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Molecular-dynamics study of self-diffusion: Iridium dimers on iridium surfaces

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Using a molecular-dynamics simulation, we have investigated the mechanisms of single dimer self-diffusion on the (111), (001), and (110) surfaces of fcc iridium. We use a realistic many-body potential, namely, the Rosato-Guillope-Legrand model potential, which involves empirical fittings of bulk properties of the solid. On the (001) and (110) surfaces, evidence of atomic diffusion by exchange mechanisms of the dimer atoms with substrate atoms are found. This is in good agreement with field-ion microscope observations. In addition, a preliminary investigation of the mechanisms of self-diffusion of iridium trimer on the (110) plane has also been carried out.

I. INTRODUCTION

The migration of individual atoms or clusters self-adsorbed on their own crystal surface is of great interest.[1-4] An important experimental tool for investigating surface diffusion is the field-ion microscope (FIM),[5-8] since it is capable of resolving individual metal atoms on metal substrates. In general, FIM experiments determine the diffusion constants of single adatoms at several temperatures and fit the results to a general Arrhenius form. Nevertheless, experimental measurements of self-diffusion have been restricted to the following metals: platinum,[9,10] rhodium,[11] nickel,[12] tungsten,[13-18] and iridium[19-29] due to the high field needed for the imaging. In parallel efforts, a number of theoretical studies were also performed by Tully, Gilmer, and Shugard,[30] Liu *et al.*,[31] McDowell and co-workers[32-36] Feibelman,[37] and Kellogg and Feibelman.[38]

Due to the periodic arrangement of the substrate atoms, adsorbed atoms experience a periodic potential along the surface. Based on the hard-sphere model of the surface, the adatoms are expected to jump along the direction of the least corrugation height. From the energy point of view, hopping along the directions with the least corrugation height requires passing through bridge sites, where the binding energy is expected to be large and barrier to diffusion correspondingly low. In the conventional picture of surface diffusion on metals, atom migration takes place by a series of displacement over the minima in the potential barrier between adjacent binding sites. Most experimental data are consistent with this intuitive picture. However, there are a few exceptions to this rule. An exception is that on the fcc(001) surface of some metals, surface diffusion proceeds by an exchange mechanism. Recently, motion by diagonal replacement has been observed in self-diffusion of the Ir(001) by Chen and Tsong,[23,24,26,27] and of Pt(001) by Kellogg and Feibelman.[38] A theoretical work on Al(001) by Feibelman[37] finds that on this surface diffusion also occurs by an exchange mechanism. On Pt and Ir(110), diffusion by cross-channel atomic exchange can also occur.[10,25,27,28] Recently, we concluded from a calculation that an exchange mechanism is favorable for the iridium adatom migration on various iridium surfaces.[39] It is of considerable interest to establish conditions which determine whether ordinary hopping or a particular exchange mechanism is preferred in the diffusion of an iridium cluster such as a dimer or trimer on iridium surfaces.

The dynamic processes occurring at a metal surface are governed by adsorbate-adsorbate, adsorbate-substrate, and substrate-substrate potentials. Pair potential forms such as the well-known Morse[40,41] and Lennard-Jones[42,43]-type potentials were popular in describing metallic bonding because of their computational simplicity. These types of potentials were used successfully to treat inert impurities, such as He in metal, but are not applicable to chemically active impurities.[44,45] Moreover, calculations with a Morse potential yielded reasonable values of activation energies for Pt and Rh, but gave a very poor result for Ni.[31,40] It is now known that these two potentials do not properly describe the interactions in bulk metals, since the binding is due to delocalized electrons where nonadditive potentials play an important role. Recently, a significant advancement in the empirical description of interatomic potentials has been made by introducing a many-body (cohesive) term in addition to the pairwise potential,[45-53] which includes the embedded-atom method (EAM),[45,46] the Sutton and Chen[48] potential (i.e., many-body Finnis-Sinclair potential), and the Rosato-Guillope-Legrand[49] potential. In these model potentials, there are two terms. The first term models the effect of the local electronic density, and the second term is a two-body potential which can be fitted as a Morse function (attractive plus repulsive) or an exponential (repulsive) form. Our simulation here is based on the Rosato-Guillope-Legrand model potential.

In this study, self-diffusion on the (001), (110), and (111) surfaces of iridium is examined from a microscopic perspective using molecular-dynamics techniques. Computer simulations are performed on a system of 648 classical atoms confined within a cubic box of fixed volume and subjected to periodic boundary conditions. The time evolution of the ensemble is then followed by an iterative numerical solution of the equations of motion of the system. However, the numerical algorithms used for the solution of the equation of motion require integration step lengths comparable to the time scale of the fastest motion, usually a vibrational period of 10^{-2} ps. While simulation of processes which occur within $1-10^3$ ps is practical, direct simulation of slow events which occur over microseconds or longer is usually prohibitive. In comparison, FIM observations are done under the temperatures where an atomic exchange or hopping occur on a time scale of "second." Therefore, it is imperative to develop procedures for extending the applicability of molecular-dynamics simulations to a longer time scale. In practice, exchange events are termed "infrequent" rather than "slow," since only appropriately energized (i.e., at higher temperatures) the exchange processes probably occur very quickly. Thus all dynamical information about the diffusion can be obtained by running trajectories at the bottleneck (i.e., the top of the potential-energy barrier) and by carrying out short integrations forward in time. Therefore, by working at a higher surface temperature $T=800$ K, we can also investigate the mechanism for dimer diffusion on these surfaces. Finally, we are interested in investigating trimer self-diffusion on the Ir(110) surfaces, but not on the Ir(001) and Ir(111) surfaces. This is due to the complexity of the Ir_3/Ir(001) and Ir(111) systems. Experimentally, diffusion of Ir trimers on the Ir(100) and Ir(111) surfaces has been studied by Chen and Tsong[26] using the FIM technique.

II. COMPUTATIONAL MODEL

Our calculations of the interaction potential and dynamics have been described in detail elsewhere.[39] Therefore, we present only an outline of the calculation.

A. The interaction potential

Let us briefly describe the form of a phenomenological many-body potential, which is a function of atomic positions and a density variable, by means of an appropriate analytic expression. It mimics the forces induced by the electronic system on the atoms. In this approach the total potential energy of an arbitrary arrangement of atoms is given by

$$U_{\mathrm{tot}}=\sum_i U_i \ , \tag{1}$$

which is written as the sum of two terms:

$$U_i=\tfrac{1}{2}\sum_{j\neq i}\phi_{ij}(r_{ij})+F_i(\rho_i) \ , \tag{2}$$

where

$$\rho_i=\sum_{j\neq i} f_j(r_{ij}) \ , \tag{3}$$

where U_{tot} is the total internal energy of an assembly of atoms, U_i is the internal energy associated with atom i, ρ_i is the total electron density at atom i due to the rest of the atoms in the system, $F_i(\rho_i)$ is the energy required to embed the atom i into the local electronic charge density ρ_i, $\phi_{ij}(r_{ij})$ is the conventional two-body central potential between atom i and atom j separated by the distance r_{ij}, and $f_j(r_{ij})$ is the contribution to the electron density at atom i due to atom j. The EAM functions are determined empirically by fitting to a number of measured properties of the solid such as the equilibrium lattice constants, elastic constants, bulk modulus, heat of sublimation, and vacancy formation energy.[45,46] However, the interaction potential used in our calculations was developed by Rosato, Guillope, and Legrand (RGL),[49] Gupta,[50] Guillope and Legrand,[51] and Tomanek and coworkers.[52,53] It is also described as a summation of two terms which are shown in Eq. (2). The first term represents the repulsive pairwise interaction of Born-Mayer type, which is written as

$$\phi_{ij}(r_{ij})=A\exp[-p(r_{ij}/r_0-1)] \ . \tag{4}$$

The second term is an attractive band energy which is described as

$$F_i(\rho_i)=-\left\{\sum_{j\neq i}\xi^2\exp[-2q(r_{ij}/r_0-1)]\right\}^{1/2} \ . \tag{5}$$

In these expressions, ξ is an effective hopping integral, r_{ij} is the distance between atom i and atom j, and r_0 is the first-neighbor distance. The parameters q and p describe the distance dependence of the "effective" hopping integrals and the repulsive pair bonds, respectively, and are related to bulk elastic constants. The parameters A, p, q, and ξ are determined by fitting the experimental values of the cohesive energy, lattice parameter, bulk modulus B, and shear elastic constants C_{44} and $C'=\frac{1}{2}(C_{11}-C_{12})$. Then the following relations can be derived:

$$\xi=\frac{p}{p-q}\frac{E_c}{Z^{1/2}} \ , \tag{6}$$

$$A=\frac{q}{p-q}\frac{E_c}{Z} \ , \tag{7}$$

where Z is the bulk coordination numbers.

B. Dynamic calculations

The evolution of the atoms in time and space is determined by the numerical solution of the classical equations of motion which can be integrated using the "velocity" form of the Verlet algorithm. This standard method was introduced by Allen and Tildesley.[54] Each surface is arranged by stacking between 8, 12, or 9 defect-free square or rectangular atomic layers, and each layer contains 81, 54, or 72 atoms, respectively. Therefore, systems of 648 atoms are considered. Numerical simulations are performed using conventional spherical cutoff, minimum image technique. The cutoff radius is chosen as 14 bohr in the present work. The initial velocity components are assigned from a Maxwellian distribution.[55,56] Periodic boundary conditions are applied in the x and y directions parallel to the surface, but not in the z direction where the motion is free. An adsorbed dimer of the same species as the bulk is then added and allowed to diffuse over the surface. Since the vibration period in simple metals is about 1 ps, the time step for the simulation of this study is chosen to be 0.01 ps. We carry out the calculations by tracing the motion of individual atoms over a time period of 20 ps, which includes three different types of molecular-dynamics (MD) simulations. First, the quenching procedure is started from the unrelaxed positions of atoms on the surface. Due to the interatomic interactions, the surface system is allowed to relax to the minimum-energy configuration. This is accomplished by setting the velocity of each atom to zero whenever the scalar product of the velocity and force becomes negative. This procedure is able to rapidly quench the system into the relaxed zero-temperature structure. After the relaxed structures of the surface are determined, a 5-ps constant-temperature (canonical) equilibrium run is made to ensure that the system is equilibrated at the desired temperature. During this procedure, the atomic velocities are renormalized at every numerical time step so that the mean kinetic energy corresponds to the specified temperature for the first 500 steps. Afterwards, the system is left undisturbed in a 15-ps constant-energy (microcanonical) simulation. In this way no artificial temperature control technique is applied. In the simulation, the total energy fluctuates by less than 0.01%.

III. RESULTS AND DISCUSSIONS

The diffusion of a single adatom on various iridium surfaces has been examined in detail in our earlier study.[39] Here we investigate the mechanisms of surface migration of Ir dimers using a similar method. However, it appears that self-diffusion of an Ir dimer is a more complicated process than that of an Ir atom. Generally speaking, the activation energy of a dimer is slightly higher than that of a single atom, thus dimers migrate more slowly than individual atoms. Also the activation barriers for adatom diffusion on the (001) and (110) surfaces are always larger compared to the diffusion barrier on the (111) surface. As the understanding of atom or cluster self-diffusion on metal surfaces is still limited, it would be interesting to find out how atoms in a small cluster move, by either hopping or exchange, during the migration. In this section we therefore present results from MD simulations of the diffusion of Ir dimers on the Ir(111), (001), and (110) planes. The self-diffusion characteristics for the various planes of the iridium dimers and trimers derived from earlier experiments and this study are summarized in Table I. Possible explanations for the observation of some interesting processes of surface migration are then discussed.

A. Dimer diffusion on the (111) surface

On the (111) surface, there are two relatively shallow but distinct adsorption sites marked *A* and *B* in Fig. 1, corresponding to hcp and fcc stacking, respectively. Based on the observation in our earlier simulation,[39] a jump of the adatom is accomplished when it moves from the hcp sites (bound surface) to the adjacent fcc sites (bound bulk), and then moves to another adjacent surface sites. Wang and Ehrlich[21] find that hcp site is favored in their studies of Ir(111) as the energy with an Ir atom at a surface site is determined to be 0.016 eV lower than for an Ir atom at a bulk site. In our previous work,[39] this value was calculated to be 0.03 eV. Similarly, in this study the energy difference of the dimer between these two sites is calculated to be 0.04 eV. Since these values are extremely small compared to the common chemical binding energy (i.e., several eV), we can conclude with confidence that the iridium dimer has a very small preference for sitting in any adsorption site at the diffusion temperature. This is similar to the case for a single adatom that we found earlier.[39] In this effort, we have found

TABLE I. Arrhenius parameters for atomic self-diffusion.

System	Mechanism	D_0 (cm^2/s)	V_a (eV)	Event No.	Ref.
dimer/iridium					
(111)	hopping across bridge site		0.425		57 (expt)
	hopping across bridge site (intratranslation)		0.341	15	present
	hopping across bridge site (intrarotation)		0.285	22	present
	hopping across bridge site (intertranslation)		0.467	3	present
	hopping over atop site		2.794	0	present
(001)	direct exchange		1.078	39	present
	indirect exchange		1.582	1	present
	hopping across bridge site		2.407	0	present
	hopping over atop site		4.112	0	present
(110)	exchange	$2.6\times10^{-4\pm0.7}$	1.18 ± 0.12		25 (expt)
	exchange		1.268	12	present
	hopping along channel	$3.7\times10^{-5\pm1.3}$	1.05 ± 0.14		25 (expt)
	hopping along channel		1.192	28	present
	hopping across bridge site		3.311	0	present
	hopping over atop site		4.662	0	present
trimer/iridium					
(110)	exchange		1.371	13	present
	hopping along channel		1.303	27	present

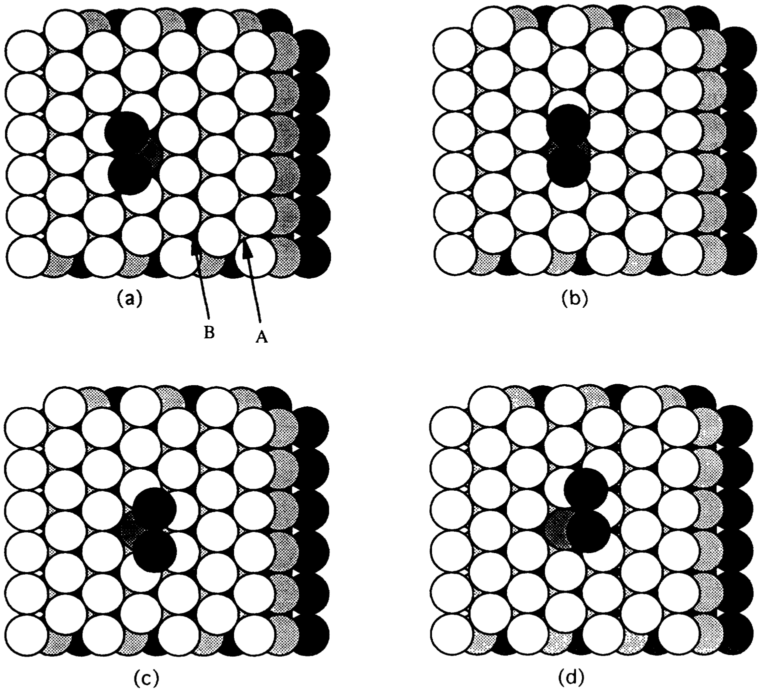

FIG. 1. Movement of iridium dimer on the Ir(111). An Ir dimer moves (a) from a hcp surface site "*A*" to (c) an adjacent fcc bulk site "*B*," and then jumps (d) to another adjacent hcp surface site. The dimer jumps over the bridge site in step (b). The solid circles represent the dimer, and the shaded circle represents a particular lattice atom which is the center of the localized cell. The substrate atom positions are taken at the lattice sites. The diffusion paths [(a)→(b)→(c)] and [(c)→(d)] describe an intracell translation and an intercell translation, respectively.

that there are three types of motions in dimer diffusion: intracell translation, intracell rotation, and intercell translation. These are distinguished by the movement of the dimer around a given lattice atom which is described by a shaded circle near the center of the picture in Figs. 1 and 2. Note that "intracell" means that the movements of the two atoms of the dimer are confined within a cell of six adsorption sites around a given substrate atom. In Fig. 1, a migration path combining an intracell translation [(a)→(b)→(c)] with an intercell translation [(c)→(d)] is shown. In Fig. 2, there are also two types of motions; intracell rotation [(a)→(b)→(c)] and intercell translation [(c)→(d)], involved in this diffusion path. It is interesting to note that the motion of the intracell rotation [Fig. 2(a)→2(b)→2(c)] looks like the dimer has rotated by 60° on the surface. The activation energies of a dimer for intracell translation, intracell rotation, and intercell translation are calculated to be 0.341, 0.285, and 0.467 eV, respectively. The activation energy for intercell motion is slightly higher than that for intracell motion, which reflects that the motions of intracell rotation, and translation would occur more often than that of intercell translation. This is consistent with the FIM result which yields the activation barrier $V_a=0.425$ eV for self-

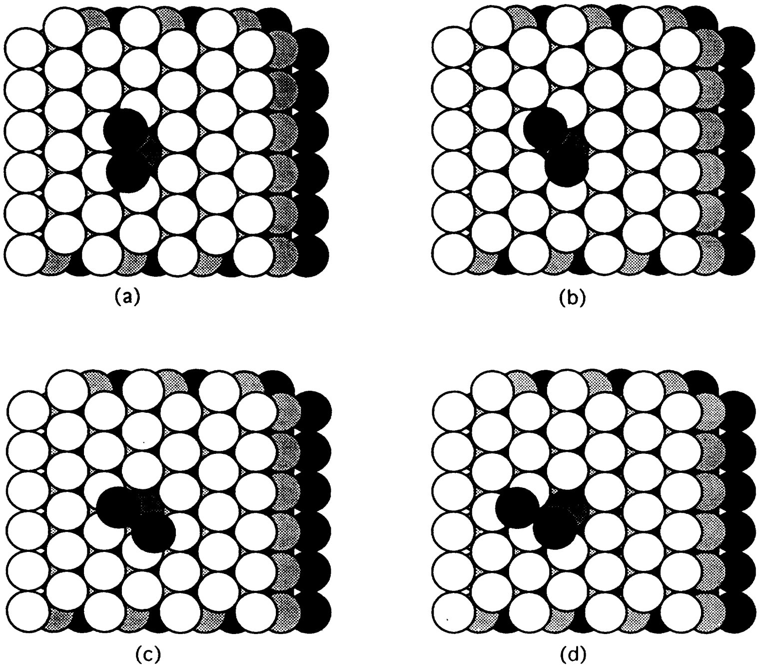

FIG. 2. Movement of the iridium dimer on the Ir(111). An Ir dimer moves (a) from a hcp surface site to (c) an adjacent fcc bulk site, and then jumps (d) to another adjacent hcp surface site. The dimer jumps over the bridge site in step (b). The diffusion paths [(a)→(b)→(c)] and [(c)→(d)] describe an intracell rotation and an intercell translation, respectively.

diffusion of a single dimer on the (111) Ir surface.[57] In the present simulation, there is a total of 40 diffusion events. Fifteen intracell translation events and 22 intracell rotation events are observed, but there are only three intercell translation events. It is then concluded that the motion of intracell rotation may play a crucial role in dimer diffusion because this has the lowest activation energy. Due to the very high activation barrier, none of the events occur by jumping over an atop site (i.e., a site on the top of a substrate atom). Qualitatively, this is in agreement with the FIM results.[57] By examining the whole simulation on this plane, we also find that none of the events involves an exchange of dimer atoms with substrate atoms. This is due to its densely packed structure. The hard fcc (111) surface does not allow the adsorbed atoms to penetrate appreciably into the substrate, so that the dimer should remain well above the surface and is expected to hop easily over the surface.

B. Dimer diffusion on the (001) surface

In general, activation energies for diffusion on the less densely packed (001) planes are higher than for diffusion on the densely packed (111) plane. Roughly speaking, the position of the binding sites can be understood as the places where the adatoms can most easily form bonds with a relatively large number of substrate atoms. The (001) surface of a face-centered-cubic lattice has square symmetry, and each atom has a coordination number of eight with four nearest neighbors in the surface layer. The adsorptions of atom are generally at the fourfold hollow sites. The potential wells associated with the equilibrium sites are deeper than those on the (111) plane, and consequently the adatoms spend a long time in such a site before jumping. Unlike the results obtained for the surface diffusion on (111), the adatom has a relatively low mobility on this plane. In our earlier simulation of single-adatom self-diffusion on the (001) face of iridium,[39] two different migration mechanisms have been demonstrated: (1) the adatom jumps from a fourfold hollow site to an adjacent fourfold hollow site over a twofold bridge site, and (2) the adatom moves into an adjacent lattice site and the surface atom moves to a fourfold hollow site. The energies needed for direct jumps of the adatom across a bridge site and that for the atomic replacement are 1.57 and 0.77 eV, respectively. Therefore, it is found that jumps of the adatom by the second mechanism occur much more often. Experimentally, activation energies of the adatom diffusion are found to be 0.84 eV for the exchange mechanism.[23,24] So far two possible processes for the migration path of dimers on this isotropic surface, a direct exchange mechanism and an indirect exchange mechanism, have been observed. In the first process, shown in Fig. 3, one (i.e., the lower atom) of the dimer atoms pushes a neighboring surface atom out of its position and replaces it, and the displaced surface atom moves to a new fourfold hollow site. This mechanism results in a displacement of the dimer center of mass equal to $a/2\hat{i}+a/2\hat{j}$ were "a" is the nearest-neighbor distance and a rotation of 90° with respect to the dimer axis. In the second process, shown in Fig. 4, one of the dimer atoms hops into an adjacent surface site, and the other one pushes two substrate atoms so as to cause one of them to pop up to the surface. This mechanism results in a center-of-mass displacement of $a/2\hat{i}+3a/2\hat{j}$ and also a rotation of 90°. It is evident in Table I, the activation energy for direct hopping over an atop site of the dimer obtained by static calculations is $V_a=4.112$ eV, and the activation energy for jumps across a bridge site is $V_a=2.407$ eV. For indirect exchange diffusion, it is

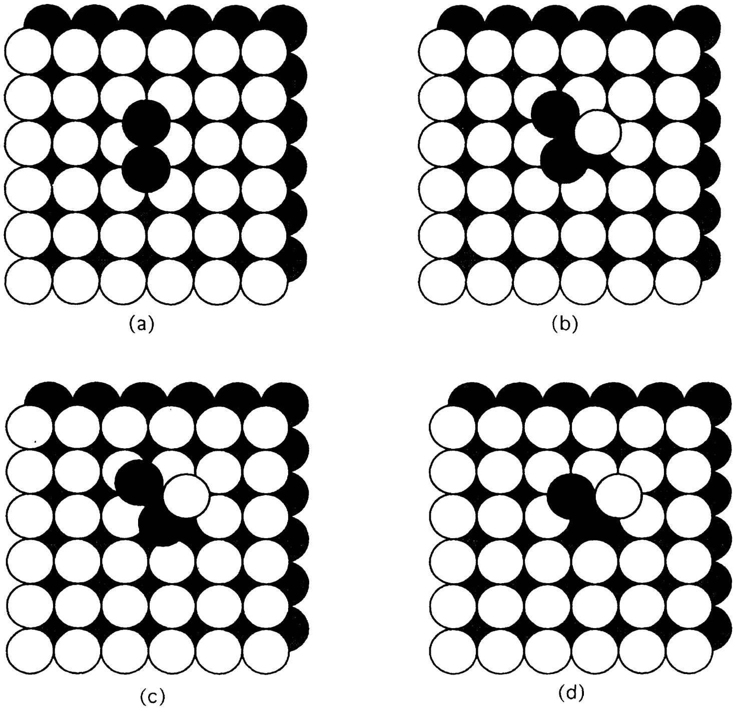

FIG. 3. The diffusion path [(a)→(b)→(c)→(d)] of Ir_2 on the Ir(001) plane by a direct exchange mechanism. The solid circles represent the dimer.

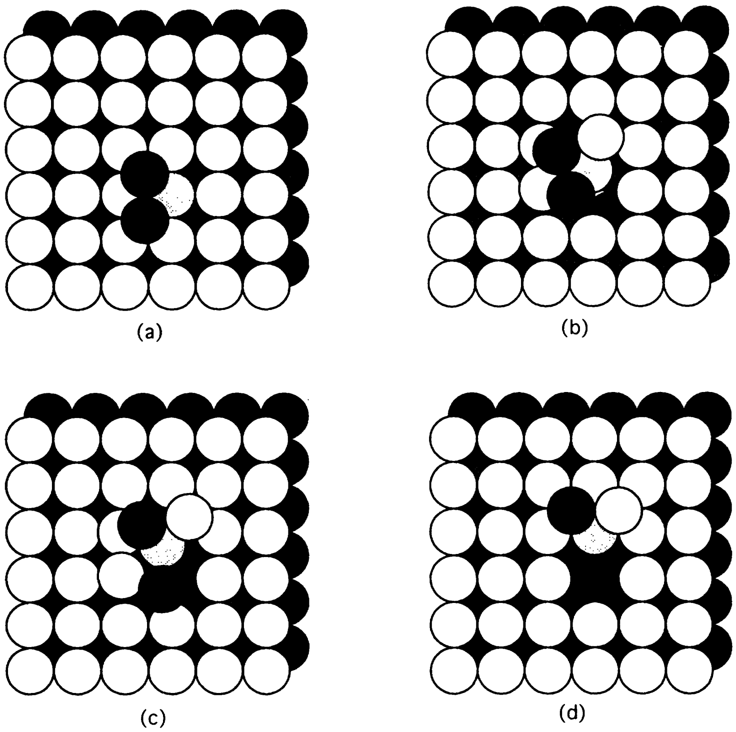

FIG. 4. The diffusion path [(a)→(b)→(c)→(d)] of Ir_2 on the Ir(001) plane by an indirect exchange mechanism. The solid circles represent the dimer.

$V_a = 1.582$ eV (Fig. 4), and for direct exchange diffusions it is $V_a = 1.078$ eV (Fig. 3). It is clear that adsorption on a bridge site or an atop site is highly unlikely due to its unfavorable binding. Based on the data in Table I, we can conclude that the dimer prefers to diffuse by having one of its atoms exchange position with a substrate atom rather than to jump across a bridge site or over an atop site. There are a total of 40 diffusion events in our simulation: none of the events are by jumping across a bridge site or over an atop site, one is an indirect exchange event, and 39 are direct exchange events. These observations are in quantitative agreement with the results from calculations of the activation barriers.

C. Dimer diffusion on the (110) surface

From a conventional picture, migration on the (110) surface is one dimensional. As expected from the atomic arrangement of the surface plane, atoms move only in the direction of the surface channels. In the case of iridium surface, however, there are two types of migration mechanism for the adatom or dimer from the FIM experiments.[23,25] Basically similar behaviors are also found for adatom diffusion in our earlier theoretical simulation:[39] (1) the adatom jumps along the surface channel; and (2) the adatom in one channel replaces a wall atom, with the wall atom moving to the original channel or an adjacent channel. A particularly striking feature of migration of the second kind is that diffusion occurs in the direction perpendicular to the close-packed rows of surface atoms, by an atomic replacement mechanism. The activation energies of adatoms along the surface channels and across the channels by an exchange mechanism are calculated to be 0.83 and 0.75 eV, respectively.[39] In a FIM experiment, the energy needed for an Ir adatom to hop along the atomic channel is found to be 0.80 eV, or 0.09 eV larger than that needed to replace a substrate atom in the cross-channel jump.[23,28] In the present calculation of the dimer case, it is found that an adsorbed dimer in one channel replaces two wall atoms, with two wall atoms moving to an adjacent channel (Fig. 5). Out of a total of 40 events, 12 are by exchange motions. Note that the two atoms of the dimer in exchange diffusion might possibly experience a time lag in reaching the transition state. The dimers can also hop along the surface channel as single adatoms, as shown in Fig. 6. There are 28 events shown in Fig. 6 in which the dimer diffuse by a conventional hopping mechanism. No event of hopping across a channel over a bridge site or an atop site is observed. All these observations can also be explained by a static calculation of the activation energies which are listed in Table I. The activation energies of the dimer diffusion have been found to be $V_a = 1.268$ eV for the exchange mechanism. Also, the activation energies of dimer migration along the surface channels and across the surface channels over a bridge site and an atop site yield $V_a = 1.192$, 3.311, and 4.662 eV, respectively. Since direct cross-channel jumps by dimers requires large activation energies, they do not occur. However, there is only a 0.076-eV difference between the activation barriers for the exchange and hopping along the channel mechanisms. We would therefore expect both mechanisms to be present in FIM experiments at the diffusion temperature, and this was proved to be true. We would also like to point out an interesting aspect here. For a single Ir adatom, diffusion across the channels is easier than along the channels.[27,28,39] In the case of dimers, the along-channel diffusion is slightly easier due to its slightly lower activation behavior. This has been observed experimentally,[25] and our simulations indeed confirm this feature. In order

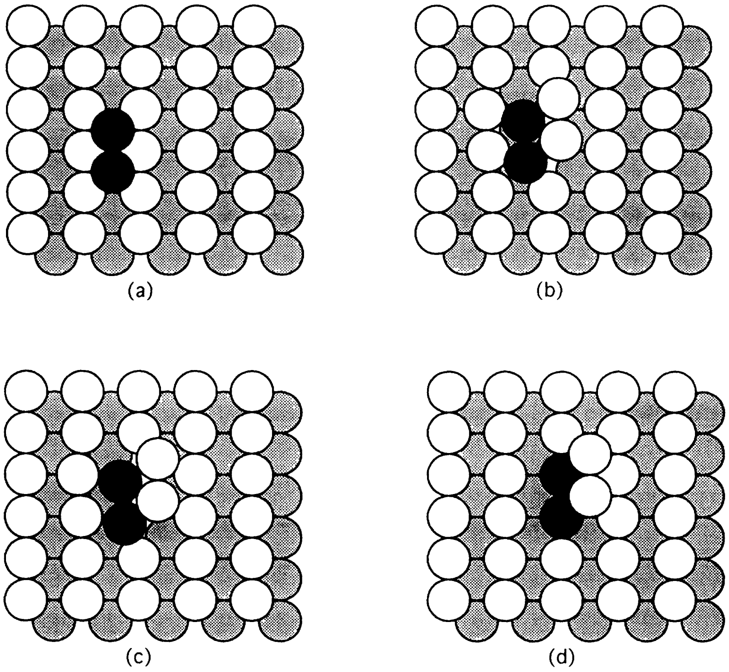

FIG. 5. The diffusion path of Ir_2 on the Ir(110) plane by an exchange mechanism [(a)→(b)→(c)→(d)]. The solid circles represent the dimer.

to learn more about the diffusion behavior of small clusters on this plane, we also calculate the energy barriers for both along-channel and cross-channel diffusion of iridium trimers. As can be seen in Table I, the activation energies of trimers along the atomic channels and across the channels by an atomic replacement mechanism obtained by static computations are $V_a = 1.303$ and 1.371 eV, respectively. This result indicates that a direct jump along the channels is energetically favored over exchange diffusion across the channels, although the difference in the activation barriers is very small. Also, it is not surprising that the tendencies of surface migration of dimers and trimers are quite similar. In the study of the atomic steps involved in the (1×1) to (1×2) reconstruction of the Pt(110), Gao and Tsong[58] find that the [110] atomic rows near the layer edge tend to break up into two to several atom row fragments. These row fragments can move along the surface channels or across the channels of the terrace. Based on their findings, it perhaps allows us to more reasonably interpret the result we obtained for the cross-channel displacement. We would intuitively expect that iridium dimer and trimer diffusion is also in two dimensions in the (110) surface. Furthermore, an important feature was also found in the present simu-

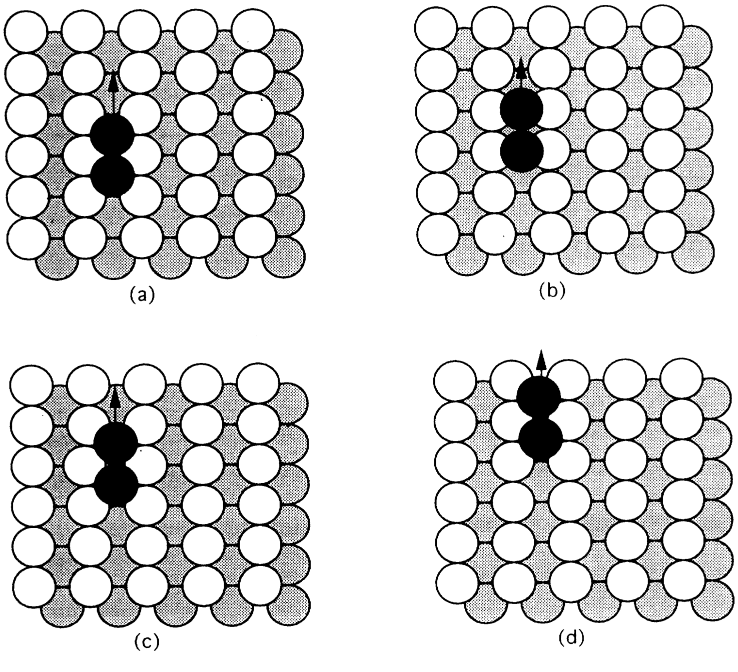

FIG. 6. Surface diffusion of Ir_2 on the Ir(110) plane along the atomic channel [path: (a)→(b)→(c)→(d)]. The arrows show dimer diffusion path, and the solid circles represent the dimer.

lation: the structure with adsorbed dimers/trimers oriented parallel to the atomic rows is far more stable than that oriented perpendicular to the atomic rows.

D. Possible explanations for the mechanisms of atomic exchange

When an atom approaches a surface, it will disturb the local environment of the lattice. Interactions with the substrate cause the neighboring substrate atoms to relax out from their normal lattice positions. The response of the stress pressure is the so-called "strain." It describes the stretches in various directions which causes the deformation. Simply stated, the strain is induced by the approaching atom. This strain can eventually be relieved when the surface atoms pop out of the substrate. It is then concluded that this elastic deformation probably makes the atomic replacement process more favorable. So far our results have confirmed the existence of the exchange mechanism, depending on the strength of the atomic bond (i.e., interatomic potential) and crystal structure. In addition, the kinetic energy of the atoms increases substantially with increasing surface temperature, and this leads in turn to an excitation of the phonons which plays a vital role on the diffusion mechanism. On the (001) and (110) surfaces, looseness of the structure allows broader oscillations of substrate atoms. Thus the possibility of the occasional spontaneous generation of a transition state will be enhanced. It is therefore easy for the adatoms to replace one of the substrate atoms in an exchange process. On the other hand, the "hard" fcc(111) Ir surface does not allow the adatoms to penetrate into the substrate, so that it is very unlikely to find an exchange event.

IV. SUMMARY

The goals of this study are to find out how an adsorbed dimer migrates on crystal planes with different atomic structures at the atomic scale, and to visualize the exchange diffusion steps as clearly as possible. A classical calculation has been performed for the dynamic motion of dimers on metal surfaces using the many-body RGL potential. In this work, we model several specific systems and compare with experimental results. On the (111), self-diffusion of Ir dimers occurs by hopping of dimer atoms, but it is a more complex process than that of single Ir atoms. Dimer diffusion on this plane is found to involve three different types of migration mode: intracell translation, intracell rotation, and intercell translation. On the (001) surface, our calculation finds the activation energy for exchange diffusion to be considerably lower than that by a simple hopping mechanism. This is why diffusion of a dimer by an exchange mechanism should occur much more often than by ordinary hopping. We also note that a displacement of the dimer on this surface is always accompanied by a rotation of 90° with respect to the dimer axis. Similar to FIM experimental observations on the anisotropic (110) surface, atomic motion both along and across the close-packed [110] atomic rows can occur. The cross-channel diffusion takes place mainly by an interesting atomic exchange mechanism. In addition, we have also performed static computations to find the activation energies for diffusion of the dimers on three low index (001), (110), and (111) surfaces. This information can provide enough evidence to explain the atomic events on various planes. Based on our finding from this simulation, we suggest that the replacement mechanism depends strongly on the crystal structure of the surface, the strength of the atomic bond, and the surface temperature. However, further examinations of the dynamics and energetics of small Ir clusters on iridium surfaces should be carried out to clarify the mechanisms of surface migration as well as the atomic steps involved in surface reconstructions.

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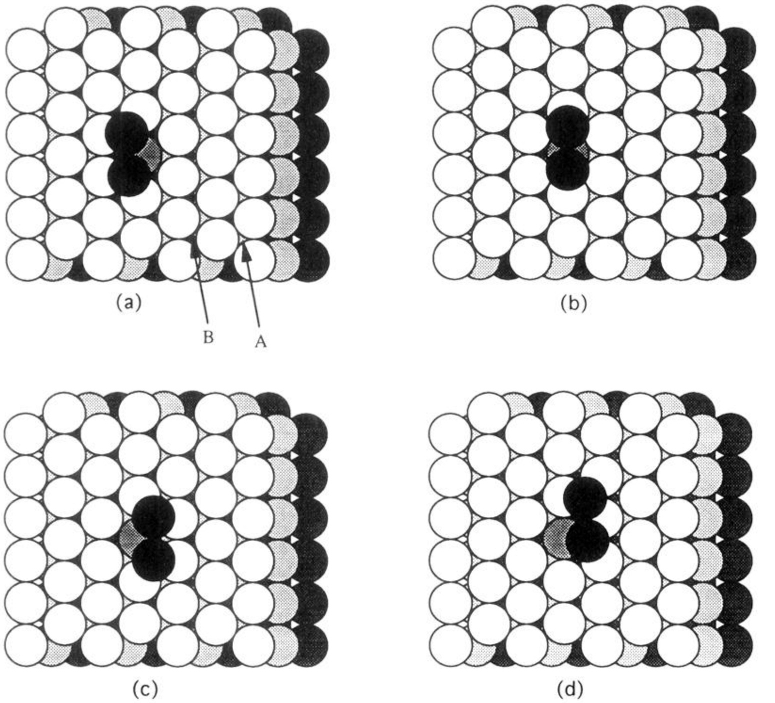

FIG. 1. Movement of iridium dimer on the Ir(111). An Ir dimer moves (a) from a hcp surface site "*A*" to (c) an adjacent fcc bulk site "*B*," and then jumps (d) to another adjacent hcp surface site. The dimer jumps over the bridge site in step (b). The solid circles represent the dimer, and the shaded circle represents a particular lattice atom which is the center of the localized cell. The substrate atom positions are taken at the lattice sites. The diffusion paths [(a)→(b)→(c)] and [(c)→(d)] describe an intracell translation and an intercell translation, respectively.

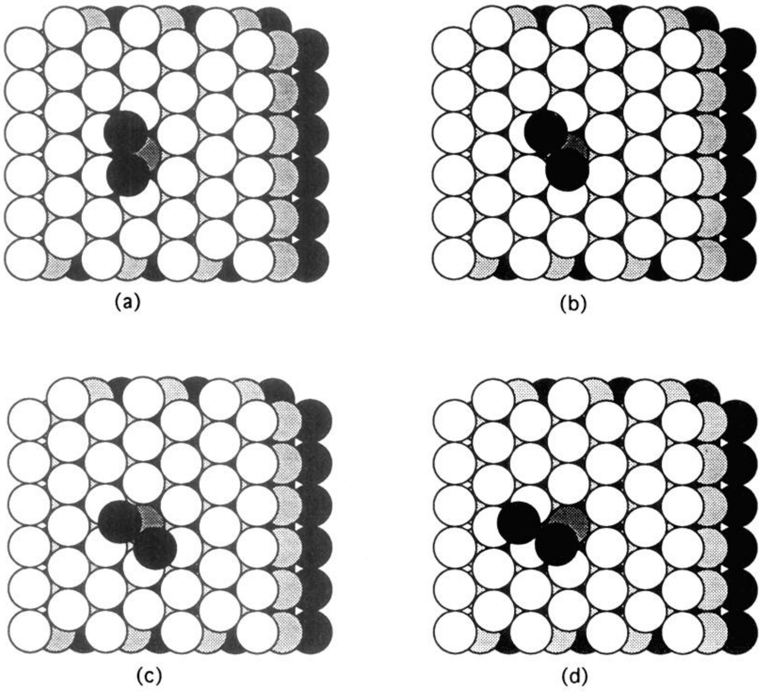

FIG. 2. Movement of the iridium dimer on the Ir(111). An Ir dimer moves (a) from a hcp surface site to (c) an adjacent fcc bulk site, and then jumps (d) to another adjacent hcp surface site. The dimer jumps over the bridge site in step (b). The diffusion paths [(a)→(b)→(c)] and [(c)→(d)] describe an intracell rotation and an intercell translation, respectively.

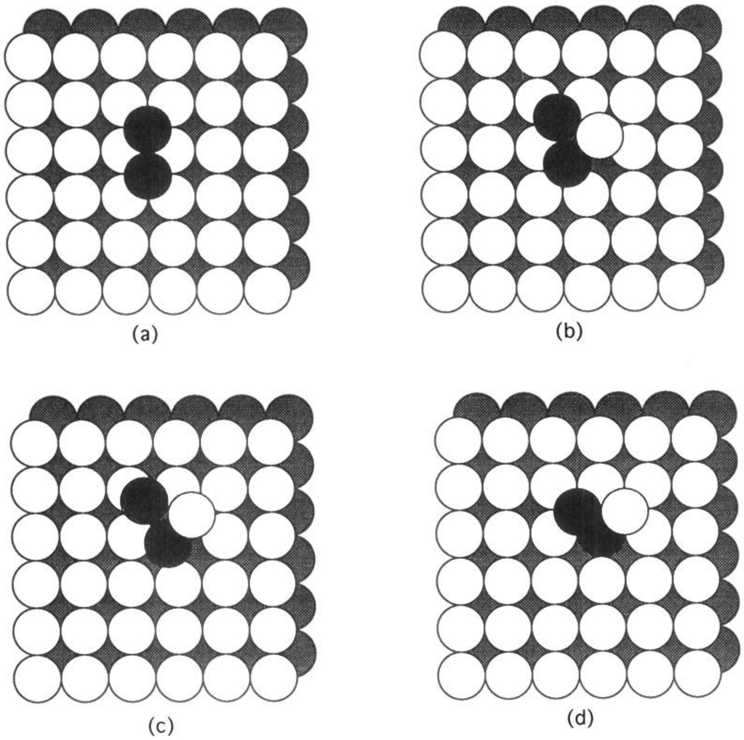
(a) (b) (c) (d)

FIG. 3. The diffusion path [(a)→(b)→(c)→(d)] of Ir_2 on the Ir(001) plane by a direct exchange mechanism. The solid circles represent the dimer.

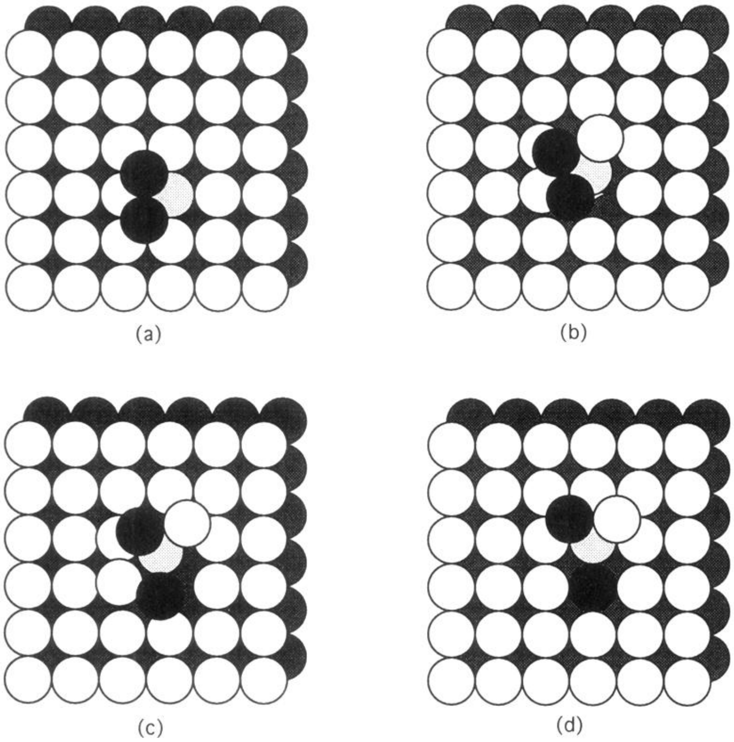

FIG. 4. The diffusion path [(a)→(b)→(c)→(d)] of Ir_2 on the Ir(001) plane by an indirect exchange mechanism. The solid circles represent the dimer.

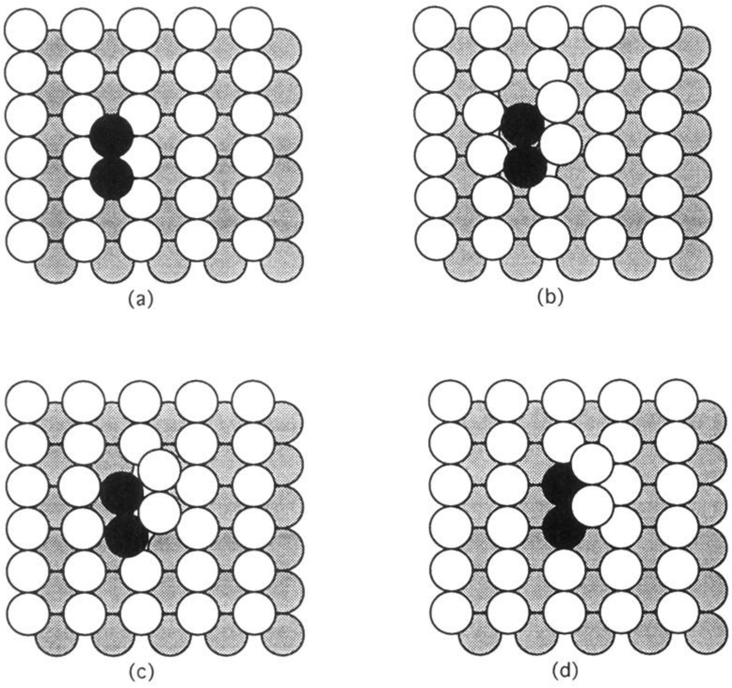

FIG. 5. The diffusion path of Ir_2 on the Ir(110) plane by an exchange mechanism [(a)→(b)→(c)→(d)]. The solid circles represent the dimer.

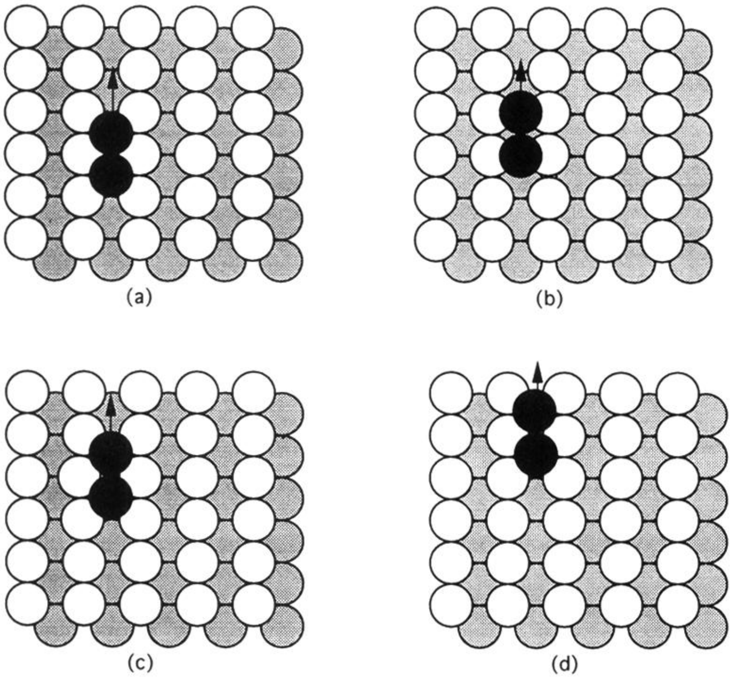

FIG. 6. Surface diffusion of Ir_2 on the Ir(110) plane along the atomic channel [path: (a)→(b)→(c)→(d)]. The arrows show dimer diffusion path, and the solid circles represent the dimer.