

03,08

Influence of field frequency during plasma-chemical deposition on the structure and properties of silicon–carbon coatings

© A.I. Popov¹, A.D. Barinov¹, P.A. Edelbecova², V.M. Yemets¹,
I.N. Miroshnicova¹, T.S. Chukanova¹

¹ National Research University „Moscow Power Engineering Institute“,
Moscow, Russia

² Institute of Nanotechnology of Microelectronics, Russian Academy of Sciences,
Moscow, Russia

E-mail: popovai2009@gmail.com

Received October 31, 2023

Revised November 16, 2023

Accepted November 27, 2023

The results of the electrophysical, mechanical properties, surface morphology and structure studies of silicon–carbon coatings prepared by plasma-chemical deposition of an organosilicon precursor at different frequencies of the axial electric field are presented. It is shown that the reason for changes in the characteristics of coatings with variations in the field frequency is a change in the ratio of the concentrations of carbon atoms with different hybridization of electron orbitals. The dependences of all studied characteristics on the field frequency have two different sections. At frequencies from 0.1 to 1.0 MHz, significant and non-monotonic changes in the properties of coatings are observed with variations in the frequency of the electric field. At frequencies above 1.0 MHz, the properties of the resulting coatings are practically independent of frequency. Based on an analysis of physical properties and Raman spectroscopy studies, a model of coating structure evolution with a change in the field frequency during their deposition is proposed.

Keywords: silicon–carbon coatings, chemical composition, phase composition, electrical conductivity, elastic modulus, Raman spectra, carbon atoms, electron orbitals hybridization.

DOI: 10.21883/0000000000

1. Introduction

Creation of silicon–carbon coatings consisting of carbon, silicon, oxygen and hydrogen atoms was a result of search for the ways to improve the performance of amorphous carbon diamond-like films. Introduction of a considerable amount (up to 25–30 at.%) of silicon and oxygen atoms into amorphous carbon ensured a decrease in hardness of the structural network and, thus, made it possible to reduce mechanical stresses considerably and to improve the amorphous state stability of coatings while maintaining their performance at a sufficiently high level. This, in turn, resulted in solution of the adhesion problem and improvement of thermal stability of materials [1] to ensure considerable expansion of the range of applications for the coatings in question. However, the expansion of the range of applications requires enhancement of material properties control.

Properties of amorphous silicon–carbon films are generally controlled by means of chemical modification of their properties by transition metals [2,3]. However, the absence of long-range order in the atom arrangement of these materials makes it possible to use structural modification for control of properties, i.e. targeted in-process modification of the coating structure with permanent chemical composition. Since high-frequency plasma-chemical decomposition of organosilicon precursors is the most commonly used method of production of silicon–carbon coatings, then

substrate holder bias potential (defining the energy of particles deposited on the substrate) [4], film bombardment by inert gas ions during film growth [5] or laser emission exposure [6] are used as structure modifying factors. All investigations mentioned above were conducted on films produced by plasma-chemical deposition at a fixed axial electric field frequency (1.76 MHz). At the same time, the field frequency defines to a great extent plasma parameters and effects the substrate holder self-bias during deposition. As a result, deposition in fields with various frequency shall form various coating structures and, therefore, their physical properties will be changed. This may be proved by a set of studies where films of various materials ($a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$, SiO_x , SiN_x) were deposited at low frequencies (up to tens of kHz) [7–9]. In [5], silicon–carbon coatings were deposited at field frequency 100 kHz. The papers listed above report a considerable difference in the properties of produced coating from the samples deposited at high field frequency. At the same time, it should be noted that, in all papers mentioned above, coatings were deposited only on individual fixed frequencies, and no systematic investigations of the electric field frequency effect on the structure and properties of resulting coatings are described in literature. This study is an attempt to fill this gap by investigating the structure and properties of silicon–carbon coatings made by plasma-chemical deposition at various electric field frequencies.

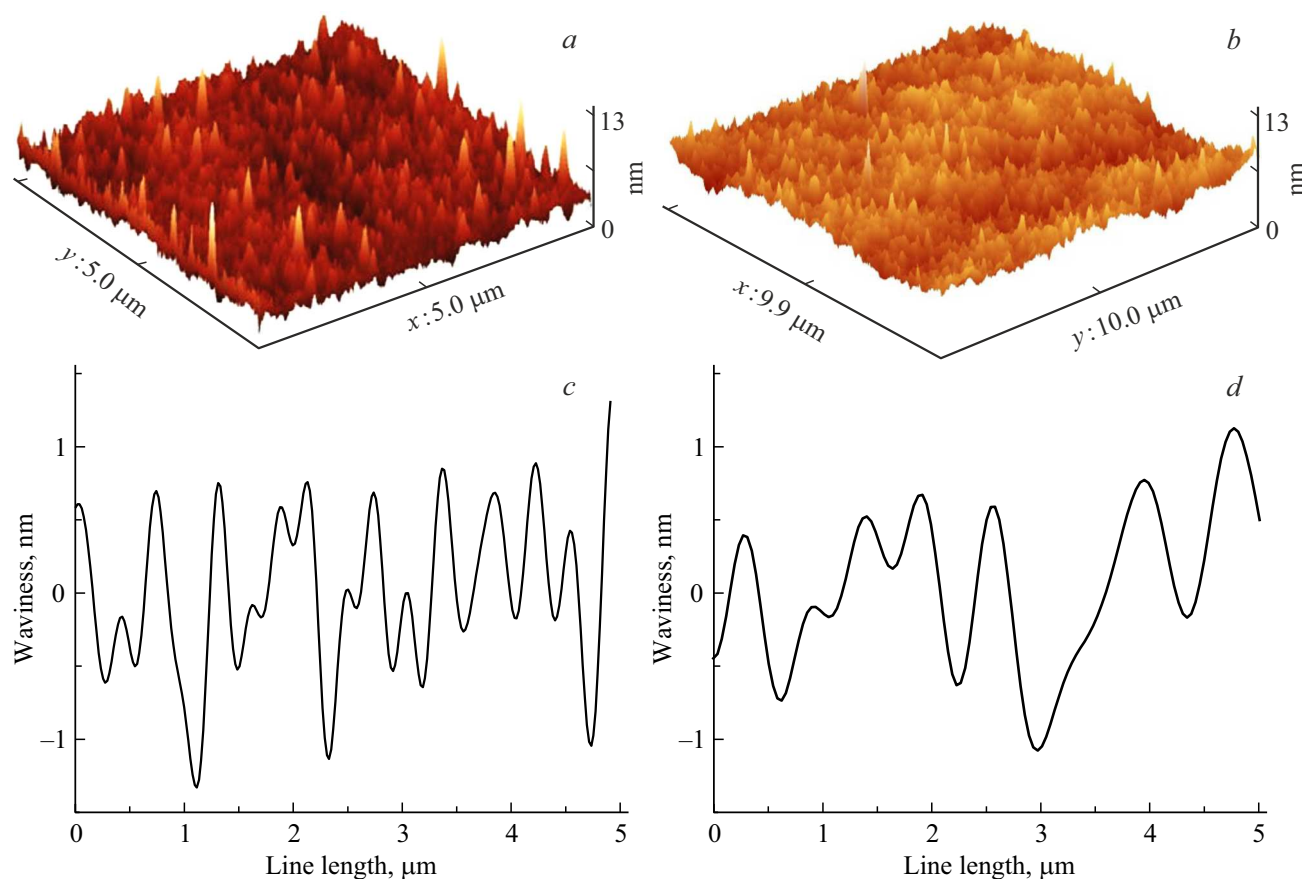


Figure 1. AFM images (*a, b*) and surface waviness (*c, d*) of silicon–carbon coatings deposited at a field frequency of 0.1 MHz (*a, c*) and 1.5 MHz (*b, d*).

2. Coating processes and study methods

Silicon–carbon coatings were produced by plasma-chemical decomposition of organosilicon precursor of polyphenyl methylsiloxane. To perform the process at various electric field frequencies, modernization of the system described in [5] was carried out to allow the process to be conducted at a fixed frequency of 1.76 MHz. As a result of the modernization, the axial electric field frequency during plasma-chemical decomposition of the precursor could be set in the range from 0.1 to 2.0 MHz. Permanent voltage on the substrate holder was maintained in all experiments and was equal to -200 V, and the temperature was within 120 – 130°C . Single crystal silicon were used as substrates. Electrophysical measurements were carried out on sandwich construction samples with metal electrodes. Thickness of silicon–carbon coatings was from 0.5 to $2.0\ \mu\text{m}$.

Chemical and phase composition and coating surface morphology were studied by scanning electron microscopy (Vega II SBU with Inca x-Act energy-dispersive detector), transmission electron microscopy (Tecnai G2 20) and atomic-force microscopy (NteGRA Prima) methods. Conductivity was measured on ASEC-03E automated elec-

trophysical study system. Mechanical properties were measured using NHT2-TTX nanohardness meter with Berkovich diamond pyramid as an indenter. Maximum load was equal to 5 mN. Coating thickness was measured using M 130 profilometer. Raman scattering spectra were carried out using inVia Qontor (Renishaw) Raman confocal microscope with emission wavelength 532 nm.

3. Experimental study of coatings deposited at different electric field frequencies

Chemical analysis of silicon–carbon coatings deposited at different axial electric field frequencies has shown that in the test frequency range from 0.1 to 2.0 MHz, content of the main elements remains permanent within the accuracy of the experiment and is as follows: carbon 73.5 ± 1.5 at.%, silicon 13.5 ± 1.0 at.%, oxygen 13.0 ± 1.0 at.%. Concentration ratio of carbon and silicon atoms is equal to 5.5 ± 0.2 . High-resolution transmission electron microscopy shows that there are no crystalline inclusions in all test samples. Amorphous state of the material is also confirmed by the diffraction analysis data.

Sample surface morphology was studied by the atomic-force microscopy (AFM) method. Examples of coating surface images for coatings deposited at different electric field frequencies are shown in Figure 1, *a* and *b*. Waviness height and pitch (Figure 1, *c* and *d*) reflecting the low-frequency component of the relief were used as quantitative surface morphology characteristics [10,11].

The investigations have shown that, at low electric field frequencies (lower than 0.8 MHz), the waviness height decreases (to 30%) with increasing field frequency, and at frequencies higher than the specified value, the waviness height remains almost permanent. The waviness pitch tends to increase with an increase in field frequency during coating deposition (see Figure 1, *c* and *d*).

Investigations of coating conductivity have shown that there are two segments on the dependences on electric field frequency during sample deposition (Figure 2): high-frequency segment (frequencies more than 1 MHz) and low-frequency segment (frequencies from 0.1 to 1.0 MHz). In the high-frequency segment, conductivity values almost do not depend on the field frequency in manufacturing and are equal to 10^{-10} – $10^{-11} \Omega^{-1} \cdot \text{cm}^{-1}$ at room temperature, and the conductivity activation energy is within 0.20–0.25 eV. By contrast to this, the dependence in the low-frequency segment is non-monotonic with a peak at frequencies near 0.4 MHz. Absolute conductivity variations achieve 4 orders of magnitude and the conductivity activation energy is equal to 0.40–0.50 eV.

Dependences of mechanical properties of silicon–carbon coatings on the electric field frequency in deposition have behavior similar to the addressed conductivity dependences.

Figure 3 shows the dependence of the modulus of elasticity of coatings on the electric field frequency during deposition. As shown in the figure, an increase in frequency from 0.1 to 0.4 MHz results in growth of the modulus of elasticity up to 80 GPa. With further increase in frequency

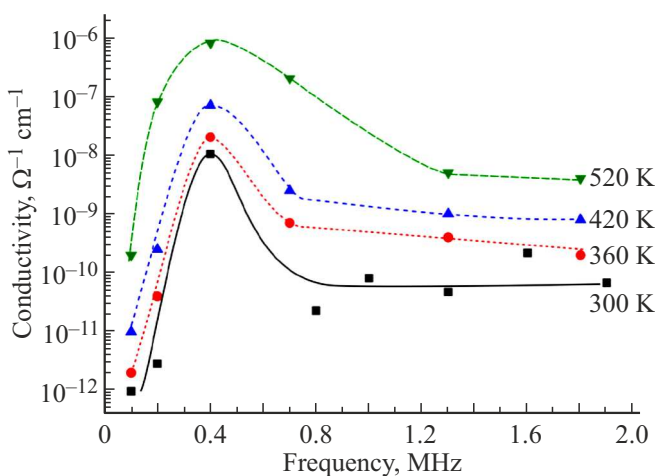


Figure 2. Dependences of the silicon–carbon coating conductivity on the field frequency during coating deposition (digits at the curves correspond to the measurement temperature).

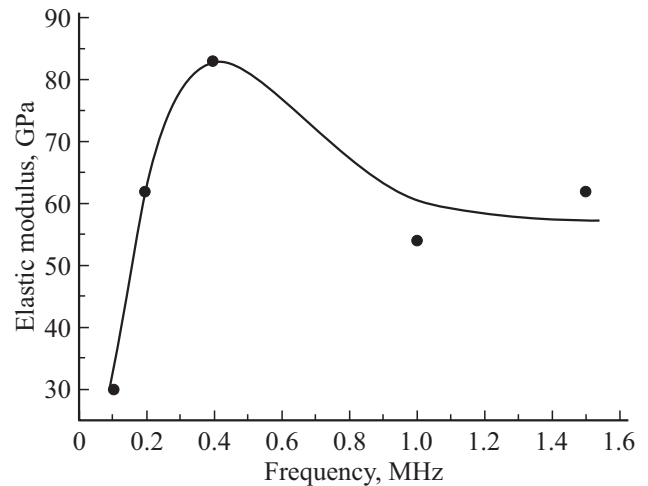


Figure 3. Dependence of the modulus of elasticity of silicon–carbon coatings on the field frequency during coating deposition.

up to 1 MHz, this parameter decreases, then its stabilization is observed.

4. Analysis and interpretation of findings

The constancy of chemical and phase composition of the coatings synthesized at different electric field frequencies as described in the previous section demonstrates that the observed variations of physical properties are caused by structural changes in the material. Considering high carbon content (72–75 at.%) in this case, it can be assumed that the ratio of fractions of carbon atoms with various hybridizations of electron orbitals plays the main role in formation of coating properties. To get the information on this ratio, Raman-scattering spectroscopy was conducted on the test samples. Ratio of concentrations of carbon atoms with sp^3 - and sp^2 -hybridization of electron orbitals and the Raman spectrum evolution with field frequency variation during coating deposition were assessed by the parameters of *G*- and *D*-peaks of carbon atoms using the model offered in [12]. Though the model was developed for carbon films, it allows qualitative assessment of the concentration of carbon atoms with sp^3 - and sp^2 -hybridization of electron orbitals and in case of silicon-carbon coatings (see, for example, [13]).

The Raman spectra of silicon–carbon coatings had an irregularly shaped peak within the frequency range of 1300 – 1600 cm^{-1} . Its decomposition into Gaussian-shaped *D*-peak (at frequencies near 1350 cm^{-1}) and *G*-peak (in the frequency region 1500 – 1580 cm^{-1}) for coatings deposited at different field frequencies is shown in Figure 4. The figure shows that the field frequency at coating deposition influences both the intensity and carbon atom peak positions in the Raman spectra.

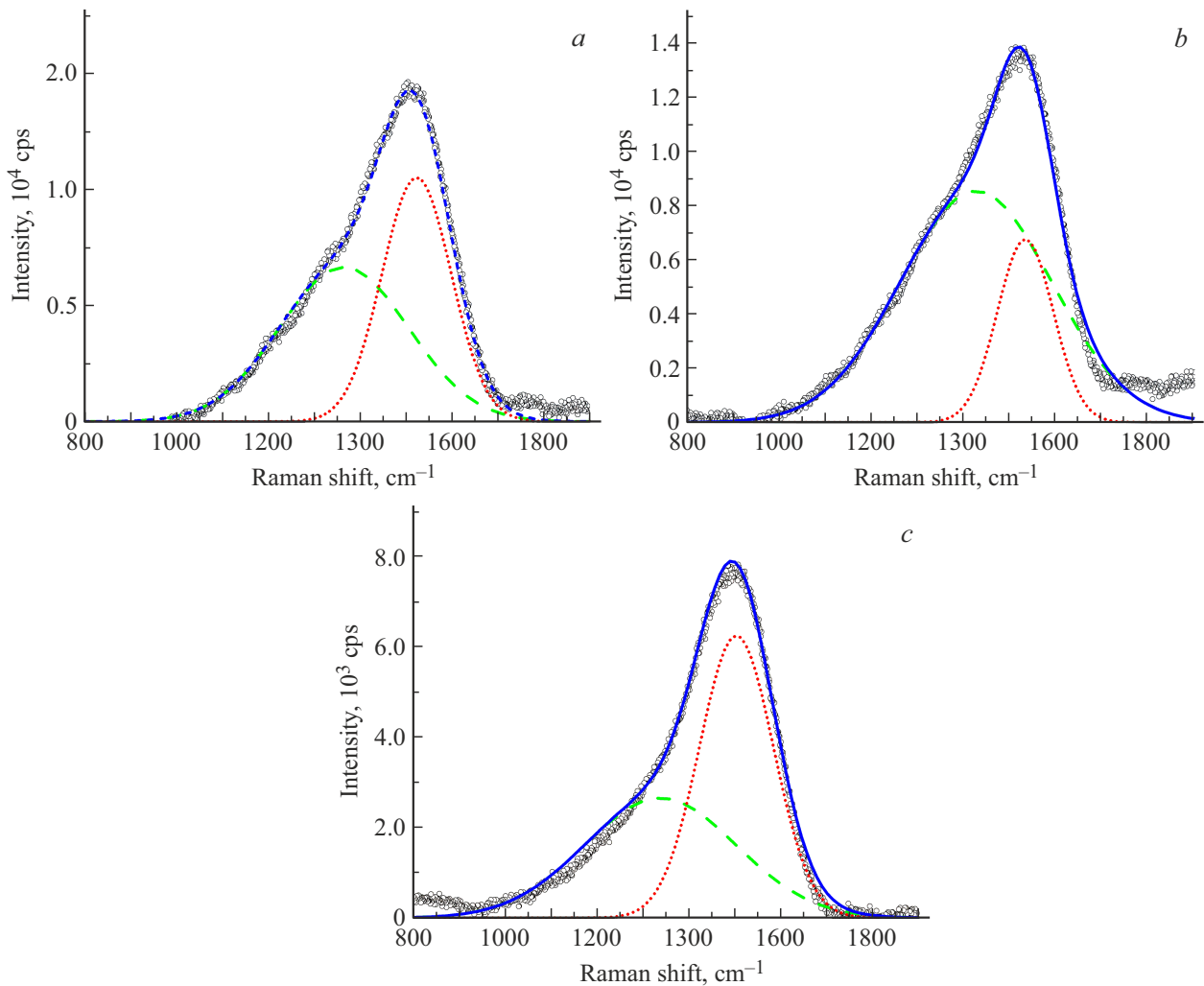


Figure 4. decomposition of the Raman spectra peak (solid line) for coatings deposited at 0.2 MHz (a), 0.4 MHz (b), 1.2 MHz (c) into *D*- (dashed line) and *G*-peaks (dotted line).

Figure 5 shows the variation of *G*-peak position and of the ratio of peak intensities I_D/I_G depending on the field frequency during coating deposition.

As shown in the figure, for coatings deposited at high electric field frequencies (more than 1 MHz), *G*-peak intensity is 2.5 times higher than *D*-peak intensity and is weakly dependent on frequency. In this case, *G*-peak is within the frequency range of 1500–1510 cm^{-1} . In accordance with [12], the ratios of peak intensities I_D/I_G that are considerably lower than 1 with *G*-peak position in the left-hand side of the frequency range typical for the peak are indicative of considerable concentration of carbon atoms with sp^3 -hybridization of electron orbitals. Decrease in the electric field frequency during coating deposition results in sharp growth of *D*-peak intensity and its intensity at 0.4 MHz considerably exceeds *G*-peak intensity. In addition, *G*-peak moves into the high frequency region up to $\sim 1535 \text{ cm}^{-1}$. The growth of peak intensity ratio I_D/I_G with the specified shift of *G*-peak is caused by a decrease in the concentration of carbon atoms with sp^3 -hybridization

of electron orbitals due to their transition into the state with sp^2 -hybridization. With further decrease in the field frequency to 0.2 MHz, the intensity ratio I_D/I_G again becomes lower than 1 and *G*-peak moves in the opposite direction to 1523 cm^{-1} . Such spectrum evolution is indicative of a decrease in concentration of sp^2 -hybridized carbon atoms in the produced coating.

The Raman scattering spectra analysis explains the dependence of the silicon–carbon coating conductivity on the electric field frequency during deposition as shown in Figure 3. Low conductivities (10^{-11} – $10^{-10} \Omega^{-1} \cdot \text{cm}^{-1}$) at deposition frequencies more than 1 MHz are caused by the prevalence of carbon atoms with sp^3 -hybridization of electron orbitals that form a diamond-like structure of coatings (increased number of σ -bonds). Decrease in field frequency during deposition to 0.4 MHz results in decrease in the concentration of sp^3 -hybridized atoms and growth of concentration of sp^2 -hybridized carbon atoms that ensure formation of a graphite-like structure with high conductivity (increase in the number of π -bonds). Sharp decrease in

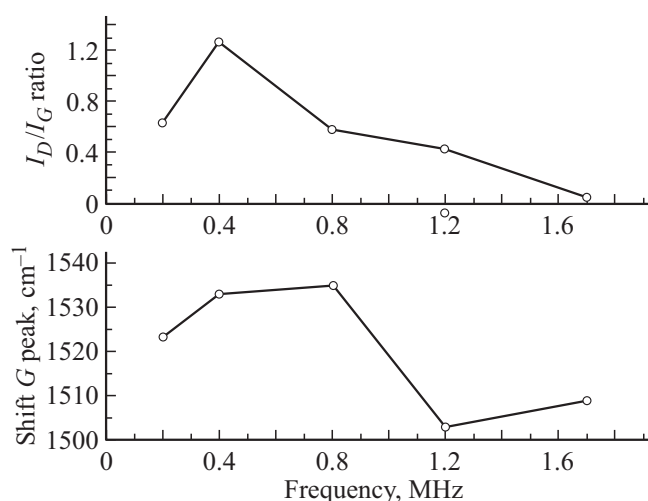


Figure 5. I_D/I_G (a) peak intensity ratio and G-peak position (b) vs. field frequency during coating deposition.

coating conductivity observed with further decrease in field frequency to 0.1 MHz occurs due to a decrease in graphite-like fraction in the material structure. It should be noted that the Raman spectra analysis does not allow the identification of the prevailing carbon atom hybridization (sp^3 or sp^1) in coatings produced in this electric field frequency range.

Thus, the Raman-scattering spectroscopy data shows that the effect of the electric field frequency during deposition of silicon-carbon coatings on their conductivity is caused by variation of concentrations of carbon atoms with different hybridization of electron orbitals. However, difficulties emerge in explaining the dependence of mechanical properties of coatings on the field frequency during deposition. Since graphite has the minimum values of mechanical properties among allotropic modifications of carbon, then the growth of the concentration of carbon atoms with sp^2 -hybridization shall cause decrease in absolute values of these properties. At the same time, Figure 4 shows that the modulus of elasticity is maximum for the coatings deposited at a field frequency of 0.4 MHz when the concentration of carbon atoms with sp^2 -hybridization of electron orbitals is maximum. The same type of dependences is also observed for other mechanical properties (microhardness, plasticity index, plastic resistance). Therefore, deposition at frequencies near 0.4 MHz results in production of coatings having both high conductivity and high mechanical properties. Taking into account the prevalence of sp^2 -hybridized carbon atoms in these conditions, this fact may be explained by formation, at the specified deposition frequency, of coatings with a glass-like carbon structure consisting of highly distorted and interlaced layers with sp^2 -hybridization [13]. The presence of interlacing ensures high mechanical properties and the layered structure defines high conductivity of the material.

It is interesting that abrupt decrease in both conductivity (by 3–4 orders of magnitude) and of modulus of elasticity (by a factor of 2.5–3) of coatings occurs with decreasing field frequency to lower than 0.4 MHz. As described above, the Raman-scattering spectroscopy data is only indicative of a decrease in concentration of sp^2 -hybridized carbon atoms, while the question on what kind of hybridization of atomic electron orbitals becomes prevailing in the coating deposition conditions still remains open. This question needs further investigation. However, the observed combination of low values of both conductivity and mechanical properties may be indicative of formation of polymer carbon modification molecules [15] with sp^1 -hybridization of atomic electron orbitals.

5. Conclusion

The investigations have shown that the axial electric field frequency variation in plasma-chemical decomposition of polyphenyl methylsiloxane considerably effects the structure and properties of produced silicon-carbon coatings with permanent chemical and phase compositions of the coatings. Moreover, there are two clearly pronounced segments on the dependences of electrophysical, mechanical properties and surface morphology of coatings on field frequency: high-frequency segment (frequencies higher than 1 MHz) on which almost no properties variations are observed, and low-frequency segment (frequencies lower than 1 MHz) featuring considerable non-monotonic variations of properties with field frequency variation.

Simultaneous analysis of the physical properties data and Raman spectra of coatings produced in different conditions suggested the following pattern of material structure evolution with electric field frequency variation. Plasma-chemical deposition at high electric field frequencies provides coatings with a diamond-like structure where carbon atoms with sp^3 -hybridization of electron orbitals prevail. The resulting material has low conductivity (10^{-10} – 10^{-11} $\Omega^{-1} \cdot \text{cm}^{-1}$) and quite high mechanical properties (modulus of elasticity achieves 60 GPa).

A decrease in electric field frequency during deposition below 1 MHz results in growth of sp^2 -hybridization of carbon atoms that achieves its peak at frequencies near 0.4 MHz. Therefore, the conductivity increases by 2–3 orders of magnitude. In this case, increase in the modulus of elasticity by $\sim 30\%$ is also observed. Such combination of electrophysical and mechanical properties with prevailing sp^2 -hybridization of carbon atoms results in conclusion that a structural network of glass-like carbon is generated in these conditions.

With further decrease in the field frequency (below 0.4 MHz), the concentration of sp^2 -hybridized carbon atoms decreases and abrupt variation of both conductivity and mechanical properties of a material occurs. This is probably due to the occurrence of sp^1 -hybridization with some carbon atoms.

Funding

The study was supported by the Russian Science Foundation, grant No. 22-29-00864 (<https://rscf.ru/project/22-29-00864/>).

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] A. Popov. *Disordered Semiconductors: Physics and Applications*. 2d ed. Pan Stanford Publ. (2018). 327 p.
- [2] A.D. Barinov, A.I. Popov, M.Yu. Presnyakov. *Neorgan. materialy* **53**, 706 (2017). (in Russian).
- [3] A.I. Popov, V.P. Afanasiev, A.D. Barinov, Yu.N. Bodisko, A.S. Gryazev, I.N. Miroshnikova, M.Yu. Presnyakov, M.L. Shupegin. *Poverkhnost. Rentgenovskie, Sinkhrotronnye Neitr. Issled.*, **9**, 49, 2019 (2023). (in Russian).
- [4] A.S. Grenaderov, A.A. Soloviev, K.V. Oskomov, M.O. Zhul'kov. *ZhTF* **91**, 1286 (2021). (in Russian).
- [5] A.I. Popov, A.D. Barinov, V.M. Emets, T.S. Tchukanova, M.L. Shupegin. *FTT* **62**, 1612 (2020). (in Russian).
- [6] E.V. Zavedeev, O.S. Zilova, A.D. Barinov. *Diamond Rel. Mater.* **74**, 45 (2017).
- [7] A.A. Sherchenkov. *Materialy elektronnoy tekhniki*, **48** (2003), 168 (2019). (in Russian).
- [8] T. Yamaguchi, N. Sakamoto, H. Tagashira. *J. Appl. Phys.* **83**, 554 (1998).
- [9] M. Shimosuma, K. Kitamori, H. Ohno, H. Hasegawa, H.J. Tagashira. *Electron. Mater.* **14**, 573 (1985).
- [10] Odnomernye parametry sherokhovatosti [Electronnyi resurs] / Rukovodstvo pol'zovatelya Gwyddion. Available at: <http://gwyddion.net/documentation/user-guide-ru/roughness-iso.html>.
- [11] S.G. Lakeev, P.I. Misurkin, Yu.S. Polyakov, S.F. Timashev. *Fluktuatsionnye i degradatsionnye protsessy v poluprovodnikovykh priborakh*. Sb. nauch. tr. MEI, M. (2011), P. 5. (in Russian).
- [12] A.C. Ferrari, J. Robertson. *Phys. Rev. B* **61**, 14095 (2000).
- [13] A.S. Grenadyorov, A.A. Solovyev, V.O. Oskirko, K.V. Oskomov, V.A. Semenov, V.S. Sypchenko, A.A. Saraev. *Vacuum*. **219**, part A. 112706 (2024).
- [14] V. Uskokovic. *Carbon Trends* **5**, 100116 (2021).
- [15] T.G. Shumilova. *Almaz, grafit, karbin, fulleren i drugie modifikatsii ugleroda*. UrO RAN, Yekaterinburg (2002), 88 p. (in Russian).

Translated by E.Ilinskaya