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Fullerene Films Deposited by Evaporation in Vacuum Using Spot-Focused Annular Electron Beam

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Abstract—A rapidly focused annular electron beam can provide for the effective evaporation of a fullerene mixture in a vacuum of ~10^{-2} Pa. A 1-kW beam focused into a spot within 0.1–1 s produces explosive evaporation of a fullerene target at an extremely high efficiency of heating. A comparison of the Raman and electronic absorption spectra of the initial fullerene powder and a film deposited upon its evaporation shows that C_{60} and C_{70} fullerenes are evaporated without rupture of C–C covalent bonds. The electron beam evaporation in vacuum has been successfully used to obtain fullerene films on substrates with an area of ~0.1 m^2. © *2005 Pleiades Publishing, Inc.*

Methods for the deposition of fullerene films via thermal evaporation in vacuum are well known [1–3], but the use of high-energy electron beams for the evaporation of initial fullerene powders is still insufficiently studied. It would be of interest to use a characteristic feature of the action of an intense electron beam that consists in explosive spraying of the target, whereby the covalent C–C bonds in evaporated fullerene molecules can be retained. In addition, the electron-beam evaporation simplifies the coating of large-area (>1 m^2) substrates, since this method of heating can provide for an ultimately high deposited power density (>10^9 W/m^2).

This Letter describes a new method of the electron-beam evaporation of targets in vacuum, which has been specially developed for the deposition of fullerene films.

The initial C_{60}/C_{70} fullerene mixture was synthesized in a plasmachemical reactor using arc discharge at a pressure of 10^5 Pa [4, 5]. The fullerene fraction was isolated from the obtained products by extraction with benzene. The initial mixture composition was as follows (weight fraction): C_{60}, 0.8; C_{70}, 0.15; higher fullerenes, 0.04; $C_{60}O$ and $C_{70}O$ oxides, 0.01. The targets were prepared by pressing the fullerene mixture into disks with a diameter of 20 mm and a thickness of 3 mm under a pressure of ~32–34 kgf/cm^2.

An experimental setup for the pulsed evaporation of powdered fullerene mixtures is schematically depicted in Fig. 1. The setup is based on a plasma electron gun *1* [6, 7], where electrons are generated in hollow-cathode magnetron discharge plasma. The discharge is initiated and continuously power-supplied using a current source *3*. Electrons with a total current of 50 mA are accelerated by a voltage of 20 kV applied to anode *2* from a high-voltage source *4*. Then, the beam of high-energy electrons enters an electromagnetic lens *5* con-

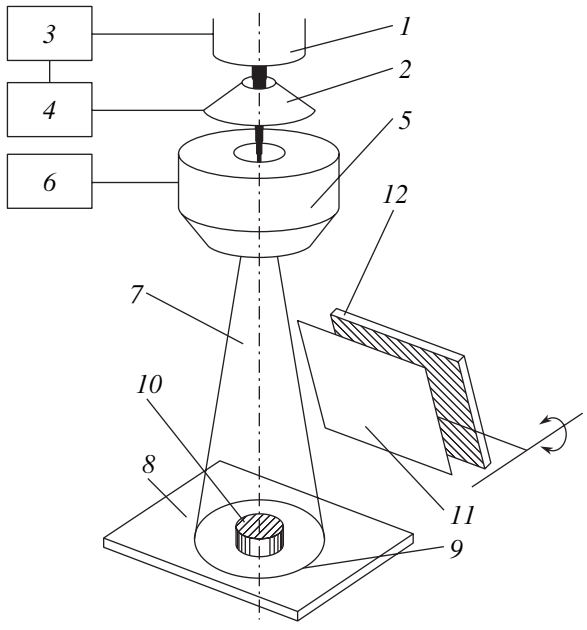

Fig. 1. Schematic diagram of the experimental arrangement: (*1*) plasma electron gun; (*2*) accelerating electrode; (*3*) discharge current source; (*4*) high-voltage source; (*5*) electromagnetic lens; (*6*) electron beam control unit; (*7*) annular electron beam; (*8*) graphite collector; (*9*) electron beam projection; (*10*) fullerene disk target; (*11*) shutter; (*12*) substrate.

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trolled by the electron beam control unit *6* [8], which produces annular electron beam *7* at the output. The beam strikes graphite collector *8*. Initially, electrons are projected into ring *9* with an outer and inner radius of 50 and 48 mm, respectively, coaxial with disk target *10*. The lens can be controlled so as to provide for a rapid narrowing of the annular beam, whereby the ring projection of the beam on the collector surface is focused into a 3-mm spot. The electron beam power in these experiments was on the order of 10^3 W. Shutter *11* can be removed to expose substrate *12* to the flux of particles evaporated from the target. The particles are deposited onto the entire surface of substrate (amorphous glass) with dimensions 30×30 cm.

The film thickness was measured using a microinterferometer (MII-4) of the Linnik type. The films were characterized using the Raman and electronic absorption spectroscopy techniques. The Raman spectra were measured on a Bruker RFS 100/S Fourier transform spectrometer equipped with a YAG:Nd laser operating at $\lambda = 1064$ nm and a power of 10 mW. The electronic absorption spectra of fullerene solutions were recorded using an Uvicon Model 943 double-beam spectrophotometer.

The sample films were grown in a vacuum of 2×10^{-2} Pa. Initially, the electron beam *7* is focused so that its projection *9* occurs at the periphery of the disk target *10*, while shutter *11* screens substrate *12* from direct flux of evaporated carbon particles. In the zone where the electron beam strikes the graphite holder *8*, the temperature is about $\sim 1.7 \times 10^3$ K and the pressure of carbon vapor is relatively low (on the order of 10^{-8} Pa) [9]. From this initial state (Fig. 1), the annular electron beam is rapidly contracted (using lens *5* controlled by unit *6*) in the radial direction so as to approach the disk target. When the electron beam touches disk *10*, the intense evaporation of fullerenes simultaneously begins over the entire circumference of the target. At this moment, shutter *11* is removed so that particles leaving the electron-beam-heated zone can reach the surface of substrate *12* and condense to form a film (at a substrate temperature of 300 K). The annular electron beam projection is contracted to the disk center within ~1 s, which leads to instantaneous evaporation of the target material. When the beam is spot-focused at the disk center and the target is completely evaporated, shutter *11* is returned in the initial position.

The film deposited on the substrate in the course of explosive evaporation of the fullerene mixture was 1–2 μm thick and had a brown color. The film covered the entire substrate surface with an area of ~0.1 m^2. The X-ray diffraction measurements showed the films formed on the substrate at 300 K to be X-ray amorphous. However, the films obtained by deposition onto a substrate heated to 393 K, followed by annealing for 0.5 h at 373 K in vacuum, exhibited a crystalline structure.

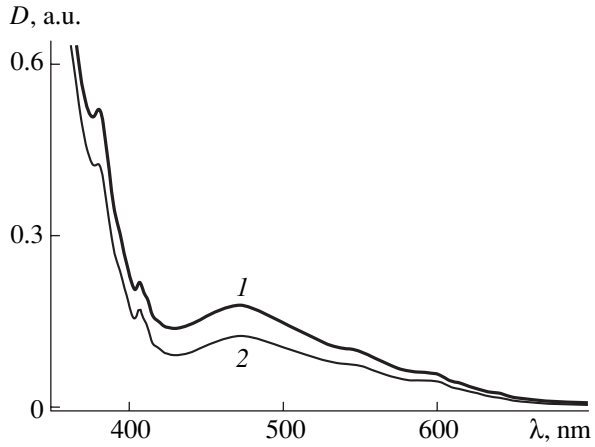

Fig. 2. Electronic absorption spectra of (*1*) an electron-beam deposited fullerene film and (*2*) the initial fullerene mixture.

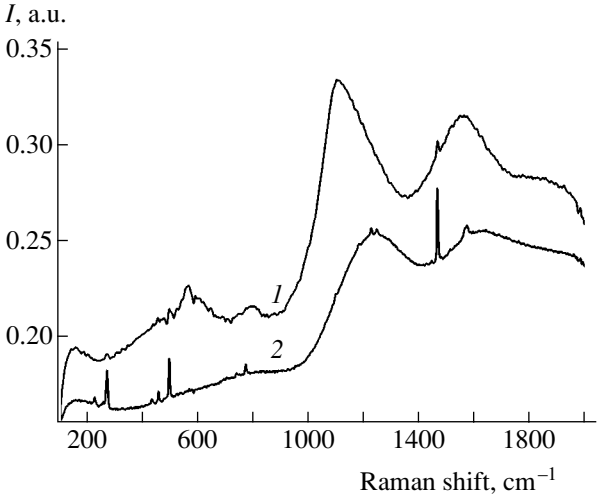

Fig. 3. Raman spectra of (*1*) an electron-beam deposited fullerene film and (*2*) the initial fullerene mixture.

The films grown as described above were soluble in nonpolar solvents. The electronic absorption spectrum of such a solution was close to that of the initial fullerene mixture (Fig. 2). This was indicative of the fact that the electron-beam evaporation of fullerenes C_{60} and C_{70} proceeds without rupture of C–C covalent bonds. However, the Raman spectrum of a deposited film displayed, besides sharp peaks corresponding to fullerenes C_{60} (495 and 1468 cm^{-1}) and C_{70} (271 cm^{-1}), some additional broad bands (Fig. 3). This result suggests that the state of fullerene molecules in the film differs from that in the initial powder. Since the film thickness is relatively small, the interaction of fullerene molecules with the substrate can be a significant factor.

In conclusion, the electron-beam-induced explosive evaporation of a fullerene mixture at temperatures above 1.7×10^3 K (significantly exceeding the sublimation temperature of fullerenes, $(7.23–7.73) \times 10^2$ K) can

be used for the deposition of fullerene films. In this study, such conditions have been provided for the first time using an annular electron beam rapidly focused into a spot. Using a plasma electron gun, electron beams with a current above 1 A and a beam power >20 kW can be generated, providing for the possibility of fullerene film deposition on the substrate surface with an area >1 m^2 due to a sufficiently large amount of evaporated material.

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