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Research of Structure and Conductivity of Films Systems C_{60}-Bi

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The structure and conductivity of films of system C_{60} -Bi received is investigated with a joint deposition from two Knudsen's cells in vacuum ~ $5 \cdot 10^{-4}$ Pa on substrates from artificial mica. Is established that with temperature ~ 470K and ratio of density of flows of atoms Bi and molecules C_{60} less than 0,5 in an interval of thickness 40–50 nm, grow of epitaxial single crystal films with close-packed hexagonal structure. Feature of the high-resolution electron microscopy images of condensates is the presence of irregular conglomerations of low concentrations bismuth is noted in the form of deposits 3–10 nm in size distributed across the volume of the film. The conductivity of films in a mode thermocycling was measured in an interval of temperatures 510–300K directly after of condensation without bleed-in of air in the vacuum chamber.

Keywords: fullerenes; bismuth; composite; film; conductivity; structure

INTRODUCTION

The fullerenes thin films are of interest because those are a convenient model to study thin film structures as well as because there is a certain prospective of their practical application [1]. It is just composite

materials based on fullerenes that are believed to be of promise in practical fields.

EXPERIMENTAL

To study the structures of pure fullerenes and C_{60}-Bi composites, we have used the high-resolution electron microscopy (direct resolution of crystallographic planes, selected-area diffraction (SED) and X-ray diffractometry (θ-2θ scanning in Cu—$K\alpha_1$ emission). The composite films were produced using thermal evaporation from two effusion sources. The evaporated substance amounts were monitored using a quartz microbalance. (001) plane of synthetic mica fluorophlogopite (FP) were used as substrates. The films were deposited at the substrate holder temperatures T_s from 400 to 500 K in a vacuum of about 10^{-4} Pa. 30 to 100 nm thick films were used for electron-microscopic investigations (a PEM-U microscope); X-ray studies were made using a DRON-3M diffractometer and films of about 500 nm thickness. The microscope resolution was 0.2 nm confirmed by the direct resolution of (200) atomic planes in thin single-crystal gold films. Data obtained in "thick" film measuring on a MII-4 interferometer were used to calibrate quartz microbalance as a device to measure the film thickness. The films were deposited onto substrate holders having either a constant temperature over the surface or a temperature gradient. The conductivity of films in a mode thermocycling was measured in an interval of temperatures 510-300K directly after of condensation without bleed-in of air in the vacuum chamber, and then the same measurements were made after remove of films on an atmosphere.

RESULTS AND DISCUSSION

Fig.1 presents SED and electron-microscopic image of the pure fullerenes and C_{60}+Bi structure on FP substrate. The studies carried out

show that perfect films with metastable1 HOP lattice grow epitaxially on FP at T_s = 450 to 500 K and the fullerenes molecular flow density 1.2×10^{17} to 6×10^{17} m^{-2} s^{-1} up to a thickness 70 to 80 nm. The experimental value of the lattice misfit is f_m ≈5 % being in a good agreement with the calculated one[2]. The structure images with the direct lattice resolution exhibit (010) and (110) type planes with interplane distances of 0.873 and 0.503 nm, respectively.

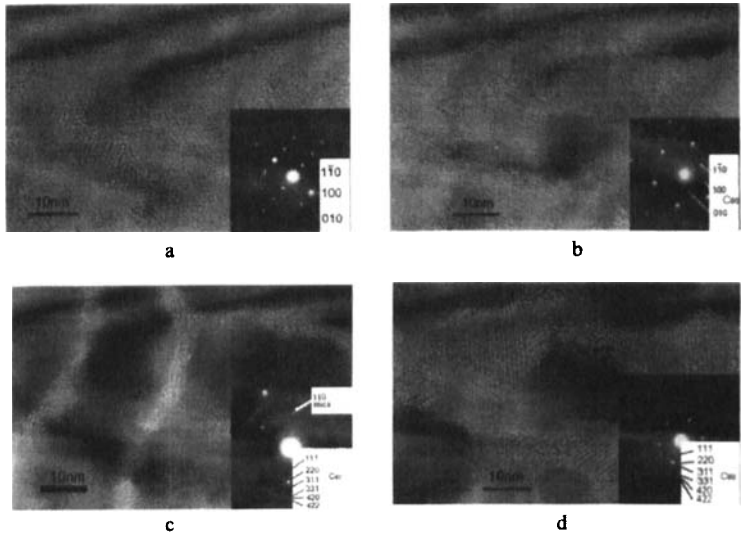

FIGURE 1 Structure of fullerenes films on FP mica nm, Ts=470 K: a) structure of pure fullerenes film; b, c,) structure of fullerene +bisuth film; d) structure of double-layer fullerene+bismuth film.

The regimes at which the films of pure C_{60} were deposited were used for the deposition of composite C_{60} + Bi. Fig. 1 shows electron microscopy images of condensates with different Bi concentrations in the film. They are characterized by the presence of contrast in the form

of dark spots. There are no reflexes with interplane distances corresponding to metallic Bi in the SED of these films. Moreover, no halo can be seen , which could be unambiguously associated with the expected amorphous particles Bi scattering. It is impossible to determine correctly the phase state of Bi agglomerations by electron microscopy.

There is an alternative: Bi either forms the agglomerations in the octahedron voids of fullerenes lattice, or separates out the fullerenes as independent particles in the amorphous state. An attempt was made to investigate the nature of the agglomerations by the layer-by-layer condensation C_{60} layer was the first to be deposited and then Bi was deposited. The structures formed as the result of the deposition (see Fig. 1d) are completely identical with the earlier ones. This experiment also does not give the final solution. Bi deposition onto the carbon film under the identical conditions causes at the same time the crystalline particles growth. We consider that at the layer-by-layer Bi deposition onto C_{60} at the chosen deposition rate and substrate temperature the Bi atoms being sorbed on C_{60} surface diffuse in volume and make the density of the adatoms lower, to the values at which the critical nucleus can't be formed. The substrate temperature decreasing and Bi atoms flux density increasing are to result in the particles growth on the surface. In other words, under the conditions, when the atoms arriving at the surface during the deposition are absorbed by volume, the critical thermodynamic and kinetic parameters of the critic nucleus formation appear during the condensation. To estimate the interaction of Bi with fullerene the values of electric conductivity of pure and doped Bi films of fullerenes were measured (see Fig. 2). Apparently, Bi contribution to electric conductivity change is not great. The influence of O_2 on the electric conductivity is more significant [3]. The electric conductivity of C_{60} and C_{60}-Bi films was measured in vacuum directly after the condensation in the temperature range 510-300 K, as well as after the exposure of the films at the decreased pressure to the atmosphere with the oxygen partial pressure 10 Pa for 50 hours. The films were

deposited on the surface of stepless mica with previously applied silver contact areas.

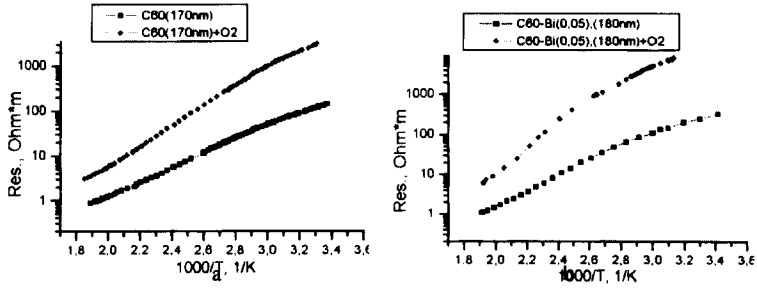

FIGURE 2. Temperature dependence of resistivity fullerene and fullerene + bismuth films.

The film deposition regimes complied with the regimes of formation of the films for structural researches. Doping of C_{60} films with bismuth only slightly changes the films conductivity. At the same time it is necessary to stress that oxygen influences significantly the decreasing of the electric conductivity of both pure C_{60} films and C_{60}-Bi films. The activation energy of E a carriers determined from the temperature dependence of electric conductivity for C_{60} films is 0.5-0.7eV, for C_{60}-Bi is 0.4-0.8 eV, which is less than the value of the prohibited zone width for bulk samples 1.5-1.9 eV. It is related to the density of the structure defects and, probably, with gas admixtures absorbed at the growth. When the films are saturated with oxygen their conductivity decreases and E_a increases for C_{60} films up to 0.6-1.1eV and for C_{60}- Bi up to 0.6-1.4eV. It is caused by the compensation effect. It is necessary to note that the electric conductivity measurements for all the films saturated with oxygen were conducted after the preliminary heating of the films in the high vacuum up to 500 K, and during the heating the partial loss of the absorbed oxygen occurred.

CONCLUSIONS

When C_{60} is deposited on the surface of fluorophlogopite the fullerenes films have a metastable close-packed hexagonal structure up to the thickness h=80 nm. The further building up of the film causes the appearance and the growth of FCC phase of fullerenes which is thermodynamically stable at the temperatures 250 K and over , with plane (111) oriented parallel with mica surface. Fullerene and bismuth coprecipitation onto the heated substrates when the relation Bi /C_{60} in the flux is less than one results in the films with the crystal structure of fullerenes with Bi atoms located in the octahedral voids of the fullerenes. At Bi/C_{60} ratio ≤ 0.1 the bismuth atoms are accumulated in the neighbouring voids of the lattice and form nano-dimensional conglomerations. Increasing of Bi quantities causes the growth of the conglomeration sizes and the deterioration of the perfectas degree of the films.When substances slightly interacting with fullerene, e.g. Bi, are condensed, the freely permeable fullerenes crystal lattice may absorb the atoms adsorbed on the surface, thus decreasing the probability of a critical nucleus formation and thereby inhibiting the film formation. The absorption process is limited by diffusion and is dependant on temperature of the surface of growth; thus, the formation of a nucleus on the fullerenes substrate is described by a new set of critical thermodynamic and kinetic parameters.

Doping of the fullerenes film with bismuth only slightly changes their electric conductivity and the activation energy of the charge carriers. Exposure of the fullerenes and metalfullerenes films to the atmosphere changes the transfer processes in the films significantly due to saturation of the crystal lattice voids with oxygen, thus making it necessary to investigate the kinetics of the transfer processes in situ under the ultrahigh vacuum conditions.

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