

---

---

SURFACE  
AND THIN FILMS

---

---

## Structure of Diamond-Like Silicon–Carbon Films Alloyed by Vanadium

O. M. Zhigalina<sup>a,b,\*</sup>, D. N. Khmelenin<sup>a</sup>, S. M. Pimenov<sup>c</sup>, M. L. Shupegin<sup>d,e</sup>,  
I. G. Dyachkova<sup>a,e</sup>, and V. E. Asadchikov<sup>a</sup>

<sup>a</sup>*Shubnikov Institute of Crystallography, Federal Research Centre “Crystallography u Photonics,”  
Russian Academy of Sciences, Moscow, 119333 Russia*

<sup>b</sup>*Bauman Moscow State Technical University, Moscow, 105005 Russia*

<sup>c</sup>*Prokhorov General Physics Institute of the Russian Academy of Sciences, Moscow, 119991 Russia*

<sup>d</sup>*National Research University “Moscow Power Engineering Institute,” Moscow, 111250 Russia*

<sup>e</sup>*Research Institute of Advanced Materials and Technologies, Moscow, 115054 Russia*

\*e-mail: zhigal@crys.ras.ru

Received December 11, 2017

**Abstract**—The structure of diamond-like silicon–carbon films formed on silicon substrates by magnetron and plasmatron codeposition using a closed-field magnetron and a plasmatron activated by tungsten cathode has been studied by transmission electron microscopy. The main feature of the films alloyed by vanadium to concentrations of 12–31 at % was found to be a layered structure of the film cross section. It was established that vanadium alloying leads to the formation of vanadium carbide (VC) nanocrystals; the nanocrystal size increases from 1–2 to 10 nm. At the maximum vanadium content, VC nanocrystals have an anisotropic shape: they are extended in the direction perpendicular to the film–substrate interface.

DOI: 10.1134/S1063774518050334

### INTRODUCTION

Diamond-like  $a$ -C : H, Si : O silicon–carbon films [1, 2] belong to nanocomposite materials. One of the most important features of these films is the possibility of introducing different metals into them in high concentrations [3], which significantly broadens the ranges of controlled variation of some physical properties of these films. In this way, one can change, e.g., the electrical conductivity from  $2 \times 10^{-13}$  to  $1 \times 10^3 \Omega^{-1} \text{ cm}^{-1}$ , Young’s modulus from 60 to 400 GPa, the residual elastic stresses from 10 GPa to 100 MPa, and the friction coefficient from 0.05 to 0.35. The films of almost all compositions are characterized by chemical inertness. Currently, metal-containing  $Me$ -( $a$ -C : H, Si : O) films have been intensively investigated. The main objects of study are wearproof coatings with a low friction coefficient [4, 5]; infrared anti-reflection coatings [6]; and functional coatings for microelectronics and microelectromechanical systems (MEMS) [7], power electronics, and electric engineering devices [8]. A peculiarity of these investigations is the wide ranges of variation in the composition (up to 50 at % of metal) and technological parameters of the  $Me$ -( $a$ -C : H, Si : O) films. The concentration dependences of the properties of nanocomposite films have a percolation character [3]. The shape of a specific percolation curve describing some concentra-

tion dependence is determined by a number of parameters, including the matrix structure, nanophase structure and morphology, and the difference between the examined properties of the pure matrix and pure nanophase. This study continues the series of works devoted to the structural and morphological peculiarities of nanoparticles of diamond-like silicon–carbon films alloyed with a transition metal from Groups IV–VI of Mendeleev’s periodic table. Vanadium-alloyed films were chosen for these investigations for the first time. Vanadium was used due to its possibility of forming a carbide nanophase with maximum hardness, which is highly promising for fabricating wear-resistant tribological coatings.

### EXPERIMENTAL

The V-( $a$ -C : H, Si : O) films were formed by simultaneous vacuum codeposition of materials from two different sources. One source was a closed-field magnetron and the second was a tungsten-cathode-activated plasmatron. The vanadium precursor was a target made of pure (99.99%) vanadium and the plasmatron precursor was PFMS-2/5 L siloxane liquid (the chemical name is methylphenylsiloxane) vapor. The vacuum facility and its technological capabilities were described in detail in [9]. Deposition was per-

**Table 1.** Chemical composition of the films

Sample	Content, at %			
	C	O	Si	V
P120	60	11	17	12
P40	60	10	13	17
M40	52	10	12	26
M120	48	13	8	31

formed in an argon atmosphere; the substrates were single-crystal silicon wafers  $20 \times 20 \times 0.4$  mm in size, located on a metal holder 200 mm in diameter. The substrate holder was under a high-frequency (1.76 MHz) voltage. The plasma flow energy was controlled from the dc bias of  $200 \pm 50$  V, arising on the substrate holder during deposition. The growth rate was  $1 \mu\text{m/h}$ . These parameters ensured low (below 1 GPa) residual elastic stress, which made it possible to form films thicker than  $5 \mu\text{m}$ . The film composition is given in Table 1.

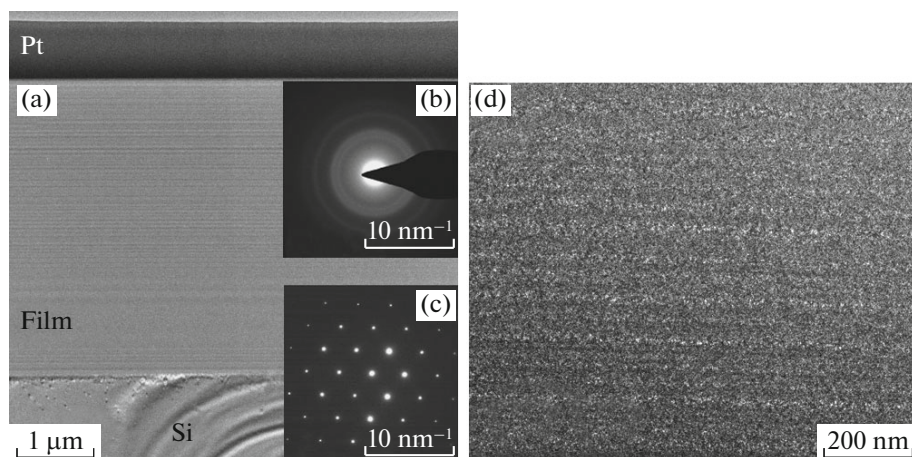
The film structure was investigated by transmission electron microscopy (TEM), high-resolution electron microscopy (HREM), scanning transmission electron microscopy (STEM), electron diffraction, and energy dispersive analysis (EDA) on a FEI Tecnai Osiris microscope with an accelerating voltage of 200 kV. Elemental analysis and chemical element distribution mapping were performed on a special SuperX EDS system with four silicon detectors. The system is designed to obtain rapidly (for several minutes) large-area maps of chemical element distribution.

Electron microscopy images were processed and analyzed using the Digital Micrograph, Esprit, TIA, and JEMS software.

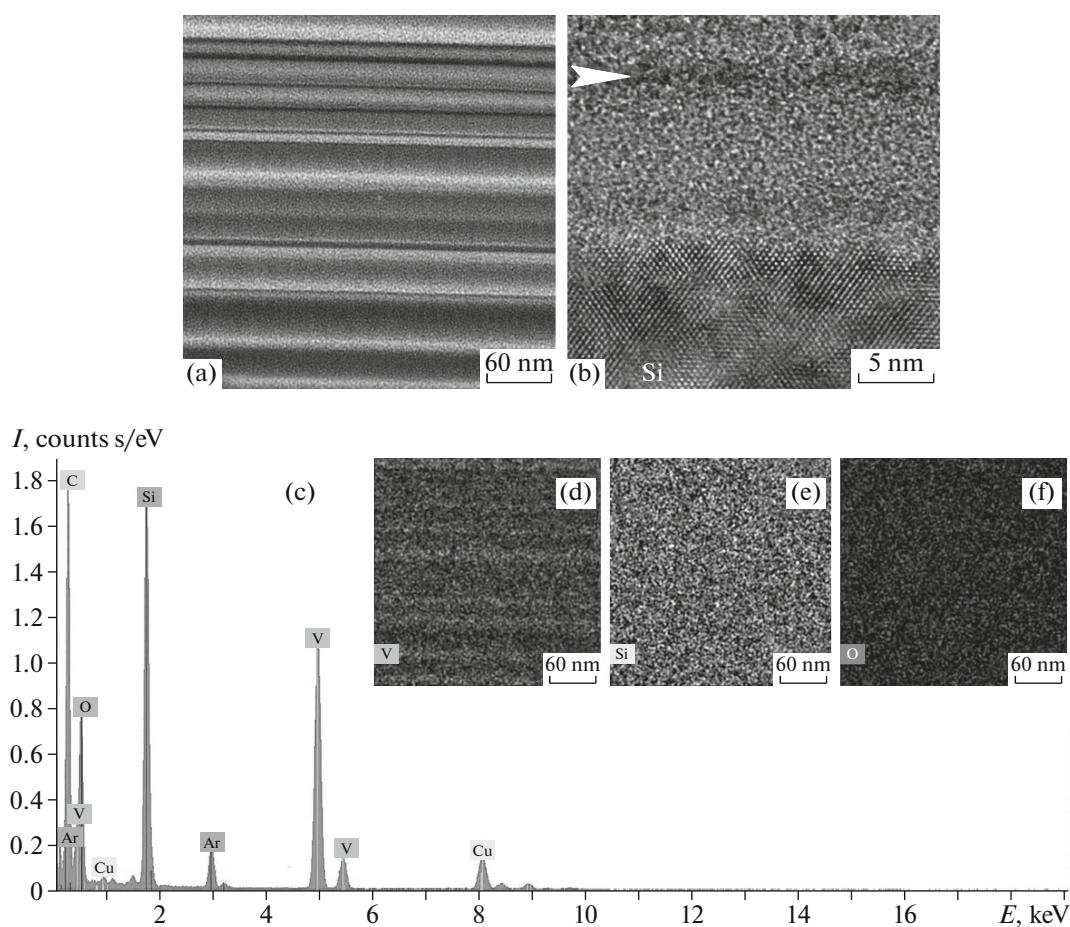
Cross-sectional TEM images of the films were obtained on thin cross sections cut perpendicular to the film surface by a focused ion beam in a FEI Scios Dual Beam scanning electron microscope column in the following way. The sample surface was protected from damage by the ion beam using a platinum coating with a thickness of about  $3 \mu\text{m}$ ; after that, a lamella with a thickness of  $1 \mu\text{m}$ , a width of  $6\text{--}12 \mu\text{m}$ , and a depth of  $6\text{--}12 \mu\text{m}$  was cut from the sample part with undamaged surface. The lamella was transferred onto a copper semiring with a built-in manipulator, and the cut specimen was welded. Further thinning occurred with a gradual decrease in current at an accelerating voltage of 30 kV, with sample tilted by  $\pm 1.5^\circ$  relative to the ion beam. The amorphous layer was removed from the lamella surface using final cleaning at an accelerating voltage of 2 kV, with sample tilted by  $\pm 5.5^\circ$  relative to the ion beam.

## RESULTS AND DISCUSSION

Figure 1a presents a general view of the cross section of a film containing 12 at % vanadium on a silicon substrate. During deposition, the film surface was coated by a Pt protective layer about  $1 \mu\text{m}$  thick. According to the TEM and STEM data, the film thickness was  $3.8 \mu\text{m}$ . It can be seen that the film structure is homogeneous and contains neither visible defects nor discontinuities (Figs. 1a, 1b). In the region of silicon substrate (Figs. 1a, 1c), there are bending contours, which are apparently due to the stress induced during nonuniform ion-beam thinning in the scanning electron microscope column. Enlarged TEM images of a part of cross-section exhibit a contrast in the form of strips oriented parallel to the film-substrate interface (Fig. 1d).



**Fig. 1.** Cross-sectional structure of the film with 12 at % vanadium: (a) general view, (b) microelectron diffraction pattern of the film, and (c) microelectron diffraction pattern of the Si substrate. The band axis is [110]. (d) Dark-field image of a fragment of the cross section. Rows of disperse crystals 1–2 nm in size are observed. The interplanar distances in the microelectron diffraction pattern correspond to those for VC.



**Fig. 2.** Elemental composition of layers in a part of cross section for the film with 12 at % vanadium: (a) STEM image with *Z* contrast of the analyzed part; (b) HRTEM image of the cross-section structure at the film–substrate interface; (c) energy-dispersive spectrum; and (d–f) V, Si, and O distribution maps. An amorphous layer with a thickness of about 15 nm on the silicon substrate surface is observed. The chemical element distribution maps show that vanadium is nonuniformly distributed throughout the film cross section.

A STEM image with *Z* contrast also reveals dark and bright strips of different thicknesses. This fact suggests that such a contrast in electron microscopy images is caused by chemical inhomogeneity of the film throughout its volume (Fig. 2a).

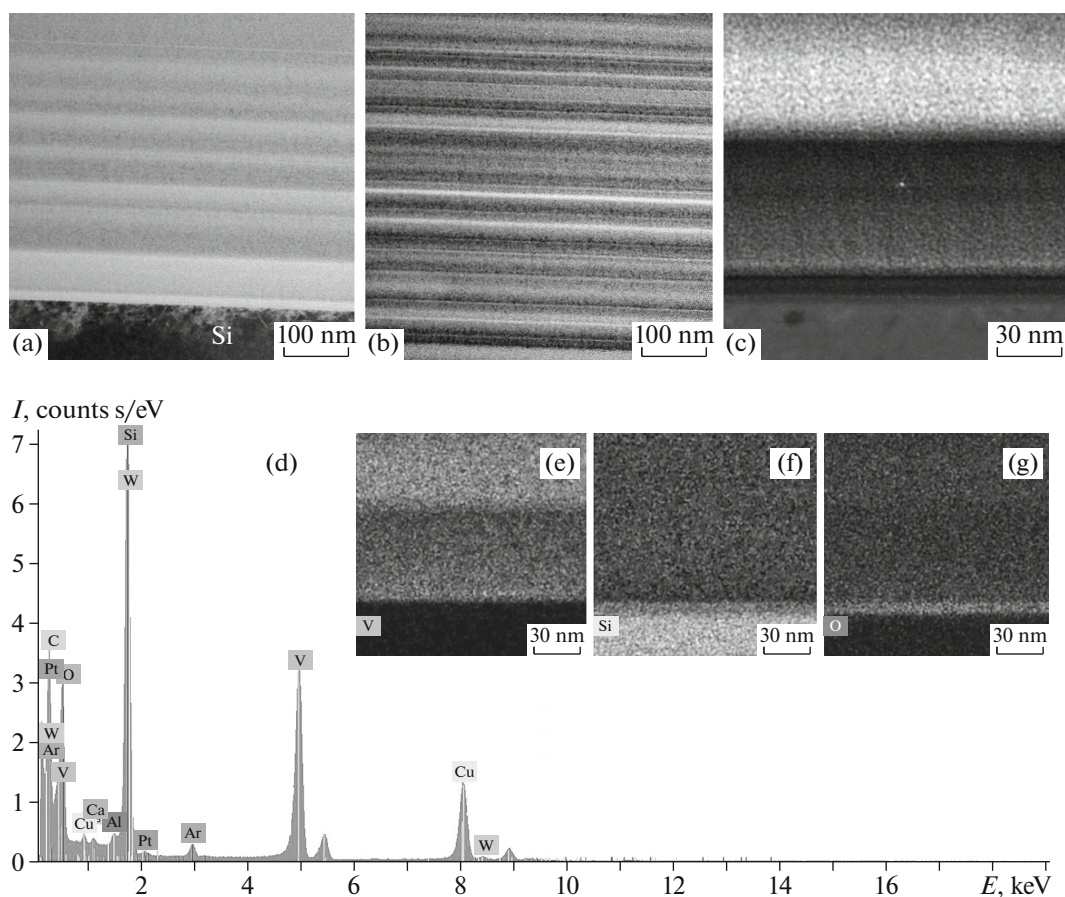
Diffraction patterns from different parts of the film are identical and have a form of broad rings (Fig. 1b). This pattern suggests, on one hand, dispersive nanocrystalline state of the film and, on the other hand, possible presence of an amorphous layer formed on the film surface during sample preparation. An interpretation of the diffraction pattern yielded interplanar spacings  $d_{hkl} = 2.39, 2.07, 1.45, 1.25,$  and  $1.2 \text{ \AA}$ , which correspond to the presence of only vanadium carbide phase and VC stoichiometry.

Indeed, the dark-field image in Fig. 1d shows rows of the disperse crystals. Their size was estimated from the dark-field and HRTEM images to be 1–2 nm. The chemical element distribution maps also demonstrate

a nonuniform layered vanadium distribution in the film cross section. The spectrum contains carbon, silicon, oxygen, and vanadium peaks. The presence of copper and argon is explained by the specific features of sample preparation and the use of a copper half-ring for lamella welding (Fig. 2).

The HRTEM image of the interfacial region revealed an amorphous layer with a thickness of about 15 nm on the silicon substrate surface (Fig. 2a).

The cross-sectional image of the film containing 17 at % vanadium is presented in Figs. 3a–3c. According to the TEM and STEM data, the film thickness was  $3.75 \mu\text{m}$ . As in the first case, one can see a strip nonuniformity caused by an increase in the content of alloying element (vanadium) in the film. As compared with the previous sample, the observed contrast from the crystal layers became more pronounced, especially in the upper part of the film (Fig. 3b). Generally, the size of VC nanocrystals increases and amounts



**Fig. 3.** Structure of a fragment of cross section for the film with 17 at % vanadium: (a) interfacial region; (b) region from the upper part of the film; (c) STEM image with *Z* contrast of the analyzed part; (d) energy-dispersive spectrum; and (e–g) V, Si, and O distribution maps.

mainly to 3–4 nm; there are also individual crystals up to 5 nm in size. The growth of nanocrystals is confirmed by the sharper rings in the diffraction pattern. The diffraction pattern and HREM images show that VC particles are randomly oriented.

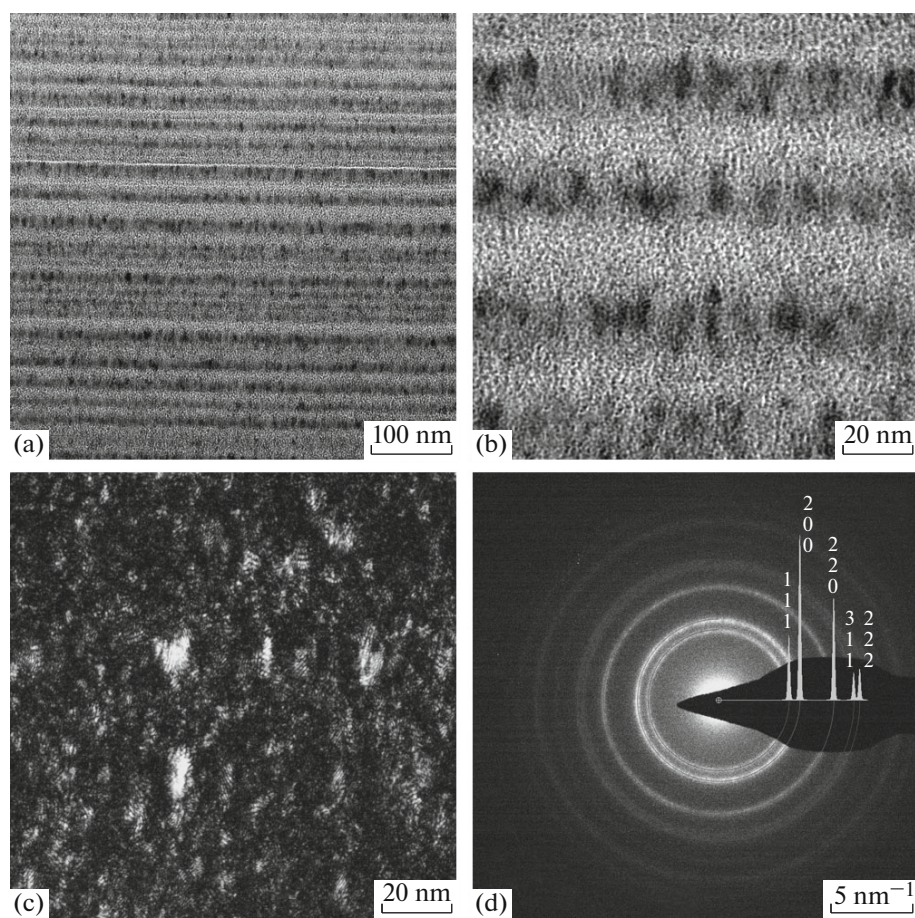
The distribution maps of chemical elements (V, Si, O, and C) for the film–substrate interfacial region show that the thickness of the amorphous layer on the silicon substrate is the same as in the first sample. This layer is silicon oxide (Figs. 3d–3g), which apparently has a thermal origin.

In the spectrum shown in Fig. 3d, the vanadium peak is higher than in the sample with 12 at % vanadium. In addition, after thinning by a focused ion beam, this sample had the maximum thickness, which allowed us to detect the nonuniform distribution of both vanadium and oxygen in the cross-section part in the film layers. Both these elements, vanadium and oxygen, are identically localized in the layers (Figs. 3e, 3f).

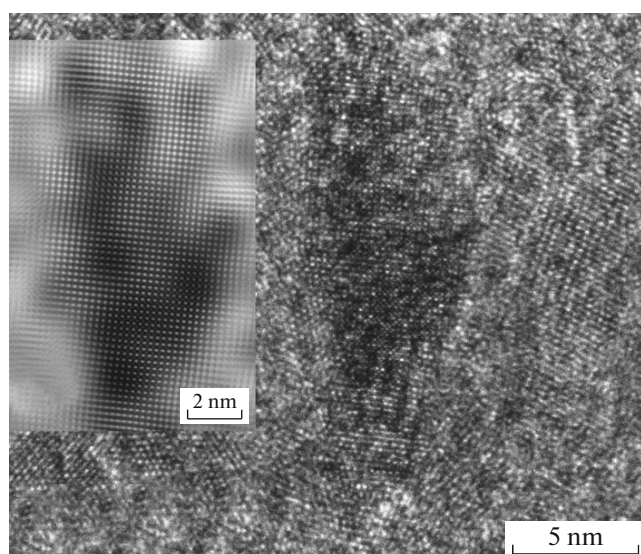
The cross-sectional structure of the film with 26 at % vanadium is in general analogous to the struc-

tures of the above-described samples. The film thickness is 2.95  $\mu\text{m}$ . Note that the nanocrystal size increases to 5–8 nm. The thickness of the layers with the vanadium carbide crystals is  $\sim 10$ –40 nm. The size of separate crystals in the layer may attain 10 nm.

When the vanadium content increases to 31 at %, the film structure turns into a set of 10–40 nm-wide dark and bright contrast tracks (Figs. 4a, 4b). In the dark-contrast strips, one can distinguish crystals extended perpendicular to the film–substrate interface, the height of which is approximately equal to the layer thickness (Figs. 4b, 4c). In the brighter strips, judging by the dark-field images, small equiaxed crystals are located. The HREM images and a filtered image of one of such VC crystals are presented in Fig. 5. An analysis of the diffraction patterns and HREM images revealed no other phases, except for vanadium carbide, despite the significant increase in the vanadium content in the film.



**Fig. 4.** Vanadium carbide nanocrystals in the film with 31 at % vanadium: (a) TEM image of layers with crystals, (b) bright-field TEM image of individual crystals, (c) dark-field TEM image of individual crystals for the same part, and (d) microelectron diffraction pattern with the superimposed VC diffraction pattern calculated using the JEMS software. The size of separate crystals in the layer may reach 10 nm.



**Fig. 5.** HRTEM image of vanadium carbide crystals. The inset shows a filtered image of a separate extended crystal.

## CONCLUSIONS

We used TEM, electron diffraction, and EDA methods to study the structure and phase composition of silicon–carbon films alloyed by vanadium to concentrations of 12–31 at %, which were formed on silicon substrates by magnetron and plasmachemical codeposition. It was found that the films have a layered cross section; the layers are formed due to the nonuniform distribution of VC nanocrystals with vanadium carbide stoichiometry. In the film with 12 at % vanadium, the nanocrystal size is no larger than 1–2 nm, and nanocrystals are randomly oriented. As the content of alloying element increases, the nanocrystal size increases as well and amounts mainly to 2–3 nm at 17 at % vanadium, 3–4 nm at 26 at % vanadium, and 5–8 nm at 31 at % vanadium. In the film with a vanadium content of 31 at %, the vanadium carbide crystals have an anisotropic shape: they are extended in the direction perpendicular to the film–substrate interface.

## ACKNOWLEDGMENTS

Electron microscopy investigations were carried out using equipment of the Shared Research Center of the Institute of Crystallography, Russian Academy of Sciences and supported by the Ministry of Education and Science of the Russian Federation and the Federal Agency for Scientific Organizations (contract no. 007-ГЗ/Ч3363/26). The works on a synthesis of vanadium-alloyed diamond-like silicon–carbon films were supported by the Russian Science Foundation, project no. 15-12-00039. This study was carried out in the framework of the government contract with the Ministry of Education and Science of the Russian Federation, project no. 16.9350.2017/8.9.

## REFERENCES

1. V. F. Dorfman, *Thin Solid Films* **212**, 267 (1992).
2. Š. Meškiniš and A. Tamulevičienė, *Mater. Sci. (Medžiagotyra)* **17** (4), 358 (2011).
3. V. F. Dorfman, *Thin Solid Films* **330**, 76 (1998).
4. T. W. Scharf, J. A. Ohlhausen, D. R. Tallant, and S. V. Prasad, *J. Appl. Phys.* **101**, 063521 (2007).
5. S. M. Pimenov, E. V. Zavedeev, N. R. Arutyunyan, et al., *J. Appl. Phys.* **122**, 145301 (2017).
6. D. Franta, I. Ohlídal, V. Buršíková, and L. Zajíčková, *Thin Solid Films* **455–456**, 393 (2004).
7. V. A. Vlasenko, S. N. Belyaev, A. G. Efimov, et al., *Tech. Phys. Lett.* **35** (15), 737 (2009).
8. S. M. Rotner, V. A. Mokritskii, and S. V. Grasooskii, *Tr. Odesskogo Politekhn. Univ.*, No. 2, 26 (2006).
9. M. L. Shupegin, *Zavod. Lab. Diagn. Mater.* **79** (2), 28 (2013).

*Translated by E. Bondareva*