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Abstract. We have investigated the response of C_{60} molecules adsorbed on Si(100)-(2 × 1) to manipulation induced by a scanning tunnelling microscope. Our results show that the C_{60}–Si(100)-(2 × 1) interaction is greater than the C_{60}–C_{60} interaction. Attempts to move a molecular pair result in the transfer of one molecule across a dimer row due to barrier lowering caused by the intermolecular interaction. Our results suggest that C_{60} is chemisorbed and this is confirmed by Si 2p core-level photoemission spectra.

Lateral manipulation using a scanning tunnelling microscope (STM) may be used to probe the interactions experienced by atoms and molecules adsorbed on solid surfaces [1–3]. Following initial work by Eigler and Schweizer [1] this approach has been used to study the interaction of electrons at the surface of noble metals with adsorbed transition metal atoms [2] and more recently the anisotropy of a molecule–substrate interaction for a high-index surface [3]. The use of this technique to investigate molecular interactions has so far been restricted to metal substrates and a low-temperature environment since the adsorbate–substrate combinations studied to date have energy barriers which are too low to suppress diffusion at room temperature. The extension of this work to room-temperature operation requires a much larger diffusion barrier and therefore a much stronger adsorbate–substrate interaction and progress towards this goal has been limited by the difficulty of initiating manipulation of strongly adsorbed molecules. In a number of recent papers controlled manipulation of molecules at room temperature has now been reported [4–7]. However, progress to date has encompassed only placement of adsorbates and no investigations of the interactions of strongly adsorbed molecules have been reported.

In this paper we describe a series of experiments in which molecular manipulation is used to investigate the intermolecular and molecule–surface interactions of C_{60} adsorbed on the Si(100)-(2 × 1) surface. This adsorbate–substrate combination has recently been the focus of intense interest and several different models for adsorption have been proposed [8–10]. By using STM manipulation we are able to discriminate between these models. We show that the response of C_{60} to manipulation implies that C_{60} is chemisorbed [10] and this result is confirmed by synchrotron radiation photoemission experiments.

We use an ultrahigh vacuum (UHV) STM (Oxford Instruments SPM group, formerly WA Technology, Cambridge, UK) operating at room temperature. Electrochemically etched W tips cleaned in vacuum by heating were used throughout. The Si(100) samples were degassed at 750 °C overnight, flash annealed at 1200 °C for 20 s and then held at 800 °C for 3 min before being cooled to room temperature. C_{60} was sublimed from a Knudsen cell at a rate of 2×10^{-3} monolayers s^{-1}. Photoelectron spectroscopy (PES) experiments were performed at the Synchrotron Radiation Source, Daresbury, UK, using incident photon energies of 120 and 140 eV and a hemispherical analyser (resolution $\sim$0.3 eV). For the PES experiments C_{60} was sublimed from a resistively heated Ta envelope.

Figure 1(a) shows an STM image in which C_{60} molecules appear as circular features and the rows of the Si(100)-(2 × 1) reconstruction run up the image. The rows arise from the dimerization of top-layer atoms [11]. The Si(100)-(2 × 1) surface and the adsorption site for C_{60} are shown schematically in figure 2. We find that C_{60} is adsorbed in the troughs between the dimer rows at the four-dimer site (labelled A in figure 2) in agreement with previous studies [9, 10].

Displacement of an adsorbate across a surface was first demonstrated by Eigler and Schweizer [1]. This original work was performed at low temperature but we have recently demonstrated that it may also be performed at room temperature [4, 5]. Following our work further demonstrations of room-temperature manipulation have been published [6, 7]. To induce manipulation on the Si(100)-(2 × 1) surface the tip–sample separation is first reduced by decreasing the gap resistance to a value $\sim$1 GΩ. The tip is then moved across the surface in a controlled manner (typically through a total distance of 3 nm in steps
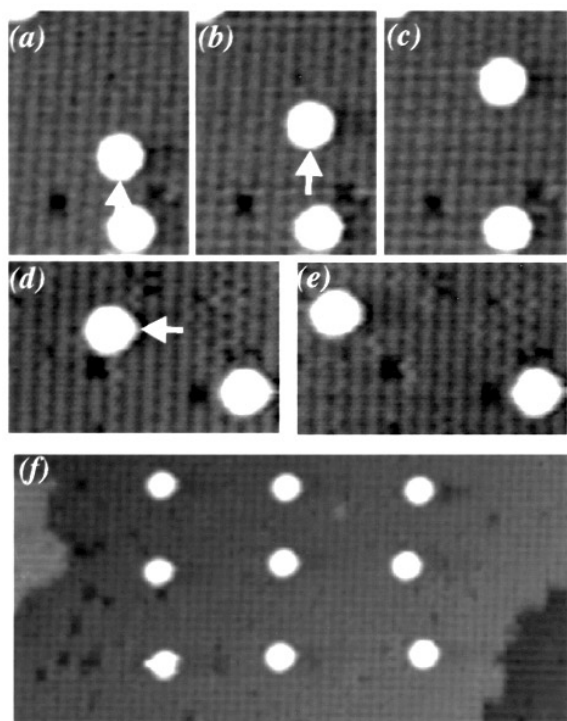
Figure 1. Demonstration of molecular manipulation:
(*a*)–(*c*) parallel to the Si(100)-(2 × 1) dimer rows, scan area
7.5 × 10 nm^2; (*d*), (*e*) across dimer rows, scan area
10 × 6.3 nm^2. The arrows indicate the direction of tip
displacement. (*f*) A 3 × 3 array of C$_{60}$ molecules, scan
area 40.5 × 19.7 nm^2. For (*a*)–(*f*): scan parameters,
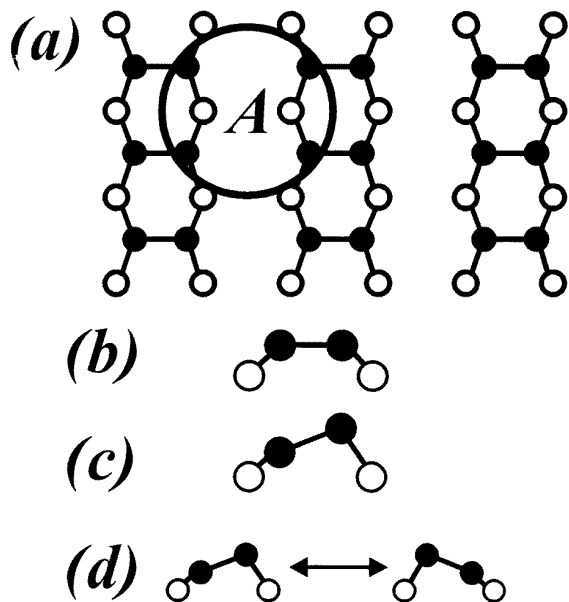−3.5 V, 0.1 nA; manipulation parameters, −1.0 V, 1.0 nA.

Figure 2. (*a*) Schematic of the Si(100)-(2 × 1) surface and
the adsorption site for C$_{60}$ labelled A; (*b*) symmetric and (*c*)
buckled Si dimers; (*d*) hopping between buckled states
which occurs at 300 K. ●, top layer Si atoms, ○, second
layer Si atoms.

of 0.6 nm). This movement may be chosen to be either
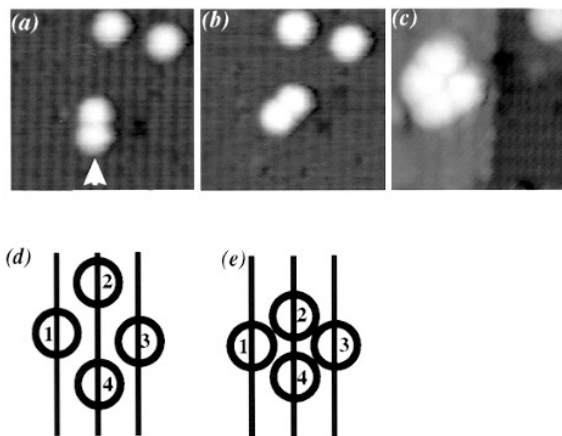parallel or perpendicular to the dimer rows. A digital

Figure 3. (*a*) A pair of C$_{60}$ molecules (*d* = 1.15 nm) prior to
manipulation. The result of an attempt to reduce the
intermolecular separation by moving the lower molecule
towards the upper molecule is shown in (*b*). The arrow in
(*a*) indicates the direction of tip displacement. Manipulation
parameters: −1.0 V, 1.5 nA. (*c*) A molecular cluster
assembled using the STM tip. (*d*) Schematic diagram
showing the position of the molecules in (*c*): ——, the
minima of the troughs. (*e*) c(4 × 3) arrangement. According
to a recent theory the cluster shown in (*c*) and (*d*) should
spontaneously relax to the configuration in (*e*); however,
this is not observed.

feedback loop is used to update the tunnel current after each
step. The gap resistance is then increased to ∼30–40 GΩ,
causing the tip to withdraw from the surface, and the tip
is returned to its original position. For the Si(100)-(2 × 1)
surface we have not observed any difference in response to
manipulation for forward and reverse bias.

For the Si(100)-(2 × 1) surface we observe a highly
anisotropic response of C$_{60}$ to STM manipulation. This
is shown in figure 1 in which the response of C$_{60}$
to manipulation either parallel (figures 1(*a*)–1(*c*)) or
perpendicular (figures 1(*d*) and 1(*e*)) to the dimer rows
is illustrated. In figures 1(*a*)–1(*c*) the effect of two
successive 3 nm displacements of the tip is shown. For
the manipulation perpendicular to the rows (figures 1(*d*)
and 1(*e*)) five parallel lines separated by 6 Å were swept
out forming an area of 3 × 3 nm^2. As shown in figure 1
it is possible to induce manipulation perpendicular to the
rows although the success rate for this direction is ∼15% as
compared with ∼95% for manipulation parallel to the dimer
rows. Note also that following attempts at manipulation
across dimer rows (figures 1(*d*) and 1(*e*)) we observe
some displacement parallel to the dimer row. However,
for displacement parallel to the rows the molecule is
guided along the troughs on the Si(100)-(2 × 1) surface.
This facilitates more precise and controllable placement.
Figure 1(*f*) shows a simple pattern. We have undertaken
further manipulation experiments to determine whether
the manipulation results from a repulsive or attractive
interaction. After application of a modified procedure, in
which the tip is not retracted before returning to its original
position, the C$_{60}$ remains at the extreme of the tip excursion.
This implies that the manipulation in figure 1 results from
a repulsive interaction.

A model for the interaction of C$_{60}$ with the Si(100)-(2 × 1) surface has recently been proposed [8]. According to this model a strong molecule–surface interaction causes the adsorption of C$_{60}$ in the troughs between dimer rows. While the interaction with the surface causes the molecule to sit in troughs, the position of the molecule along the trough, which is determined by the component of forces parallel to the dimer rows, is assumed to be determined entirely by interactions with other adsorbed molecules. The intermolecular interaction is taken to be van der Waals [12] in origin, and the molecules are assumed to be physisorbed. Note that the equilibrium intermolecular separation according to this model is therefore given by $d_0 = 1.005$ nm. We have used STM manipulation of pairs and small groups of molecules to evaluate this model. Figures 3(a) and 3(b) show the result of an attempt to reduce the separation of a C$_{60}$ pair by moving the lower molecule along the trough towards the upper molecule. The initial position of the tip was chosen so that it was sufficiently far away from the upper molecule so that no manipulation would result in the absence of the lower molecule, that is there should be no direct interaction between tip and upper molecule. Prior to manipulation the separation, d, of the C$_{60}$ pair is 1.15 ± 0.02 nm (equal to $3a$, where a (= 0.384 nm) is the surface lattice constant). Figure 3(b) shows an STM image taken after application of the manipulation procedure and shows that the upper molecule has been forced to move across a dimer row into an adjacent trough. The final molecular separation is 1.09 ± 0.02 nm. Note also that both molecules move 'up' the image by ~0.8 nm.

We have repeated this experiment many times and the important aspects of the results shown in figure 3 are reproducible. In particular we have never observed a separation of molecules along a trough which is less than 1.15 ± 0.02 nm, a result which is inconsistent with [8] in which a value equal to the intermolecular separation d_0 is predicted. We have also assembled molecular clusters. According to the model described above the cluster in figure 3(c) should relax to an ordered (local c(4 × 3)) arrangement, but this is inconsistent with our data (see figures 3(d) and 3(e)).

There are two possible explanations for these differences. First, the molecules are not physisorbed, but chemisorbed, and the resulting charge exchange between adsorbate and substrate modifies the intermolecular potential leading to a different equilibrium separation. A second (and on the basis of our STM results more likely) possibility is that the positions of the molecules along the trough are determined by the molecule–surface interaction rather than intermolecular forces.

Both explanations imply a much stronger interaction between C$_{60}$ and Si(100)-(2 × 1) than is consistent with physisorption. This is confirmed by photoemission spectra from the Si(100)-(2 × 1) surface before and after C$_{60}$ deposition. Figure 4(a) shows the Si 2p core-level spectrum acquired from the clean surface. The spectrum is decomposed into a number of spin–orbit split Voight components and is in agreement with previous work [13]. The various components arise from Si atoms in different
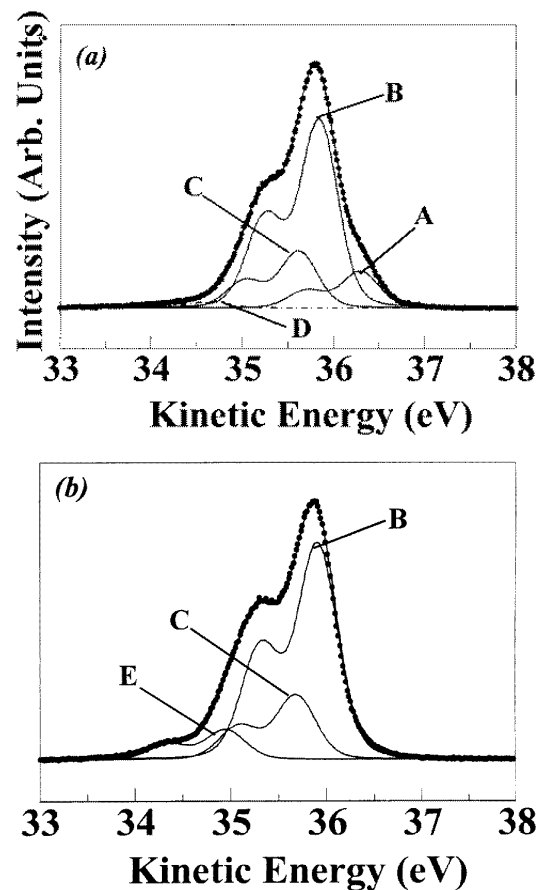

Figure 4. Si 2p core-level photoelectron spectrum from (a) the clean Si(100)-(2 × 1) surface and (b) Si(100)-(2 × 1) after deposition of ~0.2 monolayer C$_{60}$. The photon energy used in each case was 140 eV.

bonding configurations or chemical environments. The most intense peak (B) corresponds to atoms in a bulk configuration, peak C is related to second layer atoms and peak D has been identified as an electron energy loss feature [14, 15]. We focus on peak A, which arises from the 'up' atom of a buckled dimer.

Buckling of dimers on the Si(100)-(2 × 1) is illustrated in figures 2(b)–2(d). A symmetric dimer (figure 2(b)) may adopt a lower energy configuration by buckling, that is raising one and lowering the other atom (figure 2(c)). The energy barrier for thermal activation between the two buckled configurations is low and transitions occur on a time scale less than the acquisition time of an STM image pixel [16]. The STM image is therefore an average of the two configurations and the dimers have a symmetric appearance, apart from a small number which are pinned by defects. However, the effects of buckling may be detected in photoemission which probes the surface on a much shorter time scale. Peak A is related to the 'up' atom of the buckled dimer [15].

Deposition of 0.2 monolayers of C$_{60}$ induces distinct changes in the Si 2p spectrum (see figure 4(b)). Note that for physisorption we would expect no significant differences in the Si 2p spectrum following C$_{60}$ deposition. Peak A is no longer present and a new peak (E) is resolved at lower energy. This shows that the bonding and net

charge on the surface Si atoms have been modified by C_{60}, providing direct evidence for chemisorption of C_{60}. Our results may be explained in terms either of charge transfer into the lowest unoccupied molecular orbital of C_{60} or the formation of Si–C bonds. We believe that the latter explanation is unlikely as the core-level shift induced by C_{60} deposition ($+0.9$ eV) is much greater than expected for Si–C bond formation [17].

We have exploited an anisotropic surface reconstruction to investigate the interactions experienced by an adsorbed molecule on a solid surface. Our results imply that C_{60} is chemisorbed on Si(100) and this is confirmed by photoemission studies.

Acknowledgments

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