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Computer simulation of surface diffusion of copper, silver and gold

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Abstract. The binding energies to copper, silver and gold (111) surfaces of self-atom clusters have been calculated. The activation energies of motion of these ad-atom clusters, vacancies and divacancies on copper, silver and gold (111) surface, and of the conversion of ad-atom clusters on (111) and (100) have been calculated by use of n-body embedded atom potentials and molecular dynamics.

Keywords. Simulations; surface diffusion; copper; silver; gold; ad-atoms; ad-atom clusters.

1. Introduction

Surface phenomena are becoming important in view of their technological applications as well as in basic sciences. The crystal growth of surface by expitaxial growth is widely used by electronic industries. Surface diffusion is very important for the expitaxial growth. In this paper the binding energies for ad-atom clusters to (111) surface, and the activation energies of the motion and conversion were calculated using molecular dynamics and n-body embedded atom method.

2. Potential

In metals, the conduction electrons travel from one atom to another atom, and the interaction cannot be represented by a pairwise potential but many-body potentials. The interaction between the ith atom and the jth atom depends not only on the distance between them but also other factors. By the embedded function, surface problems can be treated.

2.1 *Oh and Johnson's potential*

The n-body embedded function proposed by Oh and Johnson (1988, 1989) is used in this paper. The total energy is given as

$$E_{\text{total}} = \Sigma E_i, \tag{1}$$

$$r_{ij} = |r_i - r_j|, \tag{2}$$

$$E_i = F(\rho_i) + (1/2)\,\Sigma \Phi(r_{ij}), \tag{3}$$

$$F(\rho) = a(\rho/\rho_e)^n + b(\rho/\rho_e), \tag{4}$$

$$\rho_i = \Sigma f(r_{ij}). \tag{5}$$

Here E_{total} is the total internal energy, E_i the internal energy associated with atom i, ρ_i the electron density at atom i due to all other atoms, $F(\rho_i)$ the embedding energy of atom into electron density ρ_i, $\Phi(r_{ij})$ is the two body central potential between atoms i and j separated by r_{ij}, and $f(r_{ij})$ the contribution to the electron density at atom i due to atom j at the distance r_{ij} from atom i. Further,

$$f(r) = f_{\text{old}}(r) - f_c(r), \tag{6}$$

$$f_{\text{old}} = f_e \exp\{-\beta(r/r_e) - 1\}, \tag{7}$$

$$f_c(r) = f_{\text{old}}(r_c) + g(r) f'_{\text{old}}(r_c)/g'(r), \tag{8}$$

$$\Phi(r) = \Phi_{\text{old}}(r) - \Phi_c(r), \tag{9}$$

$$\Phi_{\text{old}}(r) = \Phi_e \exp\{-\gamma(r/r_e - 1)\}, \tag{10}$$

$$\Phi_c(r) = \Phi_{\text{old}}(r_c) + g(r)\, \Phi'_{\text{old}}(r_c)/g'(r_c), \tag{11}$$

$$g(r) = 1 - \exp\{\delta(r/r_e - r_c/r_e)\}. \tag{12}$$

For copper, Oh and Johnson (1988) give $\beta = 5$, $\gamma = 8{\cdot}5$, $\delta = 20$, $r_c = 1{\cdot}9r_e$, $\Phi_e = 0{\cdot}36952$ eV, $a = -4{\cdot}0956$, $b = -1{\cdot}6979$, $n = 0{\cdot}44217$, and $\rho_e = 12{\cdot}793$. For silver, $\beta = 6$, $\gamma = 7{\cdot}5$, $\delta = 20$, $r_c = 1{\cdot}9r_e$, $\Phi_e = 0{\cdot}85184$ eV, $a = -5{\cdot}0929$, $b = -2{\cdot}9961$, $n = 0{\cdot}65777$, and $\rho_e = 12{\cdot}551$. For gold, $\beta = 6$, $\gamma = 8$, $\delta = 20$, $r_c = 1{\cdot}9r_e$, $\Phi_e = 0{\cdot}54608$ eV, $a = -39{\cdot}701$, $b = 32{\cdot}428$, $n = 0{\cdot}92504$, and $\rho_e = 12{\cdot}551$.

2.2 *Doyama and Kogure potential*

The n-body embedded function proposed by Doyama and Kogure (to be published) was also used in this paper. The total energy is given by

$$E_{\text{total}} = \Sigma E_i, \tag{13}$$

$$r_{ij} = |r_i - r_j|, \tag{14}$$

$$E_i = F(\rho_i) + (1/2)\, \Sigma \Phi(r_{ij}), \tag{15}$$

$$F(\rho) = D\rho_i \log(\rho_i), \tag{16}$$

$$\rho_i = \Sigma f(r_{ij}), \tag{17}$$

$$\Phi(r_{ij}) = A_1(r_{c_1} - r_{ij})^2 \exp(-c_1 r_{ij}), \tag{18}$$

$$f(r_{ij}) = A_2(r_{c_2} - r_{ij})^2 \exp(-c_2 r_{ij}). \tag{19}$$

Values of parameters A_1, A_2, C_1, C_2 and D are given in table 1. In table 2, experimental and calculated values are listed.

3. Binding energies of atom clusters to (111) plane

3.1 *Oh and Johnson's potential*

The binding energies of atom clusters to the (111) surface for copper, silver and gold have been calculated. A crystal used has (111) surface, contains 2310 atoms, 11 atoms in ⟨110⟩ direction, 14 atoms in ⟨112⟩ direction and 15 atoms in ⟨111⟩ direction. 506 or 420 atoms near the centre of (111) surface were relaxed. Let the binding energy of an N ad-atom cluster be B_N. Each ad-atom has three bonds ($3E_1$) to the (111) plane. Let the binding energy per bond in the ad-atom cluster be E_2 and the number of bonds m. The results are shown in tables 3–5 for copper, silver and gold, respectively. For copper, the binding energy of the first ad-atom to (111) plane (2·60 eV) is lower than that of the atom sticking to the next to the atom adsorbed (3·02 eV). The binding energy of the last atom to complete a hexagon

Table 1. Determined potential parameters.

	Cu	Ag	Au
A_1	$8{\cdot}28945997705 \times 10^{3}$	$9{\cdot}10810768184 \times 10^{3}$	$5{\cdot}18021878920 \times 10^{5}$
A_2	$1{\cdot}83251035107 \times 10^{-2}$	$5{\cdot}25514178418 \times 10^{-2}$	$1{\cdot}83065797788 \times 10^{-2}$
C_1	10·72729128641	10·8172151010 79	15·57704835828
C_2	$3{\cdot}19759369823 \times 10^{-1}$	1·38555356572	$1{\cdot}28671308081 \times 10^{-5}$
D	13·07921251628	11·28152486706	11·93177438785

Table 2. Experimental values used to fit potential parameters and calculated values.

			Cu	Ag	Au
C_{11}	(cal)	[10^{12} dyne/cm^2]	1·806	1·22	1·37
	(exp)		1·684	1·24	1·86
C_{12}	(cal)	[10^{12} dyne/cm^2]	1·201	0·837	0·913
	(exp)		1·214	0·934	1·57
C_{44}	(cal)	[10^{12} dyne/cm^2]	0·710	0·489	0·492
	(exp)		0·754	0·461	0·42
E_c	(cal)	[eV]	3·54	2·85	3·93
	(exp)		3·54	2·85	3·93
E^F_v	(cal)	[eV]	1·3	1·10	1·01
	(exp)		1·3	1·1	0·96
E_s	(cal)	[ergs/cm^2]	73	17	52·3
	(exp)		73	17	55
a	(exp)	[A]	3·61496	4·0862	4·07864
Q			$8{\cdot}78 \times 10^{-3}$	$1{\cdot}49 \times 10^{-2}$	3×10^{-1}

Table 3. Binding energies of ad-atom clusters to copper (111) surface using Oh and Johnson potential.

Number of atoms in cluster N	Configuration	Total binding energy $B = 3n_1 E_1 + n_2 E_2$ (eV)	Number of nearest neighbours $3n_1 + n_2$	Energy per bond $B/(3n_1 + n_2)$	Energy per bond within clusters B_2
1		2·60	3(3 × 1)	0·87	
2		5·62	7(= 3 × 2 + 1)	0·80	0·42
3		8·97	12(= 3 × 3 + 3)	0·76	0·39
4		12·28	17(= 4 × 3 + 5)	0·72	0·38
4		11·94	16(= 4 × 3 + 4)	0·75	0·39
5		15·57	22(= 5 × 3 + 7)	0·71	0·37
6		18·82	27(= 6 × 3 + 9)	0·70	0·36
6		18·47	25(= 6 × 3 + 7)	0·74	0·36
6		18·85	27(= 6 × 3 + 9)	0·70	0·36
7		22·37	33(= 7 × 3 + 12)	0·68	0·35
7		21·76	32(= 7 × 3 + 11)	0·68	0·32

with one atom at the centre (7-atom cluster) (3·55 eV) is higher than other cases. The difference between the binding energy of an atom at a normal site (*N*-site: form fcc structure) and that of an atom at hexagonal site (*H*-site) which forms a stacking fault was calculated to be 0·004 eV. For silver, the binding energy of the first atom to (111) plane (2·13 eV) is lower than that of the atom sticking to the next to the atom adsorbed (2·38 eV). The binding energy of the last atom to complete a hexagon with one atom at the centre (7-atom cluster) (2·9 eV) is higher than other cases. The difference between the binding energy of an atom at a normal site (form fcc structure) and that of an atom at a *H*-site which forms a stacking fault was calculated to be 0·0085 eV. For gold the binding energy of the first atom to (111) plane (2·90 eV) is lower than that of the atom sticking to the next to the atom adsorbed (3·42 eV). The binding energy of the last atom to complete a hexagon with one atom at the centre (7-atom cluster) (4·04 eV) is higher than other cases. The difference between the binding energy of an atom at a normal site (form fcc structure) and that of an atom at a *H*-site which forms a stacking fault was calculated to be 0·0028 eV.

3.2 *Doyama and Kogure potential*

The binding energies of atom clusters to the (111) surface for copper, silver and

Table 4. Binding energies of ad-atom clusters to silver (111) surface using Oh and Johnson potential.

Number of atoms in cluster N	Configuration	Total binding energy $B = 3n_1 E_1 + n_2 E_2$ (eV)	Number of nearest neighbours $3n_1 + n_2$	Energy per bond $B/(3n_1 + n_2)$	Energy per bond within clusters. B_2
1		2·13	3(= 3 × 1)	0·71	
2		4·51	7(= 3 × 2 + 1)	0·64	0·25
3		7·19	12(= 3 × 3 + 3)	0·60	0·24
3		6·85	11(= 3 × 3 + 2)	0·62	0·24
3		6·85	11(= 3 × 3 + 2)	0·62	0·24
4		9·82	17(= 3 × 4 + 5)	0·58	0·26
4		9·51	16(= 3 × 4 + 4)	0·59	0·25
4		9·20	15(= 3 × 4 + 3)	0·61	0·23
4		9·20	15(= 3 × 4 + 3)	0·61	0·23
5		12·44	22(= 3 × 5 + 7)	0·57	0·26
5		11·87	20(= 3 × 5 + 5)	0·59	0·25
5		11·56	19(= 3 × 5 + 4)	0·61	0·23
5		11·56	19(= 3 × 4 + 4)	0·61	0·23
6		15·04	27(= 3 × 6 + 9)	0·56	0·25
6		15·04	27(= 3 × 6 + 9)	0·56	0·26
6		15·04	27(= 3 × 6 + 9)	0·56	0·26
7		17·94	33(= 3 × 7 + 12)	0·54	0·26

gold using Doyama and Kogure potential have been calculated for the same crystal structure as the one used in the preceding subsection. The results are shown in tables 6 and 7 for copper and silver respectively. For copper the binding energy of the first ad-atom to (111) plane (2·42 eV) is lower than that of the atom sticking to the next to the atom adsorbed (2·92 eV). The difference between the binding energy of an atom at a normal site (form fcc structure) and that of an atom at a *H*-site which forms a stacking fault was calculated to be 0·013 eV. For silver the binding energy of the first atom to (111) plane (1·87 eV) is lower than that of the atom sticking to the next to the atom adsorbed (2·3 eV). The difference between the binding energy of an atom at a normal site (form fcc structure) and that of an atom at a *H*-site which forms a stacking fault was calculated to be 0·0041 eV.

4. Motion of an ad-atom on (111) and (100) (figure 1)

4.1 *Oh and Johnson's potential*

For copper the binding energy of an atom on (111) surface at the N-site and at the H-site was calculated to be 2·61 eV and 2·60 eV, respectively. The activation energy for the motion of ad-atom from N-site to H-site, $E_{1A}^{M}(N \rightarrow H)$ (111), was calculated to be 0·043 eV with relaxation of 507 atoms around and including the ad-atom. The activation energy for the motion of ad-atom from H-site to N-site, $E_{1A}^{M}(H \rightarrow N)$ (111), was 0·039 eV which are quite small. The energy difference between N-site and H-site was 0·004 eV.

For silver the binding energy of an atom on (111) surface at the N- and H-sites was calculated to be 2·126 eV and 2·118 eV, respectively. The activation energy for the motion of ad-atom from N-site to H-site, $E_{1A}^{M}(N \rightarrow H)$ (111), was calculated

Table 5. Binding energies of ad-atom clusters to gold (111) surface using Oh and Johnson potential.

Number of atoms in cluster N	Configuration	Total binding energy $B = 3n_1 E_1 + n_2 E_2$ (eV)	Number of nearest neighbours $3n_1 + n_2$	Energy per bond $B/(3n_1 + n_2)$	Energy per bond within clusters B_2
1		2·91	3(= 3 × 1)	0·97	
2		6·32	7(= 3 × 2 + 1)	0·90	0·50
3		10·16	12(= 3 × 3 + 3)	0·85	0·48
3		9·62	11(= 3 × 3 + 2)	0·87	0·45
3		9·60	11(= 3 × 3 + 2)	0·87	0·44
4		13·83	17(= 3 × 4 + 5)	0·81	0·44
4		13·41	16(= 3 × 4 + 4)	0·84	0·44
4		12·94	15(= 3 × 4 + 3)	0·86	0·43
4		12·90	15(= 3 × 4 + 3)	0·86	0·42
5		17·51	22(= 3 × 5 + 7)	0·80	0·42
5		16·75	20(= 3 × 5 + 5)	0·84	0·44
5		16·27	19(= 3 × 5 + 4)	0·86	0·43
5		16·24	19(= 3 × 5 + 4)	0·85	0·42
6		21·12	27(= 3 × 6 + 9)	0·78	0·41
6		21·18	27(= 3 × 6 + 9)	0·78	0·40
7		25·16	33(= 3 × 7 + 12)	0·64	0·40

to be 0·0559 eV with relaxation of 507 atoms around and including the ad-atom. The activation energy for the motion of ad-atom from *H*-site to *N*-site $E_{1A}^{M}(H \rightarrow N)$ (111), was 0·0464 eV. The activation energies are quite small. The energy difference between *N*- and *H*-sites was 0·0085 eV.

For gold the binding energy of an atom on (111) surface at the *N*- and *H*-sites was calculated to be 2·91 eV and 2·90 eV respectively. The activation energy for the motion of ad-atom from *N*-site to *H*-site, $E_{1A}^{M}(N \rightarrow H)$ (111), was calculated to be 0·084 eV with relaxation of 507 atoms around and including the ad-atom. The activation energy for the motion of ad-atom from *H*-site to *N*-site, $E_{1A}^{M}(H \rightarrow N)$ (111), was 0·074 eV. The activation energies are quite small. The energy difference between *N*-site and *H*-site was 0·010 eV.

The activation energy for the motion of an ad-atom on (100), E_{1A}^{M} (100), were calculated to be 0·50 and 0·81 eV for copper and gold, which are much higher than that on (111). (111) plane has the highest atomic density and, is smooth, but

Table 6. Binding energies of ad-atom clusters to copper (111) surface using Doyama and Kogure potential.

Number of atoms in cluster N	Configuration	Total binding energy $B = 3n_1 E_1 + n_2 E_2$ (eV)	Number of nearest neighbours $3n_1 + n_2$	Energy per bond $B/(3n_1 + n_2)$	Energy per bond within clusters B_2
1		2·424	3	0·81	
2		5·336	7(= 3 × 2 + 1)	0·76	0·49
2	(110)	5·314	7(= 3 × 2 + 1)	0·76	0·47
3		8·648	12(= 3 × 3 + 3)	0·72	0·46
4		11·420	16(= 3 × 4 + 4)	0·71	0·43
4		11·116	15(= 3 × 4 + 3)	0·74	0·47
4		11·097	15(= 3 × 4 + 3)	0·76	0·47
5		15·176	22(= 3 × 5 + 7)	0·69	0·44
5		14·009	19(= 3 × 5 + 4)	0·74	0·47
5		13·990	19(= 3 × 5 + 4)	0·74	0·47
5		14·415	20(= 3 × 5 + 5)	0·72	0·46
5		13·914	19(= 3 × 5 + 4)	0·73	0·45
6		18·401	27(= 3 × 6 + 9)	0·68	0·43
6		18·425	27(= 3 × 6 + 9)	0·68	0·43
6		17·679	25(= 3 × 6 + 7)	0·71	0·45
6		16·292	24(= 3 × 6 + 5)		

(100) plane does not have the highest atomic density. The surface is not very smooth. Therefore, it is reasonable that the activation energy for the motion of a single ad-atom on (100) is higher than that on (111).

4.2 *Doyama and Kogure potential*

For copper the binding energy of an atom on (111) surface at the *N*- and *H*-sites was calculated to be 2·61 eV and 2·60 eV respectively. The activation energy for the motion of ad-atom from *N*-site to *H*-site, $E_{1A}^{M}(N \rightarrow H)$ (111), was calculated to be 0·055 eV with relaxation of 507 atoms around and including the ad-atom. The activation energy for the motion of ad-atom from *H*-site to *N*-site, $E_{1A}^{M}(H \rightarrow N)$ (111), was 0·042 eV. These are quite small. The energy difference between *N*-site and *H*-site was 0·013 eV.

For silver the binding energy of an atom on (111) surface at the *N*-site and at

Table 7. Binding energies of ad-atom clusters to silver (111) surface using Doyama and Kogure potential.

Number of atoms in cluster N	Configuration	Total binding energy $B = 3n_1 E_1 + n_2 E_2$ (eV)	Number of nearest neighbours $3n_1 + n_2$	Energy per bond $B/(3n_1 + n_2)$	Energy per bond within clusters B_2
1		1·867	3	0·62	
2		4·174	7(= 3 × 2 + 1)	0·60	0·44
3		6·837	12(= 3 × 3 + 3)	0·57	0·41
3		6·460	11(= 3 × 3 + 2)	0·59	0·43
3		6·452	11(= 3 × 3 + 2)	0·59	0·43
4		9·459	17(= 3 × 4 + 5)	0·56	0·40
4		9·097	16(= 3 × 4 + 4)	0·57	0·41
4		8·737	15(= 3 × 4 + 3)	0·58	0·42
4		8·730	15(= 3 × 4 + 3)	0·58	0·42
5		11·381	20(= 3 × 5 + 5)	0·57	0·41
5		11·020	19(= 3 × 5 + 4)	0·58	0·42
5		11·012	19(= 3 × 5 + 4)	0·58	0·42
5		10·973	19(= 3 × 5 + 4)	0·58	0·41
6		14·667	27(= 3 × 6 + 9)	0·54	0·39
6		14·658	27(= 3 × 6 + 9)	0·54	0·38
6		14·647	27(= 3 × 6 + 9)	0·54	0·38

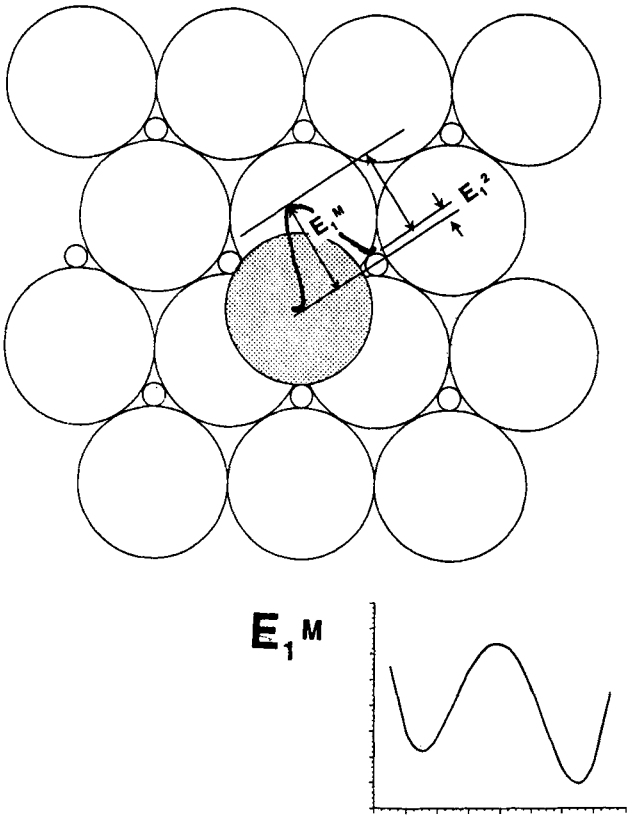


Figure 1. Motion of an ad-atom on (111). From *N*-site to *H*-site and from *H*-site to *N*-site.

the *H*-site was calculated to be 1·867 eV and 1·864 eV. The activation energy for the motion of ad-atom from *N*-site to *H*-site, $E_{1A}^{M}(N \rightarrow H)$ (111), was calculated to be 0·058 eV with relaxation of 507 atoms around and including the ad-atom. The activation energy for the motion of ad-atom from *H*-site to *N*-site, $E_{1A}^{M}(H \rightarrow N)$ (111), was 0·054 eV. The activation energies are quite small. The energy difference between *N*-site and *H*-site was 0·004 eV.

5. Di ad-atoms on (111) and (100) (figure 2)

5.1 *Oh and Johnson's potential*

For copper the binding energy of a di ad-atom to (111) plane was calculated to be 5·62 eV (table 3). The binding energy of the second atoms was 3·02 eV which is higher than the first ad-atom to the (111) surface (2·60 eV). The activation energy for the motion of a di ad-atom on (111), E_{2A}^{M} (111), was calculated to be 0·30 eV with relaxation of 420 atoms around and including the ad-atoms. A di ad-atom moves by butterfly motion, without breaking the bond between two ad-atoms.

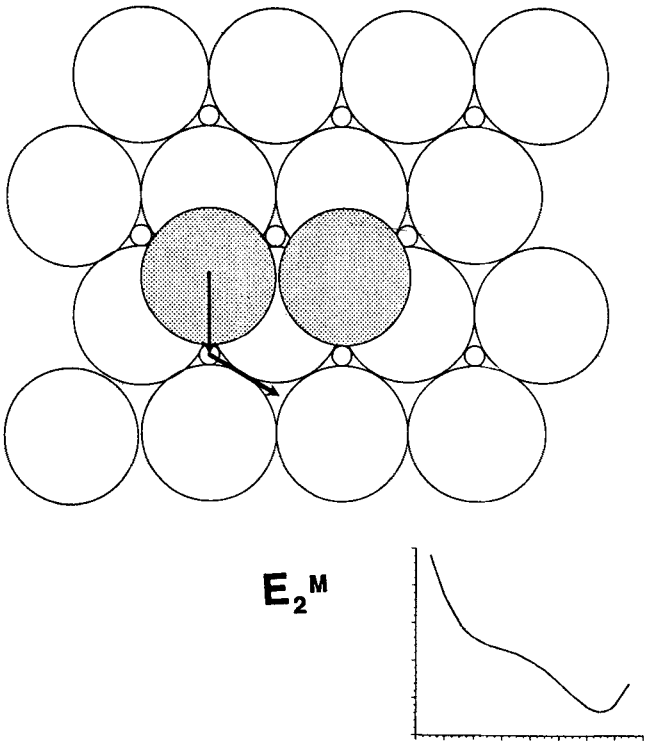


Figure 2. Motion of a di ad-atom. The di ad-atom has to be partially broken while it moves.

The activation energy for the motion of a di ad-atom is much higher than that of a single ad-atom. An atom (atom 1) of a di ad-atom was moved away from the other atom (atom 2).

For silver the binding energy of a di ad-atom to (111) plane was calculated to be 4·51 eV (table 4). The binding energy of the second atoms was 2·38 eV which is higher than the first ad-atom to the (111) surface (2·1 eV). The activation energy for the motion of di ad-atoms on (111) was calculated to be 0·148 eV with relaxation of 420 atoms around and including the ad-atoms. The activation energy for the motion of di ad-atoms is much higher than that of a single ad-atom. An atom (atom 1) of di ad-atoms was moved away from the other atom (atom 2).

For gold the binding energy of a di ad-atom to (111) plane was calculated to be 6·32 eV (table 5). The binding energy of the second atoms was 3·42 eV which is higher than the first ad-atom to the (111) surface (2·90 eV). The activation energy for the motion of a di ad-atom on (111), E_{2A}^{M} (111), was calculated to be 0·14 eV with relaxation of 420 atoms around and including the ad-atoms. A di ad-atom moves by butterfly motion, without breaking the bond between two ad-atoms. The activation energy for the motion of a di ad-atom is much higher than that of a single ad-atom. An atom (atom 1) of a di ad-atom was moved away from the other atom (atom 2).

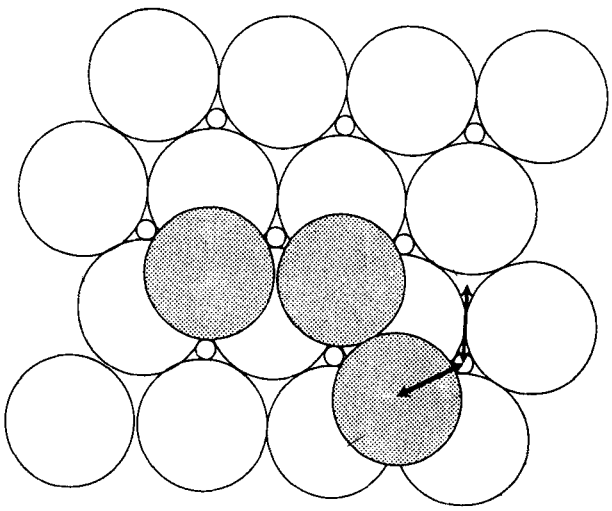
For the motion of a di ad-atom on (100), one of the di ad-atom of the di ad-atom in the nearest neighbour distance has to be broken first into the next

nearest neighbour position and the other ad-atom moves. For copper the activation energy for the conversion, $E_{2A}^{M}(\text{nn} \rightarrow \text{nnn})$ was found to be 0·60 eV and $E_{2A}^{M}(\text{nnn} \rightarrow \text{nn})$ was 0·30 eV. Therefore, the activation energy for the motion of di ad-atom on (100) is 0·60 eV for copper. The activation energy for the break up of a di ad-atom from the nearest neighbour to $2d$ (d is the nearest neighbour distance) in [110] was found to be 0·90 eV for copper.

5.2 *Doyama and Kogure potential*

For copper the binding energy of a di ad-atom to (111) plane was calculated to be 5·34 eV (table 6). The binding energy of the second atoms was 2·92 eV which is higher than the first ad-atom to the (111) surface (2·42 eV). The activation energy for the motion of a di ad-atom on (111), E_{2A}^{M} (111), was calculated to be 0·12 eV with relaxation of 420 atoms around and including the ad-atoms. A di ad-atom moves by butterfly motion, without breaking the bond between two ad-atoms. The activation energy for the motion of a di ad-atom is much higher than that of a single ad-atom. An atom (atom 1) of a di ad-atom was moved away from the other atom (atom 2).

For silver the binding energy of a di ad-atom to (111) plane was calculated to be 4·17 eV (table 7). The binding energy of the second atom was 2·30 eV which is higher than the first ad-atom to the (111) surface (1·87 eV).



$$\frac{E_3^{180} \rightarrow E_3^{120}}{E_3^{120} \rightarrow E_3^{180}}$$

Figure 3. Motion of a 3 ad-atom. $E_3^{180} \rightleftarrows E_3^{120}$ conversion.

6. Motion of 3 ad-atoms on (111) and (100) (figure 3)

6.1 *Oh and Johnson's potential*

The most stable configuration of a tri ad-atom is triangular for copper, silver and gold. The configurations of the tri ad-atom shown in figure 3 will be called 60° tri ad-atom, 120° tri ad-atom and 180° tri ad-atom, respectively. The activation energies for the transformation from 60° to 120° tri ad-atoms, $E_{3A}^{M}(60 \rightarrow 120)$ (111), was calculated to be 0·413 eV and 0·632 eV, for silver and gold, respectively. The activation energies for the transformation from 120° to 60° tri ad-atoms, $E_{3A}^{M}(120 \rightarrow 60)$ (111), were calculated to be 0·083 eV and 0·116 eV, for silver and gold, respectively, which are quite low. The activation energies for the transformation from 180° to 120° tri ad-atom, $E_{3A}^{M}(180 \rightarrow 120)$ (111), was calculated to be 0·156 eV and 0·118 eV for silver and gold respectively. Those from 120° to 180°, $E_{3A}^{M}(120 \rightarrow 180)$ (111), were 0·140 eV.

The activation energy for the conversion of tri ad-atom 90° to 90°, $E_{3A}^{M}(90 \rightarrow 90)$ (100) was found to be 0·43 eV for copper. The activation energy for the conversion of tri ad-atom 90° to 135°, $E_{3A}^{M}(90 \rightarrow 135)$ (100), was found to be 0·67 eV for copper. The activation energy for the conversion of 180° tri ad-atom to 135°, $E_{3A}^{M}(180 \rightarrow 135)$ (100) was found to be 0·60 eV for copper. The energy for a 180° tri ad-atom to convert into 90° next neighbours $E_{3A}^{M}(180 \rightarrow 90\text{nnn})$ (100), was found to be 0·70 eV for copper.

7. A surface vacancy on (111)

7.1 *Oh and Johnson's potential*

It was found that ad-atoms move quite easily on (111) plane. How does a vacancy on (111) plane move? The formation energy of a surface vacancy is then 1·66 eV. The activation energy for the motion of a surface vacancy on (111) was calculated to be 0·958 eV. A vacancy on (111) plane is much harder to move compared with an ad-atom. For silver formation energy was found to be 4·163 eV. Since the binding energy of an ad-atom is 2·60 eV, the formation energy is then 1·66 eV. The activation energy for the motion of a vacancy on (111) was calculated to be 0·958 eV. A vacancy on (111) plane is much harder to move compared with an ad-atom. For gold, formation energy was found to be 4·163 eV. Since the binding energy of an ad-atom is 2·60 eV, the formation energy is then 1·66 eV. The activation energy for the motion of a vacancy on (111) was calculated to be 0·785 eV. A vacancy on (111) plane is much harder to move compared with an ad-atom.

8. A surface divacancy on (111)

8.1 *Oh and Johnson's potential*

For copper the formation energy of a divacancy on (111) was calculated to be 8·190 eV. Since the binding energy of di ad-atoms is 5·62 eV, the formation energy is 2·57 eV. It is well known that a divacancy is much easier to move compared with a vacancy in fcc metals. How is the motion of divacancy on (111) plane?

The activation energy for the motion of a surface divacancy on (111) was calculated to be 0·916 eV. A divacancy on (111) moves as hard as single vacancy on (111). The saddle point for the motion of divacancy is the centre of the trivacancy.

For gold, the formation energy of a divacancy on (111) was calculated to be 8·190 eV. Since the binding energy of di ad-atoms is 5·62 eV, the formation energy is 2·57 eV. It is well known that a divacancy is much easier to move compared with a vacancy in fcc metals. How is the motion divacancy on (111) plane? The activation energy for the motion of divacancy on (111) was calculated to be 0·916 eV. A divacancy on (111) moves as hard as single vacancy on (111). The saddle point for the motion of divacancy is the centre of the trivacancy.

For silver the formation energy of a divacancy on (111) was calculated to be 8·190 eV. Since the binding energy of di ad-atoms is 5·62 eV, the formation energy is 2·57 eV. The activation energy for the motion of divacancy on (111) was calculated to be 0·916 eV. A divacancy on (111) moves as hard as single vacancy on (111). The saddle point for the motion of divacancy is the centre of the trivacancy.

9. Vacancies and divacancies in bulk

9.1 *Oh and Johnson's potential*

The activation energies for the motion of a vacancy and divacancy was calculated to be 0·79 eV and 0·59 eV for gold. The experimental values are 0·82 eV and 0·66 eV, respectively.

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