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Moving a silver atom on a Si(001) surface with a tip?

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Abstract

To improve the understanding of atom manipulation, moving a single silver atom on a Si(001) surface by the tip apex of an STM is investigated theoretically. Two adsorption sites on Si(001) were tested: (i) the cave site between two dimers belonging to two adjacent dimer rows, and (ii) the bond site on the dangling bond of one surface silicon atom. We have found that a sliding or a pushing process by the tip is not feasible when the silver adatom is located in the cave site. However, it is possible to push the Ag atom in the case of bond-site adsorption, with a tip height ranging between 2.53 and 3 Å above the surface. © 1997 Elsevier Science B.V.

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The significant improvements in atomic and molecular assembly techniques during the last decade have opened up the possibility of fabricating atomic-scale devices. Several techniques have been proposed for assembling individual atoms on a surface [1–10], but the manipulation of atoms or molecules by the tip apex of an STM remains the most promising because each adsorbate is positioned one after the other at the required site on the surface. Hence, successful manipulations of Xe on Ni(110) [1,3,6] or copper porphyrin on Cu(100) [9] have been performed. Different procedures have been used on metal surfaces. Eigler et al. [1] adjusted the STM tip position above the Xe atom such that a lateral movement of the tip

apex slid the adatom on the surface (sliding process). The tip can also be located above the Xe atom and a voltage pulse applied on the tip to transfer the adatom [3]. The tip is then moved and a negative pulse is applied to deposit Xe in another position (vertical process). The tip can also approach close the adsorbate (a copper porphyrin molecule on Cu(100)) and then push it (pushing process) [9]. On a semiconductor surface, molecules like C₆₀ have been manipulated using the pushing process [10,11], but no studies has been devoted to the STM tip manipulation of adatoms on such surfaces. This involves further difficulties in comparison with previous manipulations. Firstly, the adsorbate is chemisorbed, unlike Xe on Ni(110) or porphyrin on Cu(100). Consequently the energy barriers for both diffusion and extraction are strong. For example, the vertical

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process cannot be used in our case since the electric field required to pull out the silver atom would be too strong and too delocalized. Only sliding or pushing processes seem feasible. Secondly, it is easier to push large objects like porphyrin with a tip than a single atom, because the internal degrees of freedom of the manipulated object may adapt to the constraint if the pushing process is not well optimized. In this Letter we present simulations of the manipulation process of a single Ag atom chemisorbed on Si(001)-(2 × 1).

In view of the very slow displacement of the tip apex usually achieved experimentally in manipulations as compared to the relaxation time of the adsorbate on a surface, a molecular mechanics approach was preferred to a molecular dynamics approach. This means that the tip apex is moved step by step towards Ag and the energy of the tip apex–silver–Si(100) slab is optimized to find the new Ag and slab atom equilibrium positions. The tip apex is also supposed to move at a constant height, which has the disadvantage of enhancing the mechanical constraints in the junction as compared to a constant-current mode. In principle, a constant-current manipulation process can also be simulated with a rigid Si(100) surface, but the computation time required for a further relaxed surface is out of the range of the computation

times presently available. Thus, the pushing process is the only viable possibility in this case.

The silicon (001) surface has been extensively studied because several controversies exist as to its reconstruction. Recent *ab initio* calculations and low-temperature STM experiments concluded that the ground state is an asymmetric dimerization in a staggered $c(4 \times 2)$ pattern [12–21]. At room temperature, it seems that an asymmetric (2×1) structure is favored. The symmetric (2×1) structure observed experimentally may be asymmetric dimers which oscillate so rapidly that they appear to be symmetric on the timescale of STM experiments [14,17,21]. When a silver atom is deposited on the Si surface, experimental studies have concluded that adsorption occurs in the cave site [22–27]. However, calculations have found that the cave and bond sites (Fig. 1) are energetically very close, and that the energy barrier between them is only 0.19 eV [28], as seen in Fig. 2. At room temperature, the bright ovoidal print observed in STM experiments is not necessarily due to the rapid flipping of the Ag atom between the two adjacent bond sites [28]. Due to the lack of experimental or theoretical confirmation, in this Letter we investigate the motion process for both Ag adsorption sites.

The calculations were performed within the

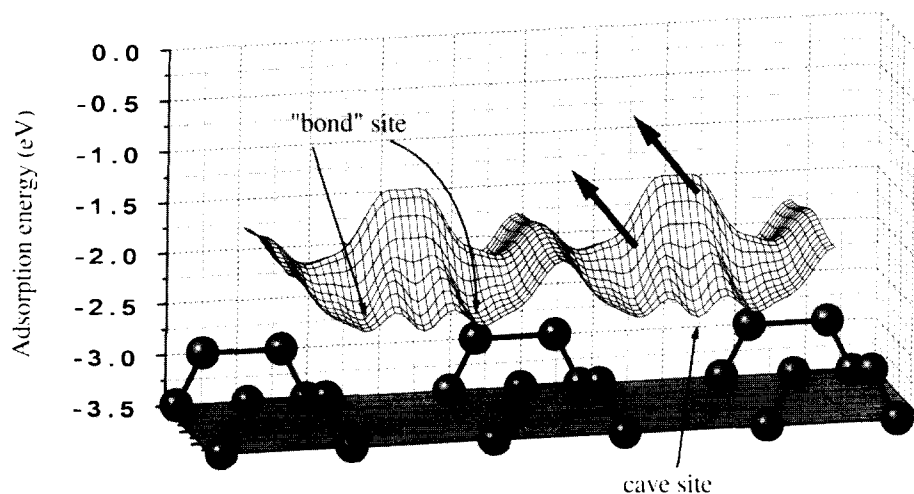


Fig. 1. 3D map of the adsorption energy of one atom Ag deposited on Si(001)-(2 × 1). The black spheres represent the Si surface and subsurface atoms. Two thick arrows have been added to show the tip movement directions when Ag is adsorbed in the bond site (left arrow) and the cave site (right arrow).

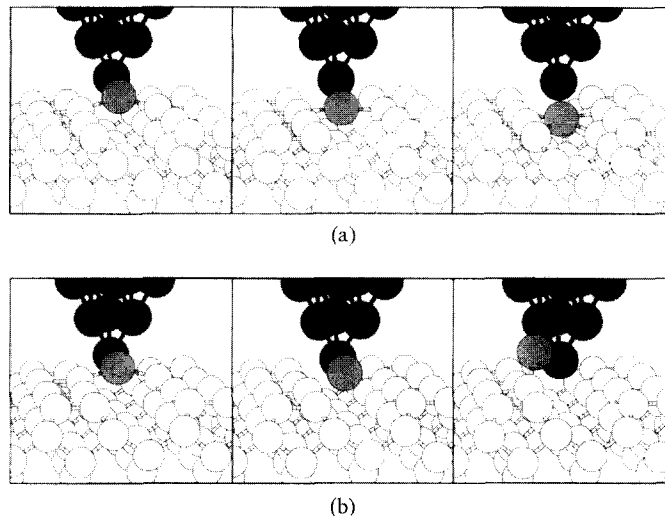


Fig. 2. Snapshots of the tip-Ag-Si(001) system with Ag adsorbed in the cave site. Two different tip heights (1.5 Å (a) and 1 Å (b)), are represented.

atom superposition and delocalization (ASED) method [29], an enhanced extended Hückel molecular orbitals (EHMO) model. Such a semi-empirical method gives a symmetric (2×1) structure which is energetically better than the asymmetric (2×1) structure for the Si(001) surface [28]. However, the energy differences are very small and of the order of the uncertainty, so we expect correct tendencies for motion processes involving larger energies. Moreover, the height difference between asymmetric dimer atoms is small, and we expect that such differences will not drastically change the tendencies we observed. We used the same silicon and silver EHMO parameters used by Okon et al. [28].

The silicon surface is represented by a four-layer slab, each layer containing 4×4 Si atoms (eight dimers). Hydrogen atoms are added to passivate the bottom and sides of the slab, leaving a clean (001) surface on top. We checked that this slab size is enough to avoid unwanted side effects. At first, the Si atoms are relaxed independent of the silver adsorbate, then frozen in positions representing a symmetric (2×1) structure. In order to avoid time-consuming calculations, only the silver adatom and all the silicon atoms located at a distance from Ag lower than a fixed distance R are allowed to relax. We checked the validity of

this assumption by performing calculations for two different values of R , i.e. 3 and 5.4 Å. The STM tip is modeled by a gold (111) tip of ten atoms. The first tip layer contains six atoms, the second three atoms and the apex a single gold atom. The EHMO parameters for gold were those calculated by Komiya et al. [30]. The tip atoms are not allowed to relax because their possible deformations would not introduce major changes in the manipulation processes. Moreover, it is important that neither the tip nor the silicon surface are irreversibly damaged, since the motion process must be repetitive. After relaxation, the tip is displaced by 0.2 Å in the direction parallel to the Si dimer rows, and the same process is repeated step by step to reproduce a manipulation process. This value seems to be a good compromise between a reasonable computation time and the need for an adiabatic displacement of the tip. We have performed several simulations for both adsorption sites, different tip height being used in order to obtain the different possibilities (the tip height is defined as the distance between the apex atom of the tip and the first layer of an ideal unrelaxed Si(001) surface).

Fig. 3 shows snapshots of the atomic positions obtained from calculations performed with the silver adatom located in the cave site. Fig. 2a

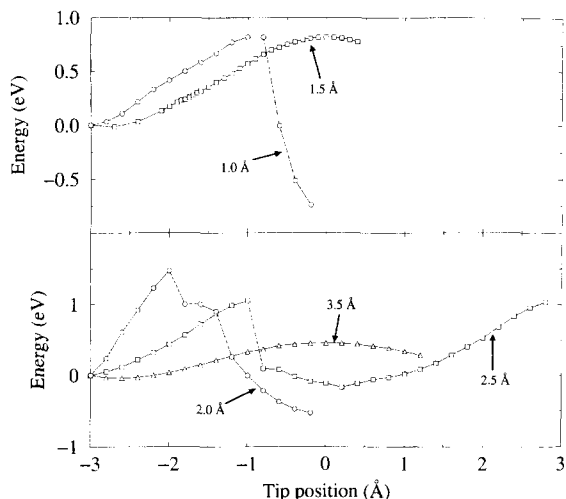


Fig. 3. Energy curves of the total energy versus the tip position for a cave adsorption site (upper panel) and a bond adsorption site (lower panel). The zero tip position corresponds to the adatom's initial location. The energy of the system relaxed with the tip located in its initial position (i.e. 3 Å from the adatom) is the reference energy. We represent the beginning of the next pushing process for a tip height of 2.5 Å in order to show that the process can be repeated.

shows the adatom behavior for a starting tip height of 1.5 Å. We can see that the Ag atom is progressively repelled by the tip apex and “sinks” into the valley between the two adjacent dimer rows. The silicon surface is maximally deformed once the tip is located just above the Ag adatom. The energy curve plotted in Fig. 4 shows the energy barrier of 0.8 eV crossed by the tip to pass above the Ag adatom, the maximum energy curve corresponding to the configuration with the tip just on top of the silver atom. Although one can observe subsequent deformation of the silicon surface in the proximity of the silver atom, there is no diffusion into the slab. Kimura et al. [27] observed silver diffusion into silicon with a deposition temperature of 760 K. However, it disappears with a reduction in temperature to 520 K. The addition of thermionic vibrations associated with the tip constraints may result in such unwanted diffusion. As the tip progresses, the adatom returns back to its initial position, the attractive energy between the tip and Ag being too weak to balance the diffusion barrier in this direction. Decreasing the tip height to 1 Å leads to major changes in the

adatom trajectory (Fig. 2b). The Ag atom is first shifted between the two neighboring dimer rows because the small energy barriers between cave and bond sites (Fig. 2) prevent it moving sideways. However, as the Ag atom is repulsed by the tip and climbs the large energy bump (1.16 eV) between two cave sites (Fig. 2), these energy barriers vanish sideways and the silver atom slips and escapes towards the next bond site (Fig. 3). There is therefore a controlled movement of the silver adatom in the direction of the dimer rows, but the manipulation process cannot continue further since the tip and the adatom are now misaligned. If the tip progresses, the constraints will not be strong enough to push the adatom again. Therefore, it appears that the cave site is not a convenient site for controlled tip-apex manipulation by a pushing process. Moreover, the height of the Ag atom in the cave site is very low in the surface. Ag is “embedded” between two dimer rows, and requires a very sharp tip apex to manipulate it successfully in this way.

Pushing Ag adsorbed in a bond site appears to be easier, since the Ag height is greater in this site on the Si(001) surface. An examination of the adsorption energy map (Fig. 2) shows that the energy barrier between two consecutive bond sites can be estimated to be 0.44 eV, and is therefore lower than between two cave sites. Fig. 4 shows snapshots of the atomic positions when the silver atom is located in the bond site. Calculations with tip height of 3.5 Å show that the adatom moves sideways as the tip approaches (Fig. 4a). Once the tip has passed over, Ag returns back to the starting bond site. When the tip is lowered to 2.5 Å (Fig. 4b), the Ag stays in the required pushing direction and crosses the energy barrier to reach the next bond site. The successful pushing of the adatom is clearly represented in Fig. 4, the adatom jump toward the next bond site corresponding to the strong decrease in the total energy. Note that the increase in energy due to the clearing of the barrier between two bond sites is larger (~ 1 eV) than the energy barrier estimated from Fig. 2 because of the additional constraints imposed by the tip. When Ag is pushed over several bond sites, the Ag potential-energy curve (Fig. 4) is periodic, demonstrating that the process can be

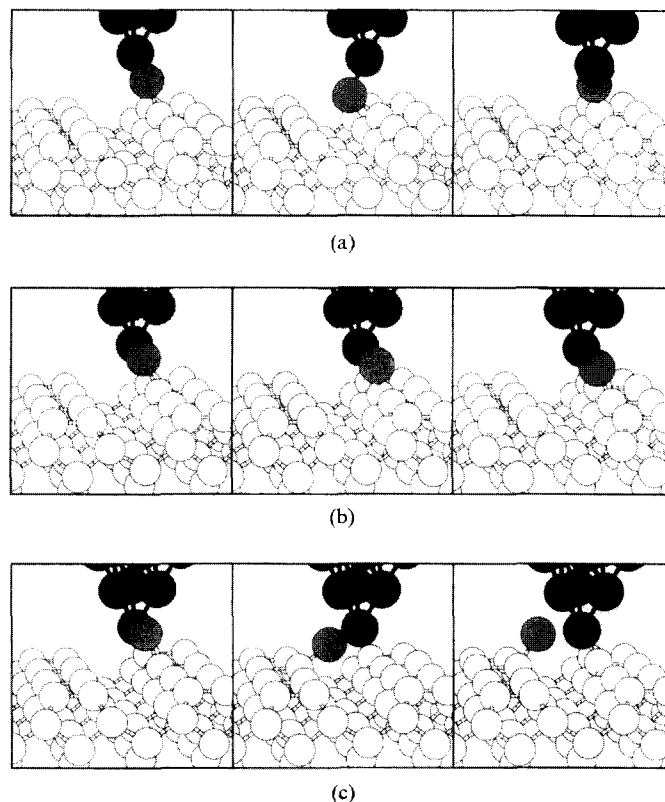


Fig. 4. Snapshots of the tip–Ag–Si(001) system with Ag adsorbed in the bond site. Three different tip heights (3.5 Å (a), 2.5 Å (b) and 2 Å (c)) are represented. Note the successful motion of the silver atom in the center strip of the figure.

driven again. The lower tip-height limit for Ag to be pushed along the bond sites is 2.5 Å. Fig. 4c shows that with a lower tip height (e.g. 2 Å), Ag escapes sideways towards the opposite bond site. Several other calculations performed with lower tip heights led to similar behavior.

In conclusion, we have calculated the atomic manipulation process of a silver atom on the Si(001)-(2 × 1) surface with a gold STM tip. Two starting adsorption sites were considered for Ag: the cave and bond sites. Varying the tip height, we showed that a pushing process at constant height will not work starting with a cave site. When the tip height is greater than 1.5 Å, the adatom moves down to escape tip repulsion, whereas a lower height results in a lateral shift toward the bond site, aborting the pushing process. However, we have found promising results when the silver atom is adsorbed in the bond site. Indeed, for a tip

height ranging from 3 to 2.5 Å, the displacement of Ag in the direction of the dimer rows is controllable. For greater tip heights the silver adatom dodges the tip, whereas for lower heights it jumps laterally to the other symmetric bond site, aborting the manipulation.

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