C$_{60}$ adsorption on the Si(110)-(16 × 2) surface

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Abstract

The interaction of C$_{60}$ with the Si(110)-(16 × 2) surface has been studied using a scanning tunnelling microscope (STM). For a submonolayer coverage isolated C$_{60}$ 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$_{60}$ 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 tunneling 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$_{60}$ [10,11]. For a submonolayer coverage isolated molecules are observed on both the (111) and (100) surfaces implying that C$_{60}$ undergoes limited diffusion at room temperature [1,3–8].

Recently we have reported a non-equilibrium phenomenon which is observed when C$_{60}$ 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$_{60}$ 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$^2$ is cut from a p-type wafer and loaded into an ultra-high vacuum system with a base pressure
~1 x 10\(^{-10}\) Torr. It was then outgassed at 700°C overnight and annealed at 1200°C for 60 s. The sample temperature is reduced abruptly to 1000°C and then decreased in 100°C steps every 2 min down to 600°C at which point the heater power is turned off. Pure C\(_{60}\) powder (> 99.9%) is sublimed from a Knudsen cell which is held at 320°C to give a deposition rate of ~3 monolayers per hour. During deposition the sample is held at room temperature and the pressure was less than 2 x 10\(^{-10}\) Torr.

3. Results and discussion

Fig. 1a shows STM [13] images for a low coverage (~10\(^{-3}\) monolayer) of C\(_{60}\) molecules. The parallel rows running in the [112] direction form the “16 x 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 [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]. 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 (~60%) as compared with the lower (40%) terraces of the “16 x 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 ~70% are adsorbed at the row centre. This point may be understood in terms of simple steric arguments since the spherical 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 C\(_{60}\) on the Si(110)-“16 x 2” surface, and there is no evidence that C\(_{60}\) diffuses at room temperature.

Fig. 2 shows an STM image following further deposition of 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 C\(_{60}\), 1.005 nm [19]. The rows of the underlying Si(110)-“16 x 2” may also be resolved in the image. The distribution of 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...
ordered. However, we show below that there are similarities in the interaction of C_{60} with Si(110)-"16×2" and that of Si(111)-7×7 [1,10,11] relating to the relative strength of the interaction of the first C_{60} monolayer and the underlying Si as compared with higher layers in a C_{60} multilayer.

The surface morphology following further deposition of up to one monolayer of C_{60} has been discussed in a recent paper [12] and shows a number of interesting kinetic effects. Fig. 3 was taken shortly (~1 h) after deposition of 0.3 monolayers on a disordered monolayer. This image shows disordered second layer C_{60} islands distributed randomly on the disordered C_{60}/Si(110) layer. The height of disordered C_{60} islands corresponds to one layer (~0.9 nm) and their typical width is ~20 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 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
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°. Fig. 4b shows
a high magnification (40 × 40 nm²) 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 V, and
tunnel current, I=0.1 nA. Between the acquisition
of these images the tip was scanned in the central
200 nm square highlighted in Fig. 4a using para-
eters, V_s=1.2 V and I=1 nA. Increasing the tip
current and reducing the sample voltage results in
a reduction of the tip–sample separation and con-
sequently 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 × 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
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 pre-
pared in a similar way to that shown in Fig. 4
After annealing at ~200°C the ordered islands are
completely desorbed leaving only the disordered
monolayer terminating the Si(110)-“16 × 2” sur-
face 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 mono-
layer by annealing at high temperatures (up to
600°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 modifi-
cation of C_{60} multilayers by STM scanning and
annealing are very similar to those described in a
recent study on Si(111)-7 × 7 [10, 11]. For
Si(111)-7 × 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 Si(110)-“16 × 2”.

Also observed for the Si(111)-7 × 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 Si(110)-“16 × 2” surface. After pre-

Fig. 5 (a) Taken after removal of islands by annealing at
~200°C (30 × 30 nm², sample voltage 3.5 V, tunnel current
0.1 nA). (b) Shows the surface after exposure to atmosphere
(30 × 30 nm², sample voltage 3.5 V, tunnel current 0.1 nA).
paring a monolayer terminated Si(110)-“16 × 2” sample as shown in Fig 5a we expose the sample to atmosphere for ~30 min (Fig. 5b) and then re-load the sample into UHV. Following exposure and a low temperature anneal (~200°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 × 2” are still clearly resolved implying that the Si has not undergone extensive oxidation. This implies that as for Si(111)-7 × 7 the presence of a C₆₀ monolayer inhibits oxidation.

4. Conclusion

In conclusion we have investigated the properties of C₆₀ on Si(110)-“16 × 2”. With regard to annealing, response to manipulation and the passivating effect of a monolayer these properties show great similarities with C₆₀ on Si(111)-7 × 7 and are a result of a strong interaction between the first C₆₀ layer and the Si and a much weaker interaction between this layer and higher layers of C₆₀.

Acknowledgements

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References

[13] The STM, electronics and software were provided commercially by Oxford Instruments SPM Group
[14] E J van Loenen, D Dijkmamp, A J Hoeven, J Microsc 152 (1988) 487, these authors discuss the nomenclature of “16 × 2” and point out that it is inconsistent with conventions for assigning the periodicity of reconstructions