Structure, Optical and Mechanical Performance of Silver-Doped Diamond-Like Carbon Composite Film

Jialin Fang[a], *Yuwei Liu*[a], *Xiaohong Jiang*[a,*],
A.V. Rogachev[b], *D.G. Piliptsou*[a,b*], *E.A. Kulesh*[b]

International Chinese-Belorussian Scientific laboratory on Vacuum-Plasma Technology

[a]*Nanjing University of Science and Technology, 200, Xiaolingwei street, Nanjing 210094, China;*

[b]*Francisk Skorina Gomel State University, 104, Sovetskaya Street, Gomel 246019, Belarus*

**jiangxh24@njust.edu.cn; *pdg_@mail.ru*

7th International Congress on Energy Fluxes and Radiation Effects (EFRE 2020)
September 14 - 26, 2020, Tomsk, Russia

Statement of the problem

DLC — a metastable form of carbon with a mixture of sp^2 and sp^3 bonds.

The properties of DLC are determined not only by concentration of sp^3 and sp^2 bonds, but also in size, degree of organization and distribution Csp^2 and Csp^3 clusters.

Properties of doped DLC:
High thermal resistance,
high wear resistance,
low mechanical stress.

the properties of doped DLC is strongly influenced by structure, chemical composition and chemical interaction of the elements.

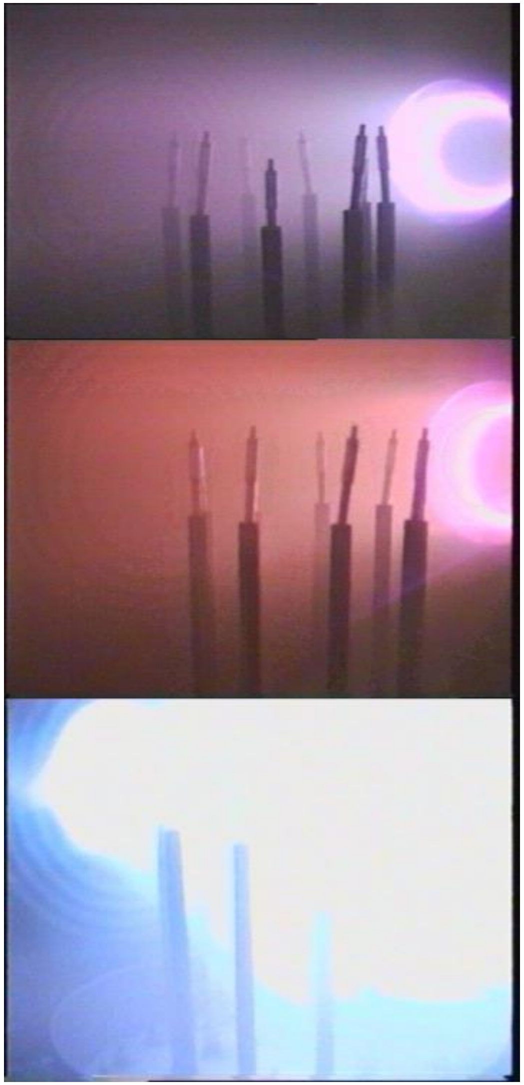
The nature of the doped elements has a catalytic or inhibitory effect on the synthesis of carbon clusters, their size and ratio of phases with sp^3 and sp^2 configuration of carbon.

The DLC phase is largely depends on the parameters of dispersion and catalytic activity of doped elements.

Physico-chemical processes occurring at interfaces in allowed systems, influencing the structure, composition and properties of coatings are determined by parameters of the formation of these layers, modes and conditions of the subsequent coating treatment, the nature and parameters of the doped elements.

The aim of this work is to study the effect of Ag concentration on the structure, mechanical and optical properties of carbon film. Knowing these values (transmission spectra, refractive index and bang gap) will allow us to develop the design of a α-C:Ag with a different Ag content.

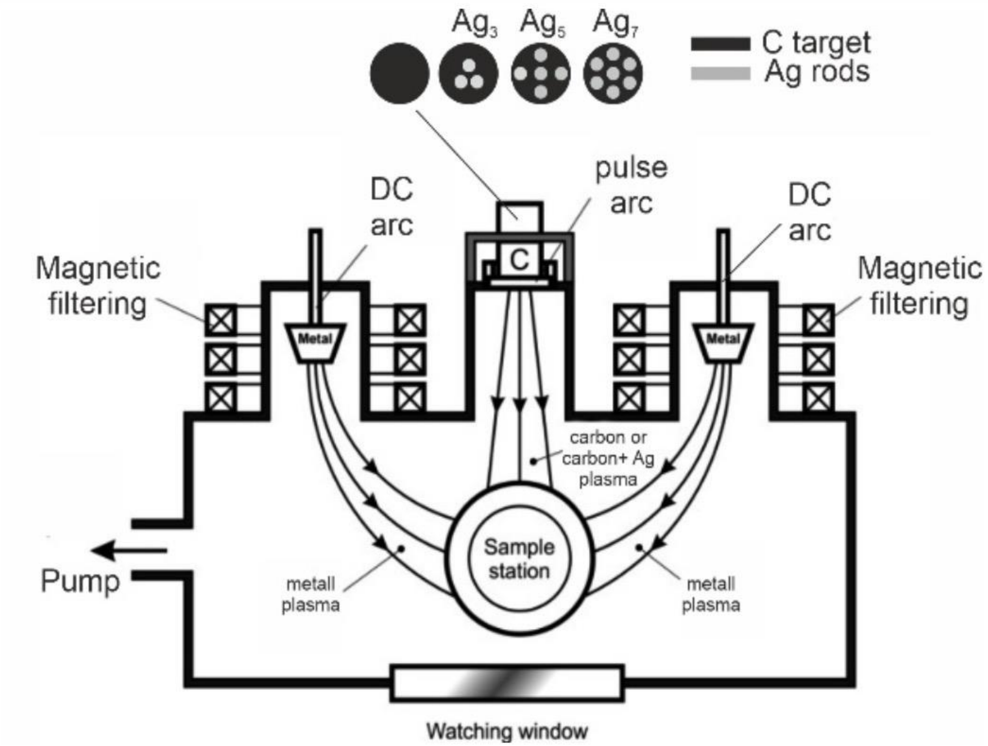
I The stage of formation of coatings



1. ionic surface cleaning and heating

2. applying a metal underlayer

3.applying an α-C:Ag



α-C:Ag coatings were obtained by sputtering a composite graphite target containing silver of various concentrations by pulsed arc discharge at the following parameters:
pulse duration τpulse = 150 μs,
pulse frequency f = 10 Hz,
discharge voltage Upulse = 350 V.

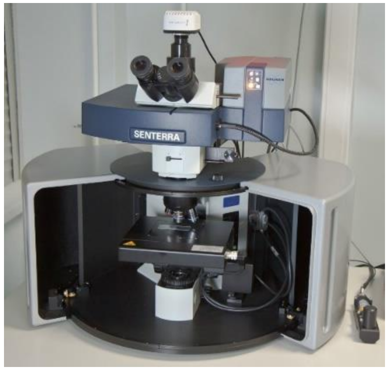
II Atomic concentration of elements and thickness of composite carbon coatings

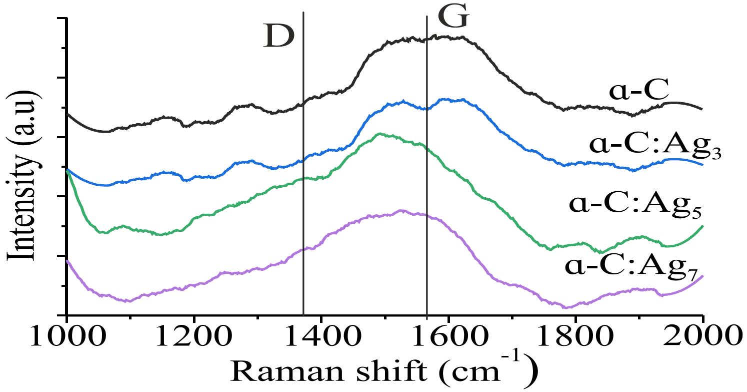
Sample	**C, at. %**	**Ag, at. %**	**O, at. %**	**Thickness, nm**
α-C	87.4	-	12.6	159.6
α-C:Ag_3	72.0	12.8	10.4	129,4
α-C:Ag_5	64.1	16.3	18.3	127.0
α-C:Ag_7	60.7	21.3	10.2	135.8

The concentration of elements by laser ellipsometry and the concentration of elements in the coatiin the coating were determined by X-ray photoelectron spectroscopy using PHI QUANTERA II (Japan). The results of determining the thickness of the coatings ng are shown in table.

The ratio of C/Ag atomic concentrations in the coating was changed by varied a sprayed surface area of the composite cathode occupied by graphite to the placement area of inserts produced of silver with a purity of 99.999%. When choosing the ratio of areas, we were guided by pre-defined rates of graphite and silver sputtering.

III Results And Discussion: A.Structure





Raman spectra of carbon coatings with different concentrations of silver

Raman spectra can be represented as the sum of two peaks D and G with centers at 1380 cm^{-1} and 1560 cm^{-1}. The D-peak is usually attributed to the presence of disordered diamond-like carbon and the G-peak to that of graphite carbon. The results of the mathematical processing of the spectra are shown in Table.

Sample	I_D/I_G Ratio	G peak position cm^{-1}	G peak width, cm^{-1}
α-C	0.86	1621	104.3
α-C:Ag_3	0.68	1552	128.5
α-C:Ag_5	0.27	1519.3	103.5
α-C:Ag_7	0.13	1497	172.4

Based on the analysis of Raman spectroscopy data, we can conclude about the microstructure of carbon coatings: they consist of sp^2-hybridized carbon atoms dispersed in an sp^3-bonded carbon matrix, with increasing silver concentration, the coating structure becomes more disordered (increasing in the width of the G peak), which implies an increase the number of carbon atoms in the sp^3 state of hybridized bonds.

III Results And Discussion: *A. Structure*

Fig.1 The volume structure was studied by transmission electron microscopy

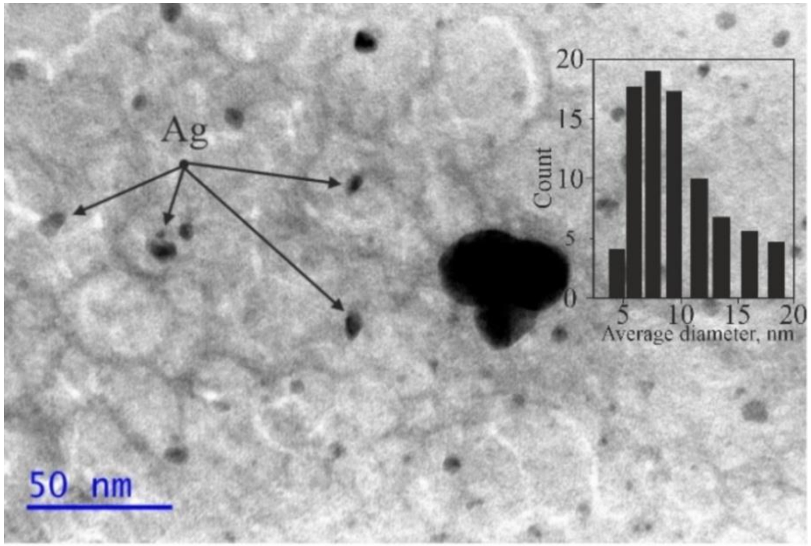
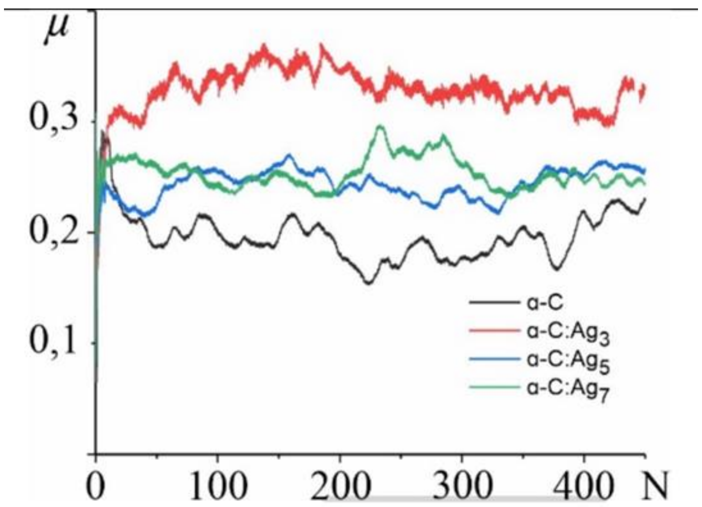


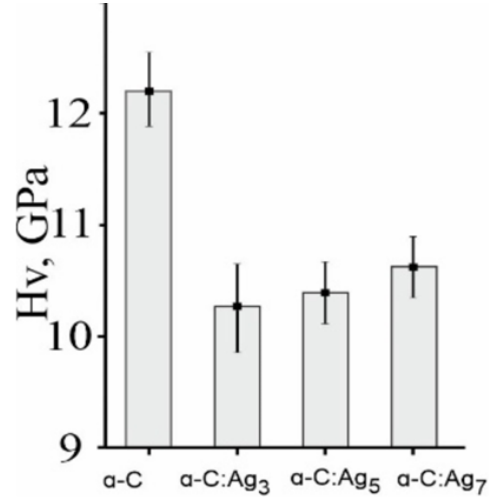
Fig.2 TEM image and particle size distribution for α-C:Ag5 coating

At a low Ag concentration of 12.8 at. %, an amorphous structure was observed identical to the microstructure of non-doped a-C coatings, which indicates that all Ag atoms were completely dissolved in the volume of an amorphous carbon matrix. However, when the concentration of the alloying element reached 16.3 at. %, the Ag atoms began to combine and form an amorphous metal phase with a cluster diameter of no more than 3 nm. At a high concentration (Fig. 2), it can be seen that metal nanoparticles are present in the coating, and using diffraction, the presence of crystalline structure with interplanar distance parameters characteristic of silver crystals that are fairly evenly distributed in the volume of the carbon matrix is established. (Dark spots correspond to Ag particles, while the bright region corresponds to the carbon matrix).

III Results And Discussion B. Mechanical Properties



Friction curves of silver-doped carbon coatings

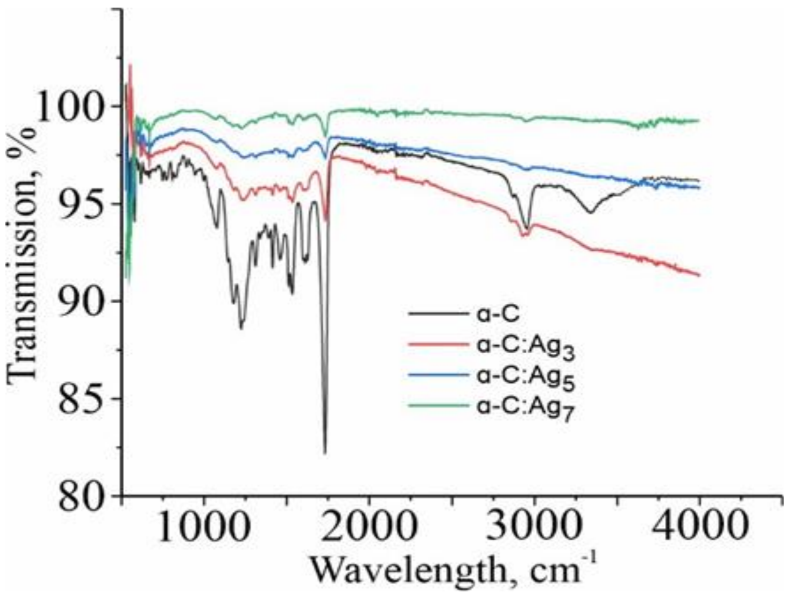


Dependence of microhardness of coatings on silver concentration

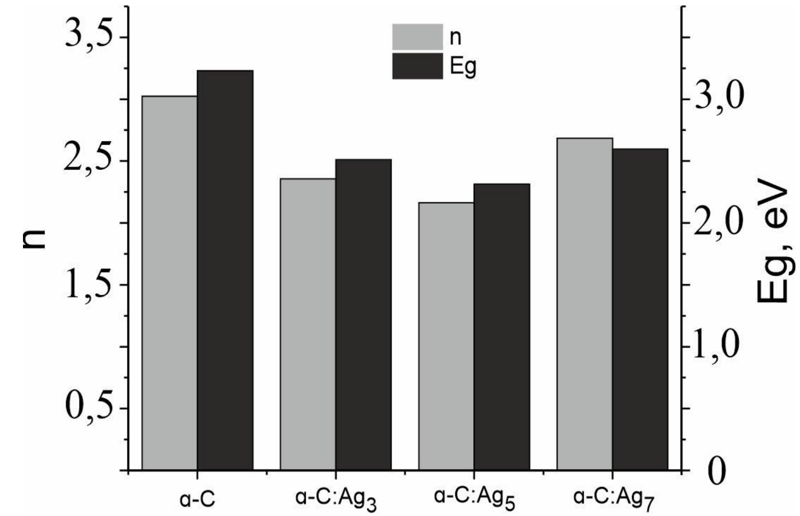
It was found that the **friction coefficient** for doped coatings is higher than for α-C, but it is observed to decrease with increasing silver concentration. The maximum values of the friction coefficient were established for a-C:Ag_3 coatings with a silver concentration of 12.8 at. %. For higher concentrations of Ag in a-C coatings, the changes in the friction coefficient are identical and are within the standard deviation for each test.

The influence of a softer substrate will reduce the **composite hardness** of the coating-substrate system. It can be seen in Fig. 5 that the microhardness of the composite coatings decreases by 15 % upon alloying, however, with an increase in silver concentration, its insignificant increase is observed, which is determined, according to Raman spectroscopy data, by a decrease in the size of Csp^2 carbon clusters (Hall-Petch law), and also by a change in the structure of silver clusters from amorphous to crystalline, which determines the increase in microhardness with increasing silver concentration to 21.3 at. %.

III Results And Discussion C. Optical Performance



IR transmission spectra of the a-C:Ag coatings with different concentrations of silver



The band gap Eg and the refractive index n of coatings with different concentrations of silver

It was found that with increasing silver concentration, a change in the shape of the spectrum occurs and an increase in the transmittance from 86% to 97% is observed. In the short-wavelength region of the spectrum, absorption is enhanced. Taking into account the fact that the obtained coatings are non-hydrogenated and there is no effect of C–H groups on the formation of the spectrum, it can be assumed that the change in the transmission spectrum is determined by the change in the structure of the coating and the electronic configuration of both silver and carbon atoms

The ***Eg*** for carbon coatings with an amorphous structure, in accordance with the cluster model, depends on the size of π-coupled clusters and decreases with increasing Csp^2 carbon clusters. As shown by Raman spectroscopy, the number of Csp^2 clusters decreases with increasing silver concentration in the coating, which determines the increase in the width of the Eg.

The ***refractive index n*** for the coating α-C and α-C:Ag_7 are at the same level and amount to 2.72. At a silver concentration of 16.3 at. %the refractive index reaches a value of 2, which, according to the data shown in Fig. 6, indicates the possibility of using these coatings for antireflection of germanium substrates

Conclusion

The effect of the concentration of Ag on the microstructure, mechanical and optical properties of the resulting coatings was studied.

1. The results of studying the microstructure of ɑ-C:Ag coatings by Raman spectroscopy showed that there is a decrease in the size, degree of ordering, and the content of Csp^2 clusters with an increase in the concentration of Ag in the coating.
2. Transmission electron microscopy showed that with an increase in the concentration of Ag in the coating, a transition is observed from an amorphous carbon structure with silver atoms dissolved in the volume of the amorphous carbon matrix to the formation of metal nanoparticles fairly uniformly distributed inside the carbon matrix.
3. The change in the coefficient of friction and microhardness of coatings was established depending on the amount of silver.
4. The increase in transmission in the IR range for doped coatings is shown.
5. A change in the refractive index and band gap is established, which is explained by both the restructuring of the carbon matrix structure and the change in the optical absorption edge due to doping of the carbon coating with silver.

СПАСИБО ЗА ВНИМАНИЕ !

谢 谢！

THANK YOU FOR YOUR ATTENTION!

This work was supported by Intergovernmental Cooperation Projects in the National Key Research and Development Plan of the Ministry of Science and Technology of PRC (projects No. 2016YFE0111800, for 2016–2019) and SPSR "Physical materials science, new materials and technologies" of the Republic of Belarus (task 4.1.24).