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Submonolayer Growth with Anomalously High Island Density in Hyperthermal Deposition

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We present a rate equation model for submonolayer island growth under conditions where hyperthermal deposition techniques such as low-energy ion deposition are employed to achieve smooth layer-by-layer growth. By asymptotic analysis, we demonstrate that the model exhibits stationary behavior with well-defined dynamic and growth exponents β and χ, respectively, in the limit of small and high detachment rates. We verify these predictions by using the particle coalescence simulation method. The simulations reveal the existence of a relatively sharp transition regime with an increasing detachment rate of adatoms from high values of the growth exponent $\beta \approx 1$ to much smaller values of β determined by detachment and island diffusion processes. Our numerical results for the island size distribution indicate an anomalously high number of small islands, in agreement with available experimental data.

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Hyperthermal deposition (HTD) techniques have become an important tool in improving and controlling the properties and growth of thin films during deposition. They include low-energy ion deposition (LEID) [1] and ion beam assisted deposition (IBAD) techniques where energetic ion beams with energies ranging from a few eV up to a few keV are used. When the ratio of bombarding ions to the deposited atoms is moderately low ranging from 0.1% to 10%, thin films with improved smoothness can be obtained under less stringent deposition conditions than in ordinary molecular beam epitaxy [2,3].

In HTD it has been observed that island growth is in striking contrast to ordinary thermal deposition: the island density is larger, the average island size is smaller [2,3], and distributions are considerably broader [1,3]. Various atomistic processes such as ion enhanced mobilities, cluster dissociation [1], and defect creation [2,4] have been suggested to explain this. However, in particular, in LEID it is a remarkable fact that the growth properties do not seem to depend much on the details of ion bombardment. With different deposition energies an anomalously high density of small islands is observed with very similar distributions [1]. This is unexpected, since the number of additional detachment events due to deposition is relatively low, and thus it is not obvious how an anomalously high island density is maintained.

In this Letter we propose a simple rate equation (RE) model for ion-assisted deposition. It demonstrates that in systems where HTD maintains smooth submonolayer growth the enhanced detachment of atoms together with island mobility results in island growth with new regular scaling properties and an anomalously high density of small islands with size distribution which is also of scaling form. The transition to this new region of growth is relatively sharp with respect to the physical parameters and it occurs in a region which is easily accessible by LEID or IBAD experiments. Our results are also in good agreement with existing experimental data.

In HTD island growth is a manifestly reversible process which is characterized by enhanced adatom detachment [1,4]. Moreover, in growth of metallic films islands may have substantial mobilities [5,6], which means that the growth can be described by neglecting spatial correlations between the growing islands [7–10]. This implies that island growth with mobile islands and breakup can be modeled using REs for a reversible aggregation-detachment process $A_i + A_j \rightleftharpoons A_{i+j}$ of clusters of sizes i and j with the rates of aggregation and detachment specified by reaction rates $K(i, j)$ and $F(i, j)$, respectively. The REs for the areal density n_s of islands of size $s \geq 1$ can be written as [10]

$$\frac{dn_s}{dt} = \frac{1}{2}\sum_{i+j=s}[K(i,j)n_i n_j - F(i,j)n_s] - \sum_{j=1}^{\infty}[K(s,j)n_s n_j - F(s,j)n_{s+j}] + \Phi\delta_{1,s}, \quad (1)$$

where Φ is the deposition flux of adatoms in monolayers per second (ML/s). The rate $K(i, j)$ for islands of sizes i and j with diffusivities D_i and D_j is given by the Smoluchowski formula $K(i, j) \propto (D_i + D_j)$, which is consistent with the point island model to be used in the present study [7,11]. Diffusion coefficients of islands in cases of interest here—metal islands on metal surfaces—have an inverse power law dependence on island size $D_i \propto i^{-\mu}$, with μ in the range $1 \leq \mu \leq 2$. We concentrate on cases where $\mu = 1$, $3/2$, or 2 corresponding to the most common single particle adatom processes in this case [6]. The reaction rate of aggregation is in this case taken to be a homogeneous kernel $K(i, j) = D_0(i^{-\mu} + j^{-\mu})$, where

D_0 is the adatom surface diffusion coefficient. The justification for this choice for moving islands is well known and discussed in more detail, e.g., in Refs. [5,7,11].

The detachment rate of adatoms from islands of size $i + j = s$ is taken to depend on island size but only detachment of single adatoms is allowed and hence it is given by $F(i, j) = F_0(i + j)^{\alpha}(\delta_{1i} + \delta_{1j})$ with parameter α. In LEID this is a physically obvious choice because in it bombarding energies from 10 to 100 eV are involved, adatom detachment dominates, and island breakup into larger pieces is not expected to occur [4,12]. Moreover, since every deposition event at the vicinity of an island boundary can be assumed to detach adatoms at least with a probability proportional to the island perimeter (i.e., $s^{1/2}$), $\alpha = 1/2$ is a reasonable lower limit. This was also confirmed by molecular dynamics (MD) simulations on an ion bombardment enhanced detachment in an island size region up to 25 atoms where values of $0.4 < \alpha < 0.6$ were found [12]. For completeness, however, the whole parameter region $0 \leq \alpha \leq 1$ will be discussed here.

Putting in the relevant reaction rates into Eq. (1) leads to REs with a complicated structure. Similar REs but with more simple aggregation rates than here display a rich variety of behavior [13]. Because the reaction rate for detachment is not a homogeneous function and there is now no detailed balance between the reaction rates (cf. Ref. [13]), an analytical solution seems unfeasible. Moreover, there is no guarantee of the existence of the usual scaling type of solutions or uniquely defined scaling exponents for the mean island size and density.

It is still possible, however, that there are stationary phases of growth where scaling solutions exists and *effective* scaling exponents can be defined. To extract such behavior, we first consider an analytic scaling ansatz. The probability density that an atom selected at random is contained in an island of size s is given by $p(s, \theta) = sn_s(\theta)/\theta$, and the average size $\bar{s}$ of the island is defined as $\bar{s}(\theta) = \sum sp(s, \theta)$ [14]. In irreversible growth in the submonolayer regime the average size is known to scale as $\bar{s}(\theta) \sim R^{\chi}\theta^{\beta}$ [14], where χ and β are the growth and dynamic exponents, respectively. Another central quantity in submonolayer growth is the scaling function $g(x) = \bar{s}p(s, \theta)$, with $x \equiv s/\bar{s}$, which is independent of the coverage θ and of the parameters $R = D_0/\Phi$ and $\kappa = F_0/D_0$ [14,15]. This scaling holds also for more general situations of reversible growth [16] and growth with moving islands [5,7].

We next assume the validity of the scaling forms for $\bar{s}$ and $g(x)$ and substitute these in the rate equations of Eq. (1). We obtain differential equations governing $\bar{s}$, the adatom density n_s, and the average island density $N = \sum n_s$ [11]. By requiring stationarity of the solutions, we obtain estimates for the dynamic and growth exponents as follows:

$$\beta = \frac{2}{1+\mu}, \qquad \chi = \beta/2, \qquad \text{for } \theta \ll \theta_{\max}; \tag{2}$$

$$\beta = \frac{1}{\mu+\alpha}, \qquad \chi \to 0, \qquad \text{for } \theta \approx \theta_{\max}. \tag{3}$$

Here $\theta_{\max}$ represents the coverage where a maximum in the island density occurs. The limit $\theta \ll \theta_{\max}$ corresponds to growth in the absence of detachment ($\kappa = 0$), and only in this region the relation $\chi = \beta/2$ holds. In the region $\theta \approx \theta_{\max}$ adatom detachment begins to govern growth because there are enough islands to provide a supply of detached adatoms exceeding the number of deposited atoms. In this case growth becomes independent of R and κ.

In order to fully explore the rich dynamics contained in Eq. (1) *without* any scaling assumptions, we have simulated island growth by using the particle coalescence method (PCM) [9]. The basic idea is to treat islands as pointlike objects, which is a good approximation at small coverages. In PCM, islands occupied only single lattice sites, and aggregation and breakup occur with rates determined by the kernels $K(i, j)$ and $F(i + j)$. In this way the reaction kernels in the REs can be specified exactly since the geometric effects arising from the complicated morphology of real islands are not taken into account [9,10]. For details of the simulation method see Ref. [11].

The PCM simulations were carried out with island diffusion characterized by $\mu = 1, 3/2$, and 2, and detachment described by $\alpha = 0, 1/2$, and 1. Parameters κ and R were in the range $10^{-6} \leq \kappa \leq 10^{-1}$ and $10^5 \leq R \leq 10^9$, with special attention paid to the region where $1 \leq \kappa R \leq 100$. Some simulations were carried out also for $\mu = 3, 6$, and 10 in order to check the convergence towards the limit of immobile islands. The simulations show that $\bar{s}$ and N indeed follow a power law type of behavior only in a limited region of the parameters, and only in this region can well-defined scaling exponents be extracted. In this regime we also observed fast convergence towards the island size distributions of scaling form.

Reversible growth and small detachment rates yield $\beta \approx 0.8$–1.0 indicating nearly linear growth. For size-independent detachment ($\alpha = 0$), in particular, we find that $\beta \approx 1$ in agreement with Monte Carlo simulations of Ref. [16] for reversible growth. With size-dependent detachment (with $\alpha = 1/2$), the dynamic exponent β and the growth exponent χ decrease from $\beta = 1.0$, $\chi = 0.5$ for $\mu = 1$, to $\beta = 0.75$, $\chi = 0.37$ for $\mu = 3$. This is consistent with previous results for irreversible growth with mobile islands, where in the region $1 \leq \mu \leq 3$ values in the range $0.45 \leq \chi \leq 0.40$ were found [5].

We confirmed the validity of our analytic prediction $\beta = 2/(\mu + 1)$ in the absence of detachment by performing simulations with $\mu = 1, 3/2$, and 2 for $\kappa = F_0/D_0 \to 0$ (with $\alpha = 1/2$). The exponent χ was also found to be in very good agreement with Eq. (1). The value $\beta = 2/(\mu + 1)$ holds until $\mu \approx 2$, after which $\beta = 2/3$ asymptotically follows for very large values of $R \approx 10^9$–10^{10} as predicted for immobile islands [5,14]. For moderate values of $R < 10^8$ with mobility exponents $\mu = 6$ and 10 there is very slow convergence towards $\beta = 2/3$. Similar slow convergence was noted in Ref. [5] in the case of submonolayer growth with mobile islands.

Reversible growth and large detachment rates yield values of the dynamic exponent depending on both μ and α as predicted in Eq. (2). In Table I we summarize our numerical results and compare them with the analytic predictions. As can be seen, the agreement is reasonably good.

Transition to a regular region of growth and its detailed nature is of particular interest here and of fundamental significance for LEID. This transition occurs with an increasing detachment rate in reversible growth and is indicated by change from $\beta \approx 1$ to much slower growth with β. In the latter case the value of β is determined by exponents characterizing detachment and island diffusion. The arguments above suggest that this transition should be particularly clear when island diffusion is fast. In Fig. 1 we show the overall behavior of dynamic exponent β as obtained from PCM simulations for various (μ, α). In the limit of small detachment $\beta \approx 0.8$ and $\chi \approx 0.4$ irrespective of α. Indeed, from Fig. 1 we can see that when $1 \leq \kappa R \leq 100$ there is a sharp transition to a qualitatively different type of growth characterized by much smaller dynamic exponents $\beta \approx 0.45$ for $\alpha = 1/2$, and $\beta \approx 0.37$ for $\alpha = 1$. As expected, slower growth is obtained for enhanced detachment. The growth in this region where enhanced detachment dominates seems to be unexpectedly regular and the value of β does not depend on the rate κ after the transition. From our numerical data we find that there is good data collapse with κR^{κ}, where $\kappa = (\alpha + 1)/2$ and the crossover region can be fitted by an exponential function.

The growth exponents χ also follow the expected behavior in different regions of growth. In the regime corresponding to low values of detachment rate we checked the relation $\chi = \beta/2$ to hold. On the other hand, in the region of slower growth there is no dependence on the parameter R as expected, and $\chi \approx 0$. This also means that although in the region of reversible growth it may still be possible to relate the value of χ to a critical size of islands (see Ref. [16]), in the limit of enhanced detachment with $\chi \approx 0$ this becomes physically meaningless, because all islands can be dissociated.

TABLE I. Dynamic scaling exponents for a regular region of growth with anomalously high density of small islands. Values denoted by subscripts a are analytical estimates given in text. Error in $\delta < 0.1$.

(μ, α)	β	β_a	δ	δ_a
(2, 1/2)	0.46(1)	0.40	3.0(1)	2.5
(2,1)	0.38(1)	0.33	3.2(1)	3.0
(3/2, 1/2)	0.56(1)	0.50	2.2(1)	2.0
(1, 1/2)	0.72(1)	0.67	1.7(1)	1.5

Scaling of island size distributions is expected also on the basis of the fact that well-defined scaling exponents exist for large detachment rates. In Fig. 2 we show scaled island size distributions corresponding to the steady values of growth exponents at large values of detachment rates, with $(\mu, \alpha) = (2, 1/2)$. Results for other values of μ are very similar. In the region of regular growth the data collapse to a single curve. The distribution is exceptionally flat with $g(x) \approx$ const for $x < 1$, indicating anomalously high density of small islands, roughly proportional to $n_s \sim s^{-1}$ for $s < \bar{s}$. We find that these distributions can be well described by the modified exponential $g(x) \propto x^{\delta} \exp(-cx)$, with values of δ summarized in Table I. For smaller island sizes there is an additional exponential part $\exp(-x/x_0)$ with $x_0 \approx 0.2$, which is most likely due to the random (Poissonian) aggregation of small islands.

It is far from obvious how the numerically discovered scaling function is a solution to the REs here. Important insight can be obtained by noting that the values for the exponent δ we have found here shown in Table I agree well with the prediction $\delta_a = \alpha + \mu$ which is based on an aggregation and breakup model with *homogeneous* breakup kernels [11], with the same total rate as the inhomogeneous model of detachment here. Although the model studied in Ref. [11] is phenomenologically different and similar analysis is not feasible at the present case, the agreement suggests that in the case of detachment the island size dependence of the total rate still governs the aggregation/breakup process but due to anomalously high density of small islands (and thus high probability of aggregation) there is a competing process of nearly random aggregation.

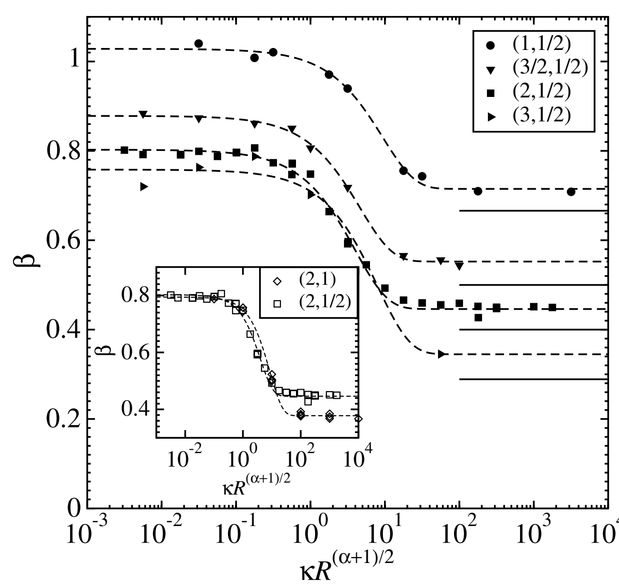

FIG. 1. Growth exponent β for systems with $(\mu, \alpha) = (1, 1/2)$, $(3/2, 1/2)$, $(2, 1/2)$, $(3, 1/2)$, and (2,1) (inset) as a function of the parameter $\kappa R^{(\alpha+1)/2}$. Note the sharp transition to growth characterized by β given by Eq. (3) (solid lines).

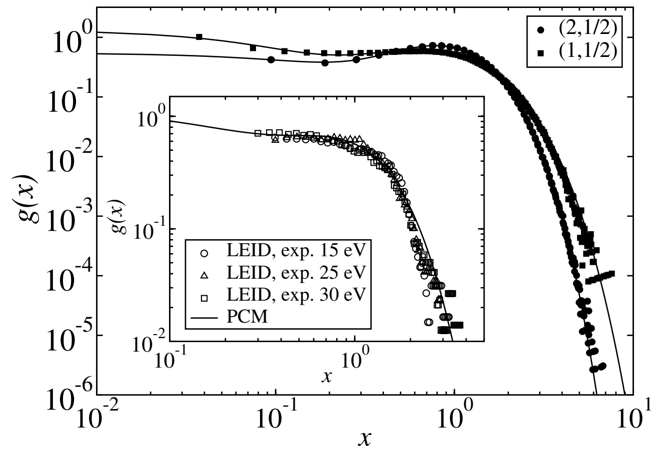

FIG. 2. Fits to the simulation results for the scaling function (solid lines) and data for cases $(2, 1/2)$, $R = 10^5$, and $\kappa = 10^{-2}$ (circles) and $(1, 1/2)$, $R = 10^6$, and $\kappa = 10^{-2}$ (squares). In the inset the experimental data on LEID from Ref. [1] are compared with PCM simulations for $(2, 1/2)$, $R = 10^5$, and $\kappa = 10^{-2}$.

Comparisons of available experimental results with the PCM simulation results are carried out in Fig. 2 where the experimental data of Degroote *et al.* [1] are scaled to yield the function $g(x)$ compared then with PCM results, with remarkably good agreement. In LEID experiments of Degroote *et al.* enhanced detachment is suggested to dominate the behavior of island size distributions. In the experiments, it is estimated that $\kappa \approx 0.1$, but recent MD simulations of Co deposition on Ag indicate much lower values of $\kappa \approx 0.01$ [12]. As the present results show, even such a low ratio of detachment to deposition is sufficient to lead to an anomalously high island density and maintain regular growth. Interestingly, the parameter region $\mu \approx 1.5$–2 with $10 \leq \kappa R \leq 100$ where regular growth occurs corresponds to those experimental parameters in LEID and other HTD techniques where layer-by-layer growth is observed.

To summarize, we proposed here a rate equation model for submonolayer growth with aggregation and enhanced adatom detachment corresponding to hyperthermal deposition conditions. The model reveals that with increasing detachment rate there is a relatively sharp transition to regular submonolayer growth with an anomalously high density of small islands. In this regular growth mode the island size distributions are of scaling form and the average island size and mean island density follow power law behavior with well-defined effective scaling exponents. We wish to emphasize that this behavior is nontrivial since the present rate equations are not of the usual simple form with homogeneous kernels and the rates do not fulfill the condition of detailed balance. Scaling can be observed only in a restricted range of the physical growth parameters. However, what makes the present results particularly intriguing is that the transition to the new regular growth mode sets in within a parameter range corresponding very closely to that found to be useful in HTD experiments. Indeed, our island size distributions are in good agreement with available experimental data. Thus, we expect that the predictions here could be easily checked.

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