Surface hardening of optic materials by deposition of diamond like carbon coatings from separated plasma of arc discharge

AS Osipkov¹, VM Bashkov¹,², AO Belyaeva¹,² R Stepanov¹, YM Mironov¹, AL Galinovsky¹

¹ Bauman Moscow State Technical University, 2-ya Baumanskaya str. 5, Moscow, 105005, Russia
² New Plasma Technologies LLC, B. Semenovskaya str. 49, off 202-205, Moscow, 107023, Russia
osipkov@bmstu.ru

Abstract. This article considers the issue of strengthening of optic materials used in the IR spectrum by deposition of diamond like carbon coatings from separated plasma arc discharge. The report shows results of tests of bare and strengthened optical materials such as BaF₂, MgF₂, Si, Ge, including the testing of their strength and spectral characteristics. Results for the determination of optical constants for the DLC coatings deposited on substrates of Ge and Si, by using separated plasma, are also presented. Investigations showed that surface hardening of optical materials operable in the IR range, by the deposition of diamond like carbon coating onto their surface, according to this technology, considerably improves operational properties and preserves or improves their optic properties.

1. Introduction
Optoelectronic systems, operating in IR range are widely spread in different fields of contemporary science and engineering. Such systems enable monitoring of various processes and objects at night and in low visibility conditions.

Enhancement of operational characteristics and efficiency improvement of such systems are inseparably linked with use of specific optical materials, such as: special kinds of glass (oxygen-free glass, and optical ceramics based on polycrystalline ZnSe ZnS, and used in the manufacture of optical components for IR devices, substrates and filters), optical crystals (CaF₂, MgF₂, BaF₂, KBr, NaCl, used to create lenses for infrared lenses, prisms, and window input devices for spectral measurements), and semiconductor materials (e.g. Si and Ge, which are used to create optical elements for thermal imaging systems operating in the range of and 3-5 and 8-12 microns).

Optical surfaces of the aforementioned materials are often soft and hygroscopic; as a consequence they can be easily damaged during operation through the effect of atmospheric moisture, dust and various mechanical impacts. Protecting such surfaces assumes strategic and actual importance.

Research into optical coatings is carried out in numerous institutions. Among Russian institutions engaged in such research one should note the scientific and industrial corporation Vavilov State Optical Institute, NII OEP PLC, the research institute Radioelectronics and Laser Technology, and Bauman Moscow State Technical University; and outside of Russia, centres such as Nano-Care AG (USA), Corning (USA), and Izovac Ltd. (Republic of Belarus), however the results of studies achieved are uncoordinated and cannot currently be used to create a nomenclature of optical materials.
Therefore this study is aimed at the development and introduction of the technology to increase abrasive surface solidity and micro-hardness of optic materials from various classes – “soft” materials for UV and IR range, semiconductors, metals, polarized films and intermediate layers of switches of laser radiation. The basic methods of strengthening optic materials can be divided into two groups: creation of compressive stresses in the surface layers of optic materials (e.g. hardening, ion exchange, surface crystallisation) and local surface strengthening (e.g. thermal and thermochemical polishing, deposition of strengthening coatings chemically connected with the surface). The last method is one of the most efficient ways of strengthening, but currently carbon-based coatings are of particular interest [1].

The aim of this study is to evaluate the potential for the protection of optical elements operating in the IR range by the deposition of a diamond like carbon (DLC) coating on the surface by the electro-arc technique with laser ignition of carbon plasma and separation of plasma flow [2].

To achieve this goal the following scientific technical tasks were solved:

1. Deposition technology for DLC coating of non-organic “soft” (BaF2, MgF2) and semiconductor (Si, Ge) materials in the IR Range was developed.
2. Production of prototypes materials with DLC coatings deposited onto their surfaces.
3. Development of techniques for investigating the performance and optical properties of these prototypes.

2. Potential of hardening coatings to provide anti-reflection optical performance

The aim of this study is to not only increase the hardening characteristics of the optical materials, but also to preserve or improve their optical properties, by reducing the coefficient of reflection from their surface. Therefore the possibility of increasing transmission by means of enhanced anti-reflection performance as a result of the deposition of hardening coating requires special attention.

The refractive indices of the optical materials requiring hardening mentioned above, vary over a wide range of values from 1.4 to 4. It is known that for optimal single-layer anti-reflection, the refractive index of an applied coating has to meet the following condition

\[ n_f \approx \sqrt{n_s} \]  

where \( n_f \) is the refractive index of a film and \( n_s \) is the refractive index of a substrate material.

Thus, to increase the transmission of substrates made from highly-refractive materials (Si, Ge), which have refractive indices in the range from 3.5 to 4, it is necessary to deposit hardening films with refractive index about 1.7 to 2. For substrates with refractive indices in the range from 1.4 to 1.6 (BaF\(_2\), MgF\(_2\), CaF\(_2\), KBr), coatings should have refractive indices of approximately 1.15 to 1.3.

3. DLC deposition technology and research methods

Diamond like carbon coatings are a class of coatings consisting of \( \text{sp}^3 \)- and \( \text{sp}^2 \)-hybridised carbon atoms. As a result of their unique chemical and physico-mechanical properties these coatings are widely used in various engineering fields from optics to heavy mechanical engineering and medicine. These properties include high hardness (5000-10000 Hv), low friction coefficient (0.15-0.08), high wear resistance and chemical inertness.

These coatings are usually produced by chemical vacuum deposition using HF plasma (the most common method), or magnetron sputtering of a graphite target and pulse laser sputtering (ablation). The properties of DLC coatings depend on the methods and conditions of deposition, because these give a different hydrogen content in the coating material and thus a different ratio of the \( \text{sp}^2 \)- to \( \text{sp}^3 \)-hybridised carbon atoms.

In this work we investigated coatings deposited by the electro-arc technique, with laser initiation of an arc and separation of a plasma flow. This was performed on the rig East 01 (New Plasma
Technologies LLC, Russia, Figure 1). The technological process is based on the separated arc evaporation of carbon from rotating cylindrical graphite target (cathode).

![Figure 1. Schematic of a rig for diamond like carbon coating deposition.](image)

1,5: solenoid; 2: camera filter; 3,4: titanium target; 6,7: trap particles; 8,12: solenoids for plasma confinement (Helmholtz coils); 9,11: water cooling; 10: ion gun; 13: camera filter; 14: carbon filters; 15: anode; 16: graphite cathode; 17: window for the laser; 18, 19: filtration system.

When developing this technology, the nano-composite hardening was created using an approach based on the formation of various combinations of the following three effects: multiphase hardening, grain size effects, and the effect of suppression of grain boundary shift by the formation of strong contacts.

By varying the parameters marked by *, the following technological modes were defined: power of laser radiation: 20 mJ; frequency of laser radiation: 20 Hz; cathode voltage*: 250 V; hold-in solenoid current*: 2 A; supply* of working gas (Ar): 15 cm$^3$/h; deposition time*: 60 min; chamber temperature*: 34 °C; rotating velocity* of the turntable on which the samples were fixed: 3 rpm; carbon source voltage*: 200 V; and chamber pressure*: $10^{-5}$ Mbar.

Measurements of thickness, roughness, micro-hardness and optical characteristics of deposited layers and tests of their surface hardness were performed for applied DLC coatings. Moreover, the similarity of coatings to diamond was estimated, i.e. the ratio of sp$^2$-and the sp$^3$-hybridised carbon atoms in the coating. Roughness and thickness of coatings were measured by means of atomic-force microscopy using a rig Ntegra Spectra (NT-MDT, Russia). For thickness measurement of a substrate, a step on its surface was created by masking a part of the sample before coating deposition.

Surface hardness measurements of the samples before and after the deposition of hardening layers were performed on Nanoindenter Hysitron TI750 UBI with Oliver-Farrah's (ISO 14577) using a Berkovich-type indentor, which is a tri-hedral diamond pyramid with an angle at the vertex of about 142°. Surface hardening was estimated according to OST 1901-95 where it was defined quantitatively by its ability to resist surface abrasion under load. The abrasion resistance was characterised quantitatively by examining the scratch formed through a magnifying glass. All coatings were sorted into five groups on the basis of mechanical hardness.
The ratio of sp\textsuperscript{2} and sp\textsuperscript{3} hybridised carbon atoms in the coating was estimated by means of Raman spectroscopy using the rig Ntegra Spectra. The carbon phase of the coating was observed in the range from 1100 to 1700 cm\textsuperscript{-1}. The phase decomposition was carried out using the technique described in [3]. The D-peak was prescribed by Lorentzian, G-peak – by Breit-Wigner-Fano function.

Spectral characteristics of the DLC coatings deposited were measured using a PerkinElmer Lambda 950 spectrometer, in the range from 0.2 to 3 microns, and an IR-Fourier spectrometer VERTEX 70 V, from 3 to 20 microns.

To define the optical characteristics of the films and thicknesses, according to the results of multispectral transmission measurements of a film-substrate system, a quasi-decision selection method was undertaken on the basis of the minimisation of the residual function [4]

\[
F = \sum_{i=1}^{N} \left[ T(\lambda_i)^2_{\text{exp}} - T(\lambda_i)^2_{\text{mod}}(n_1, k_1, d_1) \right]^2
\]

where \( N \) is the number of radiation wavelengths at which measurements are made; \( T(\lambda_i)^2_{\text{exp}} \) and \( T(\lambda_i)^2_{\text{mod}} \) are the experimentally measured and modelled (respectively) values of the transmission coefficients at wavelength \( \lambda_i \), and \( n_1, k_1 \) and \( d_1 \) are the refraction coefficients, absorption and film thickness respectively.

For the model of the film transmission on the substrate, a variant of the matrix method [5] was used. This allows the user to take into account the possible deviations from an ideal case, such as inhomogeneity of layers and roughness of transitions between them, and the existence of “thick” layers.

The minimisation of equation (2) is a complex optimisation problem, as the residual function has a large number of local minima, and cannot always be defined in all areas of a search. The number of parameters can reach 10 and more, and include: film thickness, coefficients of model dependence, \( n_1(\lambda) \) (e.g. coefficients of Sellmeier equation), or coefficients of model dependence, \( k_1(\lambda) \).

Nowadays there are a number of software products for the determination of film parameters using multi-spectral measurements, however the majority of such programs are problem specific and do not allow flexible solving of numerous problems arising while determining of optical characteristics of diamond like nano-films. A special software program [4] providing measurements of thickness and optical characteristics of diamond like carbon nano-films was developed in the visual programming environment LabVIEW 2011, in which two optimisation algorithms are implemented using the method of consecutive square programming [6], and the method of differential evolution [7].

### 4. Results
The Raman spectroscopy analysis of the chemical composition of the deposited carbon layers showed (Figure 2) that the ratio of sp\textsuperscript{3} and sp\textsuperscript{2}-hybridised carbon atoms varies from 40 to 65% on the substrates oriented directly perpendicular to the plasma flow. On the parallel substrates, this indicator is much lower (from 17 to 35%) which might be due to different conditions of carbon film growth.

Analysis of the mechanical characteristics of the surface layer (Table 1) of the optical materials considered, deposited on various types of substrates, showed that DLC coating deposition leads to a surface hardness increase from 18% for Ge, to 250% for a substrate made from soft BaF\textsubscript{2}, accompanied by an increase in elastic modulus of the hardened surface of between 10 and 36%. Thus the tests of mechanical hardness of samples of Ge and Si showed that DLC coating deposition provides a surface hardening corresponding to “0” hardness class according to OST 1901-95.

An increase of surface roughness was observed on substrates from soft materials. This is might be due to surface layer erosion of such materials under the influence of ion beams. The matter demands further study, and the optimisation of the technological process for these materials.
Figure 2. Typical Raman spectrum of DLC-coating and its decomposition (Ge substrate, sp$^3$ – 48%)

Table 1. Mechanical characteristics of DLC coatings

| Substrate material | Coating thickness, nm | Substrate material hardness, GPa | DLC-coating hardness, GPa | Substrate surface modulus of elasticity, GPa | Hardened surface modulus of elasticity, GPa |
|--------------------|-----------------------|---------------------------------|--------------------------|---------------------------------------------|--------------------------------------------|
| BaF$_2$            | 72                    | 1.7                             | 4.3                      | 66.03                                       | 90.4                                       |
| MgF$_2$            | 71                    | 7.2                             | 14.7                     | 136                                         | 162.4                                      |
| Si                 | 65                    | 12.10                           | 20.15                    | 116.5                                       | 130.7                                      |
| Ge                 | 101                   | 12.10                           | 14.36                    | -                                           | -                                          |

Measured spectral transmission characteristics of the studied on the samples are presented in Figures 3 and 4. On the basis of the analysis of the received spectral characteristics one can conclude that after hardening, DLC coating deposition preserves the spectral range of transmission of the prototypes in the IR range for BaF$_2$ and MgF$_2$, and also some anti-reflection for Ge and Si samples is observed.

Figure 3. Spectral characteristics of transmission of bare and strengthened MgF$_2$ and BaF$_2$
Results of determination of optical constants for DLC on substrates of Ge and Si are presented in Figure 5. Distinction of optical coefficients for DLC coatings on substrates of Ge and Si may be due to different conditions of carbon layer formation while deposition, and as a consequence, the different structure of a formed DLC film.

5. Hardening of anti-reflective coatings
Surface hardening of “soft” optical materials while preserving their optical properties can be considered as an important practical result, capable in increasing considerably the operational properties of these materials. At the same time semiconductor materials, as a rule, also require anti-reflection characteristics. During execution of this research, samples of substrates were made using the semiconductor materials Ge and Si with thin layer Al2O3-Ge anti-reflection coatings. Hardening
layers of DLC were subsequently deposited onto the surfaces of the aforementioned substrates. The measured transmission characteristics are given in Figure 6. Results of micro-hardness measurements of the hardened anti-reflective coatings are given in Table 2.

![Image](a) ![Image](b)

**Figure 6.** Optical characteristics (refractive and absorption coefficients) of DLC coating on substrates of (a) Ge, and (b) Si.

| Substrate | Hardness, GPa |
|-----------|---------------|
| Si        | 11.1          | 9.8           | 15.3          |
| Ge        | 12.5          | 4.1           | 16.8          |

**Table 2.** Results of micro-hardness measurements of Si and Ge samples covered with hardened anti-reflection coating.

The data analysis presented in Figure 6 and in Table 2 indicates that, with development, the DLC coating technology has the potential to preserve the desired IR transmission characteristics for optical details of the semiconductor materials Ge and Si and with anti-reflective coatings, and to improve their mechanical strength properties.

6. **Conclusion**

Experimental research showed that surface hardening of optical materials operated in IR range, by deposition of diamond like carbon coatings, using our developed technology of electro-arc deposition with separation of plasma flow and laser ignition of an arc, considerably improves the operational properties of these materials and preserves or improves their optical properties. The developed DLC deposition technology, including anti-reflective coatings, should be of great practical interest for developers of optical systems for modern thermo-vision devices working in conditions of aggressive mechanical impacts on optical elements.
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