

## Disorder-Order Ripening of C<sub>60</sub> Islands

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C<sub>60</sub> forms nonequilibrium disordered islands on the Si(110) surface which progressively decay over several weeks. Over the same period ordered islands with a minimum height of three monolayers are observed to grow. This process has been monitored using an ultrahigh vacuum scanning tunneling microscope operating at room temperature. We discuss these observations in terms of the van der Waals interaction between C<sub>60</sub> molecules and argue that the initial formation of the disordered phase is kinetically driven. [S0031-9007(97)02858-5]

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There are several nonequilibrium processes which determine the evolving morphology of a surface during crystal growth. Under appropriate conditions islands of adsorbed material first nucleate and grow. Following this a phenomenon known as ripening or coarsening may occur during which the smaller islands decay while the larger islands grow. Ripening may be considered to be a relaxation of the adsorbed islands towards the true equilibrium configuration in which the island boundaries and their associated free energy are minimized. This is known as Ostwald ripening, and it has been shown that in this regime the average island size has a universal power law dependence on time [1]. Although much of the original work in this area was developed to explain three dimensional ripening phenomena, many of these ideas have recently been applied to the formation and relaxation of two dimensional islands [2–6]. A common aspect of most of this work [3–6] is that the configuration of atoms and molecules in the growing and decaying droplets are identical and, since they are produced by homoepitaxial growth, correspond to the crystal structure of the substrate.

In this Letter we report a new nonequilibrium growth phenomenon which is observed when C<sub>60</sub> is deposited on a disordered substrate. Disordered islands of C<sub>60</sub> are nucleated and we then observe an evolution of the surface morphology over the course of several weeks. Although there are some similarities with conventional ripening the growing and decaying islands have quite different molecular ordering. In particular, while the decaying islands are highly disordered, the growing islands consist of C<sub>60</sub> molecules close packed in an ordered hexagonal arrangement. Our results imply that the disordered clusters do not correspond to an equilibrium configuration of molecules and that their formation is driven by the kinetics of the deposition process and the disorder of the substrate.

In our experiments C<sub>60</sub> is adsorbed on a clean Si(110) surface. A 7 × 3 mm<sup>2</sup> piece of a *p*-type wafer (resistivity ~ 1 Ω cm) was loaded into an ultrahigh vacuum (UHV) system, outgassed at 700 °C and annealed at 1200 °C for 1–2 min. Scanning tunneling microscopy (STM) [7] images of the surface at this stage reveal the

characteristic “16 × 2” reconstruction [8,9]. C<sub>60</sub> is then deposited from a Knudsen cell at a deposition rate of ~3 monolayers per hour.

Figure 1 shows an STM image following deposition of just under 1 monolayer of C<sub>60</sub>. The corrugations running diagonally spaced by ~5 nm correspond to the rows (height 0.19 nm) of the underlying reconstructed Si(110) surface [8,9]. The C<sub>60</sub> molecules appear as circular features and are distributed in a disordered arrangement across the surface. It is possible to identify C<sub>60</sub> molecules in four-, five-, and six-fold coordination. There is a striking absence in Fig. 1 of either isolated second layer C<sub>60</sub> molecules or any evidence for the formation of second layer C<sub>60</sub> islands. This implies that C<sub>60</sub> molecules which are incident on parts of the surface already terminated by C<sub>60</sub> are free to diffuse to areas of clean Si where they are preferentially adsorbed.

The monolayer coverage of C<sub>60</sub> on Si(110) is qualitatively different to that observed on either of the other principal Si surfaces on which ordered layers are formed [10–12]. However, the C<sub>60</sub>/Si(110) monolayer shows many similarities with recently reported properties [13] of the C<sub>60</sub>/Si(111) monolayer in that it is strongly bound

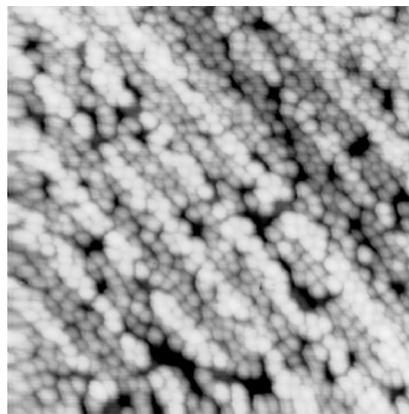


FIG. 1. Constant current (sample voltage,  $V = 3$  V,  $I = 0.3$  nA) STM image of Si(110) after deposition of slightly less than 1 monolayer of C<sub>60</sub>. Image size is 40 nm × 40 nm.

to the Si, but forms a chemically unreactive termination which interacts weakly with further adsorbed layers [14]. The molecules in the second and higher layers interact with each other and also the first layer  $C_{60}$  via the van der Waals interaction, while the first layer is bound strongly to the Si. This accounts for the ease of diffusion of second layer  $C_{60}$  molecules.

This monolayer plays a critical role in our experiments by providing a stable disordered template which acts as a substrate on which further  $C_{60}$  layers may be deposited. Following a further deposition of  $\sim 0.35$  monolayers of  $C_{60}$  second and third layer islands are formed which evolve over several weeks. This evolution is the focus of our experiments and is illustrated in Figs. 2(a)–2(d). Images taken shortly after deposition [Fig. 2(a)] show contrast levels corresponding to the disordered  $C_{60}$  monolayer discussed above (darkest level) and second and third layer islands (lighter levels) which have a diffuse appearance and a typical width of  $\sim 15$  nm. The density of islands is  $\sim 2 \times 10^3 \mu\text{m}^{-2}$ . The morphology gradually changes with time. After 10 h [Fig. 2(b)] islands which are 3 monolayers high are observed (in the remainder of our paper island height is measured from the top of the disordered monolayer so this corresponds to 4 monolayers above the Si surface). These islands are clearly faceted with edges intersecting at an angle close to  $120^\circ$ . The faceted islands grow at the expense of the second layer islands over the following weeks [see Figs. 2(c) and 2(d) taken after 2 and 15 days] and become progressively larger until all the second layer islands have disappeared [Fig. 2(d)].

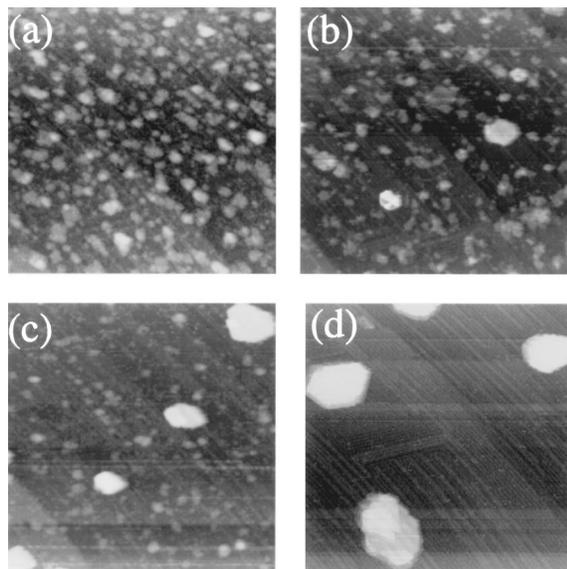


FIG. 2. Constant current STM images ( $300 \text{ nm} \times 300 \text{ nm}$ ) of Si(110) taken at various times [(a) 2 h, scan parameters 3.5 V, 0.1 nA, (b) 10 h, 3.0 V, 0.2 nA, (c) 2 days, 3.0 V, 0.1 nA, (d) 15 days, 3.5 V 0.1 nA] after the deposition of 0.35 monolayers of  $C_{60}$  on the disordered  $C_{60}$  monolayer/Si(110). The darkest contrast level in all images is the disordered  $C_{60}$  monolayer.

The faceting observed for the 3 layer islands as compared with the diffuse appearance of lower layer islands implies a difference in molecular ordering. This is confirmed by higher magnification images. Figure 3(a) shows an STM image of a diffuse layer island in which the random molecular arrangement may be resolved. In contrast, Figs. 3(b) and 3(c) show images of a faceted island which reveal a highly ordered hexagonal arrangement of molecules with an intermolecular spacing equal, within experimental error, to the value observed for fullerene crystals, 1.005 nm. The orientation of the hexagonal ordering varies from island to island and is not related to the principal axes of the underlying reconstructed surface.

Our images show that the lateral dimensions of the faceted islands increase with time from an average value of 20 nm at 10 h to 50 nm at 15 days. In addition, their average height increases from  $\sim 3$  to  $\sim 4$  monolayers. We do not observe any faceted islands less than 3 monolayers high.

Figures 2(a)–2(d) are typical of changes observed in a number of experiments and are a small selection of the images acquired during one particular run. To consider these effects quantitatively we have measured the height and area of a representative sample of ordered and disordered islands from images taken at various times. Typical areas which are analyzed are  $\sim 200 \times 400 \text{ nm}^2$  which can contain up to 100 islands. We then calculate the total volume of the disordered and ordered islands. Assuming a constant density the volume of an island is proportional to the number of constituent molecules. In Fig. 4 we show the fraction of molecules in ordered and disordered islands as a function of time. Data points from three different experimental runs are shown, and the results show a high degree of reproducibility. The time dependence of the fraction of molecules in disordered islands is described well by an exponential decay,  $N_d = \exp(-t/\tau_d)$ . A single parameter fit gives  $\tau_d = 41.7$  h.

To illustrate the height difference between ordered and disordered islands we show in Fig. 5 histograms of the proportion of adsorbed molecules in islands of various heights at several times during an experimental run. It

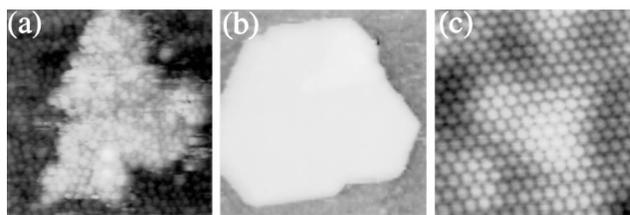


FIG. 3. High magnification images of (a) a disordered island ( $25 \text{ nm} \times 25 \text{ nm}$ , 3.5 V, 0.05 nA); (b) an ordered faceted island ( $60 \text{ nm} \times 60 \text{ nm}$ , 3.0 V, 0.1 nA); (c) a higher magnification scan of the island in image (b) showing the ordering of the  $C_{60}$  molecules ( $14 \text{ nm} \times 14 \text{ nm}$ , 3.0 V, 0.2 nA). The background contrast variation of the ordered layer has an amplitude of  $\sim 0.05$  nm, much smaller than the diameter of  $C_{60}$ , 1.0 nm.

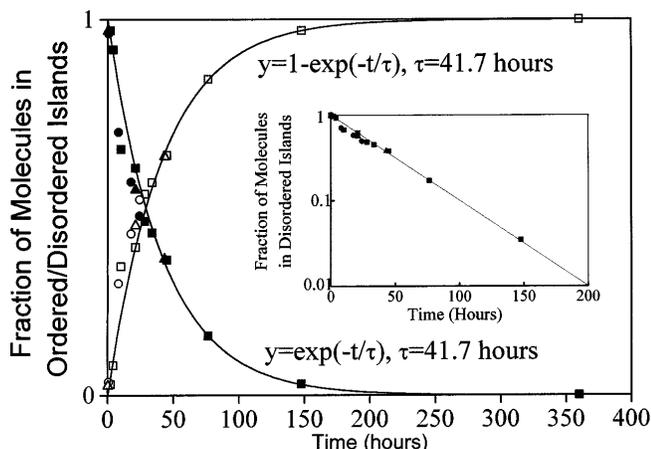


FIG. 4. The fraction of the total adsorbed material in the second and higher layers which is incorporated in disordered (filled symbols) and ordered (open symbols) islands as a function of time. The circles, squares, and triangles are data points taken from different experimental runs.

is clear that all ordered islands have a height of 3 or more monolayers, while most of the disordered islands are 1 or 2 monolayers high.

The effects of weak homogeneous disorder on nucleation and ripening have been considered previously [15,16] but there is currently no theory which is directly related to our experiment. However, it is possible to gain a qualitative understanding from a microscopic perspective. We compare the binding energies of  $C_{60}$  on a hexagonally ordered  $C_{60}(111)$  crystal surface and the disordered  $C_{60}$  termination shown in Fig. 1. A pair of  $C_{60}$  molecules interact via van der Waals forces with a binding energy,  $E_B = 0.27$  eV [17,18]. The interaction potential falls rapidly with separation so that the total binding energy on a  $C_{60}$  terminated surface is given by  $NE_B$ , where  $N$  is the number

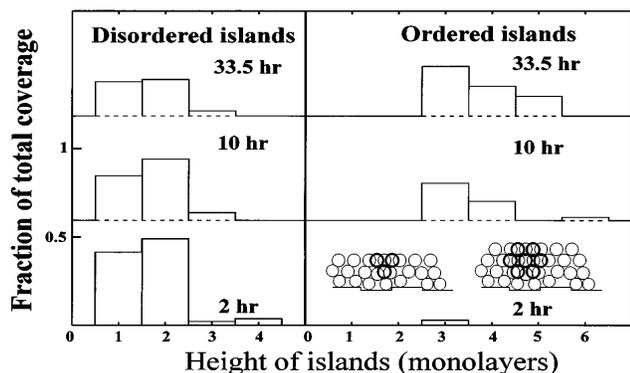


FIG. 5. Histograms of the proportion of material in disordered and ordered islands of various heights at several times. Inset shows a side view of a growing (111) facet at the edge of an island of height (from left to right) 2 and 3 monolayers. The bold circles represent  $C_{60}$  clusters nucleating a new layer on the ordered layers of the growing edge. The step on the substrate represents a row of the “ $16 \times 2$ ” reconstruction.

of nearest neighbors for which the center to center spacing is close to the value observed in bulk  $C_{60}$ . For a single molecule sitting on  $C_{60}(111)$ ,  $N = 3$ . For most adsorption sites on the disordered  $C_{60}$  terminated surfaces shown in Fig. 1  $N$  is also equal to 3, although it is possible, in principle, that sites with  $N = 4$  or 5 could also occur. In the minimum energy trajectory for hopping the  $C_{60}$  molecule remains in contact with two nearest neighbors. The activation energy for hopping,  $E_A$ ,  $\sim 0.6E_B$  [19] for  $C_{60}(111)$  and lies in the range  $0.6E_B \leq E_A \leq E_B$  for a molecule in an adsorption site with  $N = 3$  on the disordered  $C_{60}$  surface. This value is greater than  $kT$  ( $= 25$  meV at room temperature) although it is not sufficiently large to freeze out activated diffusion.

While the activation energy for a *single* molecule is larger when adsorbed on the disordered surface, the binding energy for a pair of molecules will always be lower. Two molecules adsorbed on  $C_{60}(111)$  may be accommodated in adjacent adsorption sites leading to an increase in their coordination from 3 to 4. However, two molecules adsorbed on a disordered  $C_{60}$  surface will in general not be able to take up their equilibrium separation with respect to each other and with the molecules in the layer below. The pair of molecules therefore have a lower activation energy for detachment from each other. Similar remarks apply to larger clusters of molecules. On  $C_{60}(111)$  ordered islands form. The coordination of a molecule at the edge of an island,  $N$  is equal to  $N_n$ , the number of nearest neighbors within the island plus 3 (corresponding to the nearest neighbors in the subsurface layer). The value of  $N_n$  is in the range 1–4 and the activation energy for detachment is  $\sim(N_n + 0.6)E_B$ . In contrast, for a disordered template a molecule in a cluster cannot simultaneously minimize its interaction energy with all of its nearest neighbors. This leads to a lower binding energy at the edges of disordered (as compared with ordered) islands and an exponentially higher rate for detachment. Note that a reduction in the number of nearest neighbors by 1 increases the detachment rate at room temperature by  $\sim \exp(E_B/kT) \approx 5 \times 10^4$ . An important factor in this simple explanation is the high symmetry of the  $C_{60}$  molecule and the consequent lack of directional bonding.

In our model for island formation and decay the first complete monolayer of  $C_{60}$  is strongly bound to the Si(110) surface and forms a disordered substrate for further deposition. Molecules deposited onto this complete monolayer are free to diffuse randomly until they encounter another molecule or group of molecules to which they become temporarily bound. This is the process for nucleation of disordered islands which then occurs on a time scale which is longer than the total deposition time. These molecules diffuse across the surface until they are incident on another island where they are bound. If this new island is also disordered, the process of detachment will be repeated. However, if the

island is ordered, the rate of detachment is exponentially smaller and the molecule will be effectively trapped. Thus the ordered islands gain material and grow at the expense of the disordered islands. The ordered islands may be nucleated at locally ordered areas in the  $C_{60}$  monolayer or alternatively by the spontaneous adoption of an ordered configuration by a cluster of a few adsorbed molecules.

We now present an argument based on kinetics to show that a height of three monolayers is required for an ordered island to grow. Consider the nucleation of new layers on a growing edge which we assume is a  $C_{60}\{111\}$  surface. See inset to Fig. 5 in which nucleating clusters on islands of height 2 and 3 monolayers are shown. The maximum coordination at the edge of a cluster formed on the growing facet is equal to 5 for a cluster on the edge of an island of height 2 monolayers, and 6 for a cluster on the edge of an island of height 3 monolayers [the corresponding values of  $N_n$  (see above) are 2 and 3, respectively]. The maximum energies for detachment,  $E_d$ , from these clusters and disassembly of the nucleated layers on the growing edge will be  $\sim 2.6E_B$  and  $\sim 3.6E_B$ , respectively. Note that these represent upper limits since the molecules incorporated in the lowest layer of the ordered island will experience a competition between in the disordered layers below it and the ordered layers above it. The time scale for detachment,  $T_d$ , is given by  $\nu^{-1} \exp(E_d/kT)$  where  $\nu$  is the characteristic vibration frequency of a  $C_{60}$  molecule at the edge of the cluster. Taking as a value of  $\nu$  the frequency of oscillation of a molecule around the minimum of the Girifalco potential [17],  $5.7 \times 10^{11} \text{ s}^{-1}$ , the upper limits for  $T_d$  are 2.5 s for an island two layers high and  $\sim 10^5$  s on an island three layers high. For growth of an island to proceed  $T_d \gg T_n$ , the average time between the incorporation of new molecules on the growing edge. From our data (density of ordered islands and decay rate) we find that  $T_n \sim 30$  s. A comparison of these time scales reveals that islands require a height of 3 monolayers in order to grow in accord with our experimental observations.

The observation (Fig. 4) that the material in disordered islands decays exponentially implies that the probability for adsorption of  $C_{60}$  on an ordered island is proportional to the amount of material remaining on disordered islands. This in turn implies that the ripening is not diffusion

limited. However, it is not clear whether the rate limiting step is nucleation on the growing edge or detachment from ordered islands.

We have reported a new ripening phenomenon which occurs when  $C_{60}$  is deposited on a disordered surface. Disordered islands are formed initially which then decay at the expense of ordered islands which have a minimum height of 3 monolayers.

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