

# Chemical analysis of $\text{CN}_x$ thin films produced by pulsed laser ablation

L.M. Franco\*, J.A. Pérez, H. Riascos

*Universidad Tecnológica de Pereira, Departamento de Física, Pereira, Risaralda A.A. 097, Colombia*

Available online 14 April 2008

## Abstract

We present an investigation of the effect of the process parameters, namely deposition pressure, laser fluence and substrate temperature, on growth and bonding state of carbon nitride ( $\text{CN}_x$ ) thin films deposited by Nd:YAG laser (1064 nm) ablation of a graphite target in nitrogen atmosphere. Based on the comparative and quantitative analysis of changes in measured infrared spectroscopy (IR) versus X-ray photoelectron spectroscopy (XPS) spectra and on a critical review of the existing interpretation of IR and XPS data, a growth condition that lead to the synthesis of hard and elastic films having properties close to the those fullerene-like  $\text{CN}_x$  is proposed.

© 2008 Elsevier Ltd. All rights reserved.

PACS: 61.48.+c; 81.05.Tp; 82.80.Pv

Keywords: Pulsed laser deposition; Carbon nitride; X-ray photoelectron spectroscopy

## 1. Introduction

Over the last years carbon nitrides have emerged as a new class of materials possessing remarkable properties and accordingly, a wide range of potential applications. The growing interest in describing and understanding the great variety of puzzling properties of the amorphous carbon nitrides,  $\text{a-CN}_x$ , is becoming more evident nowadays. The fabrication of  $\text{a-CN}_x$  materials is a big challenge, since a high degree in tuning the structural, optical and electronic characteristics is possible. In the present paper we made an attempt to correlate the microstructure of films deposited by PLD with their chemical compositions. The main process parameters determining the nitrogen content of the carbon nitride films fabricated by reactive PLD are the pressure of the  $\text{N}_2$  atmosphere. This approach is useful in order to understand the film behavior according to the different experimental parameters (nitrogen pressure, laser fluence, residual atmosphere) in order to master the fabrication of  $\text{a-CN}_x$  materials.

## 2. Experimental setup

The experimental setup and experimental procedure were described previously [1]. We used short pulse, Q-switched Nd:YAG laser which provided 7-ns, 500 mJ laser pulses at a wavelength of 1064 nm with a 10 Hz repetition rate. The experiment took place in a stainless steel vacuum chamber configured with 13 ports, in way spherical of 12 in inner diameter, it evacuated to 5 mTorr, and flushed with a pure nitrogen (99.999%) at different flow rates during experiments. During laser ablation, nitrogen pressure was varied from 0.13 to 6.7 Pa by a vacuum gauge and the laser fluence at 2 and 10 J/cm<sup>2</sup>. The distance of 7 cm from the target. The films were deposited on silicon substrates that had previously been ultrasonically cleaned in acetone.

## 3. Result and discussion

As deduced both from FTIR and XPS measurements, the films grown were amorphous carbon nitride ( $\text{a-CN}_x$ ) films. We present in Fig. 1 typical IR spectra obtained in the range 500–3500 cm<sup>-1</sup> at five different nitrogen pressure and fluence values 2 and 10 J/cm<sup>2</sup>, respectively. The most remarkable feature in each IR spectrum is the peak around 2270 cm<sup>-1</sup> can be attributed to the presence of the isonitrile

\*Corresponding author.

E-mail address: [linafranco1@gmail.com](mailto:linafranco1@gmail.com) (L.M. Franco).

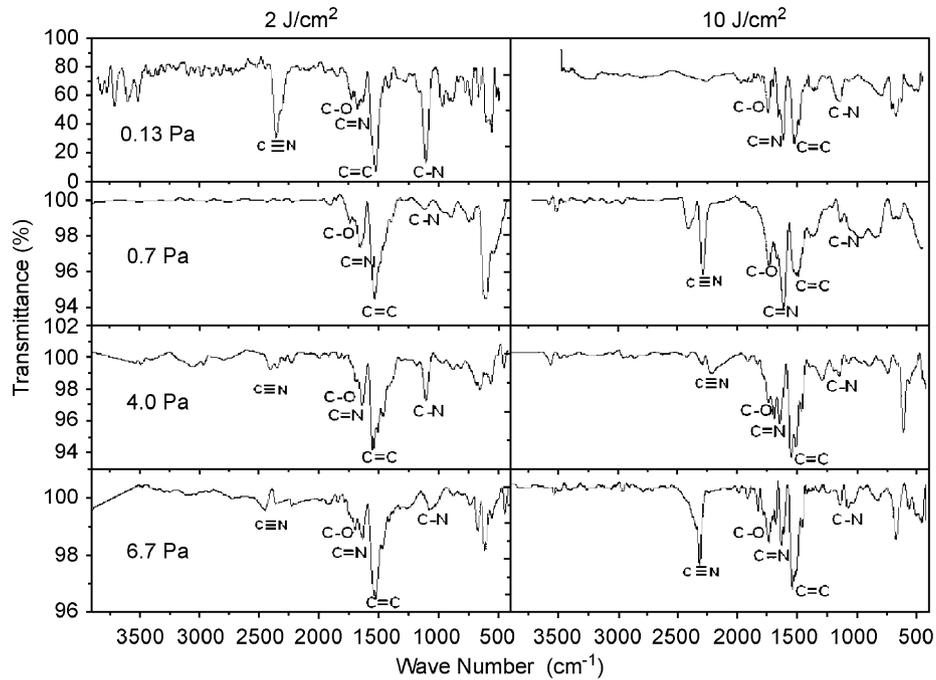


Fig. 1. FTIR spectra of the samples grown at 2 and 10 J/cm<sup>2</sup>.

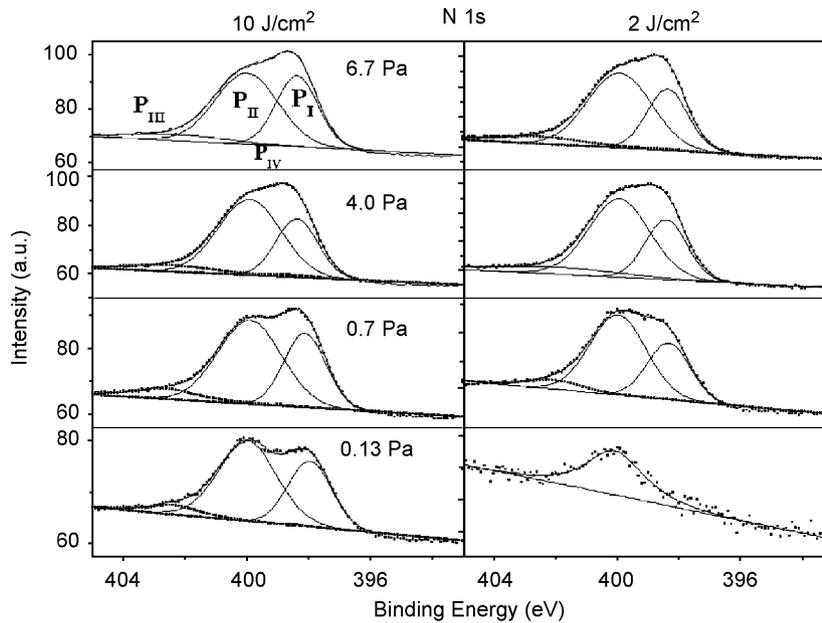


Fig. 2. XPS N1s electron spectra of films grown at various gas pressure and two fluences.

and nitrile groups ( $C \equiv N$ ), which may terminate a chain or form part of network within the structure of the films. Their low intensities indicate the low content of sp carbon in the film. The peaks at  $1640$  and  $1545\text{ cm}^{-1}$  can be assigned to CC and CN double bonds, stretching vibrations of non-conjugated alkenes and azometinic groups, respectively, [1].

The IR spectra of the samples grown at  $10\text{ J/cm}^2$  differ significantly from that of the grown at  $2\text{ J/cm}^2$ , especially

because they have a much higher intensity of the  $2270\text{ cm}^{-1}$  peak. It was reported that the  $C \equiv N$  bonding saturates all valence electrons of nitrogen. This type of bonding produces bond-terminating sites and induces the loss of connectiveness of the amorphous carbon network, which results in less densely packed structure. The observed decrease can be related to the incoming species (erosion regime), which can affect both the nitrogen incorporation and in the CN films and consequently their microstructure.

It can thus be suggested that ions near the substrates selectively etch sp and sp<sup>2</sup> hybridized carbon, i.e. the functional groups of  $-\text{C}=\text{N}$ ,  $\text{N}-\text{C}=\text{O}$ ,  $-\text{C}\equiv\text{N}$ . Because of their high reactivity with positive ions (high electron density), etching of nitrogen and sp and sp<sup>2</sup> hybridized carbon in the films is enhanced by increased ion bombardment, and tends to increase film density [2].

XPS is commonly used to analyze the chemical bonding structure of carbon-related materials. N 1s electron spectra of films grown at various gas pressure and two fluences are presented in Fig. 2. N1s spectra had broad peak corresponding to some bonding configurations related to nitrogen atoms, whose relative intensities vary with the laser fluence. In order to investigate the bonding configurations of nitrogen atoms in the CN<sub>x</sub> films in detail, the N1s electron spectra were deconvoluted into four gaussian line shapes as illustrated in Fig. 2. Up to four contributions can be fitted and are labeled as follows: Peak I (398–399 eV), Peak II (400.0–400.8 eV), Peak III (402.5 eV), and Peak IV (399 eV). The main components are peaks I and II, which are related to two-fold coordinated sp<sup>2</sup>-hybridized nitrogen (sp<sup>2</sup> C–N) bonds and sp<sup>2</sup> C–N bonds, respectively. The appearance of the XPS N 1s core level spectra, seen

in Fig. 2, is similar to previously reported ones [3]. But for the sample grown at 0.13 Pa and a laser fluence of 2 J/cm<sup>2</sup>, all films show double-peak structures. This suggests that N is bonded essentially in the above-mentioned two different bonding configurations. This is most pronounced for films deposited at 10 J/cm<sup>2</sup>; whereas Peak II is the most intense. According to the ratio of Peaks I and II, can be taken as an indicator that the microstructure of the films is fullerene-like, if the ratio of PII/PI is larger than 1. According to Figs. 1 and 2, we can conclude that the incorporation of nitrogen species into the thin films results predominantly in the formation of fullerene-like structures with sp<sup>2</sup> hybridization of carbon.

## References

- [1] H. Riascos, J. Niedhardt, G. Radnóczy, J. Emmerlich, G. Zambrano, L. Hultman, P. Prieto. *Thin Solid Films* 497 (2004) 1–6.
- [2] M. Lejeune, O. Durand-Drouhin, S. Charvet, A. Grosman, C. Ortega, M. Benlahsen, *Thin Solid Films* 444 (2003) 1.
- [3] L. Hultman, J. Neidhardt, N. Hellgren, H. Sjöström, J.-E. Sundgren, *MRS Bull.* 28 (3) (2003) 194.