

Explosive Evaporation of Fullerenes by Electron Beam and Ion Beam Sputtering in Vacuum

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Abstract – A new approach to the synthesis of films containing fullerenes and doping elements is described. The ion beam sputtering of dopant-containing fullerene mixtures in a vacuum of $\sim 10^{-2}$ Pa allowed micron-thick films containing C_{60} and C_{70} fullerenes and the corresponding dopant element (Fe, Na, B, Gd, or Se) to be grown on quartz substrates. A rapidly focused annular electron beam can provide for the effective evaporation of a fullerene mixture in a vacuum of $\sim 10^{-2}$ 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. The electron beam evaporation in vacuum has been successfully used to obtain fullerene films on substrates with an area of ~ 0.1 m².

1. Introduction

The ability to contain atoms of foreign elements inside a carbon framework is the basic property of fullerene molecules. The introduction of such impurities into fullerene molecules substantially modifies their properties and significantly expands the spectrum of their possible practical applications. Methods for the introduction of impurity elements into the cavity of a fullerene molecule are virtually the same as those used for the synthesis of fullerenes. The formation of fullerenes in the course of deposition of a carbon vapor occurring in a partly ionized state was described in [1, 2]. The dominating factors in the synthesis of C_x carbon clusters can be the electron temperature and density in the plasma [3], since these parameters influence the cross section of the collisions of charged carbon clusters. The rate of formation of C_{k+m} clusters increases when the components C_k and C_m bear charges of the opposite signs. Qualitative analysis of the process of fullerene synthesis in plasma shows that the conditions facilitating the synthesis and increasing the yield of fullerenes and their derivatives can be created in the course of thin film deposition by ion beam sputtering of a fullerene target. An especially important task is to obtain the fullerene films containing doping elements.

Deposition of fullerene films via thermal evaporation in vacuum is well known [4–6], 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 m²) substrates, since this method of heating can provide for an ultimately high deposited power density ($>10^9$ W/m²).

2. Experiment

Below, we present the results of an experimental investigation into the synthesis of films containing fullerenes and an impurity element (Fe, Na, B, Gd, or Se) by means of sputtering of a pressed mixture containing C_{60}/C_{70} fullerenes and a doping element with a beam of Ar^+ ions in a vacuum of $\sim 10^2$ Pa, and 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 fullerene mixture was synthesized in a plasmachemical reactor operating at an arc discharge frequency of 44 kHz and a pressure of 10^5 Pa [7]. The fullerene fraction was isolated from the obtained products by extraction with benzene. The initial fullerene 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 adding a powdered doping element (Fe, Na, B, Gd, or Se) in a preset amount to the fullerene mixture and pressing disks with a diameter of 20 mm and a thickness of 3 mm under a pressure of ~ 30 kgf/cm².

The sample films were grown in a vacuum of $2 \cdot 10^{-2}$ Pa in the course of sputtering of a target with a beam of accelerated Ar^+ ions. The experiments were performed in a setup [8, 9], using the scheme depicted

ted in Fig. 1. According to this scheme, ions 1 with a total beam current of 5–10 mA were formed in the plasma of magnetron discharge with cold hollow cathode [10] and accelerated to an energy of 5–10 keV, which corresponded to an ion velocity of $\sim 1.5 \cdot 10^5$ m/s. The ion beam was continuously incident onto the surface of target 2 at an angle of 45–60° over a time period of 8 h, which corresponded to a total ion fluence of $\sim 5 \cdot 10^{16}$ cm⁻². As a result, a flux of particles was sputtered from spot 3 of the ion beam projection onto the target surface. The sputtered flux was expected to consist of molecular clusters 4 (fullerene fragments), atoms 5 of doping elements (Fe, Na, B, Gd, or Se), and electrons 6. The sputtered particles were deposited onto the surface of a fused quartz substrate 7, where a film was synthesized and grown to a total thickness of ~ 1 μm under non-equilibrium conditions at a substrate temperature of 300 K.

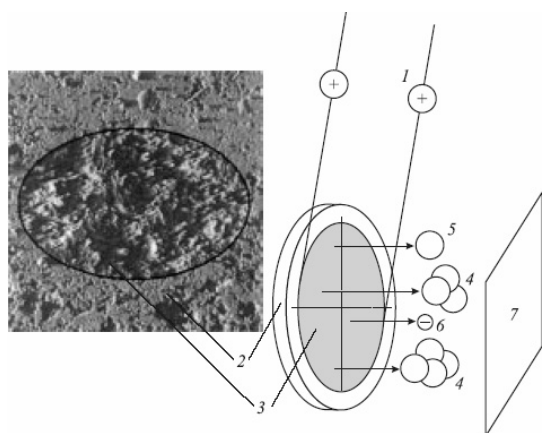


Fig. 1. Schematic diagram of the experimental arrangement: (1) Ar⁺ ion beam; (2) target; (3) ion beam spot on the target surface; (4) molecular clusters (fullerene fragments); (5) doping atoms (Fe, Na, B, Gd, or Se); (6) γ electrons; (7) substrate. The inset shows a SEM micrograph of the target surface with a sputtered area

An experimental setup for the pulsed evaporation of powdered fullerene mixtures is schematically depicted in Fig. 2. The setup is based on a plasma electron gun 1 [11], 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 controlled by the electron beam control unit 6 [12], 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 10³ 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. 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 $\sim 1.7 \cdot 10^3$ K and the pressure of carbon vapor is relatively low (on the order of 10⁻⁸ Pa) [13]. From this initial state (Fig. 2), 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.

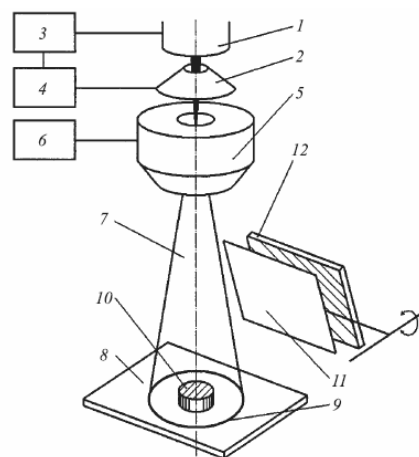


Fig. 2. Schematic diagram of the experimental arrangement: (1) plasma electron gun; (2) accelerating electrode; (3) discharge current source; (4) high-voltage source; (5) electromagnetic lens; (6) electron beam control unit; (7) annular electron beam; (8) graphite collector; (9) electron beam projection;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

The film thickness was measured using a microinterferometer (MII-4) of the Linnik type. The surface morphology of the grown films was studied using a LEO 1430VP scanning electron microscope (SEM). 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.

3. Results

The observed SEM micro-graphs of the ion beam deposited films showed smooth and even growth surface, reproducing the roughness of a fused quartz substrate. The average roughness height was ~ 6.5 nm. The film structure and phase composition were studied by X-ray diffraction on a Rigaku diffractometer using $\text{CuK}\alpha$ radiation. These measurements showed the obtained films to be X-ray amorphous. The films were insoluble in non-polar solvents and contained a large proportion of various carbon-based molecules and fragments. The Raman spectra of the deposited films displayed no bands characteristic of the C_{60} and C_{70} molecules. However, the mass spectra showed that C_{60} and C_{70} molecules are present in the films. These data confirmed the formation of fullerenes due to the merging of clusters (fullerene fragments) under the conditions of their stopping and deposition on the growth (substrate) surface. The films exhibited lower volatility as compared to that of the initial fullerene mixture. Based on these data, we may suggest that fullerene molecules in the films occur in a polymerized state. The polymerization process can be stimulated by γ electrons, which are knocked out from the film and continuously irradiate the growing film. The X-ray spectral analysis of the films (performed using an Oxford Instruments INCA Energy 300 energy-dispersive analyzer) showed the X-ray emission peaks due to doping elements (Fe, Na, B, Gd, or Se) introduced into the fullerene mixture. These data confirmed the stable transport of doping elements from sputtered targets and filling of the deposited films. In addition to the peaks of C and doping elements, the spectra contained the peaks of N, O, and Si. For example, Fig. 3 presents the typical X-ray emission spectrum of a film obtained using the ion beam sputtering of an iron-containing fullerene target. The appearance of Si and O peaks in this spectrum is probably related to the presence of a substrate. In addition, O and N can appear as a result of adsorption from the gas phase on a highly reactive surface of the deposit [14]. By changing the parameters of the ion beam sputtering process and the deposition conditions, it is possible to control both the growth of a fullerene film and the content of doping elements in the deposit. The results of investigation of the surface morphology (Fig. 1) of the initial target 2 and the sputtered area 3 showed that, within a relatively short sputtering time (8 h), the beam of accelerated ions produced a

significant change in the surface microrelief, which showed evidence for a non-uniform etching of the fullerene powder in the direction of incidence of the ion beam. The surface relief with a characteristic columnar structure observed in the ion beam spot 3 (Fig. 1) is indicative of a nonthermal ("cold") decomposition of the surface of a pressed fullerene mixture.

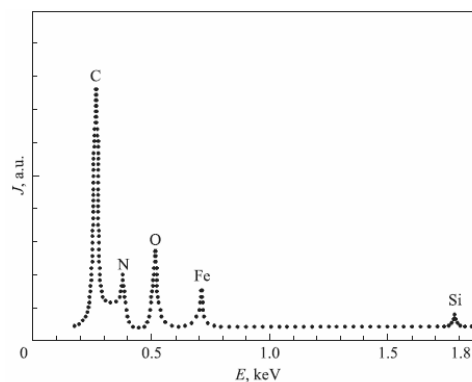


Fig. 3. X-ray emission spectrum of a thin film obtained by ion sputtering of a target containing fullerenes and iron as the doping element

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 m². 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. The films grown as described above were soluble in non-polar solvents. The electronic absorption spectrum of such a solution was close to that of the initial fullerene mixture (Fig. 4).

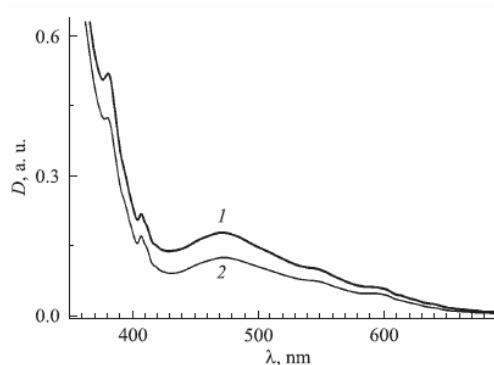


Fig. 4. Electronic absorption spectra of (1) an electron-beam deposited fullerene film and (2) the initial fullerene mixture

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. 5). 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.

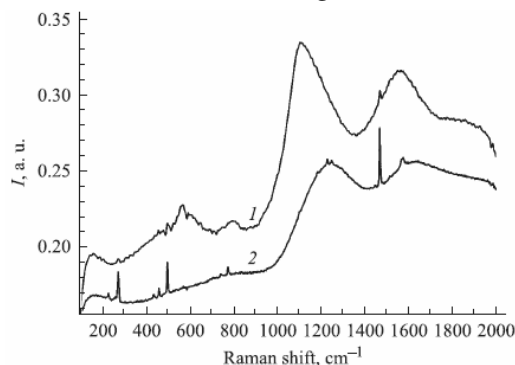


Fig. 5. Raman spectra of (1) an electron-beam deposited fullerene film and (2) the initial fullerene mixture

4. Conclusion

Thus, the ion beam bombardment leads to breakage of the carbon framework of fullerene molecules in the target mixture containing a doping element, as well as to the sputtering and transfer of clusters (molecular fragments) and doping elements to the growth surface. At the same time, the obtained results show evidence of the possible "assembly" of the carbon framework of fullerene molecules on the substrate surface, which results in the formation of films containing fullerene molecules and doping elements. This mechanism of the process of ion beam sputter deposition of fullerenes (under the conditions of uncertainty [15] in the sputtering and transfer of the carbon framework of C_{60} and C_{70} molecules with diameters of $\sim 0.71\text{ nm}$) is consistent with the detection of both molecular fragments and C_{60} and C_{70} molecules in the obtained films. It is highly probable that doping elements can enter into the matrix of the carbon framework, with the formation of endohedral fullerenes, whereas the dopant atoms not entering into the carbon framework can participate in the formation of exohedral fullerenes. Thus, it is probable that dopant atoms can occur inside the C_{60} and C_{70} molecules synthesized via the assembly of molecular fragments on the substrate, or that dopant atoms are more likely involved in the intermolecular bonds outside these molecules.

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

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 $>20\text{ kW}$ can be generated, providing for the possibility of fullerene film deposition on the substrate surface with an area $>1\text{ m}^2$ due to a sufficiently large amount of evaporated material.

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References

- [1] A.V. Elets'kii, *Usp. Fiz. Nauk.* 164, 1007 (1994).
- [2] N.I. Alekseev and G.A. Dyuzhev, *Zh. Tekh. Fiz.* 69 (12), 42 (1999).
- [3] G.N. Churilov, A.S. Fedorov, and P.V. Novikov, *Pis'ma Zh. Éksp. Teor. Fiz.* 76, 604 (2002) [*JETP Lett.* 76, 522 (2002)].
- [4] I.P. Soshnikov, A.V. Lunev, M.E. Gaevskii, et al., *Zh. Tekh. Fiz.* 70 (6), 98 (2000)].
- [5] S.V. Kozyrev and V.V. Rotkin, *Fiz. Tekh. Poluprovodn. (St. Petersburg)* 27, 1409 (1993).
- [6] E.M. Shpilevskii, L.V. Baran, and M.E. Shpilevskii, *Mater. Tekhnol. Instrum.* 3 (2), 105 (1998).
- [7] G.N. Churilov, *Prib. Tekh. Éksp.*, No. 1, 5 (2000).
- [8] A.P. Semenov, *Beams of Scattering Ions: Production and Application*, Ulan-Ude, Izd. BNTs SO RAN, 1999 [in Russian].
- [9] A.P. Semenov and I.A. Semenova, *Zh. Tekh. Fiz.* 74 (4), 102 (2004).
- [10] A.P. Semenov and I.A. Semenova, *Zh. Tekh. Fiz.* 75 (4), 48 (2005).
- [11] A.P. Semenov and I.A. Semenova, *Izv. Vyssh. Uchebn. Zaved., Fiz.*, No. 9, 69(2001).
- [12] Yu.V. Grigor'ev, Yu.G. Petrov, and V.I. Pozdnov, *Prib. Tekh. Éksp.*, No. 2, 236 (1990).
- [13] A.I. Pipko, V.Ya. Pliskovskii, and E.A. Penchko, *Pumping Equipment for Vacuum Devices*, Moscow, Énergiya, 1965 [in Russian].
- [14] T.L. Makarova, I.B. Zakharova, T.I. Zubkova, and A.Ya. Vul', *Fiz. Tverd. Tela (St. Petersburg)* 41, 354 (1999) [*Phys. Solid State* 41, 319 (1999)].
- [15] *Sputtering by Particle Bombardment*, Ed. By R. Behrisch, New York, Springer-Verlag, 1991, Vol. 3.