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## Preparation and Study of Graphene-based Films Produced on Diamond-like Carbon (DLC)

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**Abstract.** Graphene-like films on Diamond-like carbon (DLC) have been obtained on quartz by pulsed laser deposition (PLD) of carbon at room temperature with subsequent thermal annealing performed under Ultra High Vacuum conditions. The surface formation of a graphene-like film on top of the DLC has been investigated as a function of many parameters and characterized by several analytic techniques. At high thermal treatment (1373 K) and medium laser fluence ( $5.6 \text{ J/cm}^2$ ), such films exhibit high performances as transparent conductors.

### Introduction

Carbon forms many different crystalline and disordered structures. It is thanks to its three hybridisation states,  $sp^3$ ,  $sp^2$  and  $sp^1$ . Due to this fact, it is possible to generally obtain low-dimensional carbon materials, e.g., graphene, carbon nanotubes (CNTs), fullerenes.

Diamond-like carbon (DLC) is a class of amorphous carbon material that displays some of the typical properties of diamond. DLC is usually applied as coatings to other materials that could benefit from some of these properties. DLC is a semiconductor with high mechanical hardness, chemical inertness and optical transparency. It contains a significant fraction of  $sp^3$  bonds. The extreme physical properties of diamond derive from its strong, directional  $\sigma$  bonds. Diamond has a wide 5.5 eV band gap, the largest bulk modulus of any solid, the highest atom density, and the smallest thermal expansion coefficient [1,2]. DLC has some extreme properties similar to diamond, such as the hardness, elastic modulus and chemical inertness, but these are achieved in an isotropic disordered thin film with no grain boundaries. It is much cheaper to produce than diamond itself. This has great advantages for many applications.

One of the possible and very attractive applications is to use DLC as a buffer layer to grow graphene or graphene-like films [3]. This can be achieved by local thermal treatment of the DLC layer using either a laser or thermal treatment in a furnace. Since the process has still not been very much explored, it is therefore of high interest in future studies.

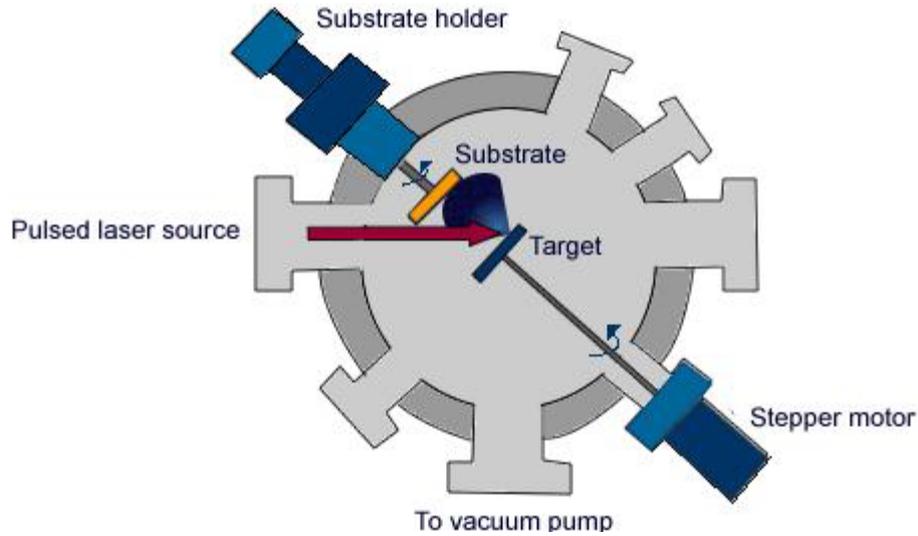
On the other hand, graphene is a two-dimensional material consisting of only one atomic layer of carbon atoms in  $sp^2$  configuration. The atoms form honeycomb lattice with extremely high Young modulus in plane and the delocalized  $\pi$ -electrons make it an excellent thermal and electrical conductor. There are many approaches to synthesize graphene, such as mechanical exfoliation, chemical vapor deposition (CVD), liquid-phase exfoliation or reduction from graphene oxide [4,5,6,7]. However, they all possess the same disadvantage, which is the necessity of transfer of the graphene film. It is very complicated and always with a poor transfer rate due to the instability of graphene normal to the plane. Our method avoids the transfer step thanks to the ability of producing graphene directly on transparent insulating substrate (quartz) using DLC as a buffer layer.

There are several ways of producing DLC: ion beam, mass selected ion beam, sputtering, cathodic arc, plasma-enhanced CVD (PECVD) and pulsed laser deposition (PLD). In this paper, we discuss the PLD production of DLC on quartz with a view to synthesize graphene on DLC. This will be reported elsewhere.

### Material and methods

The experimental setup is shown in Figure 1. The laser beam is focused inside the vacuum chamber on the surface of the target, consisting of highly-oriented pyrolytic graphite (HOPG). The target is mounted on a rotational holder which allows the rotation of the target in order to ablate the material homogeneously. There is also a substrate holder with variable temperature in front of the target where the ablated material is deposited. The pressure inside the vacuum chamber reaches the order of  $10^{-7}$  mbar.

The deposition was performed with an EMG 201 MSC KrF excimer laser at  $\lambda = 248 \text{ nm}$ , with a pulse duration of 20 ns and a repetition rate of 10 Hz. The working distance between the target and the sample was 5.5 cm. The laser fluence varies from  $2.6 \text{ J/cm}^2$  to  $8.4 \text{ J/cm}^2$ . The laser beam spot area was estimated using



**Figure 1.** PLD configuration [8].

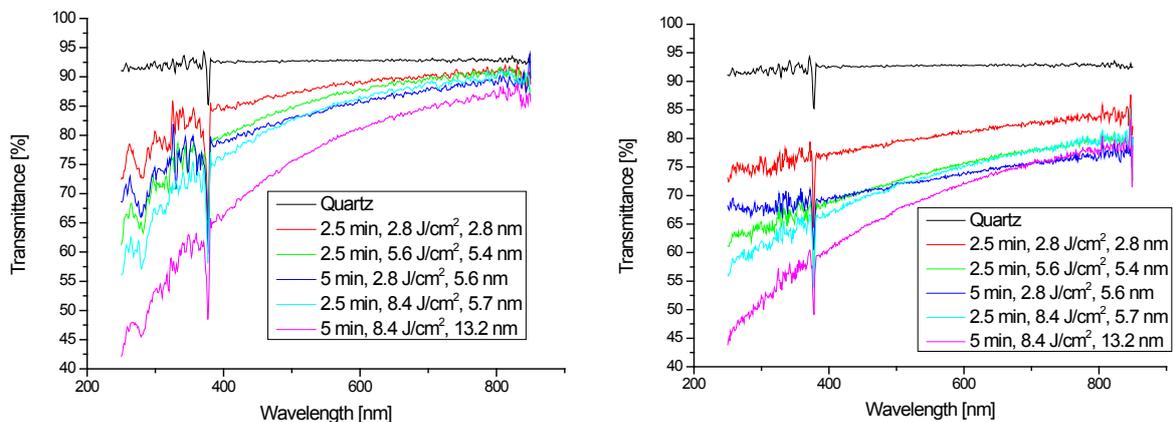
a silicon sample at  $0.0106 \text{ cm}^2$ . Carbon atoms were ablated from a high purity HOPG target. All the DLC films were grown on  $10 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$  quartz samples which were cleaned prior to the deposition in successive baths of acetone, ethanol, isopropanol and deionized water for 5 minutes each.

The influence of deposition time and laser fluence on the DLC film properties was studied. The thickness is expected to vary with the deposition time while the  $\text{sp}^3/\text{sp}^2$  content ratio is expected to vary with the laser fluence. The thickness of the DLC films was characterized by a Taylor Hobson Talystep profilometer and DekTak profilometer. The optical properties of the films were studied using UV/VIS/NIR Perkin ELMER Spectrophotometer Lambda 19. The spectra were acquired from 250 nm to 850 nm, using a scan speed of 120 nm/min. The slit width of the spectrophotometer was set to 2 nm. The spectrophotometer was calibrated using blank sample of quartz. Optical band gaps were calculated from the optical spectra of the films using Tauc's method [9]. Raman spectroscopy was performed using the LabRam Aramis spectroscopy. We used a green laser at 532 nm, with the filter giving us a laser power of 9 mW, a hole of  $500 \mu\text{m}$  (not confocal), the 1800 line/mm grating and the  $\times 50$  magnification lens.

## Results and discussion

### Optical spectra

The transmittance axis shows values from 40 to 100 %. 100 % transmittance corresponds to no sample in the spectrophotometer. The transmittance of blank quartz substrate is shown. If we take a closer look on the spectra (Figure 2), we can see that at higher laser fluences ( $5.6\text{--}8.4 \text{ J/cm}^2$ ), the transmittance decreases with decreasing wavelength faster than at low laser fluence ( $2.8 \text{ J/cm}^2$ ) which could be caused by different  $\text{sp}^3/\text{sp}^2$  ratio. The transmittance is lower after the thermal treatment because of the graphitization which occurs on the surface.



**Figure 2.** Transmission spectra as deposited (on the left), after annealing at  $800 \text{ }^\circ\text{C}$  (on the right).

### Optical band gap calculation

The optical band gap was calculated using Tauc's method. The basic assumption in Tauc's method is that the semiconductor material has parabolic band edges and energy-independent matrix elements for intraband transitions. It uses only the data acquired by transmittance measurements and is based on the Tauc's relation

$$\alpha hv = (hv - E_g)^n, \quad (1)$$

where  $hv$  is the photon energy in eV,  $E_g$  is optical band gap,  $n$  is index depending on the type of transition (0.5 for allowed direct transitions, 1.5 for forbidden direct transitions, 2 for allowed indirect transitions, 3 for forbidden indirect transitions), and  $\alpha$  is absorption coefficient, in this case given by Lambert–Beer–Bouguer's law with the assumption of 0 % reflectivity

$$\alpha = -\frac{\ln(T)}{t}, \quad (2)$$

where  $T$  is transmittance,  $t$  is thickness. By plotting  $(\alpha hv)^{1/n}$  against  $hv$  (Tauc's plot), we can determine the optical band gap from the E axis intercept of the plot (see Figure 3).

Changshi and Feng [10] proposed small modification of Tauc's method in order to improve the precision of optical band gap calculation. In most cases, the exact value of the index  $n$  is not known for certain materials, therefore the Tauc's plot cannot be obtained. To obtain the value of the index  $n$ , they have modified the Tauc's relation to the following form:

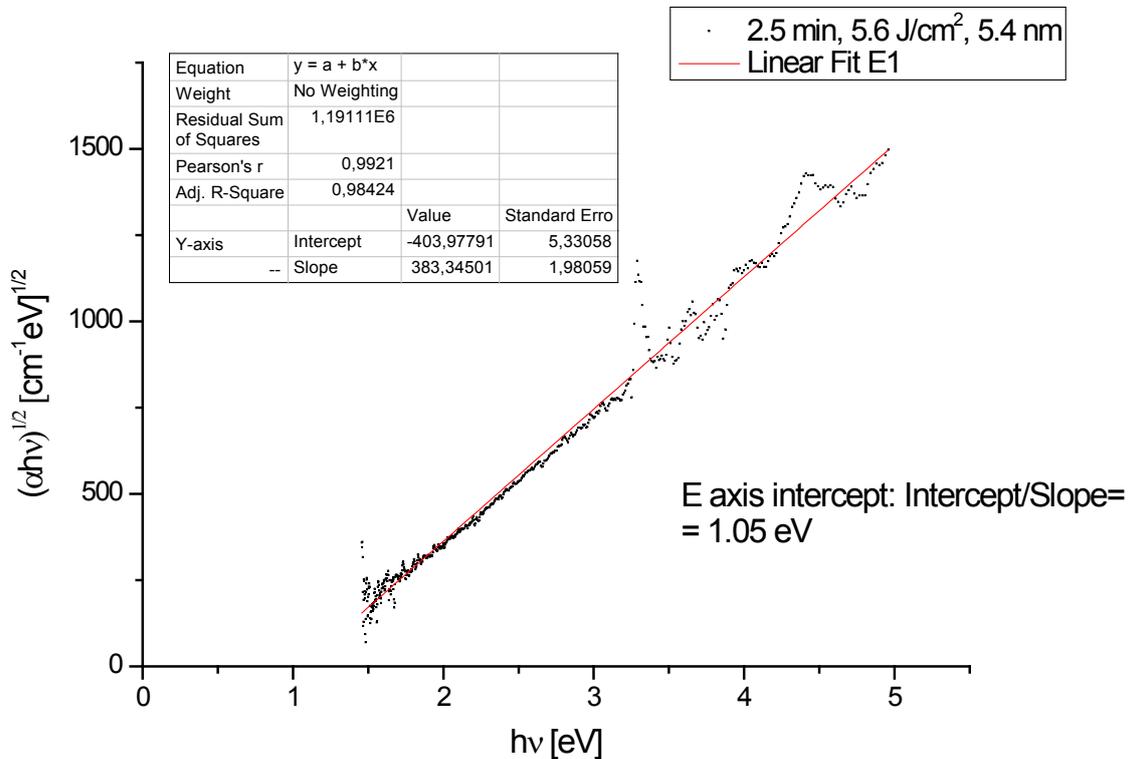
$$hv = \frac{1}{C^{1/n}} (-\ln(T) hv)^{\frac{1}{n}} + E_g, \quad (3)$$

where  $C$  is a constant taking into account the thickness of the sample.

This could be rewritten as

$$hv = p_1 + p_2 (-\ln(T) hv)^{p_3}, \quad (4)$$

where  $p_1$  stands for  $E_g$ ,  $p_2$  stands for  $1/C^{1/n}$  and  $p_3$  stands for  $1/n$ . By plotting  $hv$  against  $-\ln(T)hv$  it is possible to obtain approximate values for  $n$  and  $E_g$  by a nonlinear fit of the plot (using the function  $y=a+bx^c$ ). We have found out that the value of the index  $n$  is 2, therefore it is allowed indirect transition. The value was subsequently used in Tauc's plot to derive the optical band gap. The obtained values of the optical band gap (0.6–1.1 eV) are in accordance with the values in the literature given for similar conditions [1,11,12].



**Figure 3.** Tauc's plot of sample produced at 5.6 J/cm<sup>2</sup> laser fluence, 2.5 min deposition time

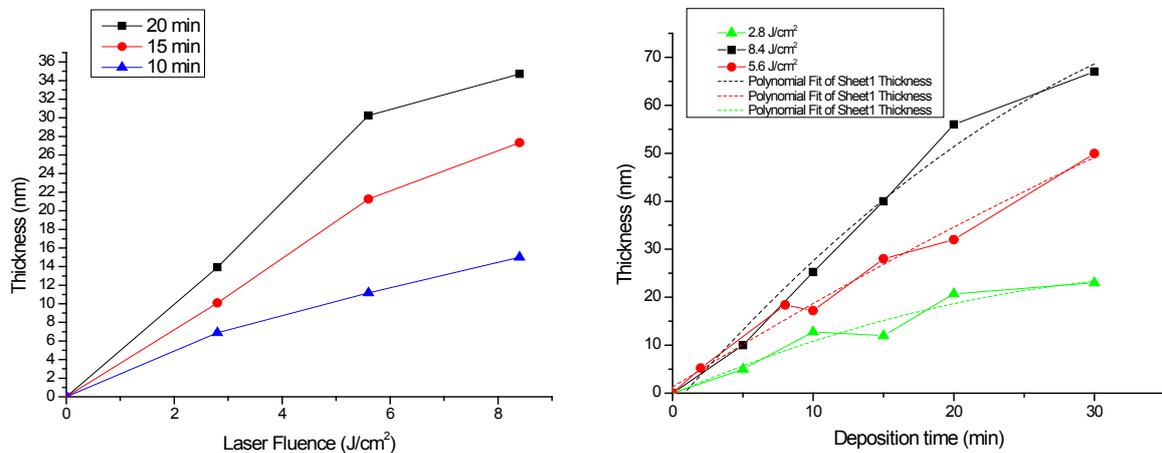
**Profilometry**

The profilometry measurements reveal that the thickness of the films does not increase linearly with increasing deposition time but rather polynomially with a trend to saturate. In Figure 4, we can see the same trend when comparing thickness with laser fluence. It can be clearly seen that saturation of the deposition rate is being approached with increasing laser fluence. The comparison between various deposition times is given.

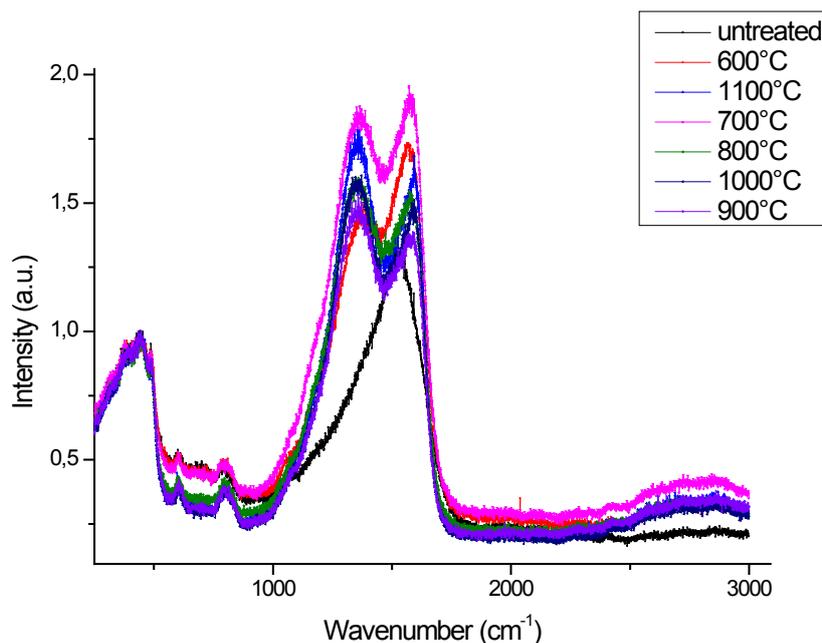
**Raman spectroscopy**

The DLC films were analyzed after the thermal treatment at different conditions. In each spectrum we can see contributions at approximately  $1370\text{ cm}^{-1}$  and at  $1580\text{ cm}^{-1}$  which correspond to D-band and G-band. The D-band is caused by disordered structure of graphene and gets higher with higher content of  $\text{sp}^3$ -hybridized carbon atoms which form diamond structure. The G-band arises from the stretching of the C–C bond in graphitic materials, and is common to all  $\text{sp}^2$  carbon systems [13]. Pure graphene exhibits strong 2D-band at around  $2700\text{ cm}^{-1}$  which signifies  $\text{sp}^2$ -hybridization, however, in our spectra we can only see very small rise of intensity around 2D-band. It is mainly because of the interactions between the layers in DLC and the nature of the material where we have thin graphite film on the surface and DLC in the bulk.

There are some contributions caused by amorphous carbon at  $1130\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$  Raman shift [14]. The intensity ratio between G-band and D-band clearly depends on the conditions of thermal treatment (temperature).



**Figure 4.** Thickness versus laser fluence (on the left) and deposition time (on the right).



**Figure 5.** Comparison of Raman spectra after different thermal treatment.

## Conclusion

The properties of DLC films prepared by PLD have been discussed. The optical properties have been investigated by transmittance measurements and the thickness of the samples have been investigated by profilometry.

The transmittance of the samples tends to decrease with higher laser fluence and deposition time which is due to higher carbon concentration. It has been shown that the Tauc's method can be used for precise determination of the optical band gap in DLC from optical spectra. The profilometry measurements show nonlinearity between the deposition time and thickness and a tendency towards deposition rate saturation at high laser fluence.

It is needed to perform another set of measurements (e.g., NRA, conductivity) which will be reported elsewhere. The XPS results of such samples have been reported previously by our research group [3].

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