

## Langmuir–Blodgett films of the fullerene C<sub>60</sub>

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Langmuir–Blodgett films of the fullerene C<sub>60</sub> have been grown. Either monolayer or bilayer films form, depending on the number of C<sub>60</sub> molecules deposited on the surface of the liquid subbase. The films on substrates of amorphous carbon have an hcp structure with the constants  $a = 1.00 \pm 0.01$  and  $1.63 \pm 0.02$  nm. © 1994 American Institute of Physics.

The fullerene C<sub>60</sub> and its condensate (fullerite) are being studied actively, with the goal of synthesizing new carbon structures and using them to develop promising functional materials with unique properties of interest to physicists and engineers.<sup>1,2</sup> The discovery of high- $T_c$  superconductivity in fullerites doped with alkali metals has spurred intense research on the fullerenes and also on compounds based on them.<sup>3–5</sup>

Because of the particular structural features and high symmetry of the C<sub>60</sub> molecule, the closest packing is achieved even in fullerite films of submicron thickness.<sup>6</sup> There is accordingly physical interest in developing a fine technology for growing C<sub>60</sub> films and in studying the structures and properties of the material in the film state. The literature contains many results on C<sub>60</sub> films grown by deposition on various substrates.<sup>1,2,6,7</sup> Another possibility, in principle, is to grow molecular films of C<sub>60</sub> by the Langmuir–Blodgett method.

The C<sub>60</sub> molecules, which are rigid, ideally hydrophobic spheres (buckyballs), are not in the category of genuinely amphiphilic molecules, which are the molecules usually selected for growing Langmuir–Blodgett (LB) films.<sup>8,9</sup> Still, it has been reported<sup>9,10</sup> that these molecules are capable of forming stable Langmuir monolayers on the surface of a water subbase. However, previous efforts to grow LB films on solid substrates have not succeeded.<sup>9–11</sup> The C<sub>60</sub> monolayers which have been formed on the surface of a water subbase have been rigid. They break when a substrate is moved through the monolayer, and they can be transferred onto a substrate only in the form of islands of the solid phase.

Our purposes in the present study were to produce LB films of the fullerene of various thicknesses, starting at a monolayer, and to study the morphology and structures of these films.

The fullerene C<sub>60</sub> (99.95% pure) was dissolved in benzene ( $10^{-4}$  M). The resulting solution was deposited on the surface of doubly distilled water (pH 6.0) in an area of 0.034 m<sup>2</sup>. Isotherms linking the surface pressure  $\pi$  at the interface on the barrier side with the area per molecule ( $A$ ) were measured, and a constant pressure was maintained and monitored during the transfer of the films onto substrates, under computer control. After the solvent evaporated, the C<sub>60</sub> surface layer was compressed by the moving barrier at a

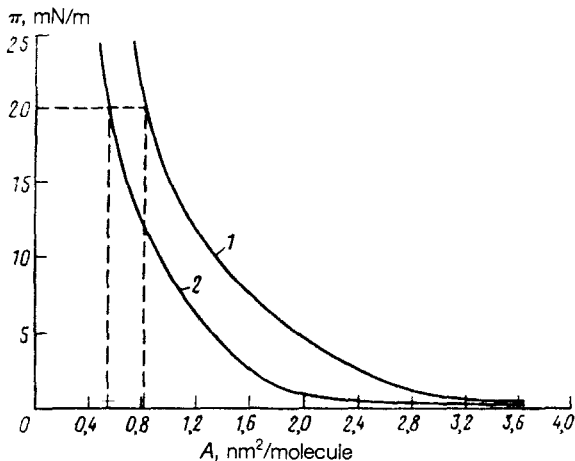


FIG. 1.  $\pi$ - $A$  isotherms at  $T=20^{\circ}\text{C}$  measured during the deposition of  $\text{C}_{60}$  on the surface of the subbase. 1—The amount of  $\text{C}_{60}$  was equivalent to  $N\sim 6\times 10^{15}$  molecules ; 2— $N\sim 9\times 10^{15}$ .

rate of  $5\times 10^{-5}$   $\text{m}^2/\text{s}$ . In the course of this compression, the surface area occupied by the fullerene molecules decreased by a factor of 8 to 8.5.

According to our study of the  $\pi$ - $A$  isotherms, the fullerene forms stable layers on the surface of the subbase. These layers can be compressed to  $\pi=25$   $\text{mN/m}$ . The compression-expansion cycles are reproducible. However, the coordinates of the isotherms, in particular, the value of  $A$  corresponding to the maximal attainable pressure (the surface pressure in the case at hand), are not constants; they vary with the amount of  $\text{C}_{60}$  which is deposited on the surface of the subbase in the initial stage of the formation of the layer (Fig. 1). For monolayers of genuinely amphiphilic molecules, this situation usually does not arise. If each amphiphilic molecule remains in contact (its "landing site") with the surface of the subbase as the surface pressure is increased, the  $\pi$ - $A$  isotherm should be reproducible upon a variation of the concentration (or volume) of the solution deposited.<sup>12</sup>

The shape of the resulting isotherms, on which there is no rectilinear region for the solid phase of ordinary Langmuir films, may be related to the formation of crystalline islands of  $\text{C}_{60}$ , even at low pressures, and a subsequent interaction of these islands. In this case it is obviously worthwhile to analyze the values of  $A$  corresponding to the maximally compressed layer, to which the applied pressure can still be held constant. The experiments yield the following values of the area per  $\text{C}_{60}$  molecule in the compressed layers at  $\pi=20$   $\text{mN/m}$ :  $A=0.85$   $\text{nm}^2$  for a film of type 1 and  $A=0.57$   $\text{nm}^2$  for a film of type 2 (curves 1 and 2, respectively, in Fig. 1). The van der Waals diameter of this buckyball is<sup>9</sup> 1.12  $\text{nm}$ ; i.e., the area of the landing site of a  $\text{C}_{60}$  molecule in the first case is close to that for the monolayer version of the packing of molecules (for comparison, the value  $A=0.96$   $\text{nm}^2$  was reported for a monolayer in Refs. 9 and 10). In the second case,  $A$  is smaller than this value by a factor of about 2. We can say, therefore, that  $\text{C}_{60}$  structures of a bilayer type form on the surface of the subbase.

Since the classical (vertical) method cannot be used to transfer rigid layers, we used the horizontal-elevator method<sup>8</sup> (the Schaefer method), in which the transfer is achieved by means of a horizontal contact of a hydrophobic plate with the compressed layer. A



FIG. 2. Electron micrographs of monolayers of type 1 (a) and of bilayers of type (b) of  $C_{60}$  films in “overlayer” regions. The numbers 1–6 specify the numbers of monolayers; the 0 represents a void.

$C_{60}$  layer compressed to 20 mN/m (Fig. 1) was transferred to the surface of a quartz plate which had been rendered hydrophobic, with a transfer factor close to one. According to measurements of electron absorption spectra of samples with 2–16  $C_{60}$  layers, for films of both types, the optical density in the primary absorption peaks at the wavelengths  $\lambda = 222, 268,$  and  $345$  nm increases linearly with the number of layers transferred. It was established experimentally that the absorption of the films of type 1 is half that of the films of type 2 for a given number of layers on the substrate. In each case the shape of the lines and the positions of the peaks of the absorption bands correspond to the spectrum of crystalline  $C_{60}$  produced by deposition in a He atmosphere.<sup>1</sup> For example, the optical density at  $\lambda_{\max} = 268$  nm of a film of type 2 consisting of a film of 10  $C_{60}$  layers is  $D = 0.58$ . This figure corresponds to a deposited film  $\sim 20$  nm thick.<sup>1</sup> Consequently, upon each contact of a substrate with a layer of type 2 compressed on the surface of the substrate, a bilayer of  $C_{60}$  molecules is transferred. This conclusion agrees with the results of the analysis of the  $\pi$ - $A$  isotherms, reported above.

For a study of the morphology and structure of LB films,  $C_{60}$  layers were transferred to the surface of an amorphous carbon film 15–20 nm thick under the conditions  $\pi_{\text{const}} = 20$  mN/m and  $T = 20^\circ\text{C}$ . The carbon film was formed by vacuum deposition on the surface of a natural cleaved face of a KCl single crystal. The carbon film was then transferred to a copper grid with a cell size of  $30 \times 30 \mu\text{m}$ . A Philips CM-20 transmission electron microscope was used for a study.

Figure 2 shows some typical electron micrographs of films produced by the two methods described above. A characteristic feature of their morphology is that, against the



FIG. 3. Typical point (a) and ring (b) electron diffraction patterns of a  $C_{60}$  Langmuir-Blodgett film.

background of a monolayer or bilayer film of uniform thickness, there are “overlayer” regions, with dimensions on the order of a few square microns, separated from each other by a distance of typically a few tens of microns. In these regions it is possible to distinguish, on the basis of the contrast, regions which are 1, 2, 3, and more monolayers thick (Fig. 2a). The overlayers observed here are a consequence of defects in the LB films. The monolayer and bilayer films generally contain voids with a typical size of  $0.1 \mu\text{m}$  and a 2D density on the order of  $10^7 \text{ m}^{-2}$ . The overlayers are thus formed from material which would have been in pores in the case of an ideal packing of molecules. Indeed, the relative area of the pores turns out to be on the order of the area of the overlayer regions.

The layers of LB films 1–2 nm thick can easily be distinguished on the basis of contrast against the background of the amorphous carbon film, whose thickness is an order of magnitude greater than that of the LB films. The reason is that the contrast in an amorphous layer differs from that in a crystalline layer. The diffraction contrast from ordered LB layers should evidently not depend on the thickness of the supporting amorphous film.

The structure of the LB films was studied in the electron-diffraction regime (with the linear dimensions of the regions studied ranging down to  $10 \mu\text{m}$ ) and also in the micro-diffraction regime for fragments of LB films with an area of less than  $1 \mu\text{m}^2$ . Essentially no diffraction patterns were observed from the monolayer and bilayer films, because of the inadequate intensity of the reflections. Some clear, nearly perfect point electron diffraction patterns (Fig. 3a) were recorded in overlayer regions with three or more monolayers. In certain regions of the monolayer films we observed some ring electron diffraction patterns (Fig. 3b), with a limited number of point reflections. Their number depends on the number of grains in the LB film which fall in the illuminated region ( $\approx 100 \mu\text{m}^2$ ). It follows that the typical size of the grains is  $\approx 3 \mu\text{m}$ .

The diffraction patterns from the  $C_{60}$  overlayers in the films of type 2 are rings like that shown in Fig. 3b. Point electron diffraction patterns corresponding to single-crystal bilayer films were observed considerably less frequently. The  $C_{60}$  films up to 60 nm thick

which were produced in Ref. 7 by vacuum condensation on NaCl and mica substrates had an fcc structure; in contrast, the ring diffraction patterns which we found correspond to an hcp lattice. It follows from an analysis of Fig. 3b that the interplanar distances  $d$  are 0.87, 0.50, and 0.41 nm. These distances correspond to (100), (110), and (200) planes of an hcp structure with a constant  $a = 1.00 \pm 0.01$  nm. When the films were tilted up to  $\pm 10^\circ$  with respect to the beam, we sometimes observed the (112) line from a nonbasal plane of the film, corresponding to the constant  $c = 1.63 \pm 0.02$  nm. These values of the constants agree with the results of Ref. 1 for  $C_{60}$  powders and microcrystals.

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