Structure changes in C_{60}–Bi composite films irradiated by accelerated electron beam

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The structure of unsupported epitaxial films of C_{60}–Bi composite with hcp lattice has been studied after irradiation by 100 keV electron beam in the electron microscope column. A short-time irradiation of the film by electrons at the average current density of 40 A/cm^2 results in the composite evaporation in the beam central area. In the film boundary region, pores are formed of dimensions well correlated with the nanodimensional areas of the segregated bismuth. The electron bombardment results in reduced interplanar spacings depending on the plane system index and the irradiation intensity. A qualitative mechanism of pore formation has been proposed.

Исследована структура свободных эпитаксиальных пленок композита C_{60}–Bi с ГПУ решеткой после облучения пучком электронов с энергией 100 кэВ в колонне электронного микроскопа. Кратковременное облучение пленки электронами при средней плотности тока 40 А/см2 вызывает испарение композита в центральной части пучка. В пограничной области пленки образуются поры, размеры которых хорошо коррелируют с наноразмерными областями сегрегированного висмута. Электронная бомбардировка приводит к уменьшению межплоскостных расстояний, зависящих от индекса системы плоскостей и интенсивности облучения. Предложена качественная модель, описывающая механизм образования пор.

Investigation of film type carbon nanostructures synthesized on the basis of C_{60} fullerene is an actual task not only from the standpoint of fundamental scientific results but also in connection with the potential use thereof [1]. The specific character of crystalline C_{60} films with hcp or fcc lattice consists in that new structure states may be induced in the matrix during specific measurements. In other words, the measuring instrument causes a transformation of the initial structure state accompanied by electricity and mass transfer during the "non-destructive" action upon the object. In [2], a model has been proposed for the p-n junction induced in the course of electrical measurement, that junction being self-organized due to electrical diffusion of the acceptor and donor impurities in the fullerite lattice. The phenomenon of electron-stimulated polymerization and amorphization in the fullerite arising during the investigation of the characteristic electron energy loss spectra has been discussed in [3, 4]. Even a low-intensity (tens of nA) irradiation by an electron beam of several keV energy for several minutes results in polymer chain formation binding an appreciable fraction of the fullerene molecules.

In this work, we cleared up the modification possibility of the C_{60}–Bi films described in [5] (where bismuth is distributed in discrete nano-dimensional areas) under bombardment with a sufficiently intense flow of elevated energy electrons. The 70 to 100 nm thick C_{60}–Bi composite films with hcp lattice were obtained by co-condensation of bismuth and fullerene from effusion cells onto fluorophlogopite (fp) substrates in the (001), [100] fp//(001), [100] C_{60} using the techniques [5]. The ratio of Bi to C_{60} flow den-

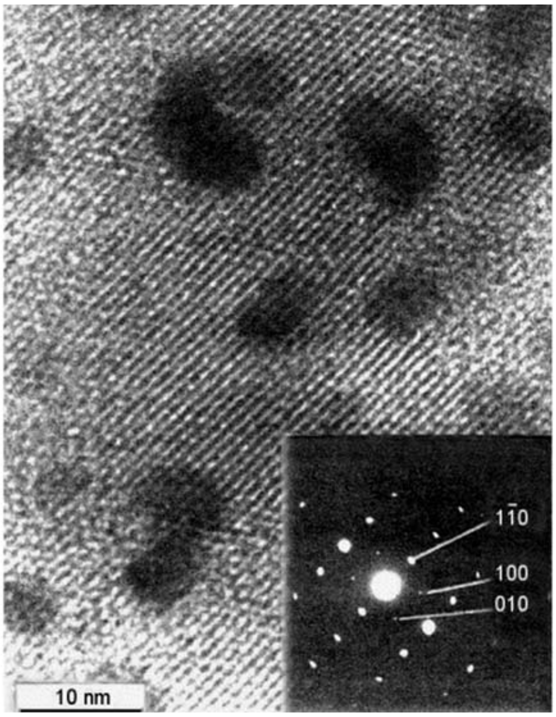

Fig. 1. Electron-microscopic image of unirradiated area of a C_{60}–Bi composite film. T = 473 K, h = 80 nm. The matrix (fullerite) has the hcp crystal lattice.

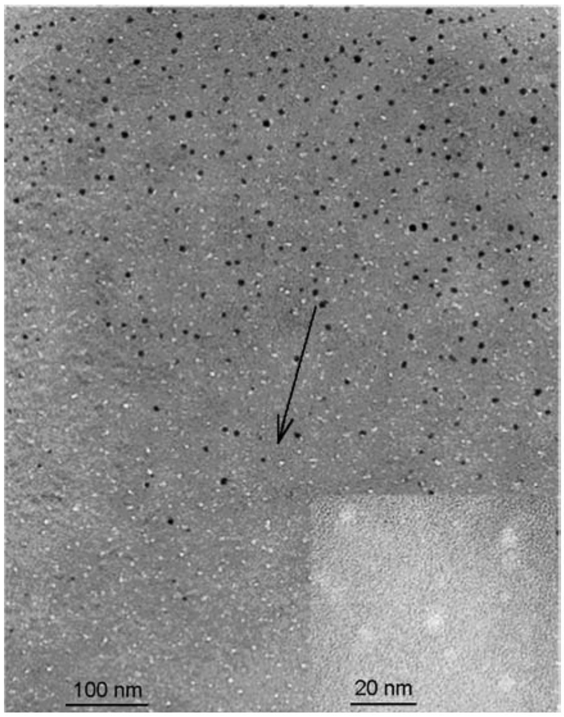

Fig. 2. Electron-microscopic panorama image of irradiated area of a C_{60}–Bi composite film. The transition area contains segregated bismuth and pores. The arrow shows the temperature elevation direction in the film plane.

sities was 1:10. The films were irradiated by a 100 keV electron beam in the EMV-100AK electron microscope column at the average electron current density j_e = 40 A·cm^{-2}. The samples were separated previously from the substrates and placed onto copper gauze for electron-microscopic studies. The electron beam was directed to the central area of the gauze cell. Then the same samples were examined using a PEM-U microscope. The presence of irregular bismuth atomic accumulations of 5 to 7 nm average size is a characteristic feature of the initial composite structure. The samples exhibit no reflections from the crystal lattice of metallic bismuth; the films studied before [5] behaved in the same fashion.

Fig. 1 presents the electron-microscopic image of the film and the diffraction pattern of the initial structure for a 80 nm thick sample. As the electron beam intensity increases, liquid bismuth drops are formed at the film surface, the drop size being growing during the irradiation. It is just the larger drops that grow predominantly. As the composition is irradiated during about 1 min, the film does not loss its continuity, the density of the segregated bismuth areas decreases, no micropores are formed in the film. Reflections corresponding to bismuth crystal lattice appear in the electron diffraction pattern.

A short-time (about 1 s) action of the beam at removed condenser diaphragm where the current density is about 40 A·cm^{-2} results in the following phenomenon. Three characteristic regions can be distinguished in the area of the intense electron beam action, namely, (1) the complete absence of the composite film; (2) the crystalline fullerite film containing irregular-arranged pores; and (3) the transition area where both nanodimensional bismuth accumulations and pores are observed (Fig. 2). To identify the pores, we have used the electron beam underfocusing/overfocusing technique that allows us to judge the local variations of the substance density in the film.

The relative changes in the interplanar spacings were measured in the irradiated sample area. The same film measurements done in the unirradiated area were used as reference data. The interplanar spacing calculation in the hcp composite crystal lattice using the diffraction patterns for different film areas has shown that the lattice period becomes reduced in the electron beam action area. The interplanar spacing relative change ε depends on the selection of the plane system and the irradiation intensity. It has been found that ε is about 2 to 2.5 times smaller for the (100) planes than for the (110) ones. The maximum ε value in the pore formation area for the (100) plane system amounted about 2 % and for the (110) one, about 5 %. We connect the results obtained with changes in the binding forces between the fullerene molecules in the crystal lattice as well as with the partial polymerization of fullerite [3, 4].

For accelerated electrons, the film is a target containing local variations of the substance density (Bi accumulations), where the bismuth atoms localized in the octahedral voids of the hcp lattice form linear chains located in the channels normal to the film surface. Under electron bombardment, in its final stage, the local changes in the film temperature are of an appreciable importance in the transition area characterized by a sharp temperature drop along the radial direction due to the sample low heat conductance. It can be supposed that, at a sufficiently high electron beam density, the energy transfer process to the composite atoms in the segregation area may be of an "explosive" character resulting in the local lattice overheating. Fullerene molecule has been found to decompose itself when heated to $T_{cr} \approx 1000°C$ [6]. In our case, the numeral estimations show that a 10^{-5} cm thick fullerene film will be evaporated during about $7 \cdot 10^{-6}$ s, the maximum heating temperature will be about 1917 K. The local heating to a $T \geq T_{cr}$ will result in a pressure elevation in that area, causing a shock wave accompanied by a diverging flow of bismuth atoms and fullerene fragments from the overheating area. Then, when the heat equilibrium will be recovered in that area where the C_{60} molecule density is reduced, a pore is formed. In the transition area at some radial distance from the beam center, where the film temperature and the electron beam density are reduced considerably, the local overheating probability is reduced towards the irradiated area periphery, that is in a good correlation with the density and pore sizes in that area.

It is very likely that C_{60} is subjected to thermal decomposition along with evaporation under the beam. In some samples, a very thin amorphous carbon film remained after the fullerene evaporation in the intense irradiation area. To date, the data available are still insufficient to estimate correctly the number of degraded molecules and to discriminate that process from the possible polymer film formation at the sample surface due to decomposition of hydrocarbons present in the residual gas medium of the microscope vacuum chamber.

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Структурні зміни у плівках композиту C_{60}–Bi, опромінених пучком прискорених електронів

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Досліджено структуру вільних епітаксіальних плівок композиту C_{60}–Bi з гексагональною щільно пакованою граткою після опромінення пучком електронів з енергією 100 кеВ у колоні електронного мікроскопа. Короткочасне опромінення плівки електронами при середній густині струму 40 А/см^2 спричиняє випаровування композиту в центральній частині пучка. У примежовій області плівки утворюються пори, розміри яких добре корелюють з нанорозмірними областями сегрегованого вісмуту. Електронне бомбардування спричиняє зменшення міжплощинних відстаней, яке залежить від індекса системи площин та від інтенсивності опромінення. Запропоновано якісну модель, що описує механізм утворення пор.