

Research Article

Diamond-Like Carbon Film Deposition Using DC Ion Source with Cold Hollow Cathode

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Carbon diamond-like thin films on a silicon substrate were deposited by direct reactive ion beam method with an ion source based on Penning direct-current discharge system with cold hollow cathode. Deposition was performed under various conditions. The pressure (12–200 mPa) and the plasma-forming gas composition consisting of different organic compounds and hydrogen (C_3H_8 , CH_4 , $Si(CH_3)_2Cl_2$, H_2), the voltage of accelerating gap in the range 0.5–5 kV, and the substrate temperature in the range 20–850 °C were varied. Synthesized films were researched using nanoindentation, Raman, and FTIR spectroscopy methods. Analysis of the experimental results was made in accordance with a developed model describing processes of growth of the amorphous and crystalline carbon materials.

1. Introduction

Film deposition or surface modification directly from the ion beam is one of the most promising methods because it allows controlling the energy of the particles of deposited material and has a number of advantages over the other most common methods of producing films in vacuum [1–4]. At an average energy of the ions, 1–5 keV, the deposition method of immersion ion implantation is implemented [5–7]. For obtaining ions with such energy it is convenient to use self-contained ion source based on DC glow discharge plasma allowing to regulate the ion energy and ion current density precisely and widely. Research to improve technology and equipment to carry out this process are very relevant in view of the accelerated development of micro- and nanoelectronics today.

Deposition of diamond-like carbon films [8] by the above-mentioned methods using multicellular ion source (IS) “Radical-M250” [3] is known. This IS forms the ion beam with a large area of cross section. To solve the same technological challenges, we proposed [9] to use the IS based

on Penning discharge with hollow cathode in crossed $E \times H$ fields. Used modification of this type of IS cannot produce ion beams of large cross-sectional area; however, it has a number of advantages over other parameters. Unlike IS “Radical-M250” in the proposed IS there is independent adjustment of the ion current density and ion energy in a wide range. Furthermore, FWHM of function of ion energy distribution in the beam of IS “Radical-M250” is 540–580 eV [3]; the same parameter at the same beam current in proposed IS can be sufficiently lower [10]. Providing a significant influence of the ion energy on properties of the synthesized films, the ion source with a narrow energy spectrum of the ions will more effectively and predictably control the properties of the synthesized films. In comparison with a deposition system based on standard filament-type cathodes such as Kaufman type IS [1, 11], the proposed cold cathode system has longer operating life in a reactive plasma.

The purpose of this study was to investigate an influence of the deposition conditions on the characteristics of amorphous carbon films obtained with the help of the ion source based on reflective discharge with hollow cathode.

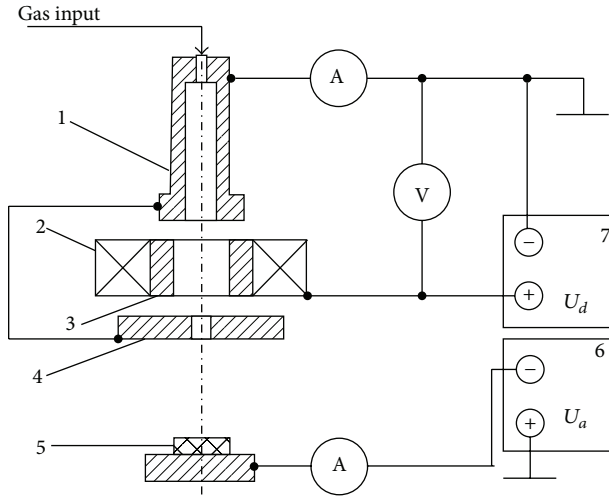


FIGURE 1: Schematic diagram of the reactive ion-beam deposition system. 1: hollow cathode; 2: magnet; 3: anode; 4: reflector cathode; 5: substrate; 6, 7: power supply sources.

2. Experiment

2.1. Experimental Setup. Figure 1 shows a schematic diagram of the reactive ion-beam deposition system. Ions were generated in the plasma of reflex-discharge which was excited in the discharge chamber formed by hollow cathode 1 with an inner diameter of 4 mm and a depth of 32 mm and cylindrical anode 3 with an inner diameter of 12 mm and reflector cathode 4 with an emission aperture about 4 mm in diameter. The magnetic field of ≈ 80 mT in the discharge chamber was created by annular magnet 2. The electrodes of the discharge chamber were cooled by running water. Through the hole in the cathode-reflector, ions penetrate into the accelerating gap and are accelerated by the electric field in the direction of the substrate 5.

Accelerating voltage U_a was regulated in the range of 0.5–5 kV by the power source 6. Energy of extracted ions in this case can be evaluated as follows:

$$E_{(i)n} = \alpha \cdot U_d + n \cdot U_a \pm \Delta E_n, \quad (1)$$

where U_d is a hollow cathode discharge voltage (350–400 V) from the power source 7, $\alpha \approx 0.8$ for this type IS, $n = 1$ – ion charge and ΔE_n is blurring of n th peak of the energy spectrum of the ions. Moreover, during the deposition of dielectric film without charge neutralizer, the ion energy can be partially reduced due to uncompensated ionic charge arising both in the vacuum volume and around the growing surface. Plasma-forming gas propane (C_3H_8) was let into the hollow cathode. In some experiments, which will be discussed separately, the plasma-forming gases methane (CH_4), dimethyldichlorosilane ($Si(CH_3)_2Cl_2$), and propane-hydrogen mixtures (1:3) were used. Pumping of the vacuum chamber was made by turbomolecular pump TMN-1500 (3) to the minimal pressure of 2 mPa. Gas flow rate Q was regulated in the range of 1.3 – 5 $m^3 \times mPa/s$. Calculations show that under these gas flow rates and used geometry the pressure in the discharge chamber was 0.8–3.4 Pa. The source

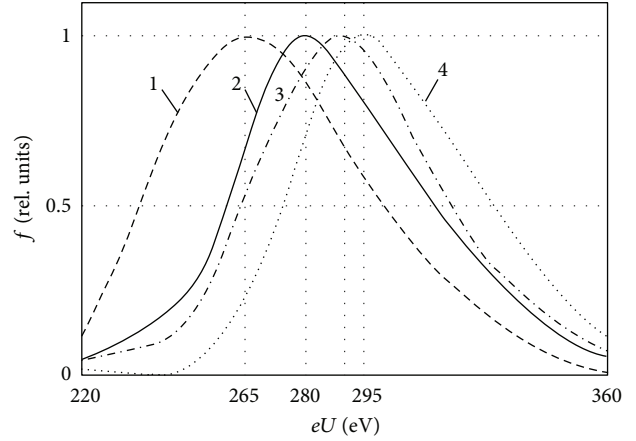


FIGURE 2: The energy spectra of ions of different gases. 1: dimethyldichlorosilane; 2: air; 3: propane; 4: argon; $I_d = 0.2$ A, $Q = 2.4$ $m^3 \times mPa/s$. ΔE , eV: 1: 64; 2: 53.5; 3: 56; 4: 55.

operated continuously. Taking into consideration some of the features of this source on hydrocarbons [9, 12], the discharge current was maintained in the range of relatively small values of 60–80 mA; the ion beam I current to the substrate was of 35–70 mA. To study the energy spectra of extracted ions at work on hydrocarbons and organ silicon compounds, the technique with a multigrid energy analyzer probe described in our previous studies [12] was used. Argon and atmosphere air were used as “control” gases in this study. Figure 2 shows obtained energy spectra.

The width of each spectrum at half-height of ΔE in all cases did not exceed a few tens of eV. The most ΔE was observed at the dimethyldichlorosilane flow.

The substrate of monocrystalline silicon KEF-4.5 (100) was set at a distance of 12 cm from the ion source. Before the synthesis of the film the substrate cleaning was performed for 5 minutes with argon ions at $U_a = 3.5$ kV, $I = 40$ mA and $p = 12$ mPa. The temperature of uncooled substrate during the deposition did not exceed $250^\circ C$ with the exception of experiments with heating of the substrate which will be discussed separately. Deposition time was 20 minutes.

The synthesized films were researched using Renishaw inVia Raman Microscope ($\lambda = 514.5$ nm), nanoindenter Nanoscan-01, and FTIR spectrometer FSM-1201.

3. Results and Discussion

3.1. Results. Carbon film synthesis experiments at the maximal acceleration voltage ($U_a = 5$ kV) showed that, at pressure 12.5 mPa or less, synthesis of the film does not occur. Deposition failed also at $p = 20$ mPa and $U_a = 1.5$ kV. Apparently, this is due to the advent of the uncompensated ion charge on the growing surface. The electric field of this charge prevents further flow of ions on the growth surface, which hinders the growth of the film. At these values of pressure and voltage the compensation of charge with the help of electrons from low-density ionized ion-beam plasma [13] is not sufficient.

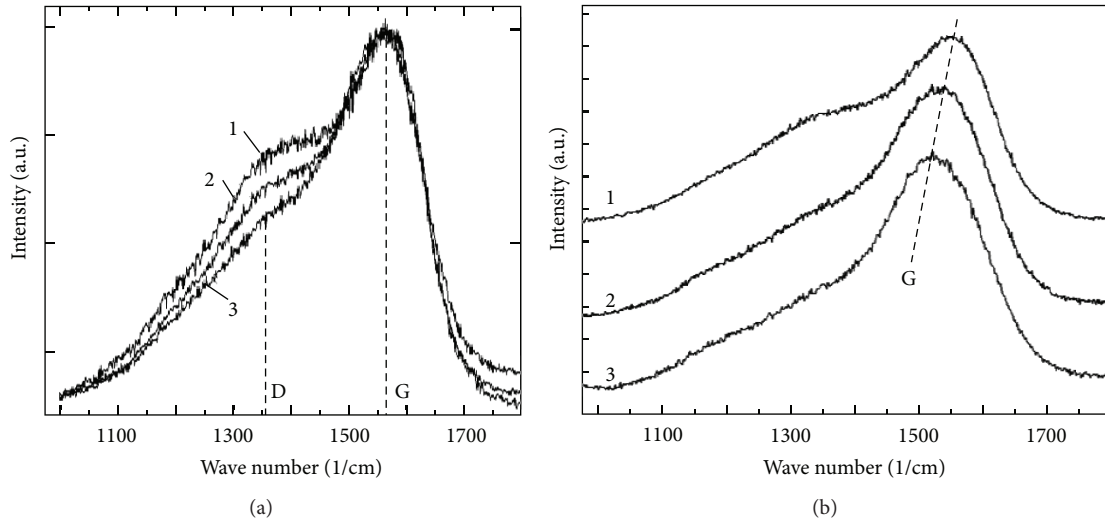


FIGURE 3: Raman spectra of samples. (a) $U_a = 5$ kV and different pressure p , mPa: 1: 42; 2: 30; 3: 20, and different substrate current I , mA: 1: 70; 2: 45; 3: 35; (b) $p = 30$ mPa, U_a , kV: 1: 5; 2: 3; 3: 1.5.

Increase of gas pressure leads to the formation of carbon films with different structures and properties. Analysis of the Raman spectra (Figure 3(a)) shows that with increase of pressure the intensity of D-band (1350 cm^{-1}) increases. In this case, G band ($\sim 1575\text{ cm}^{-1}$) does not move, but the ratio of the intensity of bands I_D/I_G increases, which, according to the data of [14, 15], indicates structural changes in the carbon film, followed by a higher content of sp^2 hybridized carbon. The spectra of the films obtained under the same conditions but with an overlap of methane or dimethyldichlorosilane as the plasma-forming gases had no pronounced differences. Only the D and G bands of carbon were observed, and the band associated with phonon interactions of silicon carbide was absent.

Onto heating substrates (600 , 700 , and 850°C) in the range of discussed accelerating voltages and gas pressures were deposited films, the Raman spectra of which have a D peak with a higher intensity ($I_D/I_G = 0.7\text{--}0.9$ rel. units) compared with the samples synthesized without the heating. This fact indicates the increasing proportion of sp^2 hybridized carbon and hence the film graphitization. Besides the gas pressure the accelerating voltage has significant influence on the film Raman spectra. With increasing U_a from 1.5 to 5 kV a transition of G band from 1540 to 1565 cm^{-1} was observed (Figure 3(b)). In addition, there is the increase of I_D/I_G at $U_a > 2.5$ kV. These observations indicate substantial changes in the composition and structure of the synthesized films [16].

Study of hardness of the samples depending on the accelerating voltage (Figure 4(a)), the gas pressure (Figure 4(b)), and the substrate temperature confirm the results of research based on the Raman spectra. Regarding the effect of accelerating voltage on the hardness of the films, it was found that the samples synthesized at approximately $U_a = 3$ kV have the highest values of hardness.

As seen in Figure 4(b), with raising pressure the hardness of the films decreases from 27 GPa to 3 GPa; that is, the

structure of the film changes from diamond-like to graphite-like. The decrease of hardness with increasing accelerating voltage occurs due to an increase of the fraction of sp^2 carbon and/or due to an increase in the concentration of chemically bounded hydrogen within the film. When methane was used as a working gas, the hardness of films was slightly increased. The films synthesized at high temperatures had low hardness (up to 3 GPa); it allows characterizing them as graphite-like.

Analysis of the samples by Fourier transmission IR spectroscopy showed two significant areas of the chemical bonds vibrations. At $1000\text{--}1800\text{ cm}^{-1}$ we can observe the field of deformational vibrations of C–H bonds, valence vibrations of carbonyl bonds, segregate C–C, and double C=C bonds. Analysis in the valence area of vibrations of C–H bonds ($2800\text{--}3200\text{ cm}^{-1}$, Figure 5, spectrum 1) showed a low concentration of chemically bounded hydrogen in the synthesized films. Meanwhile, at increase of the gas pressure $40\text{--}200$ mPa and/or reducing of the ion energy (accelerating voltage $U_a \leq 1$ kV), the intensity of valence vibrations of C–H bonds increases sharply (Figure 5, spectrum 2). These observations correspond to the increase of the chemically bounded hydrogen concentration in the film. Using a $\text{C}_3\text{H}_8 : \text{H}_2$ mixture up to 75% of volume of hydrogen has no significant effect on the intensity of the IR absorption bands of C–H bonds. The IR spectrum 2 in the area of C–H bonds valence vibrations has the following details: sp^3 $\text{CH}_3(\text{a})$ (2960), sp^3 $\text{CH}_2(\text{a})$ (2925), sp^3 $\text{CH}(\text{a})$ (2900), sp^3 $\text{CH}_3(\text{s})$ (2870), sp^3 $\text{CH}_2(\text{s})$ (2850), and sp^3 $\text{CH}(\text{s})$ (3030) (here sp^3 , sp^2 , and sp : hybridization type, the figures in brackets: wave number in cm^{-1} , (a) and (s): asymmetric and symmetric vibrations). Absorption band of 3000 and 3045 cm^{-1} correspond to the valence vibrations of sp^2 CH and aromatic groups, respectively. The intensity of the IR absorption bands is directly related to the concentration of CH_n vibrational groups, which allows us to estimate the concentration of bounded hydrogen in the film [17, 18].

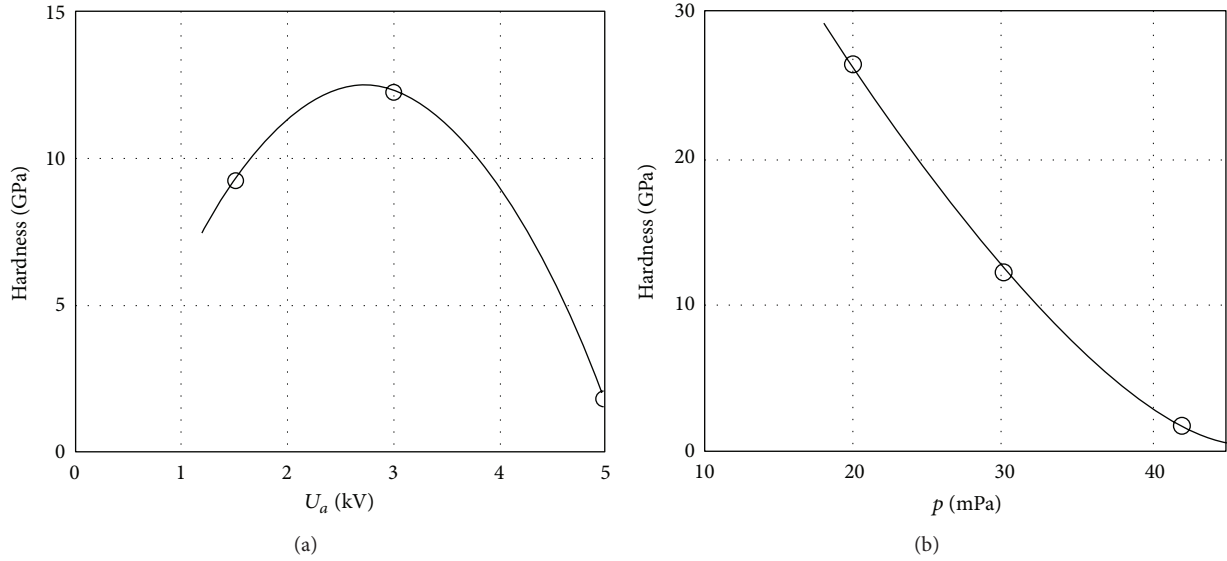


FIGURE 4: Dependence of the film hardness on the accelerating voltage at a fixed gas pressure $p = 30$ mPa (a) and the gas pressure at a fixed acceleration voltage $U_a = 5$ kV (b).

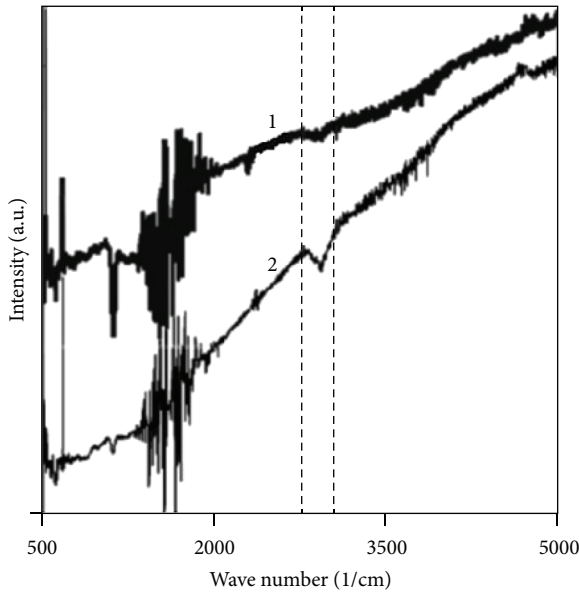


FIGURE 5: IR transmission spectra of films synthesized at $U_a = 5$ kV and $p = 20$ mPa (1) and $U_a \approx 0.5$ kV, $p = 200$ mPa (2).

This experimental research shows that with increase of the accelerating voltage and/or decrease of the pressure the intensity of IR light absorption in the range of stretching vibrations of C–H bonds decreases. It was estimated that decrease of bounded hydrogen is from 10 to 2%. Under these experimental conditions films with the high hydrogen content $> 35\%$, which can be categorized as hydrogenated polymer-like [19], were not synthesized.

There is another feature of deposited samples that was observed at FTIR analysis. The intensity of transmittance of red and infrared light for some samples was three times

higher compared to the same parameter for the pure Si substrate. This fact points to one of possible technical applications. These films can be employed as antireflective coatings in IR sensors.

3.2. Discussions. The observed changes in the hardness and the content of bounded hydrogen, depending on the synthesis conditions, can be explained by the model of nucleation and growth of amorphous and crystalline carbon films [20]. According to this model, during the deposition of the film two types of clusters are formed, which replicate and modify the surface structure of a monocrystalline substrate. Thus, clusters replicating can be formed only by carbon atoms with sp^3 hybridization, but clusters modifying the structure may consist of carbon atoms with both sp^2 and sp^3 hybridization types. In addition, modifying clusters and carbon atoms of sp^3 hybridization type can form more bonds with hydrogen than clusters formed by carbon atoms with sp^2 type hybridization.

With increasing the pressure, the rate of formation of modifying clusters is reduced more than the rate of formation of replicating clusters. Within the modeling the rates of these processes can be represented in the following form:

$$\frac{V_M}{V_S} = K_0 \left[a \frac{K_r P}{1 + K_r P} \right] \exp\left(+\frac{\Delta E}{kT}\right), \quad (2)$$

where V_M , V_S are the formation rates of modifying and replicating clusters on the surface superstructure; ΔE is the difference in the potential barriers to the formation of modifying and replicating clusters, the superstructure of the substrate surface (depending on the type of components (radicals) of which the formation of clusters come from); K_0 is ratio of constants of direct cluster formation reactions, modifying and replicating the surface superstructure of substrate (depending on the type of components (radicals) from which

clusters are formed); K_γ is coefficient of hydrocarbon radical adsorption on the surface of the silicon substrate; p is partial pressure of hydrocarbon radicals; k is Boltzmann constant; and T is thermodynamic temperature.

This expression shows that the increase in pressure, together with the amount of active particles capable to form layers at interacting with the substrate, leads to increased concentration of clusters modifying the surface and hence to increase of the fraction of sp^2 carbon. The increase in the fraction of sp^2 carbon occurs irrespective of the reasons for increasing the number of active particles in the gaseous phase (plasma). Increasing number of sp^3 clusters in the matrix changes the film structure from amorphous (a-C:H) to tetragonal (ta-C:H) carbon and therefore leads to an increase in the hardness of the films, as observed in our experiments. Increase of the pressure leads to increase of the formation rate of both sp^3 and sp^2 carbon clusters, but the rate of formation of sp^2 carbon is higher. Furthermore, at $p > 100$ mPa and $U_a < 1$ kV, the changes in the composition of deposited films can be explained by the changes in the deposition conditions under which the accelerating gap ignites the gas discharge, the energy of bombarding ions is lowered, the concentration of hydrogen in products of propane dissociation increases, and the degree of destruction of propane is reduced.

As regards the influence of an accelerating voltage determining the ion energy, its role in the formation of the film structure can be described as follows. Increasing the accelerating potential leads to a greater role of the processes of destruction of clusters. In the first place, clusters with high potential energy are destroyed. In the case of the synthesis of amorphous films under ion bombardment surface-modifying cluster predominantly form, and probability of destruction of cluster formed by sp^3 carbon is higher than in the case of cluster formed by the sp^2 hybridized carbon. As a result, with increasing acceleration of voltage in the result of competing of two processes of cluster formation and their destruction in the film, the ratio of carbon with sp^3 hybridization type decreases. At the same time the proportion of bound hydrogen is reduced. Since cluster modifying the surface structure and formed by the two carbon atoms type with sp^3 hybridization can form up to four bonds with hydrogen atoms, whereas with sp^2 type only to two bonds, then the reduction in the proportion of sp^3 carbon must be accompanied by a decrease of the concentration of bounded hydrogen. Thus, the intense ion bombardment during growth process is the main reason for the low content of bounded hydrogen in the films produced in this work. It should be noted that an increase of clusters in the matrix which modify the superstructure and which are formed by sp^2 carbon atoms, leads to a changes in the film structure from amorphous polymer-like to the amorphous diamond-like, and finally, to the amorphous graphite. Such structural changes explain non-monotonic dependence of the film hardness on the accelerating voltage.

It should be noted that the increase of the concentration of sp^2 carbon in the films with the increase of the accelerating voltage was also obtained in RF discharge plasma system with [21], in which the role of the accelerating voltage carries

substrate bias (U_{bias}). In the case of RF plasma system, samples with the highest hardness were obtained at pressures of 3.6 Pa and $U_{bias} = -400$ V, whereas in the case of synthesis with the help of IS, the conditions were different (p , T , gas composition). In addition, the concentration of bound hydrogen in the films produced by the RF plasma system was significantly higher than in the case of ion beams usage. Meanwhile, dependencies of films hardness changes on alternating accelerating IS voltage, and substrate bias voltage with RF plasma system is similar. Similar hardness dependencies of synthesized films on the accelerating voltage and gas pressure were obtained in glow discharge plasma system [22]. Dependencies of refractive index and optical gap changes on ion energy are also similar for amorphous carbon films deposited by both RF plasma system and direct ion-beam system [11]. As it was showed in [3] the hardness, density, and electrical resistance of the films depend on the ion energy during the deposition. In this case, the hardness dependency on the ion energy is described by a curve with a maximum. Thus, under these circumstances, it can be concluded that at consistent change in the deposition parameters, regardless of the type of plasma source, the nature of effects of pressure and ion energy on the structure and composition of growing amorphous carbon films remains the same.

4. Conclusions

Deposition of carbon films with the help of plasma ion source with a hollow cathode DC discharge allows varying accurately and widely different deposition conditions: the pressure and the composition of the plasma-forming gas, current density, and ion energy. Films synthesized by this method may have both graphite-like and diamond-like material structures.

Since a dependence of the hardness and the content of bounded hydrogen from the pressure and the accelerating voltage (ion energy) was identified, then for the deposition of carbon films the source with narrow energy spectrum of ions should be used. Narrow energy spreading of ions generated by the source based on hollow cathode reflective discharge allows obtaining films with more exact defined characteristics.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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