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FORMATION OF 2H-MODIFICATION GRAPHITE IN FILMS DEPOSITED WITH THE USE OF NANOSECOND LASER PULSES

V. K. Goncharov, S. A. Petrov, and M. V. Puzyrev

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A possible physical model of formation of the wurtzite phase of graphite in the crystallized regions of an amorphous diamondlike carbon film deposited on a glass substrate, heated in advance to a temperature of ~473 K, in a vacuum as a result of the exposure of a graphite target to a laser radiation of energy density $q = 3.15 \cdot 10^4$ *J/m*^{2} *is proposed.*

Diamondlike films have attracted considerable interest as a material which, due to its high hardness, heat conduction, specific electrical resistance, and optical transparency (especially in the IR region of the spectrum), can be used to advantage in microelectronics, optics, and mechanical engineering [1].

At present, the method of deposition of films from an erosion laser plasma is widely used in the synthesis of thin-film materials and structures with unique properties, many of which cannot be obtained by other methods. This is explained by the fact that this method provides high localization and concentration of laser energy on a target, congruence of evaporation of complex substances, and controlled deposition of superthin layers with a rate of up to 10^5 nm/sec at a condensate particle energy of up to 1 keV or higher [2].

It is known that a solid, when exposed to a laser beam, heats to high temperatures (from hundreds of degrees to several thousand), which can give rise to various effects, including phase transformations [3, 4]. For example, diamond, wurtzite (lonsdalite), α-carbyne, and β-carbyne are formed as a result of the laser heating of a polycrystalline graphite in air to ~3000 K and its rapid cooling by liquid nitrogen [5]. In [5], an LG-25 infrared laser with a radiation density of up to $5 \cdot 10^4$ kW/m^2 was used for heating. It has been established that the higher the heating temperature, the more frequent the diamond in the products of solid-phase transformation, and, at low temperatures, the main metastable phase is α-carbyne. It has also been noted in this work that the solid-phase transformation products, from which graphite is removed, have a higher hardness than corundum (they scratch it).

As practice shows, the procedure of lapping of the surfaces of diamond crystals cut by a laser presents more difficulties and is more time consuming as compared to that of crystals that were not subjected to laser treatment. This points to the fact that the abrasion resistance of a diamond surface increases under the action of laser radiation. In [6], it has been shown that, in a diamond subjected to laser cutting, the diamond substance undergoes graphitization and graphite undergoes not only evaporation and reprecipitation but also recrystallization, i.e., new polycrystalline diamond and diamond-graphite concretions are formed on the surface of a crystal. It was suggested in this work that it is precisely the formation of polycrystalline concretions of small crystals or the disorientation of the lattice in the process of surface recrystallization of diamond that increases its abrasive resistance. Note that both a finely dispersed graphite with an extremely low degree of structural order (turbostratic structure) and a graphite textured in the basal plane (two-layer structural modification 2H) have been revealed in the graphitization products.

The aim of the present work is investigation of the phase transformations of diamondlike films deposited in a vacuum as a result of the evaporation of a graphite target by nanosecond monopulses with a radiation energy density q close to the ionization threshold of the erosion laser plasma.

The experimental procedure is described in [7]. The energy of a laser pulse acting on a graphite target in a vacuum was 8 J. The structure and phase composition of the modified layers were investigated by transmission electron microscopy and transmission electron diffraction at an accelerating voltage of 100 kV.

A. N. Sevchenko Scientific-Research Institute of Applied Physical Problems, Belarusian State University, 7 Kurchatov Str., Minsk, 220064, Belarus; email: puzyrev@bsu.by. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 77, No. 4, pp. 86–88, July–August, 2004. Original article submitted November 5, 2003.

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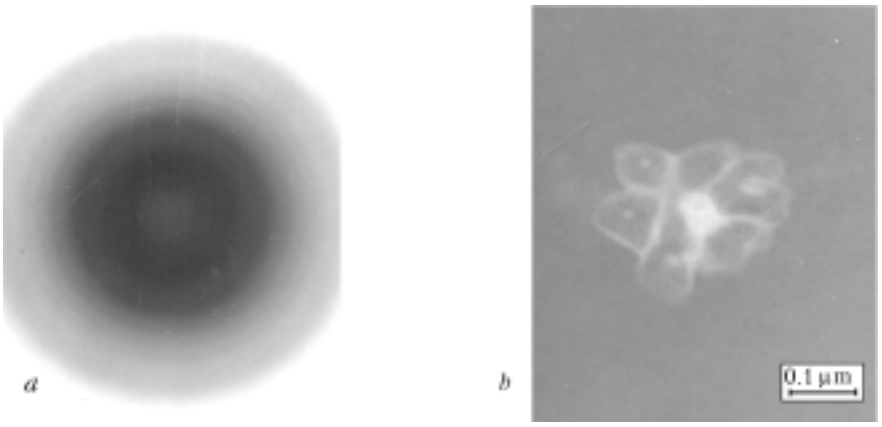

Fig. 1. Microdiffraction pattern (a) and electron microphotograph of the crystallized region of an amorphous, diamondlike carbon film (b).

Experimental Results and Discussion. As the investigations of the deposited films by the method of transmission electron microscopy have shown, thin, blackened (graphitized), amorphous diamondlike films were deposited on hot glass substrates as a result of the exposure of a graphite target to a laser radiation with $q = 3.15 \cdot 10^4$ J/m^2 in a vacuum. However, careful analysis of the microdiffraction patterns of the films obtained at an accelerating voltage of 100 kV has shown that local regions of an amorphous diamondlike film deposited in such a regime are subjected to crystallization (see Fig. 1a). On the microdiffraction pattern, shown in Fig. 1a, there is a polycrystalline ring that is due to the diamond structure of carbon: (111), $d = 0.206$ nm. As is seen from Fig. 1b, the polycrystalline formations of diamondlike carbon consist of pyramidal diamond crystallites, disoriented in the circular direction, with a deformed 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.

Undoubtedly, as in the case of exposure of Si single crystals to intense steady-state ionic beams [8, 9] and in the case of accelerated fluxes of an erosion laser plasma of heavy metals [10], of interest is the formation of the metastable wurtzite phase, in particular, a graphite with unit-cell parameters $a = 0.246 \pm 0.002$ and $c = 0.680 \pm 0.003$ nm. To investigate this structural modification, we made electron diffraction patterns of its regions inclined, with the use of a goniometer, at an angle of 40–50^o to the electron beam. Inclusions of 2H graphite were revealed in the crystallized regions of an amorphous diamondlike film. As in the case of stationary, strong-current implantation and intensive pulsed treatment of refractory metals (Hf, Ta, W) by ion-plasma flows with an energy of 10 keV, 2H-graphite inclusions, supposedly, are localized downstream of the path of C^+ ions in the crystallized matrix. It may be suggested that at $q = 3.15 \cdot 10^4$ J/m^2 the deposition of amorphous diamondlike films by laser evaporation of a graphite target is similar in composition and energy distribution of vapor particles to the deposition of films from ion beams. According to [10], when the carbon-vapor ionization threshold, equal to $5 \cdot 10^{12}$ W/m^2 at a pulse duration of 10 nsec, 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. It should be noted that carbon ions present in this erosion laser plasma are predominantly monoatomic. According to the data of [11], at a limiting value of $q = 8 \cdot 10^{11}$ W/m^2, corresponding to the graphite evaporation threshold, the mean rate of deposition of neutral particles is $5.8 \cdot 10^3$ m/sec and their mean energy (2 eV) is close to the energy of the σ-bond of the diamond atoms (3.6 eV) [12]. In our case, the laser radiation density on a graphite target is $1.1 \cdot 10^{12}$ W/m^2.

The mechanism of formation of 2H graphite is not yet clearly understood. It is known that high pressures and temperatures are required for the formation of the wurtzite phase. In [13], it was suggested that the phase transition from the diamondlike structure to the wurtzite structure in silicon is analogous to that in martensite and can be caused by a uniaxial compression stress equal to approximately 20 GPa. We think that such local pressures can arise as a result of the generation of shock waves or elastic stress waves with a large amplitude by implanted ions and as a result of their superposition. The concept of shock waves was used in [14] for an explanation of the variety of phases, including the high-pressure phases, formed in Fe in the case of implantation of N^+. It may be suggested that shock waves arise as a result of the energy dissipation in the case of maximum (peak) displacements of atoms. These waves

move with a supersonic velocity and, in doing so, form regions of extremely high pressures (tens or hundreds of gigapascals) and temperatures. Since the time of this peak is very short (10^{-10}–10^{-12} sec), the phases are formed not through the transformation of the crystal lattice in the process of diffusion but through its deformation. According to [15], the pressure at the shock-wave front is $P = q^*/\bar{R}_P$. In our case, $\bar{R}_P$ = 2.9 nm for the C^+ ion with an energy of 1 keV [16]. As is seen from the electron microphotographs, the diameter of the region where a maximum energy is released in nuclear processes is ~4 nm. Thus, the value of P is approximately 4.5 GPa. The superposition of waves from closely spaced sources should increase this value; therefore, in certain cases, the criterion proposed in [13] is true. It should be emphasized that, in the crystallized regions of an amorphous diamondlike film, inclusions of the hexagonal carbon (chaoite and α-carbyne) with unit-cell parameters a = 0.8948 nm and c = 1.4078 nm were also revealed. The conclusions drawn in [14] allow us to consider this circumstance as indirect evidence of the validity of using the concept of shock waves in the case considered.

Thus, it has been experimentally established that the wurtzite phase of graphite arises in the crystallized region of a diamondlike film deposited on a glass substrate, heated in advance to a temperature of ~473 K, as a result of the exposure of a graphite target in a vacuum to a neodymium laser radiation of nanosecond duration and an energy flux density of $q = 3.15 \cdot 10^4$ J/m^2. Moreover, in accordance with [14], the presence of α-carbyne and chaoite inclusions can be considered as an additional argument in favor of the model of formation of 2H-graphite inclusions. In this connection, it should be noted that 2H silicon was not revealed in a silicon exposed to natural ions in a steady-state hard regime.

NOTATION

a, c, parameters of a unit cell, nm; d, interfacial distance, nm; P, pressure at the shock wave front, GPa; q, laser radiation energy density, J/m^2; q^*, local energy introduced into a diamondlike carbon film per unit area, J/m^2; $\bar{R}_P$, mean projective range of a carbon ion in a diamondlike carbon film, nm.

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