Island Shape-Induced Transition from 2D to 3D Growth for Pt/Pt(111)

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We present a kinetic Monte Carlo simulation of the growth of Pt on Pt(111) capable of describing the experimentally observed temperature dependence of the island shapes and the growth mode. We show that the transition from a 2D growth mode at low temperatures to a 3D mode at higher temperatures is closely related to the disappearance of kink sites and the appearance of the triangular islands observed in the 3D growth regime.

The nucleation and growth of metal overlayers on metal surfaces provide a significant challenge to our understanding of surfaces. It is the combination of many different surface processes that determine the island shape, the density of islands, and the growth mode, that is, whether the growth proceeds in a layer-by-layer (2D) mode or a rough three-dimensional (3D) overlayer is formed. If eventually we become able to control the shapes of the islands on the surface and the growth mode, we will be in a completely new position to "design" surfaces with particular mechanical, electrical, magnetic, or chemical properties.

Even the simplest homoepitaxial systems are still not understood. For Pt deposited on Pt(111), for instance, it is observed that as the temperature is lowered, the growth mode changes first from 2D to 3D, but then back to 2D at even lower temperatures [1–3]. The first transition is expected. It is well established that the diffusion barrier down from an island is larger than the barrier for diffusion on the flat surface [4–7]. Below some temperature this process freezes out. The atoms landing on top of an already existing island cannot diffuse down and attach at the edge, but instead nucleate new islands on top of the old one. The reentrant 2D growth at even lower temperatures is much harder to understand. What is it that makes the diffusion down from islands possible again at temperatures as low as 100–200 K?

There has been a large number of suggestions for mechanisms of the reentrant growth in the literature. It has been suggested that since the islands are smaller and more irregular at low temperatures, either the size [1] or the availability of kink sites [1,3] affect the barrier for descent. Support for the size dependence has been provided by Li and DePristo [5] based on approximate total energy calculations within the corrected effective medium theory, while calculations of Villarba and Jonsson [8] using the embedded atom method have pointed out that very special exchange processes next to kinks can have a much lower barrier than any other down-diffusion processes. Other ideas in the field include the concept of "transient mobility" [9] and "downward funneling" [10]. While some of these ideas may be important, it remains to directly evaluate their importance for the growth process. A very elegant analysis by

Tersoff, van der Gon, and Tromp have shown how the concept of a critical island size may be useful in a discussion of 2D vs 3D growth [11]. In a full kinetic Monte Carlo simulation, Smilauer, Wilby, and Vvedensky [12] are able to obtain the reentrant growth transition; however, the barriers used are not relevant for Pt/Pt(111).

In the present Letter we suggest that the low temperature transition between 2D and 3D growth is driven by the change in both size *and* shape of the islands with temperature. We base our conclusions on a set of kinetic Monte Carlo simulations of the growth of Pt on Pt(111) as a function of temperature. We show that with a realistic set of parameters consistent with a number of independent experimental observations and with detailed calculations of diffusion processes using the effective medium theory [13], we can reproduce the observed reentrant behavior. We show that while the low temperature 2D growth is related to the low barrier diffusion processes at kinks which are abundant on the rough islands at this temperature, at higher temperatures the 3D behavior is closely connected to the occurrence of triangular islands. Some kinks are still present at the edges of these islands, but the fast diffusion process down from islands is solely found at kinks on the step orientations that disappear when the triangular islands form.

The kinetic Monte Carlo model we use is similar to the one proposed by Voter [14]. The simulations are done on an fcc (111) lattice [15]. In agreement with molecular dynamics simulations [5,6], atoms arriving from the gas phase stick when they are supported by three atoms in the lower layer (i.e., we neglect overhangs, and funneling is to some extent included).

The input into the simulations is a set of activation barriers and prefactors for the many possible diffusion processes. In principle the number of different barriers is very large, and their exact values are unknown. Only approximate total energy methods can at present give results for all the processes of interest here. We have used the effective medium theory (EMT) to give us an idea about the important processes in analogy with the analysis of Liu *et al.* [16]. This way we can limit the number of distinct processes in the model by making a classification depending on the local environment. The EMT barriers

are not expected to be sufficiently accurate to describe the growth process. However, if we assume the relative ordering of the barriers to be reasonably correct, we can construct a growth model by scaling the EMT barriers to get a good description of the experiment.

Figure 1 summarizes the results for a number of different diffusion processes over an island, down from an island, along the two different A and B steps, and away from an island. A large number of the features seen in Fig. 1 are in qualitative agreement with experimental observations, in particular from field ion microscopy (FIM) [4,17] and with the detailed local density functional calculations for Al/Al(111) [7].

From calculations for a large number of different diffusion processes, we have found that we can systematize our calculated barriers for in-layer processes by noting that the barrier depends on the number of in-layer neighbors in the initial state, and on whether or not the process is a dissociation away from an island.

It has been shown by Liu et al. [18] that to explain the island shapes at higher temperatures it is important to distinguish between the A and B steps. In the temperature range of interest here, where triangular islands having A steps are observed, it is sufficient to include the asymmetry at corners of A and B steps (position B in Fig. 1).

Villarba and Jonsson [8] have pointed out the importance of kink sites for diffusion down from islands. As illustrated in Fig. 2, we also find that sites next to kinks have the lowest barrier for down diffusion through an exchange process. But we find that a low barrier process only exists on the B steps. On the A steps the atom that moves out from the step does not have an easy path between two atoms underneath, but has to move over an
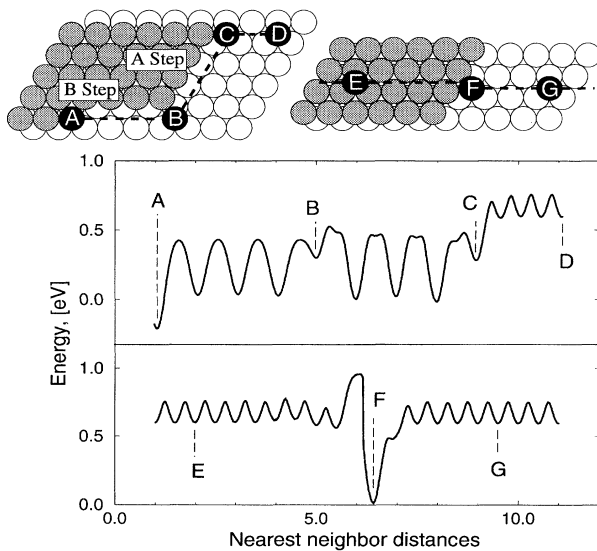

FIG. 1. Examples of effective medium calculations. An atom is dragged along the indicated path, and the energy is minimized with respect to all other degrees of freedom. Only part of the unit cell used in the calculations is shown.
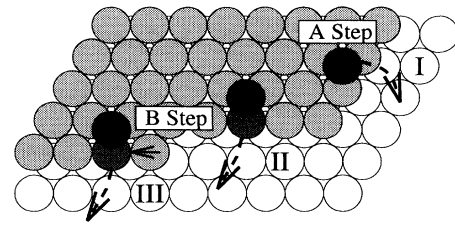
FIG. 2. The three interlayer processes included in Table I. In the transition state of process III, the kink atom is shifted to the left, lowering the energy barrier [8].

on-top site (cf. Fig. 2). The calculated barriers for the intralayer and interlayer diffusion processes are summarized in Table I.

As expected, if we use the EMT barriers directly in a kinetic Monte Carlo simulation of the initial stages of growth, we get a poor agreement with the experiment. In such a simulation too few islands are nucleated. Also these islands take a much too regular shape. However, choosing a prefactor of 10^{11} s^{-1}, and scaling all barriers for the intralayer processes up by a factor of 1.6 [19], we obtain a growth model qualitatively and quantitatively in agreement with the experimentally observed island densities and shapes [2,3]. Also, the resulting model value for the terrace diffusion (0.26 eV) agrees very well with a direct measurement of the diffusion rate at 100 K by Kellogg and Feibelman using the FIM [20]. They obtain 0.25 $\pm$ 0.02 eV assuming a prefactor of 10^{12} s^{-1}. The fact that the EMT barriers appear to be approximately 30% too low is a very reasonable accuracy for the approximate total energy method. It should be compared to the fact that a full local density functional calculation of the barrier for the normal diffusion process gave a barrier of 0.38 eV [20].

When continuing the growth simulation with the deposition of several monolayers, we also find that the EMT barriers for the interlayer processes are too low to obtain 3D behavior at any temperature above 250 K whether or not the kink process is included. In the model presented in Table I, exhibiting 3D growth above 350 K and reentrant 2D at lower temperatures, we have increased the barrier for down diffusion at straight steps by a factor of 1.6 as for the intralayer processes and the barrier for the kink process by a factor 1.5, and chosen the same prefactor for all processes.

It should be stressed that we have tried to choose a common scaling for the barriers for reasons of simplicity, and not because we believe in the existence of an exact scaling between the EMT and the true barriers. Nor is our result critically dependent on the exact value of the barriers in the model. The important point is to obtain reasonable island densities and shapes. Only one barrier is crucial, and this is the barrier for down diffusion at kink sites. The rate of this particular process has a very strong influence on the growth mode around the transition temperature, and we had to choose a slightly different scaling factor for this barrier.

TABLE I. EMT energy barriers in eV and the adjusted values used in the model simulation. N_i (N_f) is the number of in-layer nearest neighbors in the initial (final) state. For given N_i and N_f the EMT calculations are performed for a variety of local environments. The corresponding energy interval of the barriers justifies the classification. The interlayer processes are illustrated in Fig. 2.

Process type	N_i	N_f	EMT	Model
In-layer processes				
Diffusion on terrace	0	0	0.16 ⎱	0.26
Diffusion to step	0	≥ 1	0.12−0.15 ⎰	
Diffusion from top of edge toward island	0	0	0.20	0.32
Diffusion along A step	1	≥ 1	0.23−0.25	0.37
Diffusion along B step	1	≥ 1	0.18−0.20	0.29
Diffusion along step	2	≥ 1	0.4 −0.45	0.64
Diffusion along step	3	≥ 1	0.63−0.65	1.01
Diffusion along step	≥ 4	≥ 1	≥ 0.83	∞
Dissociation from step	1	0	0.50−0.60	0.80
Dissociation from step	2	0	0.71−0.74	∞
Dissociation from step	≥ 3	0	≥ 0.96	∞
Interlayer processes				
Overedge at A step, I			0.41 ⎱	0.59
Exchange at B step, II			0.37 ⎰	
Exchange next to kink at B step, III			0.26	0.39

We then turn to the simulation of the growth process. In the upper part of Fig. 3 we show the calculated island structure after deposition of 0.3 monolayer of Pt on Pt(111) at two different temperatures. Both the density and the shapes are very close to the scanning tunneling microscopy observations of Bott, Michely, and Comsa [2], confirming the validity of the model. To characterize the nature of the growth process we monitor the density of steps as a function of the growth time. For a 2D growth pattern we expect the step density to oscillate, while it should increase monotonically for 3D growth. The step density is closely related to the He scattering intensity which is used experimentally to characterize the growth mode [1]. Figure 4 shows the step density at 255, 270, and 370 K. At 370 K the growth mode is clearly 3D, while it is much more 2D-like at the lower temperatures. In agreement with experimental findings the 2D character increases with temperature up to the transition temperature. In Fig. 3 we also include a snapshot of the surface after 4 monolayers have been deposited. At 370 K six layers are exposed, and the 3D nature of the growth is evident. At 255 K, the growth is much more layer by layer like, but it is not a perfect 2D growth. Three layers are open at a time. The nonperfect nature of the low temperature 2D growth is also reflected in the fact that the oscillations in the step density are seen to decay.

The simulation gives us some insight into the important factors determining whether 2D or 3D growth is observed. In our model the low temperature 2D growth is a direct result of the very low barrier for descent at kinks. If this process is not included, we have found no set of barriers and prefactors consistent with the other experimental observations that are able to give the reentrant 2D growth mode.

As the temperature is increased the Pt islands become larger, and the step density is decreased. The diffusion along the steps speeds up and decreases the kink density. In our simulations another thing happens, too, as the temperature is increased. The asymmetry of the diffusion around corners of islands and the predominant interlayer diffusion at the B steps give rise to a change of the island shape. The islands do not become (quasi)hexagonal but rather triangular, because more atoms go to the B step than to the A step (cf. Fig. 1). The B steps essentially disappear, and since it is only the B steps that have the low barrier
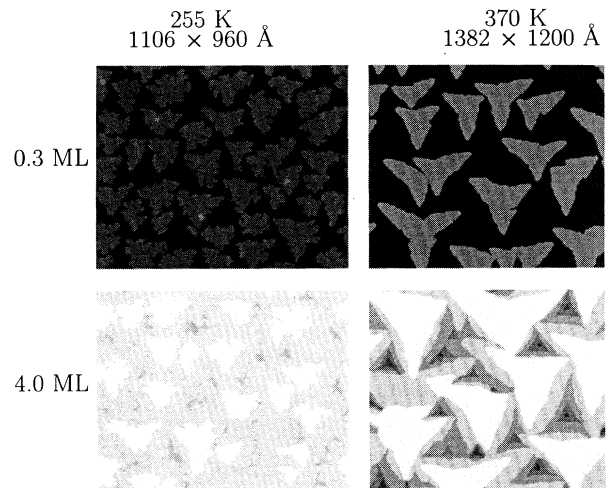

FIG. 3. Top view of the obtained surfaces after the deposition of 0.3 and 4.0 ML at a rate of 0.0033 ML/s, and at a temperature below and above the low temperature growth mode transition. The grey scale indicates the height above the surface.
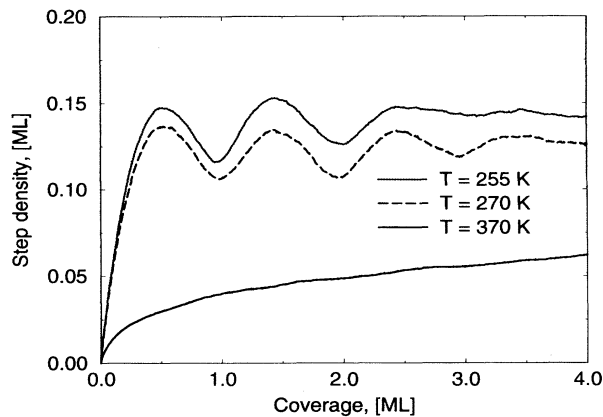
FIG. 4.   The step density as a function of coverage at three temperatures. The deposition rate is 0.0033 ML/s.

kink sites, the diffusion down from the islands is reduced further.

If we do not include any asymmetry between the A and B steps, the islands grow quasihexagonal, and even the relatively few available kinks on these compact islands make the 3D growth hard to obtain. We can only get a low temperature 2D and high temperature 3D growth if we *reduce* the calculated barrier at the kink site to 0.24 eV *and* choose an extremely low prefactor for this process of 10^8 s^{-1}. Given that the EMT consistently underestimates diffusion barriers, this seems very unlikely. When we include the asymmetry we can choose the more reasonable parameters, but the most direct justification of the included difference between kinks at A and B steps comes from observing the influence of this on the islands' shape at 0.3 monolayer (ML). All the interlayer transport occurs at kinks at B steps, since the other available processes are frozen out. In the 3D regime it means that it occurs at the corners of the triangular islands. The effect at 0.3 ML is that the corners grow faster than the edges, yielding concave curved triangles and the "fjords" in the triangles that are very consistent with the island shapes observed with scanning tunneling microscopy. Also note the experimental observation that the temperature range of the intermediate 3D growth coincides exactly with the temperature range where the islands are compact and triangular having A steps.

In conclusion, we have constructed a model including the important diffusion processes for Pt on clean and island covered Pt(111) surfaces. Using the kinetic Monte Carlo method the model can describe in great detail the observed island shapes in the temperature range 200–370 K as well as the transition between 2D and 3D growth around 340 K. The simulations point unambiguously to the importance of kink sites for the diffusion of adatoms down from an island as proposed previously [3]. As a new effect we show that the transition in the growth mode is related to a transition in *shape* of the islands from irregular at low temperatures to triangular at the higher temperatures.

The present work underlines the fact that even a qualitative understanding of the growth modes requires a detailed understanding of the underlying diffusion processes. The strong dependence of the barriers for diffusion on the local geometry gives rise to strong asymmetries in the diffusion rates which ultimately determine the growth mode.

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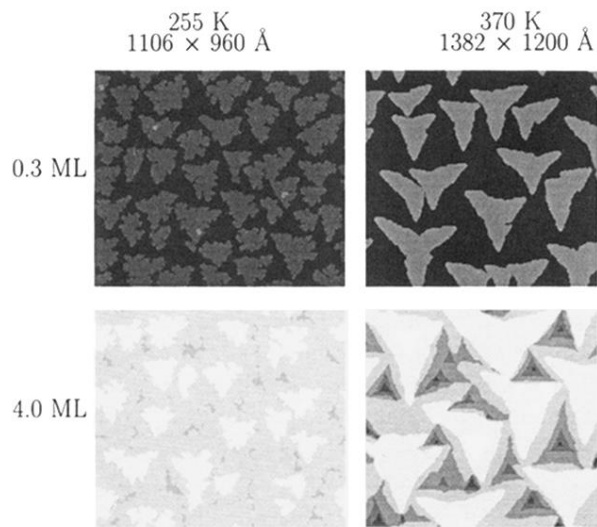255 K
1106 × 960 Å

370 K
1382 × 1200 Å

0.3 ML

4.0 ML

FIG. 3. Top view of the obtained surfaces after the deposition of 0.3 and 4.0 ML at a rate of 0.0033 ML/s, and at a temperature below and above the low temperature growth mode transition. The grey scale indicates the height above the surface.