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EFFECT OF HIGH-CONCENTRATION ENERGY FLUXES MATERIALS

# STRUCTURE OF DIAMONDLIKE CARBON FILMS SYNTHESIZED BY THE METHOD OF LASER EVAPORATION OF GRAPHITE IN A VACUUM

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*Using the methods of transmission electron diffraction, transmission electron microscopy, and electron paramagnetic resonance, we have analyzed the structure of thin carbon layers deposited on glass substrates, heated to a temperature of $T \approx 473$ K, in a vacuum as a result of the exposure of a graphite target to a pulsed laser radiation of nanosecond duration and energy 2–8 J. It is shown that carbon films with an amorphous diamond structure undergo not only graphitization but also crystallization: polycrystalline diamond- and diamond-graphite concretions are formed on their surface.*

The interest shown in diamondlike films is explained by the unique combination of their properties: high hardness, heat conduction, specific electrical resistance, chemical resistance, and abrasive resistance. Moreover, these films are optically transparent in the UV and visible regions of the spectrum and their physicochemical characteristics can be controlled in the process of growth. Diamondlike films are among the most promising materials for microelectronics, optics, mechanical engineering, and medicine.

Considerable recent attention has been focused on the search for optimum regimes of formation of diamondlike films that would be uniform in composition and perfect in structure, in particular, by the method of pulsed laser evaporation of a graphite in a vacuum. This method is simple in use and highly efficient, excludes the presence of foreign gases and provides high accuracy of the operations performed and their reproduction. Moreover, in the case where pulsed lasers are used for deposition of films, lower requirements are imposed on the vacuum because the time of interaction of radiations with the substance is very short in this case.

The first works have shown that in the case of evaporation of a graphite by a continuous $CO_2$ laser radiation with an energy flux density of $q = 5 \cdot 10^7$ W/m$^2$, on its surface there arise layers identical in properties to graphite films [1]. The exposure of a graphite target to neodymium laser pulses of duration $\tau < 10^{-7}$ sec and energy flux density $q = 10^{13}$ W/m$^2$ leads to the formation of carbon condensates with a specific resistance of $\rho = 10^3$–$10^6$ Ω·m [2]. Samples with a higher specific resistance of $\rho = 10^9$ Ω·m were obtained at a similar energy flux density of $q = 8 \cdot 10^{12}$ W/m$^2$ and very low condensation rates (< 0.01 nm/sec) [3]. The laser deposition at the above-indicated values of $q$ is similar in composition and energy distribution of vapor particles to the deposition of films from ionic beams. For example, when the carbon-vapor ionization threshold equal to $5 \cdot 10^{12}$ W/m$^2$ at $\tau = 10$ nsec, according to [4], is exceeded, the graphite evaporation is accompanied by the formation of a plasma torch consisting of ions (~10%) and neutral particles with energies, respectively, of 100–1000 eV and 10–100 eV. The carbon ions present in this torch are predominantly monoatomic. The fraction of $C_2^+$ and $C_3^+$ ions is, respectively, $10^{-5}$ and $10^{-7}$ of the monoatomic $C^+$ ions [5].

The high energies of the ionic beams (higher than 50 eV) limit the rate of growth of diamondlike films, with the result that their composition becomes inhomogeneous. These films, along with the amorphous diamond phase of

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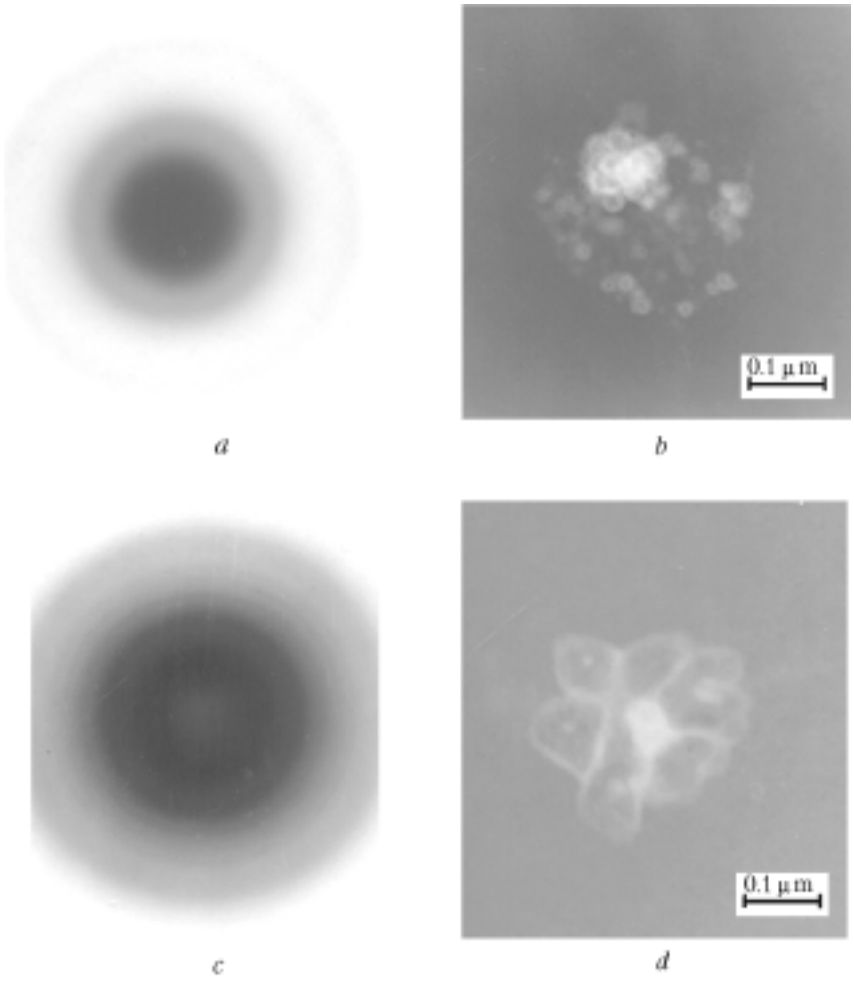


Fig. 1. Electron diffraction patterns (a, c) and electron microphotographs (b, d) of a diamondlike film deposited as a result of the evaporation of a graphite in a vacuum by nanosecond laser radiation monopulses ($\lambda$ = 1.06 μm) with energies of 3 J (a, b) and 8 J (c, d).

carbon, contain crystals of diamond and carbyne [6]. Because of this, it is appropriate to use vapor-plasma fluxes of particles with energies of less than 50 eV. According to [4], at a limiting value of $q = 8 \cdot 10^{11}$ W/m$^2$, corresponding to the carbon evaporation threshold, the mean energies of the neutral particles (2 eV) are close to the energy of the $\sigma$-bond of the diamond atoms (3.6 eV) [7].

The aim of the present work is to investigate the structure of thin carbon layers deposited on glass substrates in a vacuum as a result of the evaporation of a graphite by a nanosecond, pulsed laser radiation with an energy flux density of lower than the erosion-laser-plasma ionization threshold.

**Materials and Experimental Procedure.** Diamondlike layers were formed with the use of a pulsed neodymium laser with a wavelength of $\lambda$ = 1.06 μm, half-height pulse duration of $\tau$ = 30 nsec, and pulse energy of $E$ = 2–8 L. A laser radiation spot with clearly defined edges and a practically homogeneous distribution of the laser energy density was formed on a graphite target with the use of an optical system. The area of the radiation spot was $S \approx 254$ mm$^2$. The target was positioned in a vacuum chamber with a residual gas pressure of $1.3 \cdot 10^{-3}$ Pa at an angle of 45$^o$ to the axis of the acting radiation beam. Glass substrates of thickness $h$ = 1.2 mm, heated to a temperature of $T \approx 473$ K, were positioned along the normal to the surface of the irradiated material at a distance of $l$ = 100 mm from each other. For each value of $E$, irradiation was performed by a series of 100 monopulses.

The structure and phase composition of the modified layers were investigated by the methods of transmission electron diffraction and transmission electron microscopy at an accelerating voltage of $U$ = 100 kV as well as by the

method of electron paramagnetic resonance (EPR) in the x-ray range on a Varian E112 spectrometer at room temperature and liquid nitrogen temperature. The concentration of paramagnetic centers in the synthesized films was calculated on the basis of the known concentration of paramagnetic centers in a standard specimen with account for the estimated thickness of the deposited layer.

**Experimental Results and Discussion.** The investigations of the deposited carbon films by the method of transmission electron diffraction have shown that they have an amorphous diamond structure at all the values of $E$ = 2–8 J. This is evidenced by the presence of a pair of diffuse rings on the electron-diffraction patterns: (111), $d$ = 0.206 nm and (311), $d$ = 0.1075 nm (see Fig. 1a).

Thin, transparent (nongraphitized) amorphous diamondlike films were obtained at $E$ = 2 J. When the energy of the laser radiation acting on a graphite target reached $E$ = 3 J, the surface layer of the diamondlike films began to graphitize, which is visually seen by the blackening of the coating deposited on a heated glass substrate from the erosion laser plasma in a vacuum. On the electron microphotograph of this film (Fig. 1b), we can see rounded and faceted graphite inclusions of globular and facet morphology with sizes of less than 1 nm and of 4–50 nm and their scaly aggregates of diameter 140–240 nm.

When the measurements were performed at room temperature, an isotropic signal with a $g$-factor of 2.0023 $\pm$ 0.0005 appeared in the EPR spectra of all the films studied, except for the thin transparent films obtained at a minimum laser radiation energy of $E$ = 2 J. For the above-indicated thin films, an EPR signal was detected only at a measurement temperature of 77 K. As the laser radiation energy increased at a constant number of monopulses, the line width ($\Delta H$) changed nonmonotonically and the intensity of the signal increased. For all the samples, the intensity of this EPR signal increased practically linearly with increase in the microwave radiation power up to 100 mW. An analogous process of formation of diamondlike films, conducted by us earlier [8] at the above-indicated pulse energies without preliminary heating of the substrate, was characterized by a practically linear decrease in $\Delta H$ from 21.0 to 7.0 Gsec when the laser radiation energy increased to 6 J and was accompanied by a large spread of the paramagnetic center concentration.

At $E$ = 8 J, thin blackened (graphitized) amorphous diamondlike films with a maximum concentration of paramagnetic centers were synthesized on the substrates. Careful analysis of the microdiffraction patterns of the films obtained at $U$ = 100 kV has shown that these films contain inclusions of graphite characterized by the two-layer structural modification 2$H$ (wurtzite) with unit-cell parameters $a$ = 0.246 nm and $c$ = 0.68 nm, hexagonal graphite with unit-cell parameters $a$ = 0.8948 nm and $c$ = 1.4078 nm (carbon/chaoite), and $\alpha$-carbyne (see Fig. 1c). The above-indicated graphites have a polycrystalline structure. To estimate their structural modification, we changed the angle of inclination of the object studied to the electron beam by 40–50$^{o}$ with the use of a goniometer in the process of recording of electron diffraction patterns. Moreover, a polycrystalline ring of the diamond phase of carbon [(111), $d$ = 0.206 nm] has been revealed on the microdiffraction patterns. As is seen from the electron microphotographs (see Fig 1d), the polycrystalline formations of diamond modification represent pyramidal diamond crystals, disordered in the circular direction, with a deformed crystal lattice. The mean diameter of such a six-pointed, star-like aggregate is ~320 nm and the size of its components is ~70–130 nm.

Comparison of the results of the EPR investigations and the investigations performed by the methods of transmission electron diffraction and transmission electron microscopy allows us to suggest that the paramagnetic centers in the films deposited as a result of evaporation of a graphite in a vacuum by a pulsed neodymium laser radiation of nanosecond duration are due to the broken C–C bonds of the $sp^3$-hybridized carbon atoms grouped at the intercrystalline or interfacial boundaries. At low energies of radiation acting on the graphite target ($E$ = 2–3 J), the large width of the EPR line can be due to the presence of a small amount of nondiamond forms of carbon on the surface and in the bulk of the film. As the laser radiation energy increases to 4–6 J, the probability of formation of new crystallization centers increases, i.e., the number of small aggregates with defects increases and, since these aggregates are found under approximately identical conditions, the exchange interaction between them is enhanced as the number of electrons localized on the broken bonds increases. Because of this, the intensity of the signal increases when the EPR line narrows. At $E$ = 8 J, pyramidal diamond crystals intensively grow (their sizes increase by more than ten times) in the synthesized films in addition to the inclusions of various graphites (wurtzite, chaoite (carbon/chaoite), and $\alpha$-carbyne) with a polycrystalline structure, which, in our opinion, leads to a broadening of the line and a sharp increase in the intensity of the EPR signal.

Thus, the complex investigations of the structure of the deposited films by the methods of transmission electron microscopy and transmission electron diffraction at $U$ = 100 kV and the method of electron paramagnetic resonance have shown that carbon films with an amorphous diamond structure can be obtained as a result of the evaporation of a graphite in a vacuum by a pulsed neodymium laser radiation of nanosecond duration. It has been established that diamondlike films obtained by this method undergo not only graphitization but also crystallization: polycrystalline diamond inclusions having a large number of defects can be formed in them.

## NOTATION

$a$, $c$, parameters of a unit cell, nm; $d$, effective interfacial distance, nm; $E$, laser pulse energy, J; $\Delta H$, width of the EPR signal line, Gsec; $h$, thickness of the glass substrate, mm; $l$, distance from the graphite target to the substrate, mm; $q$, laser radiation power density, W/m$^2$; $S$, area of the laser spot, mm$^2$; $T$, temperature of the substrate, K; $U$, accelerating voltage, kV; $\lambda$, laser radiation wavelength, μm; $\rho$, specific resistance of the sample, Ω·m; $\tau$, lasing pulse duration, nsec.

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