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Effect of step-step separation on surface diffusion processes

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We present results of calculations of activation energy barriers for several processes involving a diffusing atom around a step edge on the (111), (100), and (110) surfaces of Cu using the nudged elastic band method with interaction potentials based on the embedded atom method. In the presence of a neighboring step, the Ehrlich-Schwoebel barrier for an adatom to undergo jump or exchange at a step edge is found to be independent of the separation between the steps unless they are at two-atom width apart, in which case the barrier is larger than that for an isolated step. The influence of the local step geometry on diffusion energetics is also discussed.

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I. INTRODUCTION

Understanding the details of diffusion on metal surfaces remains a subject of continuing interest in the surface science community since the atomic processes responsible for surface diffusion govern the microscopic nature of several technologically important phenomena such as thin-film and epitaxial growth, catalysis, and chemical reactions. One of the decisive factors controlling the growth mode, whether it is two-dimensional, layer-by-layer, or three-dimensional pyramidal clusters (mounds), is the energy barrier experienced by the diffusing atom at the step edge. If this barrier is small, the adatom can descend over the step edge to the lower terrace plane and the growth is expected to be two dimensional. On the contrary, if the diffusing atom encounters a high-energy barrier at the step edge, the growth is likely to be three dimensional. The existence of this step-edge barrier, called the Ehrlich-Schwoebel (ES) barrier, has been confirmed for the (111), (100), and (110) surfaces of several metals.[1–5] What is less known is whether the magnitude of this barrier depends on the terrace width. Adatoms may hop or exchange at the step edge. Results from theoretical studies based on both embedded-atom-method[3] (EAM) and *ab initio*[5] calculations show that diffusion of a single atom over a step on fcc(111) metal surface is generally through the exchange of the adatom with a step atom and the energy barrier involved in the process depends on the local step geometry.

Regardless of whether the diffusion mechanism is a hop or an exchange, the Ehrlich-Schwoebel barrier plays an important role in determining the evolution of the surface morphology. Although there has been some discussion in several experimental papers on the effect of the terrace width on the magnitude of the ES barrier,[6–10] no solid conclusion has been drawn and there is a need to establish theoretically whether a variation of this barrier with the terrace width indeed exists. We have therefore undertaken total energy calculations for single-atom diffusion over a step edge on the low-Miller-index surfaces of Cu using the nudged elastic band method[11] based on interaction potentials extracted from the EAM.[12] In this paper, we examine the dependence of the Ehrlich-Schwoebel barrier on the terrace width for a diffusing Cu adatom over two types (a tightly and a loosely packed) of step edges on the (111), (100), and (110) surfaces of Cu. We are also interested in evaluating the energies for an adatom, a step atom to detach from the step edge for varying terrace widths, to see if these energies change with the varying terrace width.

The rest of the paper is organized as follows. Section II contains a brief summary of computational details, while Sec. III embraces the theoretical techniques involved in the total energy calculations. Our results and discussions are presented in Sec. IV, and concluding remarks are summarized in Sec. V.

II. COMPUTATIONAL DETAILS

In our model systems for examining the effect of terrace width on adatom diffusion on the (111), (100), and (110) surfaces of Cu, a two-step-system is constructed by adding two more layers, with a reduced number of atomic chains, on top of a seven-layer slab of (111) and six-layer slab of (100) and (110) [see Fig. 1(a)]. For an isolated step system, on the other hand, one-half of the top layer is removed [see Fig. 1(b)]. To create a kink site along a step edge, half of the

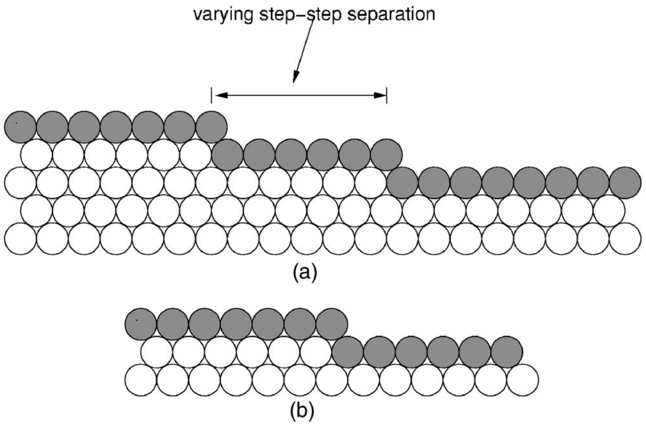

FIG. 1. (a) Isolated step system and (b) two-step system.

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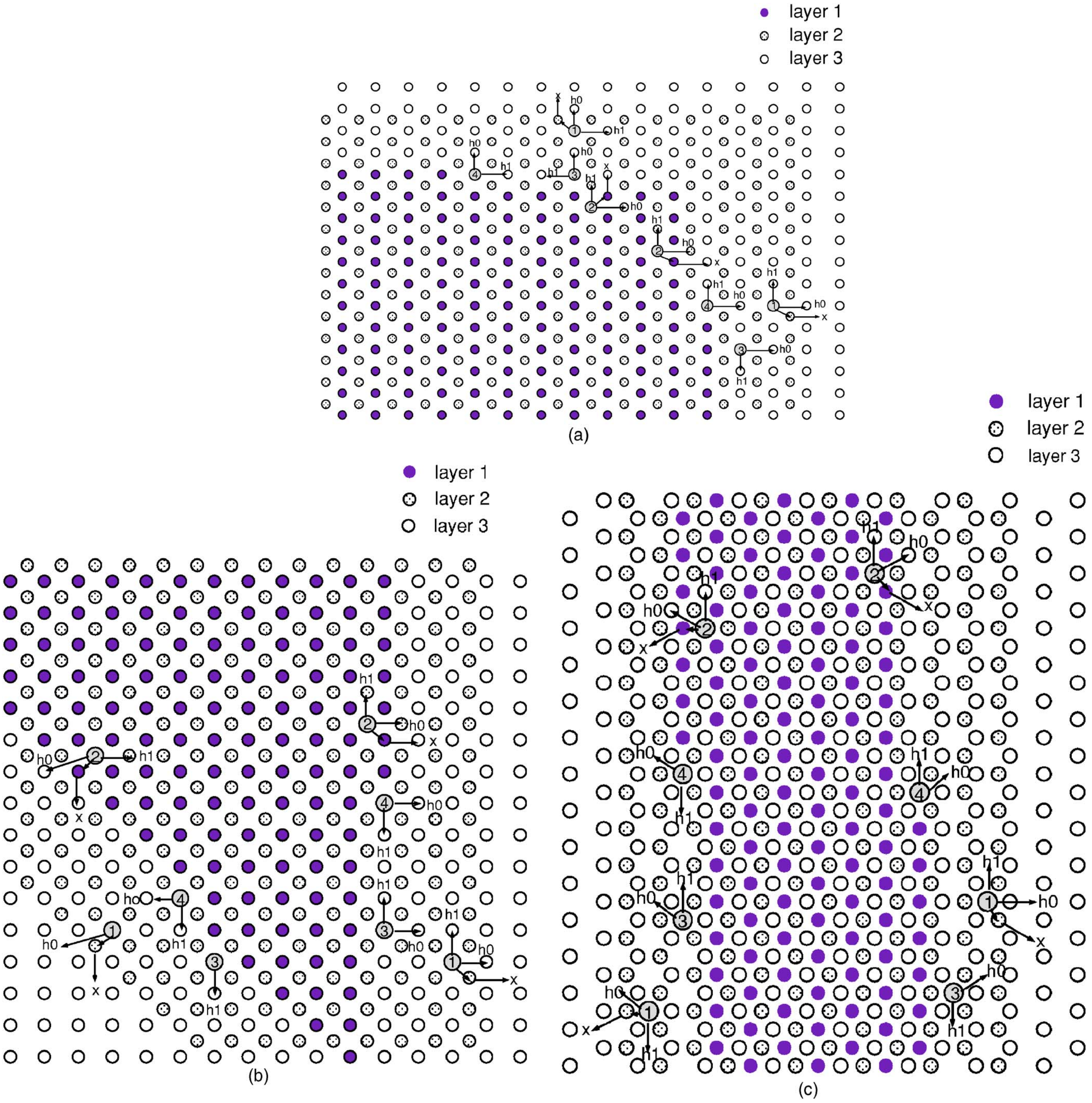

FIG. 2. (Color online) The investigated diffusion processes on (a)Cu(110), (b) Cu(100), and (c) Cu(111).

atoms along one step edge are removed. The super cell contains 20×8 sites per layer. In the surface layers some of the sites are empty so as to create the appropriate systems with two steps separated by a specific terrace width. The chosen model systems are tested to be large enough that the possibility of finite-size effects is diminished. In the simulations, the positions of atoms in the two bottom layers are maintained fixed and periodic boundary conditions are applied in the surface plane.

To describe interactions between the atoms in the model systems, we use the embedded atom method. This is a semi-empirical potential and of many-body type.[12] Although the EAM potentials neglect the large gradient in the charge density near the surface and use atomic charge density for solids, for the six fcc metals Ag, Au, Cu, Ni, Pd, and Pt and their alloys, it has proved to be reliable by successfully reproducing many of the characteristics of the bulk and surface systems.[12] We have also found the EAM potentials to be reliable for examining the temperature-dependent structure and dynamics of Cu and Ag flat surfaces[13] and for describing the energetics, phonons, and structures of Cu vicinals[14] and self-diffusion processes on the (100) surfaces of Ag, Cu, and Ni.[15]

The activation energy barrier for each of the studied processes is calculated using the nudged elastic band technique.[11] The essential feature of this method is that once the initial and final configurations of a system are known, it determines the minimum energy path between these end states by generating a "chain of states" (or images) of the system for the intermediate states in configurational space and subsequently carrying out a simultaneous optimization procedure for the intermediate images. The highest energy along this path determines the saddle point and the energy barrier for the process. The diffusion processes involved in this work are shown in Fig. 2. The largest circles represent the mobile atoms involved in various diffusion processes, and their labels 1, 2, 3, and 4 represent an adatom in the proximity of the step on the lower terrace, in the vicinity of the step on the upper terrace, attached to the upper step ledge, and at a kink site at the upper step, respectively. In Figs. 2(a)–2(c) the exchange process is indicated by $\times$, while $h0$ and $h1$ represent the hopping processes of types indicated. The diffusion process $h0$ for atoms 1 and 2 on all surfaces correspond to a hop over the step edge to the next fcc site. The process $h1$ on each surface, except for $(100)\times\{110\}$, represents an atom hopping along the step edge. For the $(100)\times\{110\}$ surface, it corresponds to a hopping atom away from the step edge toward the interior of the terrace. Similarly, $h0$ on the same surface represents a hopping atom along the step.

III. RESULTS AND DISCUSSIONS

A. Diffusion of an adatom on a flat surface

To have a systematic study, we have first calculated the energy barriers for an adatom diffusing on the flat surfaces of Cu and tabulated them in Table I. Note that for all flat surfaces the hopping mechanism is energetically more favorable than the exchange mechanism except for the hopping process crossing the channel on Cu(110). Let us note that the characteristics of diffusion processes on Cu(110) differ from those on Cu(100) and Cu(111) in that the intralayer diffusion processes are strongly anisotropic. There are two principle diffusion directions: ⟨110⟩, in-channel diffusion, and ⟨010⟩, across-channel diffusion. The isotropic nature of the diffusion processes on Cu(100) and Cu(111) might lead to island formations at first stages of a growth process on these surfaces.[16–18] In contrast, on Cu(110) growth along the channel is more likely as the diffusion barrier across the channel for the adatom is higher. Indeed, several experimental works have already proven the existence of such a quasi-one-dimensional growth stage on various fcc(110) surfaces.[19,20] Note also that the energy barriers in Table I are in agreement with those reported earlier[1,3,21] and are included here for completeness.

TABLE I. Energy barriers (in eV) for a diffusing atom, through both exchange and hopping mechanisms, on the low-Miller-index surfaces of Cu.

Process	Cu(110)	Cu(100)	Cu(111)
Exchange	0.34	0.70	1.42
Hopping	0.24 (in channel) 1.13 (cross channel)	0.49	0.01

B. Diffusion of an adatom over a step edge

Our calculated energy barriers for an adatom diffusing over an isolated step edge on the (111), (100), and (110) surfaces of Cu are presented in Table II, together with available theoretical results. As seen in the table, for all surfaces the exchange mechanism appears to be energetically more favorable than hopping. Our calculations also show the ES barrier for both hopping and exchange processes to be surface geometry dependent, in agreement with the results of other theoretical calculations. For both exchange and hopping mechanism, while the adatom diffusing over {111}-microfaceted steps on Cu(110) experiences the highest-energy barrier, compared to the other surfaces, the corresponding atom over the {111} step on Cu(111) experiences the lowest-energy barrier. The very low ES barrier of the exchange process for an adatom crossing the *B*-type steps on Cu(111) suggests a much faster mass transport over *B*-type sides of adatom islands growing on Cu(111). Note also that there is an additional barrier for the diffusion over both type of steps, relative to the diffusion on flat regions (*A*-type step, 0.31 eV and *B*-type step, 0.07 eV), which hinders the interlayer mass transport on the islands on Cu(111). Thus, nucleation on the top of the islands occurs before coalescence takes place, resulting in rising islands during a growth process on Cu(111).[16] For Cu(100), the diffusion over {110}-microfaceted steps is energetically more favorable than that over {111}-microfaceted steps, suggesting a faster mass transport over {110}-microfaceted steps of the islands growing on Cu(100). Adatoms approaching the steps along ⟨100⟩ on Cu(100) descend over the step to the lower terrace by an exchange process since the energy barrier is found to be 0.33 eV which is lower than the barrier for the diffusion at flat regions (0.49 eV). On the other hand, the barrier for the diffusion over the steps along ⟨100⟩ (0.55 eV) is somewhat higher than that for the diffusion on flat regions. Therefore, adatoms coming near the steps along ⟨100⟩ are more likely to diffuse back to flat regions of the island instead of descending down the step to the lower terraces. Furthermore, the smaller energy barrier for the exchange process over the step along the ⟨100⟩ direction, with respect to the corresponding barrier over the step along the closed-packed ⟨110⟩ direction, might be an explanation as to why the coalescence of the squarelike islands on Cu(100) happens first along the diagonal axis of the ⟨100⟩ direction upon deposition.[17] For Cu(110), the geometrical preference of the Cu adatom is reflected in both exchange and hopping processes over the steps on Cu(110), revealing a lower-energy barrier for diffusion over the step along $\langle 1\bar{1}0\rangle$. It is also interesting to note that while the in-channel hopping process over the {100}-step rise on Cu(110) is less favorable than the exchange process, it is the reverse for the adatom diffusion

TABLE II. Energy barriers (in eV) for a diffusing atom, through both exchange and hopping mechanisms, over an isolated step on the low-Miller-index surfaces of Cu. Here $(h_t k_t l_t) \times \{h_s k_s l_s\}$ represents the respective Miller indices for the terrace and step plane orientations.

Process	Work	(110)×{100}	(110)×{111}	(100)×{110}	(100)×{111}	(111)×{100}	(111)×{111}
Exchange	Present	0.54	0.72	0.33	0.55	0.33	0.082
	EAM[a]			0.33	0.54	0.28	0.085
	EAM[b]				0.51		0.085
	EMT[c]	0.57	0.69		0.63	0.45	
	DFT[d]	0.54	0.82				
Hopping	Present	0.66	1.14	0.58	0.77	0.52	0.48
	EAM[a]			0.57	0.77	0.51	0.50
	EAM[b]				0.77	0.49	
	EMT[c]	0.48	0.84		0.57	0.37	

[a] Reference 3.

[b] Reference 4.

[c] Reference 2.

[d] Reference 21.

over the {111}-microfaceted steps. Note the excellent agreement between our results for the exchange process over the {100} step with the results of *ab initio* calculations based on density functional theory (DFT) calculations.[21]. However, the calculated barrier for the exchange of adatom and the {111}-step atom is somewhat smaller than that predicted by DFT calculations. As for the comparison of EAM and EMT results, for the hopping mechanism, the EAM gives larger energy barriers compared to the results obtained from EMT. For the exchange mechanism, on the other hand, EMT results in greater energy barriers than the EAM values, except for the {111} step on the Cu(100) low-index plane. The small differences in the EAM results can be attributed to the different methods used in the total energy calculations.

In Table III, we present the energy barrier for an adatom located between the two steps and diffusing through both exchange and hopping mechanisms over the lower descending step (atom 1 in Fig. 2). The barriers are given with respect to varying step-step separation which is defined by the number of atomic rows between the two steps. It is interesting to note that the energy barriers converge to that of an adatom diffusing over an isolated step at about three atomic rows. As is also clear from Table III our calculations lead to a step-step separation of two atomic rows at which the ES barrier drastically increases. The dramatic increase in the ES barrier is much more pronounced at steps on (111). For the exchange process at the step-step separation of two atom rows, the barriers for *A*- and *B*-type steps are much larger (0.82 eV and 0.34 eV, correspondingly) than the barriers when the step-step separation is three or more atom rows (0.34 eV and 0.08 eV, respectively). In a related study of the kinetics of rapid island decay on Ag(111), this specific mechanism is identified to be one of the expected atomistic processes leading to the enhanced interlayer mass transport at short step-step separations.[10] The corresponding authors proposed a concerted two-atom-exchange mechanism which bypasses the ordinary detachment barrier of atoms from kink sites and estimated the associated barrier as the energy to form an atom along the step from a kink site plus the energy barrier to descend. Although our calculations for Cu, within the EAM scheme, give a larger energy value for forming an atom along the step from a kink site (0.28 eV), compared to the effective medium theory (EMT) result (0.17 eV), the total barrier for the proposed concerted mechanism (0.28 eV +0.34 eV) is still lower than the activation barrier for ordinary detachment processes (0.72 eV).[22] Note that the barrier for the same process on *A*-type steps is (0.28 eV+0.82 eV) much larger than the one on *B*-type steps, indicating that the

TABLE III. Energy barriers (in eV) for an adatom located between two steps (atom 1 in Fig. 2) and diffusing through exchange (x) and hopping (*h*0) mechanisms over the descending step on the low-Miller-index surfaces of Cu as the terrace width varies. The terrace width is given in terms of number of atomic rows on the terrace. The values in parantesses are the barriers for the hopping process.

Terrace width	(110)×{100}	(110)×{111}	(100)×{110}	(100)×{111}	(111)×{100}	(111)×{111}
Two rows	0.74(0.92)	0.74(1.15)	0.74(0.93)	0.82(1.16)	0.82(1.16)	0.34(1.12)
Three rows	0.54(0.66)	0.71(1.14)	0.37(0.61)	0.56(0.77)	0.34(0.52)	0.07(0.48)
Four rows	0.54(0.66)	0.71(1.14)	0.33(0.58)	0.55(0.77)	0.33(0.51)	0.08(0.48)
Five rows	0.54(0.66)	0.72(1.14)	0.33(0.58)	0.55(0.77)	0.33(0.52)	0.08(0.48)
Six rows	0.54(0.66)	0.72(1.14)	0.33(0.58)	0.55(0.77)	0.33(0.52)	0.08(0.48)

TABLE IV. Energy barriers (in eV) for an adatom diffusing along and away from the step edge (atom 3 in Fig. 2) between two steps.

Terrace width	(110)×{100}	(110)×{111}	(100)×{110}	(100)×{111}	(111)×{100}	(111)×{111}
Along the step	0.88	0.26	0.81	0.26	0.25	0.30
Away from the step	0.46	1.14	0.81	0.80	0.63	0.67

rapid decay of island might be initiated on *B*-type rather than *A*-type step edges of the adatom islands.

The ES barrier for the adatom diffusing over the {111}-step edge on Cu(110), through both exchange and hopping mechanisms, is barely changing with respect to the varying step-step separation. The increase in ES barrier for two-atom-wide terraces can be explained in the context of coordination number. The coordination numbers for adatoms located at the equilibrium site between the two steps separated by two atomic rows on (110)×{100}, (110)×{111}, (100)×{110}, (100)×{111}, (111)×{100}, and (111)×{111} are, respectively, 5, 5, 6, 5, 5, and 5, whereas it is 4 for the adatom on a wider terrace separating the two steps on (110) and (100) flat surfaces and 3 for the adatom on a wider terrace between *A*- and *B*-type steps on fcc(111). Hence, the adatoms at a transition-state configuration of two-atom-wide terrace systems lose more coordination compared to those of wider terrace systems, thus yielding a higher energy cost. From these results, one might conclude that in the absence of other defects around the step, the ES barrier plays not an assisting but a hindering role in mass transport phenomena on stepped surfaces when the edges of the islands get closer.

C. Diffusion of an adatom along and away from a step edge

In Table IV, we present energy barriers for an adatom diffusing along and away from the steps of Cu(110), Cu(100), and Cu(111). We have also calculated the barriers with varying terrace width and found small changes within the range of ±0.05 eV when the terrace width is about two to three atomic chains. The smaller energy barrier for the diffusion along the step edge compared to the diffusion away from the step suggests a smother atomic chain formation around the island during a growth process. However, a fractal-like shape around the edges of the islands is expected when a smaller energy barrier for the diffusion away from the step edge, with respect to the diffusion along the step, is encountered. As seen in Table IV, the difference in energy barriers for an adatom diffusing along the *A*- and *B*-type step edge on Cu(111) is approximately 0.05 eV, indicating no preference for the adatom as to along what type of step edge to diffuse on Cu(111) during a growth process and thus yielding almost equally sized *A*- and *B*-type step edges of adatom islands on Cu(111).[23] In fact, the Scanning tunneling microscope (STM) observations of well-shaped hexagonal islands on Cu(111) support the idea of no preferred island edge during a growth process.[7,24] On the other hand, diffusion along {111}-microfaceted steps on Cu(100) is energetically more favorable than that along the steps of {110}-microfaceted steps, suggesting preferential growth along the {111}-oriented steps. Indeed, results from the experimental works[18,25] have shown the equilibrium shapes of islands on Cu(100) to be quasisquare of the ⟨110⟩-oriented side with shorter ⟨100⟩-oriented edges at the corners of the square. Note also that while the barrier for an adatom to hop along the {111}-step edge is significantly lower than that for the adatom diffusing on a flat surface, the diffusion barrier is significantly higher than the barrier for the adatom diffusion along the {110}-step rise compared to the flat surface diffusion. This corroborates the concept of preferential growth along the {111} rising step. Our results also reveal that while the energy barrier along the two type microfaceted steps on Cu(100) and Cu(111) and the {111}-microfaceted step on Cu(110) is lower than the barrier for the diffusion away from the step, it is reverse for the diffusion involving the {100}-microfaceted step on Cu(110). Note that the diffusion away from the {100}-microfaceted on Cu(110) involves in-channel diffusion whereas that along the step of {111} possesses the characteristics of cross-channel diffusion.

IV. CONCLUSION

In summary, we have investigated activation barriers for several selected diffusion processes near a step edge on the (110), (100), and (111) surfaces of Cu and considered the effect of increasing terrace width. Calculations are performed using the nudge elastic band method with the interaction potentials extracted from the embedded-atom method. Our results reveal that the barrier for an adatom diffusing over a step edge is sensitive to both the terrace and step orientation. In addition, we find no sudden decrease in the ES barrier with decreasing terrace width. In fact, the barrier increases when the separation between the two consecutive steps is about two atomic rows. Among the investigated diffusion processes, we find no single-atom process which might lead to enhanced interlayer mass transport. Our calculated barrier for the proposed two-atom-exchange mechanism is consistent with the EMT result.[10] As pointed out in Ref. 10, the existence of defects, such as kink and vacancy sites, around the step may reduce the barrier for processes taking place in the vicinity of the step. We thus believe that extensive total energy calculations for other possible single- and many-atom diffusion processes on these particular surfaces, supported by molecular dynamic simulations, may help us further digest the observed fast-decay phenomenon.

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