High-Temperature Study of the Schwoebel Effect in Au(111)

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We investigate the adatom descent from straight steps on Au(111) by molecular-dynamics simulations. Au is modeled using many-body tight-binding potentials. Adatom descent may take place by a jump or by exchange; the static energy barriers are very similar for both mechanisms and much higher than the barrier for coming back to the inner terrace. However, the simulations at high temperatures (450–650 K) show that adatoms exchange fast and jumps are rare at both steps. These results suggest that the Schwoebel barriers for exchange are decreased at high temperature.

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The understanding of the elementary processes of adatom migration on stepped surfaces is of great interest in the study of growth mechanisms. In fact, the transitions from continuous to layer-by-layer growth and vice versa, discovered, for instance, in molecular beam epitaxy experiments on Pt(111) [1–3], depend on the effectiveness of the interlayer mass transport. Clearly, layer-by-layer growth is possible when adatoms deposited on terraces are able to descend fast: as dimers and larger clusters are usually less mobile [4–7], one adatom should descend before being reached by another one. Very often, the kinetic bottleneck hindering interlayer mobility is represented by the so-called Schwoebel barrier [8]. The Schwoebel barrier is due to the fact that an adatom reaching the border of the terrace may feel a potential barrier preventing the descent to the lower terrace; in fact, the descent may be difficult as the adatom should lose coordination at the saddle point position. The loss of coordination is different depending on the descent mechanism, which can be either by jump or by exchange, as it has been shown by experiments [7,9] and calculations [10–14].

In this Letter we investigate the mechanisms of adatom descent from straight steps on Au(111) by molecular-dynamics (MD) simulations. The system is modeled using many-body potentials of the kind developed by Rosato, Guillopé, and Legrand (RGL) [15,16]. RGL potentials are derived in the framework of the second-moment approximation to the tight-binding model; the total energy of each atom is then written as the sum of a band contribution (in the form of the square root of the second moment of the electronic density of states) and a repulsive term of the Born-Mayer type. The form and the parameters of those potentials for gold are given in Ref. [17]. RGL potentials correctly describe surface relaxation and reconstructions and predict the diffusion mechanisms on the flat surfaces of fcc transition metals, in agreement with known experimental results [18]. In the following, we calculate the static energy barriers for different elementary processes by quenched molecular dynamics [19] and then we make MD simulations in the range $450 < T < 650$ K. The high-T simulations will show that the frequency of exchanges is unexpectedly large with respect to those of the other processes.

Our system consists of a (111) slab with a terrace above it [17] (a top view is given in Fig. 1). The slab is nine layers thick in the z direction; on the surface plane the size is (15×9) and periodic boundary conditions are applied. On the topmost layer there is a seven-row terrace. The terrace is bounded on its sides by two straight steps of different symmetry, an A step (lower side of the terrace in Fig. 1) and a B step (upper side). Above the terrace we

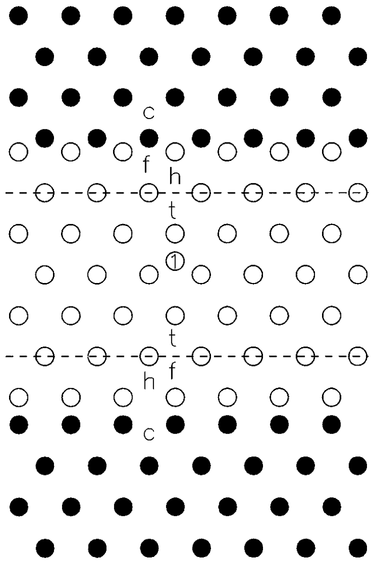

FIG. 1. Top view of the slab used in the simulation. The open and full circles represent the atoms of the upper and lower terraces, respectively. The adatom (indicated by 1) is in the middle of the upper terrace. The terrace is bounded by step A on its lower side and step B on its upper side. The terrace borders are the strips beyond the dashed lines. f and h indicate fcc and hcp sites on the terrace borders; c indicates the nearest equilibrium site on the lower terrace (in the channel) and t the nearest equilibrium site in the inner terrace.

put an adatom which may move around, reach the border of one of the steps, and eventually descend. Once the adatom is on the border many different processes may happen: diffusion along the step, reflection back to the inner terrace, or descent to the lower terrace, either by jump or by exchange.

Let us consider step *A* (on the lower side of the terrace in Fig. 1). The equilibrium sites just at the border of the upper terrace are hcp sites (as the site h in Fig. 1); their fcc neighbors (as f) are behind the atoms of the step. Once the adatom has reached an h site, there are different possibilities. The adatom may jump directly down in the channel (to the site c just in front); it may exchange with an atom of the step, the latter being pushed to one of the c sites; it may jump to an f site. If the adatom is on an f site, other processes may take place: it may jump to an h site, it may exchange with an atom of the step, or it may come back to the inner terrace jumping to the nearest t site. Along step *B* the same kinds of processes can take place, the only difference being that the sites just at the border of the step are fcc ones.

The barriers for some of the above processes are reported in Table I. The position just near the border is somewhat stabler than the one behind the step atom in both steps (in step *A* h sites are stabler than f sites; in step *B* the opposite happens); for that reason, the exchange-descent barrier from h sites E_e^{hcp} is slightly different from the one for exchange from f sites E_e^{fcc}. The jump-descent barriers E_j are higher by a few eV than E_e^{hcp} and E_e^{fcc}. On the contrary, the barrier $E_\perp$, which prevents coming back to the inner terrace (it is the barrier between sites f and t at step *A* and between sites h and t at step *B*), is noticeably smaller than the others, by a factor of 2 or more, and essentially the same as the barrier for diffusion on the flat (111) surface (0.12 eV [20]). Concerning the anisotropy between steps, we find that the barriers for step descent are slightly smaller along step *B*. The anisotropy, however, is not marked. This is different from what has been recently found in calculations (by embedded-atom and effective-medium potentials) in Ag [14] and Pt [12], where the barrier for exchange turns out to be considerably lower at step *B* than at step *A*. The effect seems to be metal dependent; we have calculated the exchange-descent barriers in Ag by means of RGL potentials and we have found a strong anisotropy (0.35 and 0.21 eV for exchange from steps *A* and *B*, respectively [21]), in agreement with Ref. [14]. The different behavior of Au and Ag may be related to the different values of the parameters in RGL potentials [15,16]. In particular, the parameter q, which governs the behavior of the potential at distances beyond first neighbors, is rather different for the two metals.

TABLE I. Energy barriers. All data are in eV. E_e^{fcc} and E_e^{hcp} are the energy barriers for exchange from fcc and hcp sites, respectively; E_j is the barrier for step descent by jump; $E_\perp$ is the barrier for migration perpendicular to the step on the upper terrace.

Step	E_e^{fcc}	E_e^{hcp}	E_j	$E_\perp$
A	0.28	0.26	0.30	0.13
B	0.25	0.26	0.28	0.12

According to the static energy barriers, one may predict the following behavior at high T, for instance, around 500 K. $E_\perp$ is considerably lower than the other barriers, the differences being considerably larger than the thermal energy at that T. Therefore, once the adatom has reached the border of one step (which is the zone between the dashed line and the atoms of the step in Fig. 1), it should diffuse along that step and then it should be reflected back to the inner terrace with a large probability, instead of descending to the lower level either by exchange or by jump. On the other hand, as the barriers for exchange and jump descent are similar (their differences being less than the thermal energy), one may expect that, even if exchange is favored, a considerable number of jumps should take place.

In order to investigate whether those predictions are correct or not, we have done many constant-energy simulations in the T range 450–650 K. Thermal dilation has been taken into account as in Ref. [17] and a time step of 7×10^{-3} ps. In each simulation, the adatom starts in the middle of the upper terrace, then it diffuses, reaches the step, and finally descends. Each simulation is stopped when the adatom has descended to the lower terrace, either by jump or by exchange. As we are interested in the descent at straight steps, we discard simulations in which one of the steps gets damaged because of atoms of the step itself which go out in the channel. Since the energy barriers are very large [17], latter events are not frequent.

The high-T results are reported in Tables II (step *A*) and III (step *B*). In those tables, t_0 is the total time spent by the adatom on the border of the step (the zone beyond the dashed lines in Fig. 1) during all simulations at the given T; n_e, n_j, and n_r are the numbers of exchanges,

TABLE II. Results for step *A* in gold. T is the temperature (in K), t_0 the total time spent on the border of the step (in ps), n_e, n_{le}, n_j, and n_r are the numbers of exchanges, long exchanges, jumps, and reflections.

T	t_0	n_e	n_{le}	n_j	n_r
450	1556	17	0	0	18
480	1761	18	0	0	20
509	1745	29	0	2	21
549	1556	41	0	3	27
593	1307	45	4	3	38
618	1003	35	3	1	24
650	1002	45	6	3	28

TABLE III. The same as in Table II, but for step *B*.

T	t_0	n_e	n_{le}	n_j	n_r
450	1672	24	0	1	18
480	1487	23	0	0	20
509	1522	46	0	1	29
549	1017	35	0	1	18
593	1118	47	0	2	29
618	1117	51	2	4	31
650	1144	67	4	1	35

jumps, and reflections, respectively. At high T, "long exchanges" may also happen. In a long exchange [22], the adatom is incorporated into the terrace at an inner site (for instance, at a t site). The number of long exchanges is n_{le}. Note that this mechanism could give some idea about the exchange mechanism on a flat (111) terrace, for which few data are available. This exchange mechanism could be especially important in the case of the incorporation of a foreign atom on this face during the formation of a surface alloy.

It is evident from those results that the above predictions do not correspond to the actual high-T results. Even at the lowest T (450 K, corresponding to a thermal energy of 0.04 eV), n_r is not larger than n_e; a particle which has reached the step border has the same probability of descending as of being reflected back. Above 550 K, especially at step *B*, exchanges are clearly more likely to occur than reflections. Concerning the step-descent mechanism, the small number of jump descents at any T is noteworthy: jumps are less than 5% of exchanges. At high T, even long exchanges are more frequent than jumps, especially at step *A*. In summary, there is an unexpectedly high frequency of exchanges with respect to that of reflections and jumps.

The physical picture leading to these results may be sketched as follows. At high temperatures, the step atoms perform large-amplitude oscillations around their equilibrium sites. The vibrations are asymmetric in the direction perpendicular to the step (y direction), being easier for a step atom to oscillate outwards than inwards. This effect is much stronger when an adatom is on the border of the step. As an example, we consider step *A* (see Fig. 2), with the adatom (indicated by 1) on an fcc site. If the adatom is on an hcp site the results are similar. At 0 K (after quenching), the step atoms are relaxed inwards, with the exception of the atom just below the adatom (atom 2). In fact, the distance of step atoms from the first inner row of the upper terrace is $\Delta y = 2.37$ Å, while the distance of atom 2 is $\Delta y_2 = 2.48$ Å. The unrelaxed distance is 2.49 Å. The distance of atom 1 is $\Delta y_1 = 0.91$ Å. As the temperature increases, the oscillation amplitude of atom 2 becomes very large; the vibration is strongly asymmetric, since atom 2 cannot move easily inwards because of the presence of the adatom and of the atoms of the inner rows. Therefore the average position of atom 2 becomes even more strongly displaced. For instance, we have measured the average positions at 450 K, by averaging over the parts of the simulations in which the adatom is on an fcc site along step *A*. Δy increases slightly (to 2.40 Å), but Δy_1 and Δy_2 are significantly changed (to 2.59 and 1.02 Å, respectively). This shows that the average configuration of atoms at high T is rather different with respect to 0 K; the anharmonicity of vibrations (the average amplitude of the y vibration of atom 2 is of 0.3 Å at 450 K) leads to a net outward displacement. The latter favors the exchange mechanism, as the adatom finds easily the space for incorporation. As a result, the frequency of exchanges is much larger than expected.

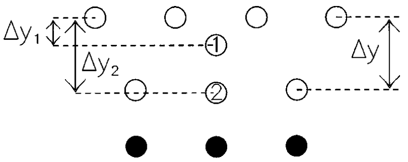

FIG. 2. Picture of step *A* with the adatom (indicated by 1) on an fcc site. The step atom just below (indicated by 2) is pushed outwards.

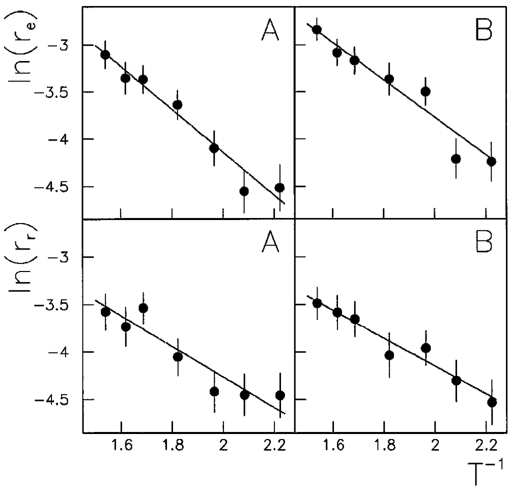

FIG. 3. Arrhenius plots of exchange and reflection rates (r_e and r_r) for steps *A* and *B*. The rates are in ps^{-1}; T is in 10^3 K.

In the following, we analyze the effect of temperature on activation barriers. In order to extract the activation energies, we assume phenomenologically an Arrhenius

TABLE IV. Parameters of the Arrhenius plots of the exchange and reflection rates r_e and r_r. $\Delta E_{e,r}$ are in eV and $r_{e,r}^{(0)}$ are in ps^{-1}.

Step	ΔE_e	$r_e^{(0)}$	ΔE_r	$r_r^{(0)}$
A	0.20 ± 0.03	1.5	0.14 ± 0.03	0.4
B	0.17 ± 0.02	1.3	0.13 ± 0.03	0.3

dependence on T for the exchange and reflection rates $r_{e,r}$ (calculated at each T as n_e/t_0 and n_r/t_0)

$$r_{e,r} = r_{e,r}^{(0)} \exp\left(-\frac{\Delta E_{e,r}}{k_B T}\right). \tag{1}$$

Unfortunately, due to the low frequency of jumps, the study of the Arrhenius plot of the jump rate would require extremely long computing times. The Arrhenius plots of r_e and r_r are represented in Fig. 3; the Arrhenius parameters, estimated by least-squares fitting, are reported in Table IV. It turns out that the dynamical barriers ΔE_e are lower than the static ones by about (25–30)% at both steps. ΔE_r is less changed with respect to the static values; it is larger than $E_\perp$, but the latter is always within the error bars. This result may suggest that the outward relaxation affects more the exchange than the reflection mechanism. Concerning prefactors, we remark that the values given in Table IV are only indicative, the errors being of the order of 50%. However, while the values of $r_e^{(0)}$ are about 10^{12} s^{-1}, $r_r^{(0)}$ is smaller. This is partially explained by noticing that the adatom, once it has reached the border of the terrace, spends a large part of its time [(55–60)% in the T range considered] in the sites just near the border (h sites along step A and f sites along step B, see Fig. 1); from those sites, it is difficult to jump directly into the inner terrace. Therefore the effective time during which reflections can occur is about one-half of t_0.

In conclusion, we have investigated the interlayer mass-transport mechanisms in Au(111), in the presence of straight steps. The static energy barriers for the relevant elementary processes have been calculated by quenched MD simulations. The high-temperature simulations have shown that the exchange-descent mechanism is always dominant; exchanges occur fast as the adatom reaches the border of the terrace, while jumps are rare. Once the atom has reached the step, the probability that it will descend is larger than the probability that it will return back to the inner terrace; i.e., the Schwoebel effect disappears. These facts contradict the predictions based on the static energy barriers. The parameters extracted from the Arrhenius plots suggest that this behavior is related to a dynamical lowering of the exchange-descent barriers.

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