2015 The 5th International Workshop on Computer Science and Engineering
doi: 10.18178/wcse.2015.04.042

Physical chemical and Protective Properties of the Diamond-Like Carbon Coatings Synthesized from Separated Plasma of Electric Arc

Mstislav O. Makeev, Ekaterina A. Zhukova, Pavel A. Mikhalev, Alexey S. Osipkov, Yury M. Mironov

Bauman Moscow State Technical University, Moscow, Russia

Keywords: diamond-like carbon coatings, protective (gas barrier) properties, electric arc plasma deposition, IR-spectral ellipsometry, Raman spectroscopy, thermovacuum impact, coating thicknesses, optical constants, diamond-like carbon coefficient.

Abstract. Research of the protective diamond-like carbon coatings by means of IR-spectral ellipsometry method and Raman spectroscopy method were carried out. Diamond-like carbon coefficients, optical constants, specific electric resistances and thicknesses of diamond-like carbon coatings were determined. Research of the mass loss of the samples at the thermovacuum impact also were performed. It is shown, diamond-like carbon coatings have well protective (barrier) properties hindering polymer material degradation in the outer space environment.

Introduction

To increase the reliability of the spacecraft's and protection of the polymer materials (used in it) for the space purposes, electron-board equipment, and optical elements from the hazards of outer space factors, it requires protective coating deposition. In the recent 20 years gas barrier protective coatings on the basis of metals and metal oxides were widely used [1, 2]. However, modern technology development requires new coatings, and their deposition methods, elaboration of which will allow to preserve useful properties of polymers (plasticity, low mass etc.) which are impossible while using metal coatings. These can be diamond-like carbon (DLC) coatings which have a number of unique properties, such as high mechanical and barrier (gas-tight) properties, biocompatibility etc [3-5]. The preferred method for the deposition of such coatings is an electric arc plasma deposition because it provides a great adhesion to the sample surface and a high DLC coefficient.

In the present work, research of the mass loss of gassing polymer samples with protective DLC coatings and without them, and the research of DLC coatings by means of IR-spectral ellipsometry (IR-SE) method and Raman spectroscopy (RS) method were carried out. IR-SE method allows determining the thicknesses and optical properties of thin films [6-8]. RS allows evaluating graphite (sp^2) and DLC (sp^3) bonds content, and qualitatively assessing the homogeneity of deposited coating [9-11]. As a result, the DLC coefficients, optical constants, specific electric resistances, thicknesses of protective DLC coatings, as well as the mass loss of the samples with protective coatings and without them were determined.

Experimental

Polyamide imide samples with diameter of 14 mm and thickness of 50 μm were used for the rearch. DLC coatings were deposited on the samples with sublayers of titanium (samples № 1-3) and without it (samples № 4-6).

Deposition of the protective multilayered DLC coatings was performed on the rig East 01 (New Plasma Technologies LLC, Russia) by means of vacuum electric arc treatment with plasma flow separation and laser initiation of the arc at room temperature in vacuum $1{,}33 \cdot 10^{-3}$ Pa ($1 \cdot 10^{-5}$ mm Hg). In the rig, laser radiation source with the wavelength of 1,064 μm was used. Sputtering was carried out in the pulsed mode with energy of 100 mJ and frequency of 25 Hz, pulse duration was 15 ns. Graphite was used as a target, distance between the target and the substrate was 5 cm. Sublayers of titanium, less than 100 nm, are used for the quality improvement of deposited DLC coatings on it. These coatings consist of a combination of different carbon allotropic modifications – sp^2- and sp^3-bonds.

The basis of the developed technique of the thermovacuum impact on the samples was standard technique of the mass loss evaluation and amount determination of the readily condensed materials regulated by the standard ASTM E595 «Standard Test Method for Total Mass Loss and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment». The essence of this technique consists in putting prepared samples in the special stainless containers. The containers are arranged in the multi-unit equipped with the heating system, in which it is possible to maintain predetermined temperature. The unit is placed in the vacuum chamber. The annealing temperature corresponds to 125 °C.

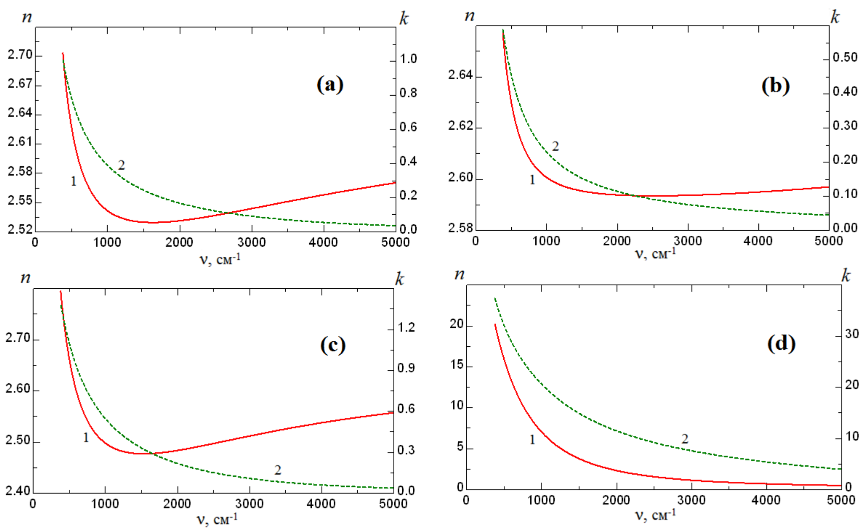
Unlike the standard technique, which involves aging during 24 hours, removing of the samples at the regular intervals was carried out. The mass loss determination of these samples and uploading in the vacuum chamber for further annealing also was performed. Assuming that the mass loss of the samples is exponential function, aging time increased then with every new loading. Total annealing time was 61 hour.

Layer thicknesses and optical constant measurements of the samples were carried out with IR-spectral ellipsometer IR-VASE of J.A. Woollam Co., Inc in the wavelength range from 300 to 5000 cm^{-1} at spectral resolution of 4 cm^{-1} and angles of incidence on the sample of 50°, 60°, and 70°. Ellipsometric model creation was carried out in the software WVASE32 [12] by which measurement processing of the ellipsometer IR-VASE is performed.

DLC coatings research by means of RS method was carried out by measurement system NTEGRA Spectra. The solid-state laser LM473 with wavelength of 473 nm and output power up to 50 mW was used as a source of exciting radiation. The size of the focal spot was 300 nm. The measurements were carried out under conditions optimal for coatings on the diffraction grating of 600/600 which shows the measurement results of a sufficiently high accuracy.

Results and Discussion

During the measurements by means of the IR-SE method, experimental spectra of the ellipsometric parameters Ψ and Δ for all the samples were obtained. On the basis of the published data [13-16] and the analysis of the obtained measurements, the optical models of polyamide imide, titanium sublayer and protective DLC coatings were developed (Fig. 1). Then, using model data, ellipsometric models for all the samples were created, and layer thicknesses of titanium and DLC coatings were determined (Table 1). The specified electric resistance (Table 1) based on the optical models of the titanium sublayer and DLC coatings was calculated, for titanium sublayer it was $7{,}5 \cdot 10^{-7}$ Ohm·m.



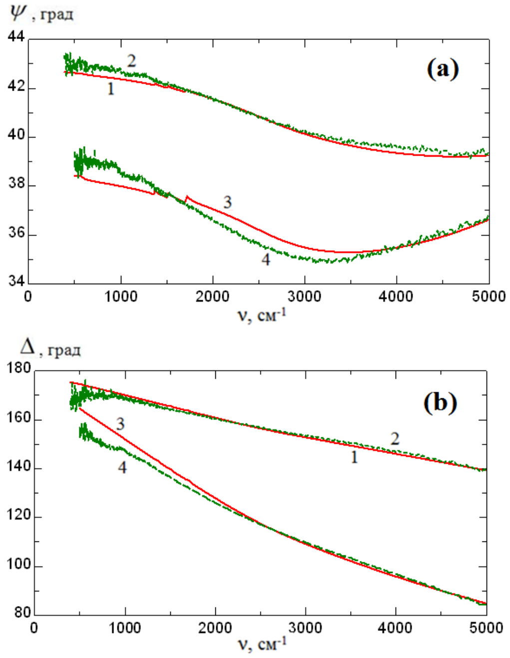
1 – refractive index (*n*), 2 – absorption index (*k*)
Fig. 1. Optical constants *n* and *k* of DLC coatings of the samples №1 (a), №2 (b), №3 (c) and sublayer of titanium (d).

Experimental and calculated on the basis of the ellipsometric model spectra of Ψ and Δ parameters are similar for all the samples under study. As an example, the spectra of sample №2 are shown in Fig. 2.

Research of DLC coating surfaces also was carried out. These coatings were deposited on the polymeric polyamide imide substrates by means of the RS method. Carbon phase of the coating was observed in the range from 1100 to 1700 cm^{-1}. The decomposition of this phase was performed by means of the technique described in [9] (Fig. 3). D-peak was set by the Lorentz function, G-peak – by the Breit-Wigner-Fano function. Decomposition parameters are represented in Table 1.

Table 1: Experimental data of the samples with DLC coatings by IR-SE and RS

Sample, №	Sublayer of titanium	DLC layer				
	Thickness, [nm]	Thickness, [nm]	Specified electric resistance ρ, Ohm m]	*G*-peak location, [cm^{-1}]	Intensity ratio of *D*- and *G*-peaks (I_D/I_G)	DLC coefficient *f*, [%]
1	167,9±2,1	48,2 ±0,8	$2{,}9\cdot10^{-4}$	1575	0,243	20
2	173,7±3,2	69,7 ±1,1	$5{,}0\cdot10^{-4}$	1588	0,230	28
3	20,5±3,9	41,8 ±1,2	$2{,}0\cdot10^{-4}$	1576	0,301	17



1 – generated data, the angle of incidence equals 50 °; 2 – experimental data, the angle of incidence equals 50 °; 3 – generated data, the angle of incidence equals 70 °; 4 - experimental data, the angle of incidence equals 70 °

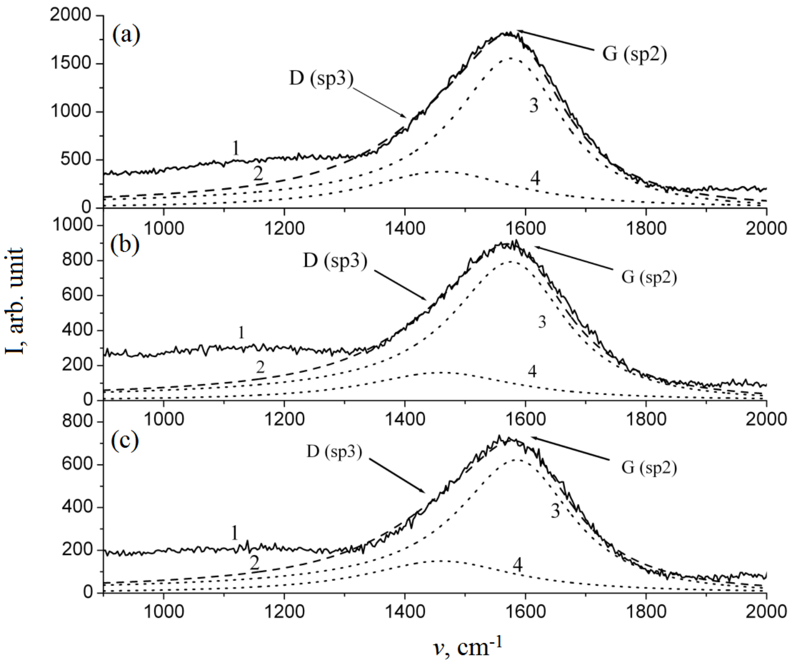
Fig. 2. Ellipsometric parameters spectra of Ψ (a) and Δ (b) of the sample №2 with deposited titanium sublayer and DLC coating.

Based on the results of the RS decomposition the quality of the DLC-coating was evaluated with DLC coefficient calculation, determined by the integral ratio of the intensities D- and G-lines [17].

The coatings, formed by electric arc plasma deposition, have DLC coefficient in the range from 17 to 28 % (table 1), that means they contain a lot of DLC bonds, which cause, on the one hand, coating Hardness increasing; and on the other hand, increase the fragility due to the surface mechanical stress increase which may lead to cracking. At the same time, the coatings under contain a lot of disordered bonds as the existence of the broadened D-peak indicates.

The analysis of the experimental research allows to conclude: the smaller the DLC coefficient of the coating *f* is, the higher is the absorption index *k* and the smaller is the electrical resistance ρ.

In Fig. 4, the dependences of the mass loss of the studying samples are presented (№ 1-6). One can observe that the mass loss of the samples with deposited DLC coatings significantly reduces (~ 3,5 times) compared with the samples without coatings. Herein, the best protective (gas barrier) properties characterize the sample № 2 with the greatest DLC coefficient and thickness.



1 – experimental spectrum, 2 – spectrum after approximation, 3 – G-peak, 4 – D-peak

Fig. 3. Decomposition of the carbon component of RS-spectra of DLC coatings №1 (a), №2 (b) and №3 (c).

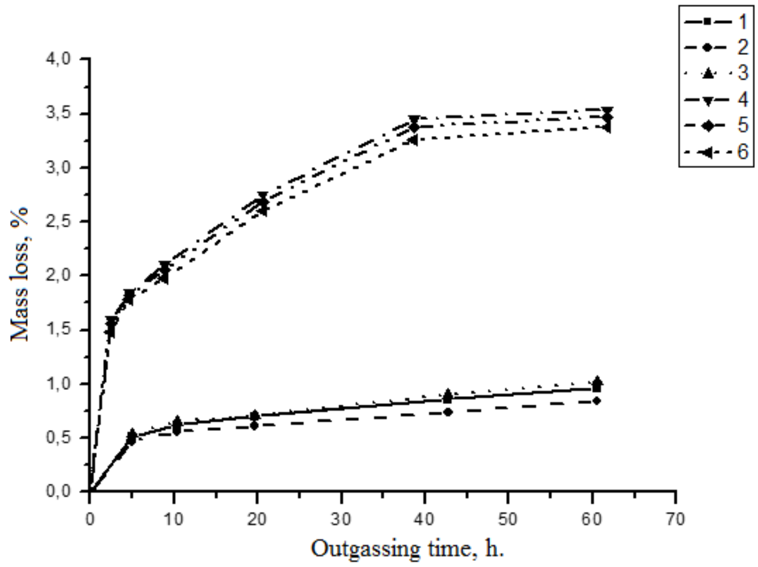


Fig. 4. Dependences of the mass loss of samples under study versus outgassing time (marking of the graphs corresponds to the numbers of the samples).

Conclusions

During the present research the following characteristics of the DLC coatings were determined:

- DLC coefficient;
- Optical constants;
- Specified electric resistances;
- Thicknesses.

Moreover, the mass loss research of the samples was carried out at the thermovacuum impact. Research results by means of IR-SE and RS agree well with each other: the smaller the DLC coefficient, the higher absorption index and the smaller electrical resistance. The mass loss research results of the samples due to thermovacuum impact also conforms to the research results of the DLC coatings properties: the smaller the mass loss of the samples is, the higher the DLC coefficient and coating thickness are. It should be taken into account that the possibility of cracking due to the surface mechanical stress increases for the coatings with a greater DLC coefficient.

Thus, it was shown, that DLC coatings have well protective (barrier) properties hindering polymeric material degradation by the impact of outer space.

Acknowledgements

The research work was carried out in the Sharing Equipment Center "Educational and engineering center of nanotechnology, nano- and microsystem technique" of Bauman Moscow State Technical University.

References

[1] P. Mercea, L. Muresan, V. Mecea and J. Membrane: Journal of membrane science Vol. 24, I. 3 (1985), p. 297.

[2] A.G. Erlat, B.M. Henry, J.J. Ingram, D.B. Mountain, A. McGuigan and R.P. Howson: Thin solid films Vol. 388, I. 1-2 (2001), p. 78.

[3] S.-M. Baek, T. Shirafuji, N. Saito and O. Takai: Jpn. J. Appl. Phys. Vol. 50, I. 8 (2011), 08JD08.

[4] G.A. Abbasa, J.A. McLaughlina and E. Harkin-Jones: Diamond & Related Materials Vol. 13 (2004), p. 1342.

[5] H. Tashiro, M. Nakaya and A. Hotta: Diamond & Related Materials Vol. 35 (2013), p. 7.

[6] J.A. Woollam, C. Bungay, J. Hilfiker and T. Tiwald: Nuclear Instruments and Methods in Physics Research. Section B: Beam Interactions with Materials and Atoms Vol. 208 (2003), p. 35.

[7] S. Gayathri, R. Krishnan, T.R. Ravindran, S. Tripura Sundari, S. Dash, A.K. Tyagi, Baldev Raj and M. Sridharan: Materials Research Bulletin Vol. 47 (2012), p. 843.

[8] M.O. Makeev, Yu.A. Ivanov, S.A. Meshkov, A.B. Gil’man and M.Yu. Yablokov: High Energy Chemistry Vol. 45, I. 6 (2011), p. 536.

[9] A.C. Ferrari and J. Robertson: Phys. Rev. B Vol. 61, I. 20 (2000), p. 14095.

[10] J. Robertson: Materials science and engineering Vol.37 (2002), p. 129.

[11] J. Hong, A. Goullet and G. Turban: Thin solid films Vol. 352 (1999), p. 41.

[12] IR-VASE User’s Manual. J.A.Woollam Co.Inc. (2006).

[13] Palik E.D: Handbook of optical constants of solids vol. 2 (N.Y.: Academic Press, 1991).

[14] A. Grill: Thin Solid Films Vol. 355-356 (1999), p. 189.

[15] F.F. Sizov, N.I. Kluy, A.N. Lukyanov, R.K. Savkina, A.B. Smirnov, A.Z. Evmenova: Technical Physics Letters Vol. 34, p. 32.

[16] Evtukh A.A., Litovchenko V.G., Klyui N.I., Marchenko R.I. and Kudzinovski S.Yu: J. Vac. Sci. Technol. B. Vol. 17 (1999), p. 679.

[17] S.S. Yap, W.O. Siew, C.H. Nee and T.Y. Tou: Diamond & Related Mat. Vol. 20 (2011), p. 294.