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Exchange mechanism for adatom diffusion on metal fcc(100) surfaces

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We study the self-diffusion of adatoms on metal fcc(100) surfaces by molecular dynamics with Pt and Ag as examples. The metals are modeled by surface embedded-atom potentials. Besides the well-known exchange diffusion mechanism, another one that appears as the diffusion of an ad-dimer is also observed, and it can be explained by the ''concerted motion'' model owing to the strong bonds formed in the transition state. The important point is that this mechanism could appear frequently even at room temperature and makes adatoms more movable on fcc(100) surfaces. [S0163-1829(98)01423-4]

The mechanism for self-diffusion of an adatom on a metal surface is of fundamental important in processes such as crystal growth and epitaxy. A lot of theoretical and experimental work has been done in the last few years, and many different diffusion mechanisms were found on fcc(100) surfaces.[1–6] The bridge-hopping mechanism is one of the main diffusion mechanisms,[1] in which an adatom hops from a fourfold hollow site to an adjacent one over the intervening twofold bridge site. Another one is the so-called exchange mechanism, where an adatom moves to the position of a surface atom that becomes an adatom at the next-nearest binding site. This interesting mechanism is suggested according to experimental observation by field-ion microscopy (FIM) and the first-principle calculation,[3–5] and is explained by a ''concerted motion'' model. The transition state for this model is an ad-dimer symmetrically located above a surface site vacated by one of the dimer atoms. Besides these two main diffusion mechanisms, it was found that the adatom could migrate by another complicated mechanism, such as the two-step exchange mechanism, the multiparticle exchange mechanism,[6,7] etc., which are found by the method of molecular dynamics (MD). MD simulation is often used to study the self-diffusion because it is capable of giving the actual trajectories of the atoms. Nevertheless, the results obtained from MD, especially quantitative results such as active energy, jump frequency of the various diffusion mechanisms, etc., are sometimes not in accordance with the fact due to the improper potential model used, so that the choice of the potential is crucial.[8] Considering this fact, in the present paper, several potentials with different parameters are used, and the study is focused on the diffusion mechanism itself and analyzing why and when the mechanism we observed could happen, etc. This avoids the influence of the inexact potential on our conclusion.

The potentials used in our simulation are obtained by the surface embedded-atom method (SEAM),[9] which is developed from the conventional embedded-atom method (EAM) for the surface environment. Therefore, the SEAM potentials could give much improved surface properties comparing with the conventional EAM potentials overall. This kind of potential has successfully described the early film deposition and the surface reconstructions.[10,11] To the self-diffusion studied here, the results given below show that the trend of the SEAM potential modifying from the conventional EAM potential at least is correct.

The system in our simulation consists of a (100) slab of the thickness of 30 layers, each layer containing 8×8 atoms; periodic boundary conditions are imposed in the surface plane. One adatom is placed on each surface. The solution of the equations of motions is achieved by the standard Verlet algorithm, with a time step 0.004 ps to ensure the total energy fluctuation less than 1.0×10^{-4}.

Several SEAM potentials $\mathcal{V}_1$, $\mathcal{V}_2$, and $\mathcal{V}_3$ given in Ref. 9 are used in the simulation for platinum. The diffusion mechanisms we observed with these potentials, however, are consistent. One is the conventional exchange mechanism mentioned above. An adatom absorbed in a fourfold site [Fig. 1(a)] interacts with a surface atom and causes it to emerge from the surface plane [Fig. 1(b)], i.e., two atoms as a dimer are now located above the surface site. After this intermediate state [Fig. 1(b)], the adatom moves to the position of the surface atom, which becomes an adatom at the next-nearest binding site [Fig. 1(c)]. This is the exchange diffusion event on fcc(100) surfaces suggested by Feibelman.[3] Another mechanism is very special, because it is in fact a diffusion mechanism for the ad-dimer, i.e., for the

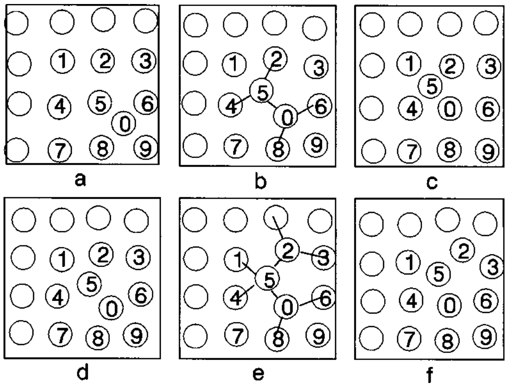

FIG. 1. The diffusion events by the conventional exchange mechanism $a\rightarrow b\rightarrow c$ and the ad-dimer exchange mechanism $d\rightarrow e\rightarrow f$, respectively, at temperature 300 K. The time sequence for the ad-dimer exchange mechanism is 0 ps $(d)\rightarrow$0.96 ps $(e)\rightarrow$1.44 ps (f).

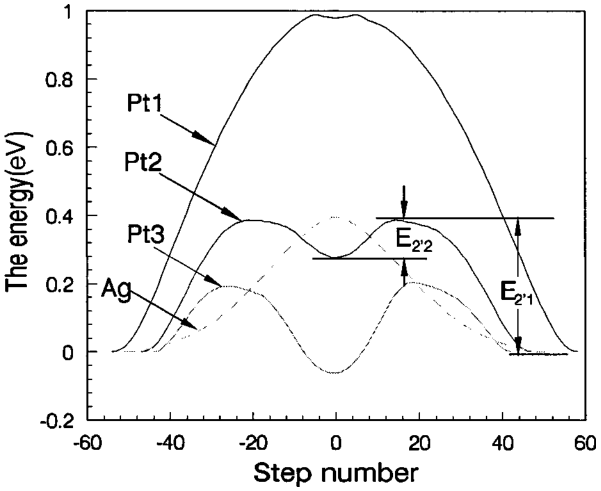

FIG. 2. The variation of the energy for the conventional exchange mechanism. Curves Pt1, Pt2, and Pt3 are for platinum with the SEAM potential $\mathcal{V}_1$, $\mathcal{V}_2$, and $\mathcal{V}_3$, respectively. The parameters are Pt1: $E_{2'1}=0.989$ eV, $E_{2'2}=0.01$ eV; Pt2: $E_{2'1}=0.387$ eV, $E_{2'2}=0.110$ eV; Pt3: $E_{2'1}=0.193$ eV, $E_{2'2}=0.225$ eV; Ag: $E_{2'1}=E_{21}=0.396$ eV.

intermediate configuration [Fig. 1(b)] of the conventional exchange mechanism. In Figs. 1(d)–1(f) we give such a diffusion process at temperature 300 K. After the dimer transition state [Fig. 1(d)], the surface atom 5 is not replaced by the adatom 0 as shown in Figs. 1(b) and 1(c), but interacts with the other surface atom 2 and also causes it to rise, as shown in Fig. 1(e). The three atoms comprising an ad-trimer 0-5-2 are now located above the surface site. This configuration is a transition state, and then the adatom 0 enters into the surface and simultaneously two others form another dimer at the nearest site [Fig. 1(f)], i.e., the dimer is transported by this exchange mechanism. It is very interesting and helpful to note that these two exchange mechanisms have good agreement. The conventional one [Figs. 1(a)–1(c)] is for adatom migration, and the transition state is an ad-dimer configuration that is the result of a concerted motion of the exchange atoms, while the new exchange mechanism [Figs. 1(d)–1(f)] is for ad-dimer migration, and the transition state is an ad-trimer configuration that is the result of a concerted motion of the three atoms. Moreover, the contribution from these two mechanisms to the transportation of the adatom as shown in Fig. 1 is the same. Owing to this fact, we regarded it as a mechanism for adatom diffusing.

To study this diffusion mechanism further, the energies of the different states are calculated by the standard approach: Choose and change a certain freedom according to the reaction path, then at each fixed increment of this freedom fully relax all the other freedoms of the active atoms. In our calculation for conventional exchange mechanism, the fixed freedom is the distance d_{59} of atoms 5 and 9 (or atoms 0 and 1, d_{01}) projected on the surface plane. To get a smooth curve, we first increase d_{59}, then decrease d_{01} after the ad-dimer state [Fig. 1(b)] step by step. In Fig. 2, the curves Pt1, Pt2, and Pt3 are calculated with the SEAM potentials $\mathcal{V}_1$, $\mathcal{V}_2$, and $\mathcal{V}_3$, respectively. Curves Pt1 and Pt2 indicate the local stability of the ad-dimer transition state, which is possible for the exchange mechanism on fcc(100) and (110) surfaces.[8,12,13] From this fact, the exchange mechanism shown in Figs. 1(d)–1(f) is not very surprising, because it is in fact a transition from the one local stable state to the other. Curve Pt3 indicates that the energy of the ad-dimer state is lower than that of the initial state Fig. 1(a). Therefore, as observed in MD simulation, the new diffusion event occurs more frequently than the conventional one. The difference of the energy curves Pt1, Pt2, and Pt3 directly comes from the different potentials $\mathcal{V}_1$, $\mathcal{V}_2$, and $\mathcal{V}_3$ used, which are obtained by modifying the conventional EAM potential more and more.[9] It means the potential $\mathcal{V}_1$ is more close to the conventional EAM potential, and as expected, the active energies of the conventional exchange mechanism from these two kind of potentials, 0.989 eV ($\mathcal{V}_1$) and 0.865 eV (with the EAM potential developed by Oh and Johnson[14]), are similar, which are all higher than the value 0.47 eV±0.1 eV obtained from the experiment.[4,15] Comparing with the conventional EAM potential and $\mathcal{V}_1$, the other two SEAM potentials $\mathcal{V}_2$ and $\mathcal{V}_3$ could give much improved surface properties overall.[9] But the active energy with the potential $\mathcal{V}_3$ seems also improper. Different from the EAM potential (or the SEAM potential $\mathcal{V}_1$), however, the $\mathcal{V}_3$ underestimates the active energy of the conventional exchange mechanism. This fact indicates that the potential $\mathcal{V}_2$, whose difference from the EAM potential is greater than $\mathcal{V}_1$ but less than $\mathcal{V}_3$, should give a reasonable result. From curve Pt2 in Fig. 2, the active energy can be estimated by the following consideration. When $KT \ll E_{2'2}=E_{2'}-E_2$, where E_2 is the energy of the ad-dimer state, $E_{2'}$ is the energy of a transition state between the initial state Fig. 1(a) and the ad-dimer state, the jump process Figs. 1(a) and 1(b) is not relative to the process Figs. 1(b) and 1(c),[16] and then the energy $E_{2'1}=E_{2'}-E_1=0.387$ eV can be approximately regarded as the active energy, where E_1 is the energy of the initial state Fig. 1(a); when $KT \not\ll E_{2'2}$, however, the two processes Figs. 1(a) and 1(b) and Figs. 1(b) and 1(c) could be relative, and the effective active energy can be estimated by $E_{2'1}+E_{2'2}=0.497$ eV.[17] In the experiment,[4,15] $T=175$ K, i.e., $E_{2'2}/KT \approx 7$. At this temperature, the active energy is about 0.387 eV to 0.497 eV, which is in good agreement with the experimental result (0.47 eV± 0.1 eV). So the SEAM potential $\mathcal{V}_2$ is more reasonable for describing the self-diffusion on the Pt(100) surface. To get the energy E_3 of the ad-trimer transition state of the ad-dimer exchange mechanism, one fixed freedom in the relaxation process is the height of atom 0 and 2, i.e., $z(0)=z(2)$ according to the symmetry of this ad-trimer configuration Fig. 1(e). With the potential $\mathcal{V}_2$, the energy difference $E_{32}=E_3-E_2=0.183$ eV.

If the exchange process Figs. 1(d)–1(f) is an independent diffusion mechanism as we expect, then it could happen when the system surmounts the potential barrier E_{32} from the ad-dimer intermediate state; another possible path is that the system overcomes the barrier $E_{2'2}$ to complete an old exchange diffusion event. From the standard result of the transition state theory, the jump frequency ratio of the ad-dimer exchange mechanism to the old one then can be written as

$$\eta=\frac{\Gamma_0}{\Gamma_0^{\mathrm{old}}}e^{-\Delta E/KT}, \tag{1}$$

where the preexponential factor $\Gamma_0=n\nu_0$, n is the number of jump directions, ν_0 is so-called "attempt frequency," $n=2$ for the old exchange mechanism, $n=4$ for the ad-dimer ex-

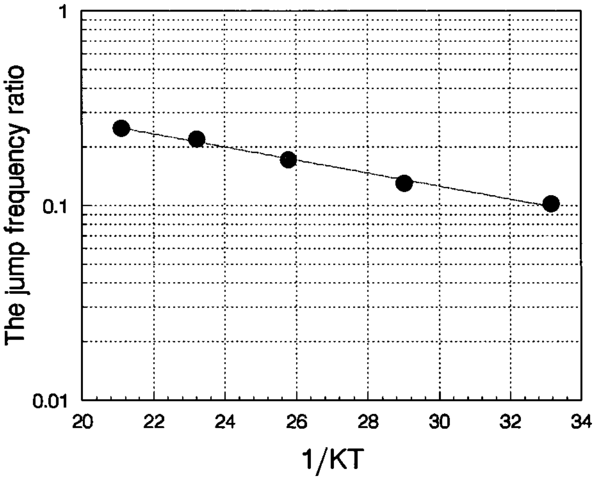

FIG. 3. The jump frequency ratio η as a function of $1/KT$.

change mechanism and then the ratio $\Gamma_0/\Gamma_0^{\mathrm{old}}=2(\nu_0/\nu_0^{\mathrm{old}})$. The energy difference $\Delta E=E_{32}-E_{2'2}$. Using MD with the potential $\mathcal{V}_2$, we simulate a smaller system that contains 16 atomic layers with 6×6 each owing to the limited capability of our computer. This makes parameters $E_{32},E_{2'2}$ change from 0.183 eV and 0.110 eV to 0.179 eV and 0.090 eV, respectively (then $\Delta E=0.088$ eV), but it does not affect the law Eq. (1) that we want to verify. In the simulation, many different ad-dimer transition states that are equilibrated at the same desired temperature are used as the initial condition, and then the number of times the system leaves the ad-dimer state by the ad-dimer and old exchange mechanism, respectively, can be obtained. The statistic results at temperatures 350 K to 550 K are shown in Fig. 3, from which the energy difference ΔE is 0.078 eV, which is basically in agreement with the result 0.088 eV obtained by the relaxation approach, the ratio $\Gamma_0/\Gamma_0^{\mathrm{old}}\approx 1.35$, and then $\nu_0/\nu_0^{\mathrm{old}}=0.68$. So our statistic results indicate that Eq. (1) is correct, or in other words, the jump frequency Γ from the ad-dimer state should be expressed by $\Gamma=\Gamma_0 e^{-E_{32}/KT}+\Gamma_0^{\mathrm{old}}e^{-E_{2'2}/KT}$, which is obviously different from $\Gamma=\Gamma_0^{\mathrm{old}}e^{-E_{2'2}/KT}$ if there is only one kind of old exchange mechanism. Therefore, the process Figs. 1(d)–1(f) as another reaction path indeed exists, and the contribution from this ad-dimer exchange mechanism to the self-diffusion, can reach about 10% comparing with that from the old one at temperature 350 K as shown in Fig. 3.

As mentioned before, two exchange mechanisms have good agreement, in which the intermediate states Fig. 1(b) and Fig. 1(e) are formed identically by extracting a substrate atom from the surface plane, it in fact indicates that the reasons why the ad-dimer exchange mechanism occurs are similar to that for the old one. Based on the first-principle calculation for Al,[3] Feibelman suggested that a substrate Al atom could be extracted from the surface plane to lead replacement diffusion when the price of the extracting can be largely recouped by the formation of shorter, stronger covalent bonds, as shown in Fig. 1(b) comparing with that in metallic form. This condition or reason for the old exchange mechanism occurring does not depend strictly on trivalency as mentioned in Ref. 3, although the calculation is for the trivalent Al. With the SEAM potential $\mathcal{V}_2$, we obtain the bond lengths $d_{06}=2.46$ Å and $d_{05}=2.48$ Å in Fig. 1(b), and $d_{08}=2.48$ Å, $d_{06}=2.51$ Å, $d_{05}=2.49$ Å, and $d_{45}=2.57$ Å in Fig. 1(e), which are all shorter than nearest-neighbor spacing 2.77 Å. This fact and the low-energy differences $E_{21}=E_2-E_1=0.278$ eV and $E_{32}=0.183$ eV show that the formation of the stronger covalent bonds is possible for Pt,[4] and then indicates that such an explanation suggested with Al is also effective for both old and ad-dimer exchange mechanisms observed on the Pt(100) surface. Another point worth noting is the relation of the two diffusion mechanisms. The ad-dimer exchange mechanism is in fact for the diffusing ad-dimer configuration, so there are more chances for it occurring when the ad-dimer state is more stable. Overall, the ad-dimer state is more stable and the covalent bonds formed in the ad-dimer state are more strong. In addition, the strong bonds mean that small energies are needed for extracting the substrate atoms from the surface plane. Therefore, the key for the ad-dimer exchange mechanism occurring is the stronger bonds formed in the transition states. It is basically in accordance with that for the old one except that the strength of the bonds for the ad-dimer exchange mechanism needs to be greater. This consistency is conformed by our MD simulation for the two different extreme cases. One is platinum, the strong bonds cause the ad-dimer configuration to be a local stable state as shown in Fig. 2, and the two mechanisms all occur. The opposite extreme case is one in which the bonds formed in the transition state are weak, and it usually makes the ad-dimer state unstable. The energy curve for Ag, for example, is shown in Fig. 2. At this time, as observed in MD simulation, the exchange mechanism is no longer an only mechanism for adatom diffusion; the hopping mechanism could appear frequently. Moreover, our observation indicates that most of the exchange diffusion events are more likely the two-step exchange mechanism suggested by Black[6] instead of the conventional exchange mechanism, i.e., the concerted motion between the exchange atoms is less due to the weak bonds (if they exist) in the ad-dimer state, and then, as expected, the ad-dimer exchange mechanism is absent. As a substitute, however, the multiparticle exchange mechanism described in Refs. 6 and 7 occurs at higher temperature. The occurrence of these complicated exchange mechanisms including the two-step exchange is possible when the bonds formed in the ad-dimer state are not very strong, and they are explained by the ''strain induced and relieved'' model.[6] Then the conclusion is that the old and ad-dimer exchange mechanisms are likely to occur when the bonds formed in the transitions state are strong enough and can be explained by the ''concerted motion'' model; when the bonds are weak, however, the two-step exchange and the multiparticle exchange mechanisms could appear and can be explained by the ''strain induced and relieved'' model, while the jump frequency of the old and ad-dimer exchange mechanisms is decreasing or vanishing, especially for the ad-dimer exchange one. This general variation for the conventional and ad-dimer exchange mechanisms with the bond strength is similar to that for hopping and conventional exchange mechanisms discussed in Ref. 18.

In conclusion, another diffusion mechanism is found by the method of molecular dynamics with the SEAM potentials. By this exchange mechanism the ad-dimer configuration that is the intermediate state of the conventional exchange mechanism could diffuse on fcc(100) surface. Similar to the conventional exchange mechanism, the occurrence of this mechanism also can be attributed to the stronger bonds formed in the transition state. Therefore, as we observed in MD simulation, this diffusion mechanism could also appear when the condition is highly advantageous to the old one, i.e., in this case, the contribution to the adatom diffusing not only comes from the preferred old mechanism as we imagined before, but also from this ad-dimer exchange mechanism. More important is that the contribution of this diffusion mechanism could be large even in room temperature.

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