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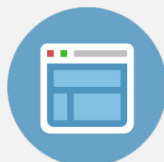
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Manipulation of C₆₀ molecules on a Si surface

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We have used the tip of a scanning tunneling microscope to position individual C₆₀ molecules on a Si(111) surface. It is possible to form simple patterns of molecules at room temperature using this technique. © 1995 American Institute of Physics.

The demonstration by Eigler and co-workers¹ that individual adsorbate atoms may be manipulated on a metallic surface using a scanning tunneling microscope (STM) is the most striking example of atomic scale modification to date. This technique has now been used to fabricate nanostructures which may be probed using a STM,² but has so far, been limited to a low-temperature environment and the use of metallic substrates. The extension of this work to include semiconductor surfaces and higher temperature operation is highly desirable and may eventually enable fabrication of a more diverse range of nanostructures.

In this letter, we show that molecular manipulation on Si surfaces at room temperature is possible. In particular we demonstrate that the tip of a STM may be used to manipulate C₆₀ molecules to form simple patterns on a Si(111) surface which has undergone a (7×7) reconstruction.

Our experiments are performed in an ultrahigh vacuum (UHV) environment. A small (5 mm × 3 mm) piece of a Si(111) wafer is loaded into the UHV system and outgassed at ~800 °C overnight. Following outgassing the sample is heated to ~1200 °C for 60 s, annealed at 800 °C for 3 min and then cooled slowly. This procedure results in a (7×7) surface reconstruction on wide terraces with a low density of defects. Submonolayers of C₆₀ were sublimed from a Knudsen cell operating at 320 °C. The sample, which was held at room temperature during deposition, is then transferred to the STM³ which is housed in an adjacent UHV chamber. For all our work to date we have used electrochemically etched W tips which are cleaned in UHV by electron beam heating to ~800–1000 °C.

A STM image of a representative part of the surface is shown in Fig. 1(a). In this topographic image the C₆₀ molecules appear as bright circular features and the (7×7) re-

construction of the Si(111) surface is also resolved. It has previously been demonstrated that C₆₀ molecules may be moved on Si surfaces by performing a STM scan with the tip held close to the Si surface and the feedback loop, which maintains constant tunnel current, effectively turned off.⁴ We have attempted to reproduce these results, but have found that this results in an unacceptably high rate of tip crashes. However, we have found that for some tips this effect may be reproduced by scanning at low voltage (<|1.5 V|) but with the feedback loop turned on. Such a procedure results in the conversion of one quasirandom pattern of C₆₀ molecules into a different quasirandom pattern.

It is not possible, however, to order the arrangement of molecules or form predetermined patterns using this approach. To achieve this objective we move the tip through the cycle which is shown schematically in Fig. 2. The tip is first moved close to the surface by reducing the voltage (the sample is negative with respect to the tip) to V_m ($|V_m| \sim 0.4$ V) and increasing the current to I_m ($|I_m| \sim 5$ nA) and is then swept a distance d across the surface while maintaining feedback control of the tunnel current. We then retract the tip by adjusting the voltage and current to values which are appropriate for scanning without moving atoms (see scan parameters in Fig. 1) and then move it back to its original position under feedback control. The tip is then moved and the “sweeping” procedure repeated across a number of parallel lines separated by ~0.6 nm. The total area swept out is $w \times d$. Typically $w = d = 6$ nm.

The aim of this procedure is to induce movement of C₆₀ molecules in the direction in which the tip moves when it is close to the surface. This direction may be $+x$, $-x$, $+y$, or $-y$ where x and y are two orthogonal axes. Figures 1(a)–(c) show an example of the movement of a C₆₀ molecule across

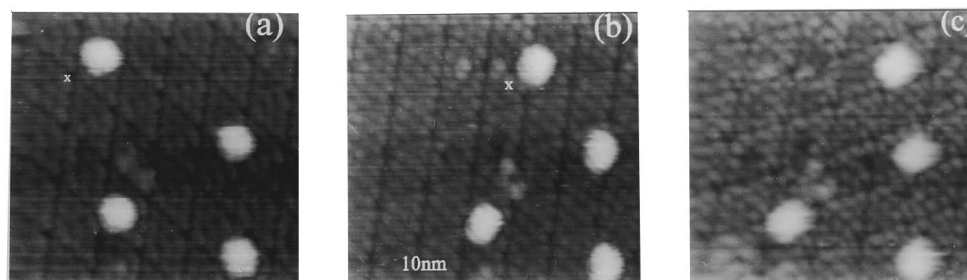


FIG. 1. Controlled movement of a single C₆₀ molecule on the Si(111)–(7×7) surface. The figures are STM topographic images with sample voltage -2.0 V and tunnel current -1 nA. The sweeping parameters V_m and I_m , as defined in the text, were -0.4 V and -4 nA. The molecule in the upper right-hand section of (a) is induced to move ~ 4 nm in the positive x direction, as shown in (b), and subsequently a further 3 nm, resulting in the arrangement of molecules shown in (c). The letter x marks the bottom left-hand corner of the $6 \text{ nm} \times 6 \text{ nm}$ area swept out by the tip in repositioning the C₆₀ molecule.

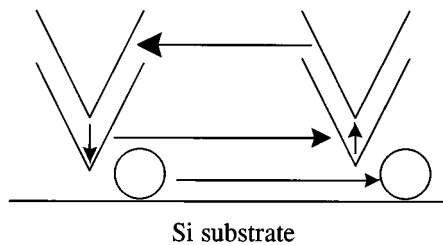


FIG. 2. A schematic illustration of the process we have used to manipulate individual C_{60} molecules on the $\text{Si}(111)-(7\times 7)$ surface.

a surface in two stages. The sweeping direction is $+x$, parallel to the horizontal axis. To move the uppermost C_{60} molecule in Fig. 1(a) it was necessary to repeat the sweeping procedure ~ 10 times. Only the last attempt was successful and this accounts for all the displacement which is apparent from a comparison between Figs. 1(a) and 1(b). Similarly the displacement between Figs. 1(b) and 1(c) occurred after ~ 10 unsuccessful attempts. The molecule is moved ~ 4 nm between Figs. 1(a) and 1(b), and then by a further 3 nm between Figs. 1(b) and 1(c). The cross in Figs. 1(a) and 1(b) marks the bottom left-hand corner of the $6\text{ nm} \times 6\text{ nm}$ area swept out by the tip. In each case the molecule has been moved to near the edge of the sweeping range. However, in many cases we observe that a molecule moves, but not to the edge of the swept region. Typically the displacement is in the range 1–5 nm even if the sweeping range $d > 6$ nm.

We have performed many attempts at moving C_{60} molecules and found their response is tip dependent. A minority of tips (generally those with higher imaging resolution) disrupt the underlying Si surface by extracting Si adatoms but fail to move the C_{60} molecules. Some tips appear to have a much higher success rate for moving C_{60} molecules than others. In addition the success rate for a given tip can vary over its useful lifetime. For example the same tip was used for the manipulations in Figs. 1 and 3 (see below) which were performed on consecutive days. As noted above ~ 1 in 10 applications of the sweeping procedure resulted in movement of C_{60} molecules for Fig. 1 whereas this figure is closer to 1 in 4 during the sequence in Fig. 3. Overall we have used

8 tips during our work. We were able to manipulate C_{60} molecules with 6 of these tips.

In order to demonstrate the potential of this approach for the manipulation of molecules into predetermined patterns we show in Figs. 3(a)–3(c) how a quasirandom arrangement of C_{60} molecules may be moved to form 5 straight line segments corresponding roughly to the shape to the letter “S”. The twelve C_{60} molecules which make up this shape are identified by the letters A–L so that their positions may be compared. In the course of this sequence of manipulations there were 40 movements of C_{60} molecules and the sweeping procedure was run ~ 150 times. This took ~ 4 h. It is clear that this fairly complex shape can be formed without significantly disrupting the adatoms of the reconstructed Si surface.

The properties of C_{60} monolayers and submonolayers on $\text{Si}(111)-7\times 7$ have been investigated by several groups.^{4–6} Li *et al.*⁵ have shown that there are several different bonding configurations for C_{60} on $\text{Si}(111)-7\times 7$ and that the interaction is not of a pure van der Waals nature—some charge transfer also occurs. It is clear that the interaction of C_{60} and $\text{Si}(111)$ is sufficiently strong that molecules are unable to diffuse across the surface at room temperature so that any rearranged pattern of molecules is stable. Nevertheless, the bonding is sufficiently weak that it is possible to move C_{60} molecules without significantly disrupting the Si surface. On the basis of our experiments so far we are unable to develop a model for the magnitude of the interaction between the STM tip and the C_{60} molecules. However, it is interesting to note that Li *et al.*⁵ anticipated that C_{60} manipulation would be possible by moving a STM tip while the sample is biased at a voltage of -0.4 V. This prediction is based on the observation that, at least for some bonding configurations there are no states lying 0.4 eV below the Fermi energy which are associated with the C_{60} molecule. With the sample biased ~ -0.4 V the tip is therefore not withdrawn relative to the underlying Si as it passes a C_{60} and a strong interaction between tip and molecule is expected which could force the C_{60} to move. Within this framework it is likely that the molecules are pushed in contrast to the pulling described by Eigler *et al.*¹ for Xe atoms on Ni.

It has previously been noted that C_{60} is preferentially

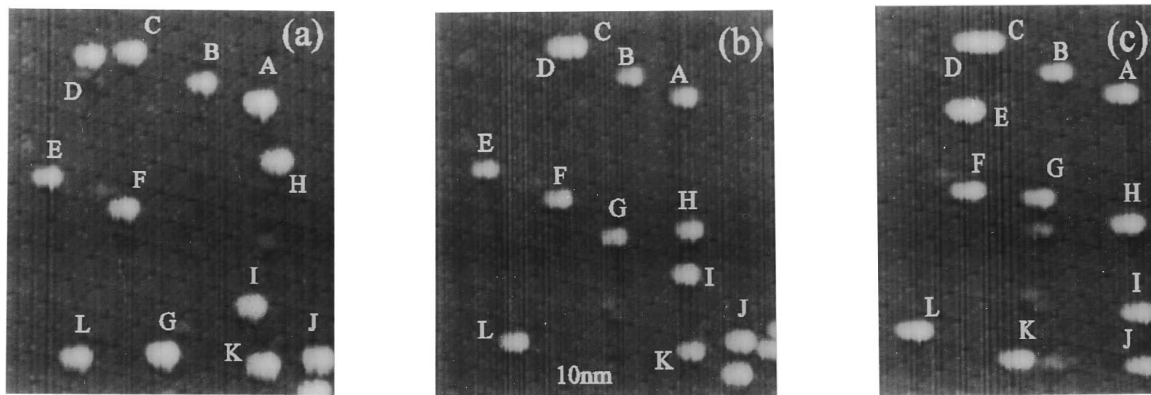


FIG. 3. (a) A quasirandom arrangement of 12 C_{60} molecules labeled A–L, before STM tip manipulation. (b) Intermediate stage of pattern formation showing considerable rearrangement of the C_{60} molecules. (c) Final ordering of molecules to form 5 straight line segments corresponding to the shape of the letter “S”. All images scanned with a bias voltage of -2 V and a tunneling current of -0.25 nA. The sweeping parameters V_m and I_m were -0.4 V and -4 nA.

adsorbed at the center adatom sites on Si(111) 7×7 (Ref. 6). This is consistent with the distribution of C_{60} molecules across the surface that we observe. Furthermore, the final positions of all the C_{60} molecules after movement by the tip are also close to these low energy adsorption sites. In particular we have not moved any C_{60} molecules to corner holes on the reconstructed surface.

In conclusion, we have shown that it is possible to manipulate the positions of individual molecules on a semiconductor surface at room temperature. Similar effects have been observed using many tips. Our results demonstrate that molecular manipulation may be used to form nanometer scale patterns on a semiconductor surface. Transfer of such patterns into a semiconductor surface, perhaps precoated with a few monolayers of adsorbate, would offer a means of fabricating

experimental electronic devices with an active region formed by one or a few individual atoms. We are optimistic that techniques to achieve this goal will be developed over the next few years.

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³The STM, control electronics and software were provided commercially by WA Technology.

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