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Accommodation and diffusion of Cu deposited on flat and stepped Cu(111) surfaces

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We present the results of a molecular-dynamics simulation of the deposition of Cu on Cu(111) using a realistic many-body interaction potential. It is shown that the transfer of the adsorption energy to the surface phonons is extremely efficient. If the adsorption takes place on a small or irregular island the energy transfer has a large probability of disrupting the island so that the incoming atom ends up *in* the island rather than *on top* of it. The implications of these observations for homoepitaxial growth and, in particular, the possibility of explaining the observation of low-temperature layer-by-layer growth are discussed.

I. INTRODUCTION

The accommodation of metal atoms on metal surfaces is an important step in the growth of metal overlayers on metal substrates. Most recently, the interest has centered upon the possibility that the incoming metal atoms have the possibility of using some of the several eV of condensation energy to move around on the surface before accommodating completely. This would be one possible explanation[1] why layer-by-layer-like growth of metals on metal surfaces has been observed for a number of systems down to very low temperatures (77 K).[1–3] A substantial mobility of the atoms on the surface is needed to achieve layer-by-layer growth, because atoms landing on an already formed island must be able to move down from the island to be incorporated into the growing layer. In the low-temperature growth experiments one would not expect such high mobilities, and even though this low-temperature reentrant layer-by-layer growth is incomplete, the question arises how the incorporation into islands can take place.

Another possible explanation is based on ordinary thermally activated diffusion.[3] From field ion microscopy (FIM) studies it has been proposed that there is a barrier for diffusion at descending steps that is higher than for ordinary diffusion on the terraces.[4] Assuming that this is a general principle, layer-by-layer growth should be impossible at low temperatures because the over-edge diffusion is frozen out. Such a transition is observed for Pt on Pt(111), but a second transition back to an imperfect layer-by-layer growth is observed at even lower temperatures.[3] This low-temperature reentrant layer-by-layer growth is explained in this picture as being due to lack of stability of adatoms on top of small islands. At the lowest temperatures the islands formed are small and irregular due to the restricted mobility. Metal atoms entering on top of these therefore preferentially move down from the island by thermal fluctuations and the layer-by-layer growth results.[3] Whereas there is theoretical evidence in support of a higher barrier for diffusion down a step edge,[5,6] there is yet no support for the hypothesis that this barrier should be much smaller for small islands.

In a series of very detailed simulations DePristo and co-workers have investigated this problem by studying the dynamics of a single metal atom condensating on a number of fcc(100) and (111) surfaces and using a number of different interatomic potentials.[7] They conclude that there is no sign of transient mobility where the adsorbing atoms use some of the condensation energy to move around on the surface. Transient mobility therefore cannot be used to explain the low-temperature layer-by-layer growth. Rather these authors suggest another dynamical effect termed *downward funneling*, by which incoming atoms are scattered away from multilayer islands on the surface.[8]

In the present paper we investigate the dynamics of the condensation process further by a series of molecular dynamics simulations for Cu on Cu(111) using the effective-medium theory to calculate the interatomic interactions. We investigate the accommodation process on flat surfaces and surfaces with islands of already deposited atoms. We find, in agreement with the results of DePristo and co-workers, that accommodation on the flat surface is very fast. Indeed, we show that it takes place even on the attractive part of the interaction potential rather than in the repulsive part as usually assumed.[9] We also show that accommodation on islands depends strongly on the island size, and we investigate the barriers for diffusion down from the island as a function of island size. It turns out that the barrier does vary with island size, but it is substantial even for the smallest possible island, the trimer. Finally, we show a complete simulation of the growth process and discuss the possible explanations of the low-temperature layer-by-layer growth process.

II. THE CALCULATIONAL METHOD

The total energy of the system of Cu interacting with a Cu(111) surface has been evaluated using the effective medium theory. We refer to Ref. 10 for the details of the method. Here we suffice to point out that it has proven able to correctly predict a large number of properties of Cu including phonons, surface phonons, surface phonon anharmonicity, disordering, and melting.[10]

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The simulations were made using effective-medium theory with the usual parameters.[10] The activation barriers for diffusion were calculated using steepest-descent minimization while the deposition of single atoms were studied using molecular dynamics with the Verlet algorithm at an initial temperature of 100 K. These simulations used a system of 147 to 180 atoms. The simulations of growth were made using a modified Langevin dynamics to stabilize the average temperature at 150 K.

We modified the conventional Langevin dynamics

$$m\ddot{\mathbf{r}} + \gamma\dot{\mathbf{r}} + \frac{\partial V}{\partial \mathbf{r}} = \mathbf{F}(\gamma, T) \tag{1}$$

where V is the potential energy of the system, $\mathbf{r}$ and m are the position and mass, respectively, of the atom, and $\mathbf{F}$ is the fluctuating force, by scaling the friction coefficient γ using the current $\bar{n}$ and equilibrium n_0 electron density for the atom

$$\gamma = \gamma_0 \frac{\bar{n}}{n_0}. \tag{2}$$

This modification ensures that the temperature can be kept under control without disturbing the growth process, as the low value for $\bar{n}$ on the incoming atom results in negligible friction and fluctuating forces for this atom until it is firmly in contact with the surface. The friction coefficient we used was $\gamma_0 = 1.8 \times 10^{12}$ s^{-1}. We verified that this value did not influence the growth process by reproducing the structure of the growing island after restarting the simulation using a value five times larger for γ_0. Both simulations were made using the same reproducible random number generator.

The system had initially 864 atoms distributed in six layers and 1008 atoms were deposited over 1.08 ns. The atoms were deposited randomly from a height of negligible interaction with the surface and the momenta of the atoms were drawn from a Boltzmann distribution at 1400 K. The parameters for the simulation were a compromise between a desired low value for the friction in the Langevin dynamics, a reasonable temperature stability, and the intrinsic drift velocity of atoms near the surface. The simulation took $\sim$ 700 h on a Sun SPARC-2 workstation. Somewhat shorter simulations were made at other temperatures and deposition rates.

III. STABILITY OF ISLANDS

The study of the properties of the islands formed in a growth process is complicated by the existence of huge numbers of isomers for the larger islands. Further an island formed during growth is not necessarily the most stable isomer.

The dissociation energy for the most compact islands containing two to twelve atoms is presented in Fig. 1. This figure shows that the heptamer, the decamer, and the dodecamer are particularly stable. The reason is that these islands form close-packed geometrical shells with the maximum number of bonds per atom.[11]

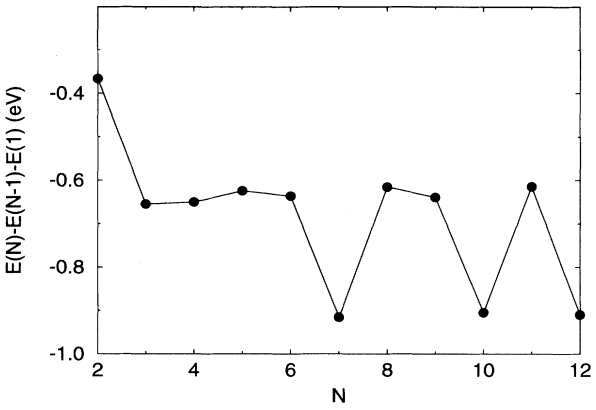

FIG. 1. Binding energy for the most compact isomer of clusters with two to twelve atoms.

IV. ACTIVATION ENERGIES FOR DIFFUSION

In Fig. 2 we show the energy as a function of position of an adatom moving down from two islands of different sizes, a heptamer, which is very stable,[11] and a trimer, which is less stable by 52 meV as the atoms in the trimer all have a low coordination number.[11] To calculate the energy along the diffusion path one coordinate has been varied along the diffusion path and the two other coordinates of the moving atom and the coordinates of all the other atoms have been allowed to vary to find the minimum energy path. Two diffusion paths are shown. One is the over-edge process indicated for the trimer in Fig. 3(a). The other is the exchange process indicated in Fig. 3(b). The activation energy for the *over-edge* mechanism is 284 meV on the trimer and 418 meV on the heptamer,

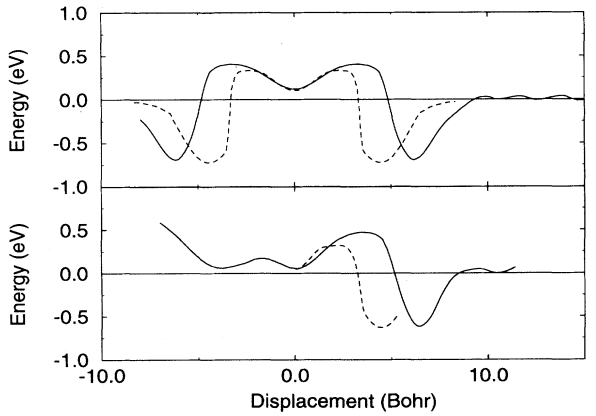

FIG. 2. Energy along two diffusion paths for adatom diffusion down from a trimer and a heptamer. The paths are indicated in Fig. 3. For the over-edge diffusion path the adatom is dragged along the direction indicated in Fig. 3 and for the exchange process an atom in the underlying layer is dragged. In both cases all other degree of freedom have been allowed to relax adiabatically along the path. The displacement of the dragged atom along the diffusion path has been used as reaction coordinate.

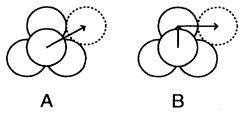

FIG. 3. Illustration of the two diffusion paths down from an island: (a) the direct or over-edge path, and (b) the exchange path.

while the activation energy on the exchange mechanism is 230 meV on the trimer and 267 meV for the heptamer. The exchange process thus has the lowest barrier for both the heptamer and the trimer. In all cases the barrier for diffusion down from the islands is substantial compared to the barrier (93 meV) for diffusion on the terrace. This is in accordance with the FIM results.[4]

The mapping of the activation barriers is complicated by the existence of both fcc and hcp sites for the adatoms on Cu(111). On the terraces a fcc site is more stable than a hcp site by 17 meV. The difference in stability is smaller for fcc and hcp sites on top of the heptamer.

The energy released when the adatom drops down from the trimer is 813 meV, somewhat larger than the 669-meV released by dropping an adatom down from the heptamer. This difference is both a reflection of the smaller stability of the adatom on the trimer and the larger dissociation energy for the tetramer than for the octamer; cf. Fig. 1.

The barrier for the over-edge process depends strongly on island size, but it is large even for the smallest island possible. The barrier for the exchange process, on the other hand, is not very island-size dependent, and again we find no indication that an adatom should not be stable on top of even the smallest island, the trimer.

V. THE ACCOMMODATION PROCESS

First we show in accordance with the findings of DePristo and co-workers[7] that atoms hitting the surface cannot use the heat of condensation to move around on the surface before thermalizing. The reason is that the energy transfer between the incoming atoms and the surface phonons is extremely rapid. This is illustrated in Fig. 4, which shows the static potential felt by a Cu atom approaching the surface and the actual development of the potential and total energy of an incoming Cu atom in the simulation. The static potential is calculated keeping all substrate atoms fixed during the approach of the new atom towards the surface.

The kinetic energy of the approaching atoms is seen to start disappearing on the attractive part of the trajectory. Usually energy transfer between an incoming adsorbate and the surface phonons is assumed to take place in the repulsive part of the interaction potential, but this is clearly not the case for the the Cu/Cu(111) potential used here.

The energy transfer is related to strong distortions of the surface. This can be observed as a marked difference between the static potential end the actual potential felt by the incoming atom in Fig. 4. The reason is that the surface atoms distort under the influence of the incoming

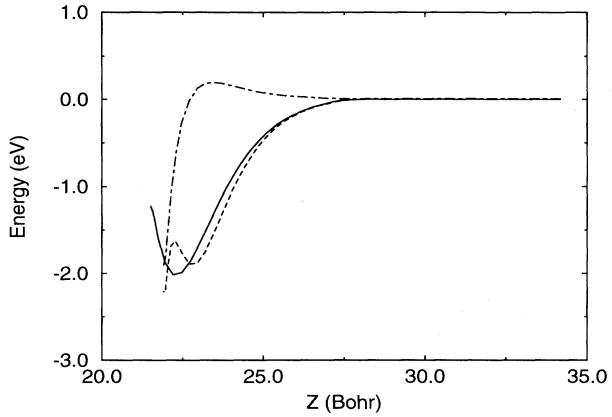

FIG. 4. The static potential felt by a Cu atom approaching a Cu(111) surface (solid curve) shown together with the actual variation of the potential energy (dashed curve) and the total energy of a Cu atom (dash-dotted curve) during a typical adsorption event.

atom. Because these distortions start while the incoming atom has a force towards the surface, the incoming atom starts losing its energy in this part of the potential well. The importance of these relaxations for the dynamics is of course largest for a system such as the present one where the equal masses of the incoming and substrate atoms make the time scales of their motion equal.

For atoms impinging on an island on the surface the dynamics is more complicated. Two typical trajectories are shown in Fig. 5. An atom impinging on the very stable heptamer behaves essentially as an atom impinging on the flat surface. The atom accommodates without much motion parallel to the surface. Note that even though the trajectory shown in the figure has the Cu atom impinging at the perimeter of the island, the large barrier shown in Fig. 2 makes sure that it stays on top of the island. This behavior is typical of islands with well-characterized stable steps. From simulations for 300 randomly chosen impact parameters we have determined the probability P_u that the incoming atom stays on top of the island after accommodation. For the heptamer $P_u = 1.00 \pm 0.14$. On the trimer, on the other hand, we find that $P_u = 0.40 \pm 0.13$, and the reason is illustrated in Fig. 5, which also includes a typical trajectory of an atom impinging on a trimer. Even though the local impact site is approximately the same as on the heptamer,

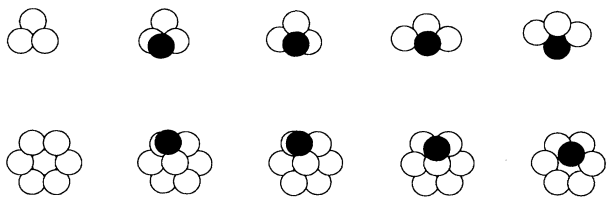

FIG. 5. Snapshots during a typical adsorption process on a trimer and on a heptamer. The incoming atom is colored black.

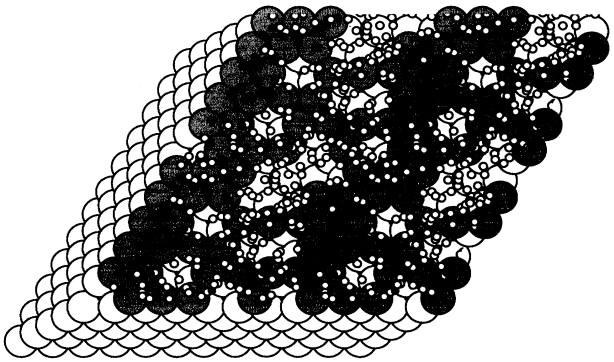

FIG. 6. Illustration of the variation of the probability that an incoming atom hitting an island stays on top of the island with in impact parameter. 300 events are marked at the point of impact. Open circles indicate that the atom ended up in the island and a closed circle indicates that it stayed up.

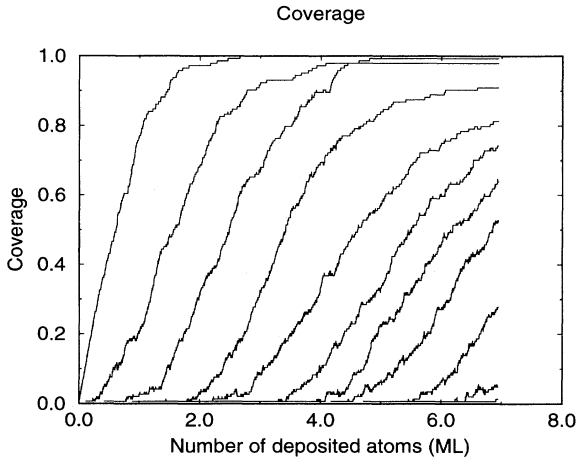

FIG. 7. Occupation of consecutive layers during the evaporation of seven monolayers of Cu on a Cu(111) surface.

the trajectory is very different. On the trimer, the impinging atom is able to disrupt the island and end up in the layer below. This difference between the trimer and the heptamer must be related to the different possibilities of the atoms in the island to move away from the incoming atoms during impact. The low P_u's are therefore expected to be typical of irregular, low stability islands.

This is illustrated further in Fig. 6, which shows the results of 300 simulations, where an atom was allowed to fall towards the same configuration of adatoms. This configuration is typical for the structure of a partially completed, grown layer. Each event is marked by an open circle at the point of impact if the atom falls down and by a closed circle if it stays on top of the island. Clearly the open circles are concentrated primarily around the irregular parts of the partly grown layer.

The conclusion is that the energy deposited in the surface atoms by the impinging atom can cause small, irregular islands to disrupt so that the incoming atom ends up in the island and not on top of it. A similar effect has been reported by Halstead and DePristo.[13] In a recent series of Monte Carlo simulations Šmilauer, Wilby, and Vvedensky[12] found that when this effect was incorporated in the mechanism, reentrant two-dimensional growth was observed.

VI. THE GROWTH PROCESS

We have also simulated the growth process, by depositing ten monolayers of Cu on a Cu(111) surface at 100 K. This simulation is not meant to resemble the experimental situation. Our deposition rate is about 11 orders of magnitude larger that the experimental ones. Since our extremely large deposition rate effectively means that we have no thermally induced diffusion during deposition, we expect that, if anything, our simulation should most closely resemble the lowest-temperature deposition experiments.

In this connection, it is interesting to note from the observed buildup of the different layers shown in Fig. 7 that, whereas the growth is definitely not strictly layer-by-layer, it is not completely three-dimensional either. The buildup of the different layers are almost parallel in time up to about seven layers indicating that although more than one layer is being filled at the time, the height-height correlation function does not increase continuously. The incomplete layer-by-layer growth of the simulation might be related to the low-temperature reentrant two-dimensional growth observed experimentally, but we cannot at this point compare our results directly with the He scattering results without some very crude approximations.

Snapshots of the surface during deposition shown in Fig. 8 reveal that the growing islands are very irregular, in agreement with the experimental situation at low temperatures.[3] Neither the conditions of the simulation nor the low-temperature experiment allows the breaking of adsorbate-adsorbate bonds, resulting in a very rough structure. We therefore suggest that the incomplete layer-by-layer growth observed in the simulation is related to the small probabilities P_u for ending up on top of the island for the irregular islands produced in the growth simulation.

If the low-temperature growth simulation is terminated and the irregular configuration of Fig. 8(a) is annealed at 650 K for 80 ps, then diffusion at the surface becomes possible at the time scale of the simulation, and more compact structures appear as shown in Fig. 8(b).

VII. CONCLUSIONS

The picture that emerges is therefore the following. There is no indication from our simulations of substantial ballistic motion of adsorbing Cu atoms on Cu(111) parallel to the surface. This is due to an extremely efficient energy transfer to the surface atoms. This indicates that ballistic motion is not the reason that reentrant layer-by-layer growth may be observed at low temperature.

We have also seen that even the smallest islands can support an adatom. The barrier for diffusion down from

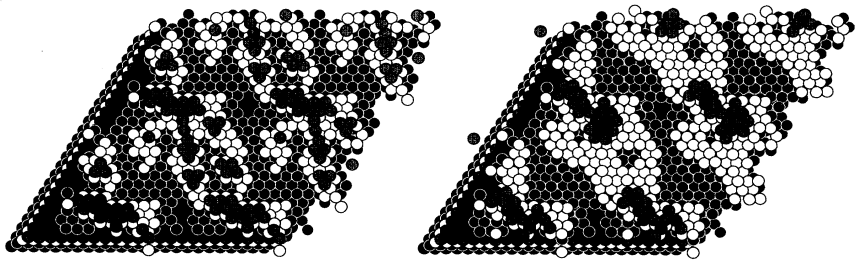

FIG. 8. (a) Snapshot of the configuration of a Cu(111) surface after one monolayer of Cu has been deposited. (b) The same surface after annealing to 650 K for 80 ps.

the island is always large compared to the diffusion barrier on the terraces. This suggests that a lack of barrier for diffusion down from the smallest islands is not the explanation of the low-temperature reentrant layer-by-layer growth either.

Rather our results indicate another possibility. During low-temperature deposition the islands on the surface are very irregular. This has been observed experimentally,[3] and our simulation confirm this picture. On these irregular islands, the probability P_u that an atom hitting the island stays up is considerably smaller than on larger, more regular islands because the impinging atom may disintegrate the unstable irregular structures. An imperfect layer-by-layer growth is therefore possible at temperatures low enough that the islands stay irregular. At higher temperatures the islands coarsen, P_u increases, and the growth becomes three dimensional. At even higher temperatures it becomes two dimensional again, as the thermal diffusion down from the islands become possible.[3]

ACKNOWLEDGMENTS

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