# Cluster Diffusion and Dissociation in the Kinetics of Layer Growth: An Atomic View

Kentaro Kyuno* and Gert Ehrlich
*Materials Research Laboratory and Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*

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Data on diffusion and dissociation of single Pt clusters on Pt(111), available for the first time from field ion microscope observations, are used to make predictions about nanoscale phenomena by solving the mean-field differential equations for growth. In the submonolayer regime, cluster dissociation is found to be much more important than diffusion of clusters in reducing the saturation island density. Cluster dissociation also significantly affects the nucleation of a second layer on top of existing clusters and must be considered on an equal footing with interlayer transport over cluster edges.

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During the last decade, a wealth of information has become available about layer growth on crystals, generated by scanning techniques with nanoscale resolution [1–4]. By working backwards from observations of growth phenomena and relying on atomistic models of crystal growth, it has become possible to infer information about the atomic events participating in growth. It is now routine, for example, to derive the diffusivity of adatoms incorporating into surface clusters from measurements of the density of clusters in submonolayer growth experiments [1,2,5]. However, useful as this approach is, it is still indirect and subject to assumptions about the atomic events limiting the observed growth [6]. Here we note that it is now feasible to reverse this procedure: for the growth of platinum layers on Pt(111) surfaces, predictions about nanoscale phenomena can be made by drawing on directly observed properties of individual adatoms and surface clusters. In this way we have been able to establish the roles cluster diffusion and also the dissociation of clusters play in the kinetics of growth on Pt(111).

In the submonolayer range, the time variation of the density $n_i$ of monolayer islands made up of $i$ atoms is given by a well established set of rate equations [1,7,8]. These involve as material parameters the diffusivity $D_i$ of clusters of size $i$, their rate of dissociation $\Gamma_i$, and the capture number $\sigma_i$, which relates the rate of incorporation of atoms into a cluster of size $i$ present at a density $n_i$ to the diffusivity $D_1$ of adatoms. If $F$ atoms strike the surface per unit time and unit area, the rate at which the density $n_i$ of islands increases with time $t$ is given by

$$dn_1/dt = F(1-\Theta) - 2\sigma_1 D_1 n_1^2 - D_1 n_1 \sum_{m=2}^{8} \sigma_m n_m + 2\Gamma_2 n_2 + \sum_{m=3}^{7} \Gamma_m n_m \,, \tag{1}$$

$$dn_k/dt = -\sigma_k n_k \sum_{m=1}^{k} D_m n_m - D_k n_k \sum_{m=k}^{8} \sigma_m n_m - \Gamma_k n_k + \Gamma_{k+1} n_{k+1} + \sum_{m=1}^{k-1} D_m n_m \sigma_{k-m} n_{k-m} \qquad 2 \le k \le 6 \,, \tag{2}$$

$$dn_7/dt = -\sigma_7 n_7 \sum_{m=1}^{7} D_m n_m - D_7 n_7 \sum_{m=7}^{8} \sigma_m n_m - \Gamma_7 n_7 + \sum_{m=1}^{6} D_m n_m \sigma_{7-m} n_{7-m} \,, \tag{3}$$

$$dn_x/dt = \sigma_4 D_4 n_4^2 + \sigma_5 n_5 \sum_{m=3}^{5} D_m n_m + \sigma_6 n_6 \sum_{m=2}^{6} D_m n_m + \sigma_7 n_7 \sum_{m=1}^{7} D_m n_m \,. \tag{4}$$

Here all islands with eight or more atoms have been lumped under $n_x$ and $\Theta$ is the fractional coverage of the surface. In Eq. (1), as an example, account is taken of atoms supplied to the surface by deposition at the rate $F$, but also by dissociation of clusters, as given by the last two terms on the right. The second and third terms on the right account for the consumption of adatoms by combination with other adatoms as well as clusters.

Equations (1)–(4) can be integrated numerically using Runge-Kutta algorithms [9] to yield the island density. We have done this for our standard conditions, at a coverage of $\Theta = 0.15$ monolayer (ML), and a flux $F$ of 0.005 ML/s. For the capture numbers $\sigma_i$ we take the constant values $\sigma_i = 3$ for $i < 8$ and $\sigma_8 = 7$, reasonable approximations that minimize the computational effort [1,7]. The necessary information about the diffusivities $D_i$ and the dissociation rates of clusters of size $i$ is available from extensive experiments with the field ion microscope, which have revealed details on the atomic level. The results of a recently completed effort on the platinum (111) plane [10–12] are summarized in Table I; this gives the activation energy for diffusion $E_D$ and the prefactor $D_0$ in the Arrhenius relation for the diffusivity, $D_i = D_0^{(i)} \exp[-E_D^{(i)}/kT]$, as well as the dissociation energy of platinum clusters up to Pt$_7$. For the frequency factor

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TABLE I. Diffusion and dissociation of Pt clusters on Pt(111) [10,12].

| Cluster | $D_0$ (cm$^2$ s$^{-1}$) | $E_D$ (eV) | $\nu$ (s$^{-1}$) | $E_{\mathrm{diss}}$ (eV) |
|---|---|---|---|---|
| Pt | $2.0(\times 1.4^{\pm 1}) \times 10^{-3}$ | $0.260 \pm 0.003$ | ... | ... |
| $Pt_2$ | $1.9(\times 4.5^{\pm 1}) \times 10^{-4}$ | $0.37 \pm 0.02$ | $4.4 \times 10^{12}$ | $0.49 \pm 0.01$ |
| $Pt_3$ | $1.1(\times 2.1^{\pm 1}) \times 10^{-3}$ | $0.52 \pm 0.01$ | $5.1 \times 10^{12}$ | $0.58 \pm 0.02$ |
| $Pt_4$ | $6.6(\times 6.1^{\pm 1}) \times 10^{-5}$ | $0.57 \pm 0.04$ | $6.6 \times 10^{12}$ | $0.75 \pm 0.01$ |
| $Pt_5$ | $1.8(\times 2.3^{\pm 1}) \times 10^{-2}$ | $0.78 \pm 0.02$ | $7.4 \times 10^{12}$ | $0.84 \pm 0.02$ |
| $Pt_6$ | $4.9(\times 5.1^{\pm 1}) \times 10^{-3}$ | $0.89 \pm 0.04$ | $8.8 \times 10^{12}$ | $1.01 \pm 0.04$ |
| $Pt_7$ | $5.1(\times 3.8^{\pm 1}) \times 10^{-1}$ | $1.17 \pm 0.04$ | $9.6 \times 10^{12}$ | $1.11 \pm 0.02$ |

$\nu$ in the dissociation rate $\Gamma_i = \nu \exp[-E_{\mathrm{diss}}^{(i)}/kT]$ we assume a value $\nu = kT/h$.

To reveal the factors affecting the density of Pt islands on Pt(111) in the submonolayer range, we first suppress both diffusion and dissociation of clusters. That is, we assume that clusters are stationary, and once *any* cluster is formed it will act as a nucleus for growth, a commonly held view in early kinetic studies [8]. These assumptions yield the essentially straight dot-dashed line in the semilogarithmic plot of the saturation island density $n_x$ versus reciprocal temperature in Fig. 1. As the temperature is increased, the island density decreases, as expected: the diffusivity and therefore the mean-square displacement of the adatoms increases, so that the likelihood of atoms incorporating into existing islands becomes increasingly important compared to the nucleation of new clusters.

What effect does cluster mobility have on the number of islands [13–17]? If clusters can diffuse once formed they may combine with other clusters, growing larger entities and reducing the number of clusters present. Allowing Pt dimers to move over the surface in accord with the diffusion parameters in Table I yields the dotted curve in Fig. 1. At temperatures above 235 K, the island density is diminished below the results for immobile, nondissociating clusters by more than 10%. Inclusion of trimer diffusion lowers the density at ~420 K, again by 10%, but below that temperature the curve allowing both dimer and trimer diffusion can hardly be distinguished from that for dimer diffusion only.

We next consider the effects of cluster dissociation on the island density, this time disregarding all cluster diffusion. Here it is useful to introduce the critical cluster size $i^*$: clusters larger than $i^*$ are assumed not to dissociate. As appears from Fig. 2, which shows the island density obtained by integration of Eqs. (1)–(4), allowing Pt dimer dissociation (that is for $i^* = 2$) reduces $n_x$ by more than 10% at a temperature of 200 K. At higher temperatures, this diminution becomes more pronounced still. A comparison of Figs. 2 and 1 makes it clear that dimer dissociation is much more significant than dimer diffusion in affecting the island density and begins to have an effect at much lower temperatures. Including dissociation of Pt trimers ($i^* = 3$), as given by the solid curve

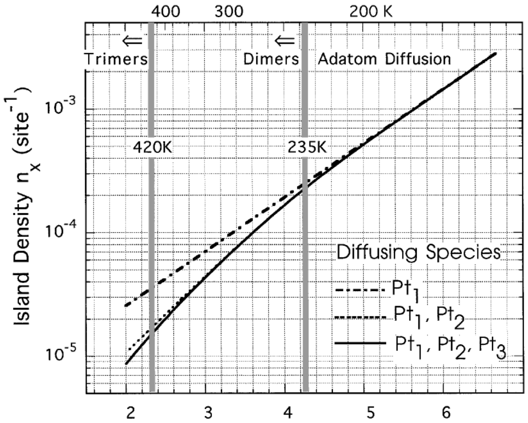

FIG. 1. Effect of cluster diffusion on saturation island density $n_x$. Calculations for atom flux $F = 5 \times 10^{-3}$ ML/s, $\Theta = 0.15$ ML, no dissociation allowed. Onset of a new cluster diffusion mode is set at the temperature at which the new channel lowers island density by ~10%.

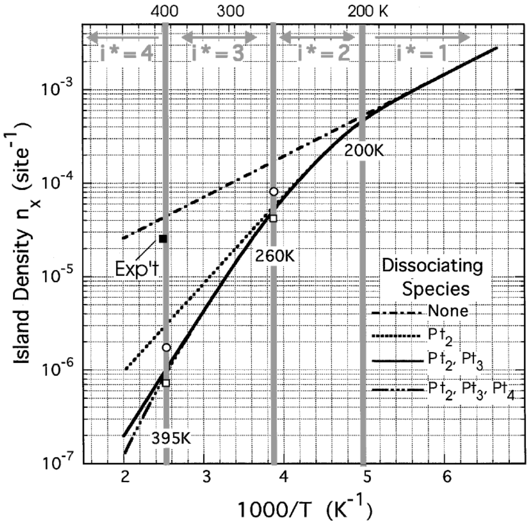

FIG. 2. Effect of cluster dissociation on island density (in absence of cluster diffusion). $F = 5 \times 10^{-3}$ ML/s; $\Theta = 0.15$ ML. Onset of new dissociation mode set at that temperature at which new channel lowers $n_x$ by ~10%. $i^*$ = critical island size. Data point at 400 K (marked Exp't) is from experiments by Kalff *et al.* [18]. Island density calculated with the uniform depletion approximation [7] for capture numbers (allowing for both diffusion and dissociation of clusters) is indicated by open circles; open squares give results using lattice approximation.

in Fig. 2, starts to make a significant difference above 260 K.

The dissociation of larger clusters has only a negligible effect up to ~400 K: the rate of dissociation of dimers and trimers is so high it dominates. Including both diffusion and dissociation does not alter these curves. In principle, cluster diffusion does lower the island density. However, for platinum, dissociation sets in over roughly the same temperature range as diffusion and eliminates the diffusing entities. In homoepitaxy on Pt(111), diffusion of clusters makes a significant contribution only at temperatures at which the clusters are no longer stable. However, dissociation of trimers as well as dimers is rapid enough at room temperature and above to markedly affect the island density.

Our predictions can be compared with actual experiments. For the growth of Pt on Pt(111), Bott *et al.* [19] have reported island densities at temperatures from 150 to ~265 K. However, Kalff *et al.* [18] just recently claimed that previous experiments on the growth of Pt(111) were contaminated by impurities, which may have had some effect on earlier results [19]. In experiments at 400 K, under what they believe are clean conditions, Kalff *et al.* find an island density of $\sim 2.7 \times 10^{-5}$. As is evident in Fig. 2, this is an order of magnitude larger than our predicted value. There clearly is a significant disparity between nanoscale observations and predictions from atomic scale properties. This disparity cannot be attributed to the capture numbers used in rate equations (1)–(4). Island densities $n_x$ calculated using the lattice approximation, an overestimate for the capture numbers [1,7], are shown by open squares in Fig. 2; they are close to our previous estimates. When the uniform depletion approximation (an underestimate) is made for the capture numbers, the island densities (open circles in Fig. 2) increase. Nevertheless, there is still an order of magnitude difference from experiments at 400 K, which suggests there may be some as yet unidentified effect which is not included in the rate equations.

Dissociation of clusters influences layer morphology not just by lowering the density of monolayer islands; it also affects the nucleation of a second layer on top of clusters. If a nucleus forms before the first layer is complete, it will cause growth to be three dimensional. Obviously a significant step-edge barrier to interlayer transport will enhance the number of adatoms on a cluster, so that the adatom concentration may exceed the critical value above which a nucleus forms. Second layer nucleation has therefore been extensively discussed in terms of the step-edge barrier $E_S$, but it should be obvious that cluster dissociation must also be considered [20], as this will diminish the likelihood of a second layer forming.

The fraction $f$ of islands of radius $r$ which have a stable nucleus on them is given [20,21] in terms of the rate of nucleation $\Omega(\rho)$ on top of an island with radius $\rho$ as

$$f = 1 - \exp\left[-\int_0^r \frac{\Omega(\rho)}{v(\rho)}\,d\rho\right]; \tag{5}$$

here $v(\rho)$ is the rate at which the cluster radius $\rho$ grows with time,

$$v(\rho) = F/(2\pi\rho n_x n_0)\,. \tag{6}$$

$n_x$ is the island density at saturation, as previously defined, and $n_0$ is the density of surface sites. Two important material parameters enter into the nucleation rate $\Omega(\rho)$. One is of course $E_S$, the additional step-edge barrier, above and beyond that for adatom diffusion, to the transport of atoms over the cluster edges. The second is the critical island size $i^*$, above which clusters do not dissociate. These parameters affect the rate of nucleation through [22]

$$\Omega(\rho) = \frac{\pi\prod_{m=1}^{i^*}\sigma_m}{(i^* + 2)\prod_{m=2}^{i^*}\Gamma_m}\left(\frac{F}{4D_1}\right)^{i^*+1} D_1^{i^*} \times \{(\rho^2 + \sqrt{3}\,a\rho S)^{i^*+2} - (\sqrt{3}\,a\rho S)^{i^*+2}\}, \tag{7}$$

where $S = \exp(E_S/kT)$.

To find the fraction of the islands on which there is a second layer when the equivalent of one monolayer has been deposited, we integrate Eq. (6) up to a radius determined from the saturated island densities, as in Fig. 2, with all cluster diffusion and dissociation considered, but neglecting coalescence. The fraction $f$ found for critical clusters of different sizes is shown for Pt on Pt(111) in Fig. 3. Two competing factors affect second layer nucleation as the temperature is increased. The island density decreases as a function of the temperature as shown in Fig. 2; that results in larger islands before coalescence. The fraction of step-edge sites, which act as sinks for adatoms on an island, therefore decreases, and second layer nucleation is promoted. However, the rate of interlayer transport over the step edges is increased by raising the temperature, which of course decreases the adatoms density and therefore the rate of nucleation. The plot in Fig. 3 demonstrates that

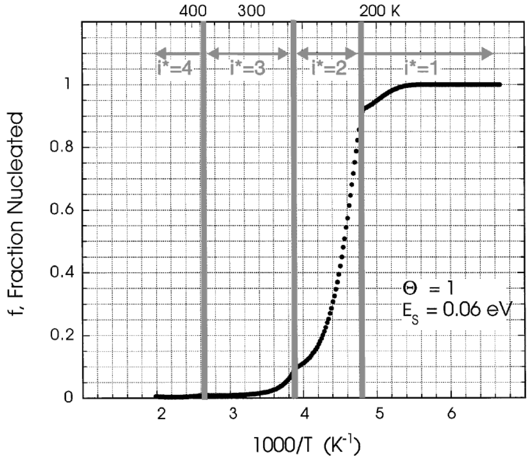

FIG. 3. Temperature dependence of the probability of second layer nucleation $f$. Estimates from Eq. (5) at $\Theta = 1$, with $E_S = 0.06$ eV [11]. Deposition rate $F = 5 \times 10^{-3}$ ML/s, $n_x$ from Fig. 2. Transition temperatures are slightly different than in Fig. 2, as they are affected by the adatom concentration.

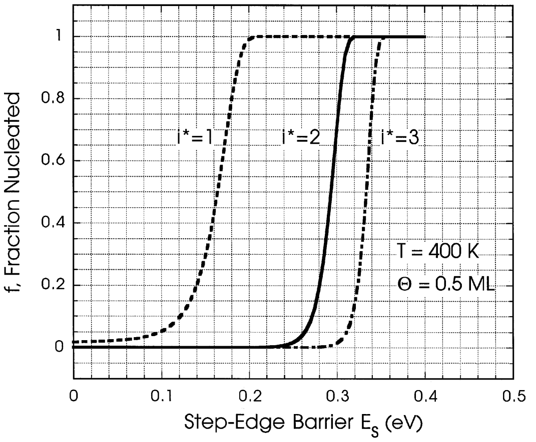

FIG. 4. Effect of additional step-edge barrier $E_S$ on the probability of second layer nucleation $f$. $F = 5 \times 10^{-3}$ ML/s, $\Theta = 0.5$ ML, $T = 400$ K. Saturation island density is taken as $2.7 \times 10^{-5}$ [18].

the latter effect dominates. Of course as the temperature is raised further, dissociation of clusters becomes more important: the critical island size rises, and the likelihood of nucleation is lowered dramatically.

Information about cluster dissociation and stability clearly is crucial to understanding nucleation on top of islands. The observed onset of nucleation has in the past been used to infer information about the magnitude of the step-edge barrier which hems in adatoms on an island, thereby promoting nucleation of a new layer [20,23]. To do this properly, however, requires data about the competitive effect of cluster dissociation, as is evident from Fig. 4. Here, as a function of the step-edge barrier $E_S$, is plotted the likelihood of second-layer nucleation for Pt(111) at 400 K and a saturation island density of $2.7 \times 10^{-5}$, reported by Kalff *et al.*, at a coverage $\Theta = 0.5$. If, for example, one-tenth of the islands are found to have a second layer on them, this would imply a step-edge barrier of $\sim$0.1 eV if the critical island size $i^*$ is 1, that is, if dimers do not dissociate. For a critical island size $i^* = 2$, however, a step-edge barrier $E_S \sim 0.27$ eV is necessary to account for the same observation. Since a critical island size of 3 is appropriate for Pt(111) at 400 K, the step-edge barrier for Pt(111) consistent with the experiments of Kalff *et al.* [18] is roughly 0.3 eV rather than the value of $E_S < 0.1$ eV derived there on the arbitrary assumption that $i^* = 1$. The step edges in these experiments appear to be predominantly of type $B$, made up of {111} facets. For $B$-type edges Feibelman [24] has in fact calculated a barrier of 0.35 eV, in seemingly good agreement with the value we infer from Kalff's experiments [25]. Caution may, however, be in order in view of the discrepancy between predictions and experiments in the submonolayer regime.

It appears that in homoepitaxial growth on Pt(111), both cluster diffusion and dissociation contribute to reducing the island density in the submonolayer regime. However, dissociation of clusters is far more important and is the dominant effect which must be adequately accounted for to achieve a reasonable description of the density of surface clusters. Cluster dissociation also plays an important role in affecting the formation of a second layer on top of clusters. It can significantly lower the rate of nucleation on clusters, promoting layer-by-layer growth, and must be treated on an equal footing with step-edge crossing to achieve a reliable view of second-layer phenomena. These conclusions should hold for growth on fcc(111) planes in general, but it will be interesting to test this proposition.

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*Permanent address: Institute of Industrial Science, University of Tokyo, Tokyo 106-8558, Japan.

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