

# Reports

## Ordered Overlayers of C<sub>60</sub> on GaAs(110) Studied with Scanning Tunneling Microscopy

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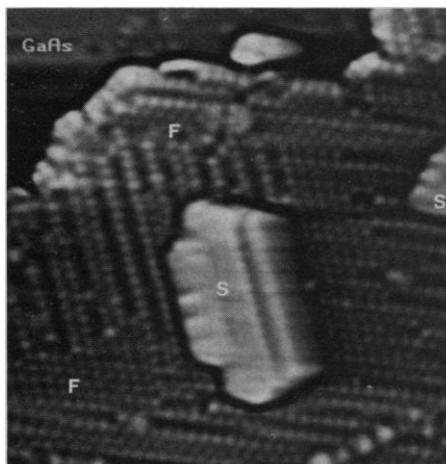
Studies of C<sub>60</sub> overlayer growth on GaAs(110) with scanning tunneling microscopy show large first monolayer islands that are locally well ordered, structurally stable, and commensurate with the GaAs surface owing to molecule-substrate interactions. Within the distorted close-packed structure, two distinct adsorption sites were identified, one of them being elevated because of stress in the C<sub>60</sub> monolayer.

RECENT BREAKTHROUGHS (1) IN the synthesis of C<sub>60</sub>, or buckminsterfullerene (2), have led to studies of the electronic (3, 4) and structural (5, 6) properties of this novel form of carbon in condensed phase. Using scanning tunneling microscopy (STM), Wilson *et al.* (5) have shown mobile hexagonal arrays of mixed C<sub>60</sub> and C<sub>70</sub> that are structurally unstable on Au(111), and these results raise questions about interactions with the support. This report demonstrates that other surfaces can exhibit stronger bonding and that distinct growth structures can be stabilized. STM results for phase-pure C<sub>60</sub> on GaAs(110) reveal large stable monolayer islands derived from distorted close-packed arrays, with distinct bonding sites. We show variations in molecular height that are due to different GaAs(110) surface sites.

The fullerenes were formed by the contact arc method (7, 8), with subsequent separation by solution with toluene. Phase-pure C<sub>60</sub> was obtained by a liquid chromatography process on alumina diluted with mixtures of hexanes. The resulting C<sub>60</sub> was then sublimed in the ultrahigh vacuum STM chamber onto substrates held at 300 K. The pressure remained below  $1 \times 10^{-9}$  torr during growth and quickly recovered to  $6 \times 10^{-11}$  torr when the source was cooled. The amount of material deposited was measured with a quartz crystal thickness monitor and was confirmed by STM images. Atomically ordered GaAs(110) surfaces were prepared by cleaving in situ. STM topographs of the occupied and unoccupied states for GaAs(110) allowed unambiguous determination of the surface orientation (9). They

also allowed a calibration of the length scale.

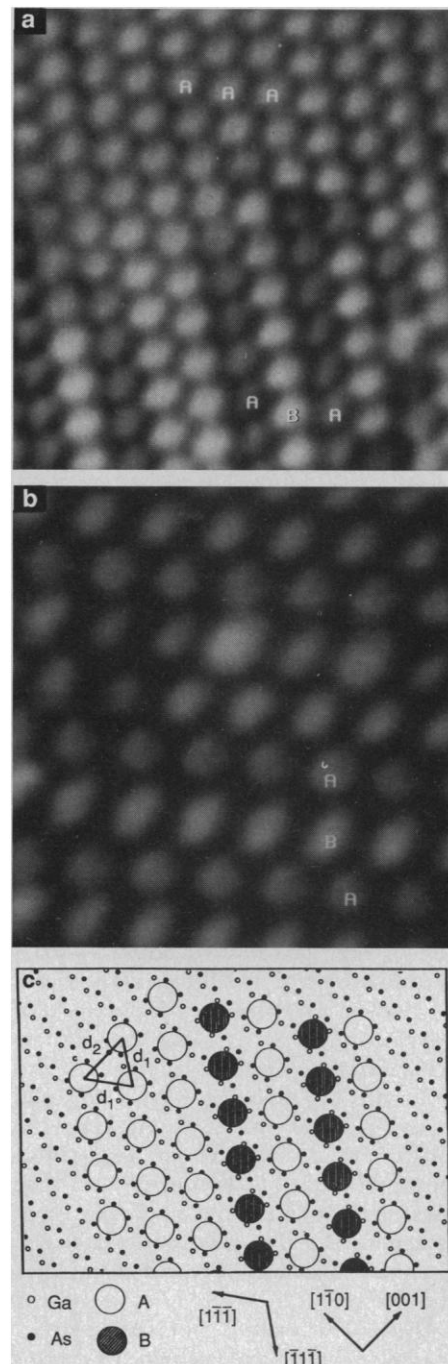
The results of Fig. 1 show that the deposition of  $\sim 0.5$  monolayer of C<sub>60</sub> produced large monolayer-high islands on the GaAs(110) surface. These islands were  $\sim 7$



**Fig. 1.** A  $380 \times 380 \text{ Å}^2$  STM image for  $\sim 0.5$  monolayer of C<sub>60</sub> grown on GaAs(110). Areas marked GaAs, F, and S correspond to the GaAs substrate, the first monolayer of C<sub>60</sub>, and the second monolayer of C<sub>60</sub>, respectively. The GaAs substrate orientations are indicated in Fig. 2c. Protrusions in the first C<sub>60</sub> monolayer represent individual C<sub>60</sub> molecules and appear as bright features.

**Fig. 2.** (a)  $110 \times 110 \text{ Å}^2$  and (b)  $72 \times 72 \text{ Å}^2$  STM topographs of the first monolayer C<sub>60</sub>. (a) depicts two domain types in the molecular layer corresponding to a pure A-site domain (upper portion) and a mixed A- and B-site domain (lower). (c) presents a model of the overlayer growth structure on GaAs(110). Sites A and B in (a) are represented by open and shaded circles. B-site rows in (a) are formed by displacing A-type molecules along the substrate  $[1\bar{1}\bar{1}]$  direction. Such rows can also be formed by displacing A-type molecules along substrate  $[1\bar{1}\bar{1}]$  direction, as shown on the bottom part of a curvature-enhanced STM image (b). The intermolecular distances indicated in (c) are  $d_1 = 9.8 \text{ Å}$  and  $d_2 = 11.3 \text{ Å}$ .

Å in height, measured 500 to 1000 Å in size, and had stable edges that consisted of straight segments. Their existence demonstrates high effective surface mobility of C<sub>60</sub> attributable to weak van der Waals interaction with the substrate. Each protrusion, shown as a bright feature, represents a C<sub>60</sub> molecule. No internal molecular structure was observed, probably because of rotational freedom, as suggested by Wilson *et al.* (5). The average apparent corrugation was  $\sim 0.8 \text{ Å}$  but it depended on the bias voltage and, to a lesser extent, the tunneling current. Planar second-layer arrays of C<sub>60</sub> were also observed (marked S in Fig. 1), as will be discussed elsewhere (10). STM imaging of



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occupied and unoccupied states of  $C_{60}$  revealed no discernible differences in the monolayer structure. For these studies, the sample bias voltages were  $\pm(1.7$  to  $3.0)$  V and typical tunneling currents were 0.5 to 1.2 nA; images shown here for the occupied states were acquired at 1.8 to 2.2 V.

The higher resolution gray-scale STM topograph of Fig. 2a shows that  $C_{60}$  molecules form ordered arrays within large monolayer islands on GaAs(110). Despite the close-packed appearance, the ordered structure in this image does not have a hexagonal symmetry. Instead linear molecular arrays run along a direction that corresponds to the  $[\bar{1}\bar{1}\bar{1}]$  direction of the substrate. The spacing between molecules in this direction is 9.8 Å. Figure 2b represents an image for this same surface in which linear arrays were aligned along the  $[1\bar{1}\bar{1}]$  direction of the substrate. Figure 2, a and b, also shows that the  $C_{60}$  molecules are bonded at different sites of the substrate, as reflected by different brightness. Lines of higher (brighter and larger) molecules, marked as B, along the above-mentioned directions are sandwiched between regular ones (marked A).

Simultaneous imaging of  $C_{60}$  islands and the adjacent substrate made it possible to determine the bonding sites of the overlayer. Figure 2c depicts the observed structure of  $C_{60}$  on GaAs(110). Two different sites, labeled A and B, correspond to open and shaded circles. The A sites, located above Ga atoms and centered on four As atoms, correspond to the darker molecules of Fig. 2a. They are  $\sim 0.8$  Å lower than B sites that are centered on four Ga atoms. The difference in height reflects the intrinsic relaxation of the GaAs(110) substrate itself; that is, the outward shift of As relative to Ga as the bond rotates  $\sim 29^\circ$  while retaining its bulk bond length (9). The upper part of Fig. 2a shows a single domain of A-type character with a  $c(4 \times 2)$  structure with respect to the substrate. In this case, nearest neighbors of  $C_{60}$  along  $[\bar{1}\bar{1}\bar{1}]$  or  $[1\bar{1}\bar{1}]$  have a separation of 9.8 Å, and those along  $[001]$  have a separation of 11.3 Å. In contrast, the lower portion of Fig. 2a reveals a domain with a mixture of A-type and B-type rows, where B-type rows can be seen as a displacement of A-type rows by 2.4 Å along the substrate  $[\bar{1}\bar{1}\bar{1}]$  direction. Such B-type rows can also be formed by displacing A-type molecules along  $[1\bar{1}\bar{1}]$ , as shown in Fig. 2b. The surface lattice structure of GaAs(110), shown in Fig. 2c, determines that such displacement can only produce the two configurations of A-B-A rows depicted in Fig. 2, a and b. Extended B-type domains were not observed.

These STM results demonstrate that  $C_{60}$  growth structures are determined by a bal-

ance between molecule-substrate and intermolecular interactions. A-type domains, dictated by registry with the substrate, have a compressed nearest neighbor distance of 9.8 Å, compared to 10.02 Å (1) or 10.04 Å (11) determined for closed-packed  $C_{60}$ . A remarkable molecule-substrate interaction is revealed by the facts that pure A-type domains exist in an extended area and that both A- and B-sites are essentially commensurate with the GaAs(110) substrate. Whereas previous studies of  $C_{60}$  on Au(111) showed structural instability (5), our results for GaAs(110) show much stronger interaction, with two favored sites. The stability of the  $C_{60}$  monolayer on GaAs(110) and its instability on Au(111) are most likely determined by the strength of molecule-substrate interactions. On the other hand, intermolecular interactions produce large monolayer islands that force molecules upward to B-type sites. Mixed domains with

A-sites and B-sites introduce movement out of the plane, pushing B-site molecules upward, and release stress in pure A-site domains.

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## The Higher Fullerenes: Isolation and Characterization of $C_{76}$ , $C_{84}$ , $C_{90}$ , $C_{94}$ , and $C_{70}O$ , an Oxide of $D_{5h}$ - $C_{70}$

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The toluene extract of the fluffy carbon material produced by resistive heating of graphite contains a variety of molecules larger than  $C_{60}$  and  $C_{70}$  in a total amount of 3 to 4% by weight. Repeated chromatography of this material on neutral alumina has led to the isolation of stable solid samples of  $C_{76}$ ,  $C_{84}$ ,  $C_{90}$ , and  $C_{94}$ . The characterization, which includes mass spectrometry,  $^{13}C$  nuclear magnetic resonance, electronic absorption (ultraviolet/visible) and vibrational (infrared) spectroscopy identifies these all-carbon molecules as higher fullerenes. In addition,  $C_{70}O$ , a stable oxide, has been isolated that is structurally and electronically closely related to  $D_{5h}$ - $C_{70}$ . This compound forms during the resistive heating process and probably has an oxygen atom inserted between two carbon atoms on the convex external surface of the  $C_{70}$  skeleton.

IN A SURPRISING DEVELOPMENT, Krätschmer and Huffman *et al.* (1) reported in 1990 the isolation of macroscopic quantities of the highly stable icosahedral-cage molecule  $C_{60}$  (buckminsterfullerene, soccer ball) (2). This new allotropic form of carbon is obtained from the benzene-soluble fraction of a fluffy soot-like material produced through resistive heating of graphite under inert atmosphere. In ad-

dition to  $C_{60}$ , the soluble extract contains  $C_{70}$  in  $C_{60}$ : $C_{70}$  ratios between 75:25 and 85:15 (3, 4). The two molecules, which are members of a homologous series of hollow closed-cage molecules, the fullerenes (2), are separable by sublimation (5), high-pressure liquid chromatography (HPLC) (6, 7), or liquid gravity chromatography (LC) on alumina (3, 4, 8). The predicted (2) icosahedral symmetry (point group  $I_h$ ) of  $C_{60}$  has been supported by comparison of infrared (IR) and Raman spectra with theoretical predictions (1, 5), by  $^{13}C$  nuclear magnetic resonance ( $^{13}C$  NMR) (3, 4, 9), and by scanning tunneling microscopy (STM) (10). The  $^{13}C$  NMR data support an ellipsoidal cage shape (point group  $D_{5h}$ ) for  $C_{70}$  (3, 4, 8, 11). The photophysical (12) and material properties (13) of the two fullerenes  $C_{60}$  and  $C_{70}$  as

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