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Photoluminescent properties of nitrogen-containing DLC films

Nickolai Klyui[a,*], Yurii Piryatinskii[b], Andriy Romanyuk[a], Vicktor Semenovich[a]

[a]Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 45 Nauki prospect, 252028 Kiev, Ukraine
[b]Institute of Physics, National Academy of Sciences of Ukraine, 46 Nauki prospect, 252028 Kiev, Ukraine

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Abstract

a-C:H:N films were studied by time-resolved photoluminescence (PL) spectroscopy. It was shown that, on the one hand, the increasing of nitrogen content in gas mixture leads to a dramatic increase of PL intensity and to downshift of the main PL band. On the other hand, in PL spectra measured from the lateral face of the films the significant narrowing of the PL bands was observed.

Keywords: Photoluminescence; DLC-films

1. Introduction

Recently diamond-like carbon (DLC) films have attracted considerable attention as a promising material for electroluminescent emission device preparation [1]. The prospect of these devices is based on the following properties of DLC films:

1. the capability of synthesizing DLC structures with an altering optical band gap (up to 4 eV);
2. intensive visible photoluminescence stimulated by the absence of the k-conservation selection rule in amorphous materials;
3. the doping of DLC with different kind of impurities during the film growth and after that;
4. high chemical and radiation hardness;
5. the capability of synthesizing large quantities of the novel mechanically durable DLC coatings.

The investigation of luminescence properties of DLC films is necessary for the development of the light emitting structures based on the DLC films.

Photoluminescence (PL) of DLC films has been described [2–5]. Among the main results obtained by different authors the non-monotonous character of PL intensity upon nitrogen doping [2,3] should be noted. In Ref. [3] high energy PL in low optical Tauc gap a-C:H:N films has been observed. Therefore the dependence of PL of DLC films on deposition parameters needs to be investigated in detail. PL in a-C:H:N films coupled with other optical properties (for example, optical band gap) might also provide an insight into the PL mechanism in a-C:H:N films.

The aim of this work is to study the effect of nitrogen on the photoluminescent properties of diamond-like carbon films. Special attention is given to the study of PL in dependence on geometry of experiment.

2. Experimental

The DLC (a-C:H:N) films were deposited by r.f. glow discharge in a parallel plate reactor. The r.f. power (13.56 MHz) was applied to the lower electrode, the upper electrode was grounded. The gas mixture (CH_4, H_2 and N_2) were introduced through the upper electrode in a shower head flow configuration. The substrates for deposition were put directly on the lower electrode which was cooled by water. The total pressure in the reaction chamber was 0.8 torr. During the plasma decomposition experiments r.f. bias voltage was fixed and equalling 1900 V. The thickness of the films was 1200 nm and the films were deposited on quartz substrates. DLC films with different nitrogen contents were deposited from mixtures of methane, hydrogen and nitrogen by a gradual replacement of hydrogen by nitrogen.

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* Corresponding author. Tel.: +7-44-265-62-02; fax: +7-44-265-85-42.
E-mail address: klyui@depy.semicond.kiev.ua (N. Klyui).

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The PL was excited by a nitrogen laser ($\lambda_{ex} = 337.1$ nm). The duration of the light pulse was 10 ns and the peak pulse power was 3 kW. Light emitted from the films was directed to the FEU-77 or ELU-FS photomultiplier through SPM-2 monochromator.

The optical constants (refractive index n and extinction coefficient k) of DLC films were measured by the spectroscopic ellipsometry from 1.5 to 5.6 eV and the laser ellipsometry at a fixed wavelength of ($\lambda = 632.8$ nm). The optical band gap (E_g) of DLC films was determined from Tauc's equation. The Auger electron spectroscopy (AES) was used to calculate the nitrogen concentration in a-C:H:N films. All measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 shows some PL spectra for a-C:H:N films obtained at different nitrogen content in the gas mixture (P_{N2}). It is seen that for the films obtained at $P_{N2} \leqslant 20\%$ the PL band maximum is situated at ~450 nm and the PL band intensity changes slightly under changing of the nitrogen content in the plasma and film. The increasing of P_{N2} up to 30% leads to drastic downshift of PL band maximum (from 450 to 580 nm). The PL band intensity remains practically constant in this case. At the same time further increasing of the nitrogen content in the gas mixture ($P_{N2} \geqslant 30\%$) results in a significant increase of the PL band intensity whereas the energy position of the band remains practically unchanged. The results obtained may be interpreted in the framework of the model proposed in [5]. At a low nitrogen content in the film the nitrogen atoms are incorporated at sp^2-cluster boundaries activating the centers of high-energy photoluminiscence [3–5]. In this case the PL intensity increases slightly with the increasing of the nitrogen content (Fig. 1) and the PL band energy position remains constant. Further increasing of the nitrogen content in the films results in the access of nitrogen to be incorporated into sp^3-coordinated matrix.

In this case the average co-ordination number of the network decreases because the nitrogen atoms have a co-ordination number of three. As a result, the internal stress caused by the distortions in the sp^2 clusters [3] is reduced. Decrease in the internal stress can promote the formation of sp^3-coordinated phase [6]. As a result, E_g must increase as shown in [7]. The same behaviour of E_g was observed in our experiment (not presented). In our case, the nitrogen atoms, being incorporated in the replacing position, can create the empty sites in the forbidden gap of a-C:H:N films [8]. As a result, an optically excited electron may non-radiatively pass to these states followed by a radiative recombination with a hole from the tail states at the top of the valence band. On the one hand, it can be responsible for a downshift of PL band; on the other, the intensity of the low energy PL must be proportional to the concentration of empty states in the forbidden gap of a-C:H:N films, and, hence, to the nitrogen concentration in the films. Fig. 2 shows the dependence of PL band intensity on the relative nitrogen content in the films determined from Auger electron spectroscopy data.

As can be seen from Fig. 2, the PL intensity of low energy component at $\lambda = 590$ nm, for films deposited at $P = 0.8$ torr, increases almost linearly with the increase in the nitrogen concentration, while the PL intensity of the high energy component at $\lambda = 450$ nm is almost constant. The latter supports the conclusion about the different nature of the PL bands observed at $\lambda = 450$ nm and at $\lambda = 580$ nm. The larger line width and greater PL intensity in the maximum of PL band at $\lambda = 580$ nm is evidence for high integral PL intensity a-C:H:N films containing more nitrogen (Figs. 1 and 2).

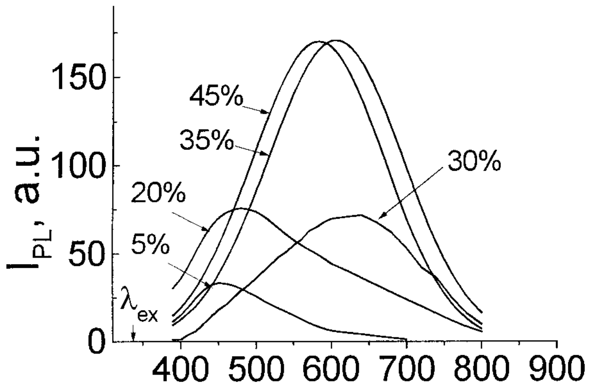

Fig. 1. PL spectra of a-C:H:N films obtained at different nitrogen content in gas mixture.

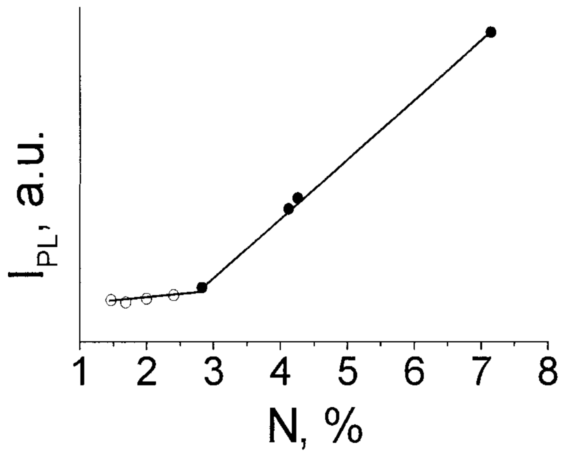

Fig. 2. Dependence of PL band intensity on relative nitrogen content (N) in a-C:H:N films. ○ — high energy PL band, ● — low energy PL band.

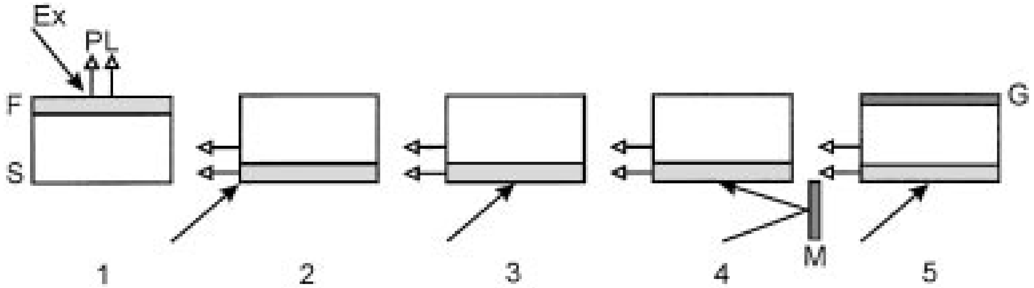

Fig. 3. Schematic presentation of experiment geometry. S — substrate, F — film, Ex — laser excitation, PL — photoluminescence, G — grinding side, M — mirror.

The latter testifies that a-C:H:N films with a high nitrogen content are promising materials for the creation of light source for visible spectral range. Moreover, the authors of Ref. [9] undertook the investigation in order to use PL properties and constructional features of *ta*-C:H films for development of a visible light source with adjustable wavelength. They observed some narrowing (monochromatization) of PL band measured from the lateral side of *ta*-C:H film [9]. We have investigated the PL peculiarities of a-C:H:N films. The PL spectra were registrated from the front and lateral side of the film under different geometry of experiment (Fig. 3).

For comparison, the measurements of the PL spectra of a-C:H film were also carried out. The results obtained are presented in Fig. 4. One can see that some narrowing of PL band is observed in the PL measurements from the lateral side of the film. This effect can be explained in a similar manner as in Ref. [9]. The light emitted by PL active centers in the films propagates in various directions. But only light emitted in the angle range limited by the angle of total internal reflection (ATIR) on the film-substrate interface propagates in the film. The light passed through the film-substrate interface propagates in the substrate within the angle range limited by the ATIR on the substrate–air interface. The interference of light propagating in limited angle range is probably responsible for the narrowing of PL band measured from the lateral side of the film.

It is evident that the energy position and half-width of the PL bands must be determined by refractive indexes and the thicknesses of the film and substrate.

These conclusions are confirmed by the results presented below. Fig. 5 shows the PL spectra measured for a-C:H:N films in different geometry of experiment shown in Fig. 3. It should be noted that the films were deposited at $P_{N2}=45\%$ and demonstrated the highest PL intensity (see Figs. 1 and 2).

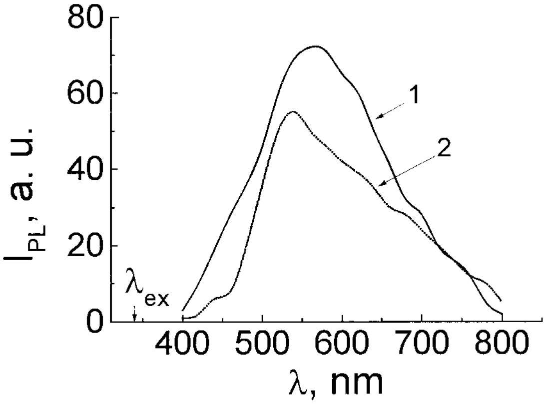

Fig. 4. PL spectra of a-C:H film. 1 — case 1, Fig. 3, 2 — case 3, Fig. 3.

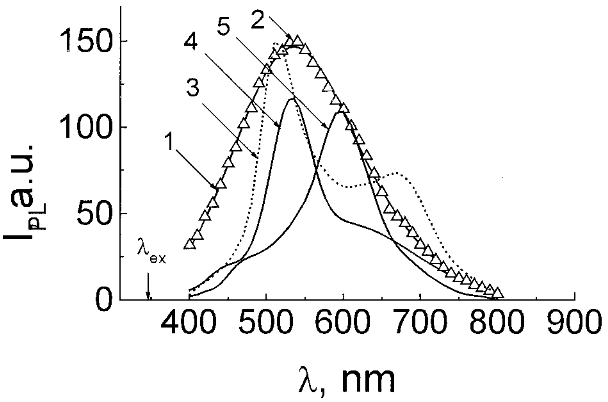

Fig. 5. PL spectra of a-C:H:N films. The curve numbers correspond to cases shown in Fig. 3.

In the PL spectrum measured in conventional geometry (Fig. 3, case 1) a broad PL band is observed (Fig. 5, curve 1). At the same time sharp narrowing and even appearance of a few distinct PL bands takes place in PL spectra measured from the lateral side of the a-C:H:N films (Fig. 3, cases 3, 4; Fig. 5, curves 3, 4). In the case shown in Fig. 3, case 2 the PL radiation practically at once is emitted from the film without any propagation in the film. If the model presented above is correct, one can expect that the PL spectrum measured in such geometry must be the same or close to the spectrum measured in the conventional geometry (Fig. 5, curve 1). Indeed, there is no marked discrepancy between them (see Fig. 5, curves 1, 2).

Some differences between the PL spectra measured in geometry 3 and 4 (Fig. 3) are caused by different excitation conditions. In the case shown in case 4 (Fig. 3) the laser beam is incident on the film at rather a significant angle. As a result of total internal reflection the laser irradiation penetrates inside the film exciting additional PL centers. The latter substantially changes the interference conditions leading to modification of PL spectrum (Fig. 5, curve 4).

It should be noted that PL from the lateral side of the a-C:H:N films–quartz substrate structure could be observed by the naked eye. Moreover, it was clearly seen that the "red" PL band was localized closer to the film, whereas the "blue" one to the substrate. In order to exclude the effect of the substrate on the measured PL spectra the backside of the quartz substrate was ground by coarse diamond powder (Fig. 3, case 5). The PL spectrum measured in such geometry is presented in Fig. 5, curve 5. It is seen that only the "red" PL band is observed in the spectrum and the "blue" one practically disappeared. It should be pointed out that refractive indexes of the investigated a-C:H and a-C:H:N films were 2.0 and 1.6, respectively. Taking into account this fact it is evident that PL radiation penetrates in a-C:H:N film within a narrower angle range than in a-C:H film because of lower value of ATIR. It provides more optimal conditions for light interference and results in the PL band half-width to be substantially narrower for a-C:H:N film–quartz substrate structure (see Figs. 4 and 5).

4. Conclusions

The obtained results show that nitrogen substantially influences the structure and optical properties of DLC films. The drastic increase in intensity and downshift of the PL band was observed for the a-C:H:N films with a high nitrogen content. It was also established that we can manage the intensity and energy position of the PL bands by changing the geometry of an experiment and excitation conditions.

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