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Thermoluminescent a-CN thin films properties as a function of plasma parameters

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ABSTRACT Amorphous carbon nitride (a-CN) thin films show luminescent properties that are of interest for many applications. Particularly interesting are their previously reported thermoluminescent characteristics. In order to optimize these properties, the plasma parameters (ion energy, plasma density and type of excited species) were studied in the present work as a function of the laser fluence and the working pressure. The plasma was produced using the fundamental line of a Nd : YAG laser with 28 ns pulse duration focused on a high purity graphite target. The laser fluences used in this work could be varied between 9 and 40 J/cm^2. Measurements and deposition of a-CN films were carried out in a nitrogen atmosphere at pressures from 3×10^{-3} to 7.5×10^{-2} Torr. We observed an optimum value of pressure, close to 7.5×10^{-2} Torr, in which the nitrogen incorporation into the film achieved its maximum value close to 29 at. % and the thermoluminescent response of the material, after irradiation with UV becomes evident.

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1 Introduction

Amorphous carbon nitride thin films have attracted the attention of many research groups because of their potential applications in a great variety of technological fields. The properties of the deposited a-C:N thin films, the density, hardness and internal stress depend mainly on the sp^3/sp^2 carbon bonding ratio. For thin films deposited by laser ablation, these characteristics are strongly dependent on the nitrogen working pressure and laser energy density used during deposition, and these have an important influence on the energy of the plasma species and on the plasma density.

Laser ablation has been extensively used in the last few years to produce a wide variety of materials in thin film form owing to its advantages over other deposition techniques. Particularly, this technique has been used successfully for the preparation of carbon- based thin films, such as diamond-like carbon (DLC), a-CN$_x$ and a-CN$_x$:H [1–3].

In this work we report on the thermoluminescent (TL) characteristics of a-C:N deposits prepared by laser ablation and exposed to UV radiation. It is worth mentioning that the TL properties of thin films may be useful in the detection and monitoring of both ionizing and non-ionizing radiation. Radiation detectors in the thin film form are of great importance in measurements of absorbed doses from weakly penetrating radiation and in the study of dose distributions in interfaces [4].

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2 Experimental

The deposition of the films and the analysis of the plasma have been described in detail elsewhere [5]. Briefly, laser ablation was performed using a Q-switched Nd : YAG laser ($\lambda = 1064$ nm, pulse duration $= 28$ ns). The target was a graphite disk, 99.99% purity. The substrates used in the present experiments were pieces of silicon cut from (100) wafers, and glass microscope slides. Prior to deposition, the substrates were ultrasonically cleaned following standard procedures. The target to substrate distance was 5 cm.

The deposition chamber base pressure was of the order of 7×10^{-6} Torr and was backfilled with nitrogen (99.99% purity) up to the working pressure from 3×10^{-3} Torr to 7.5×10^{-2} Torr. The fluence delivered by the laser was varied from 9 J/cm^2 to 40 J/cm^2 by keeping the spot size constant on the target surface and adjusting the energy per pulse. All the films were grown at room temperature.

Determination of the mean kinetic energy of ions was performed using the time-of-flight technique (TOF). To study this, a Langmuir planar 3 mm diameter probe was used. In all the experiments the probe was biased at -10 V, where saturation of the ion current take place. The signal from the probe was monitored through a 15 Ω resistor. The plasma density was determined from the ion current values across the resistor. Measurements were performed under the experimental conditions used for thin film deposition. The optical emission spectroscopy (OES) and time resolved measurements were carried out using a gated intensified CCD.

The compositional analysis was performed by energy dispersive spectrometry (EDS) and for some samples elastic forward analysis (EFA). The bond configuration was studied by FTIR spectroscopy. In order to investigate the thermoluminescence response of the deposited thin films, samples were irradiated with UV light using a low pressure Hg lamp. The TL glow curves were obtained using a Harshaw 4000 TL reader.

3 Results

3.1 *Plasma characterization*

The plasma parameters, i.e., ion energy, plasma density and the type of excited species, were studied as a function of the laser fluence and the working pressure. The mean kinetic energy of the ions was obtained from the TOF curves following the procedure described elsewhere [6]. Figure 1 shows the mean ion kinetic energy as a function of the working pressure at different values of laser fluence, at a distance of 5 cm from the target. As can be observed, the ion energy decreases as the working pressure increases, following the same behavior for each value of fluence. For the fluence of 24 J/cm^2 the ion energy changes from 73 eV at 7.5×10^{-2} Torr to 215 eV at 3×10^{-3} Torr. At a fluence value of 17.5 J/cm^2, the mean ion energy varies from 52 to 150 eV for the same pressure change. The observed reduction of the kinetic energy of the plasma species as the working pressure increases can be attributed to momentum transfer collisions between the plasma species and the background gas as the mean free path is reduced producing thermalization of the plasma plume. In the same Fig. 1, it is shown the plasma density as a function of the nitrogen pressure at a distance of 5 cm from the target. The obtained values for the plasma density fluctuate from 5.4×10^{13} cm^{-3} at 3×10^{-3} Torr to 5.5×10^{11} cm^{-3} at 7.5×10^{-2} Torr. These results reveal an exponential decay in the plasma density as the nitrogen pressure increases. This behavior could be attributed to a recombination process that becomes more important at higher pressures as the mean free path is reduced and because the plasma beam attenuates as the number of collision centers increase. At the same time, at higher pressures the plasma is confined to a smaller space; therefore, fewer particles reach the substrate.

Time and spatially resolved optical emission spectroscopy results indicate that the emitting species are always the same, no matter what pressure or laser fluence is used and these are; C^+ (at 283.66, 290.6, 299.2 and 426.65 nm), C^{2+} (at 406.89 and 418.66 nm) and atomic excited nitrogen N* (427.8 nm), with the C^+(426.65) being the most abundant species in the plasma with the longest lifetime. The behavior of the ratio of emission intensities $C^+(426.65)/N^*$ as a function of the working pressure showed a minimum at a working pressure lower than that pressure at which the maximum nitrogen incorporation into the films was detected, which is related to the fact that at higher pressures the energy of the particles hitting the growing films is lower, therefore reducing the chemical sputtering.

3.2 *Thin film characterization*

The chemical composition of the deposited films was studied from the EDS measurements. Additionally, some samples were analyzed using EFA [7] in order to verify the EDS results, obtaining a satisfactory agreement. It is worth mentioning that the EFA results revealed the presence of hydrogen in the films [3] in spite of the fact that no hydrogen was intentionally introduced into the chamber. In general, the composition results showed that the nitrogen content of the films depends on the deposition conditions, the most evident was the effect of the nitrogen pressure used, when the fluence is kept constant. The nitrogen concentration is increased when the nitrogen pressure increases. This result is consistent with previous reports [8]. On the other hand, concerning the plasma parameters, Fig. 2 shows the atomic concentration of nitrogen (N) and oxygen (O) as a function of the laser fluence used. At a nitrogen pressure of 7.5×10^{-2} Torr, the nitrogen concentration reaches a maximum value close to 29% at a fluence value of 17.5 J/cm^2, whereas the lowest value (8%) corresponds to 9 J/cm^2. The incorporation of oxygen is independent of the laser fluence probably indicating that this element is incorporated into the films when they are exposed to the atmosphere. Nevertheless, the concentration of this element is probably related to the porosity of the films. Figure 2 also shows the effect of the ion energy on the atomic concentration of oxygen and nitrogen. In this case, we can observe that as the ion energy increases from 16 to 123 eV, the nitrogen concentration decreases from 28 to 19%. From these results it is seen

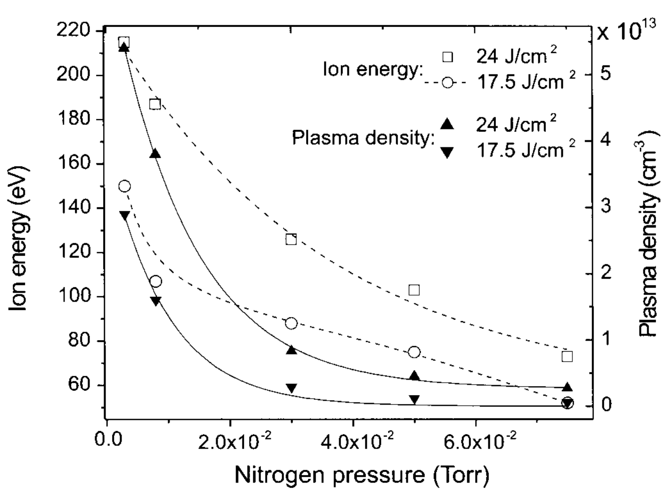

FIGURE 1 Plasma parameters as a function of the nitrogen pressure, ion energy (*dashed line*) and plasma density (*continuous line*). The lines are guides to the eye

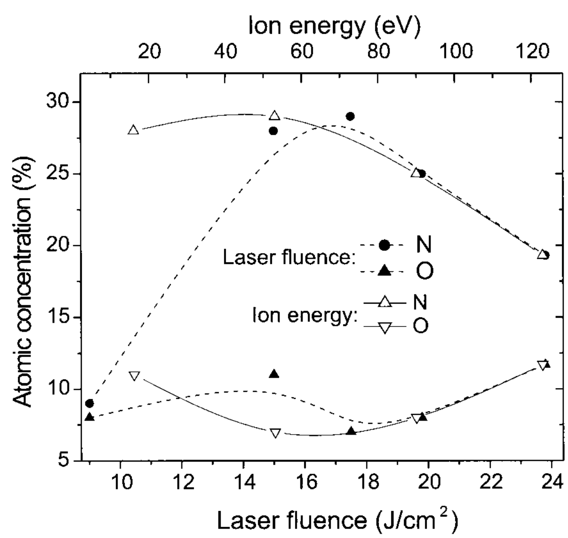

FIGURE 2 Nitrogen and oxygen atomic concentrations as a function of the laser fluence used to ablate the target (*dashed line*) and the ion energy (*continuous line*). The lines are guides to the eye

that in this laser ablation experiment enhancing the quantity of nitrogen incorporated into the films is not a trivial task as we have two non independent processes. On one side, the highest production of atomic nitrogen occurs at regimes where the ion energy causes chemical sputtering. On the other, a reduction of the ion energy takes place at pressures where one gets less atomic nitrogen.

The compositional measurements done in this work detect elements (O, N, C, H) 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 IR results reveal the presence of N−H and/or OH (2800 to 3800 cm^{-1}), and C=N (2100–2230 cm^{-1}) groups mainly. The presence of H and O can be attributed to the fact that in these films moisture is easily absorbed from the environment. Such an incorporation of water in a-CN thin films has been observed before and suggests that low-density films with high porosity are produced at higher nitrogen pressures [8].

The thermoluminescent properties were studied in thin films deposited on Si substrates. The films were irradiated with UV radiation (254 nm). The irradiation and TL measurements were performed in a N_2 atmosphere at room temperature and the irradiated samples were kept in the dark in order to avoid any influence of the environment light. The glow curves were obtained using a cycle composed of a preheat to 50 °C for 5 s followed by the acquisition from 50 to 350 °C at a heating rate of 5 °C s^{-1}. No TL response was observed from irradiated substrates without deposit. The glow curves of the irradiated samples exhibited two TL peaks, one at 97 °C and the other at 154 °C as shown in Fig. 3. It is worth noting that thermoluminescence was only observed for samples deposited at a nitrogen pressure of 7.5×10^{-2} Torr. However, probably there is a range of pressures rather that only one single pressure value in which TL response would be observed. The TL response was observed in samples with nitrogen concentration from 17 to 29%. This range of pressures is broad, leading one to conclude that the TL phenomenon is not directly related to the presence of nitrogen. A different situation was observed with the oxygen concentration. In this case almost all the films with oxygen content between 10 to 12% showed TL response, regardless of the nitrogen content. This seems to indicate that oxygen probably plays an important role in TL emission as V_{O-H} centers could be formed. It is worth noting that very little information is available in the literature concerning the mechanism of TL production in carbon-based materials. The TL parameters that characterize the glow curve of this material were obtained using a peak shape method [9]. The results revealed a second-order kinetics and an activation energy of 1.35 eV for the 154 °C peak. Concerning the plasma parameters, we found at least two regimes in which a material with TL response can be obtained. However, attempts to establish a correlation between plasma parameters and TL response has been very difficult due to the considerable number of parameters involved in the material formation as well as in its precise characterization.

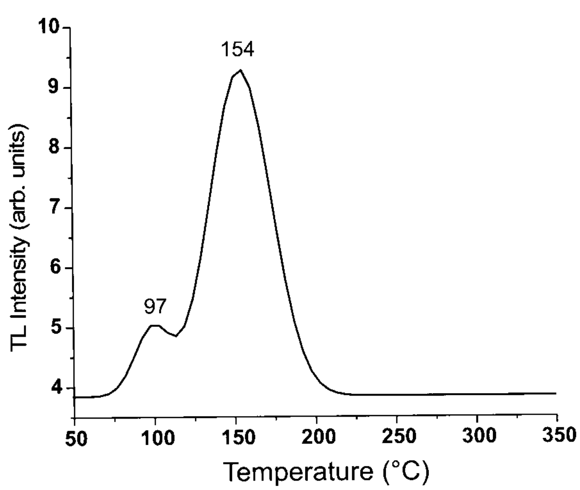

FIGURE 3 Characteristic TL glow curve corresponding to an UV irradiated a-CN_x thin film

4 Conclusions

Amorphous carbon nitride thin films with a thermoluminiscent response were deposited by laser ablation. The results show that nitrogen incorporation in the film depends on the laser fluence used for deposition and reaches a maximum value close to 29% at 17.5 J/cm^2. For higher fluences the nitrogen content diminishes. The nitrogen content also depends on the kinetic energy of plasma species used for the growth film and it shows a maximum at approximately 60 eV. The compositional results show the presence of hydrogen and oxygen in spite of the fact that no hydrogen and oxygen were deliberately introduced during deposition. The TL response seems to depend on the oxygen concentration, and/or the film porosity, independent of the nitrogen concentration in the film.

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