

Tip-induced atom extraction: effect of tip geometry and its composition

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2008 New J. Phys. 10 083044

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Tip-induced atom extraction: effect of tip geometry and its composition

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New Journal of Physics **10** (2008) 083044 (11pp)

Received 20 May 2008

Published 29 August 2008

Online at <http://www.njp.org/>

doi:10.1088/1367-2630/10/8/083044

Abstract. Atomic-scale simulations are performed to study the vertical manipulation of single Co adatoms on a Cu(001) surface using a scanning tunneling microscopy (STM) tip. Cu and Co tips with different geometries are investigated. Our results demonstrate that the details of the tip significantly affect the manipulation of the Co adatom. The differences in the manipulation of the Co adatom using different tips and the dependence on tip geometry are revealed. The possibilities and mechanism of extracting single adatoms on metal surfaces with a STM tip at zero bias voltage are explored.

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1. Introduction

Since the first successful manipulation of Xe atoms on a Ni(110) surface with a scanning tunneling microscopy (STM) tip by Eigler and Schweizer [1], atomic manipulation has opened up possibilities of designing man-made nanostructures on the atomic scale. The activation barrier of adatoms on metal surfaces or clusters can be reduced and atomic motion can

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be controlled in the presence of the tip [2]–[4]. Using the STM tip, one can construct low-dimensional nanostructures such as nanowires [5], quantum corrals [6] and electron resonators [7], etc. The STM manipulation can be performed by precisely controlling tip–sample interactions [8] and by applying an electric field between the tip and the sample [9].

Atomic manipulation usually includes two processes: lateral manipulation (LM) and vertical manipulation (VM). One can perform these two processes separately or combine them for different purposes. In a LM process, the minimum tip–atom distance required for a manipulation can be determined by measuring the threshold tunneling current to move an atom at a fixed bias [10]. The mechanism of atomic motion in a LM process has been demonstrated by Bartels *et al* [11]. Three modes, ‘pulling’, ‘sliding’ and ‘pushing’, are discerned [12, 13]. Pulling and sliding are usually applied in the manipulation of metal atoms [14], whereas organic molecules are mostly pushed on flat or stepped surfaces [15, 16] and sometimes pulled on semiconductor surfaces [17]. VM involves atomic transfer between the tip and the surface, which can be achieved by using an electric field or by direct tip–adatom contact [18]. VM towards the tip is difficult to control because the barrier vertically withdrawing an individual adsorbate off a surface is generally larger than that for LM [14]. Multiple excitation of adsorbate–substrate vibrational mode through inelastic electron effects in the presence of an electric field can be used to explain the mechanisms of VM [19].

It has been demonstrated that the VM of individual metal atoms from a metal surface or a molecule from a semiconductor surface can be achieved using a STM tip at zero bias voltage [20, 21]. In fact, experimental investigations show that it is not necessary to successfully extract atoms or molecules from the surface by applying an electric field between the tip and the sample [22]. Applied electric field might destroy the structure of adsorbed atoms or molecules [23].

It is found that atom manipulation is usually influenced by the details of the tip [15, 17], [24]–[27]. Ghosh *et al* [24] have revealed that a blunt tip is more effective than a sharp tip in the LM and VM of adatoms. Activation barrier of adsorbates on metal surfaces can be lowered much more effectively by using a blunt tip rather than a sharp one. The lowering of the barrier is also found to depend on the tip composition. A Cu tip is more effective in lowering the barrier of a Pt atom on a Pt surface as compared to a Pt tip [25]. Bouju *et al* [26] have found that the dragging mechanism for a Xe adsorbate on a Cu(110) surface depends on tip geometry. Yildirim *et al* [27] have shown that the extraction mode of a Ag adatom from a mound depends on tip geometry and composition. Very recently, the effect of tip structure and position on the manipulation has also been found for pushing and pulling a C₆₀ molecule on a Si(001) surface [15, 17].

In this paper, we present our results for the manipulation of single Co adatoms on a Cu(001) surface using Cu or Co tips. By performing atomic scale simulations, we reveal the influence of tip geometry and composition on the manipulation. The possibilities and mechanism of the VM of single magnetic adatoms on metal surfaces with a STM tip at zero bias voltage are explored.

2. Computational methods and models

In this work, atomic scale simulations are performed using the molecular statics (MS) method with *ab initio* based many body potentials [28]. This approach is based on fitting of many-body potentials to accurate *ab initio* data for surface and bulk properties. First, using the Korringa–Kohn–Rostoker (KKR) Green’s function method [29], we construct an *ab initio* data pool by calculating surface and bulk properties. Then many body potentials based on the second

moment approximation of the tight binding theory [30] are fitted to this *ab initio* data. Recent studies [31]–[37] have shown that this method describes atomic relaxations in nanostructures in very good agreement with fully *ab initio* calculations. It is demonstrated that this method can be successfully used to investigate the structure, electronic and magnetic properties of a single atom magnetic junction [38]. The technical details and parameters of interatomic potentials can be found in our previous works [28, 30, 37].

The Cu(001) substrate is mimicked by a seven-layer thick slab with 512 atoms per layer. Periodic boundary conditions are applied along the directions parallel to the surface and no such constraint is imposed along the direction normal to the surface. We model the tip by a Cu or Co pyramid of three layers arranged in fcc(001) stacking. The two bottom layers in the substrate and the topmost layer of the tip are fixed in each relaxation in order to keep their bulk properties. Fully relaxed calculations are performed at each step when approaching the tip towards the surface.

3. Results and discussions

Let us first consider a blunt Cu_{29} tip to be positioned above a Co adatom on a Cu(001) surface. There are four atoms at the apex for this tip (see figure 1). We approach the tip towards the surface vertically with a step of 0.1 Å. When the distance between the tip and the substrate reduces, both the tip-bottom atoms and the adatom exhibit strong vertical displacements. A big atomic relaxation also occurs in the substrate underneath the adatom (see figure 1). However, during the manipulation we notice that a sudden jump of the adatom to the tip takes place when the tip–substrate distance is about 8.0 Å. Here, the tip–substrate distance is defined as the distance from the topmost layer of the tip to the surface layer of the substrate.

We find that atomic relaxations have already happened before the sudden jump of the Co adatom towards the tip. Thus, the sudden jump does not mean the starting point of chemical interaction between the tip and the adatom. In order to understand this phenomenon, we retract the tip from a shorter (6.9 Å) to a longer (8.9 Å) tip–substrate distance. We find that the tip-bottom atoms and the adatom go through different paths when the tip–substrate distance is beyond 8.0 Å (see figure 1). Four Co–Cu bonds near the surface are broken, whereas another four Co–Cu bonds near the tip are formed. The adatom initially staying at the surface follows the tip and stays with the tip when retracting the tip from the surface. This means that adatom transfer happens from the substrate to the tip and this process is irreversible. This is significantly different from the case using a sharp Cu_{14} tip (there is one atom at the apex for a sharp Cu_{14} tip; see figure 3(a)), where the adatom cannot be extracted from the surface by the tip and the manipulation is reversible when approaching and retracting the tip [38].

If we use a sharp Co_{14} tip and do the same thing as with the Cu tips, we find that one can extract a Co adatom from the substrate using this tip. This can be attributed to the stronger interaction between Co atoms as compared with the Co–Cu interaction. Using a blunt Co_{29} tip, one can also extract a Co adatom. But some details are different. For the junction with the Co_{29} tip, it is found that only the Co adatom goes through different paths when the tip–substrate distance is beyond 8.4 Å (see figure 2). The tip-bottom atoms and the substrate atoms have almost the same paths when one approaches the tip to the surface and then retracts it. This means that the Co adatom attached to the Co tip does not induce so strong relaxations in the Co tip as that in the Cu tip. Our study finds that the tip length for the Co_{29} tip (3.25 Å) is shorter than that for the Cu_{29} tip (3.32 Å) at very large tip–substrate separation (without the tip–adatom

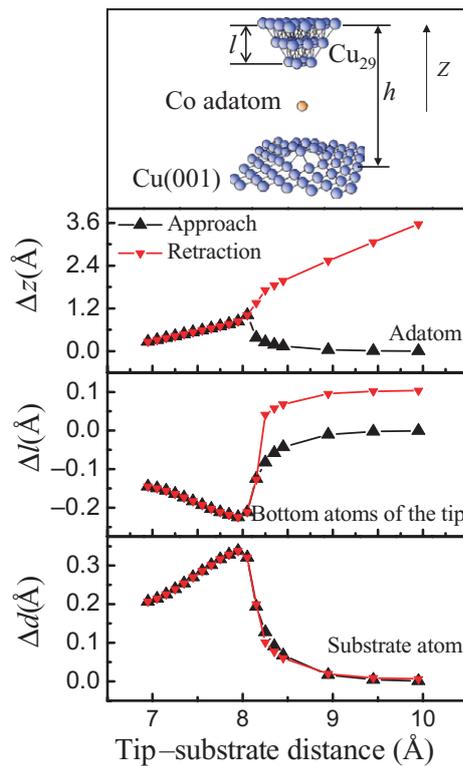


Figure 1. One-atom magnetic junction consisting of a Cu_{29} tip, Co adatom and Cu(001) substrate. The tip is above the adatom. With the decrease of the tip-substrate distance, both the tip-apex and the adatom exhibit strong vertical displacements. A large atomic relaxation also occurs in the substrate underneath the adatom. In this figure, $\Delta l = l_0 - l$ is the change of the tip length, where l and l_0 are the tip lengths with and without tip-adatom interaction; Δz and Δd are the displacements of the adatom and the substrate atom C along the z -axis, where z_0 is the relaxed adatom-substrate distance without tip-adatom interaction; h is the tip-substrate distance, which is defined as the distance from topmost layer of the tip to the Cu(001) surface.

interaction). The relaxation in the Co_{29} tip is larger than that in the Cu_{29} tip in the absence of tip-adatom interaction. Accordingly, the ability for further relaxation for the Co_{29} tip is smaller than that for Cu_{29} tip when the adatom is attached to the tip. It should be mentioned for blunt Co tips that the migration of the Co adatom along the apex layer and the aggregation of Co adatoms onto the tip might take place after the VM [39, 40], which should be paid much attention during the precise manipulation of atoms and molecules using a STM tip.

Why does atom transfer take place when using a blunt Cu_{29} tip? To answer this question, we have calculated the potential energy curves of a Co adatom positioned between the tip and the Cu(001) substrate for both sharp and blunt Cu tips at different tip-substrate distances (see figure 3). This can be done by calculating the minimum energy of the tip-adatom-surface junction for a given tip-substrate distance as a function of adatom altitude. It is revealed that, at a large tip-substrate distance, the Co adatom has two possible stable positions, one at the surface and the other at the tip. Each energy minimum is represented by a potential well and

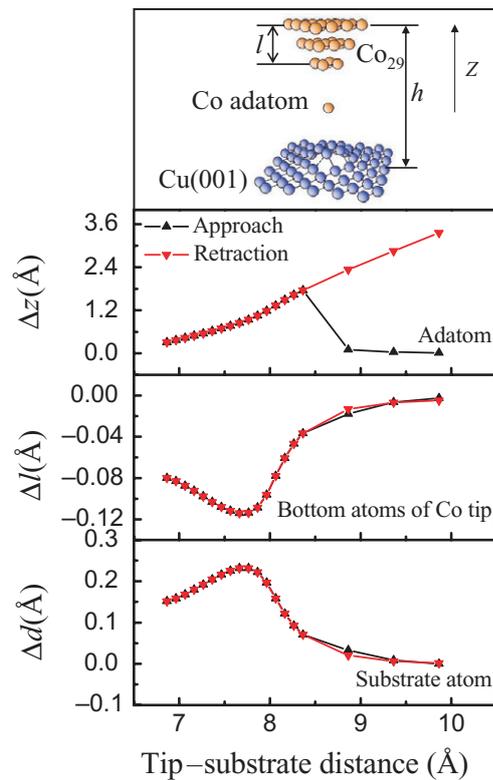


Figure 2. One-atom magnetic junction consisting of a Co_{29} tip, Co adatom and Cu(001) substrate. The tip is above the adatom. Large atomic relaxations take place in the junction when approaching the tip towards the surface. The meaning of the symbols in this figure is the same as in figure 1.

the two potential wells are separated by an energy barrier between them. Figure 3(b) shows that the potential well close to the Cu_{29} tip is lower than that near the Cu(001) surface for the tip–substrate distances, where the junction has two potential wells. For example, the energy difference between these two wells is about 15 meV at a tip–substrate distance of 8.9 Å. This means that the adatom tends to stay with the Cu tip rather than at the surface. If we use a sharp Cu_{14} tip (see figure 3(a)), the adatom cannot be picked up from the surface. Our studies find that the minimum potential well is at the surface side in this case. Thus, one is more likely to pick up the adatom from the surface with a Cu tip by changing the shape of the tip from a sharp Cu_{14} to a blunt Cu_{29} tip. This might also be a way to fabricate a sharp tip by extracting an adatom from a surface using a blunt tip if one wants to enhance the STM image resolution [14, 41]. It is also shown in figure 3 that the barrier for a Co adatom to go from the surface site to the tip site or from the tip site to the surface site can be reduced and the double potential well becomes a single potential well by decreasing the tip–substrate distance.

We have also calculated the energy difference between two potential wells as a function of the tip–substrate distance for both junctions with the Cu_{29} and Co_{29} tip, which is shown in figure 4. It is found that the energy difference changes sharply when the tip–substrate distance is beyond a certain tip–substrate distance. The energy difference increases with increasing tip–substrate distance for the junction with the Co_{29} tip, whereas it decreases with increasing

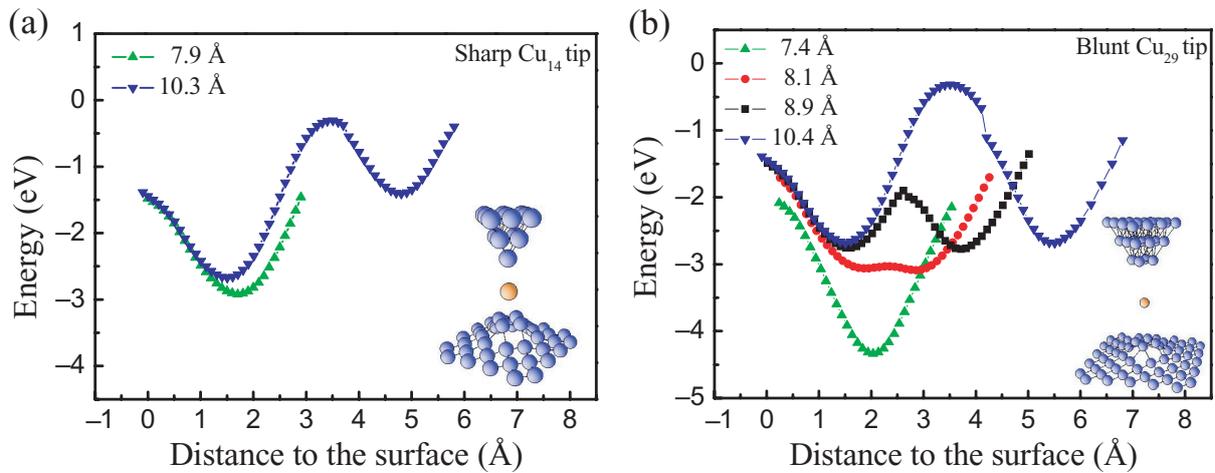


Figure 3. Calculated potential energy curve of a Co adatom positioned between a Cu tip and a Cu(001) substrate as a function of the Co adatom altitude above the surface for different tip–substrate distances: (a) for a sharp Cu_{14} tip; (b) for a blunt Cu_{29} tip. Here, the zero in energy is given by the energy of the three components of the junction (tip, Co adatom and substrate) at very large separation.

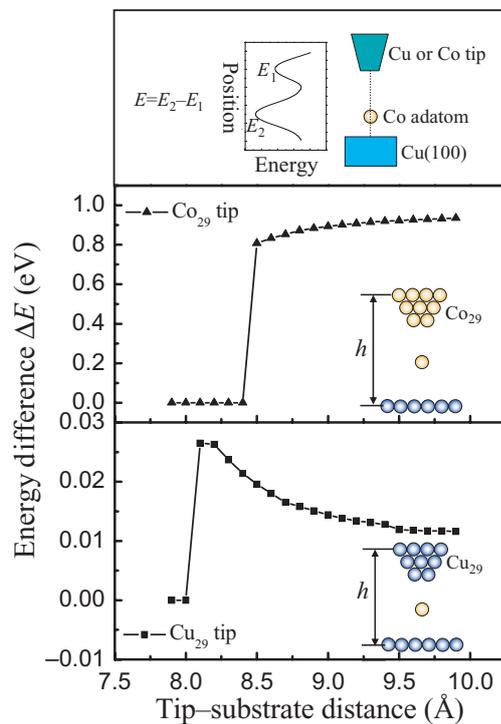


Figure 4. Energy difference between two energy minima of the Co adatom as a function of the tip–substrate distance for the Cu_{29} and Co_{29} tips.

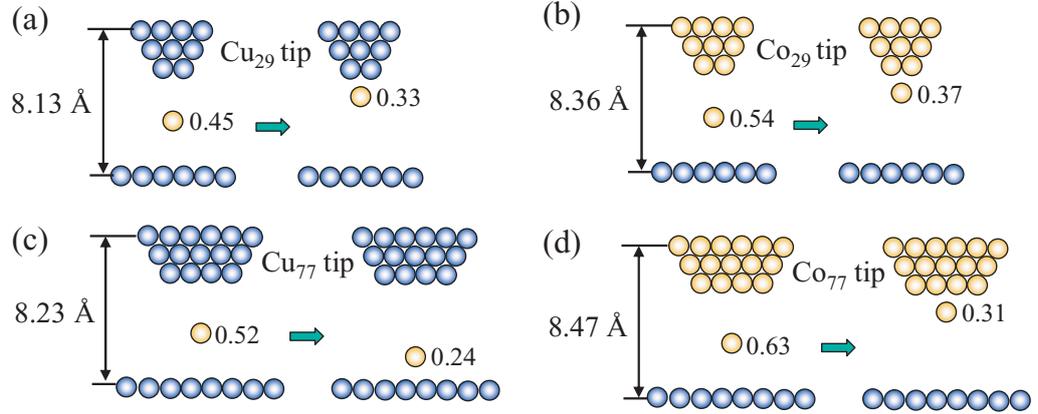


Figure 5. Atomic level stress (units: eV \AA^{-3}) on the Co adatom before and after breaking the Co–Cu bond for different tips: (a) a Cu_{29} tip; (b) a Co_{29} tip; (c) a Cu_{77} tip and (d) a Co_{77} tip.

tip–substrate distance for the junction with the Cu_{29} tip. It can also be noted that the sign of the energy difference is independent of the tip–substrate distance for these two junctions when they have two potential wells. If we increase the size of the tip-apex layer, we find that the situation becomes more complicated. For example, one can still extract the adatom from the surface using a blunt Co_{77} tip, whereas one cannot do it anymore using a blunt Cu_{77} tip.

Where does the difference come from? Firstly, let us consider the atomic stress acting on the Co adatom for the junctions containing Cu_{29} , Cu_{77} , Co_{29} and Co_{77} tips. The atomic level stress components [42] can be calculated as follows:

$$\sigma_{\alpha\beta}(i) = -\frac{1}{\Omega_0} \left[\frac{p_i^\alpha p_i^\beta}{m_i} + \frac{1}{4} \sum_j (r_{ij}^\beta f_{ij}^\alpha + r_{ij}^\alpha f_{ij}^\beta) \right], \quad (1)$$

where $(\alpha\beta) \equiv (x, y, z)$, m_i and \vec{p}_i are the mass and momentum of atom i , \vec{r}_{ij} means the distance between atom i and atom j , and \vec{f}_{ij} is the force acting on atom i due to j ; Ω_0 defines the average atomic volume. Figure 5 shows that breaking a Cu–Co or Co–Co bond is a process of stress relief for all these blunt tips. One can also find that the stress relief is much larger for the tips with a large tip-apex layer. This is easy to understand because the atoms in the large tip-apex layer are constrained by many more nearest-neighbor atoms and thus find it difficult to relax compared to those in the small tip-apex layer.

Secondly, by calculating the potential energy curves for the junction with the tip containing 16 or 36 atoms in the tip-apex layer, one can see that the minimum potential well for the junction containing either a Co_{29} or Co_{77} tip is always at the surface side for the tip–substrate distances where the system has two potential wells. But for the junction containing a blunt Cu tip, when the tip size increases from Cu_{29} to Cu_{77} , the minimum potential well shifts from the tip side to the surface side. As an example, figure 6 shows the calculated energy difference at a tip–substrate distance of 8.9 Å. For the junctions containing blunt Co tips, the energy difference is always positive, which means that the Co adatom tends to stay with the Co tip. However, for the junctions containing blunt Cu tips, when the tip size increases from a blunt Cu_{29} to Cu_{77} tip, the energy difference changes its sign. The adatom still stays at the surface when using the Cu_{77} tip. This means that one can always extract the Co adatom from the Cu(001) surface using Co tips. But for Cu tips, whether one can extract the Co adatom or not depends on the tip geometry.

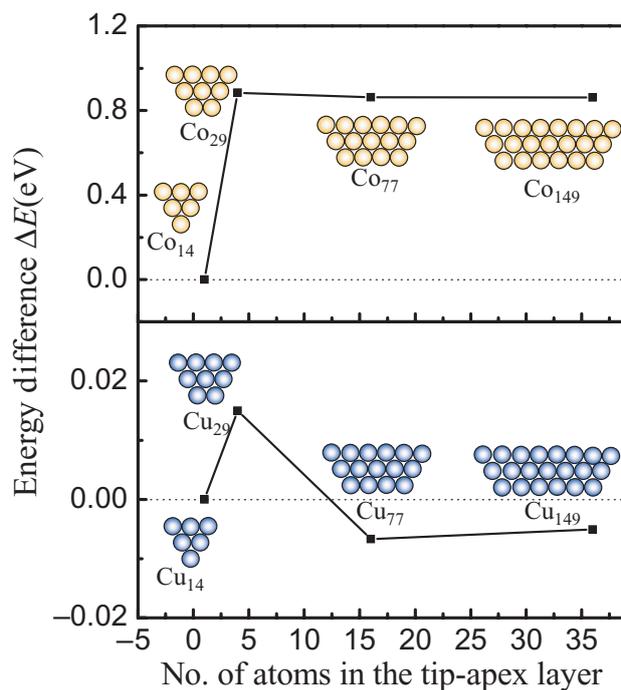


Figure 6. Energy difference between two energy minima of the Co adatom as a function of the number of atoms in the tip-apex layer for the junctions containing different tips at a tip-substrate distance of 8.9 Å. The upper panel is for Co tips and the lower one is for Cu tips. The negative value means that the adatom is more stable staying with the tip than it is staying with the surface in the junction, and vice versa.

Why can this blunt Cu_{29} tip withdraw the adatom and the others not? If we compare a sharp Cu_{14} tip with a blunt Cu_{29} tip (see figures 7(a) and (b)). It is easily understood that one Co-Cu bond connecting the tip with the adatom cannot compete with four Co-Cu bonds connecting the substrate with the adatom (see figure 7(a)). This is not the case if we compare a blunt Cu_{29} tip with other blunt Cu tips (see figures 7(b) and (c)). Both sides (one at the tip side and the other at the surface side) have four Co-Cu bonds for these blunt Cu tips (see figure 7(b)). We can explain this qualitatively from the viewpoint of coordination number (CN) [43].

In a Cu(001) surface, each atom in the first surface layer has eight nearest-neighbor coordination atoms. But for these atoms in the tip-apex layer in a Cu blunt tip (see figures 7(b) and (c)), the number of the nearest-neighbor coordination atoms depends on the number of atoms in the tip-apex layer. For these four atoms in the tip-apex layer of the Cu_{29} tip, their CN is six. Whether the Co adatom is adhered to the surface or to the tip, it would increase the CN of the atoms in the surface layer or these atoms in the tip-apex layer. By introducing the Co adatom, the CN for these four Cu atoms in the first surface layer or for these four Cu atoms in the tip-apex layer of the Cu_{29} tip (see figure 7(b)) increases by one. We have plotted the cohesive function of bulk Cu atoms as a function of the number of Cu neighbors (see figure 7(d)). From this figure, one can see that the total energy is lowered more effectively by increasing the CN of the atom with lower CN. Due to the fact that the CN for these four atoms in the tip-apex layer (6) is smaller than that for these four atoms in the first surface layer (8), the Co adatom tends to stay with the Cu_{29} tip and lower the total energy more effectively.

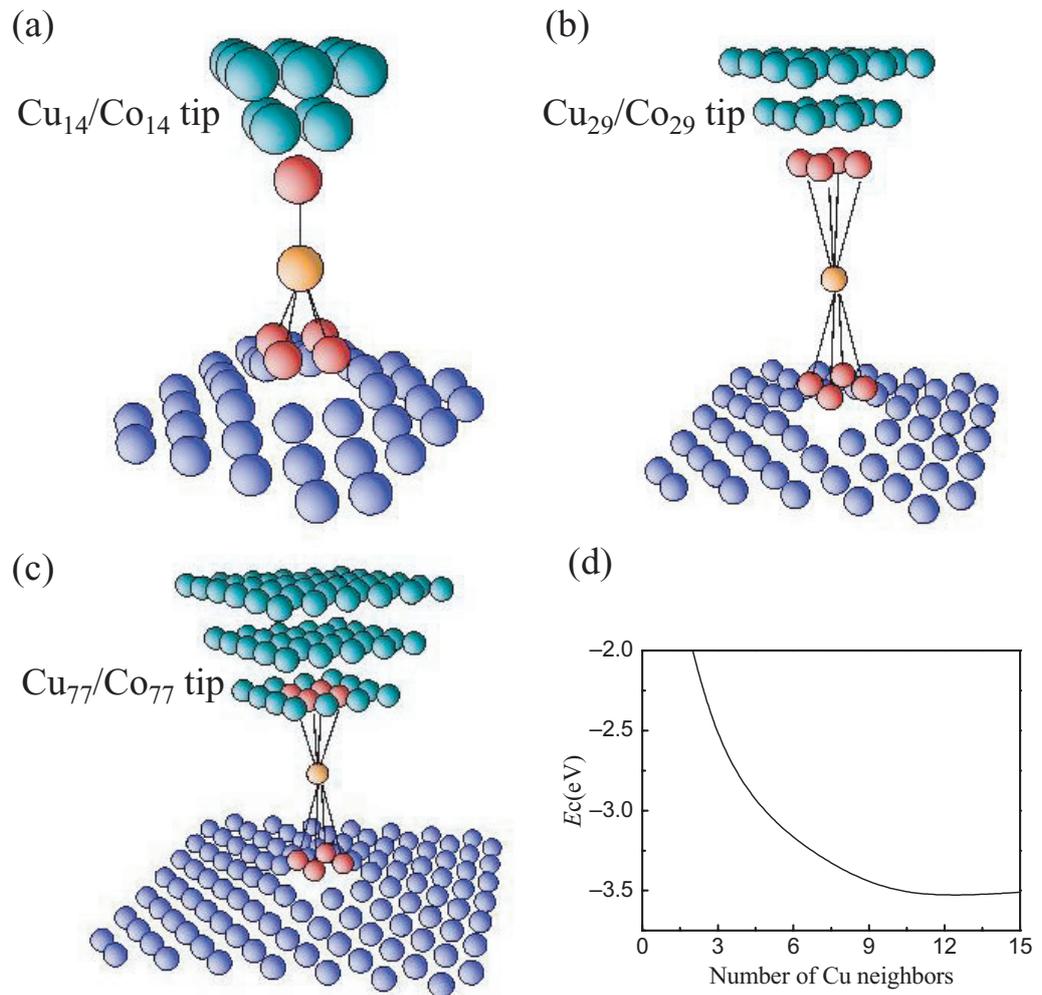


Figure 7. Co–Cu bonds are shown for the junctions with different tips: (a) a sharp Cu_{14} or Co_{14} tip; (b) a blunt Cu_{29} or Co_{29} tip and (c) a blunt Cu_{77} or Co_{77} tip. The cohesive energy of Cu as a function of its nearest-neighbors is also shown in (d).

While for the junctions containing other blunt Cu tips (for example, see figure 7(c), 16 atoms in the tip-apex layer), each of these four atoms at the tip side or at the surface side has eight nearest-neighbor atoms. However, due to the significant relaxations coming from the different layer of the tip, the CN of these four atoms in the apex layer of the tip will increase. As a result, the CN is larger than that for the atoms in the surface. When retracting the tip from the surface, the Co adatom will still stay at the surface in order to lower the energy more effectively.

The many-body contribution to the total energy might play an important role during the VM of the adatom, which has been found to participate in stabilizing an adsorbate on a surface in the presence of the apex [39]. The triple-dipole dispersive interaction between two atoms in the apex and the adsorbate tends to reduce the difference in energy between the more stable and the less stable position, especially for the adsorption of molecules on the tip [39]. Thus, it is deduced that the many-body contribution is different for different tip structures.

It should be noted that the main results in this work are qualitatively not affected if we increase the tip height but keep its shape (still the same atoms in the tip-apex layer) and stacking

of the tip for the sharp tip and the blunt tip with four atoms in the tip-apex layer. But for other blunt tips, the tip will collapse when one extracts the adatom from the surface. This is beyond the scope of this work.

4. Conclusions

In summary, we have studied the manipulation of single Co adatoms on a Cu(001) surface using Co or Cu tips. It is revealed that whether the Co adatom can be extracted or not depends on tip geometry and composition. The possibilities of the VM of single magnetic adatoms on metal surfaces with a STM tip at zero bias voltage are demonstrated. A double potential well model and the concept of CN are used to explain the shift of the minimum potential well from the tip side to the surface side or vice versa.

We believe that the findings in this work are of importance to succeed in carrying atoms or molecules one by one with a STM tip on surfaces. One can also obtain the utmost geometrical resolution with STM by this VM.

Acknowledgment

This project was supported by the Deutsche Forschungsgemeinschaft (DFG).

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