Diffusion of Cu on Cu surfaces

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Diffusion of a single Cu adatom on low-index Cu surfaces with different morphologies (with and without the presence of other Cu adatoms as well as near and over stepped surfaces) is studied using the embedded-atom method and a molecular static simulation. Migration energies of a Cu adatom in the presence of other Cu adatoms which are relevant in computer simulations of island growth are calculated. We have also calculated the formation and migration energies of an adatom and a vacancy in different layers as well as formation energies of steps on various Cu surfaces. Step-step interaction is shown to be repulsive and consistent with elasticity theory. Our calculations predict a lower activation energy for diffusion of a vacancy than of an adatom for all three Cu surfaces.

I. INTRODUCTION

Understanding surface diffusion is important in the study of many surface related phenomena such as crystal growth, thin film growth, and catalysis. Surface diffusion has been observed experimentally using the field ion microscope (FIM).[1] However, these observations are limited to a few surfaces due to limitations stemming from the response of surfaces of these materials (which are the microscope tips) to high voltage inside the FIM. Although FIM results are not available for diffusion of Cu atoms on Cu surfaces, it will nevertheless be important to study these surfaces from a theoretical standpoint. These calculations are useful to interpret recent experiments of growth of Cu on Cu surfaces,[2] as well as computer simulations of the same processes on the same surface.[3] As discussed later, there is some disagreement in the determination of activation energy barriers for diffusion and in how diffusion proceeds, i.e., by hopping to the nearest site or by the exchange mechanism.[4] In this latter case, an adatom migrates toward a surface atom and pushes it out of its site and fills the vacant place that the surface atom leaves behind. Such a mechanism has been observed experimentally using FIM(1) for Ir/Ir(001), Pt/Pt(001), Ni/Pt(001), and Pt/Ni(001) surfaces,[1] but not for copper. Diffusion by exchange has also been noticed by the embedded-atom method (EAM). First-principles theoretical calculations predict exchange diffusion for a few fcc(001) surfaces,[4] but the case for copper seems controversial (see below).

If we are concerned about the simulation of homoepitaxial growth on low-index copper surfaces, we need to calculate more than one activation energy barrier for adatom hopping. In fact, it has been recently shown,[3] that in simulating the motion of adatoms on Cu(001), one

has to consider not only the motion of an isolated adatom, but the motion of an adatom in the presence of other adatoms (such as near islands). Except for a few special cases, such as the hopping down of atoms from a higher to a lower terrace, it might not matter much, in the overall simulation, whether an atom moves by exchange or hopping.

Due to the large number of particles required to be included in the system and to the lack of symmetry, it is very difficult, if not impossible to do these calculations using a first-principles approach. However, the use of a semiempirical method, such as the embedded-atom method[5] (EAM) seems to us a good compromise between ease of computation and incorporation of the essential physics. We recall that the EAM is a semiempirical model to approximate total energy of fcc solids; this method has received considerable attention from researchers involved with classical atomistic computer simulations.[5−22] The EAM have been applied to many surface problems such as, diffusion,[6−11] shapes of the adsorbed islands,[16] reconstruction,[17] phonons,[18] and relaxations[19] to name a few. Further comments about the applicability of this method to the present problem can be found in the next section.

The main objective of this paper is to determine the migration energies of a Cu adatom on flat Cu surfaces, as well as on Cu surfaces with single atomic steps or islands. There have been a few experimental and theoretical works on the diffusion of Cu adatoms on top of Cu low-index surfaces. Breeman and Boerma[23] used low-energy ion scattering (LEIS) to find a value of the activation energy of Cu on Cu(001) of 0.39 eV. Ernst, Fabre, and Lapujoulada[24] analyzed their helium beam scattering data using nucleation theory and found this activation energy to be 0.28 eV. However, some questions were raised in Ref. 25 about this analysis and Ernst's value

would have to be revised downwards, yielding a value close to 0.1 eV. Jo and Vook[26] in an electromigration experiment on polycrystalline strips reported a value of 0.47 eV. Theoretical works yields a wide range of values as well. Breeman *et al.*[27,28] used the embedding atom method of Finnis and Sinclair and obtained an activation energy of Cu on Cu(001) of 0.79 eV. This work and others that use the EAM get a value of about 0.48 eV. Hansen *et al.* used the modified effective-medium theory[29] (MEMT) to obtain a value of about 0.23 eV for the exchange mechanism. The EAM calculations predict that such mechanism is not favored for migration on Cu(001), although it is for some other specific cases, as described below. We also compare these migration energies with energies obtained for nickel surfaces, and show that there is a general trend. This trend, which might be shared by other metal surfaces of similar kind, could be exploited to obtain quick estimates of migration energy barriers. Calculations of formation energies of various defects on Cu surfaces, such as vacancy, adatom, and steps are presented and discussed. Step-step interaction is studied and the long-range part of the interaction is compared with the elasticity theory. Most of our results are compared with either theoretical or experimental findings.

The computational methods will be outlined in Sec. II. Results and discussion are given in Sec. III. Finally, in Sec. IV, we will summarize our results and draw some concluding remarks.

II. METHOD

We have employed the EAM technique developed by Daw and Baskes[5] to model the interactions between Cu atoms. in the EAM, most of the binding energy of each atom is due to the embedding energy, which is supplemented by a two-body pair potential. The embedding function of each atom does depend on the electronic charge density at the position of that atom and, therefore, is well defined near the surface of a crystal if charge density near the surface is well known. Mapping of the surface charge density of the Cu crystal has been reported using first-principle calculations.[30]

The EAM functions are usually determined by considering functional forms for energy, embedding function of each particle, and pair potential between particles and fitting them to the bulk properties of crystalline solid. In this work, the EAM functions of Cu developed by Adams, Foiles, and Wolfer[6] are employed. These functions are fitted to a similar database as the one employed by Foiles, Baskes, and Daw (FBD),[5] except for the use of a more updated value of the single vacancy formation energy in the fitting.[6,7] Daw-Basks (DB) EAM functions,[5] as well as Voter-Chen[10] (VC) have frequently been used in the literature. Because EAM has traditionally been constructed by fitting certain functions (see below) to bulk properties, its application at the surface environments is not always as reliable as in the bulk. There have been several attempts to extend the fit of the EAM functions to surface as well as the bulk.[20,21] However, these attempts have been applied to specific problems and their reliabilities have not been fully tested against other applications. The EAM in its present state is an approximate and simple method, which works rather well for Cu. It should be mentioned that the EAM at its best application, i.e., when applied to Cu, may produce results within 5–10 % of experimental data. The EAM functions employed in this study were fitted to the bulk properties, such as elastic constants, bulk modulus, cohesive energy, single vacancy formation energy, equilibrium lattice constant, and heat of solution of dilute alloys. Although this fit has been done to bulk properties, calculated surface properties are in good agreement with available experimental data or other calculations.[2,14] The EAM functions are employed in conjunction with the molecular static (MS) simulation to calculate formation and migration energies.

The MS simulation is a computational technique for minimizing the total energy of a system of particles (atoms), with respect to the position of particles. The MS code, employed by us, is based on the conjugate gradient and works at zero temperature. The input to the MS code is a lattice file. The lattices we have used in our calculations are slabs of various sizes with two free surfaces. Two periodic boundary conditions are employed parallel to the free surfaces.

Adatom and vacancy formation energies on and in Cu(100), (110), and (111) surfaces are calculated using a slab of 20–21 layers, 100–121 atoms per layer, and periodic boundary conditions along x and y directions. The middle two layers are frozen and our results are size independent. The migration energy of an atom or a vacancy is calculated using the following formula:

$$E_m = E_{sad} - E_0 , \qquad (1)$$

where E_m is the migration energy of an atom or a vacancy, E_{sad} is the saddle-point energy, which is the minimized energy of the system plus the atom/vacancy when atom/vacancy is at the saddle point (saddle point for symmetric system is usually midway between the initial and final migrating points), and E_0 is the total minimized energy of the system with the migrating atom/vacancy at the initial point in the migration path.

As illustrated in the next sections, growth by vapor deposition on these low-index Cu surfaces proceeds by surface diffusion of adatoms followed by nucleation, growth, and then coalescence of islands. Recent simulations have shown that it is crucial to consider, in the calculation of surface diffusion of an adatom, the presence of other adatoms. In this type of simulation, atoms are deposited at random on various densities of a substrate at a fixed rate.[3,10] After arrival at a site, an atom can hop to a vacant nearest-neighbor site according to the following formula:

$$h = u_0 \exp(-E_b/k_B T) , \qquad (2)$$

where h is the hoping rate, u_0 is the hopping frequency, E_b is the energy barrier for hopping, T is the temperature, and k_B is the Boltzmann constant. It should be mentioned that the activation entropy has not been included in the calculation of E_b. It is important to realize that the E_b of hopping of one atom from the initial to a

final site depends on the local environment of atoms at those sites. In particular, for a fcc(001) surface ten neighboring sites around the atom in initial and final sites were found to influence E_b.[3,10] Based on whether these ten sites are occupied or empty a total number of $(2)^{10}$ or 1024 configurations is required.[3,10] Due to symmetry, only limited numbers of these configurations (about 544) are independent of one another.

Before presenting the method used to calculate the energetics of defects, we define the following terms: surface energy, adatom, vacancy, ledge, kink formation energies, and adatom vacancy activation energies.

Surface energy is the difference in energy of an atom per unit area in the surface and the bulk environments. Because of weaker binding energies of atoms in the surface region, due to their lower coordination number, one expects a nonzero positive value for the surface energy. Obviously, a lower surface energy is indicative of a more stable surface. In the calculation of surface energy the following formula is employed:

$$2AE_{sur} = E - NE_c ,\qquad (3)$$

where E_{sur} is the surface energy in eV/$\mathring{A}^2$, E is the total minimized energy of the slab, N is the total numbers of atoms in the slab, E_c is the cohesive energy of the atoms, A is area of each free surface of the slab, and two accounts for two free surfaces.

A related quantity, i.e., the formation energy of an adatom or a vacancy is the amount of energy that needs to be spent to create an adatom or vacancy, respectively. The formation energy of an adatom can be calculated from the following formula:

$$E_{1a}^f = E(N+1,1) - E(N,0) + E_S ,\qquad (4)$$

where E_{1a}^f is the single adatom formation energy, $E(N+1,1)$ is the total minimized energy of a system of $N+1$ atoms with one adatom, $E(N,0)$ is the total minimized energy of a system of N atoms with no adatom, and E_S is the sublimation energy of each atom ($E_S > 0$ or negative of cohesive energy). The formation energy of a vacancy can also be calculated from a similar formula:

$$E_{1v}^f = E(N-1,1) - E(N,0) - E_S ,\qquad (5)$$

where E_{1v}^f is the single vacancy formation energy and $E(N-1,1)$ is the total minimized energy of a system of $N-1$ atoms with one vacancy.

Similarly, the ledge formation energy is the difference in energy between a surface with a ledge and a flat surface. The kink formation energy is the difference in energy between a ledge with and without a kink. It is important to note that ledge or kink formation energies are calculated with respect to a flat or a surface with a single ledge, respectively. The formation energy of a surface

TABLE I. (a) Migration energies of an adatom on Cu(100) surface using AFW, VC, and DB EAM potentials. For comparison, we report the corresponding values for Cu from other references. Moves b and c are from ledge site and moves d and e are from kink site. The results in this table are all relevant to the moves in Fig. 1(a). All energies are in eV; (b) migration energies of an adatom on the Cu(110) surface using AFW and VC potentials. The results in this table are all relevant to the moves in Fig. 1(b). All energies are in eV. (c) Migration energies of an adatom on Cu(111) surface using AFW and DB potentials. The results in this table are all relevant to the moves in Fig. 1(c). All energies are in eV.

(a)

Moves	a	b	c	d	e	f	g	h
Various work								
Present work (AFW)	0.48	0.25	0.84	0.51	0.83	0.80	0.77	0.51
Ref. 9 (AFW)	0.45	0.27	0.86	0.54	0.87		0.81	0.65
Ref. 7 (VC)	0.53					0.79		
Ref. 14 (DB)	0.49	0.26	0.83	0.53		>1		0.5
Ref. 7 (AFW)	0.38					0.72		

(b)

Moves	a	b	c	d	e	f	g	h	i	j
Various work										
Present work (AFW)	0.24	1.15	0.28	1.17	0.54	1.30	0.30	0.87	1.17	0.72
Ref. 7 (VC)	0.53						0.31			
Ref. 7 (AFW)	0.23						0.30			

(c)

Moves	a	b	c	d	e	f	g	h
Various work								
Present work (AFW)	0.028	0.29	0.67	0.54	0.59	1.12	0.49	0.085
Ref. 7 (VC)	0.044							
Ref. 7 (AFW)	0.026							

with step with respect to the surface without step is calculated using the following formula:[31]

$$\lambda = (E - 2A_s E_{sur} + NE_S)/(4l_x) ,$$ (6)

where λ is the formation energy of the step in eV/Å, E is the total minimized energy of the system including the step, A_s is the area of the step as projected onto a flat surface, E_{sur} is the surface energy of a flat surface from
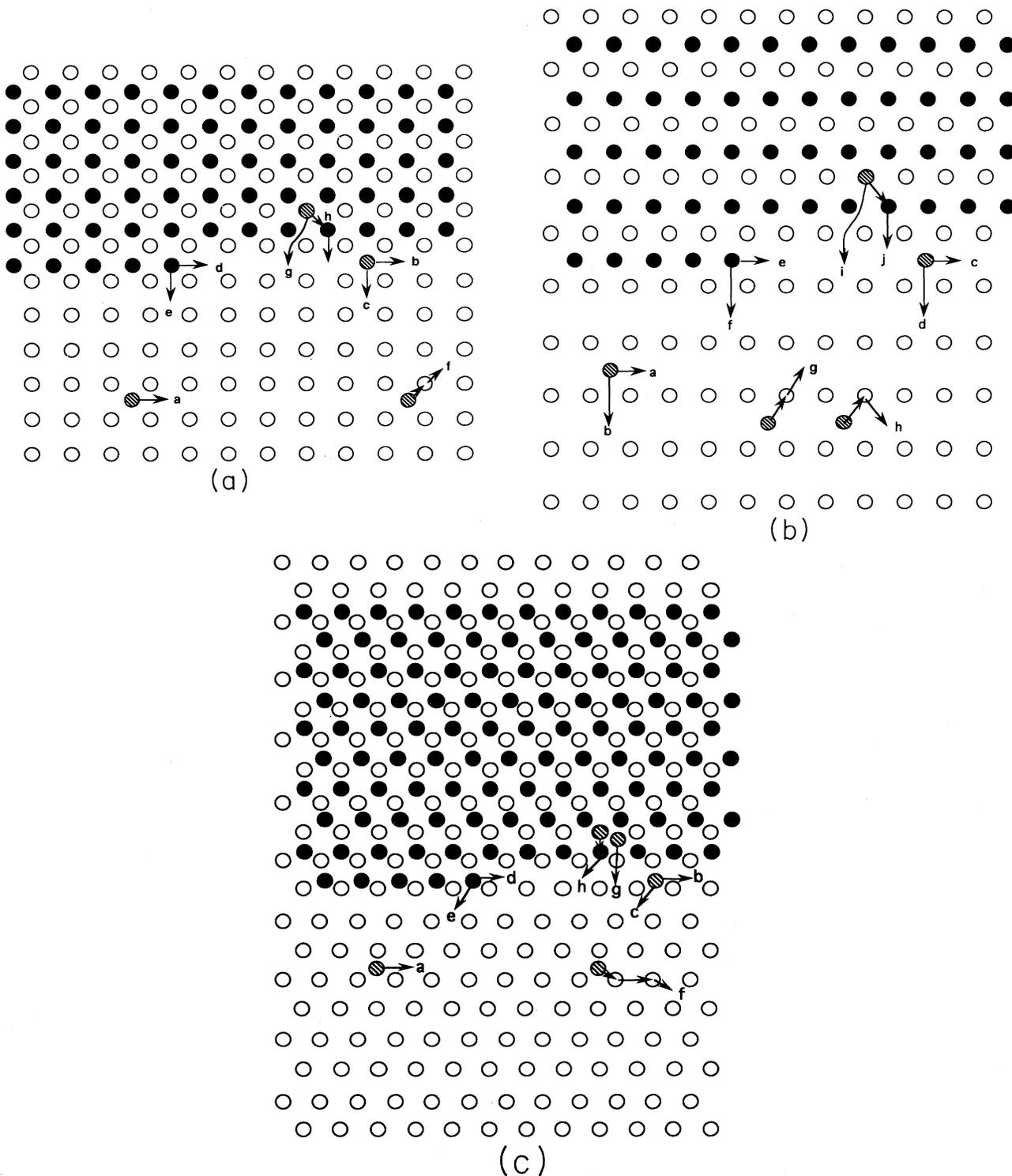

(a)

(b)

(c)

FIG. 1. (a) Various diffusion processes on Cu(100) surface (see text), lower terrace atoms (○), upper terrace atoms (●), adatom (◉).
(b) Various diffusion process on Cu(110) surface (see text), lower terrace atoms, upper terrace atoms, adatom. (c) Various diffusion processes on Cu(111) surface, step B (see text), lower terrace atoms, upper terrace atoms, adatom.

Eq. (3), N is the total numbers of atoms in the system, l_x is the periodic length of the ledge along the x direction, and 4 accounts for four ledges (two on each free surface), and E_S is the sublimation energy. It is worth mentioning that our formula for the formation energy of the step in its present form is valid for a slab with two free surface. A similar formula as Eq. (6) along with Eq. (3) can be employed for the calculation of kink formation energy.

III. RESULTS AND DISCUSSION

Here, we present and discuss the most significant findings.

A. Diffusion of a Cu adatom on flat Cu surfaces

Migration energies of a Cu adatom on flat Cu(100), Cu(110), and Cu(111) surfaces were calculated using Eq. (1) and are reported in Table I. Various migration paths are displayed in Fig. 1. Our value of 0.48 eV for the direct hopping migration energy of a Cu adatom over a bridge on a Cu(100) surface is in good agreement with the corresponding values of 0.49 eV (DB EAM),[14] 0.53 eV (VC EAM),[7] 0.45 eV (AFW EAM),[9] 0.41 eV (MEMT),[29] 0.47 eV [corrected effective medium theory (CEMT)],[29] and 0.39 eV (LEIS).[23] On the other hand, our value of 0.48 eV is in poor agreement with the value of 0.28 eV reported by Ernst, Fabre, and Lapujoulade[24] using helium beam scattering. We understand that the value reported by Ernst, Fabre, and Lapujoulade[24] could still be not final.[9] Using the same EAM functions, a value of 0.38 eV was reported in Ref. 7 for the same calculation. We believe this value to be wrong (perhaps a typographical error), since we were able to replicate all other values reported in that paper. Our value of 0.24 eV for the migration energy of move a in Fig. 1(b), i.e., diffusion of a Cu adatom parallel to the closed-packed direction, is in good agreement with the corresponding values of 0.23 eV and 0.53 eV in Ref. 7, using Adams and Vorter EAM potentials. The close agreement between our results and those using Adams potential is not

surprising, because we have used the same potential. Our value of 1.15 for the migration energy of a Cu adatom moving across a closed-packed direction on Cu(110), i.e., move b in Fig. 1(b), is much higher than the corresponding value of 0.24 eV for a move along the closed-packed direction. Energy barriers for direct move diffusion on Cu(110) surface is very anisotropic. This is somehow expected, due to geometry of the surface. Our value of 0.028 eV for move a in Fig. 1(c) is in good agreement with the values of 0.026 eV (Ref. 7) and 0.044 eV.[7]

Migration energies of an adatom involving an exchange mechanism are calculated for diffusion of a Cu adatom on flat Cu(100), Cu(110), and Cu(111) surfaces. Our moves for the diffusion by exchange are shown in Fig. 1 and results are reported in Table I. Our values of 0.80 eV and 0.30 eV for exchange migration energies on Cu(100) and Cu(110) surfaces are in accord with the corresponding values of 0.72 eV (AFW EAM),[7] 0.79 eV (VC EAM) (Ref. 7) and 0.30 eV (AFW EAM), 0.31 eV (VC EAM), respectively. Our values of 0.80 eV, 0.30 eV, and 1.15 eV for exchange migration energies of a Cu adatom on Cu(100), Cu(110), Cu(111) surfaces are, in general, higher than the corresponding values 0.22, 0.25, 0.46 eV using the MEMT.[29] It should be mentioned that the kinetic-exchange-correlation term (KEC) in the CEMT or one electron term (OE) in the MEMT has made the exchange move energetically more favorable over a direct hopping over a bridge on the Cu(100) surface. On the other hand, the EAM favors direct hopping over the exchange on Cu(100) and Cu(111) surfaces [look at Figs. 1(a) and 1(c) and Tables I(a) and I(c)]. This is presumably because the EAM does not include contributions due to the KEC or OE terms. A direct experimental measurement of the exchange barrier of a Cu adatom on a Cu(100) surface can provide ultimate validity for the various theoretical methods described here.

Our value of 0.30 eV of the energy barrier for an exchange move perpendicular to the wall [move g on the Cu(110) surface] is comparable to the corresponding direct move value of 0.24 eV along the trough (move a), but much smaller than the value of 1.15 (move b) across the trough. Note that the exchange move has the same

TABLE II. Relative migration energies of various moves with respect to the corresponding value on a flat surface. Cu(100), Cu(110), and Cu(111) rows are results of present work using AFW EAM functions of copper.

Moves	a	b	c	d	e	f	g	h	i	j
Surfaces										
Cu(100)	1	0.52	1.75	1.06	1.73	1.67	1.60	1.06		
Cu(100)[a]	1	0.60	1.91	1.20	1.93		1.80	1.44		
Cu(100)[b]	1	0.53	1.69	1.08				1.02		
Ni(100)[c]	1	0.52		1.03	1.65	1.48	1.44			
Cu(100)	1	4.79	1.17	4.87	2.25	5.42	1.25	3.62	4.87	3
Ni(110)[c]	1		0.93		1.66	3.50	1.11		3.04	
Cu(111)	1	10.4	23.9	19.3	21.1	40.0	17.5	3.0		
Ni(111)[c]	1	8.75		14.1	12.9		9.82			

[a]Reference 9 using AFW EAM functions.
[b]Reference 8 using AFW EAM functions of Ni.
[c]Reference 14 using DB EAM functions.

TABLE III. Migration energies of a Cu adatom in presence of other Cu adatoms (island) on Cu(100) surface using AFW EAM functions. All energies are in eV.

Configurations	Migration energies
a	0.811
b	0.485
c	0.563
d	0.007
e	0.459
f	0.563
g	0.479
h	0.246
i	0.636
j	0.634

net effect as a direct move. Therefore the exchange move has restored the energetic isotropy of the surface diffusion.

B. Diffusion of an adatom near a step

Energy barriers for diffusion of an adatom near a step on Cu(100), (110), and (111) surfaces are different than their corresponding values on the flat Cu surfaces. In particular, migration energy of a Cu adatom along the ledge on Cu(100) is smaller than the corresponding value on the flat Cu surface. A similar trend was found in a Finnis-Sinclair atom embedding[29] calculation of the activation energies of Cu atoms on a Cu(001) surface near edges of Cu islands.[3] This result is very important in a simulation of the motion of Cu atoms on a Cu(001) surface with Cu islands. For example, Barkema et al.[3] simulated the growth of Cu on Cu(001) and found that this lower energy for motion parallel to an island edge is responsible for the formation of rather compact islands. STM images for a similar system, deposition of Ni on Ni(001) at 300 K, show compact and squarelike islands.[32]

Migration energies of a Cu adatom moving near a step on various Cu surfaces are reported in Table I along with the results of Refs. 9 and 14 for Cu(100) surface. As it can be seen from Table I, the agreement between our values and the ones in Refs. 9 and 14 is rather good. Our values of 0.25 and 0.84 eV for modes b and c, i.e., migration energies of a Cu adatom along and perpendicular to the ledge direction on Cu(100) surface, are in good agreement with the corresponding values of 0.26, 0.83 eV from Ref. 14, using DB EAM functions and 0.27, 0.86 eV from Ref. 9, using AFW EAM functions, respectively. Our value of 0.51 eV for the exchange energy barrier of a Cu adatom diffusing over a descending step on Cu(100) surface is comparable to the value of 0.48 eV for the corresponding move on a bare Cu(100) surface. This is a surprising result, because a step edge was believed to produce a strong repulsive potential against the motions of an approaching adatom moving on the upper terrace toward the step edge.[14] Our result is consistent with a recent FIM experiment of Wang and Ehrlich[1] on Ir/Ir(100). Our values of 0.51 eV and 0.48 eV for migra-

tion energies of a Cu adatom diffusing over a descending step on Cu(100) surface or a flat Cu(100) surface are in close agreement with the corresponding values of 0.5 and 0.49 eV in Ref. 14, using DB EAM functions, but they disagree with the corresponding values of 0.65 eV and 0.45 eV in Ref. 9 using AFW EAM functions. As it can be seen in Table I, diffusion by exchange over a descending step on Cu surfaces studied here is, in general, energetically more favorable than the corresponding direct move diffusion. FIM result of Wang and Ehrlich[1] for the migration energy of a W adatom over a descending Ir step of type B or Ir(111) surface corroborates the trend of our findings. However, to the best of our knowledge, there is no similar experimental result for copper. The trend we found for migration energies of moves a and g is consistent with a similar work done on a Ni surface,[8] i.e., the migration energy for move g is greater than the corre-
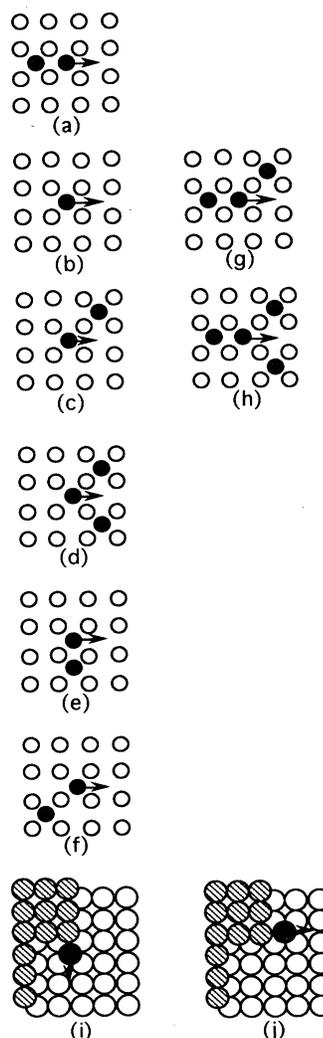

FIG. 2. Diffusion of an adatom in presence of other adatoms. Adatom is presented by an arrow to the right, lower terrace atoms (○), upper terrace atoms (●).

sponding value for move a. This has the implication that moving atoms toward the step edge are reflected back on the upper terrace. This is true only if direct hopping is the diffusion mechanism. Our value of 1.32 eV for sum of the energy barriers for moves a and c in Fig. 1(a) is in reasonable agreement with the value of 1.10 eV from a recent low-energy electron-diffraction experiment.[33] Remembering that the EAM does not include the exact electron interaction between the ledge and adatom[9] and

also the fact that entropy contribution is not included in the calculation of energy barriers here, the agreement is quite reasonable.

Relative migration energies of various moves of an adatom near a step are calculated with respect to the corresponding values on a flat surface. Our results along with the ones for Ni from Ref. 8 and a Cu step on Cu(100) surface from Refs. 9 and 14 are presented in Table II. As it can be seen from Table II, the agreement

TABLE IV. Formation and migration energies of defects as well as surface energies and binding energies of an adatom on Cu(100), Cu(110), and Cu(111) surfaces using AFW, DB, and VC EAM functions. All energies are in eV. Surface energies are in ergs/cm^2.

Surface	(100)	(110)	(111)
Vacancy			
E^f_{1v}	0.594	0.292	0.722
E_m	0.355	0.510	0.582
$Q_v = E^f_{1v} + E_m$	0.949	0.902	1.304
Adatom			
E^1_{af}	0.712	0.309	0.966
E_m	0.481	0.244	0.028
$Q_a = E^1_{af} + E_m$	1.19	0.553	0.994
Surface energy			
Present work	1319	1446	1214
From Ref. 7 (AFW)	1321	1487	1215
From Ref. 14 (DB)	1288		1181
From experiment[a]	1790	1790	1790
Formation energy			
Ledge (eV/A)	0.068	0.0054	0.103
From Ref. 9 (AFW)	0.064		
From Ref. 14 (DB)	0.061		
Kink (eV/kink)	0.108	0.245	0.059
from STM[b]	0.101		
from Ref. 9 (AFW)	0.139		
Binding energy of an adatom			
to bare surface	-2.85 $(-2.85)^c$	-3.17	-2.28
to ledge site	-3.23 $(-3.23)^c$	-3.24	-3.06
to kink site	-3.54 $(-3.54)^c$	-3.54	-3.54
Relative binding energy of an adatom			
to bare surface			
Cu	0.80	0.89	0.64
Cu[c]	0.80		
Ni[d]	0.82	0.92	0.75
to ledge site			
Cu	0.91	0.91	0.86
Cu[c]	0.91		
Ni[d]	0.92	0.92	0.92
to kink site			
Cu	1	1	1
Cu[c]	1		
Ni[d]	1	1	1

[a]Reference 34.
[b]Reference 2 using STM.
[c]Reference 9 using AFW EAM functions.
[d]Reference 8 using AFW EAM functions.

between our trend and the one for Ni and Cu is excellent for the (001) surface. For the (110) and (111) surfaces, on the other hand, the agreement varies depending on the moves.

The evaporation barriers for an adatom from flat site (fourfold hollow site), ledge site, and kink site on Cu surfaces into the vacuum are reported in Table IV. These barriers are equal to the binding energies of a Cu adatom to those sites. As it can be seen from Table IV, binding energies of a Cu adatom to a kink site on Cu(100), Cu(110), and Cu(111) surfaces are equal to the cohesive energy of a Cu atom in the bulk region. This is consistent with the results obtained in Ref. 8 on Ni surfaces. Relative binding energies of a Cu adatom, with respect to the binding energy at the kink site, are calculated for various sites on Cu(100), Cu(110), and Cu(111) surfaces and reported in Table IV along with similar values for Ni surfaces[8] and Cu(100) surface from Ref. 9. As it can be seen in Table IV, Cu and Ni have a very similar trend in their relative binding energies.

C. Diffusion of an adatom near an island on a Cu(100) surface

The migration energies of a Cu adatom in the presence of other Cu adatoms (islands) are calculated for the configurations (a)–(g) in Fig. 2 and are presented in Table III. A histogram of these migration energies is shown in Fig. 3. As it can be seen from this histogram all the migration energies are scattered around four peaks. Configurations (a)–(g) of Fig. 2 are dominant in the monolayer growth. Work is in progress to model this four-peak histogram into a simple formula. This simple formula can then be employed to approximately calculate migration energies of all 1024 configurations described in Sec. II.
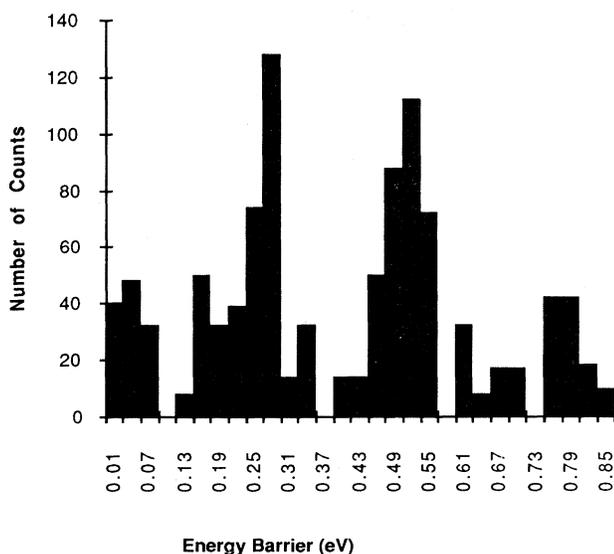

FIG. 3. The occurrence of various migration energies vs their energies.

The migration energies of an adatom from a multiple length kink sites, i.e., moves (i) and (j) in Fig. 2, onto the terrace sites are lower as compared to similar moves originating from the step edge.[14] These migration energies are reported in Table III. Our values of 0.636 eV and 0.634 eV for migration energies from multiple length kink site are in good agreement with the value of 0.56 eV from Ref. 14 for both moves. With this reduction in barriers, one can expect that with increasing substrate temperature the number of kinks will increase and mobile atoms along the ledge migrate to these multiple length kink sites from which they can evaporate to terrace sites.

D. Energetics of point defects and step formations

Single vacancy and adatom formation energies of a Cu adatom in or on free surfaces of Cu(100), Cu(110), and Cu(111) slabs, are calculated using Eqs. (4) and (5) and the MS technique and are reported in Table IV. Our value of 0.72 eV for the single vacancy formation energy in Cu(111) surface is somewhat smaller than the value of 0.92 eV deduced from a first-principle calculation.[30] However, the slab in the first-principle calculation[30] is smaller [seven Cu(111) layers with 21 atoms per layer] than ours (20–21 layers with 121 atoms per layer). We get the following trends among the single vacancy and single adatom activation energies Q_v and Q_a in or on Cu(100), Cu(110), and Cu(111) surfaces; $Q_v < Q_a$ on Cu(100) surface and $Q_a < Q_v$ on Cu(110) and Cu(111) surfaces. These trends indicate that, on the Cu(100) surface, single vacancy migration is the dominant diffusion mechanism. On Cu(110) and Cu(111) surfaces, on the other hand, the diffusion mechanism is dominated by adatom migration. Our trends of dominant diffusion mechanisms on Cu(110) and Cu(111) surfaces are in accord with the prediction of Ref. 8 for Ni, using the AFW EAM functions. On the other hand, our trend for the dominant diffusion mechanism on Cu(100) is opposite of the one in Ref. 8 for Ni. Our trend for the dominant diffusion mechanism on Cu surfaces are in accord with the prediction of Ref. 35 using a pair potential.

Surface energies of Cu(100), Cu(110), and Cu(111) surfaces are calculated and reported in Table IV, using slabs of about 21 layers with 80–90 atoms per layer with the middle three layers in their bulk environment. As expected, surface energy of the Cu(110) surface is highest among the three surfaces studied here. This is indicative of the fact that Cu(110) is the least stable surface among the surfaces studied here. Our values of 1319 ergs/cm,^{2} 1446 ergs/cm,^{2} and 1214 ergs/cm^2 for surface energies of Cu(100), Cu(110), and Cu(111) surfaces are in a good agreement with the corresponding values of 1321 ergs/cm^2, 1487 ergs/cm^2, and 1215 ergs/cm^2 from Ref. 7. Our surface energies for (100) and (111) surfaces can also be compared with the corresponding values of 1288 ergs/cm^2 and 1181 ergs/cm^2 from Ref. 14. Our values of the surface energies for the surfaces studied here are somewhat smaller than the experimental values.[34] The experimental values are usually averaged over several faces and, therefore, comparison of our results with the experiment is only qualitative. It is known that EAM, in

general, underestimates the surface energy.[7,14] It is shown in Ref. 17 that inclusion of a gradient correction to the charge density can increase the surface energy of Au(110) and brings it closer to the experimental value.

The formation energies per unit length of a ledge and a kink on Cu(100), Cu(110), and Cu(111) surfaces are calculated and presented in Table IV, using slabs of about 21 layers with the middle three frozen in their ideal bulk environment and enough atoms are removed from both free surfaces to construct two similar steps that have four rows of atoms parallel to the ledge in the upper and lower terraces. Our ledges are always along the [110] or close-packed direction. As expected, formation energy of a ledge on Cu(110) is lower than its corresponding values on Cu(100) and Cu(111) surfaces. This is in turn due to the high surface energy of (110) surface as compared to (100) and (111) ones. It is worth mentioning that the steps employed in this section have a small width and interact with one another. As it will be seen in the next section, the step formation energy vary with the step width and, hence, the calculation is meaningful only when we compare formation energies of the steps of same width on Cu surfaces with one another. Our trend ($\lambda_{110} < \lambda_{100} < \lambda_{111}$) for the formation energies of the ledges on Cu surfaces is in accord with the corresponding trend on Ni surfaces.[8] Our value of 0.108 eV for the kink formation energy (only one kink) is in good agreement with the experimental value of 0.10 eV.[2] Our trend ($\lambda_{110} > \lambda_{100} > \lambda_{111}$) for the formation energies of a kink on Cu surfaces is similar to the one observed in Ref. 8 for Ni.

E. Step-step interaction

We have constructed slabs of 21–41 layers thick, $4a$ height (where a is surface lattice constant), $5a–81a$ width. We have removed slightly more than a half of atoms of both free surfaces and made atomic steps of widths $2.5a$ up to $40.5a$. The reason we made variable thickness slabs is that depth of the relaxation along the z direction varies with increasing step width.[31] We need to make our slabs thick enough so that energies of the atoms in the middle region of the slab converge to the bulk cohesive energy. We calculated the formation energies of the steps using Eq. (6) and graphed them in Fig. 4 vs step width d. The long-range part of Fig. 4 is fitted to the function,

$$\lambda = \lambda_0 + \alpha a^2 / d^2 , \tag{7}$$

where $\lambda_0 = 0.065$ eV/Å, $\alpha = 0.0802$ eV/Å, and $a = 3.615/\sqrt{2}$ is the surface lattice constant. The functional form in Eq. (7) is in accord with elasticity theory.[31] From Fig. 4(a) or Eq. (7) one can clearly see that the elastic interaction energy between the steps is repulsive. Our value of $\lambda_0 = 0.065$ eV/Å (an isolated ledge formation energy) is in good agreement with the corresponding values of 0.064 eV/Å (AFW EAM) (Ref. 9) and 0.061 eV/Å (DB EAM).[14] The values of λ_0 and α reported in here are on a flat surface. However, it is shown in Ref. 31 that these values are the same on vicinal and flat surfaces within the estimated uncertainty, for the system studied there.
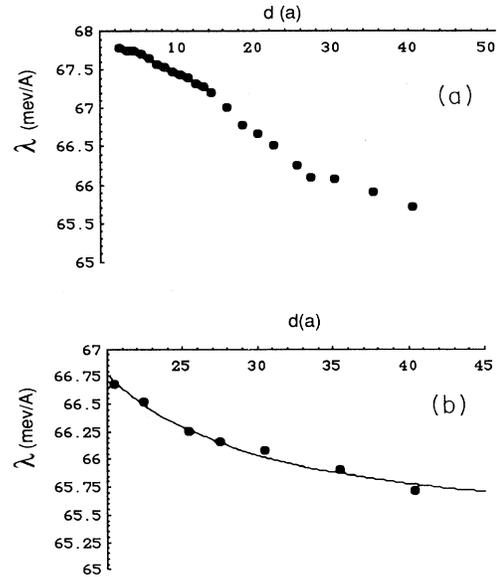

FIG. 4. (a) Ledge formation energy λ vs ledge separation $d(a)$ on a flat Cu(100) surface. The unit of a is the surface lattice constant. (b) Asymptotic part (large step widths) of (a). Points are from the simulation and the continuous curve is the fitted function to the points.

IV. SUMMARY OF RESULTS

We have calculated the energetics of adatom and vacancy diffusion of Cu atoms on low-index surfaces of copper. Our findings should be useful as input to numerical simulations of epitaxial growth and are relevant to recent experiments probing diffusion of Cu adatoms on Cu surfaces. In the following, we summarize the most significant results of our calculations.

A. General trends in the energy barriers for hopping

(1) Migration energy barriers of an adatom near islands have been calculated and plotted. Our graph shows that all the migration energies can be grouped around four distinct energy values.

(2) Our results for the migration energy barriers of an adatom near different step configurations show that relative energy (energy barriers for a given move vs energy barriers for migration of an isolated adatom) are similar for Cu and Ni low-index surfaces.

(3) Diffusion of an adatom near a step on Cu(001) surface is anisotropic. In particular, migration energies of an adatom moving along a ledge on Cu(001) surface is smaller than the corresponding value on the flat surface. On the other hand, migration energies for moves perpendicular to the ledge direction on Cu(001) surface is greater than its corresponding value on the flat surface.

(4) Diffusion of an adatom near a step on Cu(110) surface is anisotropic. In particular, migration energies of an adatom moving along a ledge on Cu(110) surface is

slightly different than the corresponding value on the flat surface. The migration energies for moves perpendicular to the ledge direction on Cu(110) surface is slightly higher than its corresponding value on the flat surface.

(5) The migration energy of a Cu adatom along the step on the Cu(111) surface is about an order of magnitude greater than the corresponding values on a flat Cu(111) surface. The migration energy of a Cu adatom moving away from the ledge is slightly smaller than for the parallel direction. This is in agreement with the experimental results showing fractal (rough) ledges of steps on (111) surfaces of other metals.[32]

(6) Migration energy of an adatom from a multiple length kink site on Cu(001) to a terrace site is smaller than the corresponding value from a single length kink site. This is consistent with a similar work on Cu(100).[14]

(7) Migration barriers of a Cu adatom (by direct hopping) over a descending step on Cu(100), Cu(110), and Cu(111) surfaces are, in general, greater than their corresponding values on flat Cu surfaces. This has the implication that atoms that land over the upper terrace during the growth can diffuse toward the step and be reflected by the step. This is consistent with a similar work done on Ni.[8]

B. General trends for energy barriers for the exchange diffusion mechanism

(8) The energy barrier for the exchange move perpendicular to the wall of a Cu(110) surface is energetically more favorable than a corresponding direct move.

(9) The energy barriers for a Cu adatom over a descending step when exchange is involved are in general lower than the corresponding direct hopping.

C. Other results

(10) The dominant mechanism of diffusion on Cu surfaces depends on surface orientation. On the Cu(100) surface, the dominant mechanism is the single vacancy migration. On Cu(110) and Cu(111), on the other hand, the dominant mechanism is migration of the adatoms. A similar work on the Ni surfaces, using the EAM, indicated the adatom diffusion to be dominant on all low-index Ni surfaces. Our work has the same trend for the dominant diffusion mechanisms as a similar work performed on Cu surfaces using a pair interatomic potential.[35]

(11) Binding energies of a Cu adatom to a kink site on Cu surfaces are equal to the cohesive energy. This result is consistent with the one in Ref. 9 on Cu(100) surface, as well as with Ref. 8 on Ni surfaces.

(12) Our value of 0.72 eV for the single vacancy formation energy in the surface layer is in fair agreement with the value of 0.92 eV from the first-principles calculations.[30]

(13) Our value for the ledge formation energy on Cu(001) surface (0.065 eV/Å is in good agreement with the values of 0.061 eV/Å (Ref. 14) and 0.064 eV/Å.[9]

(14) Step-step interaction is repulsive within the step separation range that was considered here and is consistent with the elasticity theory.

(15) Our value for the kink formation energy (0.108 eV/kink) is in excellent agreement with the corresponding value of (0.101 eV/kink) from the scanning tunneling microscopy (STM) experiment (2).

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