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Double domain ordering and selective removal of C_{60} on Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$

M. D. Upward, P. Moriarty, and P. H. Beton
Department of Physics, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom

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We have used ultra-high-vacuum scanning tunneling microscopy to investigate the interaction of C_{60} with the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surface. C_{60} molecules bond preferentially at defect sites and step edges and form double domain islands that are ordered relative to the bulk Si in exactly the same positions as previously observed for Si(111)-7×7. We discuss the dependence of molecular packing on surface geometry and reactivity and show that the islands are removed by annealing leaving Si(111) terraces coexisting with a network of strongly bound C_{60} molecules adsorbed at step edges. [S0163-1829(97)51628-6]

The ordering of C_{60} molecules on various different substrates has been investigated widely over recent years using ultra-high-vacuum (UHV) scanning tunneling microscopy (STM). C_{60} is free to diffuse on many surfaces and as a result forms highly ordered islands even when the total coverage is less than a single monolayer. The molecular ordering is generally hexagonal with an intermolecular separation which is close to that of C_{60} bulk crystals, although some departures are observed due to a competition between molecule-molecule and molecule-surface interactions.[1–4] This behavior is observed for C_{60} on GaAs(110) (Ref. 1) and noble metal surfaces.[2–4] For Si surfaces exposed to a low coverage of C_{60} isolated molecules are observed.[5–7] This implies that C_{60} is more strongly bound to the surface and unable to diffuse freely. Nevertheless, at higher coverages close to a single monolayer, C_{60} can form an ordered layer.[8–10] The ordering on Si(111)-7×7 is hexagonal with two different domains which make an angle of ±11° to the Si$[\bar{2}11]$ direction.[8,9] This has been called ‘‘double domain ordering’’[11] and might be expected, in principle, when C_{60} is deposited on any hexagonally ordered substrate with a misorientation angle determined by the commensurability of the C_{60} molecular spacing and the lattice constant of the underlying surface. However, the example of C_{60} on Si(111)-7×7 remains the only report published to date.

In this paper we describe a series of experiments on the interaction of C_{60} with the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surface. This surface provides an interesting contrast to the highly reactive Si(111)-7×7 since it has a different surface geometry and exhibits pronounced differences in surface reactivity. We find that C_{60} diffuses freely on this surface and adsorbs preferentially at step edges and defects. Further deposition of C_{60} leads to the formation of highly ordered islands which exhibit double domain ordering. The molecular ordering relative to the bulk Si is exactly the same on the Si(111)-7×7 and Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surfaces despite the clear differences in the molecule-surface interactions. These differences are highlighted by annealing the sample which causes the ordered islands to desorb, but leaves C_{60} remaining at step edges on the surface. After annealing at higher temperatures Ag is removed from the surface, leaving domains of Si(111)-7×7 surrounded by a network of C_{60} molecules which remain adsorbed on step edges.

Our experiments were carried out using (5×3) mm^2 pieces of a Si(111) p-type wafer. Samples are introduced into the UHV system and outgassed at ~800 °C overnight. The samples were flash annealed at ~1200 °C for ~120 s and then allowed to cool to room temperature. This processing results in a clean (7×7) reconstructed surface with a low defect density. The Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surface was prepared by depositing Ag onto the Si sample which was heated in the range 500–600 °C. Electrochemically etched polycrystalline W wire tips were used for STM (Ref. 12) imaging. The tips were cleaned in the UHV system by electron beam heating. C_{60} was sublimed onto a Si/Ag sample held at room temperature with a typical deposition rate of ~0.05 monolayers/min.

Figure 1(a) shows an STM image of a surface following the deposition of ~0.5 monolayers of C_{60}. The left-hand side of the image shows the hexagonally ordered Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surface. This surface has been the subject of many STM investigations over the last decade following original work by Wilson and co-workers[13] and van Loenen and co-workers.[14] Many models have been proposed for the atomic configuration with a consensus now emerging in favor of the honeycomb-chain-trimer model proposed by Takahashi and co-workers[15] and shown in Fig. 2(a). The bright features on the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ [see contrast enhanced area of Fig. 1(a)] correspond to the Ag trimers and the dark regions to the Si trimers [see Fig. 2(a)]. For a review and comparison of these models see Jia and co-workers.[16]

Also apparent in Fig. 1(a) (right-hand side) is a hexagonally ordered island of C_{60}. The intermolecular spacing in this island is 1.01±0.01 nm. The principal axes of the C_{60} and Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ are oriented at an angle which has been measured and averaged over many islands and found to be 11°. Due to the symmetry of the arrangement it is clear that an equivalent packing at an angle −11° is also possible. The two configurations at ±11° correspond to different domains. Figure 1(b) shows two islands whose principal axes are oriented at 22° and correspond to the two possible domains. From images such as Fig. 1(a) it is possible to establish the registry of the C_{60} relative to the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$. Figure 2(b) shows the molecular positions above a honeycomb network for which each

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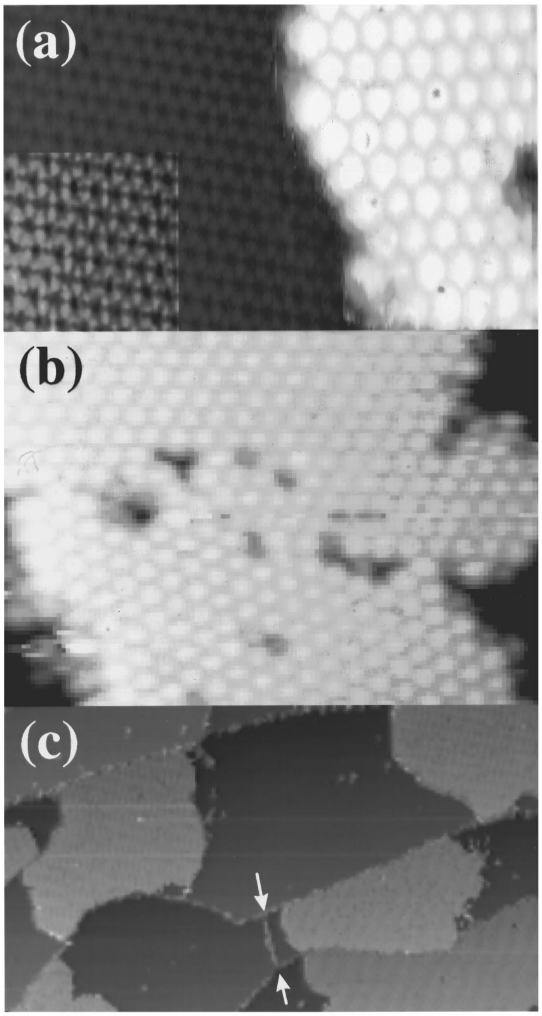

FIG. 1. (a) An STM image (15 nm×9 nm; sample bias -1.5 V, 0.2 nA) of a C_{60} island on the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surface. The bottom left corner has a different contrast to clarify the structure of the surface; (b) an image (19 nm×13 nm, -3 V, 0.3 nA) illustrating the double domain ordering of the C_{60} islands. The angle between the principal axes of the islands in the upper and lower parts of the image is 22°; (c) large scale image (190 nm ×110 nm; 2 V, 0.5 nA) showing islands that have grown to fill the entire width of a terrace. Also visible are isolated molecules bound to defects, molecules adsorbed at step edges and at an antiphase boundary (marked by arrow).

vertex is a Ag trimer and a Si trimer sits at the center of each hexagon [see Fig. 2(a)]. Thus $\frac{1}{3}$ of the molecules sit directly above a Si trimer and $\frac{2}{3}$ above a Ag trimer. For this arrangement the angle between the principal axes of the C_{60} and Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ is $\cos^{-1}(3\sqrt{3}/\sqrt{28})=10.9°$ and the intermolecular separation is equal to $a_0\sqrt{7}=1.016$ nm (a_0 is the lattice constant of the unreconstructed surface, 0.384 nm) in excellent agreement with our experimental data.

The separation of C_{60} molecules in equivalent binding sites in the ordered double domains is $a_0\sqrt{63}$, while the separation of adjacent molecules is $a_0\sqrt{7}$. In the double domains formed on Si(111)-7×7, C_{60} molecules form a hexagonal array with principal axes oriented at 10.9° to the Si[2,1,1] direction. Molecules are adsorbed at the corner holes of the reconstruction and at bridge sites between adatoms. The separation along the principal axis of the ordered layer between molecules adsorbed at corner hole sites, that is the periodicity of the surface layer, is $a_0 7\sqrt{7}$. However, the separation between adjacent molecules is $a_0\sqrt{7}$, equal to the value observed for the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surface. Noting that the principal axis of the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surface is aligned with Si[2,1,1] it is clear that although the surface periodicity of C_{60} layers on these two surfaces is quite different, their arrangement relative to the *bulk* Si is identical. This is an unexpected result which appears, on initial consideration, to imply that intermolecular interactions are the dominant factor in determining surface order.

To determine if this is the case or whether the C_{60}/surface interactions lead to the same ordering merely by coincidence we consider the problem of stacking a hexagonally ordered layer of C_{60} molecules with intermolecular spacing a_c on the unreconstructed Si(111) surface. This surface is also hexagonally ordered so that there is an angle of 60° between its lattice vectors **a** and **b** each of which has modulus a_0. A regular hexagonal arrangement of molecules can occur provided there exist integers l, m, and n which satisfy the condition,

$$l a_c = |m\mathbf{a}+n\mathbf{b}| = a_0\sqrt{(m^2+n^2+mn)}.$$

The orientation of the domains relative to the Si[$\bar{2}$,1,1] axis is given by $\Theta=\cos^{-1}\{(m+n)\sqrt{3}/[2\sqrt{m^2+n^2+mn}]\}$. The experimentally observed packing corresponds to the set of integers $l=1$, $m=1$, and $n=2$. This gives a value for a_c which is slightly larger than a_b, the intermolecular spacing in bulk C_{60}, 1.005 nm.[17] However, the difference is small, $\delta a=(a_c-a_b)/a_b=1\times10^{-2}$. In fact there is alternative packing for which $l=2$, $m=3$, and $n=3$ which gives $a_c=a_0\sqrt{27}/4=0.99$ nm with a corresponding value of $\delta a=-9\times10^{-3}$. Assuming that the intermolecular potential is the same for adsorbed molecules as for free molecules,[18] we use the potential given by Girifalco[19] and find that the energy for the ($l=1$, $m=1$, $n=2$) packing is actually slightly higher than ($l=2$, $m=3$, $n=3$) by ~0.5 meV per molecule. We therefore argue that the ($l=1$, $m=1$, $n=2$) configuration is stabilized by molecule/surface interactions and that it is energetically favorable for molecules to sit directly above trimers as in Fig. 2(b). Note that for the ($l=2$, $m=3$, $n=3$) configuration a maximum of 50% of adsorbed molecules could sit above trimers.

The implication of this argument is that the C_{60}/Si(111)-7×7 and C_{60}/Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ interactions both stabilize the same molecular configuration. This also implies that other reconstructions formed on Si(111) could stabilize different configurations, for example ($l=2$, $m=3$, $n=3$). This possibility is extremely interesting since for $m=n$ we have $\Theta=0$ and so the domains are exactly aligned with Si[2,1,1] leading to *single* domain, i.e., true epitaxial growth.

We have stressed above that the interactions of individual molecules and the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ and Si(111)-7×7 surfaces show extreme differences. In the remainder of this paper we discuss data illustrating these differences. This evidence is provided by an investigation of the

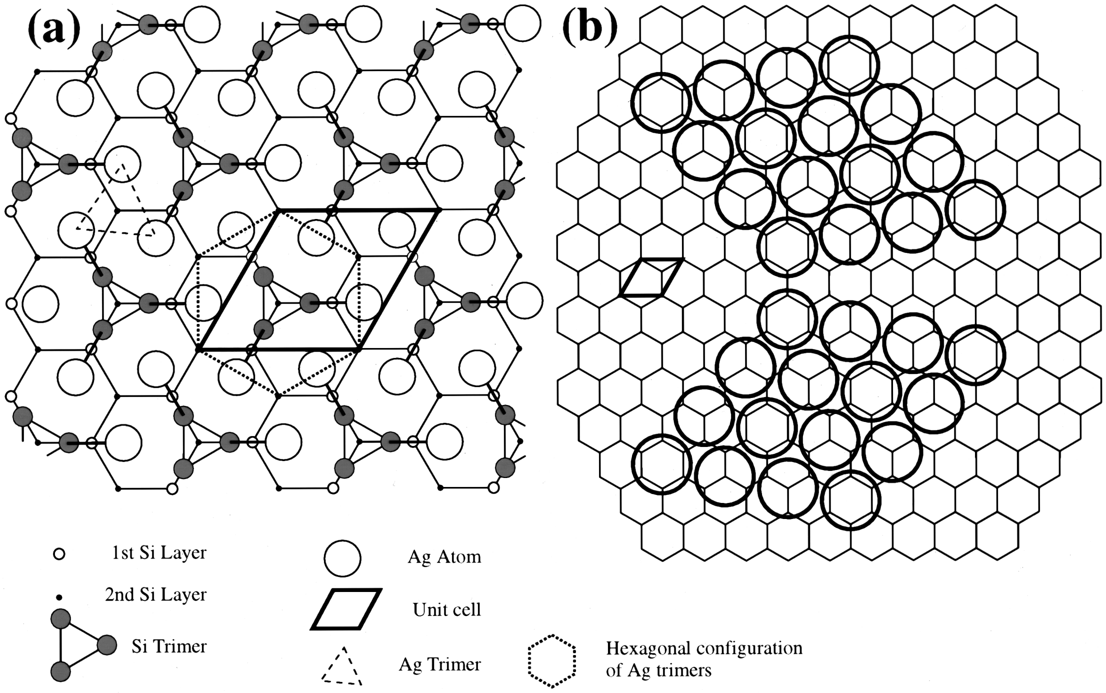

FIG. 2. (a) Schematic diagram of the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surface; (b) schematic diagram of the two domains of C_{60}. The underlying hexagonal lattice is the unit cell indicated in (a) by a dotted hexagon. Each vertex of the hexagon corresponds to a Ag trimer and the center of each hexagon corresponds to a Si trimer.

diffusion of molecules on Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ and the response of the C_{60} terminated Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surface to annealing.

A lower magnification image of the surface showing the general morphology of the surface is shown in Fig. 1(c). The large bright areas correspond to the C_{60} islands and the darker regions the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$. There are also noticeable bright lines and spots. The lines result predominantly from C_{60} molecules bonding at step edges, however, they are also bound to antiphase boundaries formed on the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ (Refs. 20 and 21) resulting in a row of pinned molecules [see Fig. 1(c)]. The spots in

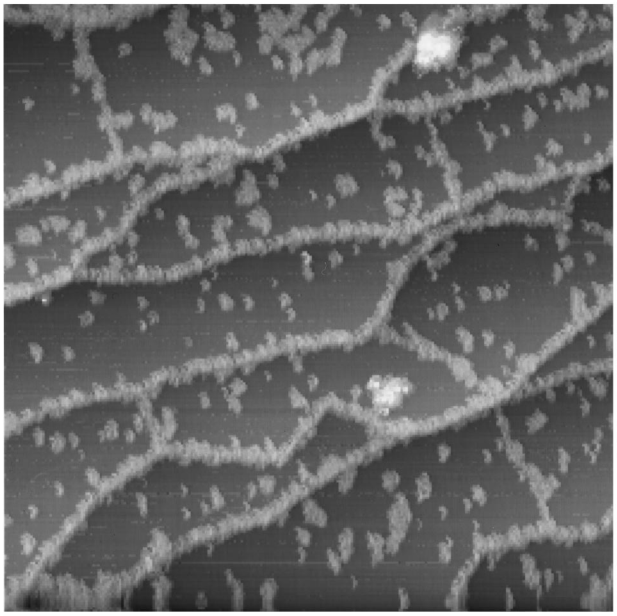

FIG. 3. STM image (300 nm×300 nm; sample bias 2 V, 0.3 nA) of the surface which results when a sample with 1 monolayer of C_{60} is annealed at 260 °C. There is a pattern of step edges lined with C_{60} molecules plus isolated groups of molecules on the terraces. The underlying surface is Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$.

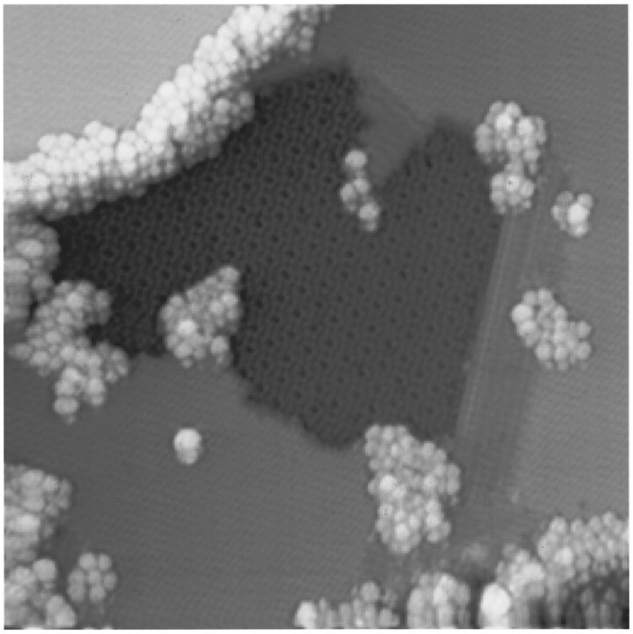

FIG. 4. STM image (50 nm×50 nm; sample bias 3 V, 0.2 nA) showing the partial removal of Ag following annealing at ~400–500 °C. In the center of the image is an area which has been reconverted to Si(111)-5×5. The remaining area is identical to that shown in Fig. 3.

Fig. 1(c) are individual or small groups of C_{60} molecules located at defect sites of the Ag surface. It is likely that defects and step edges provide preferential bonding sites due to the presence of dangling bonds.[20,21] These results show that C_{60} is free to diffuse across the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surface. This is completely different to the behavior on Si(111)-7×7 for which diffusion is not observed.

Defects and terrace steps provide preferential bonding sites on the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surface. When a C_{60}/Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surface as shown in Fig. 1 is annealed at 260 °C it is found that the ordered islands desorb, but the C_{60} molecules remain bound to the step edges and surface. This results in the surface shown in Fig. 3 which shows that the molecules at steps, domain boundaries, and terrace defects are still present, but the islands have been removed. The underlying Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surface remains unaffected. In addition, there appear to be more molecules at the steps and defects as compared with a surface immediately following deposition [see Fig. 1(c) and Fig. 3]. This increase is presumably due to additional molecules bonding at these sites rather than desorbing.

If the surface shown in Fig. 3 is annealed at ~400°–500 °C (Ref. 22) it is possible to remove Ag from the surface but leave the C_{60}. Figure 4 shows an image of a sample which has undergone a partial removal of Ag. In regions where the Ag is removed the surface converts to a 5×5 or 7×7 reconstruction, with areas bounded with C_{60} molecules, and isolated clusters of molecules. Figure 4 shows such an area in which the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ reconstruction is resolved on the lower terrace, and the (5×5) reconstruction is clearly visible in the ''hole,'' Wan and co-workers[23] have discussed the phase diagram for the Ag/Si(111) system as a function of temperature and Ag coverage. They find that Ag desorbs at 550 °C and the $\sqrt{3}\times\sqrt{3}$ and 7×7 reconstructions coexist above 400 °C. In addition they find that the surface completely reverts to a 7×7 reconstruction after annealing at 700 °C. The mixed phase of 5×5, 7×7, and $\sqrt{3}\times\sqrt{3}R30°$ which we observe coexists with C_{60} adsorbed at step edges and our results are broadly consistent with Wan and co-workers.[23]

We emphasize that this behavior is quite different to annealing of ordered layers of C_{60} adsorbed on Si(111)-7×7. For this surface the monolayer is strongly bound and cannot be desorbed.[24]

In conclusion, we have investigated C_{60} molecules deposited on Ag terminated Si(111). Molecular islands are formed which are ordered in a double domain configuration. A comparison with C_{60} islands formed on Si(111)-7×7 shows that the ordering of molecules is the same relative to the bulk Si despite pronounced differences in adsorbate/substrate interaction. These differences are highlighted by annealing at successively higher temperatures which results in a Si(111) surface with a network of C_{60} molecules adsorbed on step edges and defects.

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