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Optical properties of diamond-like carbon films subjected to ultraviolet irradiation

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Abstract. Influence of UV irradiation on optical properties of the nitrogen doped diamond-like carbon (DLC) films was studied. Transparency spectra of the initial, UV irradiated and concentrated UV irradiated films were measured. Dependences of the optical bandgap on the nitrogen content were obtained from these spectra. Raman measurements revealed a decrease in the graphitic cluster size by two times after UV irradiation. It was shown that concentrated UV irradiation leads to smaller changes in comparison with nonconcentrated UV. Physical mechanism of air oxygen embedding into the DLC structure under UV irradiation is proposed to explain the changes in the properties of the films.

Keywords: diamond-like carbon film, ultraviolet irradiation, optical properties.

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1. Introduction

The unique properties of diamond-like carbon (DLC) films make them an attractive material to improve various properties of devices. In particular, the films may be used to develop a variety of electronic devices. They allow decreasing the work function, threshold emission voltage and increasing stability of field emission cathodes [1]. When the DLC films are used as antireflection and protective coatings for solar cells (SC), the efficiency is improved by the factor 1.3-1.45 [2]. One of the ways to change parameters of DLC films is introduction of nitrogen into these films [3, 4]. Because of nitrogen has different bond configurations inside the film, it can change structure and properties of the DLC films substantially [4-6].

Although DLC structure and properties are formed during deposition, they also can be modified through post-growth ultraviolet (UV) irradiation [7-9]. Optical transparency of a-C:H films increases and adsorption edge shifts to the short-wave area after UV irradiation [7, 8]. Authors of [8] point out the possible participation of oxygen in changing the characteristics. UV irradiation results in decreasing the number of C-H bonds with simultaneous increasing in the quantity of double bonds of carbon atoms including bonds with nitrogen [7]. UV irradiation may also result in oxidation of the film surface, while the N to C concentration ratio increases after irradiation.

That structure modifications cause changes in the electronic structure of the films. The DLC films deposited from a gas source with larger amount of nitrogen have a smaller optical bandgap E_{opt} before UV irradiation. After irradiation E_{opt} approaches to E_{opt} of the films deposited from the gas source with smaller amount of nitrogen [7]. However, in our previous works we observed just an opposite behavior of the optical bandgap in dependence on the nitrogen content in DLC films [10, 11].

It is an additional evidence of necessity to study more detailed effect of nitrogen and post-growth UV irradiation on the DLC films properties.

Nitrogen in the structure of DLC films causes the photoluminescence band of about 2.75 eV (450 nm). The intensity of this band only very weakly depends on the nitrogen concentration [10]. The same band appears after UV irradiation of a-C:H:N films [7], and the intensity of the band linearly depends on the nitrogen concentration in these films.

Taking into account that amount of works devoted to investigation of the influence of UV irradiation on properties of DLC films is very small and the physical mechanism of this influence is not clear enough, the aim of this work was to study changes in optical characteristics of DLC a-C:H:N after UV irradiation.

2. Experimental

a-C:H:N DLC films were obtained by plasma-enhanced chemical vapor deposition [11]. The deposition conditions are listed in Table 1. The samples were deposited onto Si (100) and glass substrates at room temperature.

Table 1. Parameters of deposition of studied samples.

#	Number of sample	Gas mixture content N_2:H_2:Ar:CH_4	Deposition time, min	Pressure, Pa	Power, Wt
1	272	20:35:5:25	30	100	250
2	281	30:25:5:25	30	100	250
3	278	45:10:5:25	45	100	250
4	248	0:55:5:25	30	100	150

UV irradiation of DLC films was carried out by a high-pressure mercury lamp ДРШ-250, the samples were irradiated by concentrated and non-concentrated UV light. In the latter case, the samples were placed instead of the concentrator lens on the distance of 14 cm from the lamp. All irradiations were carried out throughout 2 hours in air.

The spectra of photoluminescence and transparency were measured after UV irradiation. Also, for the sample deposited from precursor gas that contains 20 % of nitrogen the Raman spectra were measured. Intensive photoluminescence was hindered to measure Raman spectra for other samples with higher nitrogen content. The data of optical density of the studied samples are shown in Fig. 1.

Tauc' dependences were calculated from the obtained spectra by using the equation [5]:

$$\sqrt{\alpha E} = B(E - E_{\text{opt}}),$$

where α is the absorption coefficient, E – energy, E_{opt} means the value of optical bandgap, B is the coefficient that takes into account the graphitic cluster size.

Optical bandgaps of the studied DLC films before and after irradiations were calculated from these curves and are shown in Fig. 2.

Raman spectra were measured only for the sample #272 prepared from precursor gas with 20 % of nitrogen, because of other samples show intensive photoluminescence. Measured Raman spectra are shown in Fig. 3, and the main parameters of the spectra obtained after fitting the experimental spectra by two Gaussians are summarized in Table 2.

Table 2. Parameters of the measured Raman spectra of the sample #272 (N_2 = 20 %).

Parameter	Initial	Irradiated by concentrated UV
ω_D, cm^{-1}	1338.4	1370.8
$\Delta\omega_D$, cm^{-1}	157.06	257.2
I_D, arb. u.	0.180	0.322
ω_G, cm^{-1}	1542.8	1542.0
$\Delta\omega_G$, cm^{-1}	139.39	128.21
I_G, arb.u.	0.736	0.762
I_D/I_G	0.245	0.423

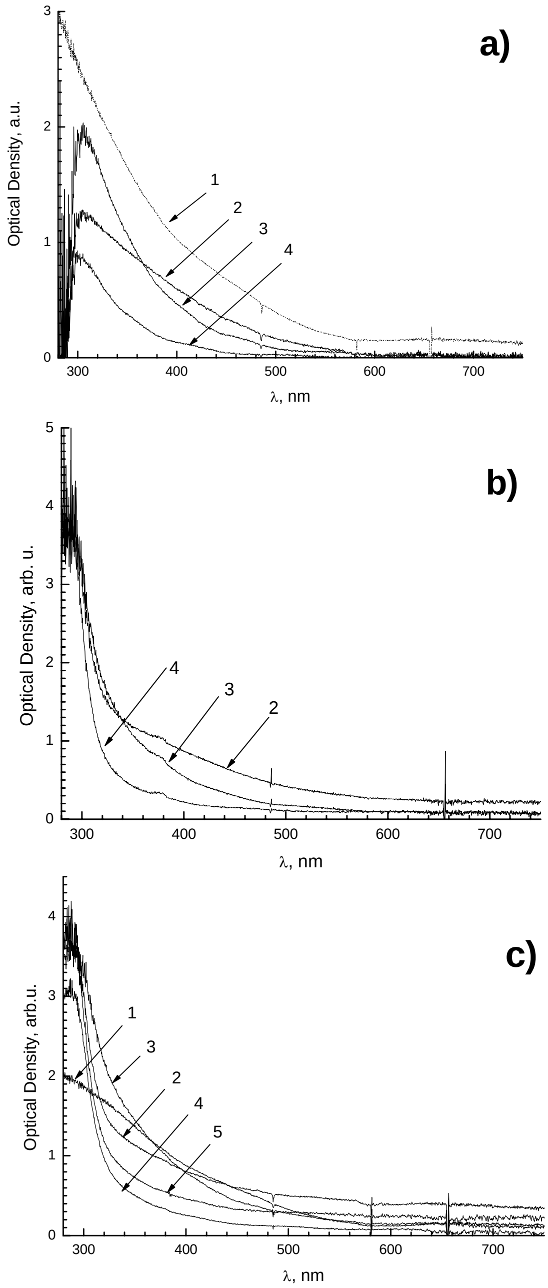

Fig. 1. Optical density of DLC films: a – initial; b – UV irradiated; c – irradiated by concentrated UV. Nitrogen content: *1* – 0; *2* – 20; 3 – 30; *4* – 45; *5* – 45 % (irradiated through glass substrate from the rear).

3. Results and discussion

Obtained dependences show that UV irradiation of the DLC films leads to significant growth of the optical bandgap (Fig. 2). At the same time, resulting values of the optical bandgap practically do not depend on the nitrogen content in the films and are close to about 3.6 eV for the films irradiated by non-concentrated UV light. Irradiation of the DLC films by concentrated UV results in optical bandgaps close to 3.4 eV.

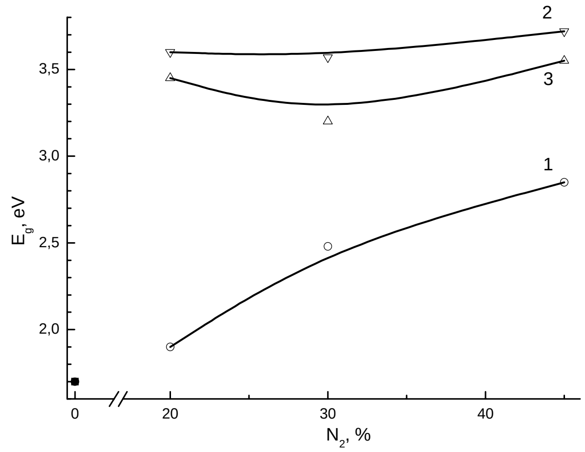

Fig. 2. Dependences of the optical bandgap versus concentration of nitrogen in precursor gas: *1* – initial samples of DLC films; *2* – UV DLC films irradiated during two hours; *3* – DLC films irradiated by concentrated UV light during two hours. Optical bandgaps of the DLC film without nitrogen (initial and UV irradiated) are shown separately because this sample was prepared in other conditions.

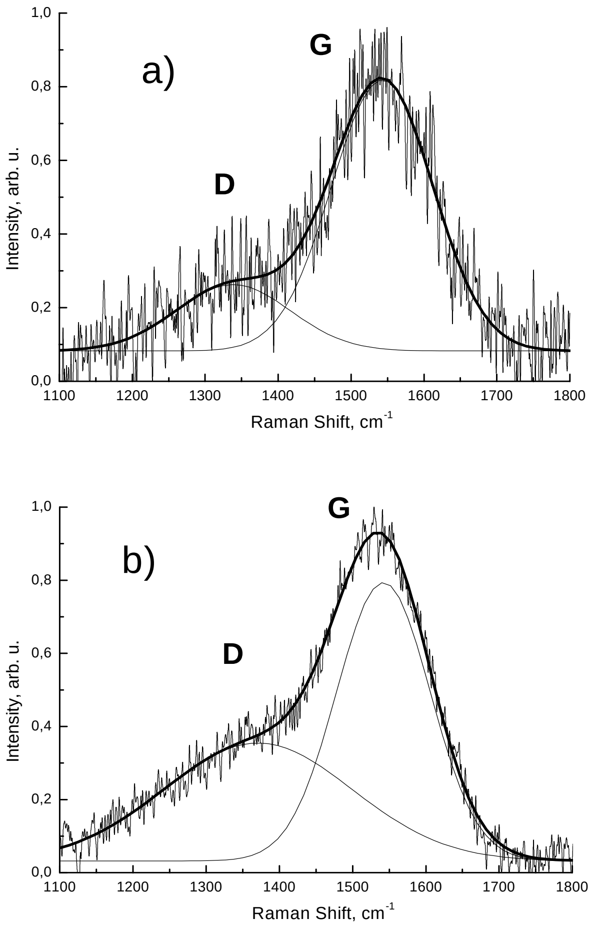

Fig. 3. Raman spectra for the DLC film prepared from the precursor gas with 20 % of nitrogen: a – initial; b – after irradiation by concentrated UV light.

Thus, increase of the optical bandgap of the DLC films after concentrated UV irradiation is lower than that for the DLC films after *nonconcentrated* UV irradiation. This behavior is caused by additional thermal influence of concentrated UV light (sample heating). As a result, hydrogen can partially leave out the samples and corresponding decrease in the optical bandgap can be observed [12].

It should be noted that UV irradiation of a-C:H films (without nitrogen) have no influence on the optical bandgap. It indicates nitrogen influence on degradation stability of the DLC films.

The mechanism of UV influence on the properties of the DLC films is probably concerned with air oxygen embedding into the DLC structure. UV irradiation activates oxygen that diffuses into the film and creates bonds with carbon, hydrogen and/or nitrogen atoms presented in the film. Presence of oxygen in the DLC film structure causes decrease of a dangling bond amount, defect states in the bandgap, appearance of additional oxygen states near π and σ diamond bands. On the whole, it leads to the increasing optical bandgap [8].

Taking into account the dependence of I_D/I_G ratio, the size of graphitic clusters in DLC film from [5] and I_D/I_G values obtained for our samples (Table 2), we conclude that after UV irradiation the size of graphitic clusters in UV irradiated DLC films is decreased.

4. Conclusions

UV irradiation of the nitrogen doped diamond-like carbon films for two hours leads to a substantial increase in the optical bandgap from 1.8-2.8 up to 3.4-3.6 eV.

I_D/I_G ratio of the Raman peaks increases by two times, that is the consequence of the decreasing number of graphitic clusters in the structure of the DLC films by two times after UV irradiation because of air oxygen embedding into the DLC structure.

It has been shown that the optical bandgap of the DLC films increases up to a certain value that weakly depends from the nitrogen content in them.

Concentrated UV irradiation causes smaller changes of the film optical properties in comparison with nonconcentrated UV irradiation. It can be related to additional sample heating during concentrated UV irradiation.

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