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# PULSED LASER DEPOSITION OF DIAMOND-LIKE AMORPHOUS CARBON FILMS FROM DIFFERENT CARBON TARGETS

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**Abstract.** The laser-plasma method was used for a diamondlike carbon films deposition. The influence of structure of graphite targets on the characteristics films was investigated. The targets of four types were used: target N1 was made from highly oriented pyrolytic graphite, target N2 was made from pure fine-grained synthetic graphite, the target N3 was also made from graphite MG1 however it was exposed additional annealed in vacuum, the target N4 was pressed from a synthetic diamond powder. It have been shown, that the best hardness of 32 GPa has been fixed for the film deposited from annealed graphite MG1. The presence of hydrogen impurity in the carbon targets influences on the films mechanical characteristics.

## 1. INTRODUCTION

Pulsed laser deposition (PLD) is an emerging thin film technology, which enables the deposition of a variety of materials with controlled composition and properties, including diamond-like carbon (DLC). The application of PLD for low temperature DLC deposition is studied in a number of works, for example Chrisey and Hubler (1994), Bonelli et al. (2002), Voevodin and Donley (1996). A strong dependence of film properties on PLD process parameters, such as laser power density and wavelength, substrate temperature and bias is typically reported (Voevodin and Donley 1996, Ong and Chang 1997, Lifshitz 1996). It is necessary to note, that there are other parameters of the laser plasma deposition process, which can influence on structure and properties of the produced films. It is a duration and form of a laser pulse, laser pulses repetition frequency, laser beam incidence angle on a target, laser beam scanning velocity on a target surface and etc. However, it is smaller attended these parameters. These parameters are fixed for the certain laser type or are selected to minimize an erosive crater size on a target surface to reduce probability of the large carbon clusters production. The material of a target is one of such parameters which insufficiently are investigated. It is obvious, that composition and energetic characteristics of the laser-produced carbon plasma plame depends on which form of carbon is used as the target material. However, high-

purity highly oriented pyrolytic graphite (HOPG) targets are most commonly used in PLD of DLC films.

So, in the present work we try to compare HOPG with other carbon target materials in the course of PLD of the carbon films.

## 2. EXPERIMENT

For the films deposition the LOTIS-TII pulsed YAG:$Nd^{3+}$ laser with a wavelength $\lambda = 1064$ nm and a pulse duration $\tau = 20$ ns (full width at half maximum FWHM) was used. The pulse repetition rate was changed from 1 to 5 Hz. Laser radiation was focused on graphite target, placed in vacuum chamber under $2{,}6\times10^{-3}$ Pa. The target was mounted at a 45° with respect to the laser beam and was constantly rotated to provide fresh surface for ablation. Velocity of the laser beam scan on the target surface was about 2 mm/s. The laser intensity was $1{,}7\times10^{8}$ W/cm$^2$. The laser beam diameter was kept constant (about 2 mm). The number of laser pulses for every experiment was 10000. Films were deposited on substrates which placed parallel to graphite target at distance 100 mm from it. Silicon and quartz glass plates were used as substrates. Films deposition was carried out at room temperature. Four different types of carbon targets were used.

The target N1 was made from highly oriented pyrolytic graphite (HOPG). This graphite has high density close to a theoretical limit 2.25 g/sm$^3$, and has diffraction of x-ray beams close to monocrystal natural graphite.

The target N2 was made from pure fine-grained synthetic graphite (MG1). This type of graphite is isotropic. Average density of this material is about 1,65 g/sm$^3$. The porosity of graphite MG1 is 25÷26 %.

It is known, that the porous graphite can contain significant amount of physically and chemically adsorbed gas impurity. The target N3 was also made from graphite MG1 however it was exposed additional annealed in vacuum $\sim10^{-2}$ Pa at 2273K during 2 hours to purify from gas. The influence of high temperature vacuum annealing on the content of hydrogen in graphite targets was estimated by secondary ions mass spectrometer (SIMS) on radicals CH and $CH_2$ emissions. The SIMS have shown the content of the hydrogen impurity in initial graphite MG1 is about 4 at.%. After vacuum annealing the CH- and $CH_2$- radicals emissions decreases in 25÷30 times.

The target N4 was pressed from a synthetic diamond powder with the average grain size of 45 microns. Polyvinyl alcohol (PVA) was used as binder. The mass concentration of the binder was 5 %. The target was a tablet by a diameter of 15 mm and thickness of 5 mm. The target was dried after pressing at T = 400 K during one day.

Profiles of the erosive “cones” formed on the target surface and films thicknesses were measured using Talystep (USA) profiler. Raman spectroscopy measurements were performed at room temperature with a Spex 1403 double monochromator using the 514,5 nm line of an argon laser at a power level of 100 mW in the backscattering configuration. The micro-hardness measurements were carried

out with a Shimadzu DUH 202 ultra-micro hardness tester using a Berkovich diamond indenter. The normal loads applied to the diamond indenter were kept in the 0,5-2 mN range.

## 3. RESULTS

The main results of the investigation are given in the Table 1 and in Fig. 1. It is obvious, that the efficiency of the material evaporation under an influence of powerful laser pulses differs for various graphite targets more than 3 times. It is possible to assume, that the efficiency of the target material evaporation correlates with the graphite thermal conductivity. The thickness of the deposited carbon films correlates with erosive craters size on targets surface. For the pressed diamond powder target the emission of a number of macro particles has been visually observed. As result the erosive crater for the target N4 was heterogeneous and the determination of its size was very difficult. It should be noted that the macro particles emission from initial graphite MG1 has been observed too, however in a significantly less degree than for diamond target. The macro particles emission may be connected with an active gassing from targets N2 and N4 at the absorption of the laser pulses energy. The reason of the gassing for the target N4 is the decomposition organic binder which exists between diamond particles. For a target N2 it is possible the gases desorption from pores surfaces.

**Table 1.** Characteristics of carbon films deposited from the different carbon targets

| Target | Evaporated volume of the target material, $mm^3$ | Film thickness, nm | Average energy of particles making carbon plasma, eV | I(D)/I(G) | Microhardness, GPa |
|---|---|---|---|---|---|
| Highly oriented pyrolytic graphite | 2,77 | 160 | 15 | 0,752 | 17 |
| Initial graphite MG1 | 0,85 | 45 | 72 | 0,275 | 10 |
| Annealed graphite MG1 | 1,05 | 35 | 91 | 0,461 | 32 |
| Pressed diamond powder | - | 20 | - | 0,394 | 29 |

Knowing the evaporated volume of the target material and energy of the laser impulse, it is possible to estimate average energy of particles making carbon plasma. Results of this estimation are also given in the Table. Kinetic energy of the particles making carbon plasma, is the important parameter defining the characte-

ristics of deposited films. It has been shown in Voevodin and Donley (1996), Lifshitz (1996), that the fraction of the $sp^3$-bonded carbon in deposited films grows with increase in kinetic energy of particles in a range from 0 to 300 эВ. Transition of the films structure from graphitic to the diamond-like occurs in the range of 80…100 эВ. Thus, it is possible to assume, that films deposited from graphite MG1 are diamond-like while films deposited from HOPG have graphitic structure.

One of the most widely used methods of the carbon films structure analysis is the Raman spectroscopy. The Raman spectra of carbon films obtained in the present work are shown in Fig. 1. In the spectra of all deposited films the broad peak with a maximum in the range of 1530...1545 $sm^{-1}$ (G-peak) dominates. Except this peak, second very weak peak with a maximum in the range of 1310…1355 $sm^{-1}$ (D-peak) is observed.

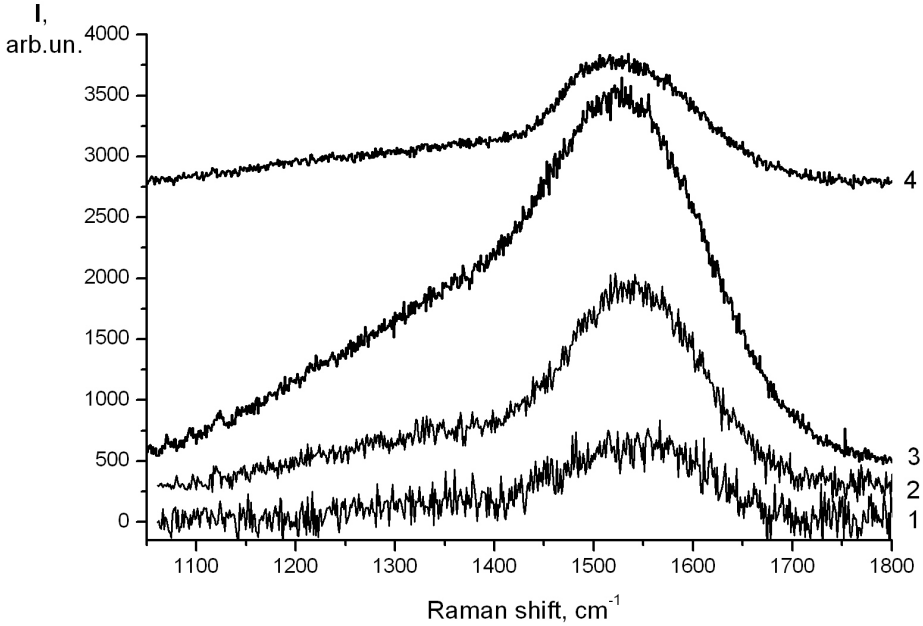


**Figure 1:** Raman spectra of carbon films deposited from the different carbon targets: 1 - initial graphite MG1; 2 - annealed graphite MG1; 3 - highly oriented pyrolytic graphite; 4 - pressed diamond powder.

According to the approach proposed in Ferrari and Robertson (2000, 2001) for description of the Raman spectra of carbon films reduction of the intensity ratio of D and G-peaks (I (D)/I (G)) evidences about increasing of the $sp^3$-bonded carbon fraction in a films. Films with G-peak domination are characterized by the high $sp^3$-bonded carbon contents and are usually named “diamond-like” (Ferrari and Robertson 2000, 2001, 2004). Results of the Raman spectra decomposition are given in the Table 1. It is clear that the material of the carbon target have the con-

siderable influence on the structure of the carbon films deposited by a LPD method. Comparing the obtained results with model (Ferrari and Robertson 2000, 2001) we can assume that the fraction of the $sp^3$- bonded carbon in deposited films decreases when the target material changes of the graphite target materials in the row of initial graphite MG1 - annealed graphite MG1 - pyrolytic graphite. The fraction of the $sp^3$-bonded carbon in the carbon film deposited from the target №4 (pressed diamond powder) is a few lower than for the film deposited from initial graphite MG1. Presence of the $sp^2$-bonded carbon at a film deposited from pressed diamond powder may be connected with the high contents (5 mas.%) of organic binder in the target material.

It should be noted that intensity of the Raman signal for the carbon film deposited from initial graphite MG1 is several times less than for the films deposited using the other graphite targets. Moreover, the this sample is characterized by the high level of a background luminescence. High degree of disorder of the film structure and/or the high contents hydrocarbon radicals in the film can be the reason of this effect. Thus, in spite of higher fraction of the $sp^3$- bonded carbon the film deposited from initial graphite MG1 can have lower mechanical characteristics than other samples.

The results of microhardness measurement of deposited films (see Table 1) are with a good agreement with the Raman spectroscopy data. The best hardness of 32 GPa has been fixed for the film deposited from annealed graphite MG1. The film deposited from HOPG has hardness about 2 times smaller. The film from initial graphite MG1 has the lowest hardness (about 10 GPa). It can be connected with the high film disorder and/or high contents of the hydrocarbon radicals in this film.

Thus, the structure of a carbon target influence on the contents of the diamond-like phase in carbon films deposited by the PLD method. The targets which were made from fine-grain polycrystalline graphite and pressed synthetic diamond micro powder allow depositing films with higher fraction of the $sp^3$-bonded carbon in comparison with targets from highly oriented pyrolytic graphite. The presence of hydrogen impurity in the carbon targets can also influence on the films mechanical characteristics.

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