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Thermal annealing of multilayer films of diamond-like carbon with a variable content of sp^3 -phase

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The effect of thermal annealing on the phase composition, structural and morphological properties of multilayer films of diamond-like carbon with a variable ratio of sp^2/sp^3 -phases was investigated. It turned out that rapid annealing in argon leads to a loss of the structural periodicity of films and an increase in the content of graphite clusters, along with a decrease of hydrogen. There was also an improvement in the surface morphology of the annealed samples compared to the original film.

Keywords: diamond-like carbon, multilayer films, plasma-enhanced chemical vapor deposition, thermal annealing.

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It is known that the properties of diamond-like carbon (DLC) films vary drastically with their composition: in certain cases, they are hard and wear-resistant [1] and dielectric in nature [2]; in other cases, they are conductive [3]. The properties of single-layer DLC coatings may be adjusted by changing the ratio of sp^2 and sp^3 carbon bonds. This can be done both at the stage of film synthesis by altering the growth parameters [4] and by subjecting the films to external influences (e.g., thermal ones; see our previous study [5]). In the present study, the effect of rapid thermal annealing on the phase composition and structural and morphological properties of multilayer DLC films with a variable sp^2/sp^3 -hybridized carbon ratio is examined. There is reason to believe that the annealing of a periodic structure of this kind will have features that distinguish it from the annealing of single-layer films.

Equipment provided by the Center for Collective Use „Physics and Technology of Micro- and Nanostructures“ (Institute for Physics of Microstructures, Russian Academy of Sciences) was used. The initial multilayer structure was obtained by plasma-enhanced chemical vapor deposition on boron-doped silicon grade silicon (100) in an Oxford Plasmalab 80 reactor. Prior to experiments, the silicon substrate was rinsed with hydrofluoric acid to remove the oxide layer. The DLC film consisted of alternating layers with higher (47%; deposition time, 45 s) and lower (32%, deposition time, 2 min) sp^3 -hybridized carbon content [6]. A total of five periods were formed. Methane supplied to the reactor through a gas distribution ring at a rate of 10 cm³/min under a pressure of 50 mTorr was the plasma source. The capacitive discharge power was 75 W. Layers with a higher percentage of „graphite“ bonds were fabricated in inductively coupled plasma at a generator

power of 250 W. A DLC sample deposited onto silicon was cleaved into four parts. Three of them were annealed in argon for 2 min at temperatures of 500, 700, and 900°C using an AcuThermo AW 410 System setup.

The films were studied by small-angle X-ray reflectometry (XRD) with a Bruker D8 Discover diffractometer. Fitting was performed using the DIFFRAC.Leptos software package (Bruker AXS). The initial model for fitting was a periodic structure (five periods) consisting of layers of carbon with nominally different densities (ρ): $< 2 \text{ g/cm}^3$ and $> 2 \text{ g/cm}^3$. The value of ρ , layer thicknesses, and interface widths were varied during modeling. The XRD curve of the DLC sample on silicon measured prior to annealing featured additional Bragg peaks associated with periodicity of the multilayer structure (Fig. 1, *a*) due to the modulation of density of layers with different percentages of sp^3 -hybridized carbon (7-nm-thick layers with $\rho = 2.2 \text{ g/cm}^3$ and 10-nm-thick ones with $\rho = 1.5 \text{ g/cm}^3$). The high intensity of Bragg peaks is indicative of the presence of a well-pronounced interface between the layers. Following thermal annealing of the film at 900°C, the structural periodicity vanished (Fig. 1, *b*) as a result of equalization of layer densities (1.8 g/cm^3). The XRD curve of the annealed sample featured Kiessig oscillations only, indicating that the film was uniform in thickness. This curve was characterized well by a model with a single carbon layer uniform in density. A similar effect was observed after DLC annealing at 500 and 700°C.

The phase composition of samples was studied by Raman spectroscopy. Raman spectra of films were recorded at a LED laser wavelength of 515 nm (Renishaw inVia confocal Raman microscope). Deconvolution was performed by approximating the spectrum line smoothed over five points

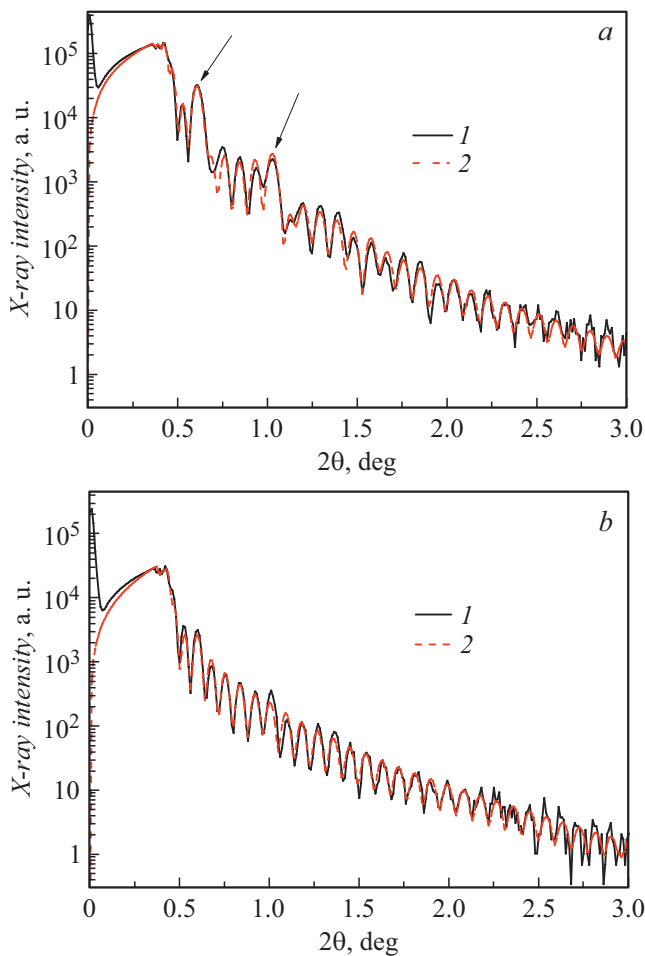


Figure 1. XRD curves of DLC films. *a* — Prior to annealing, *b* — after annealing at 900°C. *1* — Experimental curve, *2* — calculated model. Additional Bragg peaks are denoted with arrows.

Key parameters of Raman spectra of multilayer DLC films

Annealing temperature, °C	D_{pos} , cm^{-1}	FWHM_D , cm^{-1}	G_{pos} , cm^{-1}	FWHM_G , cm^{-1}	I_D/I_G
No annealing	1372	166	1552	162	0.32
500	1381	252	1600	89	0.65
700	1365	267	1598	92	0.83
900	1367	242	1593	110	1.01

with Gaussian functions. Two characteristic peaks were found within the 1050–2000 cm^{-1} range: *D* and *G* [7]. The data on their position (D_{pos} and G_{pos}), full width at half maximum (FWHM_D and FWHM_G), and intensity ratio I_D/I_G are presented in the table. It turned out that rapid thermal annealing induces a shift of the position of the *G* peak toward higher wavenumbers (relative to those corresponding to the initial structure). This shift corresponds to an increase in the fraction of sp^2 bonds in the films [8]. The *G* peak also changed its shape and became narrower (FWHM_G decreased by a factor of

1.5–1.8). In addition, the ratio of intensities of *D* and *G* peaks increased with temperature. Taken together, these changes indicate an increase in the degree of ordering of films due to the formation of larger clusters. According to the Ferrari–Robertson model, this should eventually lead to the formation of nanocrystalline graphite [7].

Another distinguishing feature of the Raman spectra of annealed diamond-like carbon films is the gentler slope of their baselines (compared to the spectrum of the as-prepared film; see Fig. 2). The slope of the spectrum is induced by photoluminescence of C–H bonds and may be regarded as a criterion for determination of hydrogen in DLC [9]. According to the results of calculation performed in accordance with the procedure outlined in [9], the percentage of hydrogen decreases from 30 to 20% in the course of annealing. When the annealing temperatures reaches 700°C, an additional broad peak at 800 cm^{-1} emerges in the film spectra. It corresponds to the TO- vibration mode of Si–C bonds of amorphous silicon carbide [10]. A narrow low-intensity peak at 2330 cm^{-1} , which corresponds to molecular nitrogen [11] that penetrates into films by diffusion from air, is also found in the spectra of annealed films.

The morphological properties of films were examined using a combination of atomic force microscopy (SMM-2000 scanning probe microscope) and white light interferometry (Talysurf CCI 2000 optical measuring system). In the process of thermal annealing, the surface of multilayer DLC films is cleaned of large defects produced during growth. A multitude of carbon „needles“ with lateral dimensions of several micrometers and a height up to 170 nm (Fig. 3, *a*) were present on the surface of the as-prepared sample. Rapid DLC annealing contributes to a significant reduction in the number of such nonuniformities, since their adhesion to the film surface is weak. Specifically, root-mean-square roughness S_q of the surface within an area of $4.5 \times 4.5 \mu\text{m}^2$

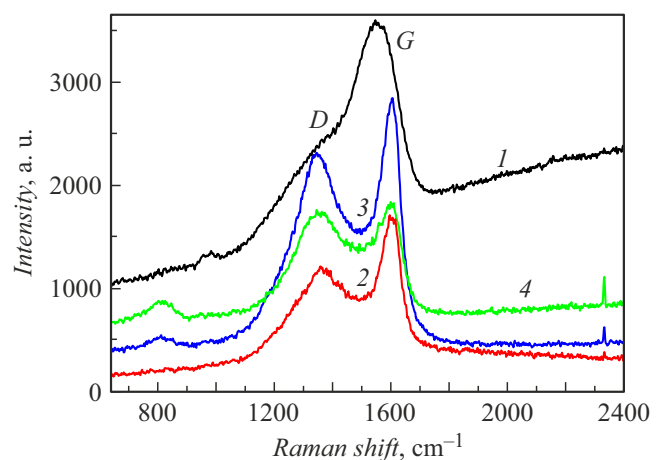


Figure 2. Raman spectrum of DLC films in the 640–2400 cm^{-1} Raman shift range. Curve *1* — as-prepared multilayer film before annealing; curves *2–4* — films after annealing at 500 (*2*), 700 (*3*), and 900°C (*4*).

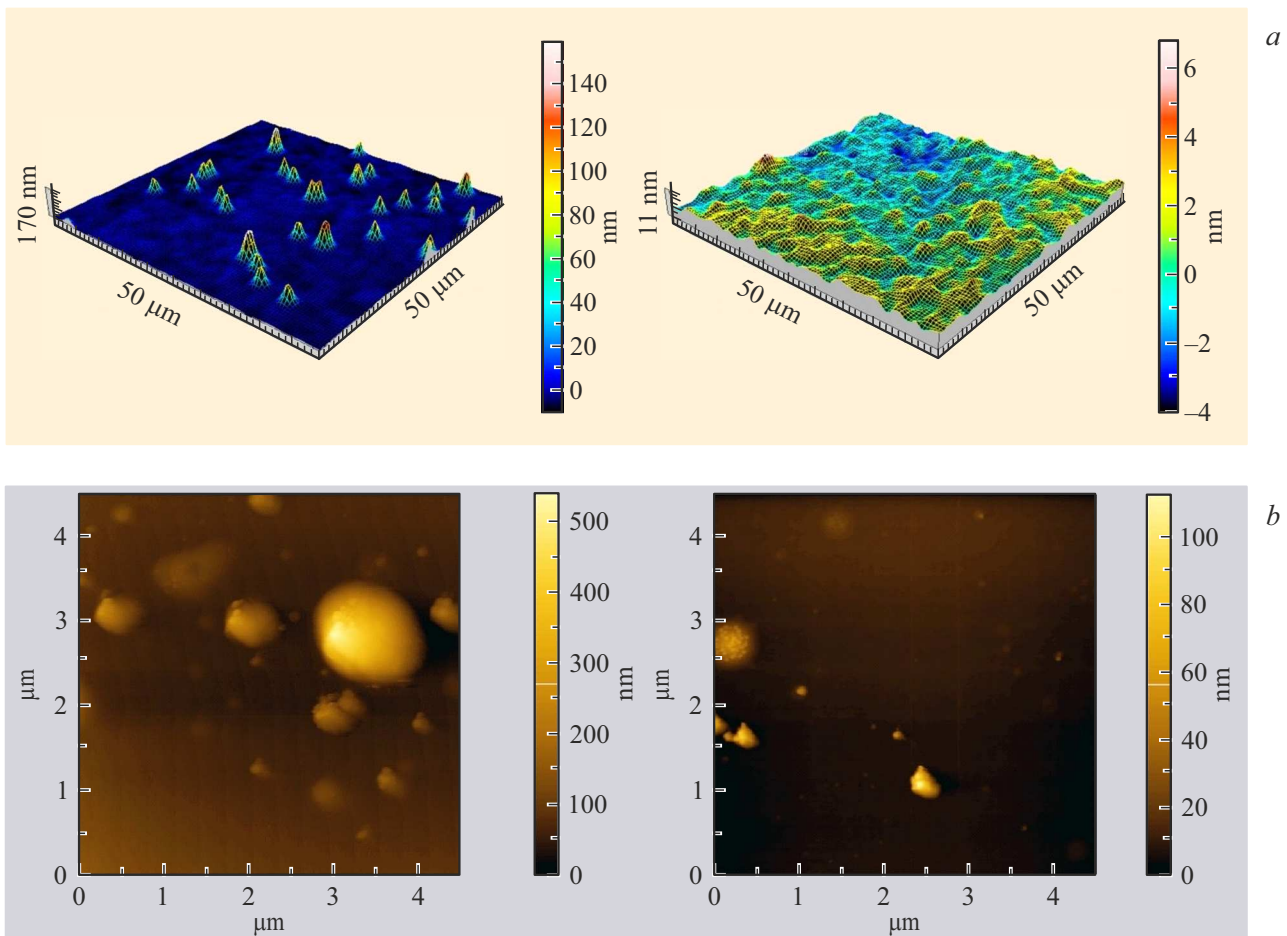


Figure 3. The surface of DLC films on silicon imaged with a white light interferometer (*a*) and an atomic force microscope (*b*). Left panels — before annealing; right panels — after annealing at 900°C.

(Fig. 3, *b*) decreased by a factor of almost 9 after annealing (from 56 to 6.4 nm), while average roughness S_a decreased by a factor of more than 7 (from 31 to 4.0 nm). The S_q values are generally consistent with the results obtained in another experiment [12] on synthesis of DLC films by the plasma-chemical method.

Thus, it was demonstrated that thermal annealing of a multilayer DLC film leads to a reduction in the concentration of hydrogen, the vanishing of additional Bragg peaks in the XRD curve, and a shift of the G peak in the Raman spectrum toward higher wavenumbers. This is indicative of an increase in the graphite phase content in the film and a loss of its multilayer structure. The obtained results may help refine the process of production of carbon memristors and non-alloyed ohmic contacts to single-crystal diamond.

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Conflict of interest

The authors declare that they have no conflict of interest.

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