Influence of adatom interactions on second layer nucleation

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We develop a theory for the inclusion of adatom interactions in second layer nucleation occurring in epitaxial growth. The interactions considered are due to ring barriers between pairs of adatoms and binding energies of unstable clusters. The theory is based on a master equation, which describes the time development of microscopic states that are specified by cluster configurations on top of an island. The transition rates are derived by scaling arguments and tested against kinetic Monte-Carlo simulations. As an application we reanalyze experiments to determine the step edge barrier for Ag/Pt(111).

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Whether thin films in epitaxy become rough or grow smoothly layer by layer depends on the onset of second layer nucleation on top of islands in the first layer: If the rate $\Omega$ of this nucleation is large, it is likely that mounds are formed before layer completion, while small second layer nucleation rates favor layer by layer growth. Detailed theories have been developed in the past to predict $\Omega$ in dependence on the island size $R$, the ratio $\alpha \equiv \left(\frac{\nu_t}{\nu_B}\right) \exp\left(-\Delta E_a/k_B T\right)$ of the hopping rates $\nu_t \exp(-E_D/k_B T)$ and $\nu_B \exp(-E_a/k_B T)$ on top of the island and over the island edge, respectively, and the ratio $D/F a^4$ of the adatom diffusivity $D = (\nu_t a^2 / 4) \exp(-E_D/k_B T)$ and deposition flux $F$; $a$ is the lattice constant. Studies so far focused on adatoms that form stable nuclei once more than $i$ of them cluster together, but otherwise do not interact.

In this Letter we show how adatom interactions strongly influence the second layer nucleation. We consider two types of these interactions: (i) Clusters of size smaller than $i+1$ are metastable, i.e. the detachment of an adatom or the break up of clusters into two pieces requires a dissociation energy $E_{dis} \gtrsim k_B T$, and (ii) the approach of two atoms by diffusion is hindered by additional barriers. As a generic model we consider a barrier $E_{ring}$ in form of a ring with radius $\xi$ around each adatom. The occurrence of such barriers was explored by Fichthorn and Scheffler based on extensive density functional calculations. Similar interaction effects can be caused by Shockley surface states.

The aim of this Letter is to develop a theory based on rate equations that allows us to take into account these interaction effects for nucleation processes in confined geometry as encountered on top of a growing island. As an application we quantify possible errors when determining the step edge barrier $E_s$ in the Ag/Pt(111) system, and we compare the results at different levels of sophistication of the underlying theory for determining the step edge barrier.

In order to take into account the adatom interactions, we refer to our rate equation approach for second layer nucleation outlined in [3]. In this approach one considers one compact island with radius $R$ that evolves in time according to some growth law $R = R(t)$. To clearly separate the different types of interaction effects, we consider the presence of either metastable clusters or the ring barrier.

We denote by $p_{n,\nu}(t)$ the probability to find the island in a state where in total $n$ atoms are on top of the island in configuration $\nu$ at time $t$. The configuration label $\nu$ specifies the way the $n$ atoms are decomposed into clusters and which pairs of atoms have a distance smaller than $\xi$ and are thus “weakly bound” by their ring barriers.

In Fig. 1 the most important states are shown together with the rates $W_{n,\nu \rightarrow n',\nu'}$ connecting them. The prob-
abilities $p_{n,\nu}(t)$ obey the master equation
\[\frac{dp_{n,\nu}}{dt} = \sum_{n',\nu'} \left[ W_{n',\nu'\rightarrow n,\nu} p_{n',\nu'} - W_{n,\nu\rightarrow n',\nu'} p_{n,\nu} \right], \tag{1}\]
where $W_{n,\nu\rightarrow n',\nu'}$ is the rate from state $(n,\nu)$ to $(n',\nu')$ and can depend on time through the growth law $R = R(t)$ (see below). Equations (1) are numerically solved subject to the initial condition $p_{n,\nu} = \delta_{n,0}$. The rates $W_{n,\nu\rightarrow n',\nu'}$ are expressed in terms of elementary rates $W_F$, $W_b$, $W_{\text{ring}}^{(n)}$, $W_F$, $W_b$ and $W_{\text{ad}}$ (cf. Fig. 1). The first two rates $W_F$ and $W_b$ refer to processes not involving the ring barrier: $W_F = \pi FR^2$ is the deposition rate of adatoms onto the island and $W_b = (D/R^2)[\kappa_1 a/(\alpha a R) + \kappa_2]^{-1}$ is the loss rate of adatoms that leave the island by surmounting the step edge barrier (ii). The coefficients $\kappa_1$, $\kappa_2$ are of order one. In order to account for the reduced mobility of pairs of atoms bound via the ring barrier compared to individual atoms, the loss rate for such pairs is approximated to be equal to that of a single atom.

The latter four rates involve the ring barrier in form of the associated Boltzmann factor $\alpha_{\text{ring}} = \exp[-\Delta E_{\text{ring}}/k_B T]$, $\Delta E_{\text{ring}} = E_{\text{ring}} - E_D$, and the ring radius $\xi$. $W_{\text{ring}} = \pi F \xi^2$ is the deposition ("flux") rate into a ring. $W_{\text{ad}} = \kappa_0 D(\pi \xi^2)$ is the attachment rate for two atoms in a circle which are confined to a separation distance smaller than $\xi$. It results from the time $\alpha \xi^2/2D$ for the two atoms to encounter by diffusion on top of an island with radius $\xi$. For the relevant case $a < \xi \ll R$ we can further derive the rates for formation and breakup of pairs weakly bound by their ring barriers. The breakup rate is given by
\[W_b = \kappa_0 \frac{D\alpha_{\text{ring}}}{a \xi}. \tag{2}\]
It results from the probability $\alpha = 2\pi \xi / \pi \xi^2$ for two atoms to have distance $\xi$ times the rate $\alpha_{\text{ring}} D/a^2$ to overcome the ring barrier. The rate for formation of an adatom pair weakly bound by their ring barriers is
\[W_{\text{ring}}^{(n)} = \frac{n(n-1)D}{R^2} \left( \kappa_1 \frac{a}{\xi \alpha_{\text{ring}}} + \kappa_2 \right)^{-1} \tag{3}\]
if in total $n$ adatoms are on top of the island. The associated time $(W_{\text{ring}}^{(2)})^{-1}$ for two atoms results from two contributions: The time $\alpha \xi^2/2D$ for first reaching the interaction distance $\xi \ll R$ and the time for overcoming the barrier. The latter is given by $[(2 \pi \xi a / \pi R^2) \times (\alpha_{\text{ring}} D/a^2)]^{-1}$, where the term $2 \pi \xi a / \pi R^2$ is due to the probability for a pair to have a distance in the interval $(\xi, \xi + a)$ and the term $\alpha_{\text{ring}} D/a^2$ is the rate to overcome the ring barrier. The rate $W_{\text{ring}}^{(2)}$ for a single pair has to be multiplied by the number $n(n-1)/2$ of distinct pairs to obtain the total rate for $n$ adatoms.

The validity of all formulae for the elementary rates is tested against kinetic Monte-Carlo (KMC) simulations performed on a hexagonal lattice for the (111) surface. As an example we show in Fig. 2 scaling plots for the two rates $W_{\text{ring}}^{(n)}$ and $W_b$ demonstrating the good agreement of the KMC data with the predictions of eqs. (2,3). All constants $\kappa$ in Eqs. (2,3) are of the order of one. The approach outlined above provides a general framework to treat the problem of second layer nucleation and may be applied and extended to a variety of situations. It furthermore allows one to gain detailed insight into the microscopic pathways followed during the nucleation process.

To apply our theory we consider the determination of step edge barriers in second layer nucleation experiments. In these experiments one measures the probability $f[R(t)]$ that a stable cluster has nucleated on top of the island until time $t$ (i.e. the fraction of "covered islands"). In systems with a substrate mediated ring barrier, second layer nucleation will be aggravated and nucleation sets in later. A repulsive ring barrier therefore has an effect similar to a reduced step edge barrier, and thus yields an apparent measurement value $\Delta E_{S}^{(0)}$ smaller than the "true" $\Delta E_{S}$. On the other hand,
metastable dimers facilitate the formation of a stable nucleus, leading to values $\Delta E_{9}^{(0)}$ larger than $\Delta E_{9}$.

To estimate the significance of the interactions, we first present results for the relative error $[\Delta E_{9} - \Delta E_{9}^{(0)}]/\Delta E_{9}$ as a function of the interaction parameters. By solving Eq. (4) we obtain the curves $f[R(t); \Delta E_{9}]$ that refer to processes including interactions. On the other hand, we can solve the rate equations neglecting the interaction ($\Delta E_{9} = 0$), thus obtaining $f_{0}[R(t); \Delta E_{9}^{(0)}]$. By fitting the curves $f_{0}$ to the “true” curves $f$ we obtain the apparent $\Delta E_{9}^{(0)}$. For the ratio of attempt frequencies $\nu_{s}/\nu_{t}$ for adatom hopping over the step edge and on a terrace, we use the generic value of one (for a general discussion on attempt frequencies, see [7]). Using a generic growth law $R(t) \propto \sqrt{t}$ (with the prefactor $(D/Fa^{4})^{1/2 (n=2)} \sqrt{FA^{2}}$ from standard nucleation theory [12]) we show in the upper half of Fig. 6 results for the relative error as a function of $\Delta E_{9}^{(0)}$. In the lower half of the figure we include the results of an analogous analysis for $i = 2$ with metastable dimers (for a setup of the corresponding rate equations, see [3]). Because the dependence on $D/Fa^{4}$ is only weak, this parameter is not varied in the plots. We see that for small $\Delta E_{9}$, even weak interactions $\Delta E_{9}^{\text{int}}$ lead to a large relative error. Closer inspection shows, that for fixed ratio $\Delta E_{9}^{\text{int}}/\Delta E_{9}$, the relative error decreases with increasing interaction energy (cf. the dashed line in Fig. [3]). In the case of metastable dimers, the error reaches a plateau when the dissociation energy becomes so large that a dimer is stable on the time scale of the formation of a stable trimer. This signifies the transition to the $i = 1$ case.

For Ag/Pt(111) detailed second layer nucleation measurements of the type discussed above were performed by Bromann et al. [13]. The system Ag/Pt(111) is particularly suited as a reference, since it has the advantage that many of the relevant parameters were determined both by experiment [13, 14, 15, 16] and by first-principle calculations [3, 7, 8, 9]. Experimentally, the diffusion barrier $E_{D}$ for Ag adatom diffusion on strained Ag islands grown on Pt(111) is $E_{D} \approx 60 \text{ meV}$ [13]. It has been shown by density functional calculations [4] that silver adatoms diffusing on top of an already existing silver island on the platinum surface exhibit a strong barrier $\Delta E_{9}^{\text{int}} = E_{9}^{\text{int}} - E_{D} \approx 50 \text{ meV}$ at a distance $\xi/a \approx 2.1$.

The original analysis by Bromann et al. was based on a mean field-type theory for second layer nucleation (“TDT approach”, see [3]). However, it has been shown recently that even in the absence of interaction effects it is necessary to re-analyze the data with an extended theory [3, 4] (see also [3]). In this theory fluctuation-dominated regimes occur for critical nuclei $i \leq 2$ [4], and it yields, for the experimental conditions and a prefactor $\nu_{t} = 10^{9} \text{ Hz}$ used in [13], the second-layer nucleation rate $\Omega(R) = \pi^{2} \kappa^{2} F R^{5}/(1 \alpha_{s})$ where $\Gamma = D/Fa^{4}$. By contrast to the generic growth law $R(t) \propto \sqrt{t}$ used for Fig. 3, in the analysis of Bromann et al. one has to deal with an exponential growth law $R(t)$ (for details see [3]).

FIG. 3: Relative error of the apparent additional step edge barrier $\Delta E_{9}^{(0)}$ when neglecting interactions ($\Delta E_{9}^{\text{int}} = 0$) with respect to the “true” barrier $\Delta E_{9}$ calculated for $\Delta E_{9}^{\text{int}} > 0$; upper part: $\Delta E_{9}^{\text{int}} = \Delta E_{9}^{\text{int}}$, lower part: $\Delta E_{9}^{\text{int}} = \Delta E_{9}$. The symbols refer to different values $\Delta E_{9}^{(0)}/k_{B}T = 3 (\bullet), 6 (\circ), 9 (\square), 12 (\diamond), 15 (\bigtriangleup)$. The dotted line in the upper figure is drawn for $\Delta E_{9}^{(0)} = \Delta E_{9}^{\text{int}}$. All plots are calculated with $D/Fa^{4} = 10^{9}$ and the generic growth law $R(t) \propto \sqrt{t}$.

Metastable states are not considered here, because $i = 1$ in the temperature range of the experiment. In Fig. 4 we have fitted the measured fraction of covered islands $f(R)$ yielding $\Delta E_{9}^{(0)} = 65 \text{ meV}$, which is about twice the value obtained previously based on the TDT approach (see Table I). For the much less reliable prefactor ratio [20] we find $\nu_{s}/\nu_{t} = 41$. The rate equation theory without interactions yields essentially the same value $\Delta E_{9}^{(0)} = 68 \text{ meV}$ by supporting the scaling approach [3, 4].

The next step in theoretical sophistication is the inclusion of the ring barrier. When using the value $\Delta E_{9}^{\text{int}} = 50 \text{ meV}$ [3], we find a significantly decreased value of $\Delta E_{9} = 52 \text{ meV}$. This decrease seems to be in contradiction to the reasoning above that $\Delta E_{9}^{(0)} < \Delta E_{9}$. However, the values were obtained by fitting both the prefactor $\nu_{s}/\nu_{t}$ and $\Delta E_{9}$ to the data and cannot be directly compared because the prefactors turn out to be very different (see Table I). When fitting under the constraint $\nu_{s}/\nu_{t} = 1$ [4], the value for $\Delta E_{9}$ increases from 42 meV to 48 meV in accordance with the general argument. Interestingly, the behavior of the standard error (see Table I) indicates that the system is better described when including the interactions. However, this interpretation should not be driven too far, since the standard error is only an indication of the quality of the fit, but should not be interpreted as the measurement error.

It was recently argued that the often reported small prefactors for hopping on weakly corrugated surfaces are
due to neglecting the interaction effects in the analysis of first layer nucleation experiments [11]. We therefore also analyze the data using the theoretical prediction $\nu_s = 10^{12}$ Hz [19] in the rate equation approach. The three $\alpha_s$ values obtained for each temperature shown in Fig. 4 lie very closely on a line in an Arrhenius plot (see the inset in Fig. 4). Both when using $\nu_s/\nu_t$ as fitting parameter and when setting $\nu_s/\nu_t = 1$, we find comparatively large values $\Delta E_s = 74$ meV and $\Delta E_s = 82$ meV, respectively.

In summary we have developed a rate equation theory that allows us to quantify the influence of certain interaction effects on the nucleation on top of islands in epitaxial growth. The formalism is rather general and may be extended to other types of adatom interactions and other kinds of geometrical constraints. We applied the theory to second layer nucleation experiments designed to extract the additional step edge barrier. It was shown that the value of $\Delta E_s$ depends very sensitively on whether the interactions are carefully accounted for in the analysis.

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TABLE I: Comparison of results for the additional step edge barrier for Ag/1ML Ag/Pt(111) obtained with theories of different levels of sophistication (see text). The standard errors from the fitting procedure are shown for the values of $\Delta E_s$.

| $\nu_s$ [Hz] | $\Delta E_{ring}$ [meV] | Theory | $\Delta E_s$ [meV] | $\nu_s/\nu_t$ | $\Delta E_s/\nu_s$ [meV] (\(\nu_s/\nu_t = 1\)) |
|--------------|----------------------|--------|------------------|---------------|---------------------------------|
| 10$^9$       | 0                    | TDT    | 30 ± 5           | 1             | 30                              |
| 10$^9$       | 0                    | Scaling | 65 ± 5           | 41            | 43 ± 2.2                        |
| 10$^9$       | 0                    | Rate Eq. | 68 ± 1           | 83            | 42 ± 2.6                        |
| 10$^9$       | 50                   | Rate Eq. | 52 ± 1           | 2             | 48 ± 0.4                        |
| 10$^{12}$    | 50                   | Rate Eq. | 74 ± 2           | 0.3           | 82 ± 0.8                        |
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