PHYSICAL REVIEW B **80**, 235413 (2009)

Diffusion barriers for Ag and Cu adatoms on the terraces and step edges on Cu(100) and Ag(100): An *ab initio* study

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(Received 2 September 2009; published 9 December 2009)

We present the results of density-functional-theory-based calculations for the activation energies for the diffusion of adatoms (Cu or Ag) on Cu(100) and Ag(100) with and without steps. We find that only for Cu on Ag(100), exchange is the dominant mechanism for the diffusion on terraces. On the other hand, for diffusion at step edges, exchange is the dominant mechanism except for Ag on Cu(100). This result also indicates that incorporation of Cu atoms into the step edges of Ag(100) costs only 330 meV, while the energy cost for Ag incorporation into Cu(100) step edge is much higher (about 700 meV). We find the hierarchy of Ehrlich-Schwoebel barriers to be: 170 meV for Ag on Cu(100); 60 meV for Cu on Cu(100); 20 meV for Ag on Ag(100), and -30 meV (-270 meV) for Cu on Ag(100). These barriers point to a striking difference in the growth modes for Ag layers on Cu(100) and Cu layers on Ag(100).

DOI: 10.1103/PhysRevB.80.235413 PACS number(s): 66.30.Fq, 68.35.bd, 68.35.Fx

I. INTRODUCTION

Understanding thin-film growth (growth mode, morphology, etc.) on metal surfaces has been the goal of investigations by both experiment and theory[1] for more than a decade because of the potential applications in electronic devices, chemical reactions, and catalysis.[2] This effort has intensified with the introduction of powerful experimental tools such as scanning tunneling microscopy and atomic force microscopy that are used to see surfaces and to manipulate atoms, clusters, and molecules so as to control diffusion, other reactions and microscopic events.[3] The morphology of thin films, and the size, density, and shape of adatom islands on surfaces can be altered by controlling the external growth parameters, such as deposition rate of atoms, substrate temperature, and coverage, and by the introduction of defects and surfactants (see Ref. 4 and references therein). Though it is a challenge to obtain a comprehensive picture of all parameters that govern growth of thin films, it is possible to proceed with a controlled study of the effect of each parameter on the growth mode and the end products. Toward this end, the last decade witnessed a great deal of effort in the determination of diffusion parameters on single-crystal surfaces.[5] In particular there has been a focus on understanding self-diffusion via hopping[6] in which an adatom diffuses on the surface from one equilibrium position to the next or via exchange[6] in which an adatom replaces its position with a surface atom, which then becomes an adatom at the next binding site. Research in the area still continues because the complexity of the phenomena has left several unresolved issues even for the simple case of diffusion by hopping (see Refs. 7 and 8 and references therein). As is well known, steps and kinks play an important role in determining the energetics and the dominant diffusion mechanism for adatoms on surfaces. Exchange, for example, may dominate at a step edge but not for diffusion on terraces.[9] At the step edge there is also the issue of an additional activation-energy barrier, the Ehrlich-Schwoebel (ES) barrier,[10] which corresponds to the extra energy needed for an adatom to diffuse from an upper terrace to the layer below at a step edge. The existence of this barrier prevents downward diffusion and has been shown to lead to a morphological instability[11] resulting in the formation of mounds. The presence of this barrier also presents a good rationale for three-dimensional (3D) growth, while the lack of it is expected to lead to layer-by-layer growth.[12]

Diffusion being a "rare" event leads to shortcomings in both theory and experiment in accurate determination of its parameters. Diffusion coefficients, which comprise of pre-exponential factors and activation energies, are case in point since their theoretical evaluation requires a detailed and accurate knowledge of surface energetics and vibrational dynamics.[7,13] While experimental techniques have to be sensitive to subtle changes in energetics (meV range) and dynamics over long-time scale (millisecond), in theory and modeling the focus has been mostly on extraction of activation-energy barriers, although recipes are available[14] for calculation of the prefactors. Understandably most of the work so far has concentrated on homoepitaxial systems. Of the two surfaces of interest here, Ag(100) and Cu(100), numerous theoretical studies of self-diffusion on the terraces exist. For diffusion via hopping of Ag adatoms on Ag(100), first-principles calculations based on density-functional theory (DFT) (Refs. 15–17) find the energy barrier to be between 0.45 and 0.60 eV, while various model potentials find it to lie in the range 0.46–0.48 eV (Refs. 18–20) to be compared with experimental findings of 0.40 eV (Ref. 21) and 0.35 eV.[22] For the exchange mechanism, barriers are found to be somewhat higher (between 0.62 and 0.78 eV) in theoretical calculations,[15,16,18–20] while experiments report it to be 0.46 eV.[22] Interestingly, theoretical results for the energy barriers for diffusion via hopping of Cu adatoms on Cu(100) also lie in the range of 0.48–0.69 eV,[7,16,18,23–26] while the range of experimental values is between 0.28 and 0.40 eV.[27–29] The energy barrier for diffusion of Cu adatoms on Cu(100) via exchange is, on the other hand, found to be much larger, close to 1 eV, in first-principles calculations,[7,16,23] and between 0.69 and 0.80 eV in results based on model interaction potentials.[24,25,30] To our knowledge there is no experimental data on exchange-mediated self-diffusion on Cu(100). In short, the above theoretical results indicate a preference for adatom diffusion to proceed via hopping on terraces of Cu(100) and Ag(100).

Attention has also been paid to evaluations of the ES barriers for these two surfaces in the presence of step edges. For Ag adatoms at the step edge of Ag(100) first-principles calculations find the ES barrier for exchange to be 0 meV, and that for hopping to be 100 meV,[15] signifying the importance of the former. Semiempirical methods find the barrier via hopping to lie in the range 110–220 meV,[20,31,32] while the barrier via exchange is between 30 and 160 meV.[20,31,32] Experimental studies report homoepitaxial growth on Ag(100) to proceed layer by layer and the ES barrier to lie in the range 30–70 meV.[33] These results nicely illustrate the correlation between layer-by-layer growth and almost vanishing ES barrier. The growth mode on Cu(100) is, however, more puzzling. Experimental observations[34,35] report a 3D growth mode along with the presence of mounds. Model potentials find the ES barrier via hopping to lie in the range 125–320 meV,[24,26,30–32,36] while that via exchange is between 30 and 130 meV.[24,31,32] If the values of the exchange ES barrier are correct, one would expect the growth mode to be layer by layer also for Cu(100), unless prefactors for the processes are significantly different from the normal (10^{-3} cm^2/s). To our knowledge there is no reported first-principles value of the ES barrier for Cu adatoms on Cu(100). Although from the values of the energy barriers cited above, there appear to be no systematic difference between the results from *ab initio* electronic-structure calculations and those based on model interaction potentials, and that the latter may at times give better agreement with experiment than the former, it would still be interesting to find this barrier using DFT.

Attention has recently turned also to examination of the diffusion of adatoms and small clusters for heterosystems. For the hopping of Cu adatoms on Ag(100), tight binding (TB) (Ref. 18) and DFT (Ref. 37) calculations find the activation-energy barrier to be about 0.60 eV. For Ag adatoms on Cu(100), model interaction potentials and TB studies reported the barrier to lie in the range 0.39–0.48 eV.[18,38,39] In recent simulations using TB-second moment approximation (SMA) scheme[40] for the growth of silver shells on copper and palladium nanoclusters, the diffusion of Ag adatom on the (100) facets of the truncated octahedron Cu nanoparticle reported the diffusion via jump to be 0.28 eV. Another study[41] using Rosato-Guillopé-Legrand potentials showed the diffusion barrier for Ag atoms on the (100) facets of polyhedra Ag clusters to be 0.43 eV. At the same time reflection high-energy electron diffraction measurements of Cu deposition on Ag(100) showed that the growth mode is layer by layer.[42] For Cu on Ag(100), the simulations using temperature-accelerated dynamics (TAD) (Refs. 37 and 43) predicted downward diffusion at low temperatures (77 K). For these heterosystems, there are no reported experimental results for the ES barriers. To the best of our knowledge, first-principles calculations have not also been carried out for the diffusion of Ag adatoms on Cu(100) terraces nor have they been performed for that of Cu adatom on Ag(100) via exchange.

In view of the above, we have carried out first-principles calculations of the activation-energy barriers for the diffusion via hopping and exchange of Cu and Ag adatoms on Cu(100) and Ag(100) for both homoepitaxial and heteroepitaxial systems, with and without steps. For comparison and completeness, we have included in our calculations also those processes for which calculated barriers already exist, as noted above. We have also tested the sensitivity of our results to the size of calculational supercell in order to extract as accurate a value for the diffusion barriers as feasible.

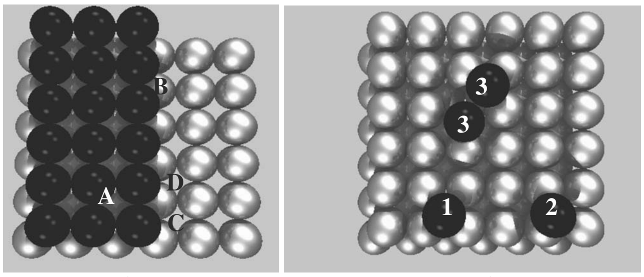
The paper is organized as follows. In Sec. II we describe the method and the calculation details. In Sec. III we present our findings for the diffusion on the (100) terraces for homoepitaxial and heteroepitaxial systems. We also discuss atomic relaxations and the bond lengths between the adatom and its neighbors at terraces and present the charge-density distributions and differences for each system. In Sec. IV we present the results for adatom diffusion near the step edges. Finally, in Sec. V we present our conclusions.

II. METHOD AND DETAILS OF THE CALCULATIONS

We perform total-energy electronic-structure calculations using DFT (Ref. 44) and the pseudopotential method as implemented in the computational code Vienna *ab initio* simulation package[45] for both homoepitaxial and heteroepitaxial diffusion of an adatom on terraces and near step edges of Cu(100) and Ag(100). For the electron exchange-correlation functional, we choose the two most popular functional of the generalized gradient approximation, Perdew and Wang 91 (PW91),[46] and Perdew-Burke-Ernzerhof (PBE).[47] We use plane wave basis set providing kinetic energy up to 18 and 20 Ry for Ag and Cu, respectively. According to our calculations, the bulk lattice constants are 4.17 Å (4.18 Å) and 3.64 Å (3.66 Å) for Ag and Cu using PW91 (PBE), respectively.

For adatom diffusion on the (100) terraces, we construct the surface cell with five atomic layers. In order to study the possible size effect on the diffusion barriers, we choose the cell periodicities in the surface plane as 2×2, 3×3, 4×4, and 5×5. For each calculation, we use a vacuum of 12–14 Å. We relax all atoms in the top four layers to their equilibrium positions while keeping the last layer fixed (all forces having converged to 0.01 eV/Å). We perform calculations using mainly PW91 and repeat some with PBE. We find at most a 20 meV difference in the diffusion barriers calculated with these two functionals. In accord with earlier studies,[7,15] we find that a basis with higher (about 30%) energy cutoff changes the diffusion barrier by about 10–20 meV. As stated in earlier investigations[7,15,48] increasing the number of *k* points also introduces a 20 meV maximum difference in the diffusion barriers, while changing the periodicity in the surface plane from 2×2 to 5×5 introduces negligible deviations (10 meV) in the diffusion barriers.

For the calculations of the diffusion barriers near the step edges via hopping, we use a surface cell with four atomic layers and periodicities of 3×3, 4×3, 3×4, and 4×4 for the stepped layer and that of 5×3, 6×3, 5×4, and 6×4 for that substrate below. The reason for repeating the calculations for different step-substrate periodicities is to determine any effect on the calculated barriers of spurious interactions introduced by periodic boundary conditions. However, questions have been raised regarding the dependence of the calculated energy barriers (via exchange) on the size of the



a) b)

FIG. 1. (a) The top view of a monoatomic terrace on fcc(100) surface with a closed-packed step running along ⟨110⟩ direction. (b) Top view of an adatom on fcc(100) at a fourfold site (1), in a transition state for diffusion via hopping (2), and a transition state for diffusion via exchange (3).

supercell. It is known that both diffusion mechanisms introduce some level of distortion of the lattice (both lateral and vertical), although much larger distortions are caused by exchange than by hopping. Not surprisingly calculated results depend on the robustness of the model systems. For example, for some metal surfaces,[48] at least 25% decrease in the exchange diffusion barriers may be obtained by simply changing the number of layers or the number of active atoms on the surface.[16,19,48] To test the effect of the supercell size, we thus perform calculations for the diffusion (via exchange) near the step edges using 6×3-3×3 and 5×4-3×4 substrate-step periodicities. For the exchange process on (100) terraces, we take the hint from previous calculations[16,19,48] and perform calculation using 5×5 cell.

To calculate the barriers for processes near step edges such as descent over the step and along the step (on a lower terrace), we introduce a close-packed {111}-faceted step (infinite stripe) running along ⟨110⟩ direction as is sketched in Fig. 1(a). For descent over the step, we determine the transition-state configuration by placing the adatom first at position A (fourfold site) in Fig. 1(a), and subsequently moving it perpendicular to the step by small increments along the diffusion direction with an applied constraint. We minimize the total energy of the system at each point (between 10 to 15 points) until the adatom reaches the next minimum-energy configuration [position C in Fig. 1(a)]. In accord with earlier studies[15,26] we find the transition state to be slightly (~0.6 Å) beyond the exact bridge site [position B in Fig. 1(a)]. One of the key diffusion processes for epitaxial growth is the diffusion along a step edge on a lower terrace, since the height of this barrier determines how steps will evolve (the shape of steps) on the surface as atoms are deposited.[15] In order to simulate this process, we place the adatom on the lower terrace at the position C and move it toward the position D in Fig. 1(a), with small increments along the direction of diffusion. Again, for each step between two equilibrium positions, we minimize the total energy of the system to determine the transition-state configuration and hence the height of the corresponding diffusion barrier.

TABLE I. Adatom bond lengths with the first nearest neighbors and atom below; adatom binding energies; and diffusion barriers on terraces.

	Bond length (Å)		E_{bind} (eV)	E_{diff} (eV)
Systems	Fourfold (bridge)	Atom below fourfold	Fourfold (bridge)	Hopping (exchange)
Ag/Ag(100)	2.79 (2.70)	3.88	2.18 (1.73)	0.45 (0.59)
Cu/Cu(100)	2.43 (2.33)	3.40	3.02 (2.49)	0.53 (0.79)
Cu/Ag(100)	2.59 (2.51)	3.48	3.45 (2.85)	0.60 (0.50)
Ag/Cu(100)	2.63 (2.52)	3.69	2.39 (2.02)	0.37 (1.02)

III. ADATOM DIFFUSION ON (100) TERRACES

In Table I, we summarize the results of calculations of adatom diffusion barriers via both hopping and exchange mechanisms. We also include in the table the results for the bond lengths and binding energies. Table I shows an interesting trend in the barriers (via hopping) on the (100) terraces. It is the lowest for Ag on Cu(100) (0.37 eV) and the highest for Cu on Ag(100) (0.60 eV). The barriers for the homosystems are in good agreement with earlier theoretical calculations which were summarized above. In addition to the differences in the electronic interactions, the large difference in the barriers for Cu adatom on Ag(100) and Ag adatom on Cu(100) may be traced to the effect of compressive vs tensile strain on the diffusion.[49,50] Here the case of Ag adatom on Cu(100) is an example of diffusion on a *compressive*-strained lattice: an adsorbate (with a larger atomic radius) diffusing on a substrate with a smaller lattice constant (3.64 Å), while that of the Cu adatom on Ag(100) provides the reverse case (diffusion on a *tensile*-strained lattice).

From Table I we note that the adatom binding energy in all cases is higher for the fourfold than for the bridge site. This is understandable since the former is the more stable configuration for an adsorbate. Also, the binding energy of a Cu adatom on Ag(100) is found to be higher than that on Cu(100) (Ref. 51) as well as that of a Ag adatom on Cu(100). It is interesting that this trend on the surface is in agreement with that of the heat of solutions of Cu and Ag atoms in bulk material.[52] From Table I we find that, within first nearest neighbors, the binding energy (fourfold site) per bond (Cu-Ag) is 0.86 eV for Cu on Ag(100) and 0.60 eV for Ag on Cu(100), to be compared with 0.76 eV for (Cu-Cu) and 0.55 eV for the (Ag-Ag) bond. For the bridge site, the binding energy per (Cu-Ag) bond is 1.43 eV for Cu on Ag(100) to be compared with 1.01 eV for (Ag-Cu) bond, 1.25 eV (Cu-Cu) and 0.87 eV for (Ag-Ag) bond. The large difference in the binding energies per bond between that for Cu on Ag(100) and Ag on Cu(100) points the fact that adatom-substrate interaction is stronger for the former.

Since diffusion involves bond breaking between adsorbate and substrate atoms and the barrier is the cost for breaking these bonds, it is understandable that the trend in the barriers (Table I) correlates with that of binding energies. The recent

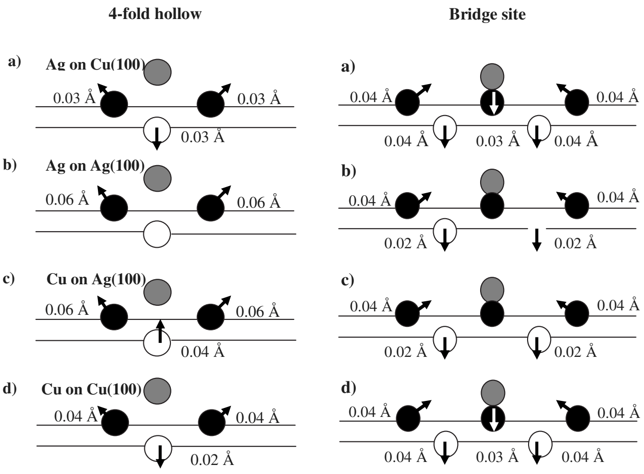


FIG. 2. Side views of a schematic representation of the relaxations upon adatom adsorption on fourfold (on the left) and bridge (on the right) sites. Gray, black, and white circles represent the adatom and first- and second-layer atoms, respectively. The values reflect the vertical displacements of the atoms with respect to the rest of the atoms of the corresponding layer.

study[53] of the diffusion of several types of adatoms on Cu(111) and Pd(111) shows that the barriers near the step edges scale linearly with binding energy hence the knowledge of the binding energy near step edge is enough to determine ES barriers. For our study in which the diffusion occurs on (100) surfaces, in contrast to the diffusion on (111) terraces, the barriers on the terraces compete with the barriers for descent over the step and hence the ES barrier is governed via both barriers.

In Fig. 1(b), a top view of the transition state (position 3) of an exchange mechanism is shown. In accord with earlier prediction, as seen from the Table I, for both homosystems diffusion via hopping is the dominant mechanism. Our calculated barriers lie in the range of the earlier predictions.[15,16,18,20,25] The new result in Table I regarding the diffusion via exchange for the heterosystem is, however, interesting. For Cu on Ag(100) in which the diffusing atom is smaller than the substrate atom, we find the barrier via exchange to be about 100 meV *smaller* than that via hopping. Ag adatom diffusion on Cu(100) shows the opposite, i.e., exchange costs 650 meV more than hopping. These results indicate that deposited Cu adatom may incorporate into Ag(100) terrace, while the incorporation of Ag adatom into Cu(100) terrace is less likely.

A. Relaxations and bond lengths on terraces

We have examined the relaxation trends and the bond lengths of the atoms in the systems for both fourfold and bridge sites. Before discussing those, let us note that the top-layer relaxation (Δd_{12}) of Ag(100) and Cu(100) terraces are found to be −2.8% and −3.6%, respectively, in reasonable agreement with previous experimental and theoretical findings.[7,15,17,54] In order to determine the change in the bonding upon adatom adsorption, we present in Fig. 2(a) schematic representation of the relaxation trends of the atoms in the first and second layers upon adatom adsorption on both fourfold and bridge sites. Note that, for surfaces without an adatom, all atoms in a layer have the same vertical positions (equilibrium configuration). Not surprisingly, the first nearest neighbors and the atom underneath are affected most by the adatom's presence. For all systems, the first nearest neighbors relax (upward) toward the adatom and occupying higher vertical positions than the rest of the atoms in the first layer. For both Ag and Cu adatoms on Cu(100), the atom below it relaxes (downward) away from it and sits at a lower vertical position with respect to the rest of the second-layer atoms [Figs. 2(a) and 2(d), left panel]. We find that for Ag and Cu adatoms on Ag(100) [Figs. 2(b) and 2(c)] the relaxation trend of the atom underneath is the opposite of that for the case on Cu(100). The atom underneath relaxes upward and gets closer to the adatom for Cu on Ag(100). For adatom adsorption on the bridge site, we find that for each system, the adatom's neighbors in the first layer relax upwards while the neighbors in the second layer relax downward with respect to the neighbors far from the adatom. While these trends are interesting, the amount of relaxation is small, being not more than 1%.

The optimized geometry of the systems shows that for the fourfold site, the first nearest neighbors relax laterally and expand the fourfold site further, while for the bridge site [position 2 in Fig. 1(b)], two nearest neighbors are pushed away to open the bridge. Upon adatom adsorption, we find that the expansion of the first-nearest-neighbor bond lengths is 3.4% for Cu adatom on Ag(100) and 1.6% for Ag adatom on Cu(100). We also find that the adatom vertical distances to the first nearest neighbors to differ up to 20% as we compare the systems with the same substrate while for the same adsorbate it differs up to 9%. We note that adatom vertical distance to the first nearest neighbors is the shortest for Cu on Ag(100) as compared to the others. This trend is in line with the bond-length change (laterally) and also the differences in the adatom atomic size relative to that of the substrate atoms.

The bond length (for fourfold site) between the Ag adatom and its first nearest neighbors on Ag(100) is found to be 2.79 Å (Table I), which is 5.4% shorter than that of the interatomic distance (2.95 Å) in the bulk. When the adatom is at the bridge site for which the coordination is reduced to two from four, the bond length becomes shorter (2.70 Å) following the typical bond-order-bond-length trend. Similarly, for Cu on Cu(100), the bond length between the Cu adatom and its first nearest neighbor is 2.43 Å, which is 5.5% shorter than the interatomic distance (2.57 Å) in the bulk. At the bridge site, we find this bond length to be reduced to 2.33 Å (4.1% shorter than that of the fourfold site). We find that the adatom bond length with the atom underneath (a second-layer atom) is the shortest for Cu on Cu(100) and the largest for Ag on Ag(100) (Table I).

For the heteroepitaxial system, Ag on Cu(100), the bond length between the Ag adatom and the first-nearest-neighbor Cu atoms is 2.63 Å, while at the bridge site, the bond length shortens 4.2% to 2.52 Å. Similarly, for Cu at the fourfold site on Ag(100), the bond length with the first-nearest-neighbor Ag atoms is 2.59 Å, while at the bridge site, the bond length shortens 3.1% to 2.51 Å. Note that the adatom

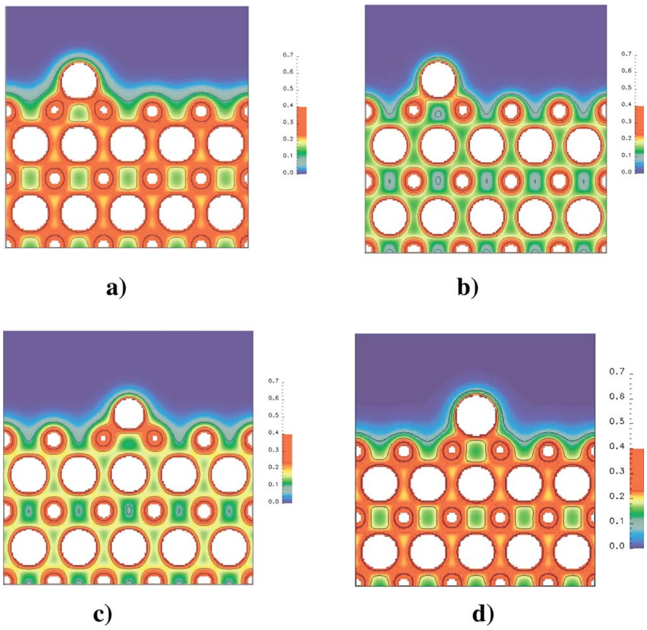


FIG. 3. (Color online) 2D charge-density contour plots perpendicular to surface plane for (a) Cu on Cu(100) (b) Ag on Ag(100) (c) Cu on Ag(100), and (d) Ag on Cu(100).

bond length (for fourfold site) with it's first nearest neighbors is shorter (1.5%) for Cu on Ag(100) than that of Ag on Cu(100), while at the bridge sites the bond lengths are the same. Note that for the former system, the adatom atomic radius being smaller than that of the substrate atoms causes the bond length within the first nearest neighbors to enlarge with it's adsorption hence it's (Cu adatom) vertical distance is closer (0.4 Å) to the surface atoms than that of the Ag on Cu(100). We also note that the bond length with the atom underneath is 6% shorter for Cu on Ag(100) as compared to the Ag on Cu(100). This is a result of the differences in the relaxation trends [see Figs. 2(a) and 2(c)] in which the atom below relaxes toward the adatom for Cu on Ag(100) while it relaxes away from the adatom for Ag on Cu(100).

In order to gain insight into the bonding strength, we present below the charge-density distributions and differences (relative to the substrate) for each system.

B. Charge-density distributions and charge-density differences on terraces

We present two-dimensional (2D) contour plots of charge-density distribution (for the plane perpendicular to the surface) between adatom and its first nearest neighbors in Figs. 3(a)–3(d) for the four systems of interest here. We find charge accumulation between the adatom and its nearest neighbors to be larger for Cu on Ag(100) than for Ag on Cu(100) [Figs. 3(c) and 3(d)]. Note that the adatom bond length with its first nearest neighbors (fourfold site) is shorter (1.5%) for the former as compared to that of the latter, (Table I). The plots for the homoepitaxial systems [Figs. 3(a) and 3(b)] show that there is stronger charge accumulation for Cu on Cu(100) as compared to that of Ag on Ag(100), revealing that the bond is more covalent in the former.

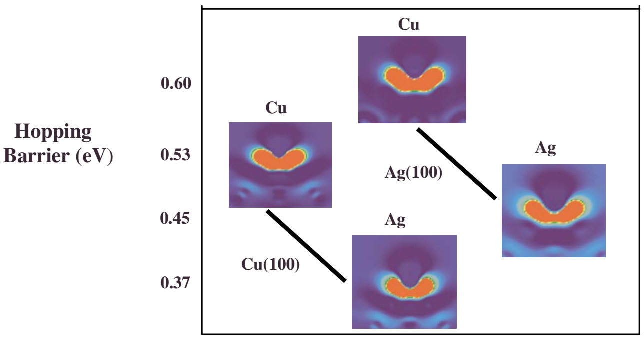


FIG. 4. (Color online) Contour plots of charge-density redistribution of the adatoms on Cu(100) and Ag(100) in the plane perpendicular to the surface. Red (light areas) and blue (dark areas) contours correspond to accumulation and depletion of charge, respectively.

As a further measure of the adatom-substrate binding strength, we evaluate the charge redistribution as determined by the charge-density difference $\Delta\rho(r)$ between that for the system with the adatom and that of the substrate and adatoms placed individually at the positions that they would otherwise occupy in the combination.

$$\Delta\rho(r) = \rho_{\mathrm{Cu/Ag(100)}}(r) - \rho_{\mathrm{Ag(100)}}(r) - \rho_{\mathrm{Cu}}(r). \qquad (1)$$

We present the charge-density redistribution plots in Fig. 4 for the plane perpendicular to the surface involving the adatom and its first nearest neighbors along with the corresponding barriers via hopping. Once again we find charge accumulation to be larger for Cu on Ag(100) than that of Ag on Cu(100). The adatom binding strength relative to substrate (as is shown by charge redistribution) is higher for the former and follows the same trend as the barriers.

IV. ADATOM DIFFUSION NEAR STEP EDGES

We now come to our ultimate goal of determining of the ES barriers for each system. Since they are calculated by subtracting the diffusion barriers for descending over a step edge and from that on terraces, we need to now turn to the calculation of the former. As we have already noted, diffusion at a step edge can proceed via either hopping [Fig. 5(a)] or exchange mechanism [Fig. 5(b)]. The earlier DFT study[15] for Ag on Ag(100) and model potential results for Cu on Cu(100) (Refs. 9, 20, 24, and 31) reported that the diffusion by descent over the step proceeds via the exchange mechanism. In Table II, we summarize the results of the barriers via both hopping and exchange for descending over the step

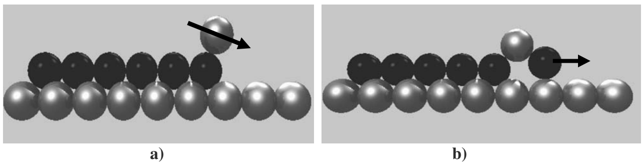


FIG. 5. Schematic representation of diffusion by descent over the step edge (a) via a hopping mechanism and (b) via an exchange mechanism.

TABLE II. Adatom bond lengths (Å) with the first nearest neighbors and the atom under; binding energies; and adatom diffusion barriers at step edges.

	Bond length		E_{bind} (eV)	E_{over} (eV)	E_{along} (eV)	ES (meV)
Systems	Fourfold (bridge)	Atom below fourfold	Fourfold (bridge)	Hopping (exchange)	Hopping	Relevant
Ag/Ag(100)	2.79 (2.70)	3.87	2.20 (1.70)	0.50 (0.47)	0.24	20
Cu/Cu(100)	2.42 (2.34)	3.39	3.06 (2.35)	0.71 (0.59)	0.32	60
Cu/Ag(100)	2.59 (2.51)	3.52	3.22 (2.57)	0.65 (0.33)	0.36	−30 (−270)
Ag/Cu(100)	2.62 (2.53)	3.68	2.44 (1.90)	0.54 (0.69)	0.20	170

(E_{over}), and for hopping along the step edge (E_{along}). The ES barriers, the adatom bond lengths (with the first nearest neighbors and atom below), and the binding energies are also presented in the Table II. For Ag on Ag(100), we find the adatom diffusion barrier (via hopping) along the step edge (on the lower terrace) to be 0.24 eV, which is much lower than that on the terraces and in good agreement with the earlier theoretical predictions.[15,20,31] This low barrier may indicate that compact islands form on this surface.[15] For the descent of the Ag adatom over the step edge of Ag(100), we find the diffusion barriers to be very similar for the hopping (0.50 eV) and exchange (0.47 eV). Earlier studies have reported this barrier (via hopping) to lie in the range 0.55–0.59 eV,[15,20,31] while the barrier via exchange lies in the range 0.45–0.64 eV.[15,20,31] We note here that, following the reports of an earlier study[48] in which it is shown that diffusion via exchange is strongly size dependent, we repeat the calculations of the exchange diffusion barriers near step edges for 5×4-3×4 in addition to 6×3-3×3 substrate-step configurations. We find that increase in the number of atoms in step chain (perpendicular to diffusion direction) decreases the diffusion barrier by 40 meV. The barrier values reported in Table II for the exchange are for the results of the calculation using the 5×4-3×4 unit cell. We also repeated the calculation for the diffusion via hopping for 5×3-3×3 and 6×4-4×4 periodicities and find that the effect on the diffusion barrier is utmost 20 meV.

For Cu on Cu(100), we find the barrier along the step edge to be 0.32 eV, which is in good agreement with the earlier reports (ranging from 0.25 to 0.40 eV).[23,24,26,30,31] For Cu adatom descending over the step edge on the Cu(100) surface, we find the barriers for hopping and exchange to be 0.71 and 0.59 eV, respectively. The earlier studies using model potentials[24,26,30] reported these barriers to lie in the range 0.56–0.79 eV. Note that our results are in excellent agreement with those from a recent TB study.[31] From the barriers, we see that diffusion via exchange is energetically more favorable than that via hopping, near the step edge. In the calculations of the barriers for the exchange process, we find that changing the number of atoms in the step chain from three to four affects (reduces) the diffusion barrier by 90 meV. The value reported in Table II is for the larger supercell.

For Cu on Ag(100), we find the barrier for diffusion along the step edge to be 0.36 eV, which is the largest for this process among the systems studied here. The barrier for the same process for Ag on Cu(100) is 0.20 eV, which is the smallest value for the rest of the studied systems. The barrier for Cu adatom descending over (E_{over}) the step edge on Ag(100) via hopping is 0.65 eV, while that for a Ag adatom at the step edge on Cu(100) is 0.54 eV. The barrier for Cu adatom's descent over the Ag(100) step edge via exchange is about 300 meV *lower* than that via hopping, thereby pointing to the former as the energetically dominant mechanism. For Ag adatom diffusion at the Cu(100) step edge, the barrier for exchange is 150 meV *higher* than that for hopping. As on the terrace, at the step edge also, hopping is the dominant diffusion mechanism for this system.

From the calculated barriers on terraces and near step edges, which are summarized in Tables I and II for Ag on Ag(100), we find the ES barrier via hopping to be 50 meV. Our calculated ES barrier is smaller than that of the earlier studies which reported the barriers to be in the range of 100–127 meV.[15,20,31] However, note that, the dominant diffusion mechanism is hopping on terraces and exchange at the step edges hence the actual ES barrier is 20 meV (Table II), which is in good agreement with the result (0 meV) of an earlier DFT study.[15] Experimental observations report this barrier to be in the range of 30–70 meV.[33] The smallness (nearly zero) of the ES barrier goes along with the observed[15,33] layer-by-layer growth mode for Ag on Ag(100). For Cu on Cu(100), the ES barrier for the hopping is 180 meV. For this surface, terrace diffusion via hopping costs less energy than exchange, while at the step edge the dominant diffusion mechanism is exchange (120 meV less than that of hopping). This actual ES barrier is thus 60 meV (Table II). The earlier predictions based on experimental observations of 3D growth mode[34,35] suggested that the ES barrier should be positive and nonzero. The studies using model potentials[9,24,26,30–32,36] reported this barrier for hopping to be in the range of 125–320 meV, and that for exchange to be 30–130 meV. Our DFT results may help refine the theoretical predictions for these barriers.

From our calculations for the heteroepitaxial systems, we find the ES barrier via hopping to be 150 meV for Cu on Ag(100). For this surface, we find exchange to provide lower adatom diffusion barriers than hopping, both at terraces and at step edges (Tables I and II). Note that the difference between the diffusion barriers via hopping and exchange for Cu adatom on Ag(100) terraces is 100 meV, pointing to a pos-

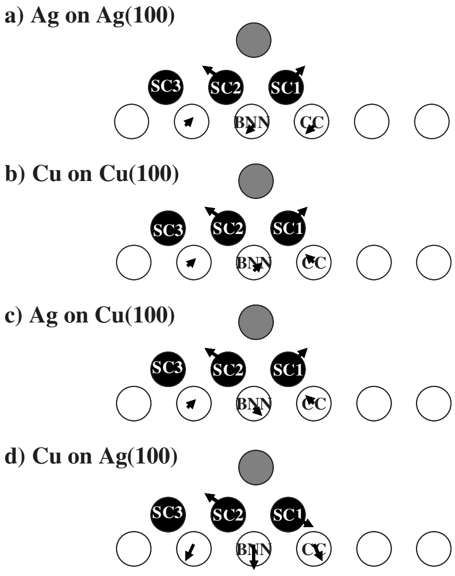


FIG. 6. Side view of a schematic representation of the relaxation trends upon adatom adsorption on fourfold site. Black, white, and gray circles represent the step atoms, the first-layer atoms and the adatoms, respectively.

sible competition between the mechanisms. If the Cu adatom reaches to the step edge via hopping then the ES barrier is −270 meV. On the other hand if Cu adatom undergoes an exchange process on Ag(100), a more likely possibility, the ES barrier would be that for Ag on Ag(100). Of course, if the exchange takes place just near the step edge the ES barrier for Cu on Ag(100) is −30 meV. The relevant ES barrier for this surface is negative either −30 meV or −270 meV. These negative barriers might be the rationale for significant terrace diffusion observed in the TAD study[37,43] and experimental observation[42] that at very low temperature (77 K) the surface grows layer by layer and the produced film is smooth. For Ag on Cu(100), the dominant terrace diffusion mechanism is hopping since the cost for exchange is about 1 eV, providing 320 meV for ES barrier via exchange. At the step edge, following the same trend as terrace, diffusion is preferred via hopping. This surface provides the relevant ES barrier to be 170 meV. To our knowledge, there are no data available in the literature for the height of the ES barrier for these studied heterosystems, except in an earlier study using TB method, on the growth of Ag shells on copper and palladium nanoclusters,[40] the step-edge barriers for Ag adatom crossing from the (100) to (111) facets is reported to be 0.67 eV via hopping, while the barriers via exchange are 0.48 and 0.67 eV. Given the heights of the ES barriers for the two heteroepitaxial systems, we expect that these systems behave differently both at terraces and the step edges hence growth mode should be expected to be different from each other.

A. Relaxations and bond lengths near step edges

Once again to investigate possible correlation between strength of bonding and bond lengths, we have examined structural relaxation of both step and substrate atoms in the presence of the adatom. In Figs. 6(a)–6(d), we present a schematic representation of the relaxation trends of the step atoms and the atoms in the first layer upon adatom adsorption on fourfold site. From the figure, we see that for each system studied except Cu on Ag(100), the first-nearest-neighbor step atoms (SC1 and SC2) move upward. The upward relaxation is the highest for Cu on Cu(100). We note that for Cu on Ag(100), the SC2 atom relaxation (upward) is the lowest as compared to the rest of the systems. It is also worth noting that the closest neighbors (at the first layer) of the step atoms show enhanced downward relaxation as compared to that of the rest of the studied systems. We find that the vertical relaxation (downward) of the atom underneath is enhanced for Ag on Cu(100). We note that the in-plane relaxation of the atoms (SC1 and SC2) is the highest for Cu on Ag(100). The optimized structure of the bridge site for Cu on Cu(100) and Ag on Cu(100) show similar relaxation trends, in which we find the first-nearest-neighbor step atoms relax upward. For Cu on Ag(100) and Ag on Ag(100), we find the step atoms (SC1 and SC2) relax downward.

Our analysis of the bond lengths at the step edges shows that the adatom's presence at fourfold site expands the first-nearest-neighbor bond length as in the case of terraces. The expansion ranges from 1.6% to 3.1% and the highest (lowest) expansion is for Cu on Ag(100) [Ag on Cu(100)]. At the bridge site, these bond lengths get closer to that of the surface without adatom.

From Table II, we find that for Cu on Ag(100), the adatom bond lengths for both fourfold and bridge sites are shorter than that of Ag on Cu(100). The decrease in the adatom bond length (at bridge site) with the first-nearest-neighbor step atoms with respect to the fourfold site is about 3% for Cu on Ag(100) and 4% for Ag on Cu(100). We find the change in the bond length to be about 8% as we compare the systems with same substrate element, while the change is 6% for the systems with same adsorbate element. We note that the adatom bond length for fourfold site (bridge site) is 1.5% (∼1%) shorter for Cu on Ag(100) than that of Ag on Cu(100). We also see that, following the same trend as for the terraces, the bond length with the atom under is the shortest for Cu on Cu(100) and the largest for Ag on Ag(100). As compared to the corresponding terraces, near the step edges, we find that the bond length with the atom underneath becomes larger (0.04 Å) for Cu on Ag(100) and the shorter (0.01 Å) for the rest of the studied systems.

B. Binding energies near step edges

The binding energies near the step edges (Table II) show that, as for terraces, they are higher for the fourfold site than the bridge site. Also, similar to the trends on the terraces, we find the adatom binding energy near the step edge to be the highest for Cu on Ag(100) and the lowest for Ag on Ag(100). The binding energy for Cu on Ag(100) is higher (0.78 eV) than that of Ag on Cu(100). The binding energy (at bridge site) decreases with respect to that of the terraces is in the range of 2–10 % with the highest decrease for Cu on Ag(100). The decrease can be understood from the fact that at bridge site of a step edge, the adatom binds to fewer neighbors than that on the terraces. Comparison of the binding energies (at fourfold site) near the step edges and on terraces (Tables I and II) shows that except for Cu on Ag(100), the rest of the systems present an increase of about 2%. We find 7% decrease in the binding energy (fourfold site) near the step edge for Cu on Ag(100). For all the systems studied, the step geometry is the same and hence the observed trends in the binding energies emerge from the dissimilarity in the electronic interactions between the adsorbate and substrate atoms.

V. CONCLUSIONS

In this paper, we have summarized the results of our first-principles total-energy calculations for the energetics of several microscopic diffusion processes that play key roles in homoepitaxial and heteroepitaxial growths on Ag(100) and Cu(100) surfaces. In agreement with earlier investigations for the diffusion on terraces, our calculations show that diffusion proceeds via hopping rather than by exchange for both studied homosystems. For the heterosystems, we find exchange to be the dominant mechanism for Cu on Ag(100), while for Ag on Cu(100) hopping is the relevant mechanism on terraces. For these heterosystems, we find that the terrace diffusion barrier (via hopping) is 0.23 eV higher for Cu on Ag(100) than that of Ag on Cu(100) which we argue to originate mainly from the differences in the electronic interactions. As compared to diffusion on the homoepitaxial system, Ag on Ag(100), we find the diffusion barrier for Ag on Cu(100) to be reduced by 80 meV. For this system, a large adatom diffuses on the substrate with small lattice constant (Cu), similar to the diffusion on a *compressively* strained lattice in which the diffusion barrier is expected to be lower than that of the unstrained surface. This can be understood from the change (decrease) in corrugation in the case of compressive strain. On the contrary, for Cu on Ag(100), for which the small adatom diffuses on the substrate with a large lattice constant, like the diffusion on a *tensile*-strained lattice, we find the diffusion barrier to increase by 70 meV from that of Cu on Cu(100). For the tensile-strain case, the increase in the corrugation enhances the diffusion barrier. Our binding-energy analysis shows that there is a linear relationship between adatom binding energies and the corresponding diffusion barriers for the terraces. The charge-density difference, which is a measure of adatom binding strength relative to the substrate, revealed that the system with higher charge accumulation (between adatom and the first nearest neighbors) has higher binding energy hence higher diffusion barrier than that of the others. We also note that for cases in which diffusion barriers had been previously calculated, our results either concur or provide validation or help narrow the range of predicted values.

In contrast to the diffusion on terraces, we find for diffusion near the step edges of Cu(100) and Ag(100) that the descent over the step is governed by exchange, confirming earlier predictions, and providing more quantitative results. For Cu adatom diffusion at the Ag(100) step edge, we show that exchange costs *less* energy than hopping. It is only for a Ag adatom's descent over the Cu(100) step edge that exchange is more costly than hopping. From the analysis of the diffusion mechanisms and the corresponding energy barriers, we find the relevant height of the ES barriers for Ag on Ag(100) to be small (20 meV), implying a good interlayer mass transport hence confirming the theoretical and experimental observations of a smooth 2D growth. For Cu on Cu(100), the relevant ES barrier is 60 meV. For the heteroepitaxial systems, our analysis shows the ES barrier for Cu on Ag(100) is negative −30 or −270 meV hence implying high mass transport at the step edges leading to possible layer-by-layer growth. The ES barrier for Ag on Cu(100) is, however, found to be much larger (170 meV), implying less mass transport from the step edge to a lower terrace and possible mound formation on the surface. These results point to the feasibility of alloying Cu atoms into Ag(100) especially at the step edges, while that for Ag atoms on Cu(100) is less likely. We await further experiments and dynamical calculation to verify our findings.

ACKNOWLEDGMENTS

The work is supported by DOE under Grants No. DE-FG02-07ER15842 and No. NSF-ITR 0840389. We acknowledge fruitful discussions with A. Kara, S. Stolbov, and S. Hong. We are grateful to Lyman Baker for careful reading of the manuscript and constructive comments.

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