Competing mechanisms in adatom diffusion on a channeled surface: Jumps versus metastable walks

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It is shown, by molecular-dynamics simulations, that in-channel Au adatom diffusion on missing-row reconstructed Au(110) takes place by two different mechanisms, jumps and metastable walks. In a metastable walk the adatom climbs up one of the (111) facets of the channel, diffuses fast along the network of metastable minima on that facet, and finally is trapped again at the channel bottom. A considerable fraction of the events giving direct mass transport to distant cells occurs by this new mechanism. [S0163-1829(98)04728-6]

The study of adatom diffusion on crystal surfaces is a key step in understanding the microscopic mechanisms involved in growth, catalysis and chemical reactions.[1] Very recently, the attention has been focused on the diffusion on anisotropic surfaces, where the most likely diffusion occurs along one well-defined direction. In such surfaces, diffusion is expected to be a one-dimensional process: diffusion trajectories among the lattice cells should essentially follow straight lines along the easy direction. The diffusion of Pd on channeled $W(211)$ (Ref. 2) and of Pt on missing-row reconstructed Pt(110) (Ref. 3) have been investigated by field-ion microscopy and scanning-tunneling microscopy, respectively. The results of these experiments have shown that a simple single-jump model is not appropriate. In fact, consistent fits of the data are possible only by introducing correlated diffusion events in which the adatom crosses several lattice cells in a single process. Moreover, in these experiments, different activation barriers for moves to nearest-neighbor (NN) and to more distant sites were estimated. In recent molecular-dynamics (MD) simulations,[4] the in-channel jump mechanism for diffusion of Pt on reconstructed Pt(110) has been investigated. In particular, the single- and double-jump rates have been calculated, and it has been shown that double jumps have indeed a higher activation barrier than single jumps.

Here we study the diffusion of Au on reconstructed Au(110) by molecular dynamics (MD) simulations, and show that, even on that channeled surface, diffusion cannot simply be considered a one-dimensional phenomenon, since a new diffusion mechanism plays an important role. In fact, we show that diffusion may happen via two completely different mechanisms: in-channel jumps and metastable walks (MW's). In-channel jump diffusion follows the usual path: the adatom starts from a given cell and move to another by crossing one or more saddle points in the in-channel direction, essentially on a straight line. If the cell of arrival is a NN of the cell of departure, the adatom makes a single jump (J_1), otherwise a multiple jump (J_2, J_3, etc.). Metastable walks follow completely different trajectories: the adatom climbs up to a metastable minimum on one of the (111) facets of the channel, then diffuses fast along that facet and finally jumps down in the channel, again either in a NN cell (MW_1 events) or in a more distant one (MW_2, MW_3, etc.). Our simulations will show that metastable walks are a considerable fraction of the events involving direct mass transport to distant cells.

In our simulations, Au is modeled by many-body potentials as developed by Rosato, Guillopé, and Legrand[5] (RGL). The form and the parameters of those potentials for gold are given in Ref. 6. RGL potentials describe correctly surface relaxations and reconstructions[5] of noble metals. They have been widely used in the simulations of diffusion in transition and noble metals[7,8,12] where they predict the diffusion mechanisms on flat surfaces in agreement with known experimental results.[8] Concerning gold, recent *ab initio* calculations of diffusion of Au/Au(100) (Ref. 9) have shown that exchange is favored compared to hopping (barriers of 0.40 and 0.58 eV, respectively). We have checked RGL potentials and they agree well with these results, giving 0.41 eV for exchange and 0.51 eV for hopping. On the (110) surface, data are available for in-channel jump (ICJ) and cross-channel exchange (CCE) diffusion in the nonreconstructed geometry. There, RGL potentials give 0.28 and 0.46 eV for ICJ and CCE, respectively, to be compared to effective medium[10] (0.27 and 0.55 eV) and embedded atom[11] (0.34 and 0.42 eV or 0.25 and 0.40 eV, depending on the parametrization).

The results here presented are obtained by microcanonical MD simulations in the range 450–625 K. At these temperatures, thermal expansion is not negligible and it has been taken into account as in Ref. 6. The solution of the equations of motion is achieved by the standard Verlet algorithm,[14] with time steps in the range 3.5–7 fs depending on T. Our system consists of a (110) slab with missing-row reconstructed surfaces. A top view of a portion of the reconstructed surface is drawn in Fig. 1, where the adatom (black circle) is in one of the in-channel minima, the dark gray circles are the top-row atoms, the light gray circles are the atoms of the second layer and the white circles the atoms of the third layer. The size of the slab is of seven and eight cells in the in-channel $[1\bar{1}0]$ (horizontal direction in the figure) and in the cross-channel [001] directions, respectively. Periodic boundary conditions are imposed in the surface plane and the slab is 17 layers thick in the perpendicular direction.

Examples of trajectories concerning typical events are given in Fig. 2. There, the trajectories of the adatom, of the

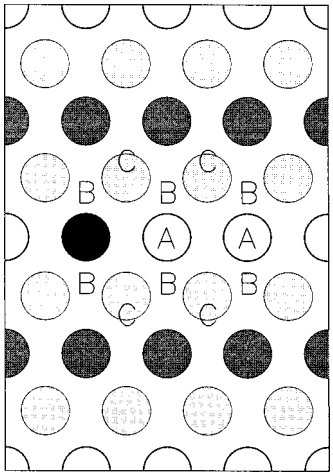

FIG. 1. Top view of a portion of the missing-row reconstructed Au(110) surface, with an adatom (black circle) in one of the in-channel minima. The dark gray, light gray, and white circles are the first-, second- and third-layer atoms, respectively.

top layer atoms and of the second layer atoms are represented in black, dark gray and light gray, respectively. All trajectories are projected into a (110) plane. The simplest diffusion events on this surface occur on a straight line, as can be seen in the left column: single, double, and triple jumps (as in the top, middle, and bottom left panels, respectively). These kinds of events have been considered in Ref. 4. However, jumps are not the only events in our simulations, since the phenomenology is much richer, as shown in the three panels of the right column of Fig. 2. There, single, double, and triple metastable walks are shown, at $T = 450$ K. In a MW, the adatom leaves the in-channel minima (sites A in Fig. 1) jumping in a metastable minimum (sites B), diffuses fast on the (110) facet of the channel through sites C and B and finally is trapped again in one of the in-channel minima. The adatom may stop for short times in any of the intermediate B and C sites; however, direct moves from a site C to a site A or to another site C, or from a site B to another site B are rather frequent, especially at the highest temperatures. The occurrence of these direct moves has been found in simulations of the high-T adatom diffusion on (111) flat surfaces of gold[12] and other metals.[16,7] In Fig. 2, because of an effect of perspective, one might have the impression that MW trajectories pass through on-top sites on the facets. This is not the case. For instance, in Fig. 3, the trajectories of the MW_2 of Fig. 2 (middle panel of right column) are projected onto the plane of the channel facet. It is evident that the walk on the facet resembles a diffusion trajectory on a flat (111) surface, with hopping via bridge sites. The adatom may also hop from a site A to a site B and then come back to the same site A (either directly or after some wandering on the facet). These events do not contribute to diffusion. We remark that the duration of a MW is short compared to the typical in-channel diffusion times: even at the highest T (625 K) the adatom spends on the average less than 2% of the total simulation time by wandering on the (111) facets.

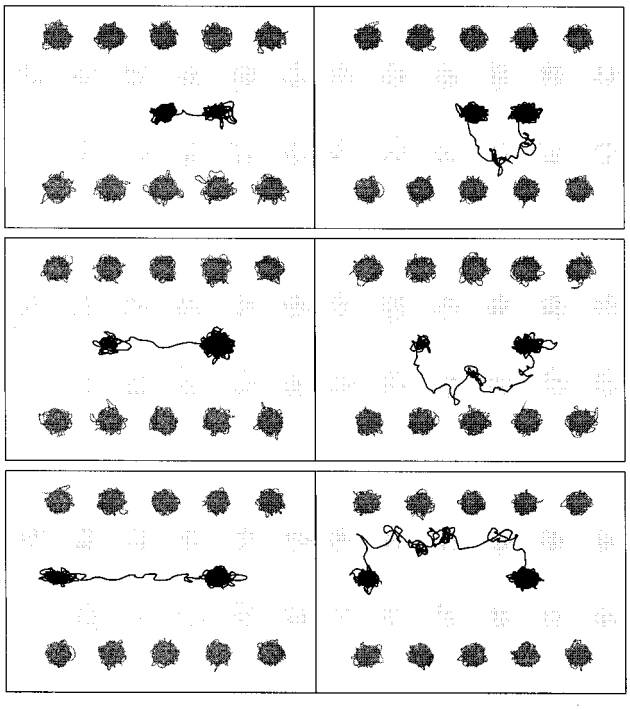

FIG. 2. Adatom trajectories in the most important elementary diffusion events, projected onto a (110) plane. The trajectories of the adatom, of the first and second layer atoms are represented in black, dark gray, and light gray, respectively. The trajectories' third-layer atoms (white circles in Fig. 1) are not plotted. Left column: in-channel jump events (single, double, and triple jumps from top to bottom). Right column: metastable walks (single, double, and triple MW from top to bottom). The simulations have been performed at 450 K.

FIG. 3. Trajectories of the MW_2 event of Fig. 2 projected onto the plane of the channel facet where it takes place.

In Table I the total events happened at six different temperatures are counted.[15] At each T, many independent simulations have been run, up to the accumulation of 1000 single jumps. This huge body of statistics (comparable to those of the experiments[3]) has been obtained with different total simulation times depending on T: for instance, we simulated for a total of 766 and 89 ns at 450 and 625 K, respectively.

In general, the fraction of the events giving direct transport to distant cells (multiple jumps and long MW's) compared to moves to NN sites is of some percents, as found in previous MD simulations on different transition and noble metal surfaces,[7,16,6,17] at temperatures of the order of half of the melting temperature. However, it must be noticed that at

TABLE I. Total number of jumps and metastable walks at the temperatures of the simulations. At each T, 1000 single jumps (J_1) were recorded.

	450 K	500 K	550 K	575 K	600 K	625 K
J_2	15	26	26	34	51	37
J_3	1	0	0	1	3	1
J_4	0	0	0	0	1	0
MW_1	40	44	59	53	54	72
MW_2	8	7	10	9	13	20
MW_3	1	5	0	5	4	1
MW_4	0	0	0	0	0	1
MW_5	0	0	0	0	0	1

any T, a considerable fraction (say, 25% on average) of these events are MW. For instance, at $T=450$ K we find 15 double jumps and 8 double MW's, and, at 625 K, 37 double jumps and 20 double MW's. Concerning triple moves, the statistics is poor; however, we find a total of 6 J_3 and 16 MW_3's. Therefore, there is a clear indication that MW's are even more important for direct transport to distant cells. Concerning single MW's, their relative frequency with respect to single jumps decreases with T.

Assuming that the temperature dependence of the rates r of the different kind of events follow the Arrhenius law $r=r_0\exp(-\beta E_a)$ ($\beta=1/k_BT$) we find for $E_a^{J_1}=0.29\pm0.01$, $E_a^{J_2}=0.43\pm0.03$, $E_a^{\mathrm{MW}_1}=0.37\pm0.02$ and $E_a^{\mathrm{MW}_2}=0.43\pm0.05$ eV. It can be noticed that $E_a^{J_2}\simeq E_a^{\mathrm{MW}_2}$ and $E_a^{J_2}\gg E_a^{J_1}$. The latter inequality is consistent with the results of simulations of single and double jumps on reconstructed Pt(110) (Ref. 4) and other metal surfaces,[7] and with the experimental findings.[2,3]

In order to elucidate the origin of the different diffusion processes, we have calculated the energy barriers for the moves between the different minima of kinds A,B,C by quenched molecular dynamics.[13] A contour plot of the adatom energy is given in Fig. 4, for the same portion of the surface represented in Fig. 1. The contour plot has been obtained fixing the x and y coordinates of the adatom and letting all the others degrees of freedom of the slab relax. This has been done on a grid of 20×20 points per unit cell. The stable and metastable minima and the preferential diffusion trajectories (both the straight trajectory along the channel and the half-hexagons on the facets) are clearly visible. We find the following static energy barriers: for single jumps $E_{AA}=0.31$ eV, for moves from in-channel minima to metastable B sites $E_{AB}=0.40$ eV, for the reverse move $E_{BA}=0.06$ eV, for moves from B sites to C sites and vice versa $E_{BC}=E_{CB}=0.10$ eV. The latter barriers are very close to those found by RGL potentials in the case of diffusion on the flat Au(111) surface.[12]

The fact that MW_1, MW_2 (and in general MW_n processes) are characterized by different activation barriers may be understood by a simple hopping model, which would also give an indication on the diffusive behavior at low T. Let us assume that the atom has just moved from the channel to a metastable site B. This happens with a rate $r_{AB}=\nu_{AB}\exp(-\beta E_{AB})$. Once the atom is there, we may ask for the probability of making a MW of length n, i.e., of jumping back in the channel in a cell at distance n from the starting one. Let us assume that the temperature is sufficiently low so that the diffusion barriers are given by the static energy barriers, as calculated above, and that direct $B\to B$ or $C\to C$ moves (or even cross-channel diffusion events, which are indeed rare) are negligible.[12,7] In this case, each time an atom is in a site B, it has a probability p of moving to sites C (to its left or its right) and a probability $1-p$ of jumping back in the channel to site A. When the atom is in C it can move only to one of the nearby B sites. p can be written as

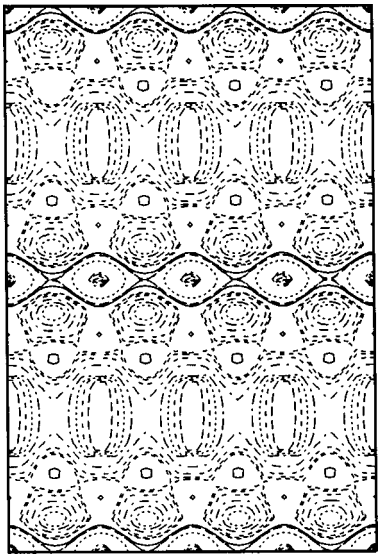

FIG. 4. Contour plot of the adatom energy (after quenching) for the same portion of the surface represented in Fig. 1. The half hexagons on the (111) facets are clearly visible.

$$p=\frac{2\nu_{BC}\exp(-\beta E_{BC})}{2\nu_{BC}\exp(-\beta E_{BC})+\nu_{BA}\exp(-\beta E_{BA})}. \qquad (1)$$

At low T $p\ll1$, since $p\propto\exp[-\beta\Delta E]$, where $\Delta E=E_{BC}-E_{BA}$. Simple random walk considerations show that the probability P_n of making a MW_n is

$$P_n=c_n\sum_{N=n}^{\infty}\frac{(2N)!}{(N+n)!(N-n)!}2^{-2N}p^N(1-p), \qquad (2)$$

with $c_n=2$ for $n\geqslant1$ and $c_0=1$. At low T, $P_n\propto p^n\propto\exp(-n\beta\Delta E)$, and the frequency of a MW_n is proportional to $\exp[-\beta(E_{AB}+n\Delta E)]$. This model leads thus to a barrier of

$$\Delta E_n=E_{AB}+n\Delta E \qquad (3)$$

for a MW_n event; our calculations for Au(110) give of $\Delta E_1=0.44$ eV and $\Delta E_2=0.48$ eV, and $\Delta E_3=0.52$ eV for MW_3. The agreement of ΔE_1 and ΔE_2 a with the activation barriers from the Arrhenius plots can be considered as reasonable, since the latter are obtained at high T, where many assumptions of the above random walk model are questionable. In any case, we remark that both the Arrhenius plots and the random walk model indicate that the activation barriers increase with the length of the MW by small amounts. On the other hand, the Arrhenius plots show that the barrier for double jumps is much larger than that for single jumps,

and, since triple jumps are extremely rare, one may infer that longer jumps are characterized by much larger barriers. In this case, the dominant mechanism for direct mass transport to large distances (more than two lattice spacings) would be via MW.

In conclusion, we have shown that the strongly anisotropic diffusion of Au adatoms on the reconstructed Au(110) surface takes place by two different mechanisms, jumps and metastable walks. Besides the usual in-channel jump diffusion, there is the possibility of a new diffusion path, in which the adatom climbs a (111) facets of the channel and then diffuses among the metastable minima along that facet, before being trapped again in the channel. This new mechanism is important for what concerns the events in which direct transport to distant sites occurs. In the T range 450–625 K, we have found that about 25% of the events leading to direct mass transport over two cells takes place via metastable walks. Moreover, our simulations indicate that metastable walks may be dominant for direct transport over three or more cells. Considerations following from the Arrhenius plots of the different diffusion processes, and from a random walk model based on the static energy barriers, suggest that the new mechanism should be important for direct transport to distant sites also at lower temperatures.

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