

## Effect of small-cluster mobility and dissociation on the island density in epitaxial growth

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We suggest that for many systems the epitaxial growth conditions are such that the mobility of small clusters, such as dimers, substantially affects the density of the islands formed by nucleation, while the dissociation of the clusters is less important. We study the effect of small-cluster mobility on the island density formed under epitaxial growth conditions with both rate equations and computer simulations. We find that the scaling derived by Villain, Pimpinelli, Tang, and Wolf from simple rate equations is in agreement with the simulations, if great care is taken to make sure that the system has reached the scaling regime. As an application we suggest a more plausible analysis of some important recent experiments. The scaling equations can be used to extract the activation barriers for monomer and small-cluster diffusion from data on island-density dependence on temperature and deposition rate.

### I. INTRODUCTION

In the early stages of epitaxial deposition, under certain conditions, the island density  $N$  satisfies the scaling relation<sup>1-3</sup>

$$N \sim \theta^{\chi/i} F^{\chi} \exp[\chi\beta(E_1 + e_i/i)]. \quad (1)$$

Here  $\theta$  is the coverage at time  $t$ ,  $F$  is the deposition flux,  $E_1$  is the activation energy for the diffusion of a single atom, and  $\beta = 1/k_B T$  is related to the surface temperature  $T$ . The size of the critical nucleus  $i$  is defined as follows. During the deposition some clusters will grow and others will tend to disappear. If the smallest cluster that will grow has  $n$  atoms, then  $i = n - 1$ . The quantity  $e_i$  is the binding energy of the critical nucleus. This is the energy of the surface having on it a cluster of  $i$  atoms minus the energy of the surface with  $i$  adsorbed atoms which do not interact with each other. The exponent  $\chi$  is equal to  $i/(i+2)$  if the diffusion of single atoms on the surface is isotropic and two dimensional, and it is equal to  $i/(2i+2)$  if the diffusion is one dimensional.<sup>3</sup> This equation is valuable because it can be used, under favorable circumstances, to extract from scanning tunneling microscopy (STM) data the activation energy of single-atom diffusion.<sup>2,4</sup> This quantity is hard to measure by other methods.

Several studies have found<sup>2,4-9</sup> that the *functional form* given by Eq. (1) correctly represents the experimental data. In some cases the fits to the data gave  $\chi = 1/3$ , as predicted by Eq. (1) for  $i = 1$ .

There are, however, cases in which the use of Eq. (1) to interpret the data leads to difficulties. In several systems<sup>5,6,8,9</sup> the exponent  $\chi$  obtained by fitting the data differed from  $1/3$ . This has been interpreted to mean that the critical island size was greater than 1. Recently, Günther *et al.*<sup>8</sup> measured the island density for Au deposited on Au(100), and found that Eq. (1) agreed with the data only if they assumed that the diffusion of the Au atoms was highly anisotropic and the critical nucleus was 3 at low temperature, and 5 at a higher temperature.

We will argue here that these results suggest that the use of Eq. (1) to interpret the data mentioned in the previous paragraph is inappropriate, and we propose a more plausible interpretation. The equation is derived under the assumption that only the mobility of single atoms is important. In recent years it has been shown—by both theory<sup>10-13</sup> and experiments<sup>14-16</sup>—that small clusters on metal surfaces are fairly mobile. The field-ion-microscope experiments of Wang and Ehrlich<sup>14</sup> show that the Ir clusters of sizes 2–12, on the Ir(111) surface, have a measurable mobility. Kellogg and Voter<sup>16</sup> have shown that small Pt clusters move readily on Pt(100). Effective-medium calculations for Pt clusters on Pt(111),<sup>12</sup> and for Fe on Cu(111),<sup>17</sup> and *ab initio* calculations for Al dimers on Al(111),<sup>10</sup> all show high mobility for small clusters. In several cases<sup>10,16</sup> it has been proposed that the mobility of the dimer is higher than that of the monomer. It is therefore reasonable to assume that, unless the temperature is carefully selected to prevent cluster motion, this process will affect island density. In cases when dimer mobility is larger than that of the monomer, dimer motion may dominate island formation. These effects are not taken into account in Eq. (1).

When the exponent  $\chi$ , obtained by fitting the experimental results with Eq. (1), is not  $1/3$ , it is customary to assume that the critical cluster size  $i$  is larger than 1. Since  $\chi$  is either  $i/(i+2)$  or  $i/(2i+2)$ , depending on the dimensionality of the monomer diffusion, it is not difficult to find a value of  $i$  for which  $\chi$  is close to the measured value. However, the assumption that one can have a critical cluster of size greater than 1 at temperatures at which dimers do not move, needs to be reexamined. The existence of a critical nucleus having  $i$  particles means that the clusters having  $i$  or fewer particles will dissociate and only those with  $i+1$  particles or more will grow. This can happen only if the atoms in a subcritical cluster can leave it with a substantial rate. There are reasons to doubt that this is true at temperatures at which cluster motion can be ignored. A simple bond-counting argument indicates that the activation energy for removing an atom from a cluster is higher than the activation energy

for single atom or dimer diffusion. This suggestion is supported by effective-medium calculations for Pt clusters on Pt(111),<sup>12</sup> and by experiments<sup>8</sup> on Pt(111) in which intraisland transport (which is indicative of atomic evaporation from islands) is detectable only at temperatures above 700 K.

To reconcile their STM measurements of island density with Eq. (1), Günther *et al.*<sup>8</sup> assumed that the diffusion of Au on Au(100) is so anisotropic that one can use the one-dimensional equation for the exponent  $\chi$  in Eq. (1). Such *strong* anisotropy is unlikely in this system. The Au(100) surface reconstructs and the structure of the atoms in the top surface layer looks like that of a (111) surface that has been stretched slightly in one direction.<sup>19</sup> The atoms in the reconstructed layer are more densely packed than in the (100)-unreconstructed surface. This suggests that while the diffusion of a single atom on this surface may be anisotropic, it is very unlikely that this anisotropy is so strong that it will lead to a one-dimensional motion. Preliminary effective-medium calculations support this conclusion.

The islands in the STM images are rectangular, and the denuded zones near steps with different orientations have different widths,<sup>8</sup> and one might interpret this to mean that single-atom diffusion is anisotropic. However, simulations have shown that the shape of an island is not dependent on whether the single-atom diffusion on the substrate's surface is anisotropic or not.<sup>20</sup> At the temperatures of interest here the main factors influencing the island shape are the differences in the binding energy and the mobility of atoms around the edge of the island.<sup>21</sup> Small differences in these parameters have been shown to lead to marked differences in shapes<sup>21</sup> on the Pt(111) surface where single-atom diffusion on the terrace is isotropic. Thus the presence of rectangular islands in the STM experiment<sup>8</sup> is likely to indicate differences in the binding energy and the diffusion barrier along island edges.

Recent information on cluster mobility and cluster dissociation suggests an alternative to the model implied by the use of Eq. (1). The nucleation mechanism depends on the temperature window in which the deposition takes place. In the lowest-temperature range, only the monomers move, and the critical nucleus size is 1. In the middle-temperature range monomers and perhaps other small clusters (e.g., dimers, trimers, etc.) move and the critical nucleus size is 1. At higher temperatures small clusters move and also dissociate. At such temperatures one has two growth scenarios. In the first, the critical cluster size is larger than 1 and the small clusters move. In the second, cluster dissociation is so rapid that the small clusters fall apart before being able to participate in the formation of another island; in this case their mobility does not affect the island density and is not a factor in the scaling relation. Island formation in these three temperature windows proceeds through different nucleation mechanisms, and is described by different scaling equations.

Since our knowledge of cluster mobility and dissociation is neither extensive nor precise, one cannot be dogmatic about this proposal. One must regard it as plausible and in need of further experimental confirmation. In

peculiar cases, such as Al/Al(111), the temperature windows are different from the ones proposed here. If the calculations<sup>10</sup> are correct, dimer motion in this system is faster than monomer motion, and it may influence the island density in the lowest-temperature window.

The scaling theory needed for examining the mechanisms proposed above has been already developed.<sup>22,23</sup> It is based on mean-field kinetic equations which are shown to lead—for certain values of the deposition parameters—to scaling relations that can be used to interpret the data. Since the kinetic equations are approximate and the scaling relations derived from them require further approximations, we first performed kinetic Monte Carlo simulations to test their validity. We have found (Sec. III) that they work well within a broad range of conditions. Now having some confidence in the validity of the scaling relations, we use them to examine the data of Günther *et al.*<sup>8</sup> We find that their results can be explained by assuming the following: at lower temperature the monomers and dimers move and the critical size is  $i=1$ . At higher temperature the dimers dissociate sufficiently quickly to prevent dimer mobility from contributing to the island density; this means that only monomer motion needs to be taken into account, and that the critical nucleus size is  $i=2$ . There is no need to assume anisotropic diffusion.

## II. SUMMARY OF THE THEORY

The scaling equation for the case when monomer and dimer motion contributes to island density and the critical nucleus size is  $i=1$  is<sup>22,23</sup>

$$N \sim \theta^{1/5} F^{2/5} \exp[\beta(E_1 + E_2)/5] . \quad (2)$$

Here  $E_1$  and  $E_2$  are the energy barriers to diffusion for monomers and dimers, respectively. The other symbols are the same as in Eq. (1). This equation assumes two-dimensional diffusion and no cluster dissociation; the critical nucleus size is therefore  $i=1$ . The scaling relations for the case when larger clusters move and dissociate are available in the literature.<sup>23</sup>

The dimer motion contributes to the island density only if<sup>23</sup>

$$(k_2/F)N^2 > 1 , \quad (3)$$

where  $k_1$  and  $k_2$  are site-to-site hopping rates for the monomer and the dimer, respectively. This condition is derived as follows. Let  $t_2$  be the average time in which a dimer meets an island, and  $t_1$  be the average time in which the dimer meets a monomer. From the random-walk theory,  $t_2 = 1/(k_2 N)$  and  $t_1 = 1/(k_1 N_1)$ , where  $N_1$  is the density of monomers and  $N$  is the island density. Under stationary conditions, we have  $F = k_1 N_1 N$ , which results in  $t_1 = N/F$ . The diffusion of the dimer affects the island density only if it meets an existing island before it has a chance to meet a monomer (i.e., if  $t_2 < t_1$ ). The condition  $t_2 < t_1$  gives Eq. (3). This relation defines the transition temperature  $T_2$ : at temperatures below  $T_2$  the dimer is not sufficiently mobile to contribute to island density, and the scaling relation (1) should be used to in-

terpret the data; above this temperature the mobility of the dimers becomes important and one should use Eq. (2).

As the temperature is increased the mobility of larger clusters and their dissociation may become important. Scaling laws for these situations have been derived.<sup>2,22,23</sup> Here we review only the case when dimer dissociation becomes important, since we found that this mechanism seems to fit the data of Günther *et al.*<sup>8</sup> Dimer motion and dissociation compete with each other. For example, if the dissociation is very rapid the dimer will not move very far before falling apart, and therefore has very little chance of meeting an atom and forming a larger cluster. Therefore, dimer motion can be ignored in the kinetic equations for island density, leading to the scaling relation given by Eq. (1) with  $i=2$ . The value  $i=2$  is used because the dimer falls apart and the trimer does not. In the opposite limit the dissociation rate is so small compared to the diffusion rate that we can assume that the dimer never falls apart: it always meets a monomer or an island before dissociating. In this case cluster mobility is important and the effect of dissociation is negligible.

One can find a quantitative criterion to distinguish between these two cases. The dissociation of small clusters contributes to the island density if and only if

$$k_1\tau_2N_1 < 1 \quad (4)$$

and

$$k_2\tau_2N < 1. \quad (5)$$

Here  $\tau_2$  is the inverse of the dissociation rate and it is given by  $1/\tau_2 = \nu_2 \exp(-\beta\epsilon_2)$ , where  $\epsilon_2$  is the activation barrier preventing dissociation. Equation (4) is the condition that a dimer dissociates before it meets and binds to a monomer. Equation (5) is the condition that the cluster dissociates before it meets an island and sticks to it.

Since small clusters on metal surfaces are known to be highly mobile, we expect that Eq. (3) is satisfied even at relatively low temperatures. Since the energy barriers preventing the dissociation of an atom from a cluster are generally much larger than barriers preventing cluster diffusion, one expects conditions (4) and (5) to be satisfied at higher temperatures. For example, if  $E_1=0.4$  eV,  $E_2=0.5$  eV,  $\epsilon_2=0.72$  eV, and  $F=0.1$  ML/s, one can estimate from Eqs. (3), (4), and (5) that dimer diffusion is important at  $T > 280$  K and dimer dissociation is important at  $T > 380$  K.

The plots of the island density versus  $\theta$ ,  $F$ , and  $1/T$  do not satisfy the scaling relation at all times during deposition, but only when the system reaches the so-called scaling regime. As we shall see from simulations it is possible to find a parameter range where the plots of  $\ln(N)$  versus  $\ln(\theta)$  and that of  $\ln(N)$  versus  $\ln(F)$  are linear, but the scaling regime has not yet been reached and the slopes of the graphs are different from those predicted by the scaling formulas. Using the scaling equations to analyze the data for this parameter range leads to erroneous conclusions: one predicts the wrong growth mechanism and erroneous activation and binding energies. One must make sure that the data have been taken in the scaling regime by applying a number of consistency checks which are discussed shortly.

### III. KINETIC MONTE CARLO SIMULATIONS

We use kinetic Monte Carlo (KMC) simulations of island growth to test the scaling relations for the case when the dimers move and dissociate. The results of the simulations are treated as experimental data from which we extract—by using the scaling relations—energy barriers to monomer and dimer diffusion. We find that, if adequate care is taken to make sure that the data have been taken in the scaling regime, the scaling relations fit the data well and provide activation energies close to the ones used as input in the simulations.

All KMC point-island simulations reported here have been done on a  $500 \times 500$  square lattice with periodic boundary conditions. Particles are randomly deposited on the lattice with a flux  $F$  and hop from site to site with the rate constant  $10^{13} \exp[-E_1/kT]$  s<sup>-1</sup>. Two monomers meeting each other form a dimer which occupies, for simplicity, a single lattice site. The dimer hops from site to site with a rate constant of  $10^{13} \exp[-E_2/kT]$  s<sup>-1</sup>. Clusters having more than two atoms do not move and are called, in what follows, islands. If two dimers or a dimer and a monomer meet, they form an island which is also assumed to occupy one lattice site. Finally, monomers and dimers stick to an island when they reach a site adjacent to it. The dimer is allowed to dissociate with the rate constant  $10^{13} \exp[-\beta\epsilon_2]$  s<sup>-1</sup>. The dissociation creates two monomers which will random walk on the lattice just like the atoms deposited by the incident beam; they have a chance to recombine or to walk away from each other. The assumption that the dimers and islands occupy one lattice site is a good approximation, since we are interested in the early stages of deposition when the islands are small. We have run a few simulations in which the islands had a finite size, and have found that the scaling relations were the same as those for point-sized islands. All simulations reported below used  $E_1=0.4$  eV,  $E_2=0.5$  eV, and  $\epsilon_2=0.72$  eV. These are reasonable values for metal-on-metal epitaxy.

According to expressions (1) and (2) we expect that, in an experiment in which the flux  $F$  and the temperature  $T$  are held constant and the coverage  $\theta$  is varied, the island density changes as  $N \sim \theta^\alpha$ , where  $\alpha$  is a numerical exponent. The numerical value of  $\alpha$  depends on the growth mechanism: at lower temperature we expect the dimer motion to slow down to the point where it does not contribute to island density. In this case only the monomer motion is important, Eq. (1) should be valid, and the exponent should be  $\frac{1}{3}$ . At higher temperatures the dimer motion is important, Eq. (2) should be valid, and  $\alpha$  should be  $\frac{1}{5}$ . There is no scaling relation at the intermediate temperature since we have  $N^3[1+(3k_2/(5F))N^2] \sim \theta$ , and Eqs. (1) or (2) follow when one or the other term in the left-hand side is dominant.

The results of the simulations for the dependence of  $N$  on  $\theta$ , at constants  $F$  and  $T$ , are shown in Fig. 1. For low temperatures (200–240 K) we have used a flux of  $10^{-4}$  ML/s. In the coverage range between 2% and 20% the curves are linear, as predicted by the scaling relations. At 200 K the exponent is 0.3, which is close to  $\frac{1}{3}$ . The discrepancy is due to statistical errors in the simulation

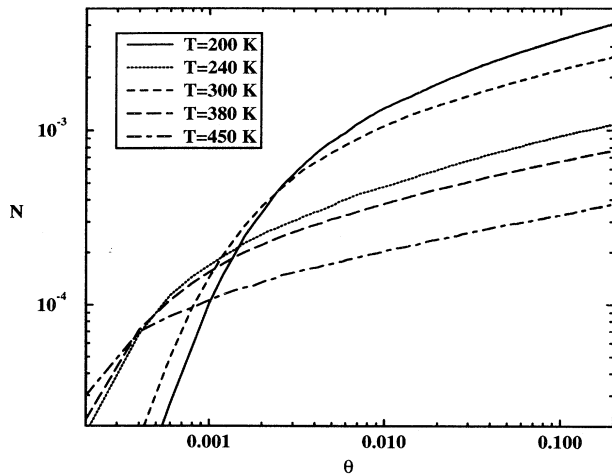


FIG. 1. The dependence of the island density on coverage for various temperatures and a deposition rate of  $F=0.1$  ML/s. Monomers and dimers can move, but dimer breaking has not been allowed. The parameters used in the simulation are given in the text.

and the fact that, with the so-called logarithmic correction,<sup>3,24</sup> the exponent predicted by scaling will be slightly smaller than  $1/3$ . For simulations at higher temperature we had to use a larger flux because of computer power constraints. The deposition flux acts as a clock in the simulation. At high temperature the atoms on the surface execute a very large number of moves in the time between successive arrivals of atoms on the surface. For this reason we do not have enough computer power to run the simulation until a sufficiently large number of atoms is deposited on the surface. Increasing the flux to  $0.1$  ML/s helps us avoid this bottleneck. We find that at  $380$  and  $450$  K the exponents are  $0.21$  and  $0.22$ , respectively. This is close to the value of  $1/5$ , expected from Eq. (2).

It is interesting to note that the curve obtained at  $220$  K is also linear, even though this is the intermediate temperature range where the scaling relations do not hold. The exponent is  $0.27$  and this is neither  $1/3$  nor  $1/5$ . Furthermore, we have also performed simulations at  $220$  and  $240$  K with a constant flux of  $0.1$  ML's. In this case the plot of  $\ln(N)$  versus  $\ln(\theta)$  was linear when  $10\% < \theta < 20\%$ , and the exponents were  $0.41$  for  $220$  K and  $0.35$  for  $240$  K. These exponents do not correspond to the predictions made by the scaling relations. This happens because the system has not yet reached the scaling range, i.e., the growth conditions when the scaling relations are valid. The use of the dependence of island density  $N$  on the coverage  $\theta$  to interpret the experimental results is further complicated by the fact that coverage scaling does not take place if the mean island size is comparable to the mean island-to-island distance.<sup>3</sup> Fortunately neither flux scaling nor the temperature dependence of island densities<sup>3</sup> is affected by the fact that the islands have a size.

According to Eq. (3) the crossover from the case when only monomer diffusion is important to the case when the

dimer motion must be taken into account occurs when  $k_2 N^2/F$  is of order 1. We have estimated  $k_2 N^2/F$  at fixed surface coverage  $\theta=20\%$  for several temperatures, and found that this condition is satisfied at  $270$  K. Since  $N$  varies slowly with  $\theta$  this crossover temperature should be insensitive to the coverage at which we determined it. This estimate of the transition temperature is in rough agreement with the observation that the exponent changes from  $0.30$  to  $0.21$  as we go from  $200$  to  $280$  K.

Scaling relations (1) and (2) also predict that in experiments in which the flux is varied while the coverage  $\theta$  and the temperature are held constant, we should observe  $N \sim F^\gamma$ . The exponent  $\gamma$  is  $1/3$  when only the monomer migrates and the critical nucleus is of size 1, and  $2/5$  if the dimer motion is important. It is possible to change the flux and keep the coverage  $\theta$  constant since the latter is equal to  $Ft$ . Changing  $F$  and keeping  $\theta$  constant means that for each value of  $F$  we will analyze the island density at the time  $t=\theta/F$ , where  $\theta$  has the desired fixed value. The dependence of the island density  $N$  on the flux  $F$  obtained in our simulations is shown in Fig. 2. We kept the temperature constant at  $T=360$  K, and the final coverage at  $20\%$  and varied  $F$  between  $1$  and  $1/100$  MS/s. We have found that the island density is proportional to  $F^\gamma$ , which  $\gamma=0.35$ . This is smaller than the value  $2/5$  predicted by the scaling equation (2). When we kept  $T=230$  K, and varied  $F$  between  $0.09$  and  $9 \times 10^{-5}$  ML/s, we found  $\gamma=0.30$ , which is also about  $10\%$  below the theoretical value of  $1/3$ . These discrepancies are diminished when the logarithmic correction<sup>3,24</sup> to the single-particle lifetime is made in the rate equation. This correction lowers the predicted exponent and improves the agreement with the simulation. These corrections are necessary because in our simulations we have used small diffusion constants

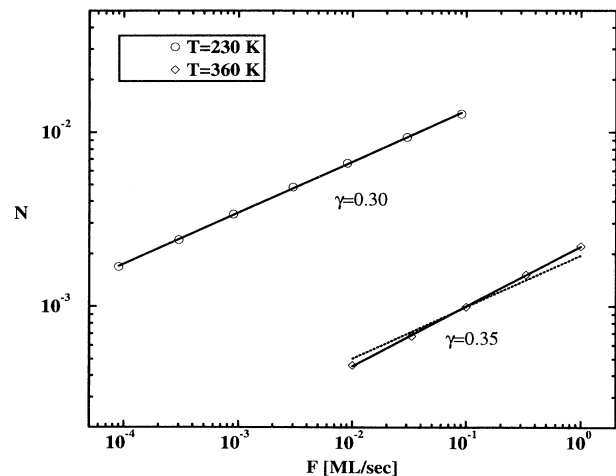


FIG. 2. Island density  $N$  as a function of deposition rate  $F$  at a fixed coverage of  $20\%$  and for two different temperatures. Solid lines are the linear fits to the simulation data. The dotted line, which has the same slope as the upper solid line, was added as a guide to the eyes to show that the difference in slopes at two different temperatures is larger than the statistical errors (which are smaller than the sizes of the symbols).

and high fluxes to decrease the computer time needed for completing the runs. The scaling relations are known to be less accurate under these conditions. The conditions encountered in metal-on-metal epitaxy are in a regime of parameters where the scaling relations are more accurate.

The rate equations also suggest that the relation  $k_1 N_1 N / F = 1$  holds at all deposition times, except for the earliest stages. If the logarithmic corrections<sup>3,24</sup> are included this becomes  $\pi k_1 N_1 N / [F \ln(1/\pi N)] = 1$ . Using the data from our simulations we have found that the latter relation holds for  $\theta > 5\%$  within the statistical error.

Finally, scaling relations (1) and (2) predict that the island density changes as  $N \sim \exp[-\delta/T]$  when the temperature is varied and the coverage  $\theta$  and flux  $F$  are held constant. The scaling relations predict that the exponent  $\delta$  is equal to  $E_1/3k_B$  at low temperatures—for which only the monomer moves—and equal to  $(E_1 + E_2)/5k_B$  at temperatures for which dimer motion becomes important. No simple scaling relation is expected at temperatures in between. In Fig. 3 we show an Arrhenius plot of the simulation results. Clearly there is a crossover from monomer-dominated scaling into the mobile-dimer scaling regime at a transition temperature of about 270 K. This is consistent with the estimate based on Eq. (3) that was made earlier in this section. The exponent given by the higher-temperature straight line in the Arrhenius plot is  $0.176(E_1 + E_2)/k_B$ , which is close to the value expected from the scaling equation (2). At the lower temperatures the dimer motion becomes irrelevant, and the exponent is close to  $E_1/3k_B$ , as expected from Eq. (1).

We have also performed simulations in which the dimer was allowed to dissociate with an activation energy

of 0.72 eV. At high temperatures the dissociation becomes so efficient that, on average, the dimer breaks up before having a chance of meeting monomers or islands. Thus the system crosses over from a regime for which monomers and dimers move but there is no dissociation (i.e., the critical size is  $i=1$ ) to one for which only monomer motion is important and the critical size is  $i=2$ . At this higher temperature the island density is expected to satisfy the scaling relation (1). We find that in the simulations the Arrhenius plot of the island density—at constant  $\theta$  and  $N$ —changes slope, and the exponent given by the highest-temperature data satisfies the prediction of Eq. (1) with  $i=2$ , as expected.

We have also compared the simulation results with those obtained by solving the rate equations numerically. The dependence of island density on coverage or temperature, obtained by solving the kinetic equations numerically, is similar to that obtained from the simulations, but the quantitative agreement is not good. For some runs the largest discrepancy is 20%, but for others it can be as high as a factor of 2. There is no contradiction in concluding that the rate equations do not work well but that the scaling relations—which are derived from them—do. Testing the functional form and the exponent predicted by the scaling relations, in a narrow range of parameters where scaling holds, is a less stringent test of the rate equations than testing whether they give the correct value of  $N$  over the whole parameter range.

#### IV. DISCUSSION OF THE EXPERIMENTAL DATA

The simulations clearly show that when using the scaling relations to interpret experiments, one must determine whether the data have been taken in the scaling range of the parameters. A linear relationship, of the kind predicted by the scaling relations, is not sufficient. Ideally, one should test the scaling for both  $\theta$  and  $F$  and make sure that the exponents obtained from such plots are consistent with each other. Moreover, plots over a large temperature range can signal the transition from one growth mechanism to another and therefore from one scaling relationship to another. Unfortunately, performing such tests requires a large set of data. However, if these data are not available the physical conclusions and the numbers extracted through the use of the scaling relations are uncertain. In addition, as we mentioned earlier, an experimental test of scaling for  $\theta$  is quite difficult due to finite-size effects.<sup>3</sup>

In spite of this caveat it is worthwhile to examine some recent experiments. Günther *et al.*<sup>8</sup> studied Au epitaxy on a reconstructed Au(100) surface. They found that, at 315 K, the island density scales with the deposition flux with an exponent of  $0.37 (\pm 0.03)$ . In addition, the island density satisfies the equation  $\ln N \sim -0.17 \text{ eV}/k_B T$  for  $315 \text{ K} < T < 380 \text{ K}$  and  $\ln N \sim -0.5 \text{ eV}/k_B T$  for  $400 \text{ K} < T < 435 \text{ K}$ . To interpret the data, Günther *et al.*<sup>8</sup> assumed initially that the island growth takes place by isotropic monomer diffusion and is not affected by dimer diffusion. This means that Eq. (1) should be valid. The

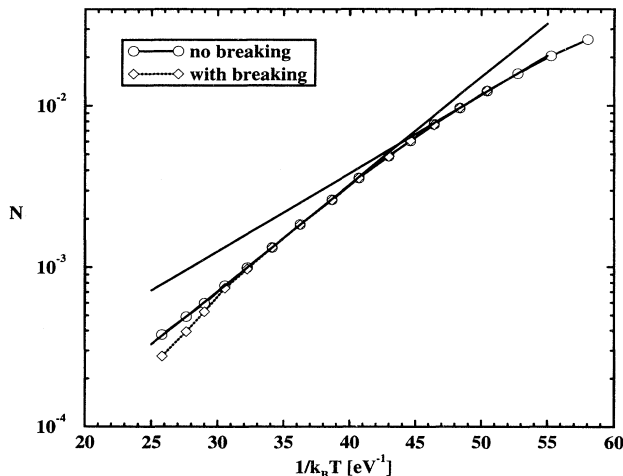


FIG. 3. Arrhenius plot of the dependence of the island density on temperature. The graph shows a crossover from monomer diffusion to monomer and dimer diffusion. The transition temperature is 270 K. The dashed curve shows the results of simulations which allowed dimer breakup. Dimer breakup becomes important at higher temperature, and the curve for this case has a different slope. The crossover to this slope occurs at about 380 K.

exponent obtained by using that equation to fit the flux dependence of  $N$  at constant  $T$  and  $\theta$  suggested a critical size  $i=1$  at 315 K; the temperature dependence fitted to Eq. (1) with  $i=1$  leads to a barrier to monomer diffusion of  $E_1=0.5$  eV. By using these parameters Günther *et al.*<sup>8</sup> simulated the growth and found an island density that is 7–10 times larger than that given by the STM data. They concluded that this contradiction rules out the scaling relations used for interpreting the data, and the mechanism implied by them. Next they assumed that the monomer diffusion is so anisotropic that one could use the relation for one-dimensional diffusion for the exponents in the scaling Eq. (1). This assumption and a critical island size  $i=3$  lead to a satisfactory fit of the data at  $T=315$  K. This also provided the following parameter values:  $E_1=0.2$  eV and a trimer binding energy  $\epsilon_3=0.6$  eV. They have also suggested that at temperatures between 400 and 435 K the same model (i.e., anisotropic monomer motion) is valid, but the critical island size  $i=5$ . From what we know at present about activation and binding energies these numbers are reasonable; furthermore, their analysis has been thorough, and great care has been taken to achieve some self-consistency in the interpretation through the use of simulations.

Nevertheless, as we mentioned in Sec. I, there are reasons to believe that the activation energy for dimer motion is smaller than that for dimer dissociation. Therefore a more plausible mechanism for the measurements made at 315 K is to allow monomers and dimers to move and to assume that  $i=1$ . This assumption is consistent with the experimental<sup>8</sup> flux scaling exponent 0.37, which is close to the value  $\frac{2}{5}$  expected for the mechanism proposed by us. From the temperature dependence reported in Ref. 8 we find, by using Eq. (2), that  $E_1+E_2=0.8$  eV. The mechanism proposed by us also implies that as the temperature is lowered, one has a crossover to a mechanism in which only monomer motion matters and the critical size is 1. If low-temperature data were available we could have used it to determine  $E_1$  from the temperature scaling (at constant flux and coverage). Lacking information about  $E_1$  we have assumed that  $E_1=0.35$  eV and  $E_2=0.45$  eV, and have used these numbers in a kinetic Monte Carlo simulation of the island growth. This gave an island density that agrees well with the experiment. The simulation is not very sensitive to the value chosen for  $E_1$ . A change from  $E_1=0.35$  eV and  $E_2=0.45$  eV to  $E_1=0.4$  eV and  $E_2=0.4$  eV changes the island density by 3%.

The high-temperature data can be explained by assuming that dimer dissociation becomes so efficient that it prevents dimer migration from contributing to island density. In this case the monomer is the only moving species and the critical size is  $i=2$ . This will predict a  $\theta$  exponent of  $\frac{1}{4}$  and an  $F$  exponent of  $\frac{1}{2}$ . Unfortunately, the data needed for testing this are not available. Another possible mechanism is that at the higher temperatures the trimer starts moving.

Our proposal is in agreement with all the data available in Ref. 8, is consistent with our knowledge of the order of the energy barriers in metal-on-metal systems, and has

the advantage that it does not invoke strong anisotropy for monomer diffusion. More extensive data, on which flux scaling and possible coverage scaling can be tested and the transition from monomer motion to dimer motion and then to dimer breaking (or trimer motion) can be seen, will allow an unambiguous determination of the growth mechanism for this system.

Another example that we want to mention briefly is Pt/Pt(111).<sup>25</sup> The island density provided by the STM data was used to extract the activation energy for monomer diffusion, under the assumption that the dimer motion is unimportant. The activation energy for monomer diffusion provided by this analysis is 0.25 eV, which is very close to a recent field-ion-microscope measurement,<sup>26</sup> but disagrees with an earlier one.<sup>27</sup> Is the neglect of dimer motion justified? The STM data give an island density of  $N=8.6 \times 10^{-4}$  at  $T=205$  K, for a deposition rate  $F=3.3 \times 10^{-3}$  ML/s. Using these data to evaluate the criterion given by Eq. (3), we find that dimer diffusion must be included in the island-density analysis at  $T=205$  K as long as  $E_2 < 0.38$  eV (we have assumed a preexponential of  $10^{13}$  to estimate the diffusion coefficient of the dimer). There is some agreement that the barrier of dimer diffusion on metal surfaces is not much larger than that of monomer diffusion.<sup>10,12,16</sup> Moreover, at a higher temperature the barrier required to make the dimer motion important is lower. It is thus likely that the island-density analysis<sup>28</sup> of the Pt/Pt(111) system will also have to include dimer motion.

## V. SUMMARY

We have proposed that, given the theoretical and experimental information regarding dimer mobility and dissociation, it is reasonable to assume that dimer motion plays a role in establishing the island density during epitaxial deposition of metal atoms on metal surfaces. This implies that the scaling equations proposed by Velfe, Stenzel, and Krohn<sup>22</sup> and by Villain *et al.*<sup>23</sup> are more appropriate for data analysis than the equations used so far. We have tested these scaling equations by kinetic Monte Carlo simulations and found them to be satisfactory for a semiquantitative analysis of data. One difficulty is created by the propensity of the data to give straight-line plots under growth conditions when the scaling equations are not applicable. The scaling exponents extracted from such plots are meaningless and, if taken seriously, would suggest an erroneous growth mechanism. It is, however, possible to avoid this situation by testing that both coverage scaling and flux scaling hold and by finding whether the coverage and flux exponents are consistent with each other. Moreover, one should analyze low- and high-temperature data to detect the crossover from temperatures when only monomer motion is important to temperatures when dimer motion matters. Showing that all these data are consistent with the proposed scaling relation will increase the confidence in the analysis. It will also provide a good estimate of the activation barrier for monomer and dimer diffusion. The paucity of reliable data for these quantities makes extensive data taking and analysis worthwhile.

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