Peculiarities of Formation of Clathrate and Percolation Structures in Model Systems C60 - Bi and Bi -Sb

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Abstract— **The processes and conditions of formation of materials with specific structure of impurity subsystem have been investigated on the basis of model systems C_{60} - Bi and Bi-Sb. It is established that in classical Bi-Sb system, traditionally characterized as a system of continuous solid solutions, at low concentrations of impurity, atypical structures are formed, characterized by the formation of impurity percolation channels, and thus by the formation of peculiar composite of matrix of basic component and three-dimensional impurity frame. By the example of the C_{60} - Bi system it is shown that the formation of clathrate structures, in which the impurity sub-system forms its own sub-lattice, not inherent to the given substance in pure form, is most probable under the conditions of ion implantation of the impurity in the preformed fullerite matrix. While under the conditions of joint condensation of the components the condensation stimulated diffusion processes lead to the formation of a two-phase metal fullerene composite.**

Keywords— fullerite, clathrate, ion-implantation, composite, solid solution, percolation.

I. INTRODUCTION

Application of new materials, improvement of the existing ones and development of new methods of their obtaining allows to expand functional capabilities, increase reliability and speediness of products of electronic technology and is included in the number of major problems faced by the modern society.

One of the main methods of controlling the properties of materials is the formation of solid solutions. But the properties of the materials depend not only on their composition, but also on the structure of the impurity sub-system.

Metal fullerene clathrates are an interesting and convenient model object for studying the formation of advanced materials with an ordered impurity subsystem. In their structure metal atoms fill the cavities of the fullerite lattice and form structures not typical of the substance in their pure form, but such structures, which are set by a sublattice of intermolecular cavities. Metal fullerenes with such arrangement of impurity atoms are a new class of artificial objects, which can manifest unique physical properties.

Of particular interest are solid solutions with small additions of dilute element, in which different phase transitions are possible when the concentration of impurity changes. It is well known that solid solutions are divided into diluted and concentrated solutions and it is widely considered that the properties during the transition from diluted to concentrated solid solutions change in a continuous manner. Nevertheless, one can expect that this transition will be accompanied by percolation-type phase transitions and self-organization processes [1-5]. This could lead to non-monotonous character of the concentration dependences of the properties, which should definitely be taken into account while choosing the materials for the manufacture of the electron technology products. The studying of phase transitions is of an interest from the scientific and practical point of view, in connection with the possibility of creating various devices of micro- and nanoelectronics.

All aforesaid has determined the direction of this paper research, which was directed to determination of peculiarities and conditions of creation of innovative materials with specific structure of impurity sub-system, which can be realized artificially or at the expense of nano-orderedness in such model systems as C_{60}-Bi films and Bi-Sb solid solutions.

II. OBJECTS OF THE RESEARCH AND METHODS OF INVESTIGATION

Bi component films of C_{60} - Bi system were prepared by condensation of sublime C_{60} molecules and accelerated bismuth ions on silicon substrates in vacuum. The source of bismuth ions was vacuum arc plasma separated from the neutral component (atoms, molecules, microparticles) by means of a curvilinear plasma guide, not allowing spatial separation of single- and double-charged ions. The amount of bismuth in metal fullerene condensates and its distribution in films was determined by X-ray fluorescence analysis and scanning electron microscopy. The structure of films was investigated by X-ray diffractometry.

Polycrystals of Bi-Sb solid solutions in intervals of 0 - 2.0 at. % Sb with a step of Sb concentration from 0.1 to 0.5 at. % were obtained from high-pure (99. 999%) Bi and Sb semimetals by synthesis in evacuated quartz ampoules at (1020 ± 5) K, subsequent cooling by the air and with the following annealing at (520 ± 5) K for 1200 hours. Synthesis was carried out simultaneously for all alloys, which guaranteed the identity of conditions of their preparation.

To determine the chemical composition and structure certification of the prepared Bi-Sb polycrystals methods of electron probe microanalysis (EPM) on a scanning electron microscope JSM-6390 LV with the system of energy dispersive spectrometer INCA Energy 350; X-ray photoelectron spectroscopy (XPS) on a XPS-800 Kratos spectrometer; X-ray fluorescence analysis (XFA) and X-ray diffractometry were used. The irradiated surface area of the samples was ~ 12 mm^2, ~ 7 mm^2 and 10 nm, while the depth of the analysed layer was ~ 1 μm, ~ 5 nm and 1 – 3 μm by XFA, XPS and EPM, respectively, when investigating the chemical composition of the samples. The results of microstructural analysis showed that all Bi-Sb samples are single-phase. The average grain size of Bi-Sb polycrystals after annealing was $d \approx 300$ μm.

To study the dependences of Bi-Sb properties on composition different methods were used. In particular, measurements of microhardness (H) were made, excluding the influence of scale effect, under the load on an indentor ~ 0.39 N; measurements of longitudinal velocity (V_L) and linear ultrasound absorption coefficient (α) were made by impulse method with the frequency-compensated acoustic bridge. Measurements of electrical conductivity (σ), magnetoresistance ($\Delta\rho/\rho$), Hall coefficient (R_H) were carried out in the temperature range of 77 - 300 K. Magnetic field of 1 Tesla was used for the R_H and $\Delta\rho/\rho$ investigations.

III. Research Results and Discussions

A. Study of C_{60} - Bi

According to X-ray fluorescence analysis films, obtained by co-deposition of sublimated fullerene molecules and accelerated bismuth ions at U = 50 V were two-component condensates with the bismuth/fullerene ratio from N_{Bi}/N_{C60} = 1/10 to N_{Bi}/N_{C60} = 3/1. The results obtained by scanning electron microscopy of C_{60}-Bi films show a heterogeneous distribution of components in the resulting condensates. In the samples with the excessive metallic component the fullerite phase is represented by isolated globular segregations of about 200 nm surrounded by the regions of segregated bismuth. (fig. 1).

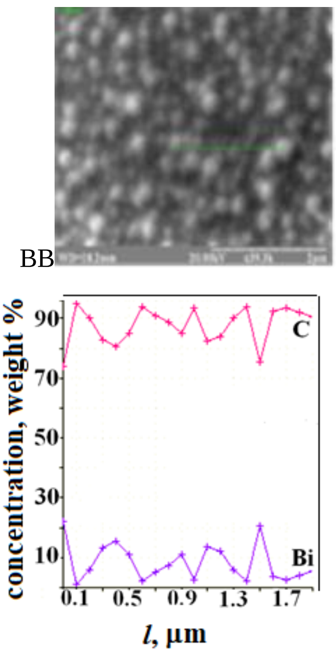

Fig.1. Surface image of C_{60} - Bi films obtained by co-deposition of bismuth ions and fullerene molecules and distribution of its components.

The structure of films obtained by the deposition of a two-component flux of sublimated fullerene molecules and accelerated bismuth ions was studied by X-ray diffractometry. Typical diffractograms of the samples are shown in Fig. 2. As can be seen from the figure, reflections corresponding to the FCC fullerite structure are present in the diffractograms at low bismuth concentrations. The ratio of the intensities of the main X-ray maxima corresponds to the theoretical and calculated values typical of fullerite FCC powder X-ray diffractograms, indicating the formation of non-textured C_{60} films. The absence of reflections from the bismuth phase indicates that the bismuth appears to be distributed in the condensate volume as X-ray amorphous nanoclusters or microinclusions.

As the content of metallic component in the films increases up to $N_{Bi}/N_{C60} \approx 1/1$, the reflections from bismuth phase appear in diffractograms, the width of which was used to determine the average size of bismuth segregations ~ 40 - 50 nm. An increase in the bismuth content in the films is accompanied by broadening of the X-ray lines corresponding to the FCC lattice of fullerite, indicating a decrease in the degree of crystallinity of the fullerite phase right up to its full amorphisation at N_{Bi}/N_{C60} = 3/1. At the same time, the formation of a separate crystalline phase of pure bismuth is observed.

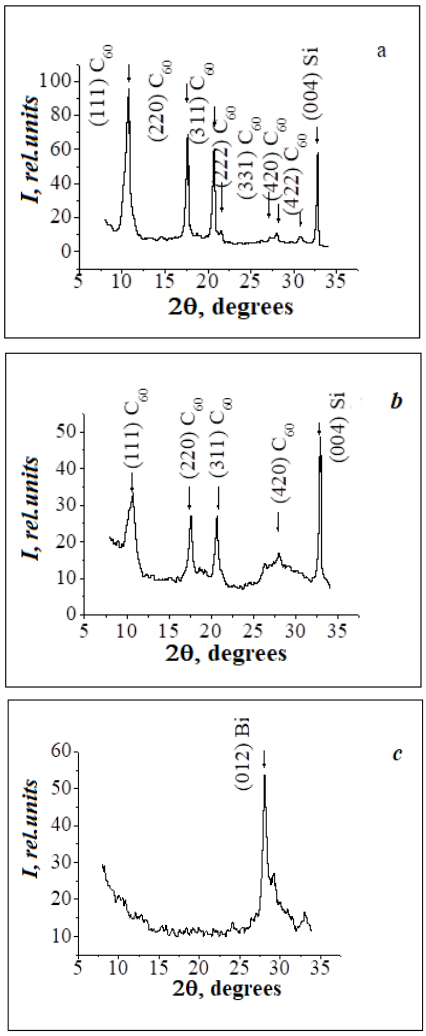

Fig. 2. Fragments of C_{60}–Bi film diffractograms.
a - $N_{Bi}/N_{C60} \approx 1/10$; *b* - $N_{Bi}/N_{C60} \approx 1/1$; *c* - $N_{Bi}/N_{C60} \approx 3/1$.

Based on the experimental data a model of C_{60}-Bi film structure formation during co-deposition of the components has been proposed. According to this model, the absence of bismuth in the fullerite crystal lattice can be explained by high diffusion rates of components during condensation, so that bismuth atoms diffuse to the boundaries of growing fullerite grains and form separate segregations. Increasing bismuth content in films leads to evolution of a metallic component at grain boundaries of fullerite FCC crystal as X-ray amorphous nanoclusters at $N_{Bi} / N_{C_{60}} = 1/10$ or as microinclusions at $N_{Bi} / N_{C_{60}} = 1$. The growth of the metallic phase inhibits recrystallization of the growing fullerite grains, resulting in a deterioration of the fullerite FCC structure perfection up to its amorphization at $N_{Bi} / N_{C_{60}} = 3$.

Based on a preliminary X-ray diffraction analysis of fullerite films deposited on silicon substrates by evaporation of fullerene powder from a Knudsen effusion cell, the investigated samples also appeared to be polycrystalline non-textured FCC lattice condensates, as indicated by the good agreement between the intensities of the main X-ray lines and the tabulated and calculated values for pure FCC fullerite powder X-ray patterns.

X-ray fluorescence analysis of fullerite films irradiated with accelerated bismuth ions has shown that ion irradiation of a C_{60} film target results in bismuth saturation of fullerite and formation of metal fullerene condensates with the integral ratio of bismuth atoms to fullerene molecules equal to $N_{Bi} / N_{C60} \approx 1$. A typical feature of the studied condensates is that in contrast to the films formed by co-deposition of components, no appreciable difference between the bismuth content in fullerite grains and at their boundaries is observed in the irradiated samples (Fig. 3).

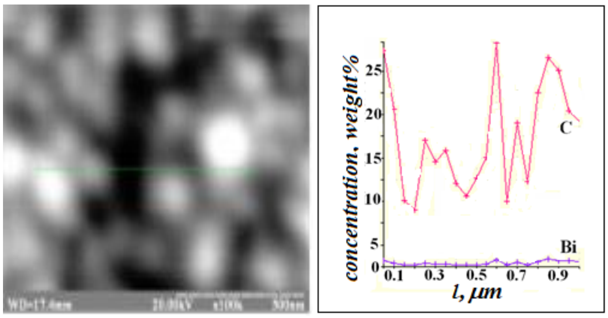

Fig. 3 Image of the surface of fullerite films irradiated with bismuth ions and the distribution of its components.

Experimental diffractograms from these samples (Fig. 4) contained reflections at angles corresponding to the interplanar distances of pure bismuth and FCC fullerite crystals, indicating the formation of a two-phase structure of the films. However, the ratio of reflection intensities from the FCC phase of this composite does not correspond to the values characteristic of pure fullerite. Based on the results of calculations described in [6], the results of diffractometry of these samples were analyzed.

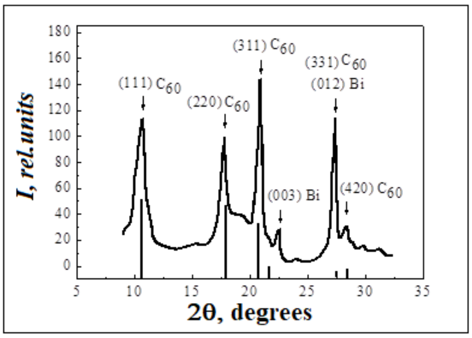

Fig. 4 Experimental diffractogram of bismuth-doped fullerite film and theoretical dashed-line X-ray of untextured pure FCC fullerite film.

The fact that the strongest line in the diffractogram is reflection (311) indicates the formation of a structure in which a part of bismuth atoms occupies the octahedral cavities of the FCC fullerite crystal. Starting from the ratio $I_{(111)} / I_{(311)} \approx 0.7$, the estimation of the filling factor of bismuth in the octahedral cavities of fullerite crystal was made; as a result, the value of the filling factor was $c \approx 0.1$.

B. Study of Bi-Sb solid solutions

On the basis of measurements of electro-physical properties in the temperature range 77 - 300 K a monotonic decrease in the whole investigated temperature range has been established, which is typical for metals, semi-metals and semiconductors with a degenerate electron gas.

For all investigated samples Hall coefficient was negative inside the whole temperature range of 77 - 300 K, indicating that all obtained polycrystals of Bi-Sb solid solutions have electronic type of conductivity.

As a result of the analysis of the dependencies of the properties on composition of solid solutions, it has been established:

- The dependence of microhardness on composition (Fig. 5a) has distinctly non-monotonic character: in the concentration intervals of 0.5 - 1.5 at.% Sb the plateau areas when microhardness practically does not change are found.
- The results of investigations of the dependence of longitudinal ultrasound velocity and linear ultrasound absorption coefficient on Sb content of polycrystalline Bi-Sb solid solutions are shown in Fig. 5b. With increasing of Sb concentration in Bi-Sb solid solutions, as one should expect, in general, there is an increase in ultrasonic velocity and a decrease in the absorption coefficient. Meanwhile, as can be seen from Fig.5b, the dependences of the longitudinal ultrasonic velocity and linear absorption coefficient from the Bi-Sb solid solution composition have a distinctly non-monotonic character; the anomalous V_L decrease and α increase at Sb concentration ~ 1.5 at.% are observed.
- On the dependences of Hall coefficient, electrical conductivity, carrier mobility and magnetoresistance on the Sb content in the concentration range of 0.5 - 1.5 at. % Sb sharp anomalous increases are also detected (Fig.6).

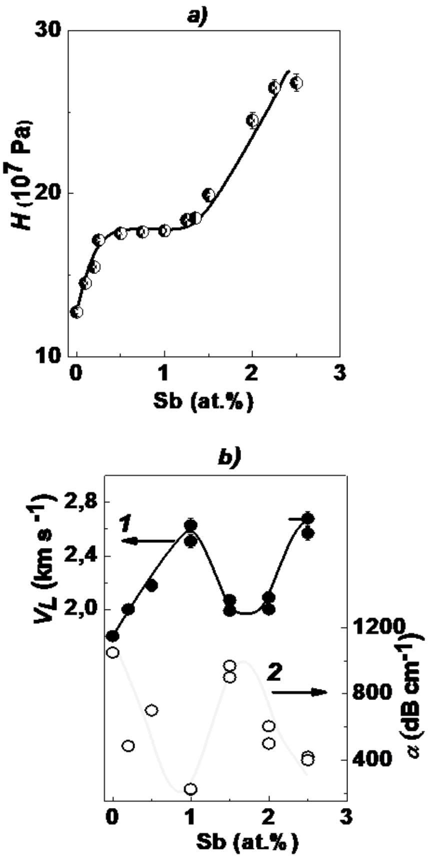

Fig.5 Dependences of microhardness H (a) and acoustic properties (b): longitudinal ultrasound velocity V_L (curve 1) and linear ultrasound absorption coefficient α (curve 2) on the Sb content for Bi-Sb polycrystals at T = 300 K.

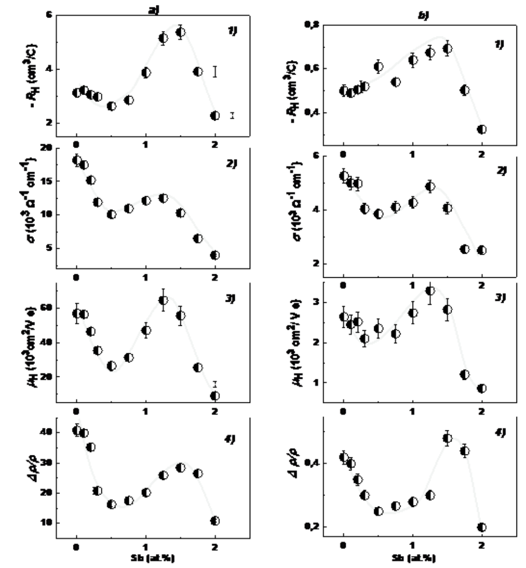

Fig.6 The dependences of Hall coefficient R_H (1), electrical conductivity σ(2), carrier mobility μ_H (3) and magnetoresistance $\Delta\rho/\rho$ (4) on the Sb content for Bi-Sb polycrystals at T = 77 K (a) and T = 300 K (b).

The presence of detected anomalies of mechanical, acoustic, electrophysical and galvanomagnetic properties from the solid solution composition, indicating the qualitative changes in the electronic and lattice sub-systems of the crystal with increasing Sb concentration, is associated with the concentration percolation-type phase transition that accompanies the transition from diluted to concentrated solid solutions. Within the framework of percolation theory [1-3] it is possible to assume that the increase in Sb concentration leads to overlapping of strain fields of neighboring atoms which is accompanied by formation of percolation channels. These channels, in turn, simplify the movement of dislocations, of electrons and of phonons, lead to a decrease in the level of elastic stresses, which is associated with the manifestation of critical phenomena, particularly, anomalies which are observed in the composition-property dependences.

Thus, in particular, the presence of a plateau section on the microhardness dependence on the solid solution composition indicates a partial removal of elastic stresses for this region. It is natural to connect the obtained results with the deviation from chaotic distribution of Sb and Bi atoms caused by reaching the percolation threshold, i.e. some critical concentration of Sb impurity atoms sufficient for their interaction and leading to collective effects in the lattice subsystem of the crystal.

It is also well known that the ultrasound velocity is closely related to material structure and properties and is a very informative parameter in the study of solid solutions, as well as in the study of phase transitions. Therefore, a significant argument in favor of the theory applied in the interpretation of the results is the anomalous decrease in V_L and sharp increase in α at Sb content ~ 1.5 at.%, which, in our opinion, also corresponds to the threshold of percolation.

The anomalous growth of electrophysical and galvanomagnetic characteristics also underlines once again the manifestation of critical phenomena, which accompany the concentration phase transition from diluted to concentrated solid solutions, based on percolation theory.

IV. *CONCLUSIONS*

1. It has been established that the deposition of two-component flux of sublimated fullerene molecules and accelerated bismuth ions results in the formation of non-textured metal-fullerene condensates, the degree of structural perfection of which is determined by the ratio of components in the films. A model of metal fullerene condensates formation has been proposed, according to which a high diffusion rate of the components at their co-condensation leads to bismuth separation mostly on the grain boundaries of the fullerite FCC crystal as X-ray amorphous nanoclusters at a resulting ratio of $N_{Bi} / N_{C_{60}} \approx 1/10$ or microinclusions at $N_{Bi} / N_{C_{60}} \approx 1$. The growth of the metallic phase causes recrystallization of the growing fullerite grains, resulting in a degradation of the fullerite FCC structure, up to its amorphization at $N_{Bi} / N_{C_{60}} \approx 3$.

2. It was experimentally shown that ion irradiation of the formed C_{60} films with accelerated bismuth ions with the energy ~ 100 eV leads to the saturation of fullerite with bismuth atoms, which, at the resulting $N_{Bi} / N_{C60} \approx 1$ component ratio, are predominantly segregated into a separate phase. Part of the bismuth atoms are located in the octahedral cavities of the fullerite FCC crystal and form a metal fullerene clathrate with an integral cavities filling factor equal to c = 0.1.

3. For Bi-Sb solid solutions in the semi-metallic region of concentrations in the range 0.5 - 1.5 at.% Sb on the dependences of the mechanical, acoustic, electrophysical and galvanomagnetic properties on antimony concentration

anomalies were established, which are associated with critical phenomena accompanying the phase transition of percolation type from diluted to concentrated solid solutions. It is supposed that after formation of percolation channels in the crystal the process of interaction of impurities acquires a collective character, simplifying the dislocation, electron and phonon movement.

4. The presence of anomalies in the region of low impurity content in semi-metallic solid solutions confirms the universal character of these phenomena for solid solutions of any type, which should be taken into account when developing and predicting the parameters of new materials based on bismuth and other elements or compounds. The results are of fundamental importance for the development of scientific understanding in the physics of solid solutions and the physics of phase transitions.

5. Thus the problem of revealing peculiarities and establishing conditions for the formation of two-component materials with atypical structure of impurity sub-system has been solved. By the example of the model system C_{60} - Bi the possibility of forming the bismuth sublattice which structure is determined by the system of intermolecular cavities in fullerite matrix has been shown. The ordering phenomena in Bi-Sb solid solutions with the formation of percolation impurity channels in the matrix of the main component have been investigated.

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