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## C<sub>60</sub> adsorption on the Si(110)-(16 × 2) surface

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### Abstract

The interaction of C<sub>60</sub> with the Si(110)-(16 × 2) surface has been studied using a scanning tunnelling microscope (STM). For a submonolayer coverage isolated C<sub>60</sub> molecules are observed with no evidence for a preferential adsorption site. As the coverage is increased, a disordered monolayer is observed and at still higher coverage disordered aggregates are observed which ripen into hexagonally ordered islands. These islands could be disrupted by the STM tip and were desorbed by annealing. Our results show that the interaction between the disordered layer and C<sub>60</sub> islands is weak. However, the first monolayer is strongly bonded to the Si surface and forms a passivating layer which is stable to exposure to atmosphere. © 1998 Elsevier Science B.V.

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### 1. Introduction

The properties of fullerene molecules deposited on the (111) and (100) Si surfaces have recently been the subject of a diverse range of experiments using ultra-high vacuum (UHV) scanning tunnelling microscopy (STM) [1–11]. Properties relating to the adsorption of individual molecules, passivation effects of fullerene overlayers, molecular manipulation experiments and the morphology of fullerene multilayers have been studied. It has been shown that a partially ordered fullerene monolayer is strongly bound to the Si(111)-7 × 7 surface and interacts relatively weakly, via van der Waals forces, with higher layers of C<sub>60</sub> [10,11]. For a submonolayer coverage isolated molecules are observed on both the (111) and (100) surfaces

implying that C<sub>60</sub> undergoes limited diffusion at room temperature [1,3–8].

Recently we have reported a non-equilibrium phenomenon which is observed when C<sub>60</sub> is deposited on Si(110) [12]. The focus of this work is a disorder-order ripening process in which ordered islands progressively grow on a disordered C<sub>60</sub> monolayer over a time scale of several days. In this paper we discuss related properties of these islands and in particular show that they are weakly bound to the disordered monolayer and may be easily disrupted or desorbed. In addition we show that the disordered monolayer is stable to exposure to atmosphere.

### 2. Experimental

A Si(110) sample with dimensions 3 × 7 mm<sup>2</sup> is cut from a p-type wafer and loaded into an ultra-high vacuum system with a base pressure

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$\sim 1 \times 10^{-10}$  Torr. It was then outgassed at  $700^\circ\text{C}$  overnight and annealed at  $1200^\circ\text{C}$  for 60 s. The sample temperature is reduced abruptly to  $1000^\circ\text{C}$  and then decreased in  $100^\circ\text{C}$  steps every 2 min down to  $600^\circ\text{C}$  at which point the heater power is turned off. Pure  $\text{C}_{60}$  powder ( $>99.9\%$ ) is sublimed from a Knudsen cell which is held at  $320^\circ\text{C}$  to give a deposition rate of  $\sim 3$  monolayers per hour. During deposition the sample is held at room temperature and the pressure was less than  $2 \times 10^{-10}$  Torr.

### 3. Results and discussion

Fig 1a shows STM [13] images for a low coverage ( $\sim 10^{-3}$  monolayer) of  $\text{C}_{60}$  molecules. The parallel rows running in the  $[1\bar{1}2]$  direction form the “ $16 \times 2$ ” reconstruction [14]. The height difference between the bright and dark rows is 0.19 nm and the width between bright rows is 5 nm. There is another equivalent domain which runs in the  $[\bar{1}12]$  direction. This reconstruction has been the subject of several STM studies and several different models have been proposed for the detailed atomic configuration on this surface [14–18].  $\text{C}_{60}$  appears as bright circular features in the topographic STM image. We have analysed the distribution of adsorption sites for images such as Fig. 1a. There is a slightly higher probability for molecules to be adsorbed on the upper ( $\sim 60\%$ ) as compared with the lower (40%) terraces of the “ $16 \times 2$ ” reconstruction. Of the molecules on the upper terrace approximately 50% are adsorbed close to the centre of a row so that there is no apparent overlap of the molecule with the row edge, while the other 50% are adsorbed at sites so that they appear in the STM images to intersect with the edge of a row. Of the molecules adsorbed on the lower terrace  $\sim 70\%$  are adsorbed at the row centre. This point may be understood in terms of simple steric arguments since the spherical  $\text{C}_{60}$  molecule may not be placed within 0.6 nm of a 0.2 nm upward step. From our data it is clear that there are many possible adsorption sites for  $\text{C}_{60}$  on the  $\text{Si}(110)$ -“ $16 \times 2$ ” surface, and there is no evidence that  $\text{C}_{60}$  diffuses at room temperature.

Fig. 2 shows an STM image following further

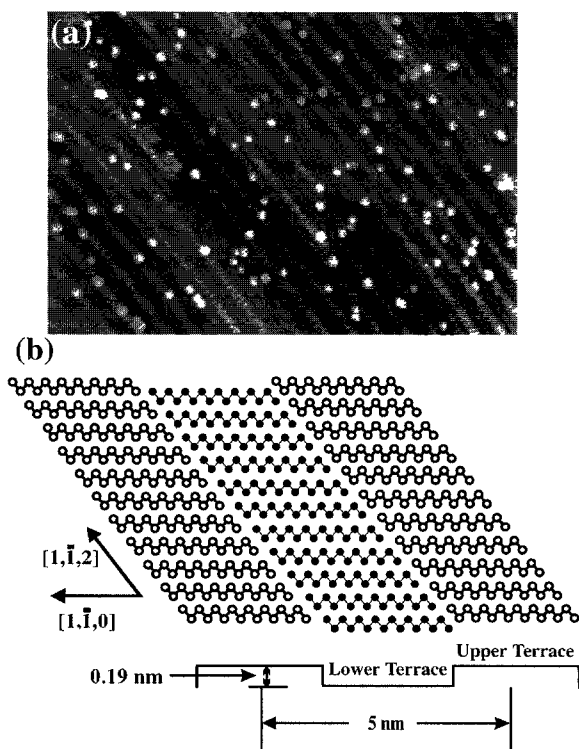


Fig 1 (a) An image of  $100 \times 70 \text{ nm}^2$  (sample voltage 3 V, tunnel current 0.35 nA) of  $\text{Si}(110)$ -“ $16 \times 2$ ” following deposition of  $\sim 10^{-3}$  monolayer of  $\text{C}_{60}$ . The “ $16 \times 2$ ” structure consists of parallel pairs of upper (bright row) and lower (dark row) terraces. (b) A schematic diagram of the terraces of the “ $16 \times 2$ ” reconstruction. The periodicity measured along the  $[1\bar{1}1]$  direction, perpendicular to the row, is 5 nm and the step height between upper and lower terraces is 0.19 nm. The filled and empty circles represent the unreconstructed positions of atoms on the lower and upper terraces

deposition of  $\text{C}_{60}$ . The coverage in Fig. 2 is 0.65 monolayers, where 1 monolayer is taken to correspond to the molecular density observed for a hexagonally close-packed layer with intermolecular separation equal to that observed in bulk  $\text{C}_{60}$ , 1.005 nm [19]. The rows of the underlying  $\text{Si}(110)$ -“ $16 \times 2$ ” may also be resolved in the image. The distribution of  $\text{C}_{60}$  molecules on the surface shows no evidence of long range order with molecules in 4-, 5- and 6-fold coordination. This disordered monolayer is therefore qualitatively different from those formed on either of the other principal Si surfaces which exhibit large regions which are well

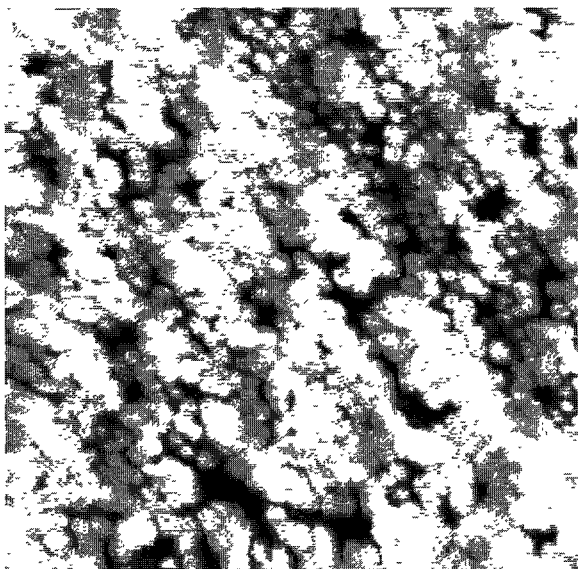


Fig 2 An STM image ( $40 \times 40 \text{ nm}^2$ , sample voltage 3 V, tunnel current 0.3 nA) of the first monolayer of  $\text{C}_{60}$  molecules on  $\text{Si}(110)$ -“ $16 \times 2$ ” reconstruction.  $\text{C}_{60}$  forms a disordered termination to the Si surface. The rows of the underlying “ $16 \times 2$ ” reconstruction are also visible.

ordered. However, we show below that there are similarities in the interaction of  $\text{C}_{60}$  with  $\text{Si}(110)$ -“ $16 \times 2$ ” and that of  $\text{Si}(111)$ - $7 \times 7$  [1,10,11] relating to the relative strength of the interaction of the first  $\text{C}_{60}$  monolayer and the underlying Si as compared with higher layers in a  $\text{C}_{60}$  multilayer.

The surface morphology following further deposition of up to one monolayer of  $\text{C}_{60}$  has been discussed in a recent paper [12] and shows a number of interesting kinetic effects. Fig. 3 was taken shortly ( $\sim 1 \text{ h}$ ) after deposition of 0.3 monolayers on a disordered monolayer. This image shows disordered second layer  $\text{C}_{60}$  islands distributed randomly on the disordered  $\text{C}_{60}/\text{Si}(110)$  layer. The height of disordered  $\text{C}_{60}$  islands corresponds to one layer ( $\sim 0.9 \text{ nm}$ ) and their typical width is  $\sim 20 \text{ nm}$ . Over a period of weeks these disordered islands decay while islands which show a high degree of ordering progressively ripen [12]. The disordered monolayer which is strongly bound to the  $\text{Si}(110)$  surface remains unchanged over this period.

Fig. 4a shows the surface morphology after the deposition of a total of 3.3 monolayers and the

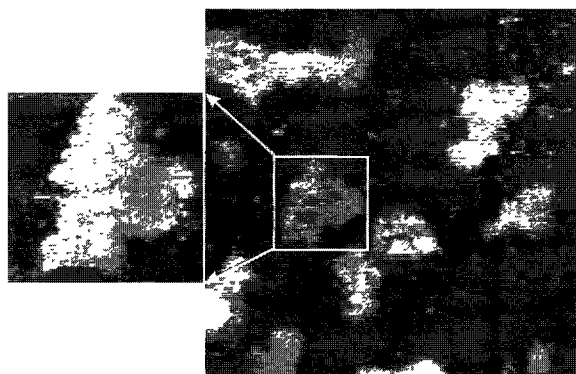


Fig 3 Taken after depositing 0.3 monolayers of  $\text{C}_{60}$  on the disordered monolayer. The height of a disordered island corresponds to one layer. The left STM image ( $25 \times 25 \text{ nm}^2$ , sample voltage 3.5 V, tunnel current 0.05 nA) shows a higher magnification of an island in the right STM image ( $100 \times 100 \text{ nm}^2$ , sample voltage 4 V, tunnel current 0.2 nA).

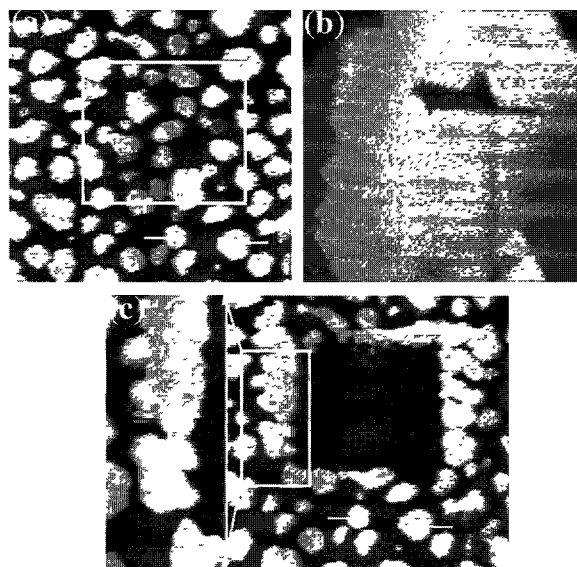


Fig 4 (a) A  $400 \times 400 \text{ nm}^2$  (sample voltage 3.5 V, tunnel current 0.1 nA) image of multilayer ordered  $\text{C}_{60}$  islands. All of the ordered islands are 3 or more monolayers high. (b) A high magnification STM image of an island ( $40 \times 40 \text{ nm}^2$ , sample voltage 3 V, tunnel current 0.04 nA). (c) Shows the disruption of the ordered islands in the white box shown in (a) ( $400 \times 400 \text{ nm}^2$ , sample voltage 3.5 V, tunnel current 0.1 nA, magnified area  $90 \times 200 \text{ nm}^2$  same scan parameters). The arrows in (a) and (c) identify islands unaffected by the disruption.

completion of the ripening process. The height of the ordered islands (measured from the top of the lowest disordered  $C_{60}$  monolayer) is 3 or more layers. The islands are clearly faceted with edges intersecting at an angle close to  $120^\circ$ . Fig. 4b shows a high magnification ( $40 \times 40 \text{ nm}^2$ ) STM image of a typical ordered island and reveals a highly ordered hexagonal close-packed arrangement of  $C_{60}$  molecules with an intermolecular spacing, equal, within experimental error, to the value observed in bulk  $C_{60}$ . Also apparent in Fig. 4b is the presence of dislocation which may be picked out by considering a circuit around the unfilled "hole" in the upper central part of Fig. 4b. Note the presence of a terrace step emanating from the left-hand side of the "hole". Starting from the top of this step it is possible to move around the hole on the same terrace and encounter the bottom of the same step. We found no preferential alignment of the hexagonal facets with the principal axes of the underlying reconstructed surface.

Under certain scanning conditions the STM tip interacted strongly with the  $C_{60}$  islands; compare Fig. 4a and Fig. 4c. The parameters used to acquire these images were sample bias,  $V_s = 3.5 \text{ V}$ , and tunnel current,  $I = 0.1 \text{ nA}$ . Between the acquisition of these images the tip was scanned in the central  $200 \text{ nm}$  square highlighted in Fig. 4a using parameters,  $V_s = 1.2 \text{ V}$  and  $I = 1 \text{ nA}$ . Increasing the tip current and reducing the sample voltage results in a reduction of the tip-sample separation and consequently gives rise to a much higher tip/sample interaction. As a result the  $C_{60}$  molecules in the islands in the centre of Fig. 4a are displaced to the edges leaving the first disordered monolayer intact. The rows of the " $16 \times 2$ " reconstruction are also unaffected by the removal of the  $C_{60}$  islands and are clearly resolved in Fig. 4c. Using the islands marked by arrows for registration it is clear the shapes of islands in the region surrounding the highlighted area have been unaffected. Interestingly, there are some islands at the edge of the highlighted region which have been partially removed. For these islands the portion which has remained in place has not been significantly changed. Compare, for example, the lower border of the island at the bottom of the highlighted area above the island identified by an arrow in Fig. 4a

and Fig. 4c. This implies that the islands have been disrupted and broken up rather than moved as a cohesive unit as described for  $C_{60}$  islands on  $\text{NaCl}(001)$  [20].

Our results imply that the bonding between  $C_{60}$  islands and the first disordered  $C_{60}$  layer is relatively weak, whereas the interaction between the Si and the first layer is stronger. To investigate the relative strength of these interactions further we have annealed a sample which has been prepared in a similar way to that shown in Fig. 4. After annealing at  $\sim 200^\circ\text{C}$  the ordered islands are completely desorbed leaving only the disordered monolayer terminating the  $\text{Si}(110)$ -" $16 \times 2$ " surface as shown in Fig. 5a. This provides further evidence for a rather weak interaction between the  $C_{60}$  islands and the disordered monolayer. We have been unable to remove the disordered monolayer by annealing at high temperatures (up to  $600^\circ\text{C}$  after which the surface is very difficult to image, due, we believe, to the decomposition of the  $C_{60}$ ).

The results described above relating to modification of  $C_{60}$  multilayers by STM scanning and annealing are very similar to those described in a recent study on  $\text{Si}(111)$ - $7 \times 7$  [10,11]. For  $\text{Si}(111)$ - $7 \times 7$  it has been shown that  $C_{60}$  bonds strongly to the Si surface but higher layers of  $C_{60}$  bond relatively weakly, via the van der Waals interaction, to the lowest  $C_{60}$  layer. Our results imply a similar effect for the  $\text{Si}(110)$ -" $16 \times 2$ ".

Also observed for the  $\text{Si}(111)$ - $7 \times 7$  surface is a passivation effect due to the  $C_{60}$  monolayer which is bound to the Si surface. We have found a similar result for the  $\text{Si}(110)$ -" $16 \times 2$ " surface. After pre-

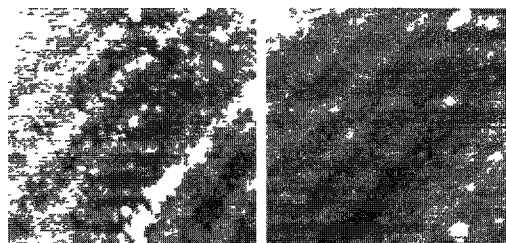


Fig. 5 (a) Taken after removal of islands by annealing at  $\sim 200^\circ\text{C}$  ( $30 \times 30 \text{ nm}^2$ , sample voltage  $3.5 \text{ V}$ , tunnel current  $0.1 \text{ nA}$ ) (b) Shows the surface after exposure to atmosphere ( $30 \times 30 \text{ nm}^2$ , sample voltage  $3.5 \text{ V}$ , tunnel current  $0.1 \text{ nA}$ )

paring a monolayer terminated Si(110)-“ $16 \times 2$ ” sample as shown in Fig. 5a we expose the sample to atmosphere for  $\sim 30$  min (Fig. 5b) and then re-load the sample into UHV. Following exposure and a low temperature anneal ( $\sim 200^\circ\text{C}$ ) to remove physisorbed material the sample surface has an appearance which is essentially unchanged from that observed prior to exposure. In addition the rows of the “ $16 \times 2$ ” are still clearly resolved implying that the Si has not undergone extensive oxidation. This implies that as for Si(111)- $7 \times 7$  the presence of a  $\text{C}_{60}$  monolayer inhibits oxidation.

#### 4. Conclusion

In conclusion we have investigated the properties of  $\text{C}_{60}$  on Si(110)-“ $16 \times 2$ ”. With regard to annealing, response to manipulation and the passivating effect of a monolayer these properties show great similarities with  $\text{C}_{60}$  on Si(111)- $7 \times 7$  and are a result of a strong interaction between the first  $\text{C}_{60}$  layer and the Si and a much weaker interaction between this layer and higher layers of  $\text{C}_{60}$ .

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