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Research Report

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M. T. Cuberes*, R. R. Schlittler, and J. K. Gimzewski

IBM Research Division
Zurich Research Laboratory
8803 Rüschlikon
Switzerland

*Present address: *Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH.*
e-mail: teresa.cuberes@materials.ox.ac.uk

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IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland
*Present address: *Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH.*
e-mail: teresa.cuberes@materials.ox.ac.uk

Abstract

We demonstrate and discuss the use of a scanning tunneling microscope operated at room temperature to push individual C_{60} molecules out from their stable adsorption sites at Cu(111) steps, trap them into nanometer-sized Cu vacancy sites formed with the tip, or reposition them one-by-one along a Cu step under complete control.

1 Introduction

Miniaturization in the microdevice industry is reaching the limits compatible with correct performance. As the devices shrink, quantum effects dominate their response. Therefore, technology requires new solutions and tools to deal with the nanoworld. Currently, the design and control operation of nanostructures constitute a primary interest in scientific research. The scanning tunneling microscope (STM) has recently demonstrated its suitability for the controlled repositioning of molecules on surfaces at room temperature [1, 2]. Such experiments seek to explore opportunities to build and operate nanodevices with an STM using molecules as structural functional units. In principle, molecules could be a priori designed (by chemical synthesis, for instance) with the ability to perform specific tasks. Although still in a primitive stage, the state of the art of STM manipulation of atoms and molecules on surfaces is improving in giant steps [3]–[9].

In the present study, we consider ways to manipulate C_{60} molecules on Cu(111) surfaces with the STM. Previous STM work has shown that, upon sublimation, C_{60} first adsorbs at the Cu steps and, as coverage increases, C_{60} islands grow from the steps towards the terraces [10]–[12]. Isolated C_{60} molecules are typically not found on Cu(111) terraces, and hence C_{60}/Cu(111) does not readily appear to be very appropriate for building nanostructures by repositioning individual molecules. However, as we demonstrate here, the tip can be used to push individual C_{60} molecules away from steps or islands towards terrace sites. Moreover, the tip can be used to form nanometer-sized Cu vacancy sites, into which individual C_{60} molecules can be pushed. In addition, C_{60} molecules can then be repositioned with an STM tip along Cu steps in a completely controlled manner [2].

Our experiments demonstrate that the ability to manipulate molecules using the STM is the result of our knowledge of the molecular behavior upon adsorption as well as our understanding of the tip–molecule and tip–substrate interactions. The STM offers a way to play with individual molecules, within the limitations imposed by nature.

2 Experimental

Sample preparation and STM measurements were performed in the same ultrahigh vacuum system. Atomically clean Cu(111) surfaces were prepared by successive neon-bombardment and annealing cycles. C_{60} was sublimated from a home-made W crucible, heated to a temperature of about 760 K, onto the Cu substrate held at a temperature of 560 K. This procedure is known to lead to the formation of a well-ordered C_{60} monolayer (ML) on Cu(111) [10]–[12]. The sublimation rate of C_{60} was controlled by a quartz microbalance mechanically translatable to the position occupied by the sample during deposition. C_{60} coverages were calibrated according to the STM images. Rates of about 1 ML min^{-1} were used. STM manipulation of C_{60} and formation of Cu vacancy sites were simplified by special software that allowed us to control arbitrarily the lateral position of the tip with respect to an STM image (Refs. [1, 2] describe the use of this software for manipulation).

3 Results and Discussion

3.1 Pushing C_{60} molecules from Cu(111) steps to terrace sites

Figure 1a shows a topography of Cu(111) covered with $\simeq$0.2 ML of C_{60} molecules. The molecules in the image are adsorbed at lower Cu step edges; no isolated C_{60} molecules occupy terrace sites. Steps on Cu(111) are preferential adsorption sites for C_{60} molecules. Bonded to the lower step edges, the molecule increases its coordination with Cu, and hence its binding energy to the surface. At the steps, C_{60} lies within a potential energy well [9] and must overcome a potential barrier to escape from the step and diffuse towards the terraces. Potential barriers for C_{60} at Cu steps are expected to be $\simeq$0.2 eV/atom for molecular diffusion towards the lower terrace and $\simeq$0.4 eV/atom towards the upper one [9]. Therefore, C_{60} molecules stabilize at Cu step sites upon adsorption on Cu(111) [10]–[12]. The potential barrier for C_{60} molecules to diffuse along the step direction is much lower than to escape to the terraces, being $\simeq$0.04 eV/atom [9]. However, Cu step atoms are mobile [13] and may rearrange around the C_{60}molecules adsorbed at the step positions, thus preventing their diffusion. In fact, in many cases, kinks among C_{60} molecules are required to explain C_{60}–C_{60} misalignments when adsorbed in rows at Cu steps [2]. Isolated C_{60} molecules adsorbed at monoatomic Cu step sites are often observed in STM images [9]. The formation of small kinks increases the coordination of C_{60} Cu and hinders a lateral molecular diffusion.

To detach a C_{60} molecule from the step in Fig. 1a, we may push it towards the lower or the upper terrace. In principle it should be easier to bring the molecule to the lower terrace because the energy barrier for molecular diffusion towards the lower terrace is lower, thus requiring a weaker tip–molecule force. However, we were only able to push molecules towards the lower terrace with poor-quality tips, never with sharp ones. As the molecules are adsorbed at the lower step-edge side, it is not always possible to adjust the tip height for a sufficient tip–molecule interaction when approaching the tip to the molecule from the upper terrace without damaging the tip or scratching the Cu surface.

In Fig. 1a, the tip was placed next to the molecules on the lower Cu terrace for manipulation. The tip parameters were adjusted to $I_{\rm t} = 10$ nA, $V_{\rm t} = -7$ mV (gap resistance $R = 500$ MΩ) to reduce the tip height [the typical imaging parameters were $I = 2$ nA and $V = 2$ V ($R = 500$ MΩ)]. Then, the tip was displaced perpendicular to the step, as indicated by the arrow, up to a distance of about 2–3 nm "inside" the upper terrace, pushing the C_{60} molecule "against" the Cu step.

Figure 1b was recorded immediately after this operation. Here, four C_{60} molecules lie at upper-terrace sites. The results demonstrate that the tip can be used to pushed C_{60} molecules from their equilibrium step sites and bring them to Cu terraces. The change in shape of the step indicates that C_{60} repositioning is accompanied by a substantial rearrangement of Cu step and terrace atoms. The topography in Fig. 1b, brought about by tip actuation, is anomolous for C_{60} on Cu(111). As stated above, isolated C_{60} molecules on Cu(111) terraces are seldom observed upon deposition [10]–[12].

With respect to the four C_{60} molecules found on the upper terrace in Fig. 1b, the two most distant from the step do not show internal molecular contrast, whereas the other two exhibit a lower corrugation ($\simeq$2.5 Å vs. $\simeq$4.0 Å) and a clear intermolecular structure. We understand that these latter molecules are trapped in the upper terrace into nanometer-sized Cu vacancies, but in effect still bonded to the second Cu layer below the surface, i.e. to the lower Cu terrace surface layer. Cu atoms may readily surround displaced C_{60} molecules when the tip is retracted. Such molecules were reproducibly observed when performing this kind of experiments. The other isolated molecules in Fig. 1b were weakly bonded to the surface, and they were observed to move around when the same surface region was repeatedly imaged until they reached a Cu step again or stuck to a C_{60} island.

For instance, according to this, molecule A in Fig. 2 is trapped inside a Cu defect, whereas molecule B is adsorbed on the surface. Figures 2a, b, and c were successively recorded with the typical tip parameters for imaging, but with no attempt made to manipulate them. The images clearly reveal that molecule B moves until it reaches a Cu step position, whereas molecule A remains immobile. The upwards movement of molecule B strongly suggests that it is being pushed by the tip that is simultaneously recording the images (scanning proceeded upwards line–by–line from the lower side of the image). Even when imaging with high gap resistances, forces exerted by the tip on adsorbed molecules can be strong enough to cause molecular movement if the barrier height for lateral molecular diffusion is sufficiently low and the molecule is weakly bonded to the surface. The fact that molecule A remains immobile in spite of being isolated amidst a Cu terrace supports our assumption that such molecules are trapped, bonded to the second Cu layer, and surrounded by Cu atoms. Owing to the increase molecular coordination to Cu, C_{60} is expected to be strongly bonded to such vacancy-site Cu defects.

3.2 Trapping C_{60} molecules on nanometer-sized Cu vacancy sites

Molecules such as B in Fig. 2, weakly bonded to the surface, are definitively not appropriate for assembling stable nanostructures. However, one can consider patterning predefined defect structures on Cu(111) terraces, and then pushing C_{60} molecules inside using the STM tip. Here we explore this possibility.

A procedure that proved useful for forming vacancy sites on Cu(111) is as follows. The tip is positioned at a chosen point on a terrace. Then, in the manipulation mode, the tip parameters are momentarily changed to $I = 10$ nA and $V = -4$ V, and returned again to the imaging mode. Figure 3 illustrates an example of the formation of defects on Cu(111) using this method. Figure 3a shows the initial topography of the Cu(111) surface. The cross in the image indicates the position selected for the formation of a defect. After positioning the tip over the cross in Fig. 3a and proceeding as described above, Fig. 3b was recorded over the same surface area. Comparison of Figs. 3a and b reveals the formation of vacancies that result from tip actuation [14].

In Fig. 3b various vacancy islands are distinguished on Cu after a single tip action. The tip shape may lead to multiple defect formation. Slightly varying the tip parameters (I ranging between 5 and 10 nA, and V ranging between -3500 and 4000 mV), it was typically possible to create just one vacancy island. We verified that the procedure to form Cu defects also damages the tip severely. In most cases, we could record only poorly resolved images.

Figure 4 demonstrates that it is possible to reposition C_{60} molecules adsorbed on Cu step sites into Cu vacancy-sites defects formed by the tip. Figure 4a shows a topographic area on Cu(111) with a Cu vacancy-island defect (labeled B) previously formed with the tip as described above. C_{60} molecules in the image are adsorbed to Cu step edges, and the defect B lies on a lower terrace with respect to the steps. In Fig. 4b two more vacancy-island defects (labeled A, C) were formed by actuating with the tip as described above at the points indicated by the crosses in Fig. 4a.

Using the tip as described in the preceding section, approaching the tip to the molecules from the left-hand side of the image, decreasing the tip height, and displacing the tip as indicated by the arrows in Fig. 4b, we pushed the molecules from the step edges towards the Cu defects A, B, and C on the Cu terrace at the right-hand side. Figure 4c, recorded after manipulation, shows that C_{60} molecules were indeed repositioned inside the previously formed Cu defects as a result of tip actuation. Once within such defects, C_{60} molecules bond to the Cu atoms around the vacancy island (in the same way as they bond to Cu monoatomic steps), thus finding a stable molecular adsorption site.

3.3 Repositioning C_{60} along Cu steps

The STM tip can also be used for repositioning C_{60} molecules adsorbed at Cu(111) monoatomic steps along the step direction, as we demonstrated in Ref. [2].

Repositioning C_{60} along Cu steps permits ease of operation, a strikingly good precision for repositioning the molecule (which can be displaced up to distances less than 1 nm), and the complete control of the directionality of molecular motion in one dimension (the step direction).

In Fig. 5, we show that these advantages are all maintained when repositioning C_{60} along meandering Cu steps. Figure 5a comprises different Cu(111) terraces, partially occupied by C_{60} molecules that form a 4×4 superstructure. We focus our attention on the rounded step situated in the lower part of the image that extents from point A to point B. We intend to reposition the molecule labeled X from the right-hand to the left-hand side of the step (i.e. from A to B). In order to manipulate molecule X, the tip is positioned between it and its right-hand neighboring molecule at the step. The tip parameters are set to the manipulation mode ($I_t \simeq 10$ nA, $V_t \simeq 7$ mV, $R \simeq 1.4$ MΩ) and the tip is displaced in the step direction. As the step is not straight, the tip movement during manipulation does not follow a straight path either. However, this does not prevent the controlled repositioning of C_{60} to a preselected step site.

In Fig. 5b molecule X in Fig. 1 has been moved in the step direction about 30 nm from its original position by tip actuation. In Fig. 5c the same C_{60} has been moved again by about 30 nm, and is now located about 60 nm from its original position in Fig. 2a. In Fig. 5f, molecule X has been moved from the right-hand side of the image to the left-hand side, a distance of about 200 Å. Similar molecular translations were repeated with the other molecules adsorbed at the step.

In some cases, the shape of the step is altered when manipulating C_{60} with the tip, see for instance Fig. 5d. When displacing the tip in the step direction for C_{60} repositioning it is possible that the tip motion deviates slightly from the step direction, which involuntarily induces the formation of kinks, thus altering the step shape. Nevertheless, with the tip parameters used for this kind of manipulation, C_{60} molecules were never detached from the step edge because of tip deviations.

4 Summary

We have investigated different possibilities to manipulate C_{60} absorbed on Cu(111). Using an STM, we can bring C_{60} to Cu terraces sites away from other C_{60} molecules, trap them at Cu defects, and reposition them controllably along Cu step edges. Our results emphasize the variety of opportunities that the STM offers for fabrication at the nanoscale.

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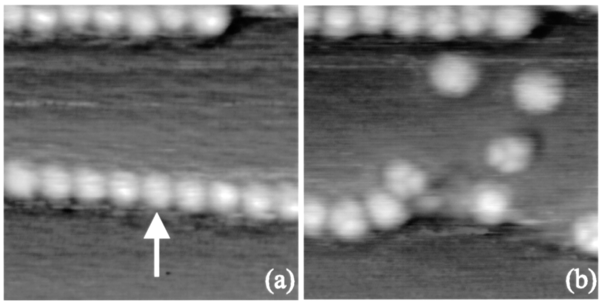

Figure 1: STM images recording during repositioning of C_{60} from step to terrace sites using the tip of an STM (surface area $\simeq$90 Å$\times$90 Å, $I_t = 2.5$ nA, $V_t = 2$ V). (a) Initial topography. The arrow indicates the direction of displacement of the tip to push C_{60} away from the step (tip parameters for manipulation $I_t = 10$ nA, $V_t = -7$ mV, $R = 1.4$ MΩ). (b) Resulting topography after tip actuation.

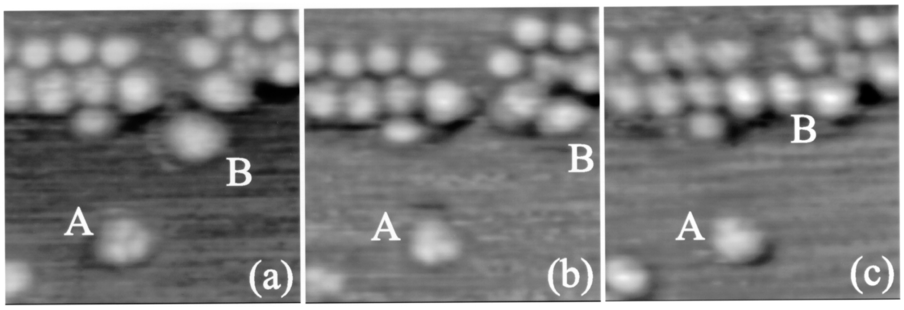

Figure 2: STM images succesively recorded over the same surface area of $\simeq$70 Å×70 Å, $I_{\mathrm{t}} = 2.5$ nA, $V_{\mathrm{t}} = 2$ V. No attempt to manipulate C_{60} with the STM tip was made here.

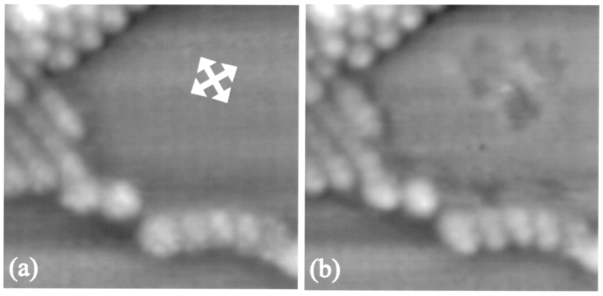

Figure 3: STM images recorded during the formation of nanometer-sized vacancy-site defects on Cu(111) using the STM tip (surface area $\simeq$90 Å×90 Å, $I_{\mathrm{t}} = 1.8$ nA, $V_{\mathrm{t}} = 2.1$ V). (a) Initial topography. The cross indicates the point where the tip is located for defect formation (momentarily switching the tunneling parameters to $I_{\mathrm{t}} = 10$ nA, $V_{\mathrm{t}} = -4$ V). (b) Resulting topography after tip actuation.

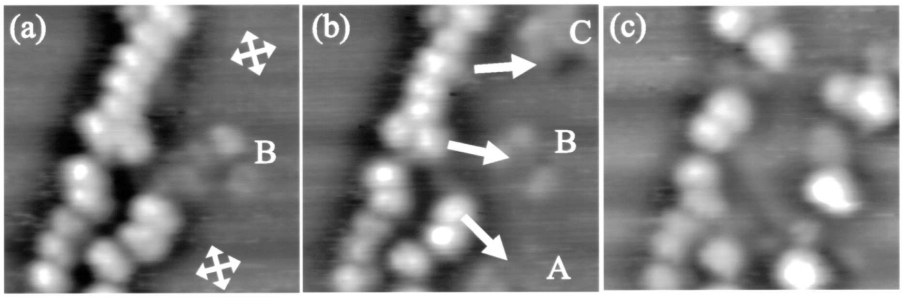

Figure 4: STM images recorded during formation of nanometer-sized vacancy-site defects and repositioning of C_{60} inside these defects (surface area $\simeq$110 Å×110 Å, $I_{\mathrm{t}} = 2$ nA, $V_{\mathrm{t}} = 2$ V). (a) Initial topography. B indicates a vacancy-sized defect, previously formed with the tip. The crosses indicate points where more defects will subsequently be formed. (b) Topography after the formation of Cu vacancy-site defects with the tip at the crosses in (a), at A and C (tip parameters for the formation of Cu vacancy defects: $It = 10$ nA, $V_{\mathrm{t}} = -4$ V). The arrows indicate the displacement of the tip to reposition C_{60} molecules (tip parameters for pushing C_{60} out of the step inside the defects: $It = 10$ nA, $V_{\mathrm{t}} = -7$ V). (c) Resulting topography after tip actuation.

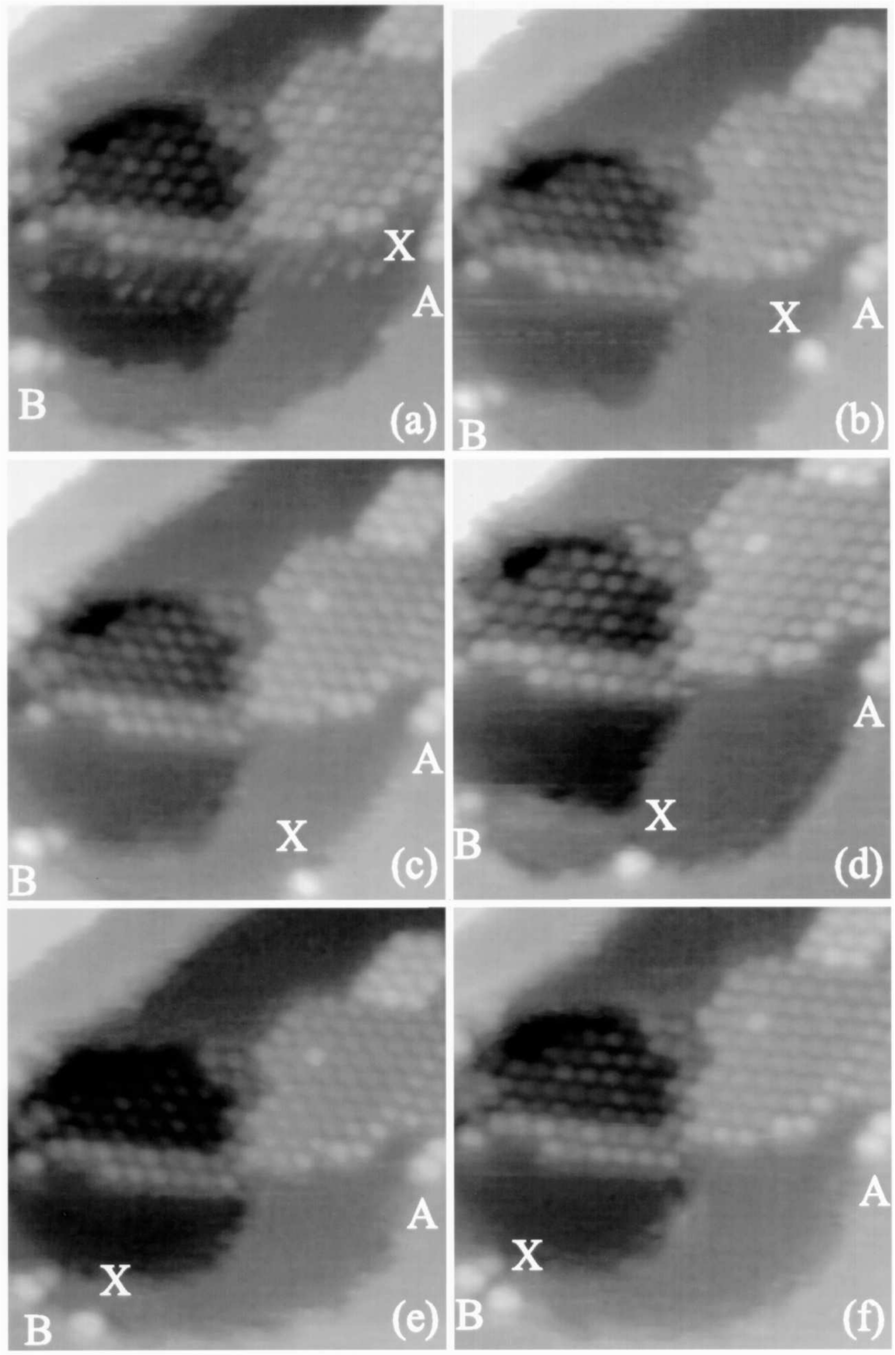

Figure 5: STM images recorded during C_{60} repositioning along a meandering Cu monoatomic step. Surface area $\simeq$200 Å$\times$200 Å, It = 2 nA, V_t = 2 V. In (a)–(f), molecule X is repositioned with the tip from A to B along the step. Tip parameters for C_{60} repositioning along the step: I_t = 5 nA, Vt = −7 mV (R = 1.4 MΩ).