Thermoluminescent response of carbon nitride thin films deposited by laser ablation

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Abstract

The effect of a high purity nitrogen working pressure on the properties of CN_x thin films grown by laser ablation has been studied. Different analytical techniques were employed to characterize the films including: Thermoluminescence (TL) measurements, Raman spectroscopy, Ion Beam Elastic Dispersion, UV–Vis spectrophotometry, FTIR, and ellipsometry. Analysis of the data shows that in spite of the fact that the system base pressure was better than 10^{-6} Torr and no hydrogen was intentionally introduced into the chamber, incorporation of hydrogen into the film was observed but only when a nitrogen gas flow was used. In this way the deposited amorphous carbon nitride films, with a nitrogen content of up to 20%, almost always contained a significant quantity of hydrogen (22%). The films show a thermoluminescent signal with peaks at 150 and 290 °C after irradiation with UV. When ^{60}Co gamma rays were used, only the 290 °C peak was observed. The Ion Beam Elastic Dispersion analysis showed the presence of lower hydrogen and nitrogen concentrations. The prepared material has a potential application as an ultra-thin TL dosemeter, and since carbon has a low atomic number it can be considered as soft tissue equivalent material for such applications. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Laser ablation has attracted great attention in the last few years as a technique with a great versatility to deposit thin films of a wide variety of materials. This technique has some advantages over other deposition techniques [1]. Particularly important is the possibility of growing films under reactive atmospheres, which has been used successfully to deposit complex oxides [2,3]. Additionally the presence of highly energetic species during the deposition process [4,5] can produce films with good adhesion and high density. These features make this technique a good candidate to grow amorphous carbon nitride thin films (a-C:N).

Amorphous carbon nitride thin films have attracted the attention of many research groups because of the potential applications in a great variety of technological fields [6]. The incorporation of nitrogen into the a-C network reduces the compressive stress resulting in thin films with better mechanical properties [7]. The properties of the deposited a-C:N thin films depend on the $sp^3/sp^2/sp$ carbon bonding ratio, density, hardness and internal stress. These characteristics are strongly dependent on the nitrogen working pressure and laser energy density, which has an important influence on the energy of the plasma species. From this point of view it is of interest to characterize the structural and optical properties of a-C:N thin films deposited by laser ablation, at a fixed laser energy density, as a function of the nitrogen gas pressure.

In this work, we report the thermoluminescent (TL) and photoluminescent (PL) response of amorphous car-

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bon nitride thin films prepared by laser ablation. The TL response was studied by exposing the thin films to ^{60}Co gamma rays and UV radiation. This property makes this material attractive for potential applications on clinical dosimetry taking advantage of its tissue-like composition. Additionally, a-C:N thin films can be prepared with thicknesses as low as 50 nm (volumes of the order of 1×10^{-2} mm^3) making them a very attractive dosimetric tool to address the difficulties associated with the measurements of depth dose distributions over very thin layers such as that of the basal cells in the skin [8]. It is worth noting that TL signal on sodium chloride thin films prepared by laser ablation has been recently reported [9].

The PL response was observed by exciting the films using a 488 nm line of an Ar laser. Other groups, using a variety of techniques, have reported that hydrogenated amorphous carbon nitride (a-CNx:H) can show a photoluminescence signal at room temperature [10,11], but there are few reports of such photoluminescence from samples made using laser ablation.

2. Experimental

2.1. Experimental setup

Laser ablation was performed using a Q-switched Nd:YAG laser with emission at the fundamental line ($\lambda = 1064$ nm) with a 28 ns pulse duration at a repetition rate of 20 Hz. The laser beam was focused on a rotating target, 20 rpm, at an incidence angle of 45°. The target was a graphite disk, 99.99%, 50 mm diameter and 2 mm thick. The substrates used in the present experiments were pieces of silicon cut from (100) wafers and glass microscope slides. The films were deposited simultaneously onto the silicon and glass substrates placed next to each other. This was performed in order
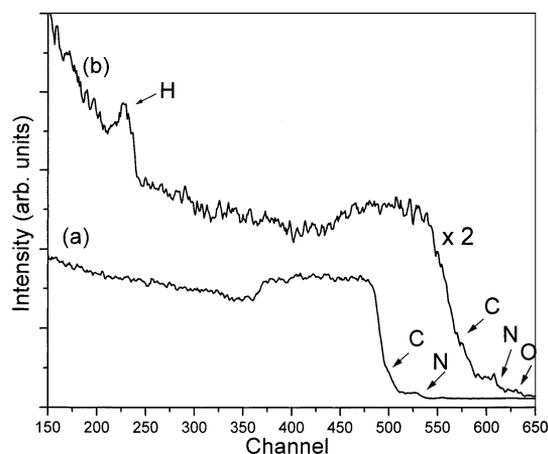
to use the most suitable substrate for characterization purposes. Prior to deposition the substrates were ultrasonically cleaned in an acetone and ethyl alcohol bath. In all the experiments the substrates were placed at 60 mm from the graphite target.

The deposition chamber base pressure was of the order of 10^{-6} Torr and was backfilled with nitrogen (99.99% purity) to the working pressure of, from 4.5×10^{-4} to 7.5×10^{-2} Torr. The thin films were grown at room temperature, a power density of 5×10^9 W cm^{-2}, and the same deposition time for all samples. The deposition time corresponds to approximately 36,000 pulses, resulting in a sample thickness of approximately 100 nm. Detail description of the experimental set up used in these experiments has been reported elsewhere [12].

2.2. Film characterization

The physical properties of the obtained thin films were characterized by Thermoluminescence measurements (TL), Raman spectroscopy, Ion Beam Elastic Dispersion (IBED), UV–Vis spectrophotometry, FTIR, and ellipsometry. The TL response was evaluated from their glow curves, which were obtained using a Harshaw TL Reader model 3500 equipped with a nitrogen supply gas to pass dried and filtered nitrogen during the reading cycle. The heating cycle used was: a pre-heat at 50 °C for 5 s followed by a readout at 300 °C for 25 s with heating ramp rate of 10 °C s^{-1}. Raman spectroscopy was used in order to study structural properties and perform the photoluminescence measurements. The Raman spectra were recorded with a Spex 1403 double monochromator using the 514 nm line of an argon laser in a backscattering configuration. The signal was detected with a photomultiplier and a standard photon counting system. The optical band gap was obtained from a Tauc plot of the ultraviolet/visible spectrometry measurements with an UV/Vis spectrometer (Philips PU8710). The refractive index was determined from ellipsometry measurements. The film thickness was measured with a Sloan Dektak IIA profilometer. Elemental analysis was performed by Ion Beam Elastic Dispersion using a 5.0 MeV ^{7}Li ion beam from a Tandem Van de Graff accelerator. The angle between the ion beam and the sample surface was fixed at 30° meanwhile the angle between the scattered particles and the incident ion beam was fixed at 45°.

3. Results and discussion

3.1. Composition

The concentration profiles of the different elements in the samples were determined from the IBED mea-

Fig. 1. Glow curves of two samples irradiated with: (a) 60 Co gamma rays and (b) UV radiation.

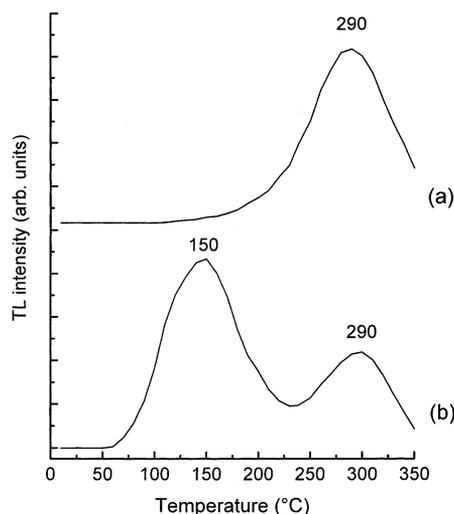Fig. 2. Glow curves of the two samples deposited on (a) glass substrate and (b) silicon substrate.

surements. Fig. 1a shows the experimental spectrum corresponding to a sample grown at a nitrogen pressure of 7.5×10^{-4} Torr in which photoluminescence was not observed. The elemental composition was calculated using the SIMNRA program [13] and the obtained result was $C_{0.84}N_{0.16}$. Fig. 1b shows an experimental spectrum of a sample that exhibits photo and thermoluminescent response. In this case the calculated elemental composition was $C_{0.51}N_{0.20}O_{0.07}H_{0.22}$. It is important to note the presence of hydrogen in this sample in spite of the fact that no hydrogen has been intentionally introduced into the chamber. This sample was grown at a nitrogen pressure of 7.5×10^{-2} Torr and only at this pressure the incorporation of hydrogen into the film was observed. The mechanisms responsible for this behavior are not still understood and will be the subject of further investigation.

The different samples showing a PL and TL response had a similar composition as that shown in Fig. 1b. This result seems to indicate that the presence of these elements in the film, within the error range, are necessary to obtain these signals, although it is not clear the role they play. The IBED measurements detect hydrogen or nitrogen both bonded and not bonded in the film. In order to determine whether these elements are bonded or not to the carbon network FTIR measurements were performed. The FTIR spectra show absorption bands at 1620, 1640, 1650, 2220 and 3000 cm^{-1} which are associated with the existence of carbon atoms bonded to either carbon or nitrogen (C=C, C=N), carbon singly bonded to either nitrogen or hydrogen (sp^3 carbon: C–N, C–H), and carbon atoms triply bonded to nitrogen [14].

3.2. Thermoluminescent properties

The a-CNx:H thin films deposited on Si substrates at a nitrogen pressure of 7.5×10^{-2} Torr, were excited using both ^{60}Co gamma rays and UV radiation (ARC Model MS416, mercury lamp). Glow curves of the studied samples irradiated with gamma rays at an absorbed dose in water of 110 Gy showed a TL signal peaking at 290 °C as it is shown in Fig. 2a. Once the samples were measured, the heating cycle was repeated and no signal was observed. In order to verify that the TL signal observed on the gamma irradiated samples was not arising from the Si substrate, pieces of 1×1 cm^2 cut from the same Si wafer were irradiated to 110 Gy and no TL response was observed for these samples. After the annealing cycle, the same samples irradiated with gamma rays were also stimulated using UV radiation. In this case the glow curves exhibited two peaks, one at 150 °C and the other at 290 °C. The 150 °C peak was approximately three times more intense than the 290 °C peak (see Fig. 2b). Once the samples were measured the heating cycle was repeated and no TL signal was observed. In order to check the reproducibility of our results, the samples were exposed to gamma and UV radiation four times and the observed responses were very similar.

A peak around at 290 °C has been observed in diamonds produced by CVD, in this case the TL response is believed to come from the nitrogen and boron impurities incorporated in the diamonds [15]. It is worth noting that the TL signal was observed only in samples deposited at a nitrogen pressure of 7.5×10^{-2} Torr. At this working pressure the nitrogen content in the film reach it's highest value close to 20% determined from the IBED measurements. These results seem to indicate that the nitrogen incorporated in the film is one of the factors that favors the TL response.

To our knowledge this is the first time that TL response of carbon nitride thin films grown by laser ablation has been reported.

3.3. Raman spectroscopy

Raman spectroscopy has been used extensively to characterize carbon films [16–18]. It is well known that the Raman spectrum of amorphous carbon thin films, such as diamond-like carbon (DLC), consists of an asymmetric band composed of two sub-bands in different proportions. One of them in the range of 1580–1600 cm^{-1}, the so-called G band arises from the in-plane stretching motion of pairs of C sp^2 bonded atoms and can be found in chains as well. A second band around 1350 cm^{-1}, the so-called D band, is associated with a breathing mode of sixfold aromatic rings and only becomes active in presence of disorder [19]. According with the three stage model proposed by
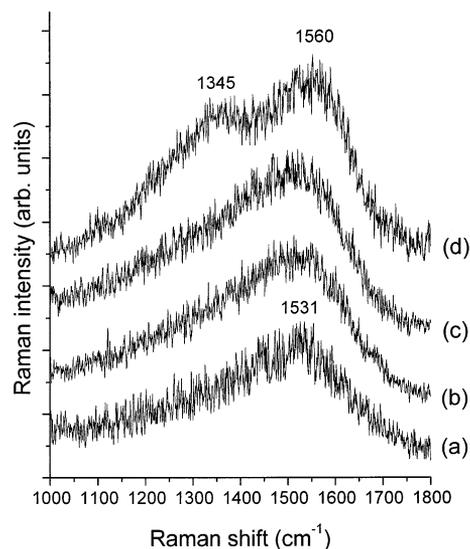
Fig. 3. Raman spectra of thin films as a function of the nitrogen gas pressure (a) base pressure, (b) 7.5×10^{-4} Torr, (c) 7.5×10^{-3} Torr and (d) 7.5×10^{-2} Torr.
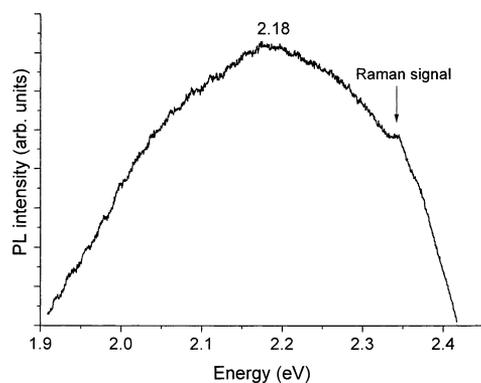

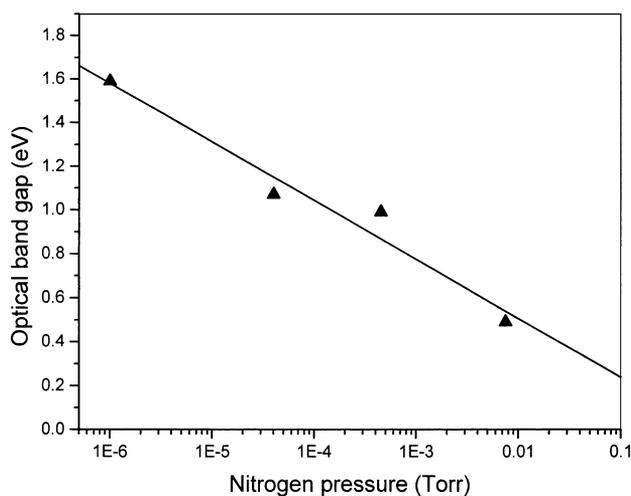Fig. 4. PL spectra of film grown at 7.5×10^{-2} Torr of nitrogen pressure.

Fig. 5. Optical band gap of amorphous carbon as a function of the nitrogen pressure. The line is a guide to the eye.

Ferrari [19], the evolution of the G peak position and the ratio I(D)/I(G) can be interpreted using an amorphization trajectory from graphite to ta-C.

Raman spectra for the carbon thin films deposited are presented in Fig. 3. These spectra are similar to those previously reported for DLC films [5,18]. In order to perform a deeper analysis the Raman spectra were fitted with a Breit–Wigner–Fano (BWF) line shape for the G peak and a Lorentzian line shape for the D peak [19,20]. The results show that the G band positions are 1531, 1516, 1527 and 1560 cm^{-1} for films deposited at a base pressure of 5×10^{-6} Torr, and a nitrogen working pressure of 7.5×10^{-4}, 7.5×10^{-3}, and 7.5×10^{-2} Torr, respectively. Additionally the ratios I(D)/I(G) are 0.18, 0.29, 0.38 and 0.69 for the same pressures. The shift of the G band towards higher frequencies and the increase of the intensity ratio $I(D)/I(G)$ can be interpreted as an increase in the sp^2 bonding fraction with an increase in the size of the graphitic clusters within the film as the nitrogen pressure increases. Then a higher nitrogen pressure induces a more sp^2 graphitic-like structure in the film.

3.4. Photoluminescent properties

Fig. 4 shows a typical photoluminescence (PL) spectrum of an a-CNx:H thin film grown at a nitrogen pressure of 7.5×10^{-2} Torr. This spectrum consists of a broad band with its maximum around 2.18 eV. In this case the excitation photon energy used was 2.54 eV (488 nm). The spectrum is similar to the PL spectra reported elsewhere [10,11]. The broad band observed is thought to be due to a distribution of luminescence centers with different energy gaps. It has been proposed that this distribution arises from the corresponding distribution of the sp^2 cluster sizes and shapes [21]. It is worth noting that nitrogen incorporation can modify this distribution in the film. It has been suggested that PL signals at energies higher than the Tauc gap in a-CH:N films are produced by luminescence centers which are associated with undisturbed sp^2 clusters having energy gaps lower than the excitation energy [22].

3.5. Optical bandgap

The optical absorbance of the obtained thin films was measured in a wavelength range of 280–700 nm with an UV–Vis spectrometer. From these measurements the absorption coefficients were calculated and the optical band gap of the films was determined using the Tauc relation [23,24]. In Fig. 5 the optical band gap as a function of the nitrogen pressure is presented. These results clearly indicate that the optical band gap decreases with the nitrogen pressure. It has been proposed that the nitrogen incorporated in the a-C network acts as a bridging atom between sp^2 clusters and this results

in an increment in the sp^2 cluster size, inducing the formation of larger graphitic domains [21]. From this idea it can be concluded that the low values of the optical band gap correspond to large graphitic clusters with more sp^2 bonded carbon. This tendency is consistent with the Raman results.

4. Conclusions

A TL response has been observed in $C_{0.51}N_{0.20}O_{0.07}H_{0.22}$ thin films grown by laser ablation in a nitrogen atmosphere. The main factor that influences the TL response of the thin films is the composition which depends on the nitrogen working pressure used. Raman spectroscopy results showed that an increase in the nitrogen pressure induces a more graphitic-like structure with more sp^2 bonded carbon. This structural change is related to the increased incorporation of the nitrogen into the film and to a reduction of the energy of the incident precursors from the plasma plume, as the mean free path is reduced. The optical band gap is reduced from 1.6 to 0.5 eV as the nitrogen pressure increases. Further work is underway in order to attempt relate the effects of the different deposition parameters to the TL response.

Acknowledgements

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