Tip-induced adatom extraction and cluster manipulation

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We present results for tip-induced extraction of a Cu adatom from Cu mound on Cu(111), and compare the characteristics to that for a similar Ag system. Molecular-dynamics and molecular static simulations were carried out using interaction potentials from the embedded atom method. Molecular-dynamics simulations revealed differences in the modes of extraction for the cases of Ag and Cu systems and their dependence on tip geometry. For the case of a sharp Ag tip, the extraction of a Ag adatom occurs via the pulling mode, while with a blunt Ag tip, the extraction is more complex involving a two-step motion. On the other hand, the relatively stronger Cu-Cu interaction leads to a sliding and/or dragging mode in which the whole three-dimensional cluster is dragged followed by the extraction of the adatom from the cluster. Molecular static simulations provide a detailed analysis of the changes in the energy landscape in the presence of the tip, resulting in a substantial decrease of the energy barrier for an adatom to descend from the mound.

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I. INTRODUCTION

Since its invention by Binning *et al.*,[1] scanning tunneling microscopy (STM) has become an important tool for imaging structure formations at surfaces,[2] yielding valuable results for many surface science problems at the nanometer scale. In recent years, STM is increasingly becoming a manipulation tool by which atoms and molecules are moved around and taken to a desired spatial location.[3–6] The scanning tunneling microscope tip causes modifications in the energy landscape in its vicinity which, in turn, controls the characteristics of the manipulation. Thus, detailed knowledge of the energy landscape in the presence of the tip may help control atomistic processes such as chemical reactions, growth, and nanostructuring, to name a few. This ability of the scanning tunneling microscope tip had already been used to manipulate laterally[3,4] and also vertically[5] individual atoms and molecular movements. Recently, the scanning tunneling microscope tip has been used to extract atoms from a metal substrate by tip crashing.[6] Of the experimental investigations aiming to shed some light on the basic mechanisms governing single atom and molecule manipulation, the work of Meyer *et al.*[7] is particularly worth mentioning in the present context. From their observation, they classified the manipulation process into two modes: lateral and vertical. In the lateral mode, a particle is moved on the surface to the desired place without losing contact with the substrate, while in the vertical mode, a particle is pulled up from its initial position by the tip and then dropped down on the surface at the desired location. They further divided the lateral manipulation into three distinct submodes, depending on the tip-particle interaction. They showed that on Cu(211), Pb and Cu atoms can be manipulated by attractive tip-adatom interactions in such a way that the atoms follow the tip discontinuously by hopping from one site to the next (pulling mode). For the case of Pb atoms, manipulation may *also* proceed through attractive forces but in a continuous way (sliding mode) with tip-particle interaction increasing very strongly. The third mode, which was observed in the case of single CO molecules, is the pushing mode resulting from a repulsive interaction between the tip and the molecule. From the theoretical side, there were several attempts[8–10] to explain the experimental findings and rationalize the physical phenomena governing manipulation.

Sorensen *et al.*[8] investigated Au adatom diffusion energetics on Au(100), in the presence of a Au tip, and found a lowering of the activation energy. Similarly, using the example of the lateral manipulation of a Cu adatom along a step on Cu(111) with a Cu tip, Kurpick and Rahman[9] showed that while the presence of a tip lowers substantially the diffusion barriers toward the tip, the barrier in the opposite direction increases. In these systems, the phenomenon was explained in terms of the coordination between the tip and surface atoms. The motion of an adatom on metal surfaces in the presence of the tip arises from changes in the potential-energy surface that are controlled by the characteristic of the interatomic potentials which in the above-mentioned systems exhibit a bond-length–bond-order correlation. At particular heights, the adatom gains new bonds with the tip atoms, which makes its motion more favorable toward the tip than away from it. Kurpick and Rahman also show that the qualitative changes in the activation energies do not depend on the details of the tip; however, the shape and form of the tip apex and the height of the tip from the adatom affect *quantitatively* the energetics. A further theoretical study of vertical and lateral manipulation on flat, stepped, and kinked metal surfaces by Ghosh *et al.*[10] revealed shifts in the saddle points and the presence of significant relaxations of the surface and tip atoms, providing more concrete factors behind the energy landscape perturbations introduced by the tip.

The issue of pulling, pushing, or sliding of the atoms by the tip has appeared once again in a recent experimental study which established that it is possible to extract individual atoms from a three-dimensional (3D) mound.[11] Since the geometrical environment of atoms on a 3D mound differs from that on flat, stepped, or kinked surfaces, the modifications to the energy landscape introduced by the presence of a tip may not be readily extrapolated from what has been learned from the earlier studies.[8–10] We already showed for the Ag(111) system that a Ag adatom can be extracted from a Ag mound by a Ag tip through the pulling mode, in qualita-

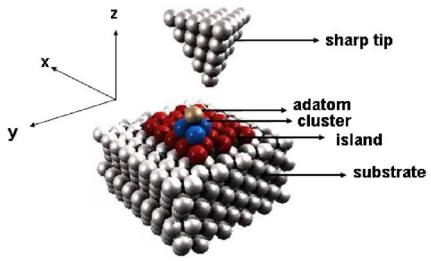

FIG. 1. (Color online) Model system for the manipulation process.

tive agreement with the experimental work of Despande *et al.*[11] The same calculations for a Cu(111) system showed differences from what has been observed for the Ag(111) system. For the Cu(111) system, we observe not only an adatom extraction by sliding mode [which is different from that of a Ag(111) system] but also manipulation of clusters which contains three to five atoms. In this paper, we provide details on the atom extraction from 3D islands for these two different systems, namely, Ag(111) and Cu(111) for which we found two different modes of extraction, reflecting the complexities behind the extraction mechanism.

In Sec. II, we present a description of our model system. In Sec. III, we give the theoretical details which are applied to this study. In Sec. IV, we present results of the Ag and Cu systems. Finally, we summarize and compare these two different extraction processes in Sec. V.

II. MODEL SYSTEM

Our prototype system for manipulation and/or extraction processes is illustrated in Fig. 1; it consists of a tip, an adatom on top of a 3D island, and a substrate. As shown in the figure, the substrate has six atomic layers of fcc(111) each containing 8×10 Cu/Ag atoms. The 3D island consists of a two-dimensional (2D) pad containing 25 Cu/Ag atoms, on top of which is a three-atom Cu/Ag cluster. The adatom (the subject of manipulation and/or extraction) is in the threefold site on top of this cluster. The tip consists of 35 (34) atoms with a sharp (blunt) tip apex. To check the system size effect, calculations for selected cases have also been done on a larger system consisting of nine layers and 20×20 Cu/Ag atoms per layer; we find the smaller size to be sufficient for these studies.

III. THEORETICAL METHODS

In this study, the atoms in our model system interact through an empirical many-body potential obtained from the embedded atom method,[12] with parametrization by Voter and Chen.[13] These potentials have had important success in explaining the characteristics of Cu and Ag surfaces, and have been proven to be reliable for examining the energetics, structure, and dynamics of these transition metals.[14–16] Our molecular-dynamics (MD) simulations were performed at a relatively low temperature (100 K) to mimic the experimental setup.[11] The positions and velocities of the atoms are calculated using a fifth-order predictor corrector method.[17] Each system is first thermalized by performing a simulation under conditions of constant number of particles, constant volume, and constant temperature (*NVT*), for 20 ps (the time step used for these calculations is 1×10^{-15} s). After this phase of thermalization of the system, we perform a simulation with constant number of particles, constant volume, and constant total energy (*NVE*) for 200 ps with the following constraints: (i) the bottom two layers of the substrate are held fixed to avoid an artificial motion of the whole MD cell due to the presence of the tip, (ii) the top two layers of the tip are held fixed to avoid a landing of the tip on the surface due to the attractive forces, (iii) two atoms of the pad are held fixed to avoid an artificial sliding of the island and the mound when the tip is moving laterally, and finally (iv) the tip is given a constant lateral velocity of 5–10 nm/ns (5×10^{-5}–10^{-4} Å per time step). After each picosecond of simulation, we store the positions of the adatom, the mound, the pad, the first surface layer, and the tip atoms. Snapshots and then movies are made from these 200 sets of data.

The molecular static (MS) simulations aim at relaxation of the system of interest to its minimum-energy configurations at 0 K. These simulations are performed using a standard conjugate gradient method,[17] which has been shown to yield the same relaxation structures as simulated annealing methods for similar systems (see Ref. 23 in Ref. 14). During the minimization process, the two bottom layer atoms of the substrate and two atoms on the island are kept rigid. All the tip atoms except the ones on the top two layers are allowed to relax to their equilibrium positions for each simulation. We already know that the presence of the tip modifies significantly the potential-energy surface[8–10] seen by an adatom on a terrace, near a step edge, or a kinked site. As a result, adatom may diffuse toward (or away from) the tip. The objective of this paper is to understand the processes by which an adatom can be extracted from a 3D cluster on Ag(111) or Cu(111). Clearly, the key to extraction is overcoming of the first barrier that adatom sees in jumping from its equilibrium position (threefold site) to the first threefold site on the wall of the mound, from which the adatom will slide easily down, as the barrier to diffuse is the same as the one on Ag(111) which is about 40 meV. The bottleneck is hence formed by the first barrier equivalent to the Schwoebel barrier found near a step.[18] The presence of the tip will ultimately change the landscape of the energetics and a detailed analysis of this barrier for several locations of the tip is needed. The sliding up, back to the original position, is possible and a successful extraction would prevent this process to happen. In other words, extraction would occur when the tip at a certain position would increase the ratio between the barriers to climb up and diffuse down. These two barriers associated with these two processes can be studied using lateral and vertical manipulation techniques, respectively. For lateral manipulation, for a fixed tip height and lateral position as measured from the adatom initial position, the total energy of the system is calculated as the adatom position is varied *laterally*. In the case of vertical manipulation, and again for a fixed tip height and lateral position as measured from the adatom initial position, the total energy of the system is calculated as the adatom position is varied *vertically*.

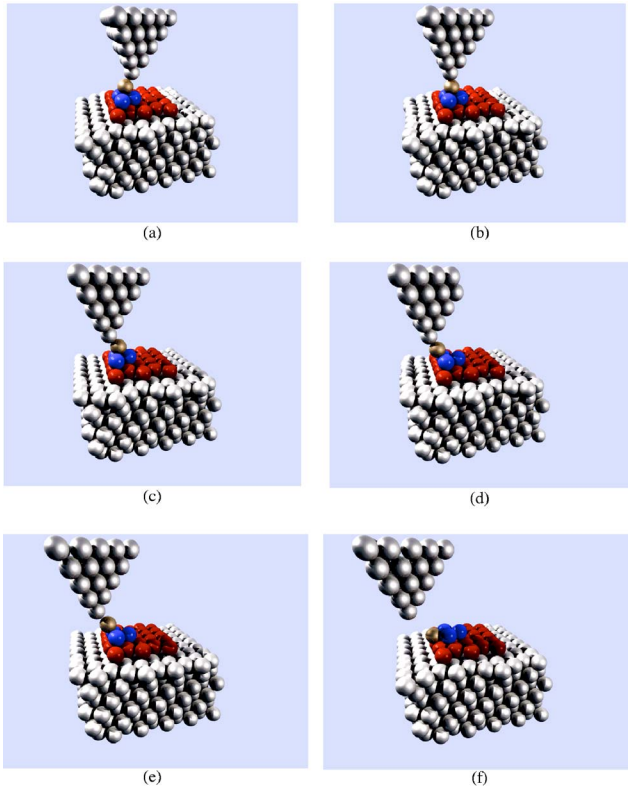

FIG. 2. (Color online) Snapshots of MD simulation for Ag sharp tip.

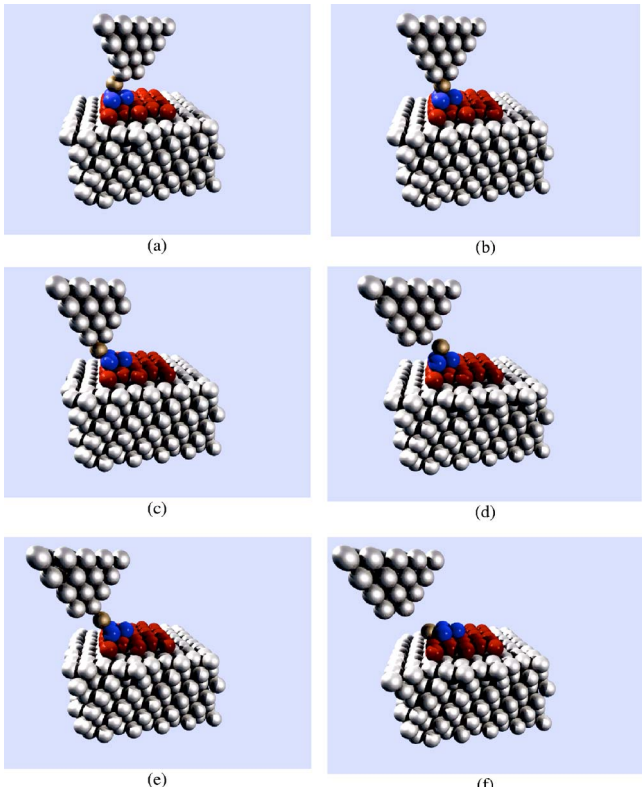

FIG. 3. (Color online) Snapshots of MD simulation for Ag blunt tip.

IV. RESULTS AND DISCUSSION

In this section, we present a summary of the results of the MD simulations for different tip heights. For every simulation, the position of the adatom is monitored to assess the success of the extraction. To study the physical properties behind a successful tip-induced extraction, we also present results of MS simulations in which the tip height and lateral positions were varied.

A. Molecular-dynamics simulations

1. Tip-induced extraction of a Ag atom from a Ag mound on Ag(111)

We have performed MD simulations for Ag tip heights (as measured from the initial position of the adatom) between 3.43 and 2.43 Å with a step of 0.1 Å. Every simulation starts with the tip apex lateral position of about 3.5 Å away (behind) from the adatom followed by the tip moving laterally toward the adatom with a constant speed of 5 or 10 nm/ns and the calculation is stopped when the tip is about 5 Å in front of the adatom. Both sharp and blunt tips with one and three atoms at the apex were used, respectively. We show a sequence of snapshots taken at 5, 40, 100, 115, 135, and 175 ps after the start of the simulation, respectively, at tip height of 2.43 Å, using a sharp Ag tip with [Figs. 2(a)–2(f)]. In Fig. 2(a), the apex atom is just behind the adatom whose lateral and vertical positions seem not to be affected by the presence of the tip. In Fig. 2(b), the apex atom is directly on top of the adatom, while in Fig. 2(c) it is just in front of the adatom. The lateral and vertical positions of the adatom are hence unaffected during these first 100 ps of the simulation. It is when the tip apex atom is about 2 Å laterally in front of the adatom [Fig. 2(d)] that we notice a change in the lateral position of the adatom with motion toward the tip. The adatom continues its monotonic motion toward the tip as it advances away from the adatom [Fig. 2(e)] and finally it is extracted from the mound as can be seen in Fig. 2(f).

A molecular-dynamics simulation using a blunt Ag tip reveals a mechanism of extraction reflecting the complex nature of the interatomic interaction as reflected below in the changes in the energy landscape. Figure 3 shows snapshots from a MD simulation where the tip apex atoms vertical position is 2.63 Å above that of the adatom. These snapshots are taken at 5, 60, 90, 135, 150, and 185 ps after the start of the simulation, as shown in Figs. 3(a)–3(f). In Fig. 3(a), the lateral position of the apex atoms is behind the adatom whose position is not affected by the presence of the tip; the same situation can be seen in Fig. 3(b) when the apex is just above the adatom. As the tip moves laterally away from the adatom, two atoms from the apex are in front of the adatom while the third is behind it, as illustrated in Fig. 3(c). In this figure, we notice that the adatom has moved with the tip attempting to overcome the barrier for extraction. In Fig. 3(d), we notice that the adatom has moved back to the top of the mound as a result of the failure of the tip to flatten enough the energy landscape for the adatom to be extracted. As the third atom of the apex is now in front of the adatom taking a similar role played by the apex of a sharp tip, the

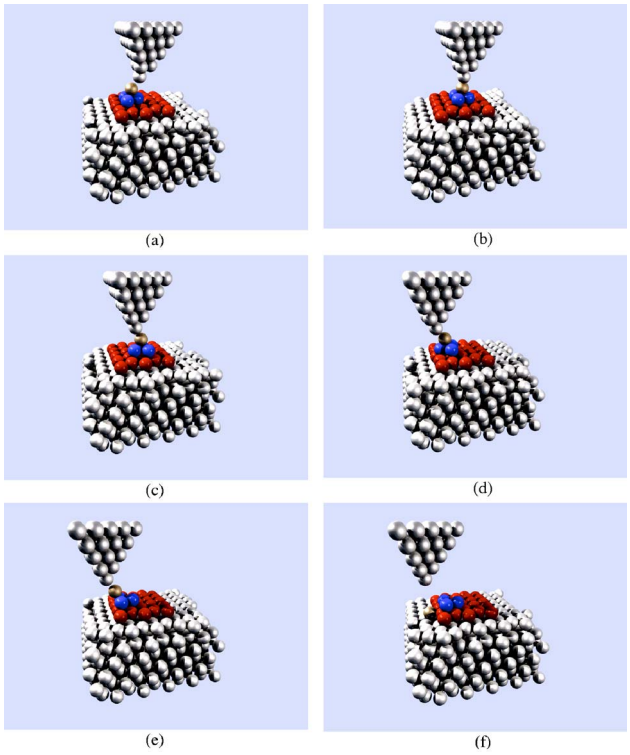

FIG. 4. (Color online) Snapshots of MD simulation for Cu system.

energy landscape is now flat enough for the adatom to be extracted, as can be seen in Figs. 3(e) and 3(f).

2. Tip-induced extraction of a Cu atom from a Cu mound on Cu(111)

For copper systems, we have used the same model as for silver where the tip and the substrate are made of copper. We performed simulations with a starting height of 2.63 Å and ran similar simulations with decreasing height by a step 0.1 Å. For all heights above 2.03 Å, the simulations did not produce any extraction of the adatom. Finally, a simulation at a tip height of 1.93 Å showed a successful extraction. A detailed analysis of the simulation movie revealed that the extraction of the Cu atom from the mound proceeds through a totally different mode than in the case of Ag atom discussed in Sec. IV A 1. We noticed that the Cu adatom was always in close contact with the tip during the manipulation phase, suggesting that in this case, the extraction is actually through a *sliding* (or dragging) *mode* involving the manipulation of the whole cluster and the adatom which reflects the very strong interaction between Cu atoms as compared to that between Ag atoms. Indeed, as the tip approaches the adatom as illustrated in Fig. 4(a) (corresponding to 42 ps after the start of the simulation), the cluster and the adatom move collectively toward the tip [see Fig. 4(b) taken just 1 ps after Fig. 4(a)]. From this moment, the tip, the cluster, and the adatom move collectively [Figs. 4(c)–4(e)]. Note that the motion of the cluster is not monotonic but rather consists of rotation (c), then a jump (d), and another rotation (e). Finally, when the tip passes the edge of the pad, the adatom is extracted (f).

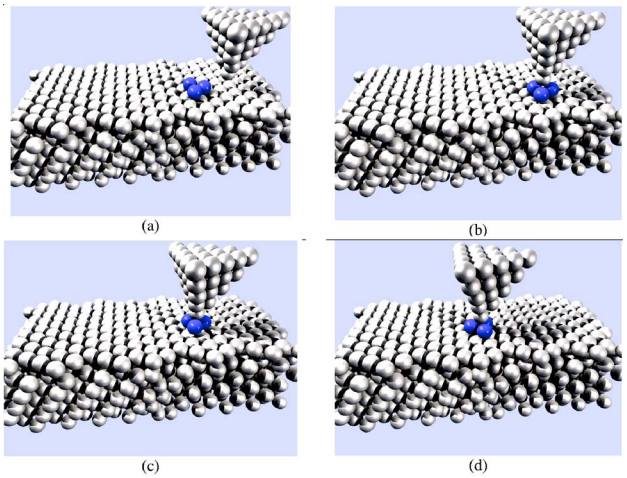

FIG. 5. (Color online) Snapshots of MD simulation for Cu trimer manipulation.

This remarkable manipulation of the whole cluster +adatom stimulated us to perform MD simulations for clusters containing three to five atoms and in both 2D and 3D configurations. We show hereafter the cases of 2D trimer and tetramer clusters on Cu(111). From Figs. 5 and 6, we note that once the cluster is in contact with the tip, it travels along with the tip with a motion consisting of a series of a rotation followed by a jump. For the case of a pentamer, once the tip gets in contact with the cluster and starts the sliding motion of the pentamer, the tip apex atom gets extracted and attaches to the pentamer as an adatom with no further motion of the cluster.

To illustrate further the difference between the Ag and Cu extraction cases illustrated in Figs. 2 and 4, we plot in Fig. 7 the lateral positions of the adatom and the tip apex versus time for simulations done at 100 K and tip heights of 2.43 and 1.93 Å for Ag and Cu, respectively. From Fig. 7(a), we note that the Ag adatom's lateral position stays almost constant when the tip moves from a position behind the adatom to positions in front of it. When the tip reaches the position

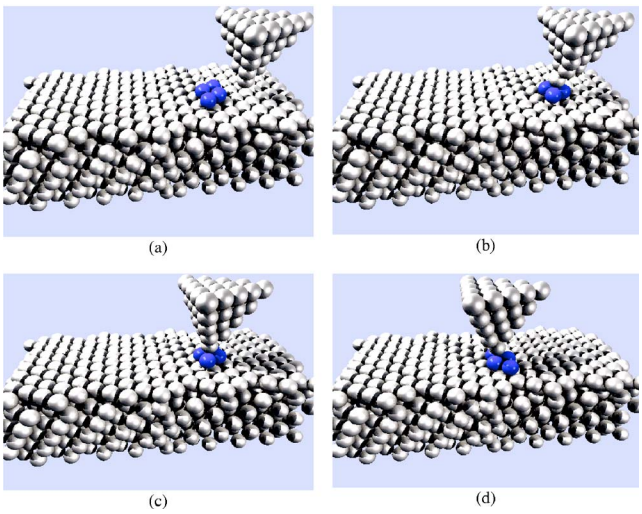

FIG. 6. (Color online) Snapshots of MD simulation for Cu tetramer manipulation.

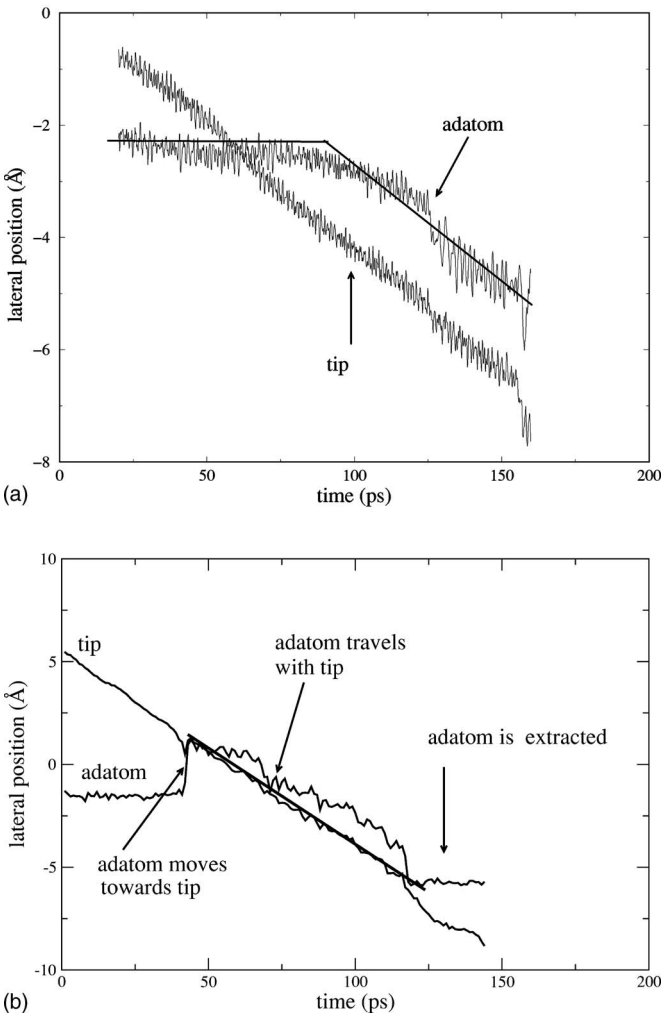

FIG. 7. Lateral position of the adatom and the tip apex vs time at 100 K for (a) the Ag system and (b) for the Cu system. Movies are at Ref. 19.

of about 2 Å in front of the Ag adatom (for which the barrier for hopping down becomes minimal as discussed earlier), the latter starts moving laterally toward the tip and finally hops down. For the case of Cu, the scenario is much different, as illustrated in Fig. 7(b). As the tip approaches the adatom (with lateral separation of about 2.5 Å), the latter moves back toward the tip and sticks to it (at about 43 ps after the beginning of the simulation). After that, the tip and the adatom move together for about 6 Å (in the time interval between 43 and 118 ps) after which the adatom is extracted.

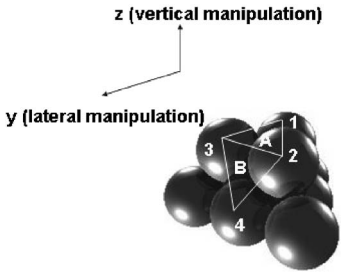

FIG. 8. The two possible adsorption sites on the mound.

B. Molecular statics simulations

In order to evaluate the manipulation capabilities of the tip, we first study the energy landscape seen by a diffusing atom in the absence of the tip. In the case of a silver atom hopping down from a Ag mound on Ag(111), in the absence of the tip, we found that the adatom encounters a barrier of 0.3 eV (A to B in Fig. 8). Once the adatom reaches point B, the adatom could climb up to A after overcoming the same barrier of 0.3 eV (B to A), as illustrated in Fig. 8. In the presence of the tip, these two barriers are modified, as can be seen from the results summarized in Table I. It is actually the difference between these two barriers that should dictate (exponentially) the probability of the adatom extraction by the tip. Indeed, if the barrier from A to B is reduced substantially, while that from B to A is moderately reduced, one will conclude that once the adatom makes it to B, it will continue sliding down. However, if the barrier from B to A is also dramatically reduced, one will expect the adatom to have a high probability to go back to its original position (A) after a

TABLE I. The activation energy barriers for the Ag adatom on the mound on Ag(111) for lateral and vertical manipulation mode.

	Energy barrier (sharp tip) (eV)		Energy barrier (blunt tip) (eV)	
Height (interlayer separation) in Å	Lateral manipulation	Vertical manipulation	Lateral manipulation	Vertical manipulation
2.43 (1.03)	0.032	0.18		
2.63 (1.11)	0.052	0.21	0.08	0.16
2.83 (1.20)	0.12	0.24	0.08	0.21
3.03 (1.28)	0.194	0.27	0.08	0.24
3.23 (1.37)	0.28	0.28	0.12	0.26
3.43 (1.45)	0.29	0.3	0.21	0.28
3.63 (1.54)	0.3	0.31	0.32	0.29

hop to B. It is then essential to study the behavior of these two barriers in the presence of the tip. When the adatom hops from A to B, we consider it to be the case of lateral manipulation, while hopping from B to A is classified here as vertical manipulation, as defined earlier. In Table I, we contrast the barrier energies to escape from the mound (lateral manipulation) and return back to the mound (vertical manipulation) as a function of the tip height and shape. We note that for both tip shapes, the difference between these two barriers is relatively high, which explains the success of the adatom extraction from the mound.

The determination of the change in the barriers involved in the extraction of a Cu atom from a Cu mound using MS simulations was not possible since we found that the whole cluster moves when the tip is close to the adatom. A restriction on the motion of the Cu cluster would significantly alter the energy landscape and hence the extracted barriers for diffusion would be meaningless.

The obvious difference between the *strong* interactions during manipulation of the Cu systems and the generally *gentle* ones for Ag systems stems from the fact that Cu and Ag have different cohesive energies and lattice constants. Manipulation of a Cu adatom in the Cu system with a (larger) cohesive energy of 3.49 eV (2.95 eV for Ag) coupled with a (smaller) lattice constant of 3.615 Å (4.090 Å for Ag) would probe larger gradients during manipulation for tip-adatom distances (of the order of nearest-neighbor separation) than those in the case of a Ag adatom in the Ag system. Consequently, one would expect copper to be "stiffer" near equilibrium positions than silver. This argument can be tested as follows: if Cu and Ag would have the same curvature at equilibrium, the phonon spectrum of one could then be extracted using the other with a multiplicative factor equal to the square root of the inverse of the ratio of the masses. Using this relationship, and starting from the Ag vibrational spectrum (with a maximum of the bulk band at about 4.6 THz), one would expect the Cu bulk band to present a maximum at 6.00 THz. In fact, the experimentally measured phonon bulk band for copper presents a maximum at about 6.8 THz, a shift of about 0.8 THz from the predicted value using the ratio of masses; a positive shift reflects the extra stiffness of the Cu potential as compared to the Ag one.

V. CONCLUSION

We have performed detailed and extensive molecular-dynamics simulations of adatom extraction from a mound by a manipulative tip for Ag and Cu systems. Successful extraction was achieved for particular tip heights which depend on the system's elemental composition. Extraction was possible at tip heights of 2.43 Å (2.63 Å for blunt tip) and 1.93 Å, above the initial position of the adatom, for Ag and Cu, respectively. For silver, in the case of a sharp tip, the extraction is clearly through a straightforward pulling mode, while for a blunt tip, the three atom apex leads to extraction through two stages, each of which can be reasoned on the basis of the local adatom environment. For copper, the situation is much more complex as a result of the relatively strong interaction between Cu atoms, which allows the tip to cause motion of the whole cluster through a sliding and/or dragging mode. In addition to these simulations of adatom extraction, we performed other simulations where 2D Cu clusters containing three, four, and five atoms were manipulated through a drag using a sharp tip. We found that for the critical size of five atoms, the tip loses its apex atom to the cluster after the tip attempts to drag this cluster. Detailed analysis of the energy landscape shows that in the case of Ag, the tip alters the landscape in such a way that when the tip is in front of the adatom and close to the edge of the mound, the energy for the adatom to hop down over the mound edge decreases very rapidly. Finally, we have traced the qualitative differences between manipulation of Cu and Ag systems to their difference in cohesive energy and lattice constant.

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