Vertical Manipulation of Individual Atoms by a Direct STM Tip-Surface Contact on Ge(111)

G. Dujardin,[1] A. Mayne,[1] O. Robert,[1] F. Rose,[1] C. Joachim,[2] and H. Tang[2]
[1]*Laboratoire de Photophysique Moléculaire, bâtiment 210, Université Paris-Sud, 91405 Orsay Cedex, France*
[2]*Centre d'Elaboration de Matériaux et d'Etudes Structurales, UPR 8011, B.P. 4347, 31055 Toulouse Cedex 4, France*
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A new type of vertical manipulation with the scanning tunneling microscope (STM), involving only direct STM tip-surface contact at zero bias voltage, is used to extract, in a very controlled manner, individual germanium atoms from a Ge(111) surface. The duration of the extraction mechanism is found to be surprisingly long, of the order of 10 ms. To explain these effects, a complete calculation of the STM tip approach and retraction sequence is performed by optimizing the total junction geometry at each step. [S0031-9007(98)05682-8]

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The ability to manipulate individual atoms and molecules with the scanning tunneling microscope (STM) has opened fascinating new areas of research [1–3]. Manipulations can be classified into two types: lateral and vertical. Lateral movements, involving the pulling, sliding, or pushing of an individual adsorbate, have been the subject of experimental [4–7] and theoretical [8,9] studies. However, vertical manipulations towards the tip apex are more difficult to control, since the energy barriers to be surmounted when pulling an individual adsorbate off a surface are generally higher than for lateral manipulations. This is especially true for strongly bound atoms from a metal or a semiconductor surface. Several basic mechanisms have been considered to explain the observed vertical manipulations. For weakly bound adsorbates (Xe/Ni(100) [2], Xe/Cu(211) [10]), vertical manipulation has been ascribed to multiple excitation of the adsorbate-substrate vibrational mode through inelastic electron effects combined with electric field effects [11] or to the transfer-on-contact process [12]. Vertical manipulation of more strongly bound adsorbates (the Si-H bond in H/Si(100) [13]) has been shown to involve vibrational or electronic excitation by inelastic interactions of electrons issued from the STM tip. Finally, extraction of individual atoms has also been achieved from semiconductor substrates themselves (Si [14–16], MoS_2 [17]) by using the electric field in the tip-surface STM junction [18].

Here, we report a new type of vertical manipulation with the STM involving only direct STM tip-surface contact at zero bias voltage. This is the first evidence that the STM tip can pick up *individual* atoms in a very controlled manner without any tunneling electron or electric field effect. We take advantage of the fact that the potential barrier to transfer a chemically bound atom from a surface to a tip may be negligible when the tip apex to surface distance is very reduced. We report the measurement of the probability for extracting a single germanium atom from a Ge(111) surface as a function of the vertical STM tip displacement, sample voltage (V_S), and duration of the tip-sample interaction. At small tip-sample distances (compared to imaging conditions), individual germanium atoms are very reproducibly extracted in a mode ($V_S = 0$) involving only direct STM tip-surface contact, without disturbing the surroundings. Furthermore, the characteristic time of the extraction process is found, quiet surprisingly, to be very long, of the order of 10 ms. The relative simplicity of this type of manipulation enabled us to perform complete calculations of the STM tip-surface interaction, leading to a detailed description of the single atom extraction mechanism.

STM experiments are performed in a UHV chamber with a base pressure $<10^{-10}$ mbar. In the UHV preparation chamber, equipped with low-energy electron diffraction, regular Ge(111)-$c(2 \times 8)$ surfaces, as shown in Fig. 1(a), are prepared by ion sputtering and annealing [19]. The procedure to extract a single germanium atom, as shown in Fig. 1, is the following. The tip of the STM (an electrochemically etched polycrystalline tungsten wire) is positioned over the desired adatom, as indicated by the numbers in Fig. 1. The feedback loop is opened, V_S is set to zero, and the tip is approached towards the adatom by Δz stepwise over 20 ms. This reduces the tip-sample distance z by Δz. V_S is set to a chosen value and kept constant for a time Δt. V_S is reset to zero and the tip is withdrawn from the surface over 20 ms as before. Then, a new STM topograph of the same area is recorded in constant current mode to examine the result of the manipulation.

It is remarkable that, in more than 98% cases, the manipulation with the tip either results in the extraction of a single adatom or has no visible effect. Only on very rare occasions ($<2\%$) does the manipulation result in the pickup of two or more adatoms or in the deposition of some atoms on the surface. We are sure that the created modification, as shown in Fig. 1, is due to the extraction of a single Ge adatom. At room temperature, the created vacancy is not stable and slowly diffuses on the surface [20]. The resulting surface rearrangements are compatible only with that of a single atom vacancy. Furthermore,

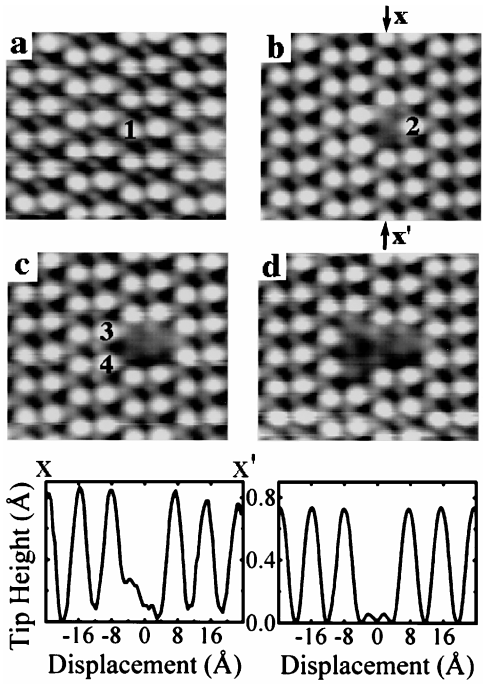

FIG. 1. A sequence of STM images [(a) to (d)] during which atoms were extracted (area 53 × 47 Å, sample bias +1 V, tunnel current 1 nA). The selected atoms are indicated by Nos. 1–4. A line profile xx' through (b) is shown at the lower left and a corresponding calculated line profile, for $I = 1$ nA at the bottom of the conduction band, at the lower right.

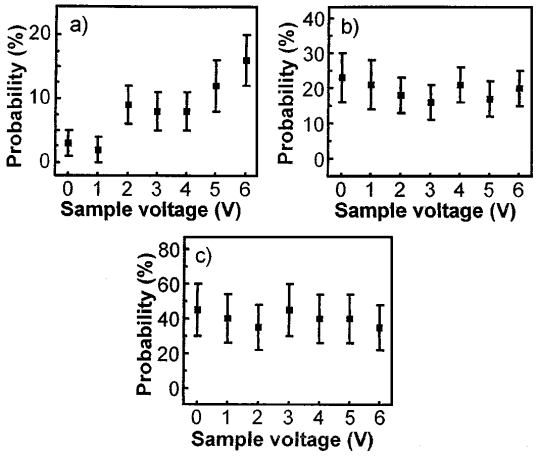

FIG. 2. A series of three graphs showing the probability of extracting a Ge adatom as a function of applied sample voltage. The tip was approached towards the surface by (a) 4 Å, (b) 6 Å, and (c) 8 Å. The interaction duration has a fixed value $\Delta t = 10$ ms. Error bars indicate the statistical uncertainties. The total number of manipulations were 470, 1400, and 112, respectively.

using the elastic scattering quantum chemistry (ESQC) technique [21], the calculated constant current image for a single adatom vacancy on Ge(111) gives a corrugation in agreement with the experimental one (see Fig. 1). These calculations also provide a good estimation of the tip apex to surface distance z when scanning the surface in a constant current mode. This is crucial to simulate a manipulation mode in STM [7–9]. For calculations performed at the bottom of the conduction band with a 1 nA current intensity under 0.5 V bias voltage, z sits between 7 and 8 Å. At 1 V, z is expected to be slightly higher by 1 Å.

In order to measure the picking up probability P of a single Ge adatom as a function of the various parameters (Δz, V_S, and Δt), we performed many series of hundreds of manipulations. Our new manipulation procedure is reproducible even though P depends to some extent on the tip used in the experiment. The most reliable tips obtained after a number of manipulations are believed to be terminated by Ge atoms. For a given tip, P can be estimated as a function of the sample voltage V_S as reported in Fig. 2 for various tip approaches Δz (4, 6, and 8 Å) and a fixed value $\Delta t = 10$ ms of the interaction duration. For a small tip approach of 4 Å, P increases as a function of the sample voltage [Fig. 2(a)]. Also, P is almost zero at low sample voltage ($V_S < 1$ V) (as well as for negative sample voltage—not shown in Fig. 2). By contrast, for larger tip approaches (6 and 8 Å), P is constant as a function of V_S [Figs. 2(b) and 2(c)] and has always the same value even at zero (or negative sample bias voltages—not shown in Fig. 2).

These results demonstrate the occurrence of two distinct manipulation modes. When the tip is far enough from the surface (z reduction smaller than 4 Å), the electric field and/or the tunnel current play clearly a crucial role in the manipulation since P becomes important only at a high sample voltage. This mode of manipulation is similar to the one previously used for Si [14–16] and MoS_2 [17]. More surprisingly, when the tip is closer to the germanium surface (approaches 6 and 8 Å), P is *constant;* the electric field and the tunnel current seem to have no noticeable effect, whatever the values of the electric field and the current intensity. In particular, *at* $V_S = 0$, P has the same value as for any value of V_S between −6 and +6 V although the tunnel current is zero and the electric field is very weak. Indeed, the work functions of the surface and the tip (which, we believe, is covered with germanium atoms) are expected to be almost identical.

To experiment more on this new direct contact manipulation mode, we performed several series of experiments at $V_S = 0$, measuring P as a function of the tip approach Δz and of the duration Δt of maximum tip approach. The results are another surprise, as Fig. 3 shows, in that, for each tip approach (5 to 8 Å), P increases as Δt increases from 1 ms through 10 ms to 50 ms. Such a behavior cannot be explained by the tunneling of the Ge adatom between the surface and the tip, because the tunneling time for an atom through a potential energy barrier is expected to be in the 1–50 ms range only at a particular z value [22]. Any slight deviation (±0.1 Å) around this z value would modify the tunneling time by several orders

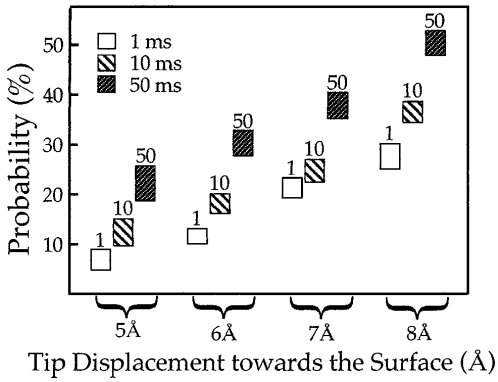

FIG. 3. A graph showing the probability of extracting a Ge adatom as a function of duration of maximum approach *and* tip displacement towards the surface. Note that the applied sample voltage in all cases is 0 V. Error bars indicate the statistical uncertainties. The total number of manipulations were 480 (5 Å), 1880 (6 Å), 1490 (7 Å), and 2180 (8 Å), respectively.

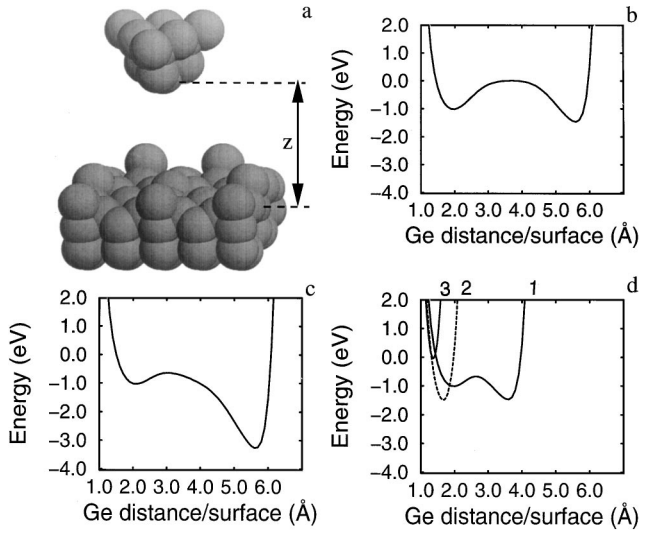

FIG. 4. Calculated potential energy curves of a Ge adatom positioned between a Ge tip apex and a Ge(111) surface as a function of the Ge adatom altitude above the surface for different tip-sample distances z. In (a), a standard ball representation of the junction considered. in (b), the imaging mode, where $I = 1$ nA, i.e., $z = 8$ Å with the tip apex lying along the surface normal of the Ge adatom. In (c), the tip apex is stopped above the Ge adatom at $z = 8$ Å. Then a sample bias voltage of $+3$ V is applied inducing the suppression of the surface Ge potential well. In (d), the merging of the two wells when the tip apex is gently approached towards the Ge adatom for $z = 6$ Å (curve 1), $z = 4$ Å (curve 2), and $z = 3.5$ Å (curve 3). The zero in energy is given by the energy of the three components of the junction (tip appex, Ge adatom, and surface) at very large separation.

of magnitude [22]. We also checked that the response time of the z movement of the tip piezo is much shorter (<100 μs) than the ms time range of the extraction by recording, during the adatom manipulation, the time evolution of the tunnel current when applying a small voltage (20 mV) to the sample. Therefore, we conclude that the adatom transfer lifetime is, indeed, surprisingly high, of the order of 10 ms.

To understand how a Ge adatom is picked up from a Ge(111) surface with the tip apex, we have performed detailed calculations, using the standard atom superposition and electron delocalization molecular orbital (ASED-MO) method [23], of the "tip apex-Ge(111) surface" atomic structure at each 0.1 Å step of the approach and retraction of the tip. This semiempirical calculation technique was preferred over first principles calculations [24] because a full optimization of this STM junction atomic structure at each step is actually way beyond the accessible computation time. Furthermore, the ESQC technique, which provides the tip-surface distance z is compatible with the Hamiltonian delivered by ASED. Finally, we have recently studied the quality of the ASED predictions on other semiconductor surfaces such as the Si(100) surface for chemisorption [25] and lateral atom manipulation [26] problems. We shall present here only a selection of the information we have obtained from the calculations.

The Ge(111) surface was described by a slab of 90 atoms in four planes with a surface of 4×5 Ge atoms [Fig. 4(a)]. The ASED parameters were optimized in such a way that the surface atomic structure of the Ge(111) surface, in the absence of the tip, converges towards the known structure [24]. Then, a tip apex composed of 13 Ge atoms with [111] facets was approached towards the surface along the normal centered on a Ge adatom [Fig. 4(a)]. The choice of the chemical composition of the tip apex was dictated by experimental facts that a tungsten tip apex is always decorated in our experiment with Ge atoms due to the coarse STM approach.

When the tip apex is far away (8 to 9 Å) from the surface, in an STM imaging mode, a Ge adatom has two possible stable chemically bound positions: one on the surface and one at the tip apex. This is confirmed by calculating the minimum energy of the "tip apex-Ge adatom-Ge(111) surface" junction for a given z as a function of the Ge adatom altitude [Fig. 4(b)]. Here, z is the distance (center to center) between the restatom layer and the tip. Note, z should not be confused with the Ge adatom altitude in Figs. 4(b) to 4(d). The zero (in both cases) corresponds to the restatom layer. The obtained double well potential also reflects the fact that the barrier for a Ge adatom to go from its surface site to a tip adsorption site is more than 1 eV, which makes this transfer process very unlikely at room temperature in the constant current imaging mode.

One way to reduce this barrier and transfer the Ge adatom on the tip apex is to apply an electric field as demonstrated experimentally here [Fig. 2(a)] and elsewhere [14–18]. In this case, with the help (or not) of inelastic electron effects, the double well potential [Fig. 4(b)] will be modified and the 1 eV barrier height

will be decreased due to the corresponding enhancement of the bias voltage. This can be seen in Fig. 4(c). In Fig. 4(d), the new possibility, presented in this Letter, is to gently merge the two wells [Fig. 4(b)] by a very fine control of z with, as a consequence, the cancellation of the potential barrier. After this merging, the energy of the junction increases [Fig. 4(d)] and, for example, at $z = 3.5$ Å, it overcomes the potential barrier height in Fig. 4(b). This enables the targetted Ge adatom to jump from the surface to the tip apex.

One critical parameter in this process is the distance between two neighbor adatoms on the surface. If this distance is smaller than the extent of the surface deformation brought about by the tip, more than one adatom will be extracted. To test this effect, we have calculated the surface relaxation during a complete "tip approach, potential well merging, tip retraction" sequence by optimizing the total junction geometry at each step [27]. It turns out that, even for a rather flat (111) tip apex, the distance between two Ge adatoms on the surface is large enough to prevent a double pickup process for a moderate constraint coming from the tip apex. We have learned also from these calculations [27] that, during the approach, a large potential basin is created by the tip apex constraint, opening the way for the targetted adatom to diffuse around the end atom on the tip apex. This explains the long duration of our pickup process. Before tip retraction, a long waiting time will permit the adatom to reside with more certainty in the vicinity of the tip apex than a short one.

In conclusion, we have demonstrated that the direct STM tip-surface contact mode can be used to reproducibly extract individual atoms from a Ge(111) surface. In measuring the extraction probability as a function of the tip-surface interaction time, we found a very surprising result, namely, that the duration of the mechanism is very long ($\sim$10 ms) as compared to intrinsic relaxation times. Complete calculations of the STM tip-surface junction atomic structure during the manipulation enabled us to explain the main features of the mechanism, one of these being that a large potential basin is created by the tip apex constraint, opening the way for the targeted adatom to diffuse around the end atom on the tip apex. It follows that, although this vertical manipulation method has been tested here on the Ge(111) surface only, it may be valid also for other semiconductor surfaces and possibly for metallic surfaces. Because of its simplicity as compared to other methods involving additional tunneling electron and/or electric field effects, this method is expected to improve significantly our ability to manipulate matter at the atomic scale.

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