

Nitrogen containing diamond-like carbon films as protective and fluorescent layers for silicon solar cells

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Thick (1300–1500 nm) diamond like carbon (DLC) films deposited on a working side of a solar cell (SC) allow us to increase its stability relating to the effect of proton and ultraviolet (UV) irradiation. So, one-stage ($E = 50$ keV) or multi-energy ($50 + 100$ keV) implantation of proton into protected SC (the S.C. + DLC films system) did not practically influence SC parameters. Moreover, SC covered by DLC film after UV irradiation shows improvement in efficiency both for implanted and unimplanted samples. At the same time the unprotected SC deteriorated after those treatments. The effects observed are connected with decreasing reflection losses due to deposition of DLC films, re-emission by DLC film of absorbed ultraviolet light in visible spectral range, and self-annealing of radiation damages in implanted DLC films due to light-induced hydrogen bonding. The results obtained have opened up a wide variety of potential applications of DLC films, especially for space solar cells.

Keywords: solar cell, diamond like carbon film.

1. Introduction

Recently, it has been shown that diamond-like carbon (DLC) films are very promising antireflecting and protective coatings for silicon solar cells (SCs) [1–4] including for space SCs [5]. The main advantages of DLC films are high hardness, chemical, and radiation stability as well as the possibility to change their optical properties under variation of deposition conditions.

In order to use DLC films as protective coatings for SCs of space application as thick as possible films should be deposited to prevent degradation of SCs under action of “solar wind”. For this aim the most suitable are nitrogen containing DLC films. It is connected with low internal mechanical stresses in the films [6] and, hence, with the possibility to grow thick coatings as well as with their high transparency and radiation stability.

Thus, the aim of this study is to show that due to deposition of DLC films the efficiency and radiation stability of silicon solar cells can be substantially improved. Parameters of silicon solar cells covered with DLC films have been investigated.

2. Experimental details

a-C:H:N films were prepared in a rf (13.56 MHz) plasma discharge by decomposition of $\text{CH}_4:\text{H}_2:\text{N}_2$ gas mixture. The deposition pressure in the reaction chamber (P) was 0.8 Torr. The bias voltage was about 1900 V. The films thickness was varied from 100 to 1500 nm. Some of the films were subjected to ultraviolet (UV) treatment by 150 W Hg-lamp and implanted by H^+ ions ($E = 50\text{--}150$ keV, $D = 10^{15}\text{--}10^{16}$ cm^{-2}). DLC films with different nitrogen contents were deposited from mixtures of methane, hydrogen and nitrogen by a gradual replacement of hydrogen by nitrogen. The films were deposited on the front side of SCs with induced p-n junction fabricated on the base of silicon.

The time-resolved photoluminescence (PL) 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 ($\lambda_{\text{ex}} = 337.1$ 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.

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3. Results and discussion

Figure 1 shows some PL spectra for a-C:H:N films obtained at different nitrogen content in the gas mixture (P_{N_2}). It can be seen that for the films obtained at $P_{N_2} \leq 20\%$ 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. Increase in P_{N_2} , up to 30%, leads to drastic downshift of PL band maximum (450–580 nm). The PL band intensity remains practically constant in this case. At the same time further increase in nitrogen content of the gas mixture ($P_{N_2} \geq 30\%$) results in a significant increase in PL band intensity whereas the energy position of the band varies only slightly.

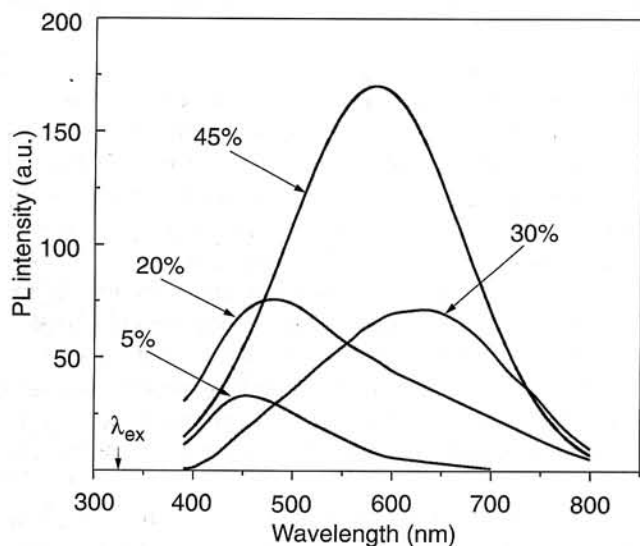


Fig. 1. PL spectra of a-C:H:N films obtained at different nitrogen content in gas mixture ($P = 0.8$ Torr).

The results obtained may be interpreted in the framework of the model proposed in Ref. 7 where it was supposed that 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 that was actually observed in our experiments [7]. It should be also noted, that downshift of PL band position and increasing PL intensity with increase in nitrogen content in the films are accompanied by increasing optical bandgap from 2.8 eV ($P_{N_2} = 20\%$) to 3.96 eV ($P_{N_2} = 45\%$). The high transparency, low hardness (< 1 GPa) and refractive index (~ 1.6) of the a-C:H:N films obtained at $P_{N_2} = 45\%$ as well as high hydrogen content in them (> 50 at.%) testify that the films are polymerlike ones.

Figure 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 can be seen from Fig. 2 that after UV-treatment PL band intensity of a-C:H:N film obtained at $P_{N_2} = 20\%$ 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 $P_{N_2} = 45\%$ even slightly increases after UV-irradiation and some upshift of PL band position takes place. These results are also 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 the centres of non-radiative recombination, such as dangling bonds. Such centres 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 excited or even broken by high energy UV irradiation [9]. As it was mentioned above the nitrogen containing centres are responsible for the PL in a-C:H:N films with high nitrogen content. It is evident that carbon-nitrogen bonds are very strong and, hence, tolerant to UV irradiation that can be a reason of the film 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 [9]. However, this effect should be studied more detailed. The dangling bonds saturation by nitrogen under action of UV radiation is most likely responsible for the increasing of PL intensity (curve 2', Fig. 2).

Another reason of 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 ($P_{N_2} = 20\%$) and low bandgap (sample 1) the UV radiation is absorbed more effectively leading to more substantial modification of the film properties.

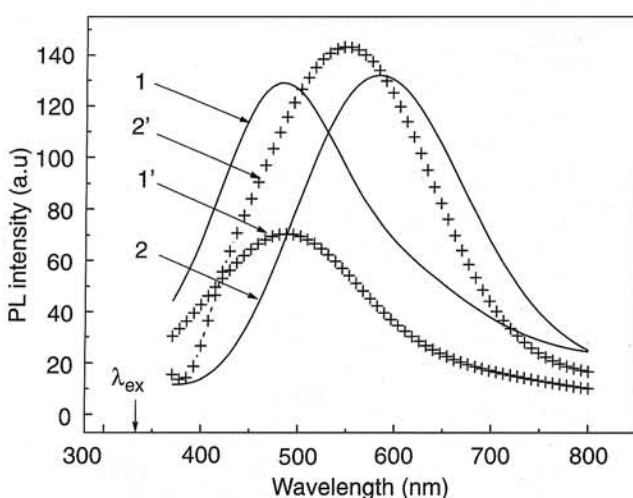


Fig. 2. PL spectra of a-C:H:N films obtained at $P = 0.8$ Torr and different nitrogen content in gas mixture: 1 – 20%, 2 – 45%, 1,2 – initial films, 1',2' – after UV treatment. For convenience the intensity of 1 and 1' PL spectra were increased 5 and 50 times, correspondingly.

In Table 1, some parameters of a-C:H:N films as well as the efficiency of SCs with and without a-C:H:N coatings are presented. The efficiencies of SCs subjected to proton implantation or UV treatment are also given.

It is seen from the Table that after deposition of thick (1500 nm) protective a-C:H:N film the SC efficiency slightly deteriorates. However, such structure is very tolerant to proton implantation (sample 1b) whereas unprotected SC after such treatment drastically degrades (sample 2a). It should be pointed out that the film thickness is quite enough to protect the SCs from the action of the most intensive "solar wind" proton flux (see Fig. 3) [10]. Arrow in Fig. 3 shows the ion energy of the implanted protons used in our experiments.

It is interesting to note that according to extinction coefficient value and film thickness (see Table) absorption losses in the a-C:H:N films have to be 15–20% at 632.8 nm. Moreover, the losses will be higher at shorter wavelengths. As we can see from Table 1, decrease in the SC efficiency after a-C:H:N film deposition is only ~1%. Such discrepancy, in our opinion, is connected with partial re-emission by DLC film of absorbed UV light in visible spectral range (see Fig. 1). Thus, the a-C:H:N film acts as a fluorescent layer. Effect of passivation of recombination active centres by DLC film should be excluded in this case, because of the film was deposited just onto antireflecting SiO₂ film. It should be noted that when a-C:H:N film was deposited onto SC after removal of SiO₂ film effect of SC efficiency increasing was observed.

Some degradation of the SC efficiency covered only 100 nm SiO₂ antireflecting film (sample 3) was also observed after UV treatment (sample 3a). At the same time, the SC efficiency with DLC film protective coating after

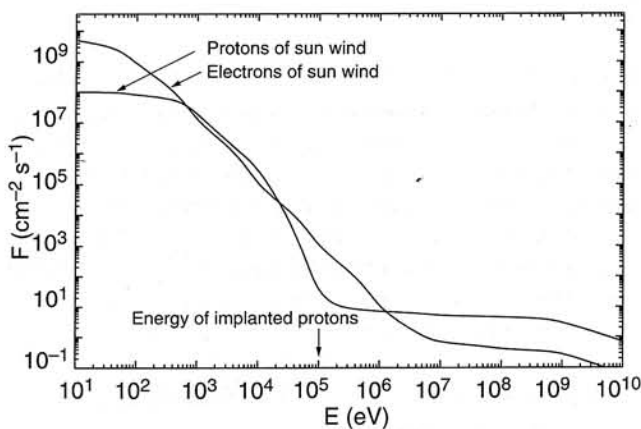


Fig. 3. Integral spectra of protons and electrons in cosmic space (after Ref. 10).

the same treatment actually improved slightly (sample 4a). It is evident that the effect mentioned is stipulated by decreasing of the DLC film absorption (see Table 1). It can be connected with band tail states compensation due to incorporation of oxygen into the film [9] or the film structure rearrangement undergoing of UV irradiation.

It should be pointed out that the possibility to vary the gas pressure and/or rf bias voltage during the same deposition process makes it possible to obtain multi-layer coatings based on a-C:H:N films and having depth gradient of refractive index. In this case, the problems of optimal antireflecting and protective effects may be solved simultaneously.

In conclusion, it has been shown that owing to high radiation stability a-C:H:N films are very promising protective coatings for silicon solar cells.

Table 1. a-C:H:N film parameters and Si SCs efficiency with and without protective coatings.

Sample No.	a-C:H:N films						SC eff. (%)	Illumination conditions
	P _{N2} (%)	P (Torr)	d (nm)	N	k	E _{opt} (eV)		
1	–	–	–	–	–	–	11.3	AM0
1a	45	0.8	1500	1.65	0.005	3.96	10.3	AM0
1b*	45	0.8	1500	1.66	0.006	3.94	10.2	AM0
2	–	–	–	–	–	–	11.3	AM0
2a*	–	–	–	–	–	–	4.3	AM0
3	–	–	–	–	–	–	12.6	AM0
3a**	–	–	–	–	–	–	11.4	AM0
4	45	0.8	1500	1.65	0.005	3.96	12.3	AM0
4a**	45	0.8	1500	1.65	0.004	4.0	13.4	AM0

P_{N2} and P is the partial nitrogen pressure and the total gas pressure in chamber during DLC film deposition process, respectively. d, n, and k are the film thickness, refractive index, and extinction coefficient, correspondingly.

*Samples 1b and 2a are the samples 1a and 2, respectively after implantation of H⁺ ions (E = 100 keV, D = 5×10¹⁵ cm⁻²).

**Samples 3a and 4a are the samples 3 and 4, respectively after UV irradiation.

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