (5) \]

where \(p_S(n)\) is the normalized steady state distribution. Consequently the nucleation probability per atom takes the form:

\[ p_{\text{nuc}} = \frac{\tau_{\text{res}}}{\tau_{\text{res}} + \tau_{\text{dep}}} W \]

where \(W\) is the probability that two adatoms \(A\) and \(B\), deposited simultaneously with distributions \(p_\Lambda(n) = p_S(n)\) and \(p_B(n) = 1/L^d\), meet before
descending. $W$ is almost independent from the exact spatial profiles of atoms $A$ and $B$ and it mainly depends on $\ell_{ES}/L$ and on the space dimensionality $d$.

Let us now assume $\tau_{res} \ll \tau_{dep}$, i.e. consider weak and strong ES barriers (for the ‘infinite ES barrier’ regime see below). Then,

$$p_{nuc} \simeq \frac{\tau_{res}}{\tau_{dep}} W \simeq \tilde{\rho} L^{d}W \simeq \tilde{\rho} N_{\text{dis}},$$

(7)

where we have used the relation $\tilde{\rho} = F \tau_{res}$ and the relation $W \simeq N_{\text{dis}}/L^{d}$ between the probability $W$ that two adatoms meet and the number $N_{\text{dis}}$ of distinct sites visited by an adatom during its diffusion on the terrace.

The relation $p_{nuc} \simeq \tilde{\rho} N_{\text{dis}}$ can be intuitively justified [15] with the following argument: the nucleation probability per atom is given by the number of distinct sites ($N_{\text{dis}}$) visited by each atom times the probability that a given site is occupied ($\tilde{\rho}$). This argument breaks down if the average number of adatoms present at the same time on the terrace (and equal to $\tilde{\rho} L^{d}$) is larger than one; such condition is equivalent to $\tau_{res} \gg \tau_{dep}$ (regime (iii)).

The nucleation rate is finally written as:

$$\omega(L) \simeq \frac{\tau_{res} W}{\tau_{dep}^{2}} \simeq FL^{d} \tilde{\rho} N_{\text{dis}}$$

(8)

and we want to compare it with the well known mean field result [3, 12]:

$$\omega_{\text{MF}} = DL^{d} \tilde{\rho}^{2} = FL^{d} \tilde{\rho} N_{\text{all}},$$

(9)

where we have made use of the relation [15] $\tilde{\rho} = \frac{F}{D} N_{\text{all}}$, $N_{\text{all}}$ being the total number of sites visited by an adatom during its diffusion on the terrace. The comparison of Eqs. (8) and (9) is fully transparent: $\omega_{\text{MF}}/\omega \simeq N_{\text{all}}/N_{\text{dis}} \equiv N$, that is mean field theory overestimates the correct nucleation rate by a factor proportional to the number of times an adatom diffusing on the island visits an already visited site.

Our comparison gets complete once we introduce a model where diffusing adatoms do not interact: even if they meet each adatom keeps diffusing until they get off. If the average number of fictitious nucleations between non interacting adatoms is $W_{\text{N}}$ we simply have $N_{\text{all}} \simeq W_{\text{N}} L^{d}$ and $\omega_{\text{MF}} = (\tau_{res} W_{\text{N}} / \tau_{dep}^{2})$, i.e. mean field theory —as expected by the relation $\omega_{\text{MF}} = DL^{d} \tilde{\rho}^{2}$— treats adatoms as independently diffusing particles.

The above results are valid for $\tau_{res} \ll \tau_{dep}$ because they derive from Eq. (7) rather than from the more general Eq. (6). What does it happen in the regime of ‘infinite’ ES effect? In this case $W = 1$ and $p_{nuc} = 1$ so that $\omega = \tau_{dep}^{-1} = FL^{d} = FN_{\text{dis}}$ while $\omega_{\text{MF}} = DL^{d} \tilde{\rho}^{2} \simeq FL^{d} \tilde{\rho} N_{\text{all}}$. Hence
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\[ \omega_{MF}/\omega \simeq \bar{\rho} L^d N_{all}/N_{dis}. \]

We can sum up our results for the nucleation rate by reporting the ratio \( \omega_{MF}/\omega \) for the three regimes introduced in Sec. 2, both in \( d = 1 \) and \( d = 2 \); this is done in Table 1 where we use the already mentioned relation between \( N_{all} \) and \( \bar{\rho} \), the well known results \[16\] that in absence of ES barriers \( N_{dis} \simeq L \) in \( d = 1 \) and \( N_{dis} \simeq L^2/\ln L \) in \( d = 2 \) and finally that \( N_{dis} = L^d \) for \( \ell_{ES} \gg L \).

| (i) \( \tau_{res} \simeq \tau_tr \) | (ii) \( \tau_tr \ll \tau_{res} \ll \tau_{dep} \) | (iii) \( \tau_{res} \gg \tau_{dep} \) |
|---|---|---|
| \( d = 1 \) \( L \) | \( \ell_{ES} \) | \( F(L\ell_{ES})^2/D \) |
| \( d = 2 \) \( \ln L \) | \( \ell_{ES}/L \) | \( F(L\ell_{ES})^2/D \) |

The result \( \omega_{MF}/\omega = \ell_{ES}/L \) —valid in the two dimensional strong barrier regime— had already been found in Ref. \[9\]. In that paper logarithmic corrections were neglected, which corresponds to disregarding the \( L \)-dependence of the factor \( W \) in the weak barriers regime.

4. The spatial distribution of nucleation events

In this Section we study what sites are the most favored for nucleation. The result is strongly dependent on the exact spatial profiles of the initial probability distributions for particles \( A \) and \( B \) \( (p_{A,B}(n)) \): we have justified below Eq. (3) that \( A \) is distributed as the stationary solution of the diffusion equation \( (p_{A}(n) = p_{S}(n)) \) while \( B \) is uniformly distributed \( (p_{B}(n) = 1/L^d) \).

The dynamical evolution of two diffusing particles on a \( d \)-dimensional terrace can be easily mapped on the problem of a single walker in a space of dimension \( d' = 2d \). If \( m \) and \( n \) label the positions of the two atoms a nucleation event occurs when \( m = n \), i.e. when the “single walker” crosses the diagonal of a square terrace if \( d = 1 \) \( (d' = 2) \) or the ‘diagonal plane’ of a four dimensional hypercube if \( d = 2 \) \( (d' = 4) \).

In \( d = 1 \) we have solved analytically \[7\] the problem for the limit cases of zero and infinite ES effect; for any value of \( \ell_{ES} \) we can compute exact numerical results for \( P(n) \) both in \( d = 1 \) and \( d = 2 \) \[8\]. Our main results in \( d = 2 \) are reproduced in Fig. 1 where we give the resulting spatial distribution of nucleation events along the diagonal of a square terrace and we compare it with Mean Field Theory: \( P(n) \sim p_{S}^2(n) \). In absence of ES barriers (Fig. 1a) MFT works remarkably well but its accuracy gets
Figure 1. \(P(n)\) along the diagonal of a square terrace of size \(L = 20\) for (a) \(\ell_{ES} = 0\), (b) \(\ell_{ES} = 4\), (c) \(\ell_{ES} = 20\), (d) \(\ell_{ES} = 100\). Full diamonds: exact theory; open squares: mean field theory; full line: “independent adatoms” model.

worse with increasing \(\ell_{ES}\) (Figs. 1b,c) and MFT fails completely for large ES barriers (Fig. 1d): in this case MFT predicts that \(P(n)\) gets flat while a clearly rounded shape is obtained.

Fig. 1 confirms that MFT is equivalent to an “independent adatoms” model and this is the reason of its failure with increasing \(\ell_{ES}\): for \(\ell_{ES} \gg L\) independent adatoms perform many more fictitious nucleations than for \(\ell_{ES} \ll L\) (see Table 1).

5. Conclusions

We think that two main aspects of our work should be emphasized. Limits and inaccuracies of mean field theory have been pointed out by several authors during the years [17, 11, 9, 18, 19] but we have performed a rigorous study for any value of the ES barriers in one and two dimensions. Furthermore we study the spatial distribution \(P(n)\) of nucleation events and we are not aware of previous similar analyses. The second aspect is that we provide a simple physical interpretation of the failure of mean field theory: it counts all the nucleations of two independently diffusing adatoms.

The nucleation rate is of primary experimental relevance because most
of the methods to determine step-edge barriers — or to evaluate other quantities derived from $\ell_{ES}$— require the knowledge of $\omega(L)$ [12, 20]. It would be therefore useful to reconsider such derivations which made use of $\omega_{MF}$: this has already been started in Ref. [9].

As for $P(n)$, a direct experimental determination is extremely complicated [21]. Nonetheless its knowledge has a theoretical interest because $P(n)$ may enter in mesoscopic models of crystal growth [22, 23], i.e. in models where surface diffusion is not taken into account microscopically but through a mesoscopic surface current plus the rule for nucleating new terraces.

Finally we mention a few extensions of our work that are presently in progress: Firstly, the problem of nucleation between adatoms of different species, i.e. particles having different diffusion constants. Secondly, the study of $P(n)$ in the limit $L \to \infty$ in order to understand what features are maintained in this limit. Finally, the nucleation on top of a fractal terrace.

References

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