PHYSICAL REVIEW B VOLUME 51, NUMBER 8 15 FEBRUARY 1995-II

Energetics and atomic steps in the reconstruction of the Pt(110) plane

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(Received 12 September 1994)

By use of molecular-dynamics simulation, details of the atomic steps involved in the (1×1) to (1×2) reconstruction of the Pt(110) surface are studied. The energetics of these surfaces is also studied and compared with available theoretical and experimental results. The surface atoms are found to rearrange into the missing-row model of the (1×2) reconstructed surface. The reconstruction involves the breaking of the $[1\bar{1}0]$ atomic rows and the spreading of these row fragments by the replacement of the atoms of the top surface layer with the channel-wall atoms of the second surface layer.

The (110) surface of fcc metals contains close-packed atomic rows in the $[1\bar{1}0]$ direction which are separated by a distance of the bulk lattice constant in the [001] direction. This anisotropic surface with highly corrugated structure can undergo a number of interesting structural phase transitions. For instance, surface atoms of the (110) surfaces of the late 5*d* metals Au, Ir and Pt tend to rearrange from the primitive (1×1) structure to the reconstructed (1×2) structure (see Fig. 1).[1–15] Most studies now agree that the (1×2) surface has a missing-row (MR) structure. In this structure, every other $[1\bar{1}0]$ atomic row of the surface layer are missing, thus the size of the unit cell in the [001] direction is double that of the bulk lattice. As indicated by Ho and Bohnen[8] with *ab initio* total-energy calculations, the tendency of Au, Ir, and Pt to reconstruct is related to strong bonding in the 5*d* metals. On the other hand, Daw and Foiles[9,10] pointed out that the missing-row (1×2) structure is lower in energy than the (1×1) structure of the Pt(110) surface.

The field ion microscope (FIM) (Refs. 16–19) is a powerful tool for investigating surface migration, as it is capable of visualizing individual metal atoms on metal surfaces. In the case of the (110) surface of Ir and Pt, two different diffusion mechanisms for the adatom and dimer have been found by FIM experiments[1,2,20–24] and by theoretical simulations.[25,26] They are (1) the adatom (dimer) in one surface channel can replace the channel-wall atom (atoms), with the channel-wall atom (atoms) moving to the original channel or to an adjacent channel; and (2) the adatom (dimer) hops along the surface channel. In a study of the atomic steps involved in the (1×1) to (1×2) reconstructions of Pt(110) and Ir(110), Gao and Tsong[1,2] found that the $[1\bar{1}0]$ atomic rows near the step edge tend to break up into two- to several-atom row fragments. These row fragments can move either across the surface channels or along the channels of the terrace. The interesting finding could provide a good account of adatom motions on the missing-row reconstruction model.

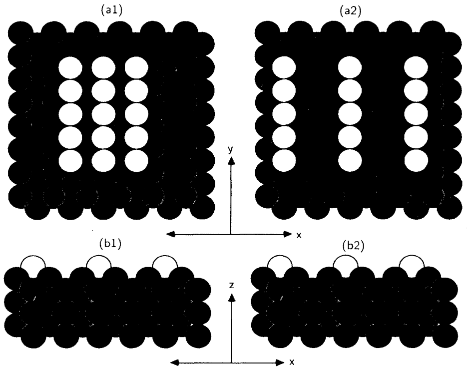

FIG. 1. (a1) and (b1) are top and side views of the Pt{110}-(1×1) structure. (a2) and (b2) are top and side view of the (1×2)-reconstructed Pt(110). The *x*, *y*, and *z* axes are the [001], $[1\bar{1}0]$, and [110] directions.

Although the geometry of the (1×2) phase is understood, the basic mechanism driving the reconstruction is still unknown. It would be interesting to elucidate the microscopic details of how the adatoms and the substrate atoms move during the reconstruction. The goal in this investigation is to obtain the dynamic results which make visualization of the reconstructed processes as clear as possible.

Our calculation of the interaction potential and dynamics has been described in detail elsewhere.[25,26] The surface temperature is taken to be 818 K (i.e., $\frac{2}{5}$ bulk-melting point) in order that a significant atomic motion of surface migration can take place within the short-time period, a nanosecond, practical for molecular-dynamics (MD) simulations. The system contains a slab of nine mobile layers. The top layer consists of 20 atoms, and the rest of the eight layers are made up of 156 atoms per layer with a 12×13 basic cell. There are a total of 132 adsorption sites in the second layer, sufficient for the 20 atoms in the top surface layer to form various superstructures up to the (2×3) size. The usual periodic boundary conditions are utilized in the two directions parallel to the surface plane in order to remove the edge effect, but the motion along the surface normal is unrestricted. The velocity version of the Verlet algorithm with a time step of 0.005 ps (i.e., 5% of the period of the atomic vibration time 10^{-13} s for simple metal systems) is employed for the numerical integration. The initial velocity components are drawn from the Maxwellian distribution at the desired temperature, and the minimum image criterion is applied. The calculations trace the motion of individual atoms over a time period of 1 ns, which includes four basic types of MD simulations. First, the quenching procedure is started from the unrelaxed positions of atoms. Due to the interatomic interactions, the surface system is allowed to relax to the minimum-energy

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configuration. This is accomplished by setting the velocity of each atom to zero whenever the scalar product of the velocity and the force become 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 20-ps canonical equilibration run is made to ensure that the system is equilibrated at the desired temperature. During this procedure, the kinetic temperature of the substrate is controlled to the specified temperature via a scaling of atomic velocities. Afterwards, the system is left undisturbed in a 0.95-ns microcanonical simulation. In this way no artificial temperature control technique is applied, and the total energy fluctuates by less than 0.01%. Lastly, a process of constant rate temperature decrease is employed to ensure that the system is quenched to the room temperature within 30 ps. Such a cooling procedure will allow the system to gradually freeze its space configuration in accordance with thermal deexcitation. The positions of the moving atoms are stabilized by the annihilation of the thermal driving force. This last procedure is needed for comparing the MD simulation result with experimental observations.

Our calculations are performed for a many-body potential, which is a function of atomic positions and the electronic density variable, by means of an appropriate analytic expression. In this approach the energy of an arbitrary arrangement of atoms is generally described by the sum of two terms. The first term is the conventional two-body central potential, and the second term is the energy required to embed the specified atom into the local electronic charge density.[27–30] In our MD simulation, we have adopted the Sutton-Chen potential model, and it has been described in previous work.[25]

FIM observations[1–3,22] and theoretical simulations[22–24] for the Pt(110) surface conclude that both atomic motions along and across the close-packed $[1\bar{1}0]$ rows can occur. In an FIM experiment,[22] the activation energies required for a Pt adatom to migrate along the atomic channels by atomic hopping and across the channels via an exchange mechanism are obtained to be 0.84 and 0.78 eV, respectively. It is more likely for the adatom to migrate across the atomic channels by replacing the channel-wall atoms. In a theoretical EAM study,[23] the adatom favors its diffusion along the atomic channels because the energy required for a Pt adatom to hop along the channel is calculated to be 0.53 eV, which is 0.15 eV lower than that needed to replace a substrate atom in the cross-channel jump. The activation energies we have obtained are summarized in Table I, together with results of FIM experiments as well as earlier theoretical computations. The activation barriers of a Pt adatom during the exchange diffusion across the channel and the hopping along the channel are 1.09 and 1.01 eV, respectively. Since the diffusion path of the adatoms is taken to be only in the diagonal direction of the square unit cell in our static computations, the actual activation barriers should be slightly smaller because of the unrestricted moving paths. Nevertheless, the energy difference of these two barriers is very small of only 0.08 eV. This calculation therefore corroborates that the adatom can diffuse either across the surface channel by exchanging position with the substrate atom, or along the surface channel by atomic hopping, and that the adatom motion is two dimensional. Furthermore, the activation energies required for direct hopping across a bridge site and jumping over an atop site of the adatom obtained by static computations are 1.35 and 1.98 eV, respectively. None of these events can be seen in our simulations.

TABLE I. Activation energies for atomic self-diffusion on the Pt(110) surface.

Surface	Mechanism	Activation energies (eV)	Reference
adatom			
	exchange	0.78	22 (FIM)
	exchange	0.68	23 (EAM)
	exchange	1.97	22 (Morse)
	exchange	1.34	24 (L-J)
	exchange	1.09	present study
	hopping along surface channel	0.84	22 (FIM)
	hopping along surface channel	0.53	23 (EAM)
	hopping along surface channel	0.64	22 (Morse)
	hopping along surface channel	1.26	24 (L-J)
	hopping along surface channel	1.01	present study
	jumping across bridge site	1.35	present study
	jumping over atop site	1.98	present study
dimer			
	exchange	1.58	present study
	hopping along surface channel	1.43	present study
trimer			
	exchange	2.17	present study
	hopping along surface channel	1.94	present study

The stability of a surface structure can be studied by examining the energetics associated with this particular geometry. We apply the energy minimization technique to the (1×1)- and (1×2)-reconstructed structures. Our result shows that the total energy per atom of the relaxed system with the (1×2) structure is 0.27 meV/atom lower than that with the (1×1) structure. It indicates that the reconstructed (1×2) structure is more stable than the (1×1) structure. In a parallel effort, the surface energies of both the (1×1) structure and the reconstructed (1×2) missing-row structure are calculated to be 26.77 and 26.12 meV/a^2, respectively, where a is a bohr. The (1×2) missing-row surface is lower in energy by 0.65 meV/a^2. It is notable that the value of the surface-energy difference, 0.59 meV/a^2, determined by EAM is close to the present value.[10] These same energetic features are primarily due to the possibility of a larger coordination number of the atoms on the more open reconstructed surface.

The results of our MD dynamic calculations from three different simulation runs are shown in Fig. 2. The top layers in all these simulation runs, except for a few scattered atoms, end up with the missing-row (1×2) structure. At the final stages of these simulation runs, we can see the pattern of a reconstructed (1×2) structure even though they are not 100% complete. The reconstructions are seen to involve the breaking of $[1\bar{1}0]$ atomic rows into one- to a few-atom clusters. Some of the single atoms of the top layer delve into the surface. Some substrate atoms of the second layer are then pushed to float on top of the surface channel. The process of this exchange mechanism is illustrated by diffusion path (a1→a2→a3) in Fig. 3. Note that this interesting event was also observed by Lynden-Bell on the (100) face of platinum.[30] Occasionally, two adatoms are also found to penetrate simultaneously by displacing two substrate atoms, while these two-channel wall atoms climb up to the next surface channel. Besides these, a number of unexpected very interesting diffusion processes are also observed. The first unexpected finding is defined as the three-atom process. In this process, the first diffusion path we observed is that one of the two adatoms exerts pressure on a nearest-neighbor channel-wall atom of the second layer and replaces it. The replaced wall atom then floats into another adsorption site in the next atomic channel. The original site of the exchanging adatom is then filled by the other adatom. This process can be seen in path (b1→b2→b3) in Fig. 3, and we refer it as an *AAS* process. Here, *A* and *S* denote adsorbate and substrate atoms, respectively. The second unexpected path in this process is that an adatom enters the substrate and pushes two neighboring channel-wall atoms so as to cause the distant one to pop up to the surface to become another adatom. The near one, where the original adatom takes its site, then moves into the distant substrate site. This movement is displayed in path (c1→c2→c3) in Fig. 3 by an *ASS* process. The second observation is the four-atom process. In this case, an adatom pushes a neighboring channel-wall atom, and it is knocked into an adsorption site in an adjacent channel. This squeezed atom then pushes two adatoms into the next surface channel, where they end up as a small chain of three atoms. This mechanism is called *ASAA*, and is illustrated by path (a1→a2→a3) in Fig. 4. Another example in this process is shown by path (b1→b2→b3) in Fig. 4 by *ASAS*, where an adatom delves into the surface and exchanges an adjacent channel-wall atom of the second layer. The lifted wall atom will float on top of the surface trough and push another adatom at the next atomic channel. By repeating the same procedure, the repelled adatom then sinks into the surface and forces another channel wall atom to take a different adsorption site in the second to the next surface channel. In this movement, all the atomic motions take place via an exchange mechanism between adatoms and the channel-wall atoms. The migration of the adatoms occurs only in the manner of crossing the surface channels (i.e., double crossing of three surface channels in all). The third interesting finding is called the five-atom process. In this event, an adatom enters the substrate and pushes a neighboring channel-wall atom, then this wall atom is forced to jump up to the next surface channel. This displaced wall atom then presses two adatoms into the next surface channel, while one of them will push another channel-wall atom and cause it to pop up back to the original surface channel. This mechanism is called *ASAAS*, and is illustrated

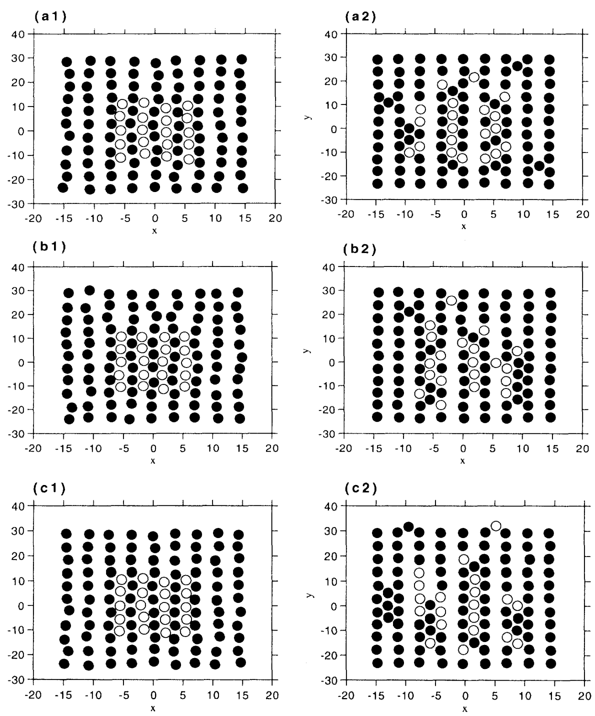

FIG. 2. Snapshots of the top view in the surface reconstruction of the Pt(110) plane. There are three MD simulation runs: (a1→a2), (b1→b2), and (c1→c2). The positions of the atomic images at the beginning are displayed in (a1), (b1), and (c1), and the final atomic configurations are shown in (a2), (b2), and (c2). The empty and solid circles represent atoms of the first and second layers in the initial states, respectively.

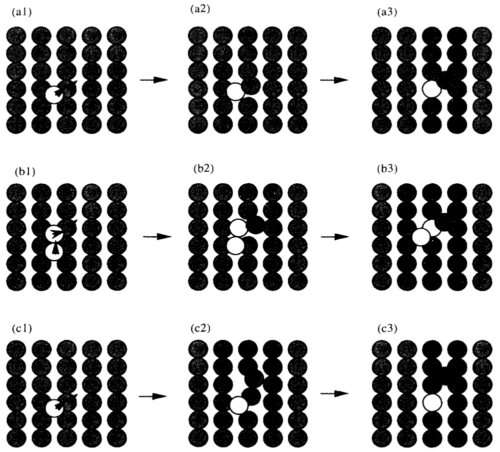

FIG. 3. Illustration of three diffusion processes a, b, and c. The first process (a1→a2→a3) represents the simple exchange process. The second and third processes (b1→b2→b3) and (c1→c2→c3) involve three atoms.

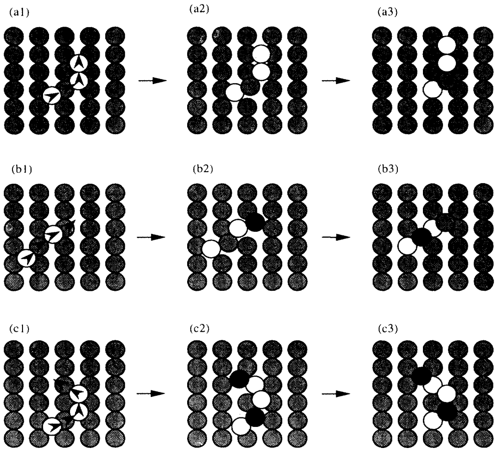

FIG. 4. Three observed diffusion process a, b, and c involving four to five atoms. The first and second processes (a1→a2→a3) and (b1→b2→b3) are the diffusion processes involving four atoms. The third one, (c1→c2→c3), is a five-atom process.

by path (c1→c2→c3) in Fig. 4. There may be even more complicated atomic processes involving many more atoms, but they occur very infrequently.

Several conclusions can be made from this MD simulation study.

(1) The atomic processes involved in the (1×1) to (1×2) surface reconstruction of the Pt(110) surface are much more complicated and varied than those concluded from FIM experiments, where only time-lapse images can be obtained even though, by using a pulsed laser technique, the time period can be as short as a few nanoseconds.

(2) The result of the energetic study of the surface structures is in agreement with the result of the dynamic simulation. As suggested by Figs. 2–4, interlayer and cross-channel diffusions via the atomic replacement mechanism play a crucial role in the dynamical behavior of surface atoms during the surface reconstruction.

(3) The many-body potential with additional repulsive interaction favors the exchange diffusion, and it can predict the existence of the missing-row reconstruction of the Pt(110) surface.

(4) The looseness of the crystal structure causes a larger vibration of substrate atoms, thus the possibility of a sporadic generation of open spaces and the change of atomic replacement are both enhanced.

(5) Due to the different amount of strain induced by the adsorbate, the substrate atoms near the row edges can be dislodged more easily than the substrate atoms far away from the layer edges.

(6) During atomic processes, the surface stresses induced by the adsorbate extending for several atoms are eventually relieved when some of the strained atoms pop out of the surface.

(7) Since the strength of the surface binding depends on the atomic coordination number, the edge atoms of the topmost layer (i.e., outer rows) behave more actively than atoms in the central area of the top layer (i.e., inner rows), in qualitative agreement with the FIM study.

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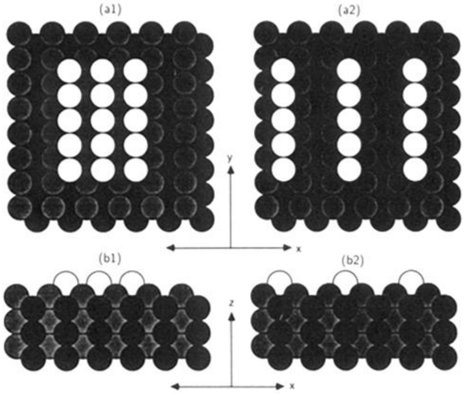

FIG. 1. (a1) and (b1) are top and side views of the Pt{110}-(1×1) structure. (a2) and (b2) are top and side view of the (1×2)-reconstructed Pt(110). The x, y, and z axes are the [001], $[1\bar{1}0]$, and [110] directions.