Poly(naphthalenehydrocarbyne): synthesis, characterization, and application to preparation of thin diamond films

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The diamond phase precursor, *viz.*, poly(naphthalenehydrocarbyne) (**1**), was prepared. Its disordered structure is built of CH fragments with sp^3-hybridized carbon atoms, and arene fragments are inserted in the structure. The use of **1** in the process of diamond layer deposition makes it possible to prepare highly qualitative thin diamond coatings with low roughness and good optical properties.

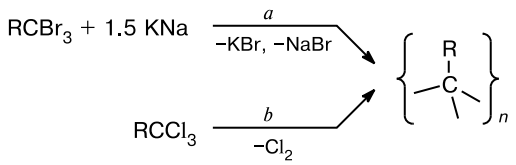
Key words: diamond precursor, poly(carbynes), nucleation, diamond films.

Uniform thin diamond films (DFs) with low surface roughness and nanocrystalline internal structure are demanded for planar electronic devices, protective optical coatings, and micro- and nanoelectromechanical systems.[2] The most important condition for preparation of such DFs is efficient nucleation, for which the method with ultradispersed diamond (UDD) deposition (usual for thick (>1 μm)[3] DFs) is inappropriate because of low density and nonuniform nuclei distribution on the substrate. It is known that the efficiency of UDD application can be enhanced by deposition of a layer of carbon[4] and ceramics SiC, SiN_x, and TiSiN (see Ref. 5). However, nuclei generation from an appropriate precursor can serve as a radical method for nucleation improvement. Poly(phenylcarbyne) has been used earlier[6—9] for this purpose. However, thus obtained films consisted of diamond-like carbon with diamond inclusions. In the present study, we describe the synthesis of poly(naphthalenehydrocarbyne) (**1**), *viz.*, a new precursor combining the aliphatic framework and aromatic fragments in its structure. Its structure and potential for using in diamond layer deposition on a silicon substrate were studied.

Results and Discussion

Synthesis of polymer 1. The general method for preparation of polymers of the poly[(R-)carbyne] series (R = Ar, Alk, H), in particular, polymers **2** and **3**, is the condensation of heme-trihalides by the action of a KNa alloy in the ultrasonic field[10,11] (Scheme 1, reaction *a*) or by electrolysis[12,13] (Scheme 1, reaction *b*). Note that these methods have several substantial drawbacks. For example, the use of an explosive KNa alloy in reaction *a* makes the latter almost impracticable. Reaction *b* is also very difficult in methodical respect (anaerobic electrolysis accompanied by Cl_2 evolution is required, the product needs purification by prolonged heating with $LiAlH_4$, *etc.*[12,13]). The product yield in procedures *a* and *b* is low, and a strong dependence of the properties of the polymers on many random factors is observed. Thus, search for convenient methods of synthesis of poly(carbynes) and, first of all, poly(hydrocarbyne) (**3**) as the most promising of them, remains topical.

Scheme 1



a. Ultrasonication. *b*. Electrolysis.
R = Ph (**2**), H (**3**)

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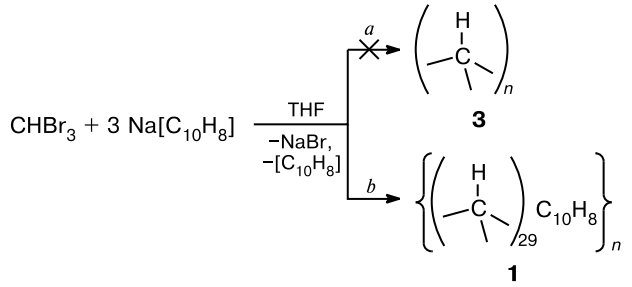
For synthesis of polymer **3**, we proposed to use the reaction in which sodium naphthalide is the condensing agent (Scheme 2, reaction *a*) (some poly(arylcarbynes)[14] were prepared similarly).

However, contrary to expectations, we obtained compound **1** (Scheme 2, reaction *b*) instead of polymer **3**. As it will be shown, compound **1** is the adduct of polymer **3** and naphthalene.

Scheme 2



Polymer **1** is a light brown powder amorphous to X-rays. The IR spectrum of **1** exhibits a band of aliphatic framework vibrations at 1058 cm^{-1} and stretching vibration bands of the C—H bonds at 2925 and 2870 cm^{-1}. The bands at 1670, 3014, and 3054 cm^{-1}, are likely due to admixtures of C=C bonds. The intense band at 752 cm^{-1} corresponds to vibrations of the arene fragments.

Like compound **3** (see Refs 10 and 11), polymer **1** is paramagnetic, and the ESR signal of **1** (at 20 °C it is a singlet with g = 2.004, which is characteristic of an unpaired electron on the carbon atom[10,11]) coincides with the signal from polymer **3**. Since compound **1** is paramagnetic, the ^{1}H NMR signals of the aliphatic framework appear as a broad resonance at δ = 1—3, which coincides with the signal in the spectrum of **3** (see Refs 10 and 11). At 6.75—7.5 ppm the spectrum of **1** contains a broad band with a maximum at δ 7.1, indicating the presence of arene fragments. The intensity ratio of the aromatic and aliphatic signals range slightly for different samples of **1** and corresponds, on the average, to one $C_{10}H_8$ molecule per 29 CH units of the aliphatic network. Note that changes in composition (the ratios range from 1 : 28 to 1 : 30) exert, most likely, no effect on the quality of the obtained diamond films; however, to confirm this rigorously, additional studies are needed.

Elemental analysis of polymer **1** shows high (up to 15%) underestimation of the carbon content. As a whole, this phenomenon is typical of poly(carbynes) and is considered[10,11] to be associated with the incomplete combustion of the samples because of their partial ceramization.

Thus, available data show that compound **1** is based on the aliphatic network framework with the carbon atoms in the sp^3 state in which the arene fragments are distributed. The type of arene binding in compound **1** remains unclear. Probably, the nature of this bond is topological rather than chemical, because it can be seen that only a minor part (~3%) of ions $[C_{10}H_8]^-$ involved in reaction *b* (see Scheme 2) is included in the structure.

In spite of the presence of arene, the aliphatic framework of polymer **1** can decompose, as shown experimentally, to form diamond clusters that are efficient nuclei of the diamond layer.

Preparation and study of diamond films deposited using polymer 1. Polymer **1** was deposited on silicon plates as a solution in a THF and diglyme (1 : 1) mixture and dried in air. The samples obtained were placed in a reaction chamber for the growth of diamond layers by the method of stabilized dc discharge (Fig. 1). The parameters of the process are given in Experimental.

The properties of the DFs obtained were studied using a wide set of methods. The typical diffraction patterns of the obtained DFs is shown in Fig. 2. Only diamond bands at 43.96 and 75.44 deg are observed in the explicit form.

According to the data of atomic force microscopy, the average roughness of the films R_a ranges from 10 to 20 nm. The morphology of the film surface with unfaceted particles (globules) is characteristic of nanocrystalline DFs.[15]

The Raman spectra of the synthesized films were characteristic of the nanocrystalline DFs.[16] The main features in the Raman spectra with UV excitation (Fig. 3) are the intense line at 1333 cm^{-1} corresponding to the first order of Raman spectra in diamond and the line with a maximum at ~1580 cm^{-1}, which is the G mode of disordered graphite due to stretching vibrations of all pairs of sp^2-hybridized C atoms in chains and aromatic rings.[17] The half-width of the G band is similar to that for amorphous tetrahedral carbon ta-C (see Ref. 17). The

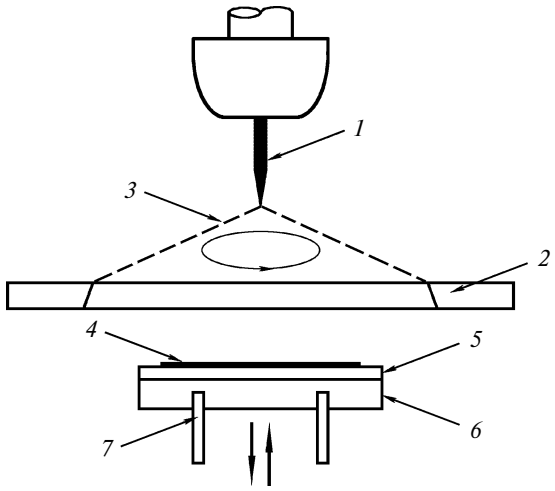


Fig. 1. Scheme of the experimental setup: *1*, hollow graphite cathode with a hole (diameter 0.4 mm) at the needle point inside which the cathode spot is situated; *2*, copper cooled anode; *3*, arc rotating discharge; *4*, silicon plate; *5*, copper disk; *6*, highly porous quartz; and *7*, movable platform.

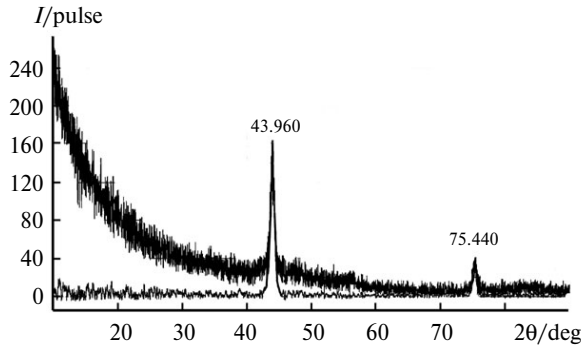


Fig. 2. X-ray pattern of the prepared DFs.

asymmetric broadening of the diamond line (half-width ~16 cm^{-1}) compared to the diamond single crystal is due to the nanocrystalline structure of DFs. According to earlier studies,[18] this half-width corresponds to the average size of crystallites in the DF in a range of 30—40 nm. The Raman spectrum (see Fig. 3) also contain a peak at 520 cm^{-1} due to the signal of the silicon film on which the film was deposited. This indirectly indicates that the film is transparent in the UV region. The films were transparent in both the IR (Fig. 4) and visible range, which is indicated by a large amplitude of Cos Δ in the ellipsometric spectra (Fig. 5). In addition to a set of bands in the far-IR region due to the two-phonon and impurity absorption of the silicon substrate, the IR spectra also contain the structural absorption band at 2800—3000 cm^{-1} due to the CH_x group stretching vibrations (see Fig. 4). The concentration of bonded hydrogen in the films was calculated by the integral intensity of this band ad reached 5 at.%, which is characteristic of nano- and ultrananocrystalline DFs with a small size of crystallites and, correspondingly, a large total surface area of intercrystalline boundaries.[19] The main contribution to the IR spectra of stretching vibrations is made by the sp^3-CH_x groups (maxima at 2875 and 2935 cm^{-1}) and the band with a maximum at ~2830 cm^{-1} (see Fig. 4), which is characteristic of micro- and nanocrystalline DFs and is caused by the presence of bonded hydrogen at the intercrystalline boundaries.[20,21]

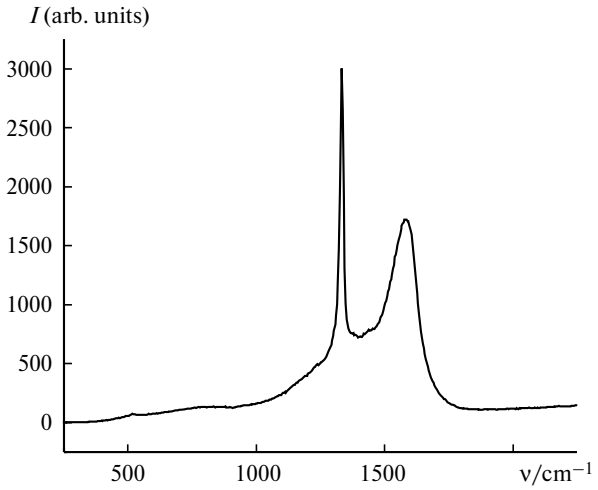


Fig. 3. Raman spectrum of the film with scattering excitation at the wavelength 244 nm.

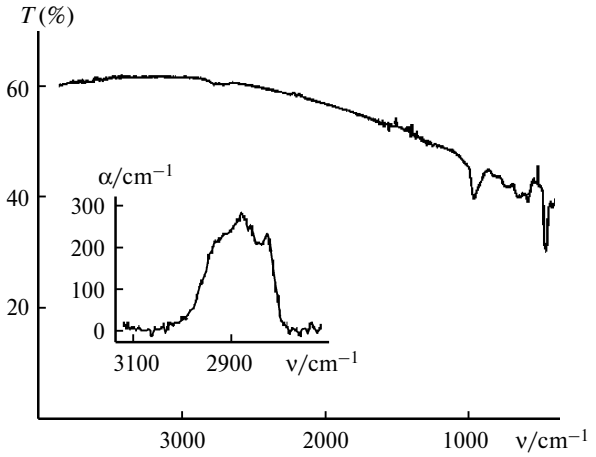


Fig. 4. Transmission spectrum in the IR region of the nanocrystalline DF deposited on a silicon supported in an arc discharge with the supported poly(naphthalenehydrocarbyne) layer. Inset: the spectrum of the absorption coefficient (α) for the film in the region of CH_x group stretching vibrations.

The data of measurements by multiangle spectroscopic ellipsometry (SE) are shown in Fig. 5. The results of SE measurements were examined in terms of the three-layer model: silicon substrate/DF/rough surface layer. This approach is characteristic of analysis of SE data for film structures with surface roughness comparable with the wavelength of the incident light. The determined parameters were the thickness, refractive index, and absorption coefficient of the DF. The surface layer thickness (15—20 nm) was specified from the atomic force microscopic data by the known[22] empirical equation and its optical properties were simulated for the media consisting of the AP by 60—70% and of air by 30—40%. The best agreement between the calculation and model was estimated as the minimum value of the function characterizing the total root-mean-square deviation of the experimental and calculated values between the ellipsometric parameters determined at the same wave lengths over the whole spectral range and at all incident angles at which the spectra were measured. It was found that the refractive index of the studied films was ~2.4 (*i.e.*, it was close to that for natural diamond) and the absorption coefficient did not exceed 0.03 in the spectral range from 400 to 1000 nm. As is known, annealing of the DFs in air results in predominant etching of non-diamond carbon and diamond regions with enhanced deficiency.[23] Consecutive annealings of the obtained DFs in air in the range from 200 to 550 °C exerted no appreciable effect on the thick-

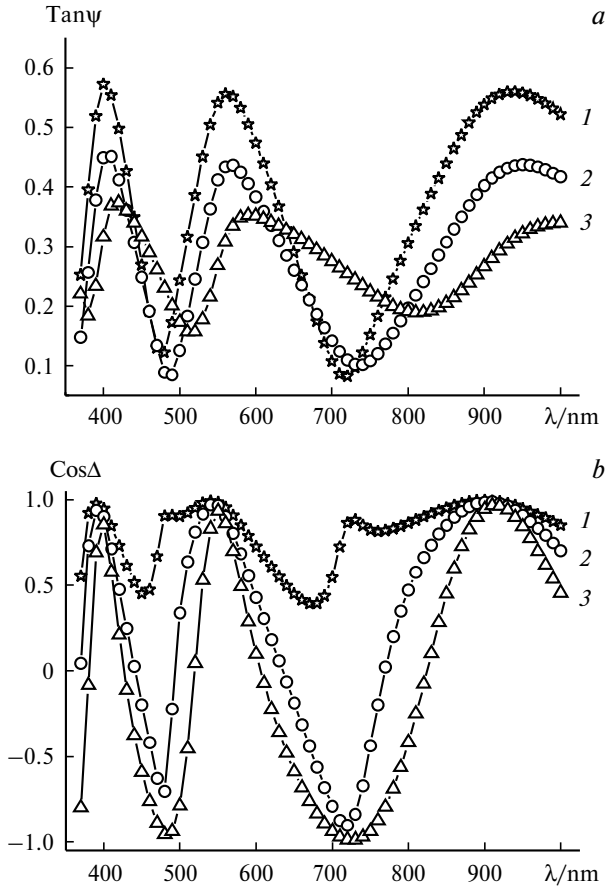


Fig. 5. Spectra of the ellipsometric parameters Tan Ψ (*a*) and Cos Δ (*b*) of the diamond film/silicon substrate structure. Points are the experimental data for incident angles: 75° (*1*), 70° (*2*), and 65° (*3*). Solid curves are simulation.

ness and optical properties of the DFs, which indicates rather high (compared to the diamond-like films) resistance of the obtained DFs to oxidation.

The above-presented data show that DF deposition using a layer of **1** make it possible to obtain continuous nanocrystalline coatings with the thickness from 0.1 to 0.4 μm. The coatings have the diamond crystalline structure, low surface roughness ($R_a \approx 10$ nm), and high optical properties.

Comparison of **1** with poly(phenylcarbyne) (**2**), whose application for nucleation is less efficient,[6—9] shows that polymer **1** substantially exceeds polymer **2b** by such an important parameter[10] as the relative content of carbon atoms with the sp^3 and sp^2 state in the structure ($sp^3 : sp^2 = 3 : 1$ for **1** and 1 : 6 for **2**). Thus, under other conditions being equal, polymer **1** is likely capable of providing more efficient nucleation than polymer **2**. In combination with availability of polymer **1** from the synthetic viewpoint, this allows one to consider **1** as one of the most promising precursors for deposition on thin DFs.

Experimental

Synthesis of poly(naphthalenehydrocarbyne) (1). All manipulations were carried out under argon atmosphere. Tetrahydrofuran was refluxed and distilled from sodium benzophenone ketyl; $CHBr_3$ was dried over $CaCl_2$ and distilled; naphthalene was dried *in vacuo* for 30 min at 40 °C. The ^{1}H NMR spectrum was recorded on a Bruker DPX 300 spectrometer. ESR spectra were measured on a Varian E13 spectrometer at 20 °C.

Sodium (5.06 g, 0.22 g-at.) as a sand was added to a solution of naphthalene (40.2 g, 0.32 mol) in THF (250 mL). The mixture was stirred for 12 h at 20 °C. A solution of $CHBr_3$ (15.52 g, 61 mmol) in THF (50 mL) was added dropwise to the resulting green solution for 15 min with stirring and cooling in an ice bath. The mixture was let to warm to 20 °C, methyllithium (3.0 mL of a 0.6 *M* solution in ether) was added, and the mixture was stirred for 1 h. Water (10 mL) was added to the mixture, the solution was separated from the precipitated salts, and the solvent was evaporated *in vacuo*. The residue was extracted at 40 °C with hexane (2×250 mL), decanting the precipitate. The residue was dissolved in CH_2Cl_2 (50 mL), and the solution was centrifuged to remove salts and concentrated by evaporation to a volume of ~10 mL. Hexane (30 mL) was gradually added to the solution obtained, and a yellowish-brown precipitate was filtered off and dried *in vacuo* at 60 °C. The yield was 0.72 g. Found (%): C, 83.1—90.4; H, 7.09—7.98; Br <0.2; Na, <0.2. $C_{39}H_{36}$. Calculated (%): C, 92.86; H, 7.14. ^{1}H NMR ($CDCl_3$), δ: 0.80—3.00 (br.s, 4.13 H, CH); 6.75—7.50 (br.s, 1 H, $C_{10}H_8$). ESR (powder): singlet, $g = 2.004$, $\Delta H = 5$ G.

Deposition of the DFs on the silicon substrate using 1. Films of **1** with a thickness of ~1 μm were deposited on standard polished plates (diameter 76 mm, thickness 0.3 mm) etched with hydrofluoric acid. A solution of **1** in THF—diglyme (1 : 1) mixture was used for deposition. After deposition of the solution, the samples were dried in air and placed in the reaction chamber of the setup (see Fig. 1).

Diamond films were prepared by the plasma-enhanced chemical vapor deposition of carbon from a mixture of methane (3%), hydrogen (77%), and argon (20%) in an arc dc discharge rotating in the magnetic field with a frequency of 100 Hz. The temperature on the silicon plate surface was 730 °C. The pressure of the flowing gas medium was 1.6 mbar.

Characterization of the obtained DFs. The X-ray phase analysis of the films was carried out on an ARL X´TRA diffractometer. Raman spectra were recorded on a Raman System 100 spectrometer (Renishaw) with scattering excitation at the wavelength 244 nm at a laser radiation power of 10 mW. The optical properties in the visible range were studied by multiangle spectroscopic ellipsometry on an ES-2 multichannel spectral ellipsometer. Infrared spectra were measured on a Bruker Spectrum 100 Optica FTIR spectrometer. An ULTRAObjective combined optical and atomic-force microscope (Carl Zeiss) was used for studying the morphology of the films, and the measurements were carried out in the semicontact mode.

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References

1. J. K. Luo, Y. Q. Fu, H. R. Le, J. A. Williams, S. M. Spearing, W. I. Milne, *J. Micromech. Microeng.*, 2007, **17**, S147.
2. A. V. Sumant, P. U. Gilbert, D. S. Grierson, A. R. Konicek, M. Abrecht, J. E. Butler, T. Feygelson, S. S. Rotter, R. W. Carpick, *Diamond Rel. Mater.*, 2007, **16**, 718.
3. V. Ralchenko, A. Saveliev, S. Voronina, A. Dementjev, K. Maslakov, M. Salerno, A. Podesta, P. Milani, in *Synthesis*, *Properties and Applications of Ultrananocrystalline Diamond*, Eds D. M. Gruen, O. A. Shenderova, A. Ya. Vul´, Springer, 2005, 109—124.
4. S. Z. Rotter, J. C. Madaleno, *Chem. Vap. Deposition*, 2009, **15**, 209.
5. Y. S. Li, C. Xiao, A. Hirose, Q. Yang, S. Shimada, *J. Am. Ceram. Soc.*, 2007, **90**, 1427.
6. X. Wang, J. Chen, Z. Zheng, Z. Sun, F. Yan, *J. Crystal Growth*, 1997, **181**, 308.
7. Z. Sun, X. Shi, B. K. Tay, D. Flynn, X. Wang, Z. Zheng, Y. Sun, *Diamond Rel. Mater.*, 1997, **6**, 230.
8. Z. Sun, X. Shi, X. Wang, B. K. Tay, H. Yang, Y. Sun, *Diamond Rel. Mater.*, 1998, **7**, 939.
9. C. Jingsheng, W. Xuejun, Z. Zhihao, Y. Fengyuan, *Thin Solid Films*, 1999, **346**, 120.
10. P. A. Bianconi, S. J. Joray, B. L. Aldrich, J. Sumranjit, D. D. Duffy, D. P. Long, J. L. Lazorcik, L. Raboin, J. K. Keams, S. L. Smulligan, J. M. Babyak, *J. Am. Chem. Soc.*, 2004, **126**, 3191.
11. V. K. Genchel´, A. V. Kucherov, A. I. Sizov, T. M. Zvukova, B. M. Bulychev, V. G. Babaev, M. B. Guseva, *Sverkhtverdye materialy* [*Superhard Materials*], 2007, No. 4, 30.
12. Y. Nur, M. W. Pitcher, S. Seyyidoglu, L. Toppare, *J. Macromol. Sci., Part A: Pure and Appl. Chem.*, 2008, **45**, 358.
13. A. M. Katzenmeyer, Y. Bayam, L. VJ, M. W. Pitcher, Y. Nur, S. Seyyidoglu, L. K. Toppare, A. A. Talin, H. Han, C. E. Davis, M. S. Islam, *J. Nanomater.*, 2009, Article ID 832 327, 4 pages, 2009, doi: 10.1155/2009/832327.
14. R. D. Rieke, US Pat. 5,436,018; *Chem. Abstrs*, 1996, **124**, 57089.
15. B. M. Bulychev, V. K. Genchel´, T. M. Zvukova, A. I. Sizov, A. F. Aleksandrov, Yu. A. Korobov, A. P. Bol´shakov, V. A. Gerasimenko, M. V. Kanzyuba, V. S. Sedov, D. N. Sovyk, V. G. Ral´chenko, V. I. Kovalev, A. V. Khomich, *Trudy XV Mezhdunar. nauch.-tekh. konf. "Vysokie tekhnologii v promyshlennosti Rossii"* [*Proceedings of the XV International Scientific Technical Conference "High Technologies in Industry of Russia"*], Ed. M. I. Samoilovich, Tekhnomash, Moscow, 2009, 440 pp. (in Russian).
16. S. Prawer, R. J. Nemanich, *Phil. Trans. R. Soc. London*, 2004, **362**, No. 1824, 2537.
17. A. C. Ferrari, J. Robertson, *Phys. Rev.*, *B.*, 2000, **64**, 075414/13.
18. Z. Sun, J. R. Shi, B. K. Tay, S. P. Lau, *Diamond Rel. Mater.*, 2000, **9**, 1979.
19. I. I. Vlasov, E. Goovaerts, V. G. Ralchenko, V. I. Konov, A. V. Khomich, M. V. Kanzyuba, *Diamond Rel. Mater.*, 2007, **16**, 2074.
20. R. P. Chin, J. Y. Huang, Y. R. Chin, T. J. Chuang, H. Seki, *Phys. Rev.*, *B.*, 1995, **52**, 5985.
21. A. V. Khomich, V. G. Ralchenko, A. A. Smolin, V. V. Migulin, S. M. Pimenov, I. I. Vlasov, V. I. Konov, *J. Chem. Vap. Dep.*, 1997, **5**, 361.
22. P. Petric, L. P. Biro, M. Fried, T. Lohner, R. Berger, C. Schneider, J. Gyulai, H. Ryssel, *Thin Solid Films*, 1998, **315**, 186.
23. A. V. Khomich, V. P. Varnin, I. G. Teremetskaya, N. A. Poklonskii, N. M. Lapchuk, A. O. Korobko, *Inorganic Materials* (*Engl. Transl.*), 2005, **41**, 812.

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