Influence of Deposition Conditions on Characteristics of Fullerenes Containing Carbonic Coatings Obtained Using High-Power Ion Beams[1]

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Abstract – A possibility of obtaining thin carbon films with high content of fullerene mixture C_{60} and C_{70} using the method of sputtering graphite targets by high-power pulsed ion beams (HPIBs) is shown. Investigation of films structural and phase composition was performed by the methods of transmission electron microscopy (TEM) and X-ray diffraction analysis (XRDA). It is shown that the formation of fullerenes depends on the parameters defining the conditions of carbon vapor condensation in a scattering vapor-plasma jet. Optimal conditions for target sputtering are defined and a possibility of controlling the composition and amount of fullerenes in films is demonstrated.

1. Introduction

The existence of carbon in the form of fullerenes and carbon nanotubes (CNT) has large prospects for application as fundamentally new materials. Fullerenes can be used for the creation of a new class of superconductors, semiconductors, magnets, nonlinear optical materials, compounds for pharmacology and medicine, new technologies for diamond synthesis and new types of energy sources [1–3]. The most commonly used electro arc and laser methods of high temperature synthesis of fullerenes and CNT in helium atmosphere use the procedure of their extraction from the resultant soot with the help of solvents [2, 4]. For a number of applications, particularly in microelectronics, a creation of fullerene thin films on a substrate is necessary.

With this purpose we used the method of thin film obtainment based on the ultrafast deposition on the substrates of high-density ablation plasma with high thermal and kinetic energy. The plasma is created at the pulsed HPIB impact on the graphite target [5]. The process consists of two consecutive stages. On the first stage the thickness of material release from the target surface is connected with HPIB parameters (depth of ion range and nature of the absorbed energy distribution, power density and beam energy density, beam geometry at a target) defining characteristics and hydrodynamical flux of a vapor-plasma flow. At relatively low HPIB power flow densities (~10^8 W/cm^2) ablation plasma gets weakly ionized already near the graphite target surface (ionization degree 10^{-1}–10^{-2}) with low temperature of electrons and heavy particles [6] and becomes an efficient source of carbonic atoms. On the second stage adiabatic spread of ablation plasma to vacuum is accompanied with its density decreasing and effective cooling. The latter is especially important for carbon vapor condensation and subsequently for condensation heat spattering which releases at carbon clusters formation [7]. At reaching a substrate the resultant products deposit in the form of a film, whose characteristics and conditions of formation are determined by the deposition rate and degree of a substrate heating by vapor-plasma flow [5, 8]. High rates of substrate cooling after the peak of heating exceeding ~10^8–10^9 K/s are an important factor for the formation of nanocrystalline film structure as it is shown in [5].

Thus, the method combines necessary conditions for the effective fullerene creation and their formation in a crystalline phase in the form of a thin film on a substrate. It was reported in [5] about the presence of fullerenes without determination of their quantity in films deposited from carbon ablation plasma. In [10] was demonstrated a possibility of obtaining films with high concentration of C_{60} and C_{70} fullerene mixture using this method. This paper presents some results of the method optimization from the point of view of obtaining the maximal content of fullerenes and their purity, which was carried out in a wide range of conditions of carbon films deposition and HPIB parameters generated on different accelera-

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tors. It has been shown that the composition and content of fullerenes in films can be controlled, which allowed to increase the C_{70} output up to 95 %.

2. Experimental part

For the creation of carbon ablation plasma, the HPIBs generated on different accelerators were used providing the following parameters: accelerator TEMP-2 (70%H^+, 30%C^+ beam composition; 350 keV energy, 60 ns pulse duration, up to 5.5 J/cm^2 energy density), diode with cylindrical (linear) focusing, ~2.5×4.0 cm^2 beam size at a target; accelerator VERA (60%H^+, 40%C^+; 500 keV, 100 ns, up to 15 J/cm^2), diode with conical focusing, ≤20 cm^2 beam area at a target; accelerator RHEPP-1 (N_2^+ or O_2^+; 700 keV, 100 ns, up to 30 J/cm^2), MAP-diode with conical focusing, ≤50 cm^2 beam area at a target.

The scheme of coating deposition is given in Fig. 1.

Graphite targets with 1,68, 1,77 and 2 g/cm^3 density located at the angle of α=40° to the HPIB axis.

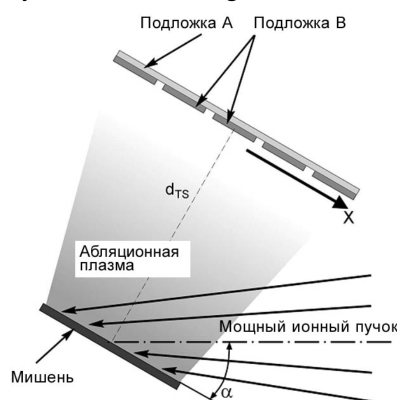

Fig. 1. Scheme of coating deposition. Substrate A – glass, substrate B – silicon, dTS – target-substrate distance

Thin film deposition was performed on the Si substrate with 10×10 mm dimensions in $5\cdot10^{-6}$ Torr vacuum. The films were formed on the RHEPP-1 accelerator in fringe regions of plasma flow with substrate location at the angle of φ=arctg x/d_{TS}. The variation of deposition conditions was achieved by modifying d_{TS} distance between target and substrate and (or) using different HPIB energy density. The film thickness was measured by Linnik interferometer and set by the number of ion current pulses. Investigation of films structural-phase composition was performed by the TEM and XRDA methods. The latter was conducted on the diffractometer "Shimadzu 600" (CuK_α radiation, grazing beam geometry, angle of incidence θ= 5°).

3. Results and Discussions

Analysis of XRDA results, presented in table 1, showed that films composition contains primarily the amorphous carbon phase and the crystalline carbon in the form of C_{60} and C_{70} fullerenes with the face-centered cubic lattice and orthorhombic lattice, respectively (fullerites).

The crystalline phase has a fine-grained structure with the average grain size ~40–50 nm. In some samples up to 5 % diamond-like carbon Diamond 8H (DLC) or 3R graphite modification is observed. It is difficult to speak definitely about the optimal conditions for this phase formation due to a small amount and instability of its yield. In the presented samples the total amount of fullerene mixture varies in the range of ~30–95 %. The data on phase-structural composition are confirmed also by film investigation using TEM method. The obtained micro-diffraction pictures (Fig. 2) contain a diffuse halo with two rings which are expressed brightly enough. This is characteristic of materials with crystalline grain dimensions ~5–7 nm.

Thus, the polycrystalline phase of carbon with the typical grain sizes of ~5–50 nm is observed in films over the entire range of deposition rates used, ~0.7–20 nm/pulse. This fact means that films cooling rate in the said range remains high enough for the nanocrystalline structure formation. However the yield of fullerenes practically does not depend on the main integral factors of films formation: the deposition rate and degree of the substrate heating by the vapor-plasma flow.

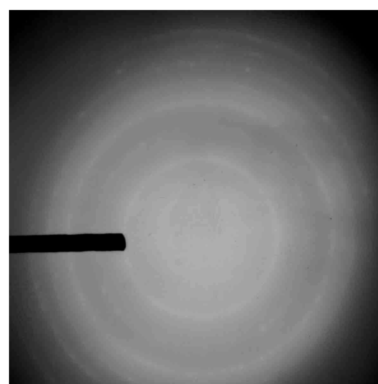

Fig. 2. Micro diffraction picture C/Si of sample № 8

The formation of fullerenes, their amount, and C_{60}/C_{70} ratio depend on the parameters defining the conditions of carbon vapor condensation in a freely scattering vapor-plasma flow. As follows from the data obtained, among such parameters one should consider the HPIB energy density, beam geometry at a target, and target-substrate distance which specify the initial temperature and the rate of carbon vapor cooling. At this the condensation mechanism seems as a process of nucleation of small carbon clusters which gradually assemble into bigger ones, also with the formation of fullerenes.

At an optimal rate of carbon vapor cooling taking into account time dependence of density and temperature in a flow, the yield of fullerenes is maximal.

In our case this corresponds to the dependence demonstrating the growth of the amount of fullerene

mixture at the fixed d_{TS} and decreasing HPIB energy density in the samples № 8–11 from 85 % to 95 % as well as the relative portion of C_{70}, up to the formation of monocrystalline film (Fig. 3). These conditions were obtained at the deposition rates range of ~1–2 nm/pulse in the mode of approximately linear increase of the temperature of heavy particles and release of target material depending on the HPIB embedded energy when according to the estimates the evaporation energy is achieved by the end of the beam current pulse. In this case for the flow cooling in the process of expansion a significant factor is also the ablation area reduction with the HPIB energy density decrease taking into consideration its actual distribution with the maximum on the target axis. This circumstance is confirmed by the high yield of fullerene mixture ~75–93 % for the samples № 1 and № 2 obtained at high deposition rates ~4.8–5.7 nm/pulse and significantly shorter $d_{TS}\approx 60$; 100 mm using a "linear" source. For such geometry of a beam at a target the rate of decreasing of main parameters of the plasma flow is significantly higher than for the case of the source with large area [8]. In all other cases, the rate of the carbon vapor cooling turns out either too slow, which is typical for high HPIB energy densities (samples № 3–7), or too fast, as for the samples № 13–16, obtained at wide angles of the samples location relative to the flow spread axis. Due to this, the main product of condensation become soot particles with increasing amount of amorphous carbon in the phase composition of films up to ~50–70 % (examples of X-ray diffraction patterns of the film for the said groups of samples are presented in Fig. 4 and Fig. 5).

Table 1. Results of X-ray diffraction analysis of carbon films

Accelerator	No	Film, irradiation condition	Energy density of beam, J/cm²	Graphitedensity, g/cm³	Coating thickness, nm	Deposition rate, nm/pulse	Targetsubstrate distance d_{TS}, mm	C_{60}:C_{70} %	DLC %	Amourphous phase, %
Temp-2	1	C/Si	5,5	1,68	345	5,75	60	60:40	–	7
	2	C/Si	4,8	1,68	288	4,80	100	20:80	–	25
Vera	3	C/Si	8,8	1,68	221	7,35	167	15:85	5	50
	4	C/Si	11,6	1,68	135	3,38	220	60:40	–	70
	5	C/Si	14,8	1,77	207	20,7	100	22:78	–	50
	6	C/Si	15,0	1,77	158	15,8	140	60:40	1	35
	7	C/Si	14,8	1,77	175	13,4	170	62:38	5	30
	8	C/Si	8,2	2,00	126,8	2,11	220	65:35	–	13
	9	C/Si	6,8	2,00	117,6	1,47	220	40:60	–	15
	10	C/Si	6,5	2,00	312,5	1,42	220	33:67	–	10
	11	C/Si	5,6	2,00	216	1,20	220	0:100	–	5
RHEPP-1	12	C/Si , 0°, N^+	14,3	2,00	145	4,00	300	10:90	–	30
	13	C/Si, 30°, N^+	14,3	2,00	81,2	0,65	300	55:45	3,(3R)	65
	14	C/Si, 45°, N^+	16,0	2,00	91,6	0,733	170	55:45	5,(3R)	70
	15	C/Si, 45°, N^+	18,2	2,00	110	0,88	450	50:50	1	65
	16	3C+Si/Si, 30°,O^+	21	2,00	71,2	1,32	170	50:50	5	70

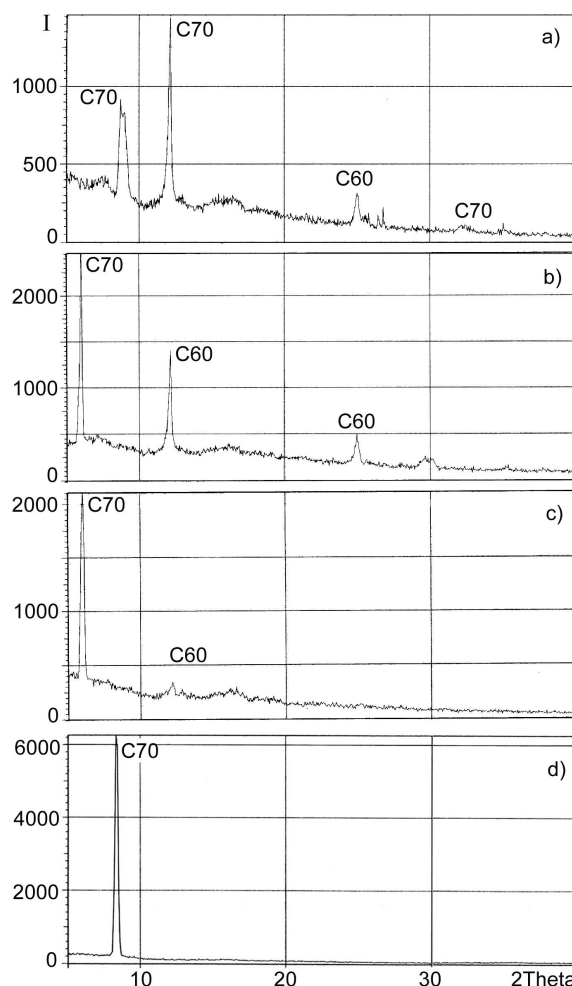

Fig. 3. X-ray diffraction pattern of the films C/Si at d_{TS}=220 mm: a) sample № 8, b) sample № 9, c) sample № 10, d) sample № 11

The conclusion of high rate of the vapor-plasma flow periphery regions cooling is supported by the results of sample № 12 analysis. The sample is located in the center of deposition for which the amount of fullerenes is considerably higher ~70 % with the predominance in the composition of C_{70}~90 %.

The obtained results can be explained in the following way. One of the distinctive features of an electric arc and laser methods of high-temperature synthesis from the one viewed here is in the use of helium atmosphere for mixing of evaporation products cloud and decreasing the temperature limit below ~2800 K for the beginning of carbon vapor condensation [4]. In our case a short duration of synthesis (several to tens microseconds) in contrast to two other methods, in which this duration constitutes ~1–2 ms, allows to use adiabatic spread of vapor plasma flow into vacuum for its cooling. There are no reasons to think that for the method viewed, the conditions for the fullerenes synthesis process will be significantly different from the specified ones. It is known [7] that maximum rate of the formation of

fullerene shells is achieved within the temperature range of ~2200–2500 K. Then one can relate the optimal conditions to the long-lasting temperature decrease within the said temperature interval along the vapor-plasma flow sufficient for the carbon clusterization and fullerenes formation.

In this case, the predominance of C_{60} or C_{70} in film composition can be explained by the exit of fullerenes from the thermal instability zone on a substrate near the upper and lower temperature limit of the said range.

We should also note a feature of the short-pulse process, which is connected with the time dependence of the carbon vapor temperature in a flow and plays an important role in fullerenes synthesis. On the one hand it interferes with the matching of various parts of a flow with the optimal conditions for fullerenes formation. On the other hand it helps to explain the fullerene mixture yield in such a wide range of deposition conditions and HPIB parameters.

Finally, it should be noted that among different kinds of graphite we used, the most stable results were obtained with the dense pyrolytic graphite of high purity, which density is 2 g/cm^3.

As an advantage of the short-pulse evaporation method with the help of HPIB, in comparison for instance with the pulsed laser evaporation, we may mention a possibility of obtaining high quality films containing fullerenes, as an end product on a large deposition area (tens-hundreds cm^2).

4. Conclusion.

A possibility in principle of thin carbon films formation with nanocrystalline structure and high content ~30–95 % of C_{60} and C_{70} fullerene mixture using the method of graphite targets sputtering by a power ion beam has been shown. Structural and phase composition of films was defined. It has been demonstrated that formation of fullerenes, their amount, and C_{60}/C_{70} ratio depend on the parameters defining the conditions of carbon vapor condensation and, first of all, the initial temperature and cooling rate of the vapor flow. The conditions for targets sputtering have been investigated and it has been illustrated that it is possible to control the amount and composition of fullerenes in films up to the formation of monocrystalline C_{70} film.

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