

## Characterization and Application of DLC Films Produced by New Combined PVD-CVD Technique

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**Abstract** A new advanced combined PVD/CVD technique of DLC film deposition has been developed. Deposition of a DLC film was carried out using a pulsed carbon arc discharge in vapor hydrocarbon atmosphere. The arc plasma enhancing CVD process promotes dramatic increase in the deposition rate and decrease of compressive stress as well as improvement of film thickness uniformity compared to that obtained with a single PVD pulsed arc process. The optical spectroscopy investigation reveals great increase in radiating components of C<sub>2</sub> Swan system molecular bands due to acetylene molecules decomposition. AFM, Raman spectroscopy, XPS and nano-indentation were used to characterize DLC films. The method ensures obtaining a new superhard DLC nano-material for deposition of protective coatings onto various industrial products including those used in medicine.

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**Key words:** Pulsed arc plasma discharge, Combined PVD/CVD, Hydrocarbon added arc, Arc, Uniformity, Swan spectra

### 1. Introduction

Tetrahedral amorphous carbon (ta-C) produced by physical methods is distinguished by specific characteristics that compare favorably with those of other diamond-like carbon thin-film materials. The high content of sp<sup>3</sup>-hybridized chemical bonds between carbon atoms imparts the properties close to those of natural diamond to ta-C material. Ta-C has better hardness and wear resistance than all known synthesized materials, including metal carbides and nitrides, cubic boron nitride and ranks below only synthetic diamonds in these properties. Its hardness is over 85 GPa [1] and wear resistance 3 × 10<sup>-7</sup> mm<sup>3</sup>/Nm [2]. However, on deposition of this excellent carbon material on large-sized substrates its high internal stress [3], rather low range of thermal stability within 400°C and slow growth rate as well as non-uniformity in coating thickness present serious obstacles to its wide industrial application.

The new method of diamond-like carbon film deposition, that in many respects allows overcoming the aforementioned problems, has been developed by the Physical-Technical Institute of National Academy of Sciences of Belarus in collaboration with the Korea Institute of Industrial Technologies. Its essence consists in using a combined method that involves a pulse cathode arc deposition (PVD method) and carbon-plasma enhanced chemical vapor deposition (PECVD) for the purpose of improving conventional deposition techniques and performance of DLC films as well.

The pulsed cathodic arc is widely used to obtain ta-C films in vacuum [4]. Owing to using a special-purpose design of the Hall plasma source, carbon plasma spreads towards substrate at a speed of 30~35 kilometers per second and, therefore, carbon ions acquire energy close to 60~75 V [5, 6]. This energy is sufficient to cause destruction of any hydrocarbon molecule on its impact with a carbon ion. The technique

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enables elimination of complex RF or MW plasma activation as well as substrate bias and heating.

## 2. Experimental conditions and characterization methods

In a series of experiments devoted DLC film deposition, the acetylene gas filled the vacuum chamber to the pressure within the range of 0.1~1.5 Pa. The chamber was preliminary pumped out to the residual pressure of  $10^{-3}$  Pa. Silicon substrates were precleaned by argon ions of 2 keV energy prior to deposition. The main voltage was applied between arc source anode and cathode with the magnitude of 300 V and the capacitor bank provided the discharge power about 100 J. The duration of discharge pulses did not exceed 300  $\mu$ s at the pulse repetition of 1.5 per a second.

In an effort to gain insight into physical and chemical processes that occur during arc carbon plasma interaction with a hydrocarbon gas, MS 3504 monochromator was employed at the spectral resolution of 0.06 nm with its connection according to *Cherny-Terner* non-symmetric scheme.

Atomic force microscopy (AFM), X-ray photo electron spectroscopy (XPS) with MgK- radiation of 1253.6 V, and Raman spectroscopy with a wave length of 514.5 nm were used for characterizing the surface morphology and atomic compositions and obtaining the information on carbon atomic bonds. The amount of a deposited carbon material was determined by weighing the aluminum foils 30  $\mu$ m thick before and after DLC film deposition carried out within 1500 discharge pulses. The accuracy of weight determination was of 0.1 mg. The substrates were placed in a vacuum chamber at a distance of 30 cm from a plasma source output normally to the plasma flow. The thickness of a coating was

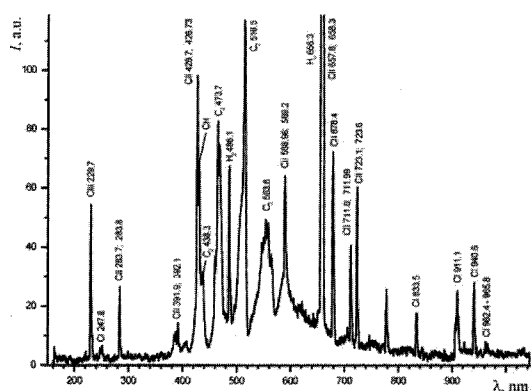


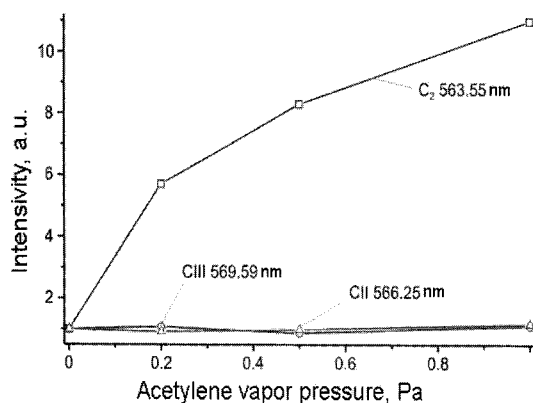
Fig. 1. Emission spectrum of the carbon plasma in the range of 200-1000 nm.

determined using interferometer MII-4. The hardness and elastic constants were measured by nano-indentation using Berkovich diamond tip. Tribological properties of DLC coatings were investigated using the tribometer pin-on-disk scheme. The ball 5.51 mm in diameter made of bearing steel was used as a counterbody. The load force was 0.4 N and RPM 120 which provided the relative speed of 7.16 m/min. Friction tracks were examined by the Hitachi S-900 scanning electronic microscopy.

## 3. Experimental results and discussion

### 3.1 Spectral investigation

The study was made of plasma emission spectra of various-energy pulsed arc discharges. The spectral range under investigation was 200 to 1000 nm. The qualitative analysis of spectra obtained without pre acetylene (Fig. 1) has shown that the basic radiating components of plasma are lines of carbon atoms, CI; ions, CII; and second-order ions, CIII, as well as molecular bands of  $C_2$  Swan system. Besides, in the spectra there are hydrogen atomic lines,  $H_\alpha$  and  $H_\beta$ , and weak lines of atomic oxygen, OI, and molecular bands of CH and CN. Admission of



**Fig. 2.** Dependence luminescence intensity of carbon ion CII, CIII and molecular carbon  $C_2$  on acetylene vapor pressure.

acetylene vapor into vacuum chamber led to dramatic increase in intensities of Swan system whereas those of other radiating components were almost not changed. For example, intensity of molecular carbon  $C_2$  at 563.55 nm increased by factors of 6, 8, and 11 when reaching the hydrocarbon partial pressure of 0.2, 0.5, and 1.0 Pa, respectively. The behavior of the intensity ratio is illustrated in Fig. 2. At the same time, emission spectra of  $C_2H_2$  molecules were not observed. The rise of acetylene pressure in the range from 0.2 Pa to 1.0 Pa resulted in increasing the intensities of  $H_\alpha$  and  $H_\beta$  spectral lines 2 to 3 times as compared to those in vacuum condition. At the same time the luminescence level of CH radicals remained almost unchanged. The enhancement of luminescence of  $C_2$  cants is indicative of changes in the plasma composition caused by increase of hydrocarbon molecules. In this respect the main outcome of the collisions of carbon plasma particles with hydrocarbon molecules is destruction of C-H bonds in acetylene molecules and formation of  $C_2$  radicals. These results are in a good agreement with the analyses based on bond dissociation energy (BDE) of acetylene molecule [7]. BDE of  $C_2H_2$  for single H-CC bond is  $E_1 = 1.20$  eV. This is

almost two times lower than triple  $HC \equiv CH$  binding energy equal to  $E_2 = 2.38$  eV. Thus, it is most likely that the ratio of  $C \equiv C$  radical number to C-H radical number will be expressed as a first approximation by function  $\exp\{-(E_1 - E_2)/kT\}$ , where  $T$  is the plasma temperature and  $k$  is the Boltzmann constant. The gas-kinetic plasma temperature (temperature of neutral component) was estimated as 0.1 eV and 1 eV derived from  $C_2$  Swan spectral intensities of rotational and vibration modes, respectively. If an average plasma temperature used is 0.5 eV, the ratio of the amount of  $C \equiv C$  radicals and C-H radicals will be 10.5 : 1.

### 3.2 Types of chemical bonds

The information on element structure and types of chemical bonds of thin-film carbon materials was obtained from X-ray photoelectron spectra. C1s core level spectra for DLC films deposited at different acetylene pressures revealed four different Gauss-Lorentz fit components with binding energies of 284.4-284.8 eV, 284.9-285.2 eV, 286.0-286.9 eV, and 287.3-287.7 eV. Based on the experimental data given in [8] the components with these binding energies correspond to  $sp^2$  bond,  $sp^3$  bond, C-O, and C=O, respectively. The relative content of chemical bonds derived from the fitting peak areas is given in Table 1. The table data support the validity of using the pulsed arc method for DLC film deposition since it ensures a high content of 4-fold coordinated  $sp^3$  sites.

The ratio of  $sp^2$  bonds to  $sp^3$  bonds is about 0.15 for the DLC films deposited in vacuum with zero substrate bias. The ratio for the bulk film material must be even lower since an upper film layer of DLC film is enriched in  $sp^2$  bonds as it is clearly demonstrated in [9, 10]. The presence of acetylene vapor in a vacuum chamber leads to some decrease in content of

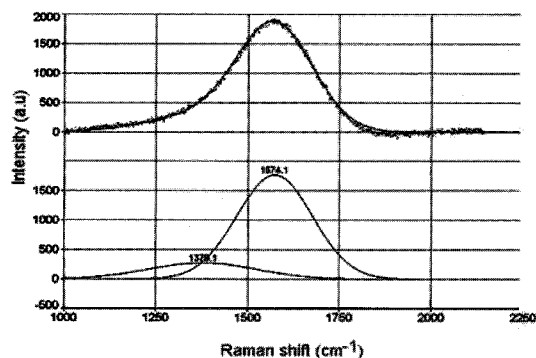
**Table 1.** Bond content of DLC coatings

Acetylene pressure, Pa	Bond content, % (Binding energy, eV)			
	Without acetylene	0.3	0.6	1.0
sp <sup>2</sup> bonded C	12.5 (284.4)	30.1 (284.5)	8.8 (284.5)	17.4 (284.8)
sp <sup>3</sup> bonded C	81.3 (285.0)	63.8 (285.2)	74.4 (285.0)	61.4 (284.9)
C – O	2.0 (286.9)	2.1 (286.7)	9.7 (286.3)	14.5 (286.0)
C = O	4.2 (287.7)	4.1 (287.7)	7.1 (287.3)	6.7 (287.6)
sp <sup>2</sup> /sp <sup>3</sup>	0.15	0.47	0.12	0.28

the four-fold s-bonds depending on the gas pressure. However, as a consequence of concurrent performing of two main processes the tendency is perhaps of a non-monotonic character. The presence of hydrocarbon molecules in a vacuum chamber favors deposition of a lot of low-energy carbon particles on a substrate which adversely affects creation of a sp<sup>3</sup> bond. An opposite trend is associated with free hydrogen release resulting from decomposition of acetylene molecules. Thus, the hydrogen can terminate sp<sup>3</sup> dangling bonds on the growing film surface and effectively stabilize them.

Table 1 also indicates that rise of acetylene pressure up to 1.0 Pa in vacuum chamber results in increase of oxygen content in DLC film more than 3 times. Oxygen, in its turn, contributes largely to coating graphitization; so, this can be considered an additional factor favorable for growth of sp<sup>2</sup> bonds content in DLC films.

Fig. 3 shows Raman spectra of a DLC film obtained in acetylene at the pressure of 0.3 Pa. The spectra generally exhibit a broad intensity distribution of 1560 cm<sup>-1</sup>. A low intensive shoulder existing at 1360 cm<sup>-1</sup> only slightly disturbs the peak symmetry. Such Raman spectrum shape is a typical one for high-quality diamond-like carbon films having a large content of sp<sup>3</sup> bonds [11]. DLC films deposited in acetylene atmosphere reveal greater skewness of Raman spectra than those deposited in vacuum and their peak positions are shifted towards low frequency as



**Fig. 3.** Raman spectrum of DLC film deposited at acetylene pressure of 0.3 Pa.

well. The deconvolution of D- and G band from a broad Raman spectrum is also shown in Fig. 3.

As to the DLC films deposited in vacuum and those deposited in acetylene at the pressure of 0.3 Pa, the ratio of integral intensity for D- and G-peak,  $I_D/I_G$ , differ considerably and are 0.12 and 0.29, respectively, while G-peak positions practically coincide for both Raman spectra (1565.4 and 1564.3 cm<sup>-1</sup>). The presence of acetylene accounts for widening of D-peak at its half height from 170.1 to 293.4 cm<sup>-1</sup>, and does not affect the width of G-peaks that remains practically invariable (224.6 and 228.3 cm<sup>-1</sup>). These results imply that graphite phase in a film deposited with acetylene is increased due to growth of a number of small graphite clusters in the amorphous sp<sup>3</sup> matrix.

### 3.3 Mechanical properties

As seen in Fig. 4, the DLC film deposition

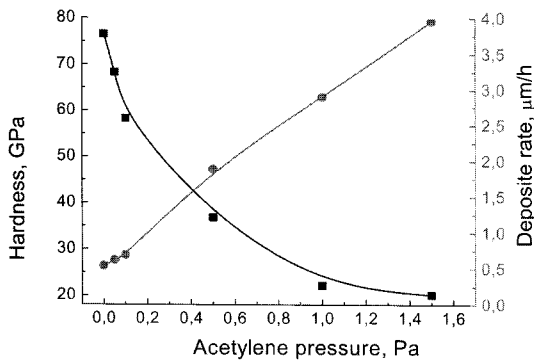


Fig. 4. Dependence of hardness and growth rate on acetylene vapor pressure.

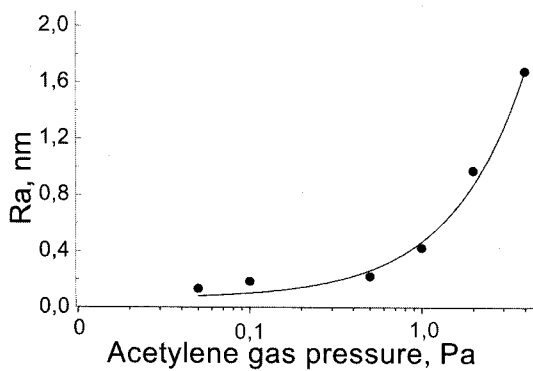


Fig. 5. Roughness of DLC coatings vs. acetylene pressure

rate almost linearly depends on acetylene vapor pressure. By this is meant that the quantity of activated acetylene radicals guided by the arc plasma towards the substrate depends directly on the number of collisions between arc-emitted carbon ions and acetylene molecules. The experience gained while investigating the combined PVD/CVD technique allows drawing a conclusion that it provides increase of DLC film deposition rate by a factor of 5–8 in comparison with that obtained by means of vacuum pulsed arc technique.

The content of the graphite-like carbon of a DLC film increases with decreasing the film hardness depending on increasing the vapor pressure. The tendency results in obtaining very

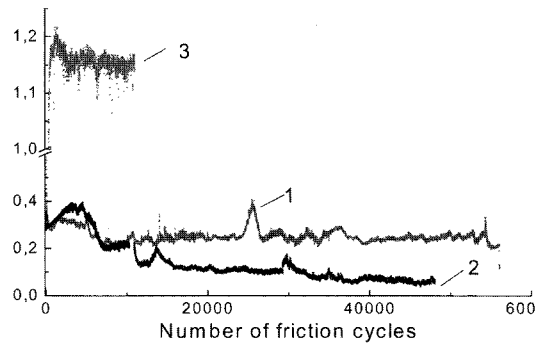


Fig. 6. Evolution of the friction coefficient vs. number of sliding cycles for DLC film (1) deposited in vacuum and (2) acetylene at pressure of 0.5 Pa. For comparison (3) is a sliding curve for uncoated silicon.

soft DLC films at the acetylene gas pressure exceeding 1 Pa. (Fig. 4). The trade-off technological solution of the problem of obtaining the low hardness at high deposition rate can be achieved at the gas pressure ranging from 0.3 to 0.8 Pa.

Fig. 5 demonstrates the dependence of a surface roughness on acetylene pressure. A remarkable change of the roughness is observed at the acetylene pressure exceeding 1.0 Pa. Such behavior of roughness changing is usually observed when using CVD methods of thin film deposition [12, 13].

### 3.4 Tribological testing

The dependence of friction coefficient,  $f$ , on the number of sliding cycles for DLC films deposited in vacuum and acetylene atmosphere at the pressure of 0.5 Pa is shown in Fig. 6. For comparison, the friction curve for uncoated silicon wafer is also presented. The friction coefficient is relatively high due to tribolayer formation during initial 30 min. After this time the value of  $f$  is stabilized for the sample (1) at the level of 0.25 while for the sample (2) the friction coefficient slowly decreases and reaches the value of 0.06. Such a low dry friction coefficient can be only compared with that of a layered solid lubricant

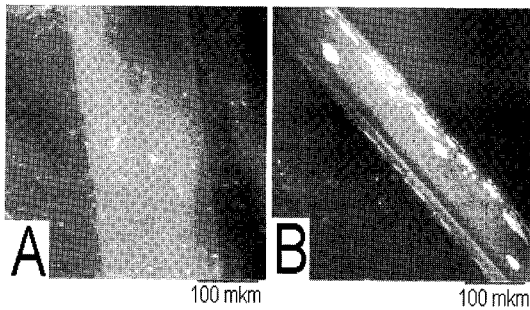


Fig. 7. SEM image of friction tracks after 7 hour tests on DLC coatings deposited in acetylene (A) and vacuum (B).

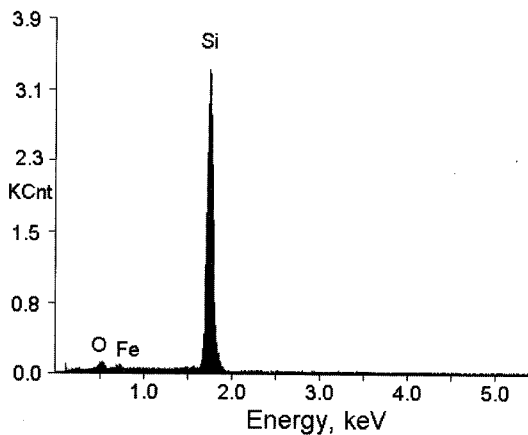


Fig. 8. EDX microanalysis spectra of the wear track for DLC coating deposited in vacuum (PVD method).

based on molybdenum disulfide or graphite. It is noteworthy to mention that the friction coefficient of uncoated steel ball against a silicon plate makes up 1.15.

The observation of friction tracks formed after 7-h sliding test (Fig. 7) has revealed weak abrasive wear of DLC films deposited by the combined method in comparison with that for the vacuum deposited DLC films. As one can see in the SEM image, Fig. 7B, in the last case the fatigue wear occurs manifesting itself in the fragmental delaminating of coating from the substrate. In this way an abrasive wear of steel rider is substantially increased. Similar results have been reported in [3]. The wear track analysis has not revealed any abrasive particles

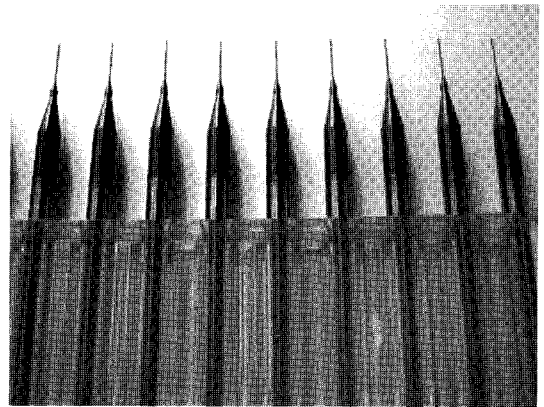


Fig. 9. Fine-sized WC drills with DLC coating deposited by combined PVD-CVD technology.

of the steel rider for the case of DLC films deposited by the combined technique. An opposite effect is found for the DLC film obtained by the pure PVD method. Fig. 8 presents energy dispersive x-ray (EDX) microanalysis of spectra consisting of iron and oxygen and peaks in the ratio of 1:3. This, probably, is the evidence of formation of  $\text{Fe}(\text{OH})_3$  iron hydrate.

#### 4. Application

The newly-developed method has been used for improving the life and performance of tungsten carbide micro-drills and routers to be used for processing of printed-circuit-boards.

Fig. 9. illustrates drills 0.25 mm in diameter with the 3.8-mm length of a working part (Kyocera Tycom Corp., USA) coated with DLC films 1.5 mm thick. Drilling and cutting tests demonstrated that the DLC coatings increased wear resistance of the micro drills and routers 1.5~2 times as much with improvement of quality of the printed-circuit-board processing and no sticking was detected.

Deposition of DLC coatings on pistons of diesel truck engines (Fig. 10) allowed reducing the friction coefficient of tribo-couple of cylinder-

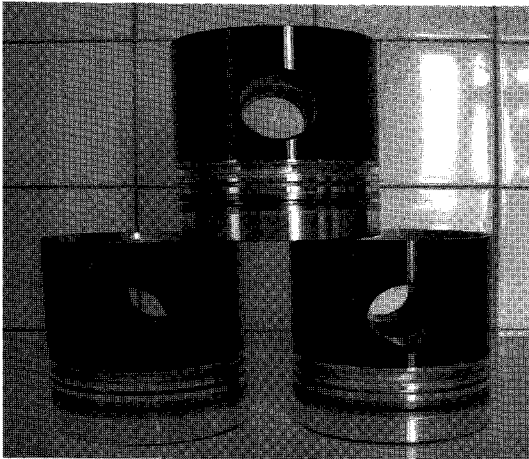


Fig. 10. Diesel engine pistons with DLC coatings.

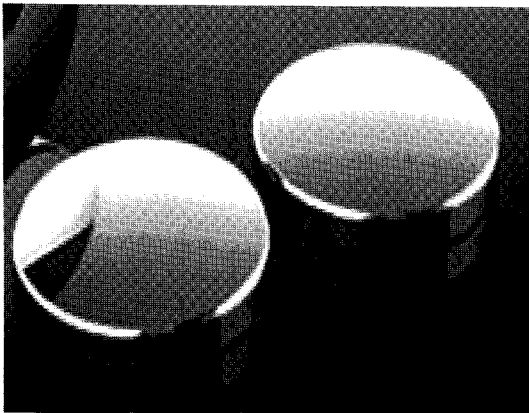


Fig. 11. Germanium lens with DLC coating as antireflection layer for infrared range.

sleeve down to 0.1 and decreasing the wear of piston surfaces. All this adds to the 4-to-6 -fold increase of piston service life.

DLC films exhibit considerable promise as materials for IR antireflection coatings to be used in optical devices as well as for absorbing coatings of body parts in order to guard against stray light in optical equipment. The PVD-CVD technology is highly suitable for deposition of such coatings owing to high uniformity of coating thickness and possibility of its controlling to several nanometers which is conditioned by a discrete impulse mode of DLC film deposition.

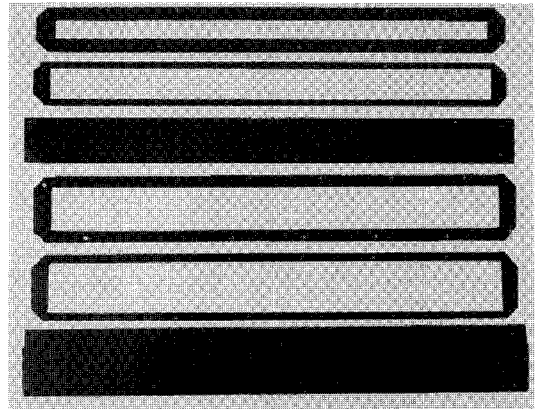


Fig. 12. DLC coating on body parts of optical instruments for artificial Earth satellites.

The bilateral DLC coatings deposited on germanium windows (Fig. 11) increase their light transmission from 0.45 up to 0.92 for wave length of 10 mm. DLC coatings were also investigated concerning their application for bodies of optical devices mounted on artificial Earth satellites. Several kinds of the bodies and frames made of invar (Ni-36% -Fe) coated with DLC films that have high light absorption and low thermal expansion coefficients are depicted in Fig. 12.

## 5. Conclusion

A high rate of deposition of diamond-like carbon coatings is the major benefit of newly-developed combined PVD-CVD method. The deposition rate exceeds that achieved when using the pulsed cathode arc burned in vacuum several times due to formation of  $C_2$  radicals resulting from acetylene molecule rupture during collisions with the carbon plasma particles. The chemical bond structure and hardness and other properties such as roughness, compressive stress, etc, are comparable with those of ta-C and hydrogenated DLC coatings and occupy an intermediate place between them. The performances may differ

depending on acetylene pressure in vacuum chamber. With further development of this method its potential for technical applications will be essentially extended.

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