Double Domain Solid C_{60} on Si(111)7×7

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We have grown fcc crystalline islands of C_{60} on a clean Si(111)7×7 surface. Scanning tunneling microscopy reveals that the islands are oriented primarily in two distinct directions independent of the island height and size. We show that this is a result of the pinning of C_{60} molecules at the corner holes associated with a disorder-to-order transition at the interface. Interlayer molecular interactions play a vital role in the process. The presence of two distinct island orientations is a manifestation of the formation of double domain solid C_{60} on the Si(111)7×7 surface.

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The epitaxial growth of C_{60} on semiconductor and other substrates has attracted much attention following the advance in synthesizing abundant quantities of pure fullerenes [1]. While it is well established that the interaction in crystals of C_{60} is governed by the van der Waals forces [2], fundamental questions about the nature of the interaction at the semiconductor-C_{60} interfaces remain unanswered. Do substrate atoms interact in concert with C_{60} molecules as a whole or do they form covalent bonds with just a few of the nearest carbon atoms within each C_{60} molecule? In either case, how can we best describe the interaction force and its strength?

On GaAs(110), Li *et al.* [3] observed that at submonolayer coverage, C_{60} molecules form monolayer islands that are well ordered and commensurate with the substrate. Their results indicate that C_{60} has fairly high mobility on the surface due to its weak interaction with the substrate. On Si(100), on the other hand, Hashizume *et al.* [4] showed that the sticking probability for C_{60} is much higher and that although island formation begins after the first disordered layer is completed, ordered fcc islands are only found above the third layer. Stronger still is the interaction between C_{60} molecules and the Si(111)7×7 surface. Neither of these two groups observed any ordered structures of C_{60} on Si(111)7×7 [5,6]. These examples indicate that the strength of the interfacial interaction varies appreciably for different semiconductor surfaces.

In this Letter we show that crystalline islands of C_{60} can, in fact, be grown on the Si(111)7×7 substrate. More surprisingly, these C_{60} islands orient themselves primarily in two distinct directions independent of their height or their size. We shall demonstrate that these two preferred orientations are clear manifestations of the formation of a double domain C_{60} solid on the Si(111)7×7 surface. The process leading to such a unique structure involves a disorder-to-order interface transition in which interplanar molecular interactions play an indispensable role. Our observations suggest that the force binding the C_{60} molecules to the semiconductor substrates is comparable to the van der Waals forces between the molecules of the C_{60} solid in general, but it is extremely sensitive to the detailed local atomic and molecular configurations.

The experiments were performed in a UHV system equipped with a homemade scanning tunneling microscope and other conventional surface preparation and characterization apparatus. The clean Si(111)7×7 and Si(111)$\sqrt{3}\times\sqrt{3}$ surfaces were prepared by annealing a piece of As doped (0.02 Ω cm) or heavily boron doped (0.001 Ω cm) Si(111) wafer at 1100∼1200 °C. C_{60} (containing 10% C_{70}) molecules were deposited at 0.05–0.1 monolayer (ML) per minute from an effusion cell onto the clean substrate held at ∼200 °C. Although the islands can grow on substrates held at room temperature during deposition, elevation of the substrate temperature enhances their growth.

All the tunneling images were acquired at a constant current set between 20 to 50 pA with the tip biased at -2.0 to -3.5 V relative to the sample. These biases exceed the 1.5 eV band gap of fcc C_{60} [2], and stable electron tunneling from the tip to the empty conduction band of the crystal was achieved. Special care was taken to avoid repeatedly sampling only a few prominent islands. Before making measurements on the island of interest we first imaged its overall shape to ensure that it had not already been studied. In addition, our tunneling microscope allowed us to position the tip laterally in 5 μm steps within a total range of 1 cm, and hence to achieve a global sampling of the specimen under study. The orientation of the principal axis of an imaged lattice was obtained by measuring the angle of a corresponding row of atoms or molecules with respect to the scan direction. Thermal drift and creeping of the piezo scanner could introduce errors into these measurements. To minimize the effect of piezo creep, we always allowed the scanner to settle before molecular resolution images were acquired after moving the tip from one island to the next. Typically, the acquisition time for each image was about 1 min, so that the thermal drift was relatively small. Nevertheless, after the initial sampling of some forty islands, we implemented a cancellation scheme [7] which reduced the drift error to less than 0.5°.

Figure 1(a) shows a typical C_{60} island and its surrounding terraces on a Si(111)7×7 surface. Higher-resolution images show that the C_{60} molecules on the terraces are largely random. Indeed, for submonolayer coverage C_{60} molecules exhibit only a slight preference for certain adsorption sites and the ad-molecule layer overall has no spatial ordering [5,6]. Step edges play no special role in the process of binding the molecules to the substrate. These observations indicate that a fairly strong interaction exists between C_{60} and the Si(111)7×7. Upon completion of the first monolayer, small disordered C_{60} islands can grow up to three layers and their boundaries exhibit chaotic patterns. The associated low energy electron diffraction patterns suggest that the Si(111)7×7 surface reconstruction persists beneath the deposited C_{60} layers, in good agreement with the recent x-ray study [8].

Ordered crystalline islands begin forming when local coverage exceeds 3 ML. The islands are characterized by well-defined facets which are nearly perpendicular to the growth plane. Figure 1(b) is a high-resolution image of the top layers of two adjacent islands. Within each island the C_{60} molecules form the closed hexagonal array that is the (111) face of the fcc crystal. Measurements taken from a large number of islands of various heights give an average nearest-neighbor distance of ~10 Å, and a spacing between the (111) planes of ~8.5 Å. The brighter species in the image are the C_{70} impurities within the top C_{60} layer [9]. The most striking feature evident in this image is the relative rotation of the $[\bar{1}10]$ axes between these two islands. When referenced to the $[\bar{2}11]$ axis of the underlying Si crystal, the left island has its $[\bar{1}10]$ axis rotated ~11° clockwise and the right one ~11° counterclockwise.

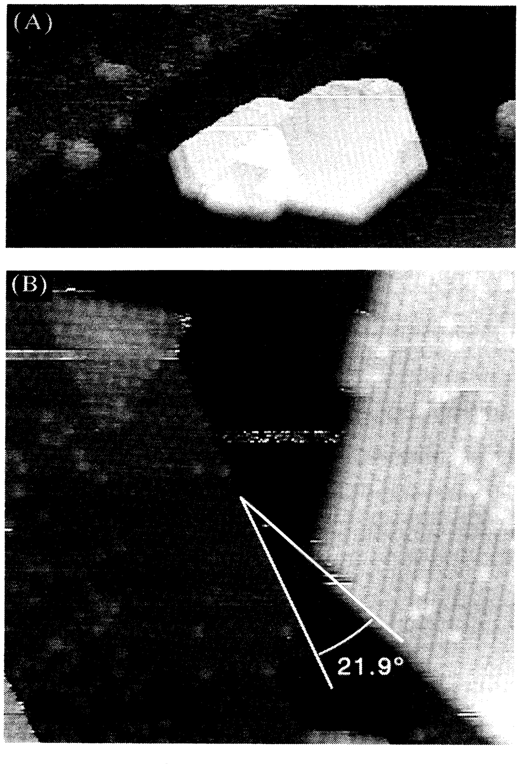

FIG. 1. (a) 3100 Å×1700 Å STM image of a 61 Å height C_{60} island on the Si(111)7×7 surface. (b) 380 Å×360 Å STM image of the top (111) planes of two islands with $[\bar{1}10]$ axes rotated ~22° from each other.

In order to determine whether the above phenomenon is a localized incident or a general property of this system, we measured the orientation of more than sixty individual islands. The size of the islands ranged from hundreds to thousands of angstroms across and from three to forty layers in height. Figure 2(a) is a histogram of the distribution of the $[\bar{1}10]$ crystal orientation relative to the $[\bar{2}11]$ axis of the underlying silicon lattice for all the islands we measured. The solid bars represent data corrected for linear drift, while the open bars represent data for which drift compensation [7] was not applied. Small nonlinear effects of the piezo scanner may still be present in the data. A conservative estimate of the error bar for each angular measurement in the figure is ±2°. We conclude from Fig. 2(a) that the C_{60} islands on the Si(111)7×7 surface are sorted, with roughly equal proportion, into two primary orientations with the $[\bar{1}10]$ axes rotated either +11° or −11° from the bulk Si$[\bar{2}11]$ axis. The width of the distribution cannot simply be accounted for by the errors in the measurement, and is currently under further investigation.

Are the characteristics observed here unique to C_{60} islands grown on the Si(111)7×7? To answer this important question we have carried out a parallel experiment

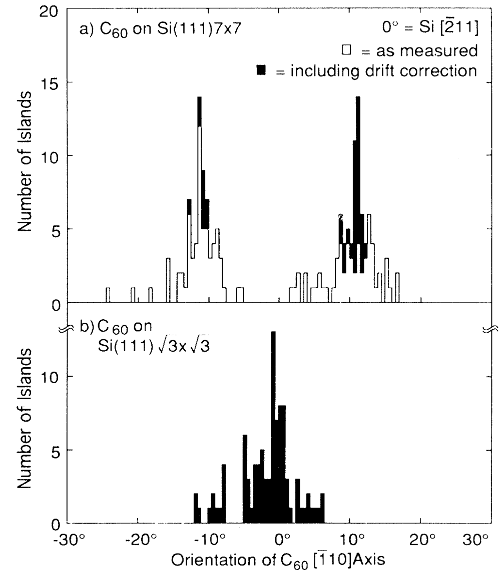

FIG. 2. $\frac{1}{2}$ degree bin histogram of the $[\bar{1}10]$ orientation of C_{60} islands on (a) the Si(111)7×7 surface and (b) the boron-induced Si(111)$\sqrt{3}\times\sqrt{3}$ surface.

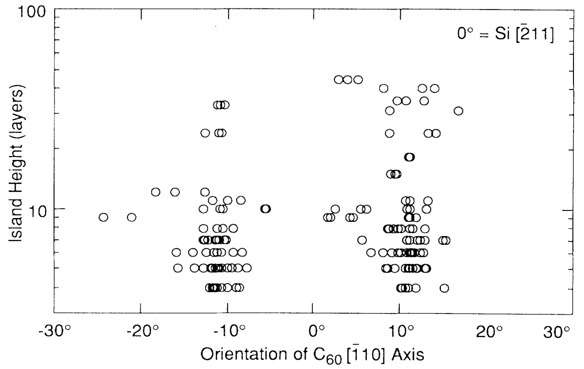

FIG. 3. Island height vs the orientations of the [$\bar{1}10$] axis of C$_{60}$ islands on Si(111)7×7.

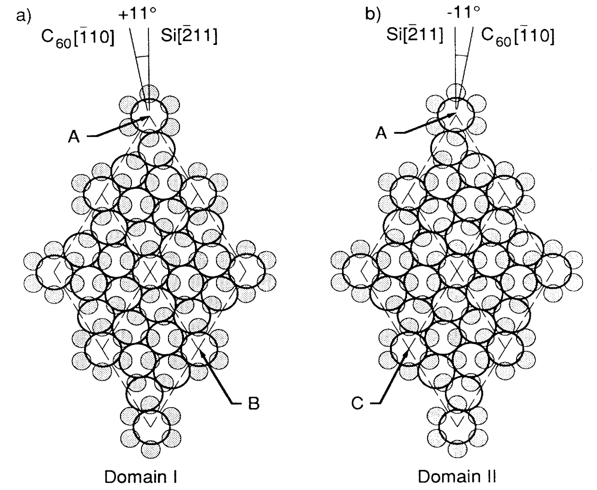

FIG. 4. Proposed double domain interfacial structure for C$_{60}$ crystals grown on Si(111)7×7.

on a Si(111) sample with a boron-induced $\sqrt{3}\times\sqrt{3}$ surface reconstruction. As in the case of Si(100) [4], the first layer of C$_{60}$ molecules does not exhibit any long-range ordering. Disordered islands begin to form after the first layer is completed, and an ordered fcc C$_{60}$ crystal structure is observed starting from the third layer. However, in contrast to the case of Si(111)7×7, only one primary orientation of the C$_{60}$ [$\bar{1}10$] axis orientation is found for the Si(111)$\sqrt{3}\times\sqrt{3}$. The data in Fig. 2(b) represents measurements of the [$\bar{1}10$] orientation of 31 individual C$_{60}$ islands on a Si(111)$\sqrt{3}\times\sqrt{3}$ substrate. Clearly, the central peak of the angular distribution is well aligned with the bulk Si [$\bar{2}11$] orientation.

Finally, we examined the possible correlation between the [$\bar{1}10$] orientation and the height of the C$_{60}$ islands on Si(111)7×7. The height is determined from the line cuts made on the image of each island. Figure 3 displays the island height as a function of the island orientation. Clearly, the orientation of the [$\bar{1}10$] axis of the C$_{60}$ islands is independent of the island height. This implies that the islands grow epitaxially and that their orientations are originated from the interface.

Collectively, our results point to a simple and startling fact that the $+11°$ or $-11°$ rotation of the [$\bar{1}10$] axis of the C$_{60}$ islands with respect to the bulk [$\bar{2}11$] direction is unique to the Si(111)7×7 surface. The most peculiar aspect of our observation might be the orientations of these C$_{60}$ islands with respect to a substrate which possesses a threefold rotational symmetry. It is quite tempting to regard these two C$_{60}$ island orientations as the manifestation of a double domain epitaxial growth of C$_{60}$ on the Si(111)7×7 surface.

In Fig. 4, we illustrate a proposed interfacial structure in which the smaller shaded circles represent silicon adatoms in the top layer of the substrate and the heavy open circles represent C$_{60}$ molecules in the first interfacial layer. The characteristic corner holes of the 7×7 reconstructed silicon surface fall at the intersections of the dashed lines outlining the surface unit cell. Careful inspection of the Si adatom configuration reveals two important features. First, in Fig. 4(a) the angle between the long diagonal or [$\bar{2}11$] axis of the 7×7 unit cell and a line *AB* diagonally spanning *two* 7×7 unit cells is precisely 10.89°. Second, the spacing between the two corner holes located at *A* and *B* is 71.1 Å, or roughly 7 times the nearest distance of the C$_{60}$. Keeping these in mind we quickly arrive at the interfacial structure shown in Fig. 4(a), in which every corner hole is symmetrically filled with one C$_{60}$ molecule and the 7×7 periodicity is still preserved. There are seven C$_{60}$ molecules in each 7×7 unit cell. A distinct domain with an otherwise identical interface structure can be generated by simply rotating the top C$_{60}$ array clockwise 22° about molecule *A* so that the row of C$_{60}$ molecules along *AB* falls along the line *AC* in Fig. 4(b). Quite remarkably, all the C$_{60}$ molecules in this seemingly complex structure reside in one of only two different binding configurations shown in Figs. 5(a) and 5(b). One C$_{60}$ molecule is at the center the corner hole, while the remaining six C$_{60}$ molecules rest squarely atop bridge sites between two silicon adatoms and are equivalent. We thus unveil the origin of the two observed

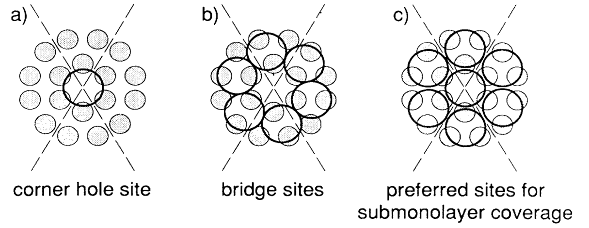

FIG. 5. (a) and (b) show the two basic configurations for the proposed interfacial structure beneath C$_{60}$ crystals, and (c) shows the preferred bonding sites for C$_{60}$ on Si(111)7×7 at submonolayer coverage.

C_{60} crystal orientations—the formation of double domain solid C_{60} on the Si(111)7×7 surface. A somewhat similar structure can be invoked to understand the formation of the single domain C_{60} on the boron-induced Si(111)$\sqrt{3}\times\sqrt{3}$ surface [10].

The lack of long-range ordering in the initial stage of growth suggests that the interface structure proposed here can be stabilized only if it is terminated by additional ordered layers of C_{60}. The bridge site configuration occupied by the majority of interfacial C_{60} molecules is quite likely under strain, for, at submonolayer coverage, these molecules favor a more relaxed configuration as shown in Fig. 5(c) [5]. They lie symmetrically atop triads of three Si adatoms. The larger intermolecular distance in the latter configuration leads to diminished attractive forces between the molecules and hence precludes long-range ordering. As the deposition progresses, these isolated molecules are bridged by additional layers of C_{60}, and the short-range van der Waals coupling among C_{60} molecules increases. When the coupling finally reaches a critical value, an interfacial disorder-to-order transition is triggered and the two distinct domains are formed as a result of the pinning of C_{60} molecules at the corner holes. This process requires a delicate balance between the intermolecular interaction and the molecule-substrate interaction. We therefore conclude that the forces binding the C_{60} molecules to the Si substrate are of the same order of magnitude as the van der Waals forces between the molecules in a fcc C_{60} solid. The fact that the corner-hole configuration prevails over all other configurations during the ordering tells us that the strength of the interaction is a sensitive function of the local atomic arrangement.

In conclusion, we have demonstrated a unique process that leads to the formation of double domain solid C_{60} on a Si(111)7×7 surface. For this van der Waals solid on a semiconductor substrate, interplanar molecular interaction is a crucial factor which helps to transform a disordered interface into an ordered one. This viewpoint unifies all the work on C_{60} growth on semiconductor surfaces that is available to date, and perhaps can be extended to understand the interfacial interactions between C_{60} and metal, ionic crystal, and other surfaces as well.

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[7] To eliminate the linear drift error, we immediately follow each image of a particular region with a second scan of the same region using a reversed scanning sequence. The error introduced by thermal drift in the angle of a particular row of atoms or molecules with respect to the scan direction can then be canceled, at least to first order, by averaging the row angles that appear on these two images.

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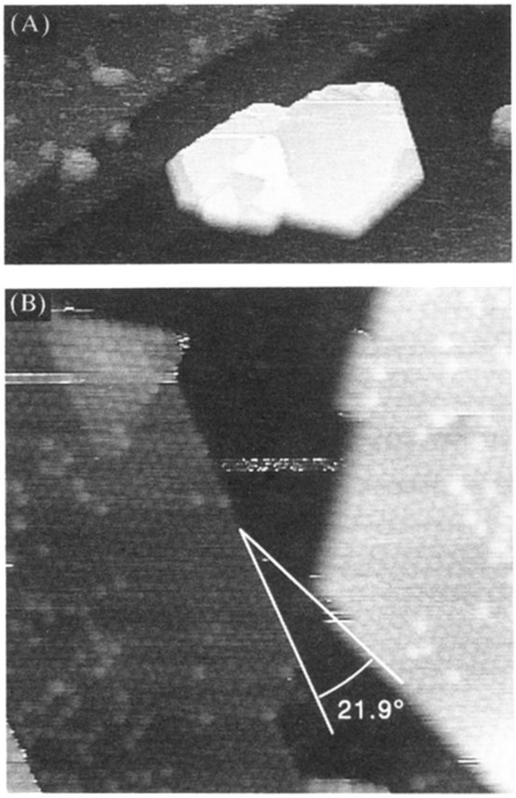
[9] Our assignment is based on the following evidence: (a) The bright species are in perfect registry with the rest of the layer and their apparent height is only 3 Å above the darker surrounding molecules and hence they cannot be ad-molecules; (b) their position is stable and never changes even after numerous scans are taken over them; and (c) they account for ~10% of the total molecules in the top layer, which equals the percentage of impurity C_{70} in the C_{60} sources used in the present experiment.

[10] Hang Xu, D. M. Chen, and W. N. Creager (to be published).



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