

Computer simulation study of self-diffusion in Pd(1 1 1) surface

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Abstract

Both the formation energies and the intra- and inter-layer activation energies of self-diffusion of a single vacancy in the first five planes of Pd(1 1 1) surface have been investigated by means of molecular dynamics (MD) in conjunction with the semi-empirical many-body potential of the modified analytical embedded-atom method (MAEAM). The results show that the effect of the surface on the vacancy is only down to the fourth layer. It is easier for a single vacancy to form and to migrate in the first layer. Furthermore, the vacancy in the second layer is favorable to migrate to the first layer. This is in agreement with the experimental results that the first layer has the highest concentration of the vacancy.

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1. Introduction

Understanding surface diffusion is important in the study of many surface related phenomena, such as corrosion [1], oxidation [2], surface catalysis and morphology [3,4], crystal growth [5], etc. Experimental techniques such as field ion microscopy (FIM), helium atom scattering and scanning tunneling microscopy (STM) have been used to study surface diffusion [6–9]. From the theoretical point of view, calculations of the energy barriers for surface diffusion have been performed on several metal surfaces by means of molecular dynamics (MD) simulations using different theories or models, such as the effective medium theory [10], the glue model [11], the embedded atom method (EAM) [12–14], the tight-binding model [15–17], etc.

In this paper, both the formation energies and the activation energies of a single vacancy diffusion intra- and inter-layer in the first five atomic planes of Pd(1 1 1) surface have been investigated by means of molecular dynamics in conjunction with the semi-empirical many-body potential of the modified analytical embedded-atom method (MAEAM) modified by Zhang et al. [18,19] from analytical embedded-atom method (AEAM) of

Johnson [20]. In our previous papers, the MAEAM has been used successfully to calculate the force and energy of Pt adatom on Pt (0 0 1) surface [21], the interfaces energy [22], grain boundary energy [23–25], the formation and migration energy of an isolated vacancy and adatom in three noble metals [26] and the activation energy of self-diffusion for immiscible alloy system and intermetallic compound [27,28].

2. Computational methods

In MAEAM, the total energy of a system is expressed as [29]:

$$E_{\text{total}} = \sum_i F(\rho_i) + \frac{1}{2} \sum_i \sum_{j(\neq i)} \phi(r_{ij}) + \sum_i M(P_i) \quad (1)$$

$$\rho_i = \sum_{j(\neq i)} f(r_{ij}) \quad (2)$$

$$P_i = \sum_{j(\neq i)} f^2(r_{ij}) \quad (3)$$

where $F(\rho_i)$ is the energy to embed an atom in site i with electron density (ρ_i) which is given by a linear superposition of spherical averaged atomic electron density of other atoms $f(r_{ij})$, r_{ij} the separation distance of atom j from atom i , $\phi(r_{ij})$ the pair-potential between atoms i and j , and $M(P_i)$ is the modified term, which describes the energy change due to nonspherical distribution of

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Table 1
Input physical parameters of Pd

Metal	a (Å)	E_c (eV)	E_{1v}^f (eV)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
Pd	3.8907	3.89	1.30	224	173	72

Table 2
Calculation parameters of Pd for MAEAM

Metal	F_0 (eV)	f_e	n	α	k_0 (eV)	k_1 (eV)	k_2 (eV)	k_3 (eV)	l_0 (eV)	l_1 (eV)	l_2 (eV)	l_3 (eV)
Pd	2.590	0.353	0.364	0.247	−0.663	0.448	−0.067	0.082	−0.033	0.711	−4.957	11.269

atomic electronic density and deviation from the linear superposition. Embedding function $F(\rho_i)$, pair-potential $\phi(r_{ij})$, modified term $M(P_i)$, and atomic electron density $f(r_{ij})$ take the following forms [18,19]:

$$F(\rho_i) = -F_0 \left[1 - n \ln \left(\frac{\rho_i}{\rho_e} \right) \right] \left(\frac{\rho_i}{\rho_e} \right)^n \quad (4)$$

$$\phi(r_{ij}) = k_0 + k_1 \left(\frac{r_{ij}}{r_{1e}} \right)^2 + k_2 \left(\frac{r_{ij}}{r_{1e}} \right)^4 + k_3 \left(\frac{r_{1e}}{r_{ij}} \right)^{12} \quad (5)$$

$(r_{ij} \leq r_{2e})$

$$M(P_i) = \alpha \left(\frac{P_i}{P_e} - 1 \right)^2 \exp \left[- \left(\frac{P_i}{P_e} - 1 \right)^2 \right] \quad (6)$$

$$f(r_{ij}) = f_e \left(\frac{r_{1e}}{r_{ij}} \right)^6 \quad (7)$$

where subscript e indicates equilibrium state and r_{1e} is the first nearest-neighbor distance at equilibrium. In this paper, the atomic electron density at equilibrium state f_e is chosen as [19]:

$$f_e = \left(\frac{E_c - E_{1v}^f}{\Omega} \right)^{3/5} \quad (8)$$

where $\Omega = a^3/4$ is the atomic volume in FCC metals.

The other seven parameters n , F_0 , α , k_0 , k_1 , k_2 and k_3 in Eqs. (4)–(6) can be determined by fitting cohesion energy E_c , mono-vacancy formation energy E_{1v}^f , lattice constant a , and elastic constants C_{11} , C_{12} and C_{44} of the metals considered.

$$n = \sqrt{\frac{\Omega(C_{11} + 2C_{12})(C_{11} - C_{12})}{216E_{1v}^f C_{44}}} \quad (9)$$

$$F_0 = E_c - E_{1v}^f \quad (10)$$

$$\alpha = \frac{\Omega(C_{12} - C_{44})}{32} - \frac{n^2 F_0}{8} \quad (11)$$

$$k_0 = -\frac{E_{1v}^f}{9} - \frac{\Omega(5481C_{44} + 2989C_{12} - 2989C_{11})}{42840} \quad (12)$$

$$k_1 = \frac{\Omega(1311C_{44} + 939C_{12} - 939C_{11})}{9520} \quad (13)$$

$$k_2 = \frac{\Omega(-33C_{44} - 32C_{12} + 32C_{11})}{1020} \quad (14)$$

$$k_3 = \frac{8\Omega(9C_{44} + C_{12} - C_{11})}{5355} \quad (15)$$

According to the analysis of Zhang and Ouyang, the pair-potential $\phi(r_{ij})$ represented by Eq. (5) is available only for the separated distance between atoms is shorter than the second neighbor distance r_{2e} and should be substituted by following cubic spline function (termed as a cutoff potential) while the separated distance between atoms is in the range from r_{2e} to r_c [18].

$$\phi(r_{ij}) = l_0 + l_1 \left(\frac{r_{ij}}{r_{2e}} - 1 \right) + l_2 \left(\frac{r_{ij}}{r_{2e}} - 1 \right)^2 + l_3 \left(\frac{r_{ij}}{r_{2e}} - 1 \right)^3 \quad (16)$$

$(r_{2e} < r_{ij} \leq r_c)$

Four parameters l_0 , l_1 , l_2 , l_3 and cutoff radius r_c are taken as:

$$l_0 = k_0 + k_1 s^2 + k_2 s^4 + k_3 s^{-12} \quad (17)$$

$$l_1 = 2k_1 s^2 + 4k_2 s^4 - 12k_3 s^{-12} \quad (18)$$

$$l_2 = -\frac{2l_1}{(\gamma - 1)} - \frac{3l_0}{(\gamma - 1)^2} \quad (19)$$

$$l_3 = \frac{l_1}{(\gamma - 1)^2} + \frac{2l_0}{(\gamma - 1)^3} \quad (20)$$

$$r_c = r_{2e} + 0.75(r_{3e} - r_{2e}) \quad (21)$$

where r_{2e} and r_{3e} are the second and third neighbor distance at equilibrium, and $s = r_{2e}/r_{1e}$, $\gamma = r_c/r_{2e}$.

By substituting physical parameters, the lattice constant a [30], cohesion energy E_c [31], mono-vacancy formation energy E_{1v}^f [32], and elastic constants C_{11} , C_{12} and C_{44} [33] of Pd metal (listed in Table 1) into Eqs. (8)–(15) and then into (17)–(20), the parameters needed for energy calculation with MAEAM can be obtained (listed in Table 2).

3. Computational procedure

A surface super-cell with 20 layers of Pd(1 1 1) atomic plane and 289 atoms in each plane is used. A mantle of the atoms fixed at their perfect lattice positions around the super-cell is used as boundary to ensure that each atom in the super-cell has a complete set of neighbors within the range of interatomic potential

except for introduction of the surface. A single vacancy in different layers is created by removing an atom from corresponding layer. The lattice relaxation resulted from the existence of the surface and vacancy is treated with the MD simulation [34,35]. The force applied to the i th atom from the other atoms is calculated by

$$f_i^\alpha = -\frac{\partial E_i}{\partial r_{ij}^\alpha} = -\left[F'(\rho_i) \sum_{j(\neq i)} f'(r_{ij}) \frac{r_{ij}^\alpha}{r_{ij}} + \frac{1}{2} \sum_{j(\neq i)} \phi'(r_{ij}) \frac{r_{ij}^\alpha}{r_{ij}} + 2M'(P_i) \sum_{j(\neq i)} f(r_{ij}) f'(r_{ij}) \frac{r_{ij}^\alpha}{r_{ij}} \right] \quad (22)$$

where the superscript α ($=x, y$ and z) in f_i^α and r_{ij}^α represents the α th component of the force (f_i) and the separation distance (r_{ij}) of atom j from atom i . $E_i = F(\rho_i) + (1/2) \sum_{j(\neq i)} \phi(r_{ij}) + M(P_i)$ is the energy contribution from atom i and Eq. (1) becomes

$$E_{\text{total}} = \sum_i E_i \quad (23)$$

The formation energy E_v^f and migration energy E_v^m of a single vacancy can be calculated by [36]

$$E_v^f = E_t^v - (E_t - E_c) \quad (24)$$

$$E_v^m = E_{\text{sad}} - E_e \quad (25)$$

where E_t^v and E_t are the total energies of the relaxed lattices with and without vacancy and E_c is cohesion energy and compensates for the missing atom. E_{sad} and E_e are the energies of the system with the vacancy in the saddle point energy configuration (activated state) and at initial equilibrium state. The sum of the formation energy E_v^f and migration energy E_v^m gives the activation energy of self-diffusion Q

$$Q = E_v^f + E_v^m. \quad (26)$$

4. Results and discussion

The formation energy E_v^f is calculated for a single vacancy formed in each of the first five atomic planes of the relaxed Pd(1 1 1) surface, and the results are shown in Fig. 1 and are

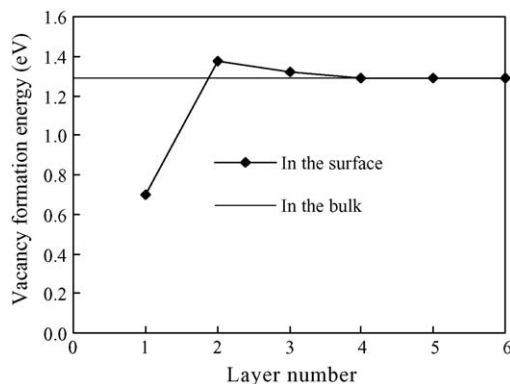


Fig. 1. Formation energy of a single vacancy in the first five layers of the relaxed Pd(1 1 1) surface.

Table 3

The formation energy E_v^f of a single vacancy in each of the first five atomic planes of the relaxed Pd(1 1 1) surface and that in the bulk

Layer number	1st	2nd	3rd	4th	5th	Bulk
E_v^f (eV)						
Present	0.699	1.375	1.319	1.289	1.289	1.289
EAM						1.4 [37]
Exp						1.7–1.85 [38,39]

listed in Table 3 together with the other available theoretical [37] and experimental [38,39] values for comparing. As can be seen that, E_v^f for a single vacancy in the first layer is lower than that in the other layers or the bulk, however E_v^f in the second or third layer is slightly higher than that in the bulk. From the fourth layer, E_v^f is close to the bulk value. And the formation energy is the lowest in the first layer and is the highest in the second layer. The reason of the former is that for a single vacancy to be formed in the first layer simply requires the least two-body bonds to be broken and thus has the lowest formation energy. The latter is because, for a next nearest-neighbor model used here, a vacancy in the second layer of Pd(1 1 1) surface requires as many two-body bonds (12 + 6) to be broken as a bulk vacancy, but the changes in embedding energy and modified term are greater for surface atoms than bulk atoms. So from the energy minimization, a single vacancy is the easiest to be formed in the first layer. This is in agreement with the fact in experiment that the vacancy has larger concentration in the first layer than the situation in the bulk [40].

Regarding the migration of a single vacancy in or below the Pd(1 1 1) surface, the variation of the system energy with the position of the vacancy migrating intra- and inter-layer has been investigated for all the nearest-neighbor (NN) jumps in the first five layers. The results are shown in Figs. 2 and 3 for intra- and inter-layer migration, respectively. The energy at the initial or final position of each jump is the formation energy of a single vacancy to be formed in corresponding layer given in Table 3 and the vacancy displacement at each NN jump is normalized to the jump vector length of $r_{1e} = (\sqrt{2}/2)a$. It can be seen that, from Fig. 2, the energy curve of each intra-layer migration is similar and symmetric. The maximum value of the energy, that is the activation energy of self-diffusion, appears at the midway of the

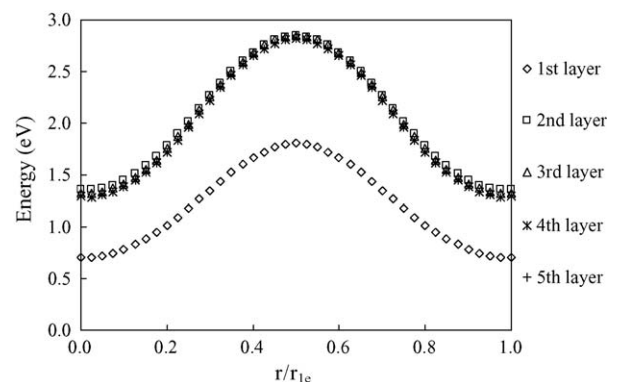


Fig. 2. Energy-displacement curve for single vacancy diffusion in intra-layer of the first five layers of the relaxed Pd(1 1 1) surface.

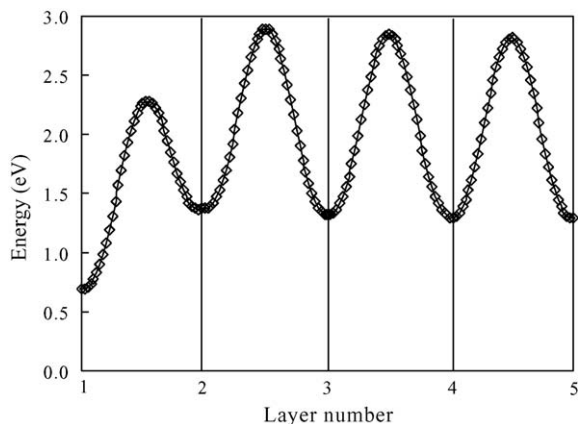


Fig. 3. Energy–displacement curve for a single vacancy diffusion in inter-layer of the first five layers of the relaxed Pd(1 1 1) surface.

migration path. The point corresponds to the maximum value of the energy is generally defined as the saddle point. This is not the case in Fig. 3 for each inter-layer migration, the energy curve is unsymmetrical and the saddle point deviates slightly the midway of the migration path. Determined the activation energies of self-diffusion Q_m^{intra} in intra-layer, Q_m^{upper} to the upper layer and Q_m^{lower} to the lower layer, respectively, for the vacancy to migrate are schematically shown in Fig. 4 together with the formation energies of the vacancy in corresponding layers.

Similarly, the formation energy E_v^f of a single vacancy in the first five layers, the activation energies of self-diffusion Q_m^{intra} in the first layer is much lower than that in the bulk, however Q_m^{intra} in the second or third layer is slightly higher than that in the bulk. From the fourth layer, Q_m^{intra} is close to the bulk value. The reason is that for a next nearest-neighbor model used here, in addition to the atoms on intra-layer, the atoms on upper two layers and lower two layers effect the vacancy diffusion intra-layer. For vacancy diffusion in the first layer, only the atoms on

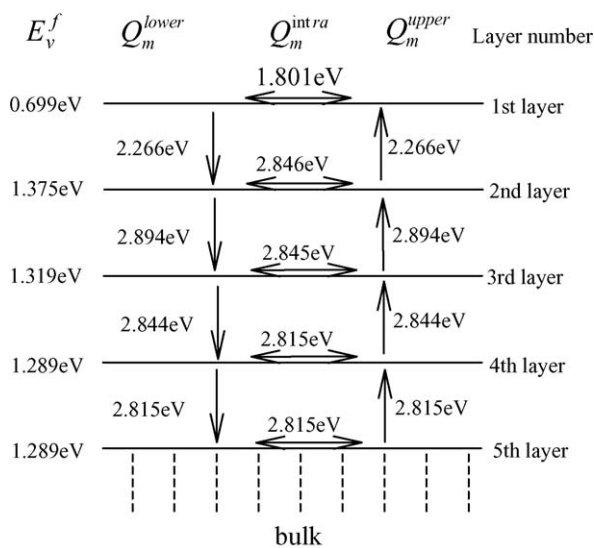


Fig. 4. The vacancy formation energy E_v^f , the activation energies of self-diffusion Q_m^{intra} in intra-layer, Q_m^{upper} to the upper layer and Q_m^{lower} to the lower layer, respectively, for single vacancy to migrate in the first five layers.

the first layer and lower two layers effect the vacancy diffusion thus the first layer has the lowest self-diffusion activation energy. Although absent the effects of the atoms on one upper layer for vacancy diffusion in the second layer and has the same number of upper two layers and lower two layers for vacancy diffusion in the third layer as that in the fourth layer, the relative larger effects coming from the surface atoms decrease in the sequence of the second-, third- and fourth-layer, so the activation energies of self-diffusion Q_m^{intra} intra-layer decrease also in the sequence of the second-, third- and fourth-layer.

For the migration of the vacancy in inter-layer, the activation energy of self-diffusion of a single vacancy migrating to upper layer Q_m^{upper} decreases with the approach of the vacancy to the surface from the third layer to the first layer. On the other hand, the activation energy of self-diffusion of the vacancy migrating to lower layer Q_m^{lower} increases with the vacancy migrating from the first layer to the third layer. Comparing the relative large number of the activation energies of self-diffusion Q_m^{intra} , Q_m^{upper} and Q_m^{lower} for a single vacancy in the second-, third- or fourth-layer to migrate in itself layer, to upper layer and to lower layer, we know that a single vacancy in the second layer is favorable to migrate to the first layer of Pd(1 1 1) surface. However, a single vacancy in the third- or fourth-layer is not easy to migrate to the upper layer due to its slightly higher activation energy of self-diffusion than that of the vacancy migrating in intra-layer or to lower layer. Below the fourth-layer, the calculated activation energies of self-diffusion Q_m^{intra} , Q_m^{upper} and Q_m^{lower} are equal to the calculated bulk value (2.815 eV) which is in good agreement with the experimental values [41,42], this means that the effects of the surface to the vacancy formation and migration are only for the vacancy in the first four layers.

5. Conclusions

The formation energies and the intra- and inter-layer activation energies of self-diffusion of a single vacancy in the first five atomic planes of Pd(1 1 1) surface have been investigated by combining the molecular dynamics with the modified analytical embedded-atom method. Following main conclusions are obtained.

The formation energy of a single vacancy is the lowest (much lower than the bulk value) for the vacancy in the first layer and is slightly higher than the bulk value for the vacancy formed in the second- or third-layer.

For migration of a vacancy in intra-layer, the activation energy of self-diffusion Q_m^{intra} increases in the sequence of the first- and second-layer, Q_m^{intra} of the second- or third-layer is slightly higher than the bulk value and Q_m^{intra} of the second layer is the highest.

For migration of a vacancy in inter-layer, the activation energy of self-diffusion of the vacancy migrating to upper layer Q_m^{upper} decreases for the vacancy in the third layer to the first layer. Comparing the relative large number of the activation energies of self-diffusion Q_m^{intra} , Q_m^{upper} and Q_m^{lower} for the vacancy in the second-, third- or fourth-layer to migrate in itself layer, to upper layer and to lower layer, we know that the vacancy in the second layer is favorable to migrate to the first layer. However, a single

vacancy in the third- or fourth-layer is not easy to migrate to the upper layer due to its slightly higher activation energy than that of the vacancy to migrate in intra-layer or to lower layer. Below the fourth layer, the calculated activation energies of self-diffusion Q_m^{intra} , Q_m^{upper} and Q_m^{lower} are equal to the calculated bulk value means that the effects of the surface to the vacancy formation and migration are only for the vacancy in the first four layers.

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