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# PROPERTIES OF DIAMONDLIKE CARBON FILMS DEPOSITED ON SILICON, QUARTZ AND GLASS SUBSTRATES USING LASER PLASMA DEPOSITION

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Abstract. Investigation of diamondlike carbon films using Raman spectroscopy method has showed, that deposited coatings according to substrate material can show graphite, nanocrystalline carbon or amorphous diamondlike carbon films' properties with the content of  $sp^3$  hybridized carbon atoms of ~20 %.

#### **1. INTRODUCTION**

Nanostructured diamondlike films have been the object of intensive study for world scientific community for several decades. This interest is caused mainly by two basic directions of use of diamondlike structures: in electronics and as a protective coating. The first direction includes exploration of ways to create lowvoltage and highly stable autoelectronic emitters for flat displays and microwave vacuum electronic devices [1], this is mainly caused both by the presence of a low emission threshold and MIS structures, thin-film transistors for solar elements, electromechanical structures on the basis of diamondlike carbon coverings building [2] with the purpose of practical realization of diamond semi-conductor electronics. The second direction is based on high durability and wear resistance of diamondlike coverings, besides they possess low friction coefficient, high heat conductivity and chemical inertness. It makes them very attractive for use as coating for critical mechanical technical units, and for magnetic storage devices [3]. The high transparency in visible and IR-range allows to use carbon films for mechanical protection of optical elements.

Properties of carbon films depend on several parameters characterizing their structure and composition. For pure carbon films, obtained using laser plasma vacuum deposition, such main parameters are the ratio of the  $sp^3/sp^2$  bonds content and a measure of orderliness of carbon atoms in a film and clusterization degree. [4]

It is known that physical properties of substance can cardinally change when transition to nanostuctured state takes place. In particular such law can be observed during formation of diamondlike carbon films. It is related to great variety of phase microstructural organizations in these films, having different forms and sizes that compose the film of carbon nanoclusters. These clusters possess unique quantum-dimensional and other properties depending on formation conditions. For example, it is known, that emission properties of diamondlike films are improved considerably with increase of defectiveness upto formation of an amorphous material which essential attribute is a diamond hybridization type of valent electrons pertinent to carbon atoms [5].

Recently a set of techniques for obtaining diamondlike carbon coatings is in use. Among them are deposition using vacuum-arc discharge [6,7], chemical-plasma deposition [6,8] or magnetron beam deposition. Every method has its own advantages and disadvantages.



The number of laser pulses -100, the temperature of the substrate -225 °C.

**Fig. 1.** Thickness of a diamondlike film dependence on acting laser radiation energies for different types of substrates

Use of lasers as an energy source for graphite evaporation has a number of advantages such as process purity (there are no impurity gases), high accuracy and productivity. Use of pulse lasers makes vacuum requirements less rough due to short time of interaction.

#### **2. EXPERIMENTAL**

The diamond-like carbon films were deposited by laser ablation of graphite, using Nd-glass laser ( $\lambda$ =1.06 µm). The pulse laser duration was 30 ns. Films were deposited in vacuum. The pressure was 10<sup>-3</sup> Pa. The graphite target had angle 45 degree to the axis of the acting laser radiation. Substrates were placed in parallel to

the graphite target. The distance from a target to a substrate was 10 cm. A system heating substrates was used during deposition. A Spectroscopic Ellipsometry, Rutherford Back-Scattering (**RBS**) and Raman Spectroscopy systems have been used to analyze the obtained films' properties.

### 3. RESULTS AND DISCUSSION

Some parameters of diamondlike carbon films such as optical transparency or coefficient or microhardness can significally depend on thickness of deposited coating. Therefore measurements of diamondlike carbon (DLC) films' thicknesses have been carried out depending on energy of acting laser radiation and substrate material. Films' thickness was measured by ellipsometry method using WVASE ellipsometer. Films were deposited on quartz, glass and silicon substrates. Corresponding to a range of influencing laser radiation energy of 2 - 8 J films were deposited on quartz substrates. The figure 1 shows that thickness significantly changes for different laser radiation energies. Besides, measurements have shown, that thickness of (DLC) films, deposited on silicon, glass and quartz substrates using the same laser energy of 5 J actually does not depend on substrate type.

In order to determine layer content of carbon atoms in samples, obtained under different conditions of films' deposition, the Rutherford He+ ions Back-Scattering method (RBS) was used [9]. Films were deposited on silicon substrates having <110> orientation.

Substrate temperature, number of laser pulses and vacuum level in the vacuum chamber had been varied during the experiment. Results are shown in Table 1. Energy of acting laser radiation was equal to 5 J. Calculations were carried out using a method that includes computer plotting of a reference spectrum and its subsequent adjustment in the area under the carbon peak in an experimental spectrum to perfect match.

№	Number of pulses	Vacuum, Torr	Temperature, K	Layer content of carbon atoms, cm-2
1	100	2•10-5	498	1,15•10 <sup>18</sup>
2	100	2•10-5	373	3,5•10 <sup>17</sup>
3	100	8•10 <sup>-6</sup>	293	$2,0 \cdot 10^{17}$
4	100	$1 \cdot 10^{-3} - 7 \cdot 10^{-4}$	293	1,9•10 <sup>17</sup>
5	380	2•10-5	293	$1.7 \cdot 10^{17}$

**Table 1.** Layer content of carbon atoms in diamondlike films deposited on silicon substrates. The energy of acting laser radiation amounts to 5 J.

Indication of layer content in the table instead of film thicknesses is related to the feature of method RBS in which ions with energies about MeV order of magnitude are used as an analyzing beam, it makes the method insensitive to the nature of chemical bounds and the electronic structure of the investigated material.

Having assumed that the nuclear density of obtained films is approximately equal to nuclear density of diamond that comes to  $1,76 \ 10^{23} \ \text{cm}^{-3}$ , it is possible to

estimate films' thickness for samples shown in table 1. It comes practically to 10 - 65 nanometers [9].

Additional research of obtained films' structure is made using the method of Raman spectroscopy. In our case parameters of the film deposited on silicon, glass and quartz substrates were investigated. Energy of acting laser radiation was 5 J. All substrates were heated to temperature of 498 K. Residual gases pressure in the vacuum chamber was  $2 \cdot 10^{-3}$  Pa. Obtained Raman spectra were processed using Lorents curves approximation.



**Fig. 2.** The trajectory of carbon transition from graphite to tetrahedral amorphous state with contingent schematic variation of G-peak position and  $I_D / I_G$  ratio [10].

Most of amorphous carbon experimental Raman spectra can be interpreted by phenomenological three-stage model [4] that defines transition of carbon from graphite to tetrahedral carbon (ta-C). This process consists of three stages as shown on figure 2: a) graphite  $\rightarrow$  nanocrystalline graphite (nc–C);

b) nanocrystalline graphite  $\rightarrow$  amorphous carbon (a–C);

c) a–C  $\rightarrow$  ta–C (  $\rightarrow$  ~ 100 % sp<sup>3</sup>, defective diamond).

Let's consider change of G-peak position and  $I_D/I_G$  ratio corresponding to obtained films (Table 2).

 Table 2. Results of Raman scattering spectra processing using Lorentz curves approximation

$I_D, cm^{-1}$	$I_{G}, cm^{-1}$	$I_D / I_G$			
Glass					
1350	1579	0,57			
Quartz					
1327	1544	0,42			
Bronze					
1330	1529	0,86			
Silicon					
1430	1561	0,72			

As we can see from the table 2 structure of the film deposited on a glass substrate lies on boundary of graphite structure to nanocrystalline graphite structure transition. Films deposited on quartz, bronze and silicon substrates are characterized by transitional structure between nanocrystalline graphite and amorphous carbon film and the  $sp^3$  carbon atoms content amounts to 10 - 20 %.

It should be noted separately that obtained spectra contain pronounced peaks near 1332 cm<sup>-1</sup> that correspond to natural diamond peaks [10].

#### 4. CONCLUSIONS

It is experimentally shown that the material of a substrate has weak effect on thickness of deposited diamondlike films. Films thicknesses depend on both energy of laser radiation affecting graphite target and substrate temperature. Films' thicknesses obtained by the ellipsometry method are consistent with the thicknesses measured on basis of mathematical processing of obtained Rutherford Back Scattering spectra.

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