

OPTICAL AND MECHANICAL PROPERTIES OF NITROGEN-DOPED DIAMOND-LIKE CARBON FILMS

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UDC 535.343.9;533.599;

535.375.5;539.533

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The optical and mechanical properties of diamond-like carbon films (DLCFs) deposited using the plasma-enhanced chemical vapor deposition technique from $\text{CH}_4\text{--H}_2\text{--N}_2$ gas mixtures with various nitrogen contents have been investigated at various radio-frequency (RF) discharge powers and gas pressures in a plasma reactor. Ellipsometry, as well as transmission and reflectance spectroscopies, was used to study the optical properties of the films. Their mechanical properties — in particular, wear resistance — were analyzed making use of the nanoindentation technique. The film thickness was also measured with a profilometer and compared with the results of ellipsometric studies. It has been demonstrated that the growth of the nitrogen content in a gas mixture and the reduction of the discharge power are accompanied by an increase of the optical bandgap and, consequently, of the carbon film transmittance, with the hardness and the refractive index of the film becoming lower at that. The rate of the film deposition considerably increases as the discharge power grows, whereas the nitrogen concentration in the gas mixture weakly influences the former.

1. Introduction

The application potential of DLCFs as protective and antireflective coatings is beyond doubts. In particular, as has been shown in a number of works, the efficiency of silicon-based solar cells, owing to the deposition of a DLCF, can be made almost half as much again [1]. Moreover, DLCFs are promising in developing the devices of vacuum microelectronics, because they reduce both the electron work function and the field emission threshold and improve the stability of the latter [2]. The typical problem of amorphous films, including DLCFs, is the availability of substantial internal mechanical stresses in them. One of the ways to reduce such stresses in DLCFs consists in the implantation of nitrogen [3]. Additionally, nitrogen considerably changes the optical and mechanical properties of DLCFs [4], giving alternative opportunities to fabricate films with preset properties.

This work aimed at finding the interrelation between the technological parameters of the DLCF deposition process — especially, the nitrogen content in a gas mixture — and the DLCF optical and mechanical properties obtained, as well as at elucidating the physical mechanisms of nitrogen influence on the film properties.

2. Experiment

The a-C:H:N films were deposited from the plasma of the RF discharge (13.56 MHz) making use of the plasma-enhanced chemical vapor deposition method, at various RF discharge powers (100–250 W) and nitrogen contents in the gas mixture (10–45%). The gas mixture $\text{CH}_4\text{:H}_2\text{:N}_2$ was used, and the nitrogen content in it (P_{N_2}) was varied by the gradual replacement of hydrogen by nitrogen. The gas pressure in a chamber was varied within the limits of 25–105 Pa. The film deposition was carried out onto substrates maintained at room temperature, for which purpose the bottom electrode of the reactor, with arranged specimens, was cooled with water. The deposition time was fixed and amounted to 15 min.

The transmission spectra of the films deposited onto glass substrates were measured with the help of an S2000 spectrometer (Ocean Optics, USA) in the range 300–800 nm, provided that light fell normally to the surface. A DH-2000 deuterium-halogen light source of the same firm was used.

While studying the mechanical properties of thin films, in particular, finding their hardness, there appears a number of problems, which restrict or even make impossible the application of the traditional methods of researches. For example, if one determines the film hardness by measuring the depth (size) of the imprint that a diamond indenter makes, the substrate would influence the results obtained if the film thickness is small, or there would emerge difficulties with the

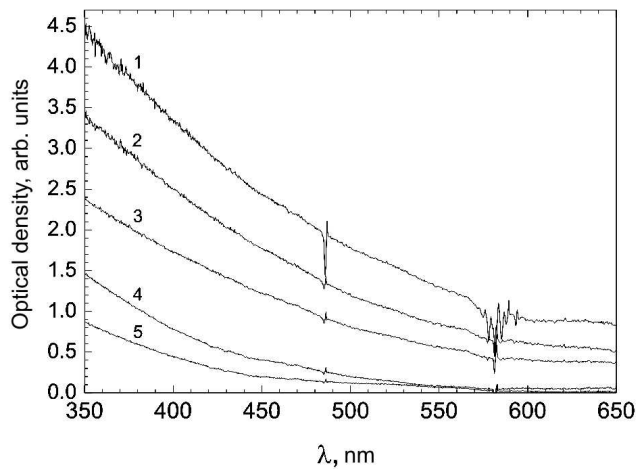


Fig. 1. Spectral dependences of the transmittance of diamond-like carbon films (DLCFs) deposited at various nitrogen contents in the gas mixture: 0 (1), 10 (2), 20 (3), 30 (4), and 45% (5)

measurements of the imprint dimensions if the loads on the indenter are small. Therefore, the nanoindentation is the best method for the determination of the thin film hardness. In the course of testing the specimen, the shift of the diamond indenter's position (its penetration into a film) is recorded both at the increasing and the decreasing of a load on it. The analysis of the diagram obtained, which describes the indenter displacements (the penetration depth versus load) makes it possible to determine both the hardness and the modulus of elasticity of a film, because the process of indenter unloading is elastic.

In order to determine the mechanical properties of thin DLCF films, we used the method that allows one to evaluate the hardness of a material by analyzing the indenter imprint depth. The researches were carried out making use of a Nano Indenter-II nanohardness tester (MTS Systems Corporation, Oak Ridge, TN, USA) with a Berkovich trihedral indenter. In the course of measurements, the dependence of the Berkovich indenter tip displacements on the indenter load was registered with a high accuracy. The device carried out the cycles of indenter loading and the measurement of its displacement 5 times per second. The measurement accuracy of the imprint depth was ± 0.04 nm and of the indenter load ± 75 nN. The punch speed of the indenter was 10 nm/s. The hardness and the modulus of elasticity of the specimen were determined following the Oliver–Pharr technique [5]. According to this method, nanohardness is calculated as the ratio between the load on the indenter and the area of the imprint's projection.

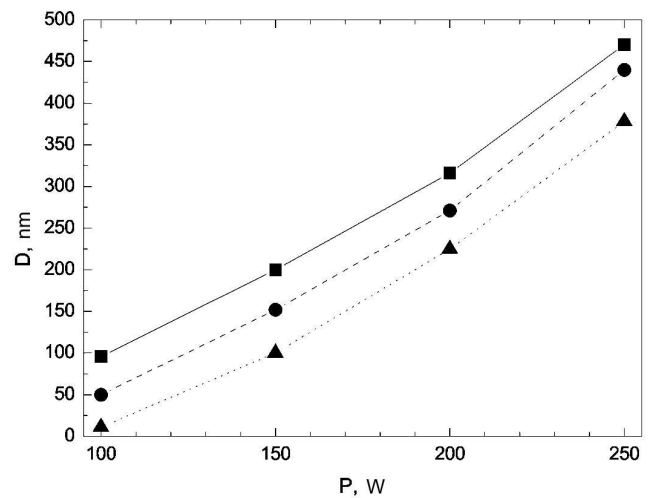


Fig. 2. Dependences of the DLCF thickness on the RF discharge power at various fixed nitrogen concentrations in working mixtures: 10 (■), 30 (●), and 45% (▲). The deposition time equals 15 min

The spectra of Raman scattered light were measured with an automated spectrometer based on a DFS-24 double monochromator. A cooled FEU-136 photoelectronic multiplier was used for the registration, in the photon counting mode of operation. The excitation was stimulated with an argon laser ($\lambda = 488$ nm). In order to prevent warming the specimen during Raman spectrum registration, the laser emission was focused onto it by means of a cylindrical lens, with the total power of exciting radiation not exceeding 40 mW.

The thicknesses of DLCFs were measured with a Dektak profilometer (the instrumental error was ± 5 nm) and an LEF-3G laser ellipsometer. The film topography was studied making use of a Digital Instruments scanning atomic force microscope (AFM) Nanoscope IV. All measurements were carried out at room temperature.

3. Results and Discussions

Figure 1 exhibits the spectral dependences of the optical density (αd) of DLCFs which were deposited from various gas mixtures, provided that the discharge power (250 W), gas pressure in a chamber (105 Pa), and deposition time (15 min) were fixed. The nitrogen content in the mixture was varied within the limits 0–45%. Taking into account a relatively insignificant difference between the thicknesses of the films that were obtained in the chosen regime of deposition at various nitrogen contents in the mixture (see Fig. 2), the

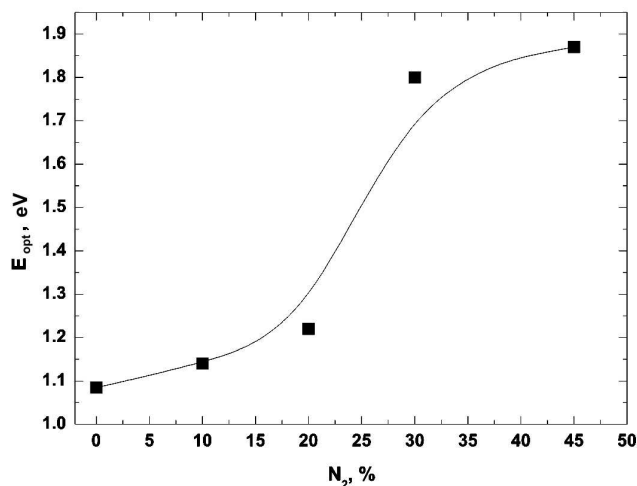


Fig. 3. Dependence of the optical bandgap E_{opt} in DLCFs on the nitrogen concentration in the working mixtures at the fixed RF discharge power of 250 W

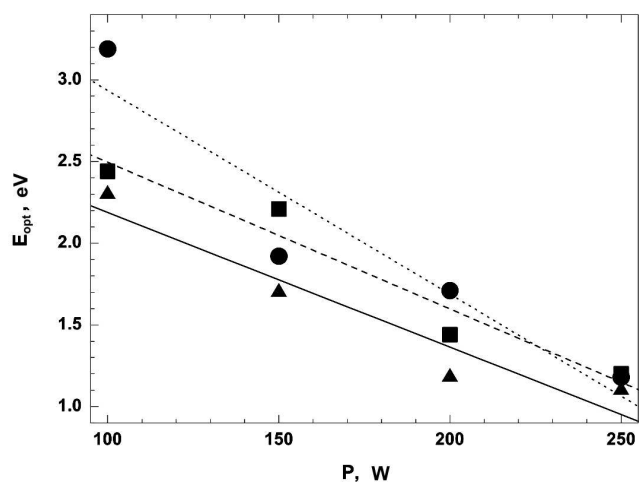


Fig. 4. Dependence of the optical bandgap width E_{opt} in DLCFs on the RF discharge power at various fixed nitrogen concentrations in working mixtures: 0 (▲), 10 (■), and 20% (●)

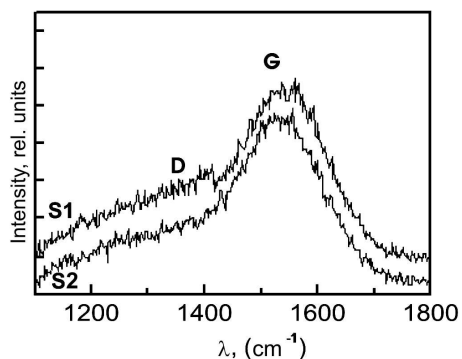


Fig. 5. Raman spectra of DLCFs obtained from a nitrogen-free gas mixture at various RF discharge powers during deposition: 250 (S1) and 100 W (S2)

conclusion can be drawn that the implantation of nitrogen into a DLCF favors the increase of its transmittance. This conclusion is confirmed directly by the dependence of the optical bandgap (E_{opt}) of the films on the nitrogen content in the gas mixture exposed in Fig. 3. The value of E_{opt} was calculated from the known Tauc relation $(\alpha h\nu)^{1/2} = B(h\nu - E_{opt})$, where $h\nu$ is the energy of photons, α the absorption coefficient, B the constant, and E_{opt} the optical bandgap width. The character of the dependence $E_{opt}(N_{N_2})$ correlates with that obtained earlier [6], which evidences for the similar mechanism of nitrogen influence on the optical properties of DLCFs. The dependences of the DLCF thickness on the RF discharge power (Fig. 2) demonstrate that the film deposition rate increases as the power grows (the deposition times were equal

for all specimens). Such an effect is related to the enhancement of the dissociation degree of methane molecules, provided that the discharge power increases [7], and, therefore, to the growth of the number of molecules which are in a reactively active state and take part in the film formation. As the nitrogen content in the gas mixture increases, the deposition rate slows down (Fig. 2), because the ratio between the N_2 and CH_4 concentrations grows [4]. The dependences of E_{opt} on the RF discharge power for the films that were deposited at a fixed content of nitrogen in the gas mixture are shown in Fig. 4. It is evident that these dependences are practically linear, and the value of E_{opt} diminishes as the discharge power grows. As was already pointed out above, the increase of the RF discharge power is accompanied by the increase of the dissociation degree of methane molecules. In addition, the number of ions in plasma, which become accelerated by the RF bias potential and bombard the growing film, also increases. All that evidently results in a more disordered film with lower transmittance and, correspondingly, the smaller value of E_{opt} [8]. The reliability of such a mechanism proves to be true by the results of additional researches carried out for nitrogen-free DLCFs. In particular, the results obtained for the optical and mechanical properties of such films are quoted in the table; and these data demonstrate that the magnitude of E_{opt} falls down as the discharge power increases. This behavior is accompanied by the increase of the film hardness H and Young modulus E . Additionally, the table quotes the

values of the ratio between the integrated intensities of G and D bands in the DLCF Raman spectra (Fig. 5). Note that the parameters of the corresponding bands in the Raman spectra (Fig. 5) were determined by fitting the experimental spectra by two Gaussian-like peaks. It is evident that the value of the ratio I_D/I_G also increases as the RF discharge power grows, which evidences therefore for the enhancement of film disordering. The results obtained completely correlate with the data of work [9], where a direct correlation between the mechanical properties of ion-doped a-C:H films and the parameters of their Raman spectra has been revealed.

Taking the application potential of DLCFs as cold cathodes in vacuum microelectronic devices into account, the researches of the roughness of their surface seem to be important. We carried out such investigations using the AFM method. The results obtained are depicted in Fig. 6. Figure 6,*a* demonstrates the surface of a DLCF, which was deposited provided a 45%-content of N_2 in the gas mixture, and testifies that the film was rather homogeneous.

The analysis of the results obtained brought about the average value of the roughness, which did not exceed 0.65 nm and was close to those determined in work [10]. At the same time, in the film region that was close to the mask (the holder) located on the surface, the roughness was substantially higher and can reach up to 2 nm. In addition, as is seen from Fig. 6,*b*, surface nonhomogeneities formed a structure that was quasi-oriented in parallel to the film—mask boundary. This effect can be probably related to the boundary effects of plasma formation and partial shadowing in the region indicated.

4. Conclusions

In order to optimize the technological regimes of film deposition and to study the mechanisms of film structure formation, a pilot batch of diamond-like carbon films has been fabricated, and the influence of the deposition conditions on their optical and mechanical properties has been researched. It has been shown that, depending on the deposition conditions (the discharge power, the gas pressure in a chamber, and the nitrogen content in a gas mixture), DLCFs with the optical bandgap width of 1.1–3.2 eV can be obtained. Such films can be used as protective and antireflective coatings in order to

Specimen	P , W	I_D/I_G	E , GPa	H , GPa	E_{opt} , eV
S1	250	2.02	111 ± 3	12.4 ± 0.6	1.1
S3	100	1.74	106 ± 2	11.5 ± 0.3	1.4

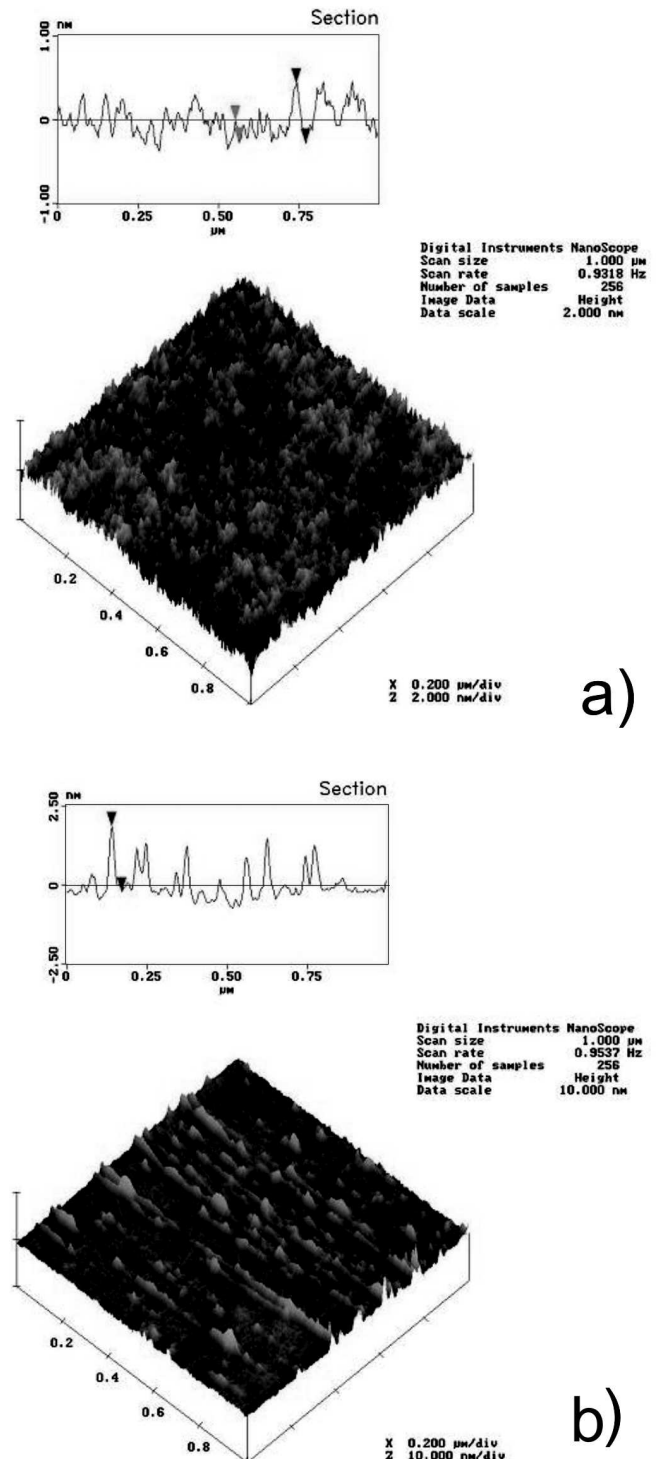


Fig. 6. AFM images of a DLCF surface: (a) at the center of the specimen and (b) near the holder (the mask)

improve the operational characteristics of solar energy photoconverters (solar cells). DLCFs can also improve

the parameters of cold cathodes in vacuum electronic devices and aligning layers in plane liquid crystal displays.

The authors are grateful to P.M. Lytvyn and V.A. Yukhymchuk for carrying out the Raman and AFM researches, respectively, and to S.M. Dub for carrying out the nanohardness measurements. The work was fulfilled in the framework of the project N 21 "Modular installation for plasma- and photo-stimulated film formation from superhard materials" of the Interdepartmental Council on scientific instrument making at the Presidium of the NAN of Ukraine and was partially supported in the framework of the INTAS project #03-51-5448 "Plasma processes for parallel and tilted liquid crystal alignment".

1. Klyui N.I., Litovchenko V.G., Rozhin A.G. et al., Solar Energy Mater. Solar Cells, **72**, 597 (2002).
2. Evtukh A.A., Litovchenko V.G., Klyui N.I. et al., J. Vac. Sci. Technol. B, **17**, 679 (1999).
3. Franceschini D.F., Achete C.A., Freire F.L. et al., Diam. and Rel. Mater., **3**, 88 (1993).
4. Silva S.R.P., Robertson J., Amaratunga G.A.J. et al., J. Appl. Phys., **81**, 2626 (1997).
5. Oliver W.C., Pharr G.M., J. Mater. Res., **7**, 1564 (1992).
6. Klyui N.I., Piryatinskii Yu.P., Semenov V.A., Mater. Lett., **35**, 334 (1998).
7. Cavalotti C., Masi M., Carrá S., J. Electrochem. Soc., **145**, 4332 (1998).
8. Seth J., Padiyath R., Babu S.V., Diam. and Rel. Mater., **3**, 210 (1994).

9. Artamonov V., Klyui N., Perez-Rodriguez A. et al., Ceramics Intern., **26**, 29 (2000).

10. Peng X.L., Barber Z.H., Clyne T.W., Surface and Coatings Technol., **136**, 23 (2001).

Received 31.10.05.

Translated from Ukrainian by O.I. Voitenko

ОПТИЧНІ ТА МЕХАНІЧНІ ВЛАСТИВОСТІ АЛМАЗОПОДІБНИХ ВУГЛЕЦЕВИХ ПЛІВОК, ЛЕГОВАНИХ АЗОТОМ

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Р е з ю м е

Досліджено оптичні та механічні властивості алмазоподібних вуглецевих плівок (АВП), отриманих методом плазмохімічного осадження (PE-CVD — plasma-enhanced chemical vapor deposition) з газової суміші $\text{CH}_4\text{—H}_2\text{—N}_2$ з різним вмістом азоту. Змінювали також потужність розряду та тиск у плазмовому реакторі. Оптичні властивості АВП досліджували еліпсометричними методами, вимірювали спектри пропускання та відбиття. Для дослідження механічних властивостей плівок використовували метод наноіндентування та вивчали їх стійкість проти спрацювання. Товщину плівок додатково визначали за допомогою профілометра і порівнювали з даними еліпсометричних досліджень. Показано, що із збільшенням вмісту азоту в плівках і зменшенням потужності розряду збільшується оптична ширина забороненої зони плівок, а отже, і їх пропускання. При цьому твердість плівок і показник заломлення зменшуються. Швидкість осадження плівок при збільшенні потужності розряду суттєво зростає, тоді як вміст азоту в газовій суміші менше впливає на цю характеристику.