

Physical-Chemical Properties of Silicon Carbonitride Films Prepared Using Laser-Plasma Deposition from Hexamethyldisilazane

V. N. Demin^a, T. P. Smirnova^a, V. O. Borisov^a, G. N. Grachev^b, A. L. Smirnov^b, and M. N. Khomyakov^b

^a*Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences,
pr. Akad. Lavrent'eva 3, Novosibirsk, 630090 Russia*

^b*Institute of Laser Physics, Siberian Branch, Russian Academy of Sciences,
pr. Akad. Lavrent'eva 13/3, Novosibirsk, 630090 Russia*

e-mail: demin@niic.nsc.ru

Received February 18, 2014

Abstract—A new method of the plasma chemical vapor deposition with the activation of the initial compounds by the plasma of the CO₂ laser in the high-speed gas flow has been applied for the synthesis of silicon carbonitride SiCN films on a substrate of stainless steel and instrumental alloys using hexamethyldisilazane vapors. The preparation of the coatings of the laser-plasma deposition in the variants of the chamber and non-chamber deposition has been studied. The properties of the prepared coatings have been studied by the methods of IR and Raman spectroscopy, atomic-force microscopy, and XRD-analysis analysis. The studies of the structure of the films using diffraction synchrotron radiation showed that the prepared silicon carbonitride coatings are X-ray amorphous. The ratio of the Si–C/Si–N bonds in coatings increases with the increase in the substrate temperature. The microhardness of the prepared coatings on stainless steel substrates is 15–25 GPa.

Keywords: laser plasma, SiCN coatings, chemical structure, structure

DOI: 10.1134/S1087659615020042

INTRODUCTION

Silicon carbonitride is a unique multifunctional material, which successfully combines the best properties of silicon carbide and nitride. The composition and properties of the coatings can vary as a function of the method and conditions of their preparation. The resistance to high temperatures, aggressive and oxidation media, high hardness, and high dielectric characteristics make silicon carbonitride a promising material for wide application in a series of modern technologies such as hardening, as well as radiation- and chemically stable protective and optical coatings.

Silicon carbonitride layers are traditionally prepared either at increased temperatures ($T \geq 1000^\circ\text{C}$) by the chemical vapor deposition (CVD) method or at relatively low temperature using radio-frequency, microwave, or glow discharge plasma (PECVD) [1, 2]. The decreased pressure in the reactor and the relevant low deposition rates hamper the preparation of layers and coatings these methods with thicknesses above the one micron necessary for solving application problems.

The powerful optical pulsating discharge (POPD) in high-speed gas flows is a new form of an optical discharge [3]. POPD is obtained in gas under the impact

of the pulsating periodic radiation of 10–100 kHz and the peak energy of laser pulsations of 500–1000 kW. At the plasma chemical synthesis of coatings the radiation is focused in the high-speed 100–1000 m/s gas fluxes providing the high cooling rate of the gas phase after the laser pulse, decrease in the sizes of the formed solid phase centers of nucleation, and the fast delivery of reagents to the processed surface. A new type of POPD in combination with the high-speed 100–300 m/s flow of the reaction gas was applied for the first time for the laser plasma chemical deposition's highly rigid coatings in the atmospheric pressure reactor [4].

The possibility of creating a high concentration of particles of the deposited components in the plasma region by supplying the initial reagents as vapors or a flow of aerosol particles in the jet of the gas-carrier makes it possible to prepare coatings with the rates much higher than the deposition rates in the conventional plasma chemical processes, in which plasma is created in rarefied gas.

In this paper we present the results of studying the physical-chemical properties of the silicon carbonitride films synthesized from hexamethyldisilazane (HMDS) using POPD plasma.

EXPERIMENTAL SECTION

The coatings were synthesized in both the chamber and non-chamber variants of the process. A detailed description of the setup for the laser plasma chemical deposition is given in [5, 6]. The non-chamber variant of the laser plasma chemical deposition setup is based on the effective protection of the reaction zone produced by the cooling gas flowing in the ring gap between the cut of the nozzle and the surface of the material, and is promising for industrial application [4].

As the initial compound, HMDS ((CH₃)₃SiNHSi(CH₃)₃) was used in the laser-plasma process. The advantages of this compound are its availability and the fact that all chemical bonds necessary for the formation of silicon carbonitride SiCN are already present in the molecule of this compound. The films were deposited on a stainless steel substrate. The substrate temperature was varied in the interval of 350–850°C. Argon supplied with the velocity of 100–300 m/s was used as the gas-carrier. A part of the argon flow passed through the source with liquid HMDS being at $T = 273, 293$ and 313 K ($P_{\text{HMDS}} = 0.10, 0.72,$ and 3.9 mm Hg, respectively) and then mixed with the main argon flow in the plasma chemical reactor. The gas mixture was of argon and 0.005–0.2 wt % HMDS. The deposition time was 1–3 min. The deposition rate varied from 100 to 1000 nm/min as a function of the parameters of the process.

A complex of modern analytical methods: an IFS-85 IR-Fourier spectrometer (Bruker), Triplemate Raman spectrometer (Spex, United States), a JSM 6700F scanning electron microscope with an EDS EX-23000 BU setup, an atomic-force microscope Solver-Pro NT MDT, and an X-ray diffractometer with the synchrotron radiation (Siberian Synchrotron and Terahertz Radiation Center) were used for studying the properties of the synthesized coatings. The thickness of the coatings was determined by measuring the reflection spectra of the coatings and calculating according to the known formulas, with allowance for the refractive index determined from the ellipsometric data.

RESULTS AND DISCUSSION

The composition, structure, and properties of the silicon carbonitride coatings and their dependence on the parameters of the synthesis were studied in detail.

The characteristic IR spectra of the coatings characterizing their chemical structure are given in Fig. 1.

It follows from Fig. 1 that the composition of the coatings depends on the distance between the substrate and the focus of the laser beam: in the sample located at a distance of 13 mm from the beam focus (spectrum 1), in addition to the absorption bands corresponding to the vibrations of the Si–C (750 cm⁻¹) and Si–N (960 cm⁻¹) bonds, one observes the peaks in

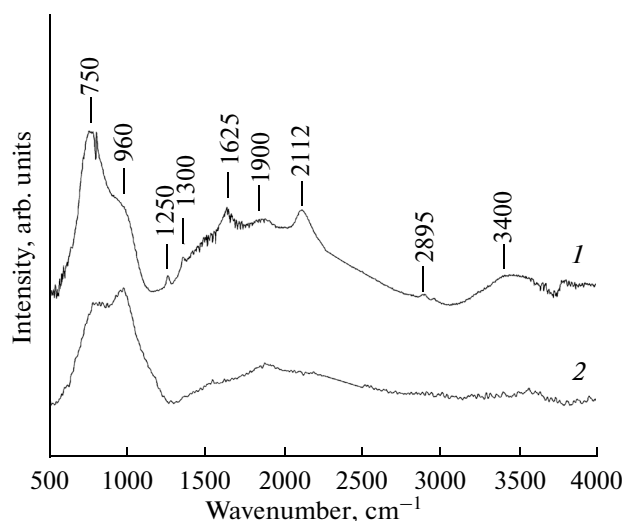


Fig. 1. Characteristic IR spectra of the SiCN coatings prepared in the chamber at the following distances between the laser beam focus and the substrate: 1—13 mm, 2—9 mm.

the region of 1600–3400 cm⁻¹ referring to the vibration modes of the carbon-containing HMDS fragments: C–H, C–C (1400–1600) cm⁻¹; Csp^2 –H, Csp^3 –H (2890–3000) cm⁻¹. The band at 2100 cm⁻¹ corresponds to the vibrations of Si–H bonds [7]. The coating on the sample located at the distance of 9 mm from the beam focus has no carbon-containing fragments (at the level of the IR spectroscopy sensitivity). The ratio of the Si–C/Si–N bonds in this sample is 0.4, which is smaller by a factor of 4.5 than that in the sample located at a distance of 13 mm from the beam focus.

Figure 2 shows the comparison of the IR spectra of films prepared in the chamber (1) and non-chamber (2) variants of processes; it follows from the figure that the non-chamber variant of the process makes it possible to prepare coatings not containing the Si–O bonds (the shoulder at $\omega = 1070$ cm⁻¹ is absent).

The ratio of the number of fragments Si–C/Si–N depends on the substrate temperature (at the fixed values of the flow rates of gases and the distance between the substrate and the plasma center) and increases with the increase in the substrate temperature (Fig. 3).

The films prepared at the distance between the substrate and the plasma focus of 9 mm and less may contain carbon, which is found by the Raman spectroscopy method (Fig. 4).

A feature of Raman spectra shown in Fig. 4 is the presence of D (~1370–1390) cm⁻¹ and G (1580–1600) cm⁻¹ peaks characteristic for graphite-like structures. The D mode is associated with the presence of six-membered rings and becomes active only in the presence of the disordered structure. The vibrational G mode of ordered graphite corresponds to the lattice

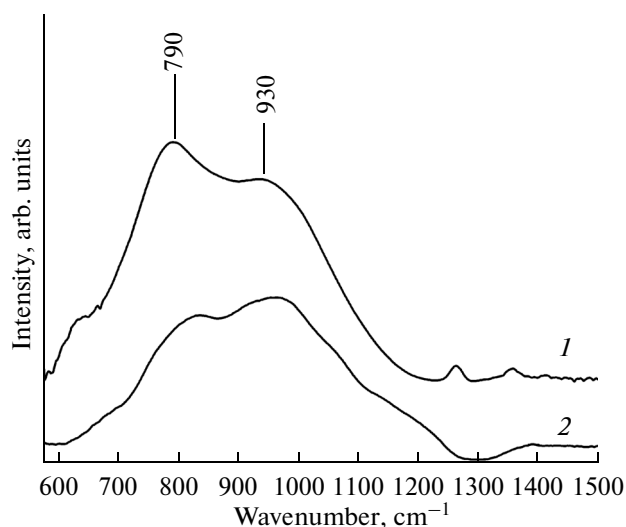


Fig. 2. IR spectra of SiCN films on stainless steel prepared in the chamber (1) and non-chamber (2) variants of the laser-plasma deposition. $T_{\text{subst}} = 700^{\circ}\text{C}$.

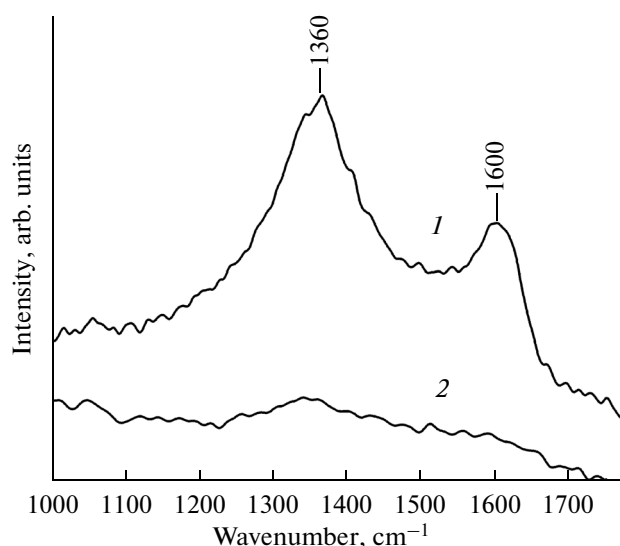


Fig. 4. Raman spectra of SiCN films on stainless steel prepared from the gas mixture of HMDS with argon (1) and argon with nitrogen (2). $T_{\text{subst}} = 700^{\circ}\text{C}$.

vibrations in the planes of graphene layers with the sp^2 -hybrid valence bonds [8]. Thus, the presence of the *D* and *G* peaks in the Raman spectra of the studied samples indicates that the clusters with the graphite-like structure are formed in it [9–11]. To estimate the sizes of clusters according to [8], it is possible to use the ratio $I(D)/I(G) = C'(\lambda)/L^2$, where the value $C' \approx 0.0055 \text{ \AA}$ (at $\lambda = 514 \text{ nm}$), and L is the size of the clusters. The size of the carbon clusters calculated according to this formula is $\sim 13 \text{ \AA}$. Using a large array of samples with the known content of hydrogen and carbon having the sp^3 -configuration, the authors [8] cali-

brated the Raman spectra and proposed an empirical equation making it possible to estimate the concentration of hydrogen and the content of sp^3 -configurations in clusters as a function of the ratio $I(D)/I(G)$. According to our estimate, the concentration of the $sp^3\text{C}-\text{C}sp^3$ bonds in carbon clusters is up to $\sim 30\%$. It follows from spectrum 2 in Fig. 4 that in the films prepared in plasma with the addition of the nitrogen flow the carbon clusters are absent (at the level of the Raman spectroscopy sensitivity).

The structure and morphology of the surface of coatings were determined using the X-ray diffraction and atomic-force microscopy methods. The X-ray diffraction data of the prepared films show that they are X-ray amorphous.

Figure 5 shows the microphoto of the surface of the films taken using the atomic-force microscope. The hill-like surface is characteristic for X-ray amorphous coatings. The average roughness size of coatings is $\sim 30 \text{ nm}$, and the average grain size is $\sim 100 \text{ nm}$.

Figure 6 shows microphotos of the cross sections of the samples with silicon carbonitride coatings on steel (a) and cubic BN (b) prepared using the FIB/SEM technique (FEI, HELIOS NanoLab 650). The character of the relief of coatings (Fig. 6) indicates that the coatings are uniform throughout thickness, and decorate well the roughness of the coated surface of materials with different structures.

To determine the hardness of the thin coating, we used a scanning nanohardness meter (NanoSkan produced by TISNUM, Troitsk, Russia). To determine the true hardness of the coatings (without the effect of the softer substrate), the nanoindentation results were processed with allowance for the hardness of the sub-

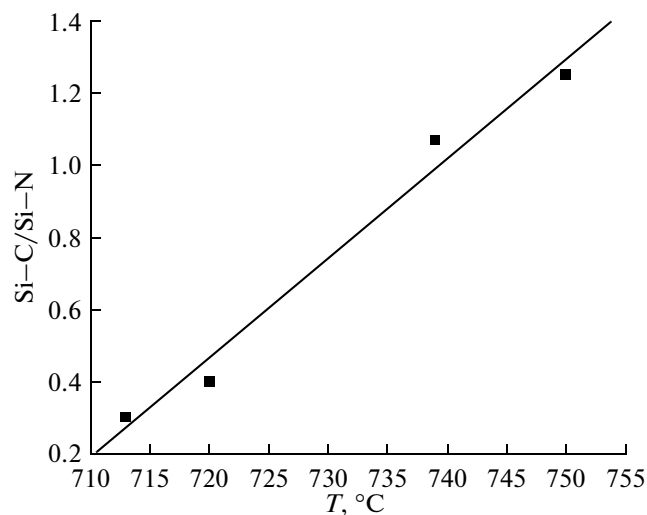


Fig. 3. Dependence of the ratio of Si-C/Si-N bonds in SiCN films on the substrate temperature.

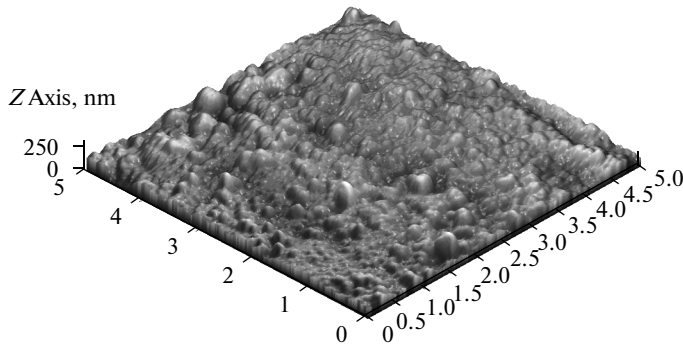


Fig. 5. AFM image of surface of SiCN films ($d = 0.6 \mu\text{m}$) on stainless steel. Non-chamber variant of the process.

strate according to the method proposed in [12]. The results of studying the microhardness of the sample, for which the ratio $\text{Si-C/Si-N} = 1$, are given in Fig. 7.

It follows from Fig. 8 that microhardness is determined by the ratio of the Si-C and Si-N fragments in the coating.

CONCLUSIONS

A new method of the plasma chemical deposition of the nanocomposite silicon carbonitride layers from the mixture of hexamethyldisilazane $\text{Si}_2\text{NH}(\text{CH}_3)_6$ and argon vapors under activation by the powerful optical pulsating discharge in the high-speed gas flow was developed.

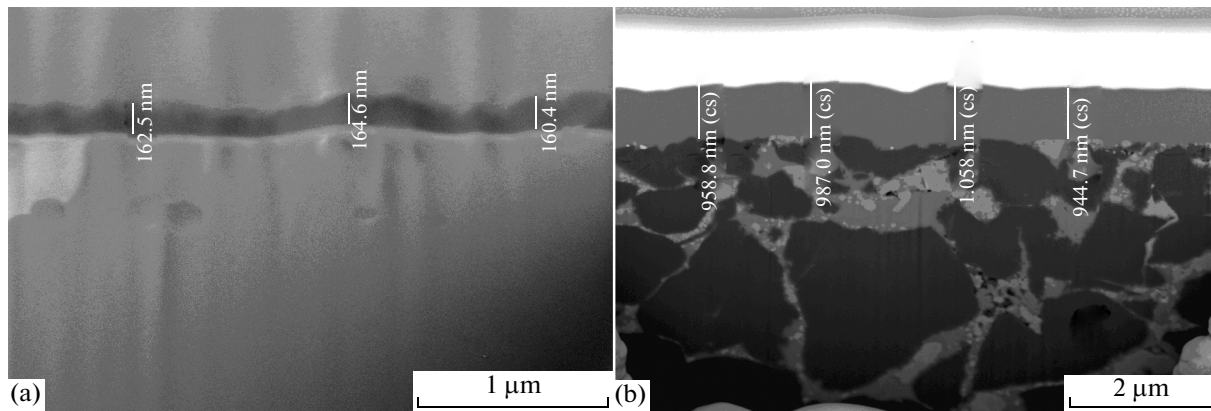


Fig. 6. Microphoto of the cross-section of the sample with the SiCN coating on: (a) steel and (b) pressed cubic BN (measurements taken on HELIOS NanoLab 650).

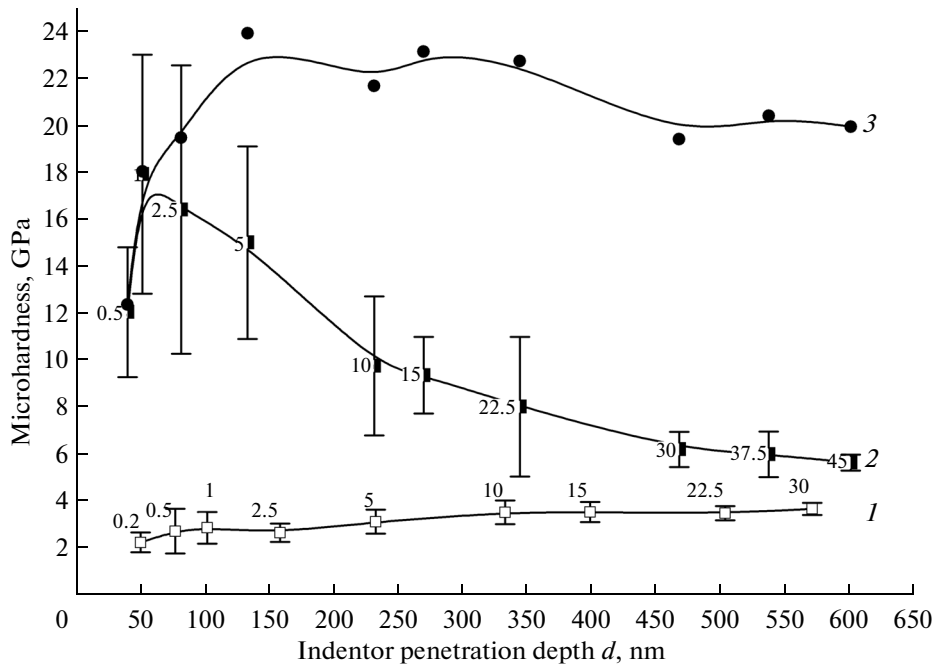


Fig. 7. Dependence of the microhardness of SiCN on the indenter penetration depth: 1—stainless steel, 2—stainless steel with the SiCN coating ($d = 450 \text{ nm}$), 3—calculation results of hardness with allowance for the thickness of coatings according to the Jonson and Hogmark model [12].

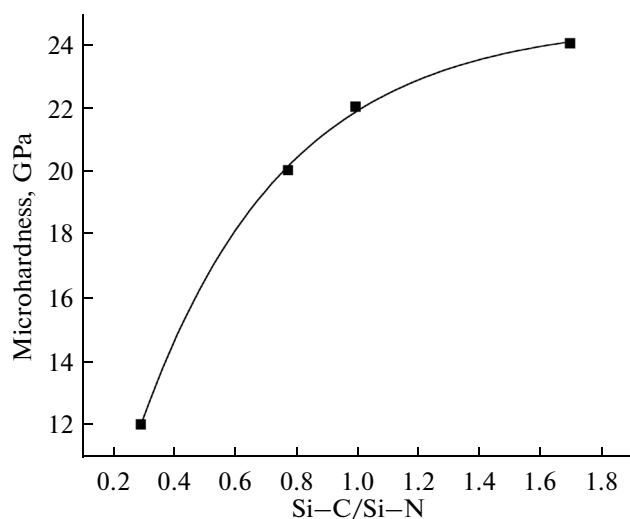


Fig. 8. Dependence of the microhardness of SiCN coatings on the ratio of Si-C/Si-N bonds found from the IR data.

The structure of the prepared silicon carbonitride films is X-ray amorphous.

The coatings are uniform throughout thickness, and decorate well the roughness of the coated surface of materials with different structures.

It was shown that the chemical composition of the coatings is determined by the substrate temperature, the distance from the beam focus to the substrate, and the composition of the gas medium for fixed values of the other parameters of the process.

The microhardness of the coatings is determined by the ratio of the Si-C/Si-N fragments and increases to 24 GPa with the increase in the content of the Si-C groups.

REFERENCES

- Smirnova, T.P., Badalyan, A.M., Borisov, V.O., Yakovkina, L.V., Kaichev, V.V., Shmakov, A.N., Nartova, A.V., Rakhlin, V.I., and Fomina, A.N., Plasma-enhanced chemical vapor deposition of silicon carbonitride films from volatile silyl derivatives of 1,1-dimethylhydrazine, *High Energy Chem.*, 2003, vol. 37, no. 5, pp. 303–309.
- Fainer, N.I., Kosinova, M.L., Rumyantsev, Yu.M., Maksimovskii, E.A., Kuznetsov, F.A., Kesler, V.G., Kirienko, V.V., Han Bao-Shan, and Lu Cheng, Synthesis and physicochemical properties of nanocrystalline silicon carbonitride films deposited by microwave plasma from organoelement compounds, *Glass Phys. Chem.*, 2005, vol. 31, no. 4, pp. 427–432.
- Grachev, G.N., Ponomarenko, A.G., Smirnov, A.L., Tischenko, V.N., and Tret'jacov, P.K., Producing of powerful optical pulsating discharge (POPD) by CO₂ pulse periodic laser radiation in supersonic gas flow, *Laser Phys.*, 1996, vol. 6, no. 2, pp. 235–240.
- Bagaev, S.N., Grachev, G.N., Demin, V.N., Smirnov, A.L., Smirnov, P.Yu., and Smirnova, T.P., Laser-plasma method for the synthesis of superhard micro- and nanostructured coatings and devices, RF Patent 2416673, *Byull. Izobret.*, 2011, no. 11, p. 2.
- Bagayev, S.N., Grachev, G.N., Ponomarenko, A.G., Smirnov, A.L., Demin, V.N., Okotrub, A.V., Baklanov, A.M., and Onischuk, A.A., A new method of laser-plasma synthesis of nanomaterials: First results and prospects, *Proc. SPIE—Int. Soc. Opt. Eng.*, 2007, pp. 6732–6736.
- Grachev, G.N., Smirnov, A.L., Zimin, M.I., Myakushina, A.A., Demin, V.N., Okotrub, A.V., Baklanov, A.M., and Onishchuk, A.A., Laser plasma-chemical facility for the synthesis of nanomaterials in high-rate gas flows, in *Sbornik trudov tret'ei Vserossiiskoi konferentsii "Khimiya poverkhnosti i nanotekhnologiya," S.-Peterbur—Khilovo, 2006* (Proceedings of the Third All-Russian Conference "Surface Chemistry and Nanotechnology," St. Petersburg, Khilovo, Russia, September 24, 2006), St. Petersburg, 2006, p. 35.
- Blaszczyk-Lezak, I., Wrobel, A.M., Aoki, T., Nakanishi, Y., Kucinska, I., and Tracz, A., Remote nitrogen microwave plasma chemical vapor deposition from a tetramethyldisilazane precursor: Growth mechanism, structure, and surface morphology of silicon carbonitride films, *Thin Solid Films*, 2006, vol. 497, nos. 1–2, pp. 24–34.
- Ferrari, A.C. and Robertson, J., Interpretation of Raman spectra of disordered and amorphous carbon, *Phys. Rev. B: Condens. Matter*, 2000, vol. 61, no. 20, pp. 14095–14107.
- Casiraghi, C., Piazza, F., Ferrari, A.C., Grambole, D., and Robertson, J., Bonding in hydrogenated diamond-like carbon by Raman spectroscopy, *Diamond Relat. Mater.*, 2005, vol. 14, p. 1098.
- Ferrari, A.C., Determination of bonding in diamond-like carbon by Raman spectroscopy, *Diamond Relat. Mater.*, 2002, vol. 11, p. 1053.
- Ferrari, A.C. and Robertson, J., Resonant Raman spectroscopy of disordered, amorphous, and diamond-like carbon, *Phys. Rev. B: Condens. Matter*, 2001, vol. 64, p. 75414.
- Jönsson, B. and Hogmark, S., Hardness measurements of thin films, *Thin Solid Films*, 1984, vol. 114, pp. 257–269.

Translated by L. Mosina