MODULATED STRUCTURE OF FULLERENE ¯ BISMUTH VACUUM DEPOSITS

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A new structure model is proposed for C_{60} ¯ Bi vacuum-deposited condensates to explain the morphology and diffraction features of such objects. The model supposes the presence of fullerite crystals with multitwin and heterophase lamellarity as well as of the crystallographic plane stacks consisting of bismuth atoms at the interlayer boundaries of fullerite grains.

Scientific communications concerning fullerite films synthesized from closed hollow carbon clusters C_{60} (fullerene) and fullerite ¯ metal film systems are published quite for 10 years [1 ¯ 3]. The enhanced interest in these new materials is initiated both by attempts to understand the nature and physical mechanism of their properties and by very good prospects for their application as high-temperature superconductors, active media in the intercalation energy storage batteries, antifrictional materials of high efficiency, ion traps, etc.

Experimental investigations in the atomic, crystalline, and grain structure and phase states of those materials is of great importance in their studies. The results accumulated up to date allow us to summarize the set of primary structure characteristics resulting from the crystal chemistry of the materials and their manufacturing conditions as well as to formulate and discuss a series of new problems and tasks directed to the further investigation of their structure features, mechanisms, and decisive physical factors defining their formation.

The following structure features are generally believed to be typical of the films under consideration. On NaCl, mica or glass substrates at temperatures exceeding 250 °C, the fullerite vacuum-deposited condensates are formed having the f.c.c. crystal structure accompanied often by the h.c.p. modification. A trend is observed to the formation of an axis texture where close-packed (111) planes of the f.c.c. modification and (0001) ones of the h.c.p. structure are arranged in parallel to the substrate plane. A high stacking fault density is noted; it is just those faults that some authors believe to be associated with h.c.p. interlayers in f.c.c. grains [3, 4].

Many morphologic characteristics of fullerite garins are manifested themselves very clearly in fullerite-metal film systems. In this sense, the work [5] is significant where the formation regularities of binary fullerite-bismuth films were studied at the co-deposition in a 10^{-3} Pa vacuum under varying deposition parameters and concentrations of components being evaporated from separate sources.

Starting from the Bi concentrations exceeding 1%, the films take the heterophase structure; round-shaped Bi particles are revealed in electron micrographs along with fullerite grains. In that work, additional structure features of fullerite films being of primary importance for the further discussion were noted beside of the above-mentioned ones, namely, (i) the Bi presence favors the fullerite grain oriented growth; (ii) the presence of Bi favors the co-excistence of the fullerite polymorphic heterophasity (f.c.c.-h.c.p.) at substrate temperatures lower than 462 K; (iii) some fullerite grains exhibit a streaky contrast in electron micrographs (see Fig.1,*a*) that becomes more pronounced after heat treatment; (iv) superstructure diffraction peaks are revealed in the film electron diffraction patterns while some reflections exhibit pronounced streaks (Fig.1,*b*) having well-reproducible directions with respect to the primary beam.

In our opinion, all the set of the above-mentioned morphology and diffraction characteristics of fillerite films and binary systems on its base can be explained in a non-contradictory manner using a unique structure model. The formation mechanism of the specific structure answering the model being proposed consists in periodical errors (changes) of the stacking sequence of close-packed planes in the course of the 'condensation assembling" of a growing crystal. Particles being condensed on the growth surface (111) of a f.c.c. crystal occupy one of three possible standard positions [6]; *A*, *B*, or *C*. Let, for example, an f.c.c. crystal be grow (the stacking order *ABC ABC*) and a stacking error be occur: *ABC ABC B*. If the further sequence will be *ABC ABC B ABC* or *ABC ABC BC ABC*..., then an usual stacking fault (interstitial or substractive one, respectively) will be formed. If the stacking order *ABC ABC BAC BAC*... will follow, the twin of the same phase is formed, while the f.c.c.→ h.c.p. phase transformation answers the *ABC ABC BC BC..* sequence or *ABC ABC BA BA..* one.

It is obvious that the probability of each variance of the further 'assembling" stacking order following to the plane stacked erroneously is influenced by the force value of the long-range interaction that the crystal

in growth exerts upon the spatial atomic arrangement in the plane being formed. It is just the foreign atoms that are among physical factors influencing considerably the realization of the above-considered growth variances. The continuous growth of a perfect fullerite crystal requires that fullerene particles should be delivered in due time to the crystallization front. When the crystallization occurs from a primary phase containing several components, the crystal growth process is hindered due to the foreign matter accumulation at the growth surface in an amount exceeding its equilibrium solubility. According to the Le Chatelier ̄ Braun principle, this hindrance can be eliminated if superfluous foreign atoms form their own crystallographic plane at the growing crystal. Several crystallographic planes may be also formed from the second component atoms.

It is just the periodically arising stacks of two or more crystallographic planes consisting of Bi atoms that are capable of screening the force action of the growing fullerite crystal on the spatial atomic arrangement at the growth plane being currently formed and thus on the sequence preservation during the further stacking. In that way, the excess Bi concentration (with respect to its equilibrium solubility) perturbs periodically the regular grain growth of the equilibrium f.c.c. fullerite modification and favors the formation of flat twins or lamellae of the metastable h.c.p. phase.

The formation of such crystal sublamellae of Bi atoms having the thickness of one or few interatomic spacings is favored by the pseudomorphism phenomenon [7]. The rhombohedric Bi structure (the space group $A7$) contains crystallographic nets with the hexagonal atomic arrangement as in (111) planes of f.c.c. lattice or in (0001) ones of the h.c.p. one. Such a fitting is shown schematically in Fig. 2,c. The treble distance between adjacent Bi atoms in its hexagonal net is 0.93 nm while the spacing in the fullerite (111) plane is 0.99 nm. Thus, the mutual deformation as small as 6% is necessary to fit these flat site patterns together. However, the pseudomorphism was observed even at greater lattice misfits [7]. Due to the mentioned fitting of Bi sublamellae with the close-packed planes of the growing fullerite crystal, the phase interface energy turns out to be rather low. The elastic deformation energy of such a lamella is also low due to its small volume. Moreover, the co-existence of such flat crystalline formations of Bi and fullerite answers the trend of this binary system towards the two-phase equilibrium state. In this connection, it may not be out of place to remember the concept of so-called contact atomic compounds [8] including layers of different compositions connected together not with van der Waals bonds but with covalent or ionic ones. The possibility of such a bond formation between fullerene clusters and bismuth atoms is discussed in [9].
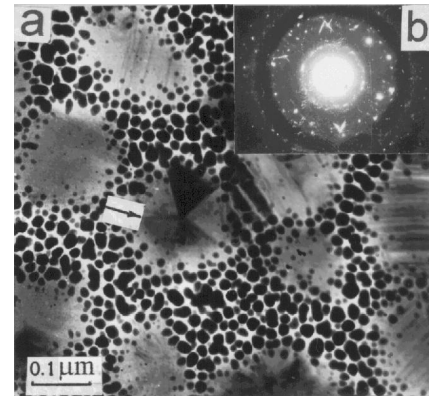

Fig. 1. Electron micrograph (*a*) and diffraction pattern (*b*) a fullerite-bismuth film
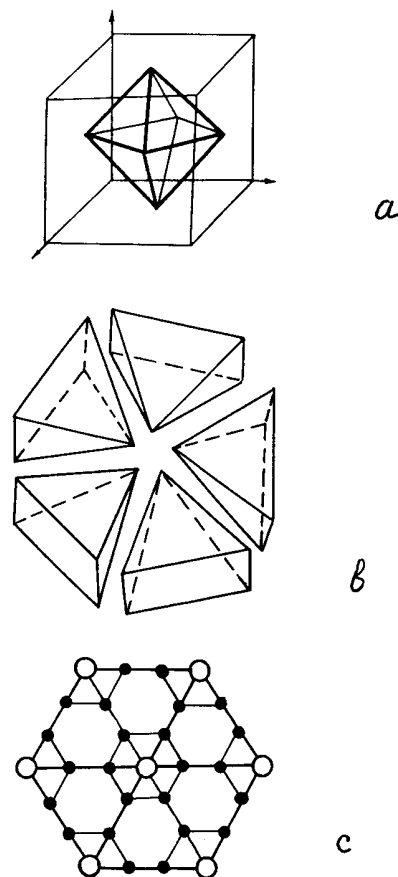

Fig. 2. Geometric relations in fullerite crystals: a ̄ arrangement of the {111} planes octahedron with respect to the cubic lattice axes; b ̄ scheme of the twin arrangement in a five-angle shaped grain; c ̄ fitting of the (111) fullerite plane (light circles) with a Bi geometric net (black circles)

Such two-dimensional Bi interlayers cannot be revealed by the routine X-ray diffraction phase

analysis due to the two-dimensional scattering character of the radiation in use. Those cannot be observed also as a superstructure in the main fullerite phase, since there is no spatial coherence along the normal to the plate plane between its plates.

Formation of the modulated structure consisting of lamellar heterophase aggregates and twins fitted together close-packed crystallographic planes results inevitably in the appearance of diffuse streaks [10] pronounced especially on [220] reflections, superreflections, and additional ("non-textured") diffraction peaks in the diffraction spectra. For example, if the fullerite crystal is oriented with its (111) plane in paralell to the substrate surface, then, in the same crystal (from here on, referred to as the 'basic" one), there are three other pairs of {111}-type planes forming angles of 70.5° with each other and thus with the substrate (Fig.2,*a*).

Twins or h.c.p. phase crystals are grown also on those tilted {111} planes of fullerite due to a stacking error of close-packed planes. In such turned h.c.p. crystals, the close-packed (0001) planes also are tilted to the substrate surface at an angle of 70.5°. As a result, as follows from crystallographic analysis, the following crystallographic planes are in the reflection position on transmission electron diffraction: (311), (331), (511), (531) of fullerite (which cannot reflect in parallel to the substrate in (111) texture) as well as (11.0), (11.2), (21.2) of the h.c.p. structure. It is just what was observed in [5]. The f.c.c. phase twin formation on tilted {111} planes of basic f.c.c. grains results in that extra reflections are appeared in the electron diffraction patterns. Such reflections are characterized by fractional Miller indices and explained by the double diffraction effects in twins [10]. On such primary fullerite twins, a next stacking error in the close-packed plane sequence gives rise to secondary twins which, in turn, are capable to give the reflection position to still other plane types of fullerene as well as to those of the h.c.p. phase that grows with its (0001) plane in parallel to {111} ones of primary and secondary f.c.c. modification twins. In such a way, a set of preferred orientations is formed in grains which are not in immediate contact with the substrate.

It is just those fullerite grains where the heterophase and twin lamellae are positioned at an angle of 70.5° to the substrate surface that exhibit the streaky contrast in electron micrographs. The successive multitwinning, i.e., the formation of primary, secondary, etc., twins, is confirmed also by the fact that several systems of parallel streaks are often observed within the same fullerite grain (Fig.1,*b*), these systems being arranged at angles close to 70.5° to each other due to the tilted orientation of lamellae. The trend of fullerite crystals to multitwinning is manifested itself sometimes as the formation of grains with the five-angle overall shape (Fig.1,*b*) in the projection on the substrate plane. The base of such a grain consists of five half-octahedral twins with side facets {111} and bases {100} having the standard dihedral angle of 70.5° at the vertex and the common <110> direction normal to the substrate plane (Fig.2,*b*). Such a pentagon is of course irregular, since the total angle formed by {111} twin facets around their common [110] edge amounts 352.5°. An angular slit of 7.5° is sometimes observable in electron micrographs (as is shown by the arrow in Fig.2,*b*).

In our opinion, along with the above-considered kinetic factor, there is a thermodynamic reason of dimensional character that is of a substantial importance for the polymorphic heterophasity formation in the lamellar grain morphology of fullerite films. Let the Gibbs' free energy G of a film be considered as consisting of two terms

$$G = G_V + G_S \qquad (1)$$

relating to the crystal volume V and its surface S, respectively. For a thin film specimen, in contrast to a bulk solid, of principal importance is that as the film thickness h decreases, the contribution of the surface component G_S may become predominating:

$$G_S / G_V \sim \sigma S / (\gamma h S) \sim b / h \qquad (2)$$

Here, σ is the specific surface energy; γ – the specific volume energy; b – a constant. Thus, for thin films (as well as for thin plates), the following relations are possible:

$$G_V \ll G_S \qquad \text{and} \qquad G \approx G_S. \qquad (3)$$

Relations (3) explain the existence of polymorphic phases in thin films: the thermodynamic criterion of the single-phase film formation defined by the energy distinction between f.c.c. and h.c.p. lattices turns out be insubstantial.

The thermodynamic dimensional factor controls also the lamellar shape of pseudomorphic Bi strata in fullerite grains till those do not attain a critical thickness h_{cr}. If the thickness of pseudomorphic flat Bi interlayers in fullerite grains becomes $h > h_{cr}$, then relations (3) for this phase component become disturbed. Therefore, an 'independent" phase is formed in films with a higher Bi content shaped as equiaxial (at least in the film plane) Bi particles. Note that the formation probability of pseudomorphic Bi interlayers is defined by the efficiency of diffusion processes within the condensation zone. Therefore, as the substrate temperature increases, the h.c.p. phase signs in the film electron diffraction patterns become substantially weaker or disappear at all, since excess Bi atoms are drawn out from the fullerite grain growth front more effectively [5].

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The system capability of 'drawing out" the excess Bi atoms hindering the further growth of fullerite grains due to the formation of pseudomorphic Bi strata on the close-packed (111) and (0001) planes of the f.c.c. and h.c.p. phases, respectively, results in a considerable intensification of the 'growth selection" phenomenon. As a result, the predominant orientation of fullerite grains with (111) planes parallel to the substrate surface, the h.c.p. phase signs, and twinning are revealed in fullerite-bismuth films at lower temperatures (420 K) rater than in pure fullerite ones (450 K).

Thus, the proposed modulated model of the fullerite-bismuth film structure allows one to provide an non-contradictory explanation for a wide variety of the morphology and diffraction characteristics of those materials. According to that model, it is just the thermodynamic factor of the condensate free energy minimization, taking into account the size effects and possibilities of the diffusion mass transfer of components during the condensation, that defines the specific morphology of crystal grains. One of the nontrivial structure features of fullerite-bismuth films consists in that several crystal-chemical arrangement types of the components may be realized therein. Those are Bi atoms in octahedral and tetrahedral voids of the fullerite lattice, sublamellae consisting of Bi atoms separating polymorphic and twinned fullerite lamellae, and proper Bi grains intermittent with fullerite grains. In addition, we indicate the polymorphic heterophasity,

the discrete twin-defined set of additional preferred orientations, the lamellar grain morphology, and the presense of specific orientation relationships between the above-mentioned structure and phase components of the condensate. Such a thermodynamically balanced morphology and phase structure must exhibit a higher temperature stability than that of pure fullerite films. Perhaps, it may define some other physical characteristics of the these materials. The proposed structure model may be useful for understanding and forecasting those   characteristics.

1. *Hebard A.F., Possensky M.J., Haddon R.C. et at.* // Nature. ‾ 1991. ‾ 350. ‾ P. 600 ‾ 607.
2. *Loktev V.M.* // Fizika Nizk. Temper. ‾ 1992. ‾ **18,** N3. ‾ P. 217 ‾ 237.
3. *Zhao W.B., Zhang X.-D., Chen K.-J. et al.* // Thin Solid Films. ‾ 1993. ‾ 232, N2. ‾ 149 ‾ 153.
4. *Hou J.G., Xu W., Haigian W., Li Y.* // J. Appl. Phys. ‾ 1998. ‾ **84,** N5. ‾ P. 2906 ‾ 2908.
5. *Toptygin A.L., Pugachev A.T., Churakova N.P. et al.* // Function. Mater. ‾ 2000. ‾ **7,** N1. ‾ P. 14 ‾ 19.
6. *Shaskolskaya M.P.* Crystallographia. ‾ Moscow: Vysshaya Shkola, 1984 [in Russian].
7. *Kosevich V.M., Ievlev V.M., Palatnik L.S., Fedorenko A.I.* Structure of Intercrystallite and Interphase Boundaries. ‾ Moscow: Metallurgia, 1980 [in Russian].
8. *Aleskovsky V.B.* Chemistry of Solid State. ‾ Moscow: Vysshaya Shkola, 1978 [in Russian].
9. *Hou J.G., Wang Y., Xu W., Zwang S.Y. et al.* // Appl. Phys. Lett. ‾ 1997. ‾ **70,** N23. ‾ P. 3110 ‾ 3115.
10. *Hirsch P.B., Howie A., Nicholson R.B. et al.* Electron Microscopy of Thin Crystals. ‾ London: Butterworths, 1965.