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Luminescence, recombination and laser damaging of a-CN:OH films grown by reactive sputtering

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In this work, porous a-CN thin films (with hydroxyl inclusions) were grown by rf sputtering system and their photoluminescence (PL) properties investigated. In particular, we investigated the stability of the films on irradiation with visible light and discuss possible recombination mechanisms of the electron-hole pairs that are responsible to the PL process. As-grown films are not stable, when light is irradiated above 10 mW on the sample having area of 3 μm^2. The material stabilisation up to 50 mW is reached after 12 min of green laser light damaging. The power dependence PL efficiency is discussed in terms of existing recombination models of amorphous semiconductors.

1. Introduction

From the viewpoints of physics, chemistry, material science, astronomy, planetary science, and electronic engineering, amorphous hydrogenated carbon nitride (a-C:N) could be an extremely important new material. Beside the attempts to prepare super-hard, (micro)-crystalline C_3N_4 phases, nitrogen incorporation in amorphous carbon is an important research field due to the strong reduction of optical band gap and structural disorderness [1]. A consequence of this is strong photoluminescence (PL) exhibited by floppy, low band gap (<1.5 eV) amorphous carbon nitride (a-CN) based thin films [2, 3]. Polymer-like hydrogenated amorphous carbon (a-C:H) film also exhibits similar PL efficiencies [4], having higher hydrogen contents (>50%), wide band gaps (>3 eV) and high resistivity. The luminescence properties of a-CN film may also be practical interest for electroluminescent devices with active layers and are much more promising than that of a-C:H [5] films. In this article we investigated the PL properties of a set of a-CN(:OH) films, focusing on the correlation between the intensity of the PL signal and excitation laser power.

2. Experiment

Films were grown at room temperature on (100) c-Si and glass substrates using radio-frequency (13.56 MHz) sputtering system with a graphite target in nitrogen atmosphere (N_2 flow rate: 80 sccm). No deliberate substrate bias was applied during deposition. The Pressure and RF power were 15 mTorr and 150 W respectively. The deposition conditions are different from those previously used with the same sputtering system [6], where the geometry of the chamber were varied by changing the distance between the electrodes. Deposition condition and different film properties of the present films are given in Table I.

Transmittance and reflectance spectra were measured on a Perkin-Elmer Lambda spectro-photometer over the wavelength range 0.3 to 2.5 μm. The absorption coefficient (α) and the optical (Tauc) gap were evaluated using standard techniques [7] and are given in Table I. IR analysis was carried out by using a Perkin-Elmer FTIR 2000 spectrometer in the transmission mode, taking the bare c-Si substrate as a reference. The spectra of samples having extreme values of self-bias are shown in Fig. 1. The film thicknesses were measured with a Tenkor profilometer.

The room temperature PL investigations were carried out at 2.4 eV laser excitation energy. A Renishaw micro-Raman monochromator was used in order to simultaneously acquire well-resolved Raman peaks and obtain information on possible sample annealing during the measurements at the highest excitation powers. In order to compare the PL intensity of the different films, we have calibrated the spectra with the Raman peak of the c-Si bare substrate at 520 cm^{-1} and normalised the measured values considering the different reflection and absorption coefficients of the films [8]. The measurements were performed at increasing excitation powers from 1 to 100 mW at the sample surface having spot area ∼3 μm^2. The dependence of the PL on the excitation power was investigated under two

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TABLE I Deposition parameters and film characteristics

Sample	Electrode spacing (mm)	Self Bias (V)	Thickness (nm)	Optical gap (eV)	α at 2.41 eV (10^4 cm^{-1})
MGF509	25	−730	135	1.15	3.0
MGF513	20	−700	125	1.20	3.1
MGF514	15	−570	100	1.25	2.7

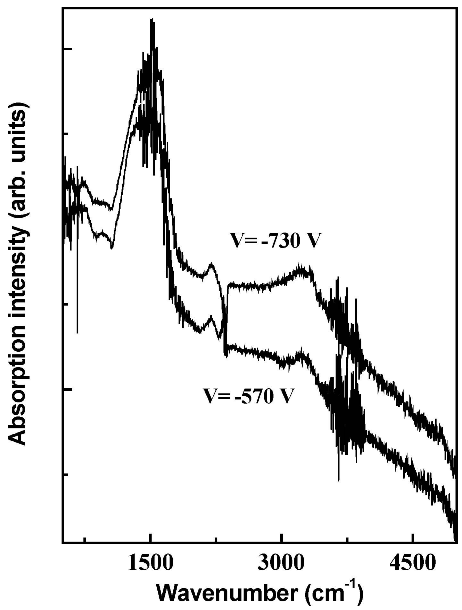

Figure 1 FTIR spectra of the films having extreme values of self-bias voltage, −730 V (MGF509) and −570 V (MGF514) normalised by their thickness. It is noted that, all nitrile groups evidenced by the stretching peak at 2200 cm^{-1} [9] are featured by lone-pair electrons which are possible role in recombination as discussed in Section 4.

different conditions:

1. On the 'as deposited' samples, and
2. After damaging using 2.4 eV laser light (16 mW/μm^2) for 12 min.

3. Results

In the light of following discussion, we focus only on the results, which are relevant to the PL analysis. The IR spectra show (Fig. 1) the presence of hydroxyl (—OH) groups in these films (3200–3600 cm^{-1}) [9, 10]. As O and H were not present in the deposition chamber, we attribute their presence to the film exposure to atmospheric water vapour after deposition, correlated with the presence of interconnected pores. The presence of hydroxyl groups may play a role in determining the local field effects and wave function confinement. So it's better to describe the films as a-CN:OH and not as a-C:N. It is observed in IR spectra that absorption is decreased with decreases of self-bias voltage and this is due to presence of hydroxyl groups in the film structure (Fig. 1). This suggests [10] an increase of compactness of the film structure as it is known that an increase of self-bias voltage films leads to porous structures with possibly lower local stresses and distortions. However, IR spectra of all films are similar to that of floppy a-CN films, grown previously [6] with the same deposition system having higher power and pressures but lower electrode spacing (and labelled in ref. [6] as (a)-type a-CN films).

In order to investigate the structural variation of the films and possible annealing effects, we have also analysed the evolution of the G and D peaks of the Raman signal superimposed with the PL and recorded at the same time by collecting photons coming from the same microscopic region of the films. The results of such Raman investigation are reported in Table II and can be summarised as follows:

(1) When the power of the excitation source is increased then the I_D/I_G ratios remains constant for the 'as deposited' film.

(2) The laser damaging procedure (i.e., the exposure of laser light for 12 min) leads to increase of I_D/I_G ratios with respect to the 'as deposited' films. However, when the power of the excitation source increases, I_D/I_G ratios of the 'laser-damaged' samples remain constant.

(3) The total area of Raman signal increases (a) more than linearly with power for the 'as deposited' samples (b) linearly with power for the 'laser-damaged' samples.

(4) In the 'as deposited' films, the width of the D peak decreases with increasing power;

In carbon nitrides, such as in amorphous carbons, the I_D/I_G ratio is related to the size of the aromatic clusters in the films [11]. Thus, points (1) and (2) indicate that the aromatic structures are not modified in shape or size by annealing effects during the measurements

TABLE II Features of Raman signal for as deposited and laser soaked films

		As deposited				After soaking			
($-V_b$)	Power (mW)	G peak width (cm^{-1})	D peak width (cm^{-1})	I_D/I_G	($I_D \pm I_G$) power	G peak width (cm^{-1})	D peak width (cm^{-1})	I_D/I_G	($I_D \pm I_G$) power
−730 V	10	*172*	291	1.30	16.5	*170*	285	1.43	13.1
	25	*169*	275	1.27	17.4	*169*	284	1.46	13.6
	50	*170*	274	1.27	17.8	*170*	280	1.42	13.9
−700 V	10	*172*	274	1.35	12.9	*165*	256	1.38	20.9
	25	*171*	273	1.34	14.1	*166*	255	1.38	21.3
	50	*166*	258	1.32	14.8	*166*	253	1.37	21.6
−570 V	10	*173*	297	1.39	21.7	*183*	294	1.52	10.5
	25	*173*	281	1.37	22.1	*177*	285	1.52	10.9
	50	*175*	264	1.35	22.3	*172*	272	1.51	10.7

at increasing powers, though such modifications occur after a prolong laser damage. At a given I_D/I_G ratio, the intensity of the Raman scattering photons increases linearly with the number of absorbed photons. The non linearity of the Raman intensity versus excitation power (point 3) indicates some structural modification without affecting the aromatic features and may affect the optical absorption coefficient and other structural features of the 'as deposited' samples. This agrees well with the current understanding of the optical properties of carbon nitrides: indeed, different than that of non-nitrogenated amorphous carbons (where optical absorption in the visible-near UV photon energy range only occurs due to π–π^* transitions inside the aromatic clusters [12]). The optical absorption properties of carbon nitrides are controlled by optical transitions and nitrogen-related lone-pair electrons [13], which are not necessarily localised inside such clusters [9].

Overall, the Raman spectra recorded simultaneously with the PL signal indicate that

(1) laser-damaged films remain stable up to 50 mW during measurements and thus, the evolution of the PL signal is not related to structural changes when the power increases, whereas

(2) structural evolution occurs during the measurements of the 'as deposited' films, though the aromatic clusters, where most of the π-electrons are confined or not directly affected

4. Discussion of the PL results

At any given excitation power, the PL spectra (exhibiting in all films almost the same peak position, $E_{PL} \approx 1.85$ eV, and width, FWHM ≈ 0.45 eV) increases with increase of self-bias voltage (see Fig. 2 and Table III), whereas there is a decrease the local distortions. It shows that PL emission occurs at $E_{PL} \approx 1.85$ eV, though their optical band gaps are ≤ 1.25 eV. It is assume that the 'H' and/or 'OH' is passivating the film surface from the atmospheric exposure after deposition and hence PL is originates from the film surface.

The results describe in Section 3 suggest the most appropriate approach to look at the 'local' (i.e., at each point of the x-axis) slope (K) of the relationship between the PL intensity (I_{PL}) and the excitation power (P) given in Equation 1. In Fig. 3, the I_{PL}/P ratio (proportional to the PL quantum efficiency, although the proportionality factor might vary from one curve to the other) is presented as a function of the power. The relation locally describes the curves as follows:

$$I_{PL}/P = \text{constant} \cdot P^K \qquad (1)$$

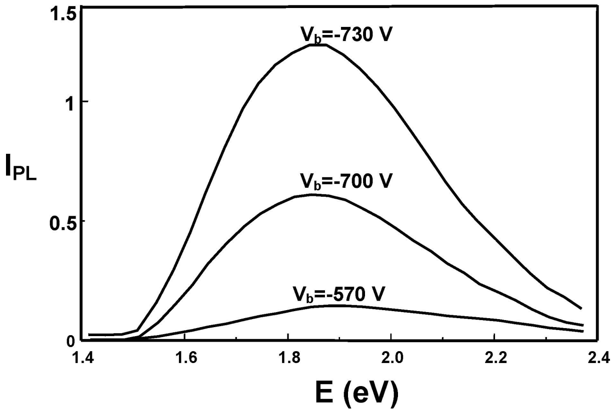

Figure 2 The PL spectra of a-CN:OH 'as deposited' films for an incident laser beam at 2.41 eV having an intensity of 16 mW/μm^2 (50 mW on a spot size of ~3 μm^2) at different self-bias voltage.

TABLE III Photoluminescence properties of the as deposited and laser soaked films

	Integrated PL Intensity∗ (arb. un.)		K (Equation 1) at 10 mW	
($-V_b$)	As dep	Laser Damaged	As dep	Laser Damaged
−730 V	96	183	0.19	0.18
−700 V	71	123	0.18	0.05
−570 V	35	66	0.15	0.06

∗Integrated PL intensities at an incident beam power of 10 mW.

From Fig. 3, several interesting remarks can be made and they are:

(1) the high intensity of the IR signal is due to presence of hydroxyl groups (3200–3600 cm^{-1}, Fig. 1) and leads to higher PL efficiencies. This suggests that 'OH' groups may play a role in the electron-hole confinement and PL process.

(2) films having the higher hydroxyl IR features are the most stable and exhibits a lower increase of PL efficiency.

(3) after the laser damaging procedure, PL efficiency increases in all samples. This is consistent with the release of stress indicated by the Raman results. Care has to be taken in assuming it as an absolute statement, as the absorption coefficients of the laser-damaged films were not monitored.

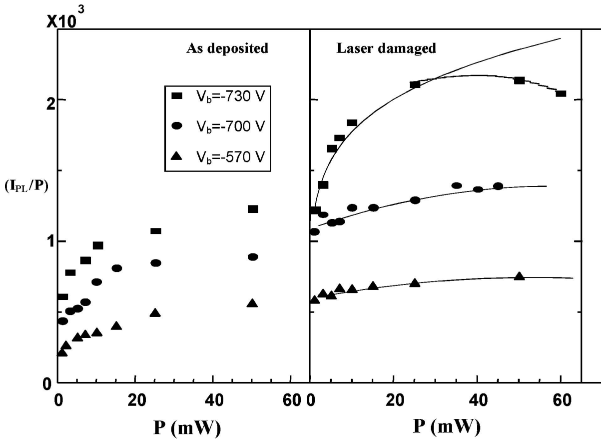

Figure 3 The dependence of the quantum PL efficiency (I_{PL}/P) on the incident power P: for as deposited films and after 12 min of laser damaging (where the continuous lines represent fitting by means of Equation 1 and the dotted line for sample MGF509 (V_b=−730 V) indicates the departure from such a fitting due to the relevance of Auger processes, see text).

(4) a change in slope is observed around 20 mW for 'as deposited' films; which indicates that the structure is stable below such power, while at higher powers change of structure (as suggested by Raman results) occur. The recorded behaviour will be a result of the simultaneous variation in the PL efficiency and the structure.

(5) continuous behaviours can be observed for (structurally stable) laser damaged films, supporting the conclusion quoted at point 3.

(6) the curve of laser damaged film (MGF509 # V= −730 V) goes through a maximum at about 40 mW (a power lower than that used for damaging).

In order to describe such behaviour, we will look at the physical models developed for a-Si:H. The constant behaviour ($K = 0$) observed at low intensity was attributed to geminate recombination (i.e., same pair produced by a single photon recombine radiatively [14]). The increasing behaviour ($K > 0$) found at higher intensities was attributed to the appearance of non-geminate (bimolecular) recombination processes [14].

In all cases (except for point 6 above, which will be discussed later) we have observed that $K > 0$ and focus on non-geminate recombination due to inhomogeneous nature of our films and differences in the nature of involved states (π and lone-pairs instead of σ and dangling bonds) with respect to a-Si:H. In our films electron-hole pairs are mainly generated in the sp^2 and sp^1 regions, and the PL process is likely to occur inside the sp^2 regions, as lone pairs, being occupied and not accompanied by anti-bonding states, may act as non-radiative centres. In order for a non-geminate radiative recombination to occur the spacing between centres should be of the order of the pair size. In such cases, the wave functions of the pairs will strongly overlap, highly increasing the probability of a non-geminate recombination and leading to a $K > 0$ value [14]. Let us assume, as customary [8], that

$$dN = -\alpha N_0 \exp[-\alpha x]dx \qquad (2)$$

where dN represents the number of photons absorbed (per unit surface per unit time) in the layer having thickness dx placed at a depth x fr.om the air-film interface, while N_0 is the number of photons (per unit surface per unit time) entering the film. Elaborating of Equation 2 the average (non randomised) distance between centres of photo-generated pairs will be:

$$d_{\mathrm{av}}(x) = (\mathrm{AEL})^{1/3}[P\tau(1 - e^{-\alpha L})]^{-1/3} \qquad (3)$$

where A is the laser beam cross section at the film surface (which, in thin films, is depth-independent) E is the photon energy, L the film thickness and τ the average recombination time of the pairs. Using the experimental values ($A \sim 3$ μm^2, $P = 10$ mW, $E = 2.41$ eV) and even assuming a very short recombination time ($\tau \sim 10^{-9}$ s) we have, $d_{\mathrm{av}}(\mathrm{x}) \approx 4$ nm (sp^2 cluster size in our films estimated by Raman analysis is $L_c > 1$ nm) [11, 12]. The extension L_π of the π-states is even higher as the presence of π-electrons also the sp^1 phase (as corroborated by IR-active groups $\sim$2200 cm^{-1}) must be considered. Thus, being L_π of the order of $d_{\mathrm{av}}(x)$, some non-geminate recombination is justified.

Radiative and non-radiative recombinations are in competition. Thus, in order to have a high K-value, it is important that the density of non-radiative recombination paths (or centres) is low, so that such paths can be easily saturated. Since a lower density of the non-radiative recombination paths leads to higher PL efficiencies, we expect (before the onset of structural changes) a higher K value for samples with higher PL efficiency. Table III corroborates this idea. The increase of PL intensity with increasing self-bias can be explained with the reduced cross-linking of the structure. Indeed, higher degree of carrier confinement increases the quantum efficiency.

Finally let us focus on the lower 'local' K-values ($K \approx 0$ or, even, in MGF509 # V= −730 V, $K < 0$) observed in the entire laser damaged (i.e., structurally stable) samples. In a-Si:H values of $K < 0$ are often present [15]. They were attributed to 'Auger' recombination processes, in which a dangling bond electron moves deeper in the valence band saturating the hole. It is clear that from the discussion above that such effects are in high competition with the non-radiative processes involving the dangling bonds and their efficiency is low resulting in a sub linear ($K < 0$) dependency of the PL intensity upon the power [15]. In carbon nitride films, role-played for those effect that are discussed above are due to the nitrogen-related lone-pair electrons. Such an effect may be important, assuming a nitrogen concentration of 10 at%, which is realistic in our films [9], the density of lone-pair electrons reach 10^{21} cm^{-3}. Thus, once saturated at lower excitation powers in regions not directly affected by lone-pairs (or possibly: the regions where the 'mixing' of the lone pairs with the π-states may result in the formation of 'spurious' bonding and antibonding states, as suggested in ref. [13]), the 'Auger' effects may become important and strongly reducing the K-value.

5. Conclusions

In summary, we have discussed the behaviour of PL of a-CN:OH (porous carbon nitrides films with hydroxyl inclusions due to atmospheric exposure) films. Despite the onset of structural variations at sufficiently high power densities, in all samples, either before or after laser damaging, the hypothesis of non-geminate recombination has been checked and found to be consistent. The role of distortions and hydroxyl groups and the possible presence of an Auger-like recombination process have been demonstrated and discussed.

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