EFFECT OF UV AND γ-IRRADIATION ON THE STRUCTURE AND OPTICAL PROPERTIES OF a-C:H:N FILMS

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The influence of ultraviolet and γ-irradiation on the properties of diamond-like carbon films with various nitrogen contents has been studied. Irradiation with ultraviolet light leads to a significant increase in the optical band gap owing to structural changes in carbon, hydrogen, and nitrogen bonds, as well as to the partial diffusion of oxygen, which is activated during the exposure, from air into the film. A reduction of the optical bandgap after γ-irradiation was observed; however, films with higher nitrogen contents demonstrate a higher resistance to radiation. Nitrogen bonds were found to experience more structural changes, whereas carbon bonds to be slightly reconstructed.

1. Introduction

Earlier [1], diamond-like carbon (DLC) films were demonstrated to be a promising object for their use as antireflective coatings in solar cells (SCs) based on silicon. At the same time, the issue concerning the stability of such coatings – and, eventually, SCs, in which they are used – under the action of external irradiation remains challenging; in particular, it may be the ultra-violet component of the solar spectrum or γ-quanta. The latter either are a component of the solar wind in the space or can be found where the radioactive background is high.

Parameters of diamond-like carbon film deposition

N	Nitrogen content in plasma, %	Deposition time, min	Gas mixture pressure, Torr	Discharge power, W
1	20	30	0.8	250
2	30	30	0.8	250
3	45	45	0.8	250

It is known that UV irradiation of films in the air environment leads to a decrease of the film thickness [2–4], an increase of the oxygen concentration in them [4, 5], an increase of film the transmittance and a shift of the absorption edge toward the short-wave range in optical spectra [2, 6], and an increase of the optical width of the energy gap in films that contain nitrogen [6]. It can be explained by the fact that UV radiation induces the break of C–H bonds in DLC films, with the establishment of either bonds with oxygens [2] or additional bonds with nitrogens [6]. However, the issue concerning the influence of ultra-violet light on the structural and optical properties of DLC films remains insufficiently researched, whereas the influence of γ-radiation on them has been practically not studied at all. At the same time, such researches are very important for the establishment of mechanisms that could be used to improve the degradation stability of SCs with antireflective DLC films with respect to the action of such radiation [7]. This has determined the subject of this work.

2. Experimental Part

In our researches, we used a-C:H:N films deposited onto silicon substrates. The method of plasma-enhanced chemical vapor deposition with various nitrogen contents in plasma (20, 30, and 45%) was applied. The technological parameters of the film deposition process are listed in the Table. Films were illuminated with UV light from

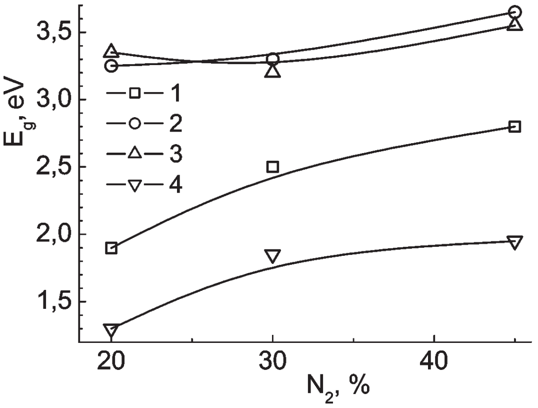

Fig. 1. Dependences of the optical width of the energy gap on the nitrogen content in a working gas mixture for initial specimens (*1*), specimens of DLC films irradiated with ultra-violet light for 2 h (*2*), specimens of DLC films irradiated with concentrated ultra-violet light for 2 h (*3*), and specimens of DLC films irradiated with γ-quanta to an exposure dose of 10^6 rad

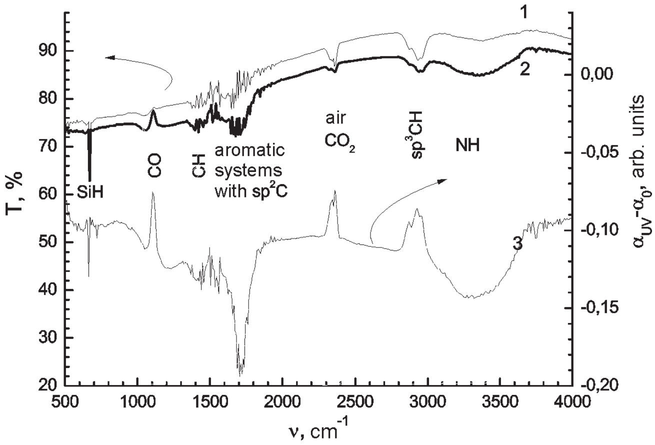

Fig. 2. IR absorption spectra of DLC films grown up from a gas mixture with 45% nitrogen before (*1*) and after (*2*) irradiation with UV light, and the difference $\Delta\alpha = \alpha_{\mathrm{UV}} - \alpha_0$ between the absorption in the irradiated and initial specimens (*3*)

a mercury lamp for 3 h. The irradiation power was 1 or 350 kW/m^2 (concentrated light). A DRSh-250 lamp was used for irradiation. Concentrated irradiation was provided making use of a quartz collecting lens. Some films were irradiated with γ-rays to an exposure dose of 10^6 rad using a ^{60}Co source.

To study the optical properties, the transmission spectra of films were measured in the spectral range 300–1000 nm, and the Tauc relation was used to determine the optical width of the energy gap, E_{opt}. In addition, the Raman spectra of light scattering in the range of *D*- and *G*-vibrational mode localization (1100–1800 cm^{-1}) and the IR-transmission spectra in the range 500–4000 cm^{-1} were measured and analyzed.

3. Results and Their Discussion

The values obtained for the optical width of the energy gap while analyzing the optical transmission spectra testify that UV irradiation of DLC films leads to a substantial growth of E_{opt} (Fig. 1). In the case of films produced from gas mixtures with high contents of nitrogen, illumination with the concentrated UV light results in a smaller increase of the optical width of the energy gap in comparison with that obtained at illumination with the nonconcentrated UV light. In our opinion, this fact is related to an additional thermal influence of concentrated UV light, which may provoke a partial release of hydrogen from DLC films.

From the analysis of the data on the IR absorption by DLC films before and after UV irradiation (Figs. 2,*a* and *b*), it follows that the latter induces a larger absorption at sp^3 CH bonds (2900–2950 cm^{-1}), which evidences the formation of new bonds between carbons and hydrogens in the diamond-like phase. Proceeding from the technique proposed in works [8, 9], we estimated the ratio between the area of peaks within the frequency interval of 2800–2900 cm^{-2} before and after UV illumination. The results obtained testify that the number of sp^3 CH bonds increased by a factor of 2.6 after the illumination.

It should be noted that the band at about 2350 cm^{-1} corresponds to the absorption at bonds of CO_2 in air, so it was not taken into account while analyzing IR spectra.

The absorption in a vicinity of 1090–1110 cm^{-1} characterizes the number of CO bonds [10]. Hence, the amount of oxygen in the film gets larger after UV irradiation. This conclusion agrees with those made by the authors of works [4, 11] that the air oxygen is easily ionized under UV irradiation by forming ozone, which, in its turn, diffuses into DLC films and forms new bonds there.

The absorption within the frequency band of 1600–2000 cm^{-1} is usually associated with the presence of aromatic rings in the substance composition [10], in other words, with the presence of sp^2-hybridized carbon atoms. In our case, the number of aromatic bonds became considerably smaller after UV irradiation, which testifies to a reduction of the number of aromatic systems with sp^2-hybridized carbon atoms in the content of *a*-C:H:N films.

Variations of the absorption at bonds between nitrogen and carbon (the single C–N 1689 cm^{-1} and the double C=N 1530 cm^{-1} ones) or hydrogen (N–H 1550 cm^{-1}

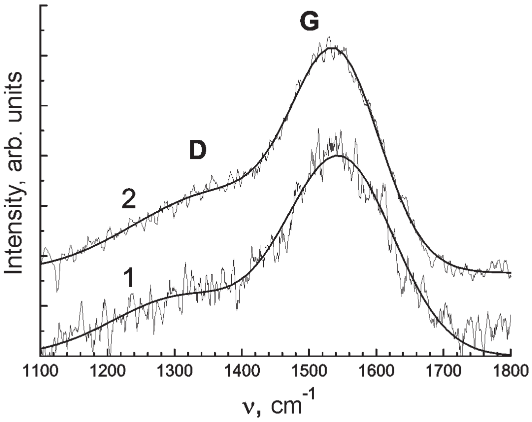

Fig. 3. Raman spectra for a DLC film specimen with 20% nitrogen before (*1*) and after (*2*) irradiation with concentrated UV light. Two peaks, which are basic for diamond-like films, are designated as *D* (disordered) and *G* (graphitic)

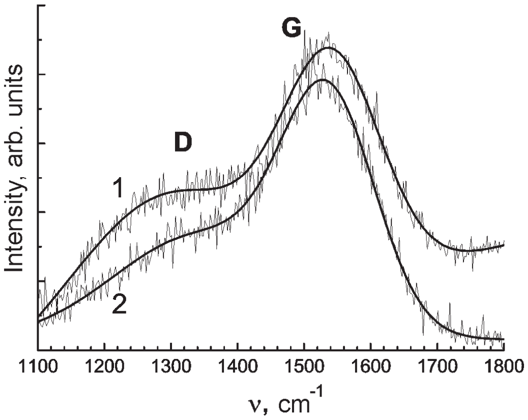

Fig. 4. Raman spectra of a DLC film grown up from a gas mixture with 20% nitrogen before (*1*) and after (*2*) γ-irradiation to a dose of 10^6 rad

and NH in the range of 3100–3600 cm^{-1}) testify to the film restructuring under the action of UV photons, namely, an increase of the number of bonds with sp^3C [9,10,12]. It should be noted separately that the number of NH bonds decreases, whereas the number of CH bonds grows; it becomes evident, if the absorption bands within the intervals of 3000–3500 and 2850–3000 cm^{-1}, respectively, are compared. The emergence of the absorption at Si–H bonds (668 cm^{-1}) confirms that hydrogen atoms release from the film under the influence of UV quanta, diffuse into the silicon substrate, passivate the dangling bonds of silicon, and form hydrogen–silicon bonds. The initial and irradiated films practically did not contain ternary bonds C≡N, which is evidenced by the absence of a characteristic band at 2250 cm^{-1} [10].

In Fig. 3, the Raman spectra for a specimen obtained from the gas mixture with 20% nitrogen content, which were recorded before (curve *1*) and after (curve *2*) irradiation with concentrated UV, are shown.

According to the results of work [13], an increase of the peak-intensity ratio I_D/I_G corresponds to a reduction of the graphite cluster sizes. Hence, UV irradiation leads to a diminishing of graphite clusters in the films. This conclusion also agrees with the conclusion based on the analysis of IR absorption spectra that the number of sp^2-hybridized carbon atoms decreases.

The measurement of the film thickness before and after irradiation with UV light showed that films 520 ± 10 nm in thickness became narrower by 22 ± 6 nm. Such changes are in agreement with the data obtained by the authors of work [4].

The analysis of the transmission spectra of DLC films after their γ-irradiations showed that, in general, the film transmittance decreases after irradiation; however, films with a higher nitrogen content are more resistant to irradiation. In addition, the optical width of the energy gap in irradiated films with a high nitrogen content turned out almost identical (see curves *1* and *4* in Fig. 1).

The analysis of the Raman spectra measured for a film grown up from the gas mixture with 20% nitrogen (Fig. 4) showed that the peak-intensity ratio I_D/I_G decreases after γ-irradiation, which testifies to an increase of graphite cluster sizes, i.e. to a partial graphitization of the film.

After γ-irradiation, the IR transmission spectra of the films—in particular, the relevant spectrum for a film grown up from the gas mixture with 45% nitrogen is depicted in Fig. 5 – revealed appreciable changes at frequencies of about 668 cm^{-1} (they correspond to the vibrations of Si–H bonds), in the frequency band of 1600–2000 cm^{-1} (bonds in aromatic systems, including those with the substituted atoms), at 2850 cm^{-1} (sp^3C–H bonds), 2920 cm^{-1} (sp^3CH$_2$ bonds), and 3100–3600 cm^{-1} (NH bonds).

For films with high nitrogen contents, the absorption decreases within the frequency interval from 1500 to 1800 cm^{-1}. This can be explained by a reduction of the number of nitrogen bonds with hydrogens and carbons in aromatic rings, which manifest themselves in this frequency range. Moreover, it is the bonds of hydrogens with nitrogens, provided the presence of the latter in DLC films, that become destroyed in the first place under the action of γ-irradiation. This process can be readily observed by analyzing the bands at about 2900 cm^{-1} (C–H bonds) and in the interval of 3100–3600 cm^{-1} (N–H bonds), when the low concentration of nitrogen (20% N$_2$ in the gas mixture) is accompanied by a reduction in

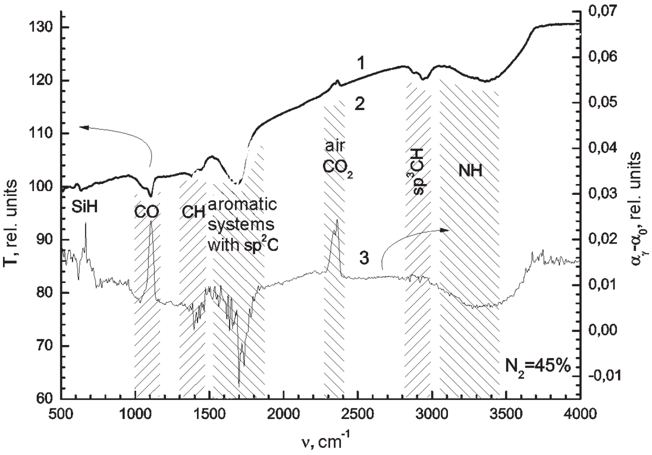

Fig. 5. IR transmission spectra of DLC films grown up from a gas mixture with 45% nitrogen before (*1*) and after (*2*) γ-irradiation to a dose of 10^6 rad, and the difference $\Delta\alpha = \alpha_\gamma - \alpha_0$ between the absorption in the irradiated and initial specimens (*3*)

the number of C–H bonds, whereas at high N_2 concentrations (45% N_2), it is the number of N–H bonds that decreases.

The mechanism of how diamond-like carbon films change their properties under the action of γ-irradiation consists in that γ-quanta break bonds, first of all, between hydrogen and nitrogen atoms. Our specific technological feature of the film deposition was that, when a film with a high content of nitrogen was deposited, nitrogen substituted some part of hydrogen in the gas mixture and, respectively, in the film content. Hence, during the γ-irradiation, more hydrogens left the film with the lower nitrogen content, which resulted in its even higher degradation. At the same time, nitrogen bonds are stronger, and the mobility of nitrogen atoms is lower in comparison with those for hydrogen atoms, which requires a more energy for the former to leave the film.

Nitrogen also plays the role of a passivating element, by occupying free bonds, instead of hydrogen. The following phenomena take place in films under the action of radiation: the graphitization (sp^2-hybridization) of atoms in the content of the sp^3 matrix of films, which were grown up from the gas mixture with a low nitrogen content; the growth of graphite cluster sizes, which is accompanied by the restructuring of sp^3CH bonds (the changes of IR absorption in the frequency range of 2800–3000 cm^{-1}); the release of hydrogen from the film (an enhancement of the absorption by SiH bonds at 668 cm^{-1} confirms that hydrogen partially diffuses into the substrate); and the formation of bonds with the less mobile nitrogen (the changes at frequencies of 1300–1800 cm^{-1}). Small modifications in the IR spectra at frequencies that correspond to bonds with nitrogen (in the interval 1500–1700 cm^{-1}) confirm the idea that nitrogen is not released from the films under the influence of high-energy quanta, but becomes involved into structural changes.

At the same time, an increase of the nitrogen content in a gas mixture used to grow films, and, hence, in the films favors a higher stability of the latter to the influence of γ-radiation. The action of γ-quanta leads, first of all, to the break of bonds between nitrogen and hydrogen atoms, whereas the sp^3 matrix remains almost invariable, and even the fraction of sp^2 hybridized carbon atoms diminishes.

The results obtained completely confirm the proposed mechanism of enhancing the degradation stability of silicon SCs with antireflective DLC films [7], which makes allowance for the hydrogen release from the film, its diffusion to the silicon SC, and the passivation of recombination-active centers (dangling bonds).

4. Conclusions

Under the influence of ultra-violet light, the structure of *a*-C:H:N films changes. This occurs owing to a number of factors. In particular, the air oxygen, being activated, integrates into the film content, which leads to the appearance of new bonds with oxygen atoms; the energy of ultra-violet quanta is enough for the bonds between hydrogen and other atoms to be broken, which results in a reduction of the hydrogen amount in the film; the irradiation with ultra-violet light induces a reduction in the number of hydrogen–nitrogen bonds, an increase in the number of sp^3 hybridized carbon atoms, and an emergence of new bonds between carbon and nitrogen atoms (in particular, an increase of C–C and C–N bonds), as well as between those atoms and oxygen ones. Such structural changes are responsible for an increase of the optical width of the energy gap and the optical transmittance of DLC films.

The action of γ-quanta on the structural properties of diamond-like carbon films consists in that the bonds between film components become broken, and hydrogen becomes partially released; nitrogen plays the role of a passivating element and occupies the free bonds substituting hydrogen; a partial graphitization of the film takes place and is accompanied by an increase of graphite cluster sizes, a reconstruction of C–H bonds, and the formation of bonds with nitrogen atoms. As a result, an increase of the nitrogen content in films favors their higher stability under the influence of γ-radiation. Irradiation gives rise to a reduction of both the film transmittance and the optical width of the energy gap; however, these changes are less in films with a higher nitrogen content.

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ВПЛИВ УФ- ТА γ-ОПРОМІНЕННЯ НА ОПТИЧНІ ТА СТРУКТУРНІ ВЛАСТИВОСТІ ПЛІВОК *a*-C:H:N

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Резюме

Проведено дослідження впливу ультрафіолетового та γ-опромінення на властивості алмазоподібних вуглецевих плівок з різним вмістом азоту. Опромінення ультрафіолетовим світлом приводить до суттєвого збільшення оптичної ширини забороненої зони внаслідок структурних змін зв'язків вуглецю, водню та азоту, а також завдяки частковій дифузії у плівку кисню повітря, що активується під час опромінення. Під час γ-опромінення відбувається зменшення оптичної ширини забороненої зони, проте, плівки з більшим вмістом азоту показують більшу стійкість до радіаційного впливу. При цьому структурні зміни стосуються переважно зв'язків азоту, з малою перебудовою зв'язків вуглецю.