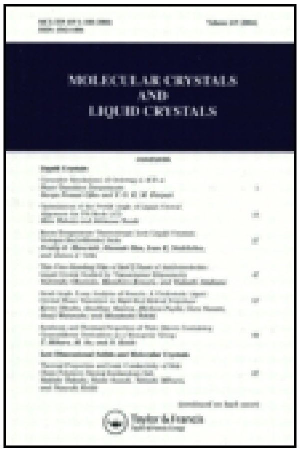

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Modification of Optical Properties of a-C:H and a-C:H:N Films Subjected to Ion Implantation and UV Treatment

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Optical properties of a-C:H and a-C:H:N films subjected to UV and proton irradiations have been investigated by photoluminescence (PL) and spectral ellipsometry (SE) methods. It was shown that the optical properties and PL mechanism of a-C:H:N films depend strongly on nitrogen concentration in the films. a-C:H:N films with high nitrogen content are more tolerant to UV-treatment. In all cases, proton implantation leads to some quenching of luminescence due to introduction of non-radiative recombination centers.

Keywords: carbon films, UV treatment, ion implantation, photoluminescence

INTRODUCTION

Amorphous hydrogenated carbon films are very attractive *to apply as* antireflecting and protective coatings for optoelectronics devices[1]. On the other side, polymerlike a-C:H and a-C:H:N films have rather intriguing lumniscent properties making them the candidates for light emitting structure production[2-5]. Besides, having high optical band gap and tranperancy these films despite low hardness can be used as protective coatings for space solar cells. In any case, it is very important to study the optical properties of the films subjected to different treatments. On the one hand, it is necessary to study the film's stability. On the other, as it was shown earlier[1, 6], UV and proton irradiations result in phase-structural transformation in the irradiated films that is of great interest of a fundamental standpoint.

In this work the effect of UV and proton irradiation on the optical properties of a-C:H and a-C:H:N films was studied by photoluminescence and spectral ellipsometry methods.

EXPEREMENTAL DETAILS

a-C:H and a-C:H:N films were prepared in a rf (13.56 MHz) plasma discharge by decomposition of CH_4:H_2:N_2 gas mixture. The deposition pressure in the reaction chamber (P) was 0.8 Torr. The bias voltage was about 1900 Volts. The thickness of the films was varied from 100 to 1000 nm. Some of the films were subjected to UV-treatment by 150 W Hg-lamp and implanted by H^+ ions ($E=50$-150 keV, $D=10^{15}$-10^{16} cm^{-2}).

The time-resolved photoluminescence spectroscopy technique was used to measure the character changes in a-C:H and a-C:H:N films before and after treatments. The PL was excited by a nitrogen laser ($\lambda_{ex}=337.1$ nm). The optical constants (refractive index n and extinction coefficient k) of DLC films were measured by the spectroscopic ellipsometry in the spectral range from 1.5 to 5.6 eV. The optical band gap (E_g) of the films was determined from Tauc's equation. All measurements were carried out at room temperature.

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 $P_{N2} \leq$ 20% the PL band maximum is situated at ~450 nm and the PL band intensity is changed 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 ($P_{N2} \geq 30\%$) results in a significant increase of the PL band intensity whereas the energy position of the band varies slightly.

The results obtained may be interpreted in the framework of the model proposed in[5]. At low nitrogen content in the film the nitrogen atoms are incorporated at sp^2-cluster boundaries activating the centers of high-energy photoluminiscence[2, 4, 5]. Further increasing of the nitrogen content in the film results in the access of nitrogen to be incorporated into sp^3-coordinated matrix. In this 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[7]. 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 that was actually observed in our experiments[5]. It should be also noted, that the PL band position downshift and the PL intensity increasing with increase in nitrogen content in the films are accompanied by increasing of optical bandgap from 2,8 eV (P_{N2}=20%) to 4,0 eV (P_{N2}=45%). High transperancy, low hardness (<1 GPa) and refractive index (~1.6) of the a-C:H:N films obtained at P_{N2}=45% as well as high hydrogen content in them (>50 at. %) testify that the films are polymerlike ones.

Fig. 2 shows PL spectra of some a-C:H:N films measured before and after UV-irradiation. The films were irradiated by 150 W Hg-lamp for 1 hour. It is seen from Fig. 2 that after UV-treatment PL band intensity of a-C:H:N film obtained at P_{N2}=20% dramatically decreases whereas the PL band position remains practically unchanged. At the same time, the intensity of PL band for a-C:H:N film growth at P_{N2}=45% even slightly increases after UV-irradiation and some upshift of PL band position takes place. These results are also the evidence of different PL mechanisms for the films with low and high nitrogen content. The PL quenching in a-C:H:N film with low nitrogen content after UV treatment is stipulated by appearance of non-radiative recombination centers, such as dangling bonds. Such centers may be formed as a result of π-bonds breaking. It should be pointed out that π-bond in carbon is rather weak (~3.5 eV) and may be exited or even broken by high energy UV irradiation[6]. As it was mentioned above the nitrogen containing centers are responsible for the PL in a-C:H:N films with high nitrogen content. It is the evident that carbon-nitrogen bonds are very strong[8] and, hence, tolerant to UV irradiation that can be a reason of the film's PL properties stability. The upshift of PL band energy position after UV irradiation (sample 2, Fig. 2) may be connected with the optical bandgap increasing[6]. However, this effect should be studied in more detail. The dangling bonds saturation by nitrogen[9] under the action of UV radiation is most likely responsible for the increasing of PL intensity (curve 2`, Fig. 2).

Another reason for a different effect of UV treatment on a-C:H:N films having various nitrogen content is a distinction of optical bandgap values. Indeed, for the film with low nitrogen content (P_{N2}=20%) and low bandgap *(sample* 1) the UV radiation is absorbed more effectively leading to more substantial modification of the film properties.

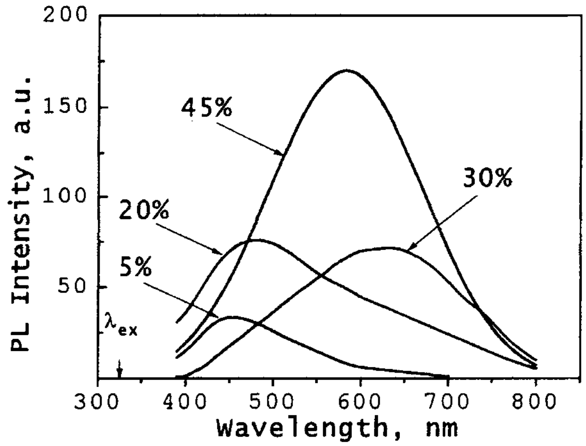

FIGURE 1. PL spectra of a-C:H:N films obtained at different nitrogen content in gas mixture (P = 0.8 Torr).

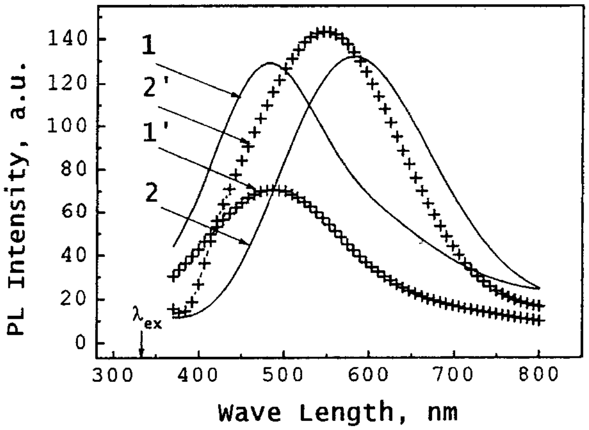

FIGURE 2. PL spectra of a-C:H:N films obtained at P=0.8 Torr and different nitrogen content in the gas mixture: 1 – 20%, 2 – 45%;1,2 – initial films, 1`, 2` -after UV treatment. For convenience the intensity of 1 and 1` PL spectra were increased 5 and 50 times, correspondingly.

Implantation of H^+ ions into a-C:H and a-C:H:N films in all cases resulted in some decreasing of PL intensity because of ion-beam induced film disordering and appearance of the centers of non-radiative recombination. However, it is interesting to note that UV irradiation of preliminary implanted films leads to marked increasing of PL intensity. In this case the implanted hydrogen under the action of UV treatment can saturate dangling bonds leading to PL intensity increasing.

In this work we reported on optical properties of a-C:H and a-C:H:N films subjected to UV and proton treatments. The possible mechanisms of the effect of nitrogen on a-C:H:N film optical properties as well as on their radiation stability were also proposed.

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