The Synthesis of Carbon Nanostructures at Graphite Evaporation by Electron Beam

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Abstract – Results of graphite evaporation by electron beam are presented. Evaporation rate as function of beam power and duration of electron bombardment was measured. Dependence of evaporation rate on beam power has threshold character. The minimum power from which evaporation begins, in our experiments was equalled 600 W. Rate of evaporation was equalled to 0.3–0.4 mg/s. Deposition rate of carbon layers on the substrates placed in 40–50 mm from a graphite target, was 0.5–1.0 μm/min. Application of complex targets containing nickel, cobalt or iron as the catalyst, does not bring essential changes in rate of evaporation and deposition. Spectra of X-ray diffraction and Raman shift of the deposited layers have shown presence of single-walled carbon nanotubes.

1. Introduction

Among beam methods of carbon nanoobjects preparation laser evaporation [1, 2] is the most known. It is produced, as a rule, in the environment of inert gas. Generation of an electron beam is simpler problem in compare with a laser beam of the same power. Nevertheless electron beam evaporation of graphite for nanostructure synthesis is applied much less often [3]. The possible reason of it consists in the settled opinion on necessity enough high gas pressure (0.1÷10 kPa) at which laser evaporation is usually made. The majority of existing electron sources appears disabled at such pressure. In our laboratory plasma cathode electron source [4] was created, capable to form an electron beam in pressure range 5÷15 Pa, which comes nearer to demanded values. The purpose of the present work consisted in application of the specified source for evaporation of graphite and research of deposition products about presence of fullerenes and nanotubes.

2. Experimental installation

All experiments have been executed on the vacuum installation equipped by oil free vacuum pump ISP-500C. The experimental scheme is presented in Fig. 1. Main elements of installation are: electron source 1, based on electron emission from plasma of hollow cathode discharge; graphite target 2 located on support 3; substrate 4 displaced in holder 5. Source 1 forms electron beam 6 which diameter in a target plane is 4 mm. Beam 6, bombarding target 2, locally heats it up to evaporation temperature; approximately 4000 K. Evaporation products are deposited on substrate 4, forming a carbon layer. Inert gas (helium in our experiments) moved directly in vacuum chamber 7. Two ways were used for nanotubes formation: catalyst adding and applying of negative potential to substrate. First way was realized by special form of graphite target, which contained metal catalyst. The target was constructed as graphite crucible with the external sizes 15 × 15 × 20 mm³ in which graphite and metal plates consistently settled down. During electron bombardment the top graphite plate was locally evaporated in the first minute. After this joint carbon and catalyst evaporation took place. In the second way graphite crucible contained only graphite plate. Substrate holder was connected to negative pole of separate power supply (not shown in Fig. 1). The temperature in a beam trace on a target during evaporation was supervised on brightness of light. Weighing of a target before and after electron irradiation was used for measurements of evaporation rate. Carbon layers were deposited on glass and silicon plates. Thicknesses of the deposited layers were measured by means of optical micro-interferometer MII-4. Surface of prepared layers was observed by means of scanning electron microscope Hitachi TM-1000. For observation in transmitting electron microscope JEM 100 CX II carbon layers were put on crystal KCl plates. X-ray diffraction analysis was made in instrument Shimadzu.
XRD 6000 for layers deposited on silicon substrates. Raman shift was measured by spectrometer Nicolet NXR 9650. On the basis of spectra analysis conclusions concerning structure of a carbon deposit have been made.

3. Results and discussion

As experiments have shown, dependence of evaporation rate on electron beam power has threshold character. Evaporation was not observed at level lower 600 W. Rate of evaporation actually did not depend on time and remained constant, at least, within first six minutes (Fig. 2). Deposition rate of carbon layers was 0.5÷1.0 μm/min at 1 kW electron beam power.

![Fig. 2. Weight loss Δm of graphite target as function of evaporation time τ for various power of electron beam: 1 – 600 W; 2 – 800 W; 3 – 1000 W. Helium pressure 10 Pa](image)

As scanning electron microscope images show, carbon deposits contain two types objects (Fig. 3). One is spherical particles 1–5 μm diameter and the other – extended objects 1–2 μm length and about 0.1 μm diameter. Transmission electron microscope image allow seeing more fine objects about 20 nm length and 2–4 nm diameter. X-ray diffraction spectra testify to presence of single-walled nanotubes (Fig. 5) in the layers deposited with catalyst using. Maxima of diffraction spectra at 2Θ = 26° specify in existence of these structures. Raman spectra confirm existence of nanotubes too (Fig. 6). Spectra contain two peaks at 1600 cm⁻¹ (G band) and 1280 cm⁻¹ (D band), which correspond to tangential mode of carbon atom oscillations. Raman spectra contain also peaks at 248.7 cm⁻¹ and 180 cm⁻¹. These peaks correspond radial breathing mode (RBM) of nanotubes [5]. It is pertinently to note, that for carbon layers, deposited without catalyst,
but with negative substrate potential Raman spectra contain only RBM peaks (Fig. 7), and have wide maximum in 1000–2000 cm\(^{-1}\) interval.

All the results give the basis for conclusion about presence of carbon nanotubes in layers, deposited by electron beam evaporation of graphite in helium atmosphere. RBM peaks allow possibility for nanotubes diameters calculation, according to the expression

\[ \Delta \nu = \frac{A}{d} + B, \]

where \( A \) and \( B \) are empirical constants: \( A = 234 \text{ cm}^{-1} \) nm and \( B = 10 \text{ cm}^{-1} \) [5]. Estimated nanotube diameters are 0.98 and 1.38 nm.

4. Conclusion

Our experiments have convincingly shown possibility of carbon nanotubes preparation by electron beam graphite evaporation in helium media. Nanotubes were grown in two variants. First is evaporation of graphite together with catalyst Ni or Fe. And second – deposition of evaporation products on negative biased substrate.

References