

Thin Fullerene-Containing Films Synthesized by Ion Beam Sputtering of Fullerene Mixtures with Doping Additives in Vacuum

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Abstract—A new approach to the synthesis of films containing fullerenes and doping elements is described. It is suggested that a cluster mechanism of the target sputtering by accelerated ions makes possible the deposition of fullerenes on a substrate with a certain probability for dopant atoms being introduced into the cavities of fullerene molecules and a higher probability of their occurrence between fullerene molecules. The proposed method has been experimentally implemented by using an Ar⁺ ion beam to sputter C₆₀/C₇₀ fullerene mixtures (synthesized in a plasmachemical reactor at a pressure of 10⁵ Pa) pressed into disk targets with a doping element (Fe, Na, B, Gd, or Se). The ion beam sputtering of dopant-containing fullerene mixtures in a vacuum of ~10⁻² Pa allowed micron-thick films containing C₆₀ and C₇₀ fullerenes and the corresponding dopant element (Fe, Na, B, Gd, or Se) to be grown on quartz substrates. © 2005 Pleiades Publishing, Inc.

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.

The growth of thin films by ion beam deposition techniques [4] involves physical sputtering of the target material, transfer of the sputtered particles to the growth surface (substrate), and deposition (growth) of a film with required composition and structure. Taking into account the temporal and spatial factors, we may consider the elementary event of this growth process as beginning with sputtering of the target and ending with

the internal physical and chemical transformations in the deposited film. From the standpoint of obtaining fullerene-containing films, the ion beam sputtering of fullerene mixtures has certain advantages. First, the flux of particles sputtered by accelerated ions from the target contains a considerable proportion of clusters of various dimensions [5]. Second, the reaction of compound formation in the case of reactive ion beam sputtering proceeds on a substrate [4, 6]. Third, a significant fraction of sputtered particles leave the target in the ionized state [7]. Fourth, the sputtering of clusters is accompanied by thermionic emission with the formation of a certain electron density in the plasma, whereby γ electrons can influence processes in the growing film. Fifth, this process makes possible simple and controlled filling of the growing film with doping elements. Finally, it is also very important that the sputtered clusters possess a relatively high temperature (~10–50 eV), which positively influences the course of the synthesis and the internal structure of the growing film even at a relatively low (~300 K) temperature of the substrate surface. Thus, the combined action and the forms of manifestation of all factors of the physical sputtering process are quite acceptable and even favorable for realization of the process of fullerene film synthesis in vacuum by means of the sputtering of fullerene mixtures containing doping elements with a beam of accelerated ions.

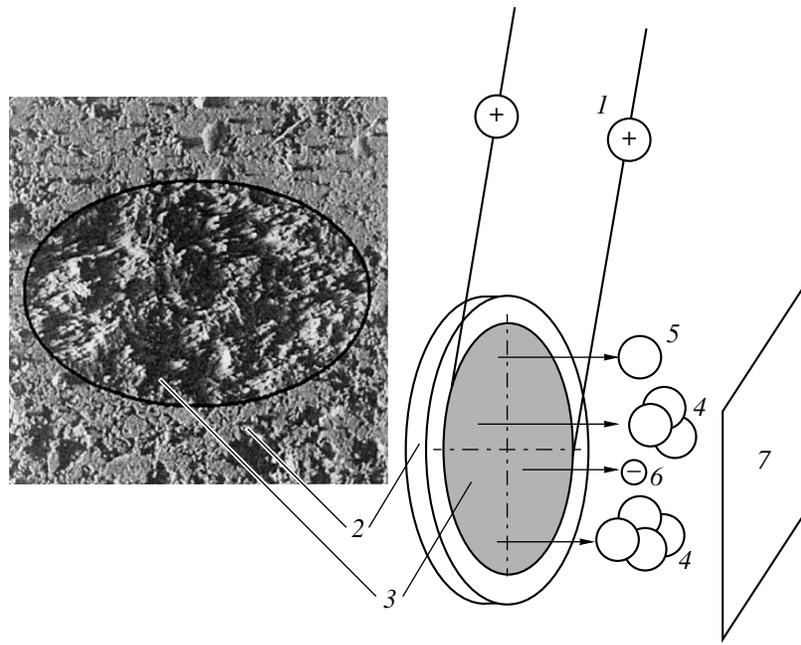


Fig. 1. Schematic diagram of the experimental arrangement: (1) Ar^+ ion beam; (2) target; (3) ion beam spot on the target surface; (4) molecular clusters (fullerene fragments); (5) doping atoms (Fe, Na, B, Gd, or Se); (6) γ electrons; (7) substrate. The inset shows a SEM micrograph of the target surface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

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.

Obviously, the large number of factors influencing the process of ion beam sputter deposition makes theoretical description of the process conditions and growth regimes an extremely difficult task. 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 $\text{C}_{60}/\text{C}_{70}$ fullerenes and a doping element (Fe, Na, B, Gd, or Se) with a beam of Ar^+ ions in a vacuum of 10^{-2} Pa.

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 [8]. 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 (see table) 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 2×10^{-2} Pa in the course of sputtering of a target with a beam of accelerated Ar^+ ions. The experiments were

performed in a setup described elsewhere [4, 9], using the scheme depicted 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 $\sim 1.5 \times 10^5$ 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 $\sim 5 \times 10^{16}$ cm⁻². As a result, a flux of particles was sputtered from spot 3 of the ion beam projection onto the target surface. According to [5, 7], 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 nonequilibrium conditions at a substrate temperature of 300 K. The film thickness was measured using a microinterferometer (MII-4) of the Linnik type.

Despite the aforementioned advantages of the ion beam deposition process, manifested by the relative

The content of doping elements in fullerene mixtures

Element	Fe	Na	B	Gd	Se
Mass fraction in fullerene mixture	0.02	0.01	0.01	0.003	0.01

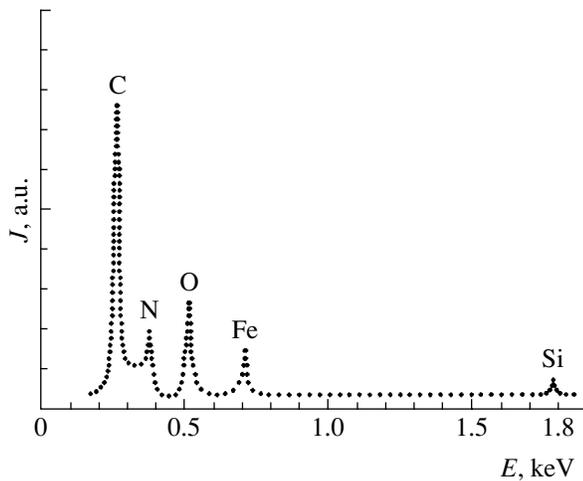


Fig. 2. X-ray emission spectrum of a thin film obtained by ion sputtering of a target containing fullerenes and iron as the doping element.

simplicity of maintaining the required regime of synthesis, the complex interrelation of separate parameters and their uncertainty lead to difficulties in the optimization of the process. The surface morphology of the grown films was studied using a LEO 1430VP scanning electron microscope (SEM). The observed SEM micrographs 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 (measured using a Bruker RFS 100/S Fourier transform spectrometer) displayed no bands characteristic of the C_{60} and C_{70} molecules. However, the mass spectra (obtained using a Bruker Biflex III time-of-flight spectrometer with laser ionization) 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 (Fe, Na, B, Gd, or Se), the spectra contained the peaks of N, O, and Si. For example, Fig. 2 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 [11].

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.

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 [5] in the sputtering and transfer of the carbon framework of C_{60} and C_{70} molecules with diameters of ~ 0.71 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. However, estimation of these probabilities require additional experiments, with investigation of the process of ion beam sputter deposition *in situ* using high-resolution mass spectrometry.

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