Tip Induced Motion of Adatoms on Metal Surfaces

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(Received 14 December 1998)

From total energy calculations we show that for certain tip-adatom separations the activation barrier for the adatom to move towards the tip disappears and the adatom experiences an attractive force in the direction of the tip. For a Cu adatom at a (100) microfaceted step on Cu(111) this happens at a lateral separation of about one lattice constant, in agreement with recent experimental findings. Simultaneously, the activation barrier in the direction away from the tip increases significantly. The details of the changes in the potential energy surface induced by the tip are found to depend on the characteristics of the tip apex and its height above the adatom.

PACS numbers: 68.35.Fx, 61.16.Ch

The scanning tunneling microscope (STM) [1,2] has been used widely for imaging surface structure and topography. It has provided fascinating insights into electron confinement and quantum size effects on metal surfaces. In recent years, the STM has become a multipurpose tool for the investigation of a variety of dynamical processes on surfaces like the diffusion of atoms and the vibrations of adsorbed molecules. One such application is in the manipulation of individual atoms on surfaces, as exhibited in the pioneering work of Eigler *et al.* [3]. This selective movement of atoms opens new avenues for controlled study of the nature of the chemical bond between atoms/molecules and surfaces and has important implications for atomistic processes such as surface alloying, catalysis and chemical reactions. We have been particularly intrigued by the work of two experimental groups who have examined the manner in which single metal atoms follow a STM tip [4,5] on metal substrates. The first experiment illustrates tip induced motion of Ag adatoms on Ag(110) through the troughs between densely packed atomic rows [4], while the second concentrates on the manipulation of Cu adatoms along the step edges of Cu(211) [5] which is a vicinal of Cu(111). Since the separation between the adatom and the tip lies in the range of a few Å, the authors interpret their results by postulating strong attractive forces between the tip and the adatom such that the adatom is "pulled" by the tip. These beautiful experiments raise several questions about the mechanisms by which the tip influences the mobility of adatoms: under what conditions does the adatom follow the tip? What is the distance dependence of this induced motion? Is the manipulation electric-field assisted or can it be ascribed mainly to interatomic forces? In other words, could a scanning force microscope produce the same results? How does the tip induced motion depend on the characteristics of the tip? These and related questions need to be answered to obtain a theoretical understanding of the physical basis underlying the manipulation of atoms on surfaces. This is important for fundamental reasons and for achieving technical advancement in nanostructuring. Most theoretical work related to STM has targetted the prediction of contrast in the observed images which requires calculations of tunnel current and barrier height [2]. A few studies have examined contact formation and adatom transfer from the tip to the surface [6,7], while some others have used atomistics simulations of tip-surface interactions to obtain estimates of the site-dependent forces acting on the tip-apex atom, as a function of the vertical tip-surface distance [8,9]. In the case of physisorbed species, through the usage of van-der-Waals–type interaction between the different species on the surface, Bouju *et al.* [10] have shown that the dragging mechanism for the adsorbate depends on the tip geometry. These studies have provided insights, but the questions raised above remain largely unanswered. In this Letter, we address these questions by performing total energy calculations, using interaction potentials derived from the embedded atom method (EAM) [11]. These potentials provide a reasonable and computationally efficient description of several transition metals and have been applied with remarkable success in various surface studies including adatom self-diffusion [12].

Our prototype system (Fig. 1) motivated by the experimental setup of Bartels *et al.* [5] consists of a Cu tip, and a Cu adatom on a Cu(111) substrate with a (100) microfaceted step. Note that, although in the experiments the tip is not made of Cu, it gets coated with Cu atoms. It is thus reasonable to assume that Cu atoms form the apex of the tip. The adatom is located in its minimum energy position at the step edge in the hollow or "fcc" site. In the absence of the tip the adatom encounters two equivalent barriers of 0.27 eV, in either direction. When a tip is placed along the step edge at a specified height and a lateral distance x away from the adatom, we expect the potential energy surface to change. For a range of values of x, we calculate the activation barriers for the adatom to move towards the tip (barrier) and in the direction opposite to it (op-barrier). In each calculation we allow all substrate atoms, except the four at the edges of the crystal and those in the bottom layer, to relax. The lateral coordinates of the adatom are also kept fixed. The impact

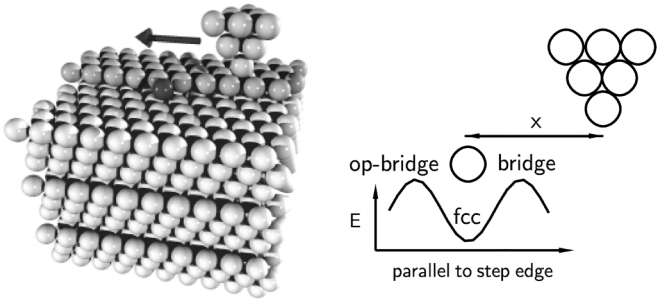

FIG. 1. At left: the model system. In the calculations the tip is moved parallel to the step edge at a constant height above it. At right: x is the lateral distance between the adatom and the tip-apex atom. The maximum energy site for the adatom between two fcc sites is called bridge or op-bridge as indicated.

of atomic relaxations, and variations of the shape, orientation, and height of the tip, on the strengths of the barriers are examined. For comparison, we extend the calculations to the manipulation of a Cu adatom along the rows of Cu(110).

We use initially a tip consisting of 10 Cu atoms arranged in fcc(111) pyramidlike stacking (see Fig. 1). Our calculated values of the barrier and op-barrier, with the adatom at a fcc site (call it A for discussion), as a function of the lateral distance x, are shown in Fig. 2. The filled circles show the results for a tip for which all atoms are assumed to be rigid and the tip height [vertical distance between the adatom and the tip-apex atom(s)] is initially set at 2.5 Å. When the tip approaches the adatom, not surprisingly the op-barrier increases and the barrier decreases. At a lateral distance of about 2.5 Å, the barrier disappears completely and the adatom

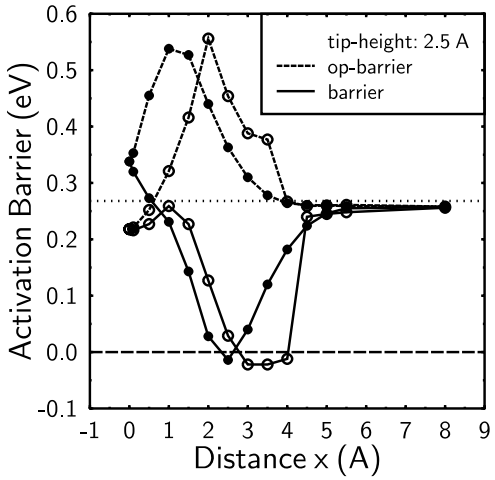

FIG. 2. Barrier (solid line) and op-barrier (fine dashed line) for adatom motion along the step edge, as a function of x, for a ten-atom tip: filled circles for a rigid tip and open circles for a relaxed tip. The dotted line indicates the barrier in the absence of the tip. Calculational errors from convergence of energy minimization are smaller than the symbol size.

experiences an attractive force towards the tip. This leads to a motion towards the tip and the adatom moves to the neighboring fcc site (call it B) directly under the tip ($x = 0$ Å) where it is trapped by the high barriers in both directions along the step edge (see Fig. 2). The motion of the adatom under the influence of the tip is easy to quantify. The decrease of the barrier gives rise to an average force of about 0.01 eV/Å between site A and the "bridge" site (between A and B) [13] and an additional force of about 0.25 eV/Å between this bridge site and site B. Within 1.5 ps the adatom is thus able to move from site A to B, under the influence of these interatomic forces and without any thermal activation. The speed involved is fast compared to typical velocities that are applied to tips to induce motion of adatoms (a few Å per second [3]). Given these high speeds and the low temperatures of 50 and 30 K in the manipulation experiments [4,5], the adatoms are not expected to experience the vibrational dynamics of the system. At 30 K, the vibrational free energy contribution is only about 1 meV, based on estimates from our earlier work on adatom diffusion [12]. Furthermore, molecular dynamics simulations, though insightful, are very tedious at such low temperatures. It is thus reasonable to examine the manipulation of atoms by tips within the framework of surface energetics using the static lattice approximation.

Next, as the tip is moved away from site B, the activation barrier for the adatom decreases in the above manner and the adatom follows the tip in subsequent hops, as observed experimentally by Bartels *et al.* [5]. The adatom prefers to follow the tip because the enhancement of the op-barrier reduces the chances of its motion in the other direction. It is interesting to note that in both experiments [4,5] and in our calculations the adatom follows the tip at a separation of about one lattice constant. In Fig. 3 the corresponding changes in the total energy of the system as the tip approaches the adatom are shown. For all three sites (fcc, bridge, and op-bridge) the total energy is lowered when the tip approaches the adatom. This is understandable since the closer proximity increases the coordination for all affected atoms. Because of their geometric positions, energy lowering starts first for the bridge site, then for the fcc, and finally for the op-bridge, leading to changes in the respective barriers.

Since atomic relaxation can have a strong effect on surface energetics, in a subsequent study we allowed the four atoms at the bottom of the ten-atom tip to relax freely. The results for the barrier and the op-barrier indicated by open circles in Fig. 2 show the characteristics to be similar to those for the rigid tip, except for some remarkable differences traceable to relaxation effects in the tip. The sudden decay of the barrier when the lateral separation x between the adatom and the tip-apex atom changes from 4.5 to 4.0 Å can be attributed to such effects. With the adatom in the bridge position and $x =$ 4.0 Å, the tip-apex atom relaxes to a position between

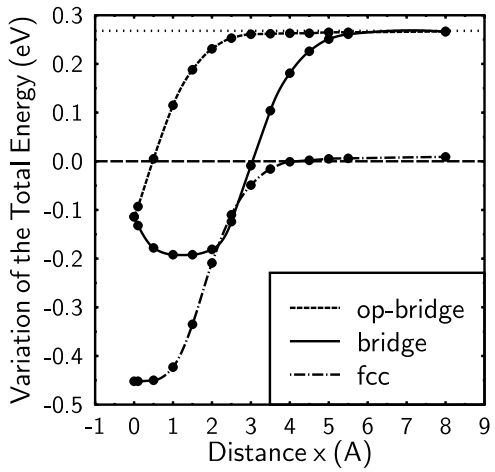

FIG. 3. Total energies corresponding to the three adatom sites: fcc (dashed-dotted line), bridge (solid line), and op-bridge (fine dashed line), as a function of x.

the step edge and the adatom, thereby lowering the total energy for the bridge site more drastically than for the fcc site. This leads to a dramatic reduction in the barrier to zero within less than 0.5 Å. These relaxation effects provide even stronger evidence for adatom manipulation by attractive forces of the tip.

In Fig. 4, for a rigid ten-atom tip, we compare the calculated changes in the barriers and op-barriers, as a function of x, for tip heights of 2.5, 3.0, and 3.5 Å. The qualitative features of the three sets of curves in Fig. 4 are very similar; however, the changes in the barrier and op-barrier become less pronounced as the tip height increases. We also find that relaxation effects are reduced when the tip height is increased. These results are understandable since the forces are expected to decrease with distance and the interatomic potentials for these metal atoms are short ranged. The question of the tip height in STM measurements is not easily answered as this is not a well-defined quantity, amenable to direct measurements. Estimates of the distance between tip apex and the sample surface are in the range of 3.0 Å [5]. Since in the theoretical analysis we are using empirical potentials which are known to have sharper cutoff ranges and do not include the smoothness from van der Waals forces, the comparison between theory and experiment is remarkably good, even though the range of interaction of the potentials is smaller than what would have given a perfect fit to the data. Note that the tip heights are the values assumed at the beginning of a set of calculations and that the range used here is similar to the ones found in molecular dynamics simulations [8,9]. The results for the different heights show how critical the tip height is in evaluating the influence of the tip on the surface atoms. A reduction in height of roughly 1 Å leads to drastic changes of the forces on the adatom.

On repeating the calculations with a smaller tip (four atoms, arranged as a tetrahedron) which was also rotated by 60 degrees to account for contributions from any eclipsed atoms in the second layer, and with a tip consisting of a single layer with 100 atoms and an atom below at the apex, we find the general trends in the barriers and op-barriers to be very similar to those in Fig. 2, within a few percent. All tips examined thus far had a single atom at the apex. We now consider a modification in which the bottom atom of the ten-atom tip is removed such that the new apex has three atoms. The results in Fig. 5 attest to significantly more pronounced changes in the barriers than in Fig. 2. The more "blunt" apex produces a larger lowering of the total energy of the system, since there is now opportunity for three apex atoms to increase their coordination with the other Cu atoms. We also find the lowering of energy to

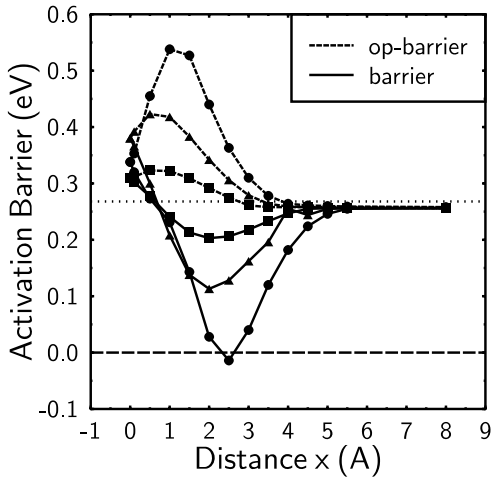

FIG. 4. Barrier (solid line) and op-barrier (fine dashed line) for a rigid ten-atom tip for tip heights of 2.5 Å (circles), 3.0 Å (triangles), and 3.5 Å (squares).

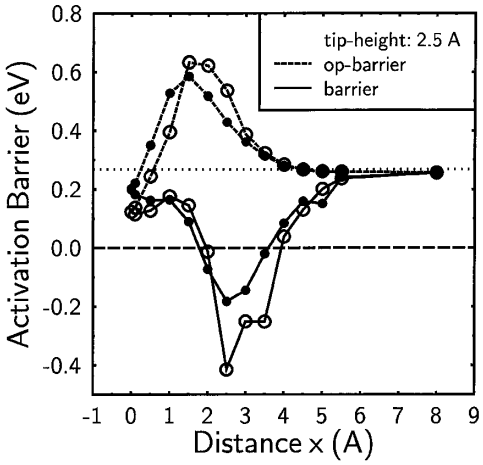

FIG. 5. Barrier (solid line) and op-barrier (fine dashed line) for adatom motion in the presence of a blunt nine-atom tip: filled circles for rigid tip, open circles for relaxed tip.

be more pronounced for the bridge than the fcc sites. It appears that though the adatom finds the fcc site, along the step edge, to be of lowest energy on the substrate in the absence of the tip, the situation changes in the presence of the blunt tip. The average attractive forces exerted by this blunt tip on the adatom are between 0.11 and 0.15 eV/Å. The time to move from one fcc site to the neighboring one is, in this case, reduced to about 0.5 ps for a lateral distance of 2.5 Å between the tip and the adatom.

On extending our study to the manipulation of a Cu adatom along the rows of Cu(110) using the ten-atom, rigid tip, at a height of 2.5 Å, as the lateral distance x is varied from 0.0 to 8.0 Å, we find features for the respective barriers and op-barriers very similar to those discussed in Fig. 2.

In summary, we have shown that the presence of a tip lowers the diffusion barriers for motion towards the tip, and increases those in the opposite direction, for adatom manipulation on stepped Cu(111) and on Cu(110). At certain values of the tip-adatom separation, the barrier for motion towards the tip disappears completely and the adatom experiences an attractive force towards the tip. These changes can be understood in terms of coordination effects between the tip and surface atoms which result in changes in the total energies for specific sites, as a function of the tip-adatom lateral separation. These results establish that tip induced motion of adatoms on metal surfaces arise mainly from changes in the potential energy surface brought about by interatomic potentials between all participating atoms. It should thus be possible to manipulate atoms with a scanning force microscope in a manner analogous to that already exhibited by STM. Furthermore, we show that although the qualitative changes in the barrier and the op-barrier for an adatom, in the presence of a tip, do not depend on the details of the tips, the quantitative results are sensitive to the shape and form of the tip apex, and the tip height. Most noticeably, with the present calculation we provide an approximately quantitative explanation of the experimental observations of the manipulation of Cu adatoms on a stepped Cu(111) surface [5]. Our conclusions for the same process on Cu(110) are also in qualitative agreement with those observed on Ag(110) [4]. The virtue of these calculations is that they are based on simple model potentials and the results are intuitive. The disadvantage is that it does not allow for inclusion of effects such as those arising from the presence of the electric fields, which in certain cases also lead to induced diffusion events as discussed by Stroscio and Eigler [3], and those from changes in the electronic structure, as, for example, tip induced changes in the density of states at the Fermi level which affect the tunneling current [15]. These latter effects may have consequences for the measured tip heights. Nevertheless, we are able to obtain a good understanding of the STM data which might be an indication that the main contribution to induced diffusion on metal systems comes from forces due to the interatomic potentials. It would indeed be intriguing to carry out more accurate first principles electronic structure calculations of these systems before we can completely rule out additional effects.

We thank G. Meyer, L. Bartels, P. Kürpick, A. Kara, and R. Koch for helpful discussions. U. K. acknowledges the Deutsche Forschungsgemeinschaft for financial support. This work was partially supported by DOE-EPSCoR/K-TECH under Grant No. DE-FG02-98ER45713. Computations were performed on the HP Exemplar system funded partially under NSF Grant No. CDA-9724289.

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