Infrared and Raman characterization of amorphous carbon nitride thin films prepared by laser ablation

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Infrared and Raman spectroscopies have been used to characterize the presence of sp^2 and sp^3 bonds in carbon nitride films providing some information about the sp^2/sp^3 ratio. The Raman results revealed that the increase in size or number of sp^2 clusters is the result of two processes, which include the increase of nitrogen content and particle bombardment, so that under certain experimental conditions a film with practically the same composition but different microstructure can be obtained. IR results reveal the presence of carbon-carbon, carbon-nitrogen, carbon-oxygen and carbon-hydrogen bonding, and their intensities depend on the laser fluence used for deposition.

Keywords: Laser ablation; Carbon nitride; Raman spectroscopy; Infrared spectroscopy

1. Introduction

In recent years the synthesis of amorphous carbon nitride thin films has generated a great interest owing to their potential applications as hard coatings, protective overcoats for magnetic storage disks, in field emission devices, gas sensors and radiation detectors, among others.

In general terms it has been shown that the mechanical and electronic properties of the carbon nitride thin films can be varied depending on the nitrogen content and the type of bonding between carbon-carbon and carbon-nitrogen atoms. The identification of the type of bonding details is very difficult, as both atoms, carbon and nitrogen, may present bonds with three different hybridizations, sp^3, sp^2 and even sp^1, so there are nine configurations of possible types of bonds [1]. Additionally, depending on the deposition technique and the experimental conditions used, the incorporation of hydrogen, oxygen, or both, into the film is also possible. The effect of nitrogen incorporation in general terms results in a reduction of the C-C sp^3 bonding fraction as it decreases as the nitrogen content is increased, indicating a transition from sp^3 to sp^2 hybridization for the carbon. Therefore, although the situation is complicated, the determination of the sp^2 fraction value or its tendency as a function of some experimental parameters is at least, in a first approximation, useful to provide some information about the sp^2/sp^3 ratio.

Vibrational spectroscopies have been widely used to characterize amorphous carbon nitride films. Infrared spectroscopy has been used for structural characterization of hydrogenated and nitrogenated amorphous carbon films owing to the sensitivity of infrared to detect carbon-carbon, carbon-nitrogen, carbon-oxygen and carbon-hydrogen bonding [2]. Therefore IR can reveal different incorporation mechanisms of nitrogen into carbon films. On the other hand Raman spectroscopy has been used extensively to characterize the presence of sp^2 and sp^3 bonds in carbon films. The Raman spectra of amorphous carbon nitride thin films are very similar to the Raman spectra of diamond like carbon (DLC), and roughly they consist of an asymmetric band composed of two bands in different proportions. One of them in the range of 1560-1600 cm^{-1}, the *G* band associated with the in-plane stretching motion of pairs or chains of C-sp^2 bonded atoms. The second band around 1350 cm^{-1}, the *D* band, is associated with a breathing mode of sixfold aromatic rings and only becomes active in presence of disorder [3]. It is worth mentioning that interpretation is very different than in the case of amorphous carbon. However, it has been suggested that the behavior of the intensity ratio I_D/I_G together with the *G* band position can be related with the sp^3/sp^2 bonding ratio and even with the nitrogen and hydrogen content [4].

Laser ablation has attracted great attention in the last few years as a technique with a great versatility to deposit a wide variety of materials in thin film form. In this method the material is evaporated from a solid target and transferred to the substrate in the form of plasma consisting of various species including neutrals, ions and clusters. This technique has some advantages over other deposition techniques; particularly important is the possibility of growing films under reactive atmospheres, which has been

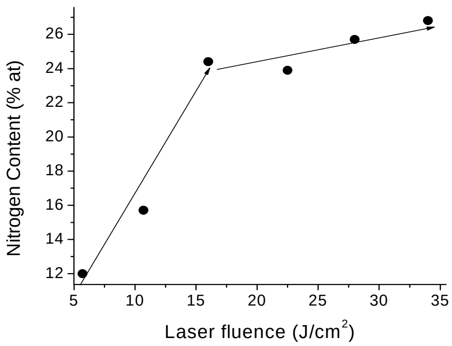
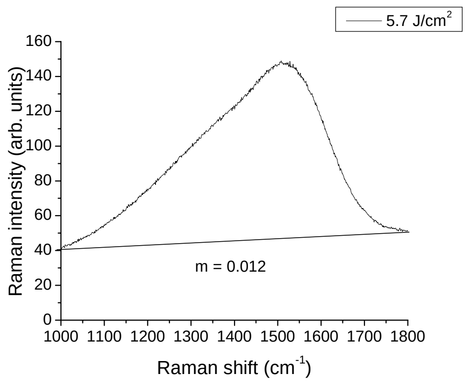


Figure 1. Nitrogen content as a function of the laser fluence used to ablate the target.



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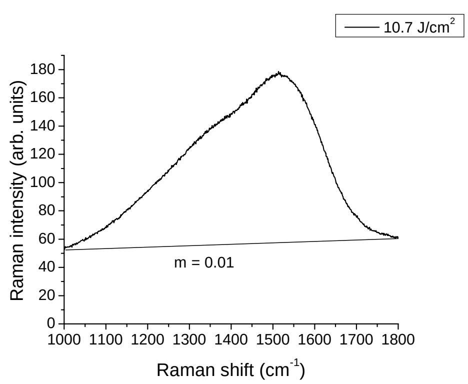

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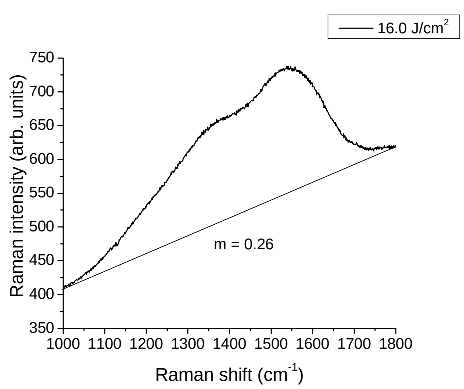

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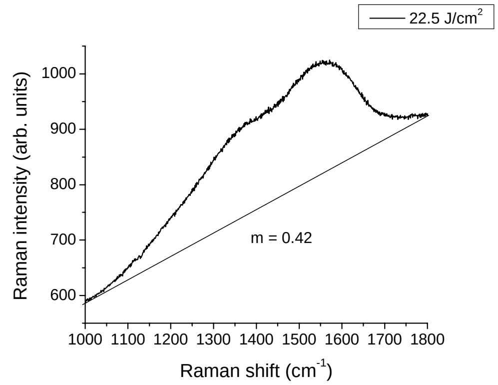

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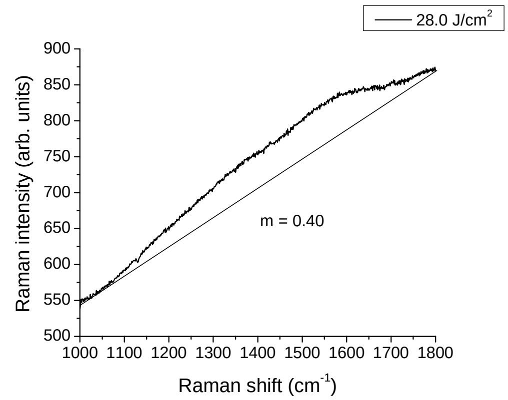

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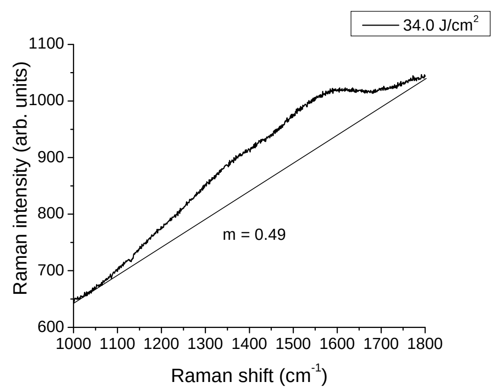

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Figure 2. Raman spectra as a function of the laser fluence.

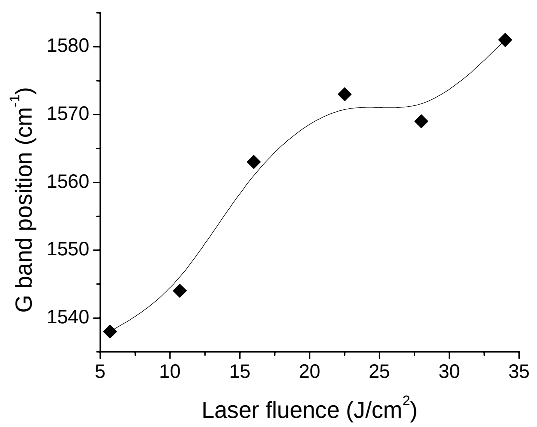

Figure 3. *G* band position as a function of the laser fluence.

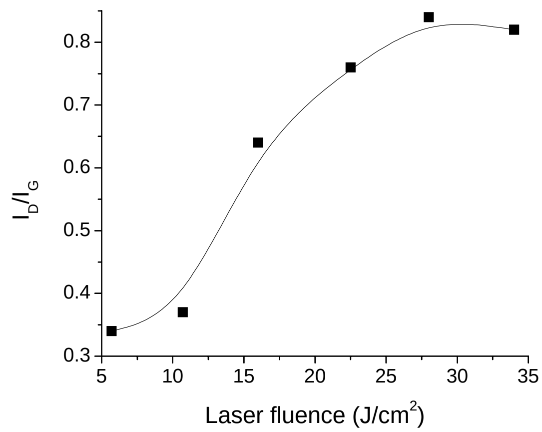

Figure 4. I_D/I_G ratio as a function of the laser fluence.

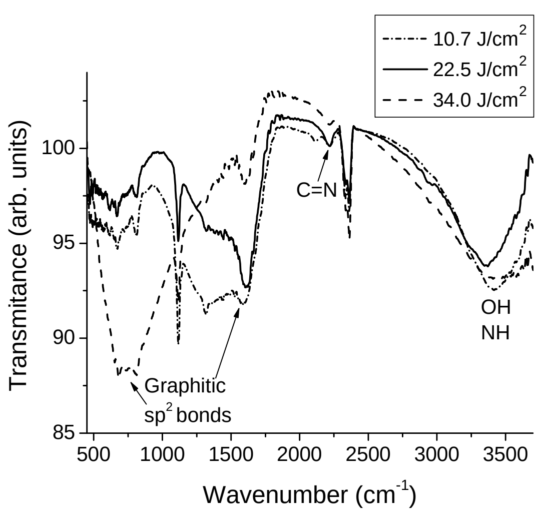

Figure 5. IR spectra of carbon nitride thin films deposited at different fluences.

used successfully to deposit complex oxides and nitrides [5]. These features make this technique a good candidate to grow amorphous carbon nitride thin films (a-C:N) as has been showed in the last years in which the preparation of amorphous carbon nitrides such as a-CNx and a-CNx:H has been reported [6].

2. Experimental

The laser ablation was performed using a Q-switched Nd:YAG laser with emission at the fundamental line (λ = 1064 nm) with a 28 ns pulse duration at a repetition rate of 10 Hz. The target was a 99.99% purity graphite disk. The substrates used in the present experiments were pieces of silicon (100). The deposition chamber base pressure was of the order of 7.5 x 10^{-6} Torr and was backfilled with nitrogen (99.99% purity) up to the working pressure, 3.0 x 10^{-2} Torr. Experiments were carried out at different laser fluences used to ablate the target, from 5.7 J/cm^2 to 34.0 J/cm^2. All the films were grown at room temperature for the same deposition time keeping the target-substrate distance at 5.0 cm.

The Raman spectra were recorded with a high resolution micro-Raman system (LabRam HR 800) using the 632.8 nm line of a He-Ne laser in a backscattering configuration. IR measurements were performed with a Nicolet Instrument Corporation, Model 510 FT-IR Fourier transform infrared spectrometer. Compositional analysis was performed by EDS using an EDAX system coupled to a scanning electron microscope (Phillips XL30).

3. Results

3.1Composition

The figure 1 shows that the nitrogen content increases from 12 at.% (for 5.7 J/cm^2) to 26.8 at.% (for 34.0 J/cm^2). As the fluence is increased it is observed an abrupt increase in the nitrogen content for values of fluence from 5.7 to 16.0 J/cm^2. For fluences greater than 16.0 J/cm^2 the nitrogen content seems to reach a saturation value of approximately 25.0 at %. It is worth mentioning that a very similar tendency at different pressures has been reported elsewhere [7].

3.2 Raman Spectroscopy

The Raman spectra of amorphous carbon nitride thin films deposited at different fluences are presented in figure 2. As it is observed the spectra show the typical features of carbon nitride. It is interesting to note that as the laser fluence increases, the photoluminescence background increases too.

In order to perform the data analysis, the Raman spectra were simulated using a Breit-Wigner-Fano (BWF) line shape for the *G* peak and a Lorentzian line shape for the *D* peak. Prior to the analysis, a linear background was subtracted. The interpretation of the Raman results was performed following the three-stage model proposed by Ferrari [3]. The results showed that as the laser fluence increased the *G* peak position was seen to shift to higher frequencies (figure 3). According to the three-stage model such a shift of the *G* peak can be interpreted as an increase in clustering. In fact, as it is observed in figure 4, the I_D/I_G ratio also increased with the laser fluence indicating also a rise in either the number or the size of the sp^2 clusters.

Additionally, these results together with the compositional one (fig.1) suggest that the clustering is the result of two combined effects. At low fluences (up to 16 J/cm^2) the incorporation of nitrogen in the film might be playing an important role, but at higher fluences, the nitrogen content in the film remains constant, therefore, in this case, the ion bombardment that undergoes the film during its growth is the predominant effect. It is worth noting, that for the case of high fluences, it is possible to obtain a material with the same composition, but different structure.

A typical signature of hydrogenated carbon samples in visible Raman spectra is the increasing photoluminescence (PL) background for higher H content. This is due to the hydrogen saturation of non-radiative recombination centers. The ratio between the slope, *m*, of the fitted linear background and the intensity of the *G* peak, $m/I(G)$, can be empirically used as a measure of the bonded H content according to the procedure proposed by A. Ferrari [4]. The obtained results reveal that the hydrogen content varies from 26.5 at.% to 33.3 at.%. It is worth noting that the hydrogen content of similar samples has been determined by EFA and a maximum hydrogen content of 32 at. % has been found [6].

3.2 Infrared Spectroscopy

In order to determine the type of bonding present in each sample, FTIR measurements were performed. In general terms the FTIR spectra show four absorption bands. The band at low frequencies, from 600 to 800 cm^{-1}, is attributed to graphitic sp^2 bonds; these normally forbidden vibrations become active when aromatic N-sp^2C bonds break the sp^2 symmetry of the graphitic rings. The second band, appears at approximately 1600 cm^{-1} and is associated with the presence of carbon atoms bonded to either carbon or nitrogen (C=C, C=N). A third band around 2100-2200 cm^{-1} attributed to the nitrogen bonded to carbon (-C=C and -N=C=N- polymeric components) is interpreted as being related to linear aliphatic CNx components. These structures are assumed to be mainly bonded at the edges of aromatic clusters in planar positions. The fourth band, from 2600 to 3700 cm^{-1}, arises from OH and NH bonds present in the film and it can be associated with the presence of water adsorbed into the film. As it is observed in figure 5 the low frequency band, associated with graphitic domains, increases as the fluence is increased, this could be interpreted in terms of a more energetic and intense bombardment of the growing film at higher fluences that give as a result the graphitization of the material.

The band related to linear aliphatic CNx components, seems to reach a maximum at 22.5 J/cm^2, in spite of the fact that at higher fluences the nitrogen content is approximately constant from 16.0 to 34.0 J/cm^2. Finally, the high frequency band remains almost constant, no matter the fluence used for deposition, indicative that probably the films adsorb hydrogen and oxygen, from the moisture atmosphere, after the growing process.

Conclusions

Amorphous carbon nitride thin films prepared by laser ablation were characterized by infrared and Raman spectroscopies. The Raman results revealed that the I_D/I_G ratio increases with the increase of the laser fluence indicating a rise in either the number or the size of the sp^2 clusters due to a two step process including the increase of nitrogen content and a more intense bombardment by plasma particles. Additionally from the ratio between the slope, *m*, of the photoluminescence background and the intensity of the *G* peak, a measure of the bonded H content was determined. The obtained results reveal that the hydrogen content varies from 26.5 at. % to 33.3 at. %. IR results reveal the presence of carbon-carbon and carbon-nitrogen bonding with intensities that depend on the laser fluence used for deposition. The IR band attributed to carbon-oxygen and carbon-hydrogen bonding remains almost constant as a function of the laser fluence suggesting that the films absorb water from the atmospheric moisture.

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