Journal of Engineering Physics and Thermophysics, Vol. 77, No. 4, 2004

NANOSTRUCTURE FORMATION ON A FILM SURFACE VACUUM-DEPOSITED FROM LASER-EROSION PLASMA

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

UDC 533.9:621.373.826

We have investigated the crystallographic nature of the nanophase structure on the surface of amorphous carbon diamond-like film vacuum-deposited on a hot glass substrate by exposing a graphite target to a pulsed neodymium laser radiation of nanosecond duration with an energy density of $1.18 \cdot 10^4$ *J/m*^{2}.

In the last few years, one of the main directions in material science has been the development of principles of obtaining materials with a nanophase structure. By nanophase materials are meant materials in which the size of particles, crystallites, or phases does not exceed 100 nm. The commensurability of the geometric size with the characteristic size of the particular physical phenomenon being considered (mean free path of electrons of photons, electric or magnetic domain size, extent of crystal lattice defects) causes various size effects, and the higher surface energy and extreme conditions for the synthesis of nanoparticles lead to a metastable state of materials that are in the ultradisperse state. In particular, the physical features of the ultradisperse state appear as a considerable improvement of the strength characteristics of nanostructure materials with the preservation of their high plasticity and low cold brittleness threshold, the semiconductor character of conduction, an increase in the temperature of the transition to the superconducting state, a decrease in the melting and phase transformation temperature, a change in the optical characteristics, etc. [1, 2]. The sizes and the size distribution of nanocrystals can effectively be modified by means of pulse laser annealing [3]. Metal nanoparticles cause the appearance of optical nonlinearity in glasses at wavelengths close to the classical resonance of electron plasma [4]. The nonlinear properties permit developing a wide gamut of optical devices (lasers, modulators, optical waveguides, and so on) [5–7].

A promising method for developing coatings with nanostructures is the application of neodymium laser radiation of nanosecond duration for vacuum evaporation of graphite. Composite systems based on nanodimensional structures deposited on a dielectric matrix consisting of layers of various allotropic states of carbon can become a base element of nanoelectronics in the near future.

The aim of the present paper is to elucidate the crystallographic nature of nanodimensional structures on the surface of a carbon diamond-like film obtained by the above method with a laser radiation energy density below the ionization threshold of the laser-erosion plasma.

Material and Experimental Procedure. In the present work, to obtain plasma, a pulsed neodymium laser with a wavelength of 1.06 μm, a pulse duration of 30 nsec, and a pulse energy of 3 J was used. The beam was focused on a graphite target into a spot of area ~254 mm^2. The target was placed in a vacuum chamber with a residual gas pressure of $1.3 \cdot 10^{-3}$ Pa at an angle of 45^o with the laser beam axis. In the direction of the normal to the irradiated substance surface at a distance of 100 mm substrates of 1.2 mm-thick glass were positioned. Carbon diamond-like films (DLF) were deposited on the glass substrates (hot substrates) heated to a temperature of ~473 K. In the experiment, for a laser radiation energy value of E = 3 J, irradiation by a series of 100 monopulses was carried out.

The structure of the modified layers was investigated by the method of transmission electron microscopy (TEM) and transmission electron diffraction (TED) at an accelerating voltage of 100 kV.

Experimental Results and Discussion. As the TED investigations of the deposited films have shown, under the action in vacuum on a graphite target of pulsed laser radiation with E = 3 J thin blackened (graphitized) amorphous DLFs were deposited on hot glass substrates. The electronograms show a pair of diffusion rings: (111) — d =

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. 83–85, July–August, 2004. Original article submitted November 5, 2003.

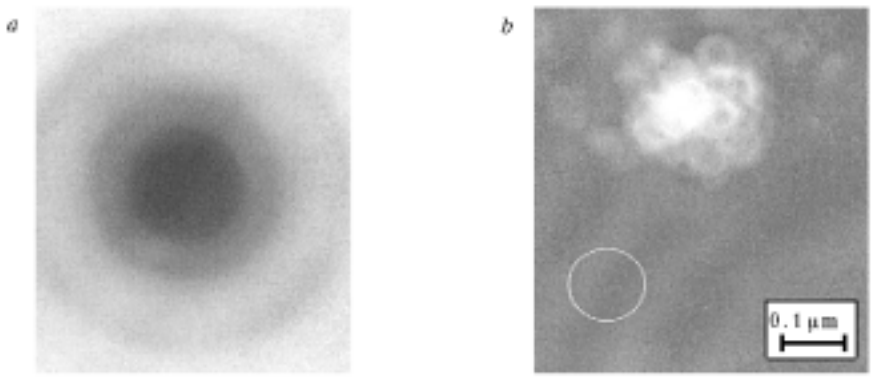

Fig. 1. Electronogram (a) and electron microphotograph (b) of amorphous carbon DLF deposited on a hot glass substrate by vacuum irradiation of graphite by a neodymium radiation with an energy density of $1.18 \cdot 10^4$ J/m^2. The white circle shows the location of the nanophase structure.

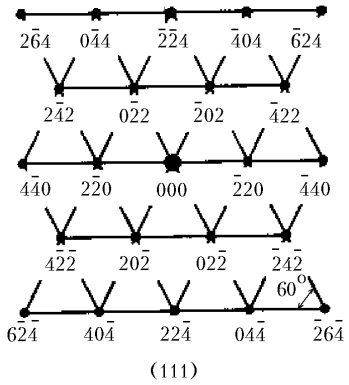

Fig. 2. Schematical representation of the TEM pattern of the nanostructure synthesis zone.

0.206 nm and (311) — d = 0.1075 nm, where d is the effective interplanar spacing (Fig. 1a). Analysis of the TEM patterns (Fig. 1b) for the above films has revealed on the amorphous DLF surface extended homogeneous portions without any inclusions of nondiamond phases and zones with graphite inclusions of rounded or faceted form (globular or facet morphology) of dimensions less than 1 nm and 4–50 nm and their scaly aggregates of diameter from 140 to 240 nm.

Moreover, in the vicinity of these aggregates, obviously, due to the local heating as a result of the condensation of graphite particles evaporated from the above-mentioned zone, favorable thermal conditions for the nanostructure nucleation are created on the amorphous DLF surface. The legitimacy of such a suggestion is that the location of nanoformations is only in the close vicinity of scaly aggregates. The region of their localization is equal to 80–100 nm, and the nanoparticle size is 2–4 nm.

The estimates made in [8] have shown that the measured threshold energy density $q = 1 \cdot 10^4$ J/m^2 enables the graphite (not diamond) surface to reach the graphite sublimation temperature T = 3700 K. In our case, the laser radiation energy density was equal to $1.18 \cdot 10^4$ J/m^2. Direct graphite–diamond transition occurs at 3000 K and a pressure of 11–12 GPa [9].

As is seen from the electron microphotographs, the spatial location of nanoparticles creates a strictly periodic structure with a definite crystallographic orientation and a characteristic diffraction contrast against the background of amorphous diamond-like film. By virtue of this, it may be suggested that nanoparticles represent carbon inclusions of the diamond structure and one can calculate the observed periodic structure according to all the rules of calculation of electronograms for monocrystals [10]. As a result, the diffraction spots were uniquely identified for the diamond phase of carbon with (111)-orientation (Fig. 2). Upon the reflex identification operation, a check for equality of the angles

between the experimental radius vectors and those calculated by the formulas for the tentative lattice of the phase was performed. The complete agreement between the angles and values of the interplanar spacings makes it possible to determine the crystallographic nature of the nanodimensional formation: we have the cubic structure of a diamond with lattice parameter α = 0.35667 nm.

Thus, the investigations performed have shown that it is possible to obtain a nanodimensional structure on the surface of amorphous carbon diamond-like film by the method of vacuum laser deposition with the use of the pulsed radiation from a neodymium laser of nanosecond duration with an energy density of $1.18 \cdot 10^4$ J/m^2. It has been established that nanoparticles form a periodic crystallographic structure of carbon of a diamond modification of (111)-orientation.

NOTATION

a, lattice parameter, nm; *d*, effective interplanar spacing, nm; *E*, laser radiation energy, J; *q*, laser radiation energy density, J/m^2; *T*, sublimation temperature of graphite, K.

REFERENCES

1. Andrievskii and A. M. Glezer, Dimensional effects in nanocrystalline materials, *Fiz. Met. Metalloved.*, **88**, No. 1, 50–73 (1999).
2. P. A. Vityaz', Promising nanophase materials based on ultradisperse diamonds, in: S. A. Astapchik and P. A. Vityaz' (eds.), *Theoretical and Technological Principles of Strengthening and Recovery of Products of Machine Building* [in Russian], Coll. of Sci. Papers, Tekhnoprint, Minsk (2001), pp. 4–8.
3. A. L. Stepanov, D. E. Hole, and P. D. Townsend, Modification of size distribution of ion implanted silver nanoparticles in sodium silicate glass using laser, *Nucl. Instr. Meth. Phys. Res.*, **14B**, Nos. 1–2, 89–98 (1999).
4. Z. Dai, S. Yamamoto, K. Narumi, A. Miyashita, and H. Naramoto, Gold nanoparticle fabrication in single crystals SiO_2 by MeV Au ion implantation, *Nucl. Instr. Meth. Phys. Res.*, **14B**, Nos. 1–2, 108–112 (1999).
5. A. Nakajima, T. Futatsugi, N. Horiguchi, and N. Yokoyama, Formation of Sn nanocrystals in thin SiO_2 film using low-energy ion implantation, *Appl. Phys. Lett.*, **71**, No. 25, 3652–3654 (1997).
6. J. A. Wolk, K. M. Yu, and E. D. Bourett-Courchesne, Synthesis of GaN nanocrystals by sequential ion implantation, *Appl. Phys. Lett.*, **70**, No. 17, 2268–2270 (1997).
7. H. Dejun, Zh. Wanru, and K. T. Chan, High energy ion implantation enhanced intermixed technology and its application on fabrication of optical waveguide, *Nucl. Instr. Meth. Phys. Res.*, **132B**, No. 3, 599–606 (1997).
8. V. P. Ageev, L. L. Builov, V. I. Konov, A. V. Kuz'michev, S. M. Pimenov, A. M. Prokhorov, V. G. Ral'chenko, B. V. Spitsyn, and N. I. Chapliev, Interaction of laser radiation with diamond films, *Dokl. Akad. Nauk SSSR*, **303**, No. 3, 598–601 (1988).
9. *Encyclopedia on Chemistry* [in Russian], Bol'shaya Rossiiskaya Éntsiklopediya, Moscow (1998), pp. 42–43.
10. K. W. Andrews, D. J. Dyson, and S. R. Keown, *Interpretation of Electron Diffraction Patterns* [Russian translation], Mir, Moscow (1971).