

**The influence of nitrogen pressure on the structure of a-CN<sub>x</sub> thin films prepared by PLD method.**

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**Abstract**

The structure of amorphous CN<sub>x</sub> thin films have a variety of chemical bond, and the investigating of these bonds ratios is very important because these ratios determine the appropriate technical use of these films. Therefore, In this paper we aim to investigate the relation between the conditions of preparation (deposition pressure) of a-CN<sub>x</sub> thin films prepared using PLD (Pulsed Laser Deposition) method and the film's structure. Results have shown that the deposition pressure variation does not affect the concentration in the same manner for all bonds in the film. Moreover, the sp<sup>2</sup> cluster size and the order degree are related to the numerical value of the deposition pressure

**Keywords:** XPS spectroscopy; Carbon nitride; Raman spectroscopy; Laser, Deposition.

**1. Introduction**

Amorphous CN<sub>x</sub> thin films are characterized by a mix of CN bonds with different patterns of sp<sup>2</sup> and sp<sup>3</sup> hybridization. These thin films characteristics depend mainly on the percentage of these two phases [1-2]. The importance of the amorphous phase arises because synthesizing of Cubic-C<sub>3</sub>N<sub>4</sub> phase requires applying high degrees of heat, which does not fit most applications.

Therefore, it is resorted to produce amorphous CN<sub>x</sub> thin films with high content of CN bonds with SP<sup>3</sup> hybridization, which have characteristics similar to the ones contained in Cubic-C<sub>3</sub>N<sub>4</sub>, which can be prepared also at room temperature [1-2].

Amorphous carbon (a-C) and amorphous  $CN_x$  thin films (a- $CN_x$ ) has the attention of the scientific community [1-9] because they have very important structural properties [4, 6-9]. Moreover, these kinds of films have a variety of uses such as optoelectronics, protective coatings, making electronic elements, capacitors, infra-red detectors and gas sensors.

In this work, we investigate how deposition parameters such as deposition pressure affect the micro structure of a- $CN_x$  thin films prepared using pulsed laser.

## 2. Materials and Methods

The a- $CN_x$  thin films have been deposited onto n-type Si (100) and glass substrates. The films were prepared using Nd:YAG pulsed laser (RD-YG-300/  $\lambda = 1064$  nm, laser fluence =  $12.8 \text{ J cm}^{-2}$ ). Five samples of carbon nitride thin films were prepared in an environment of pure nitrogen (purity 99.999%). The  $N_2$  pressures varied from 10 to 1000 Pa. Raman spectra of the samples were measured using a Jobin-Yvon T64000 (operating with a 514.5 nm line of argon laser with resolution  $2 \text{ cm}^{-1}$ ). The chemical composition of our films were measured by using a LEYBOLD LHS11 MCP- XPS spectroscopy. The SEM photos were recorded by using a JEOL-type JSM 6400F scanning electron microscopy.

## 3. Results and Discussion

A detailed description of the spectra obtained by all used spectroscopes compressively is mentioned in our previous works [4,6-9].

Fig. 1 plots XPS spectrum of the sample prepared using pressure of 100 Pa. In this figure we distinguish the peaks C1s, O1s and N1s.

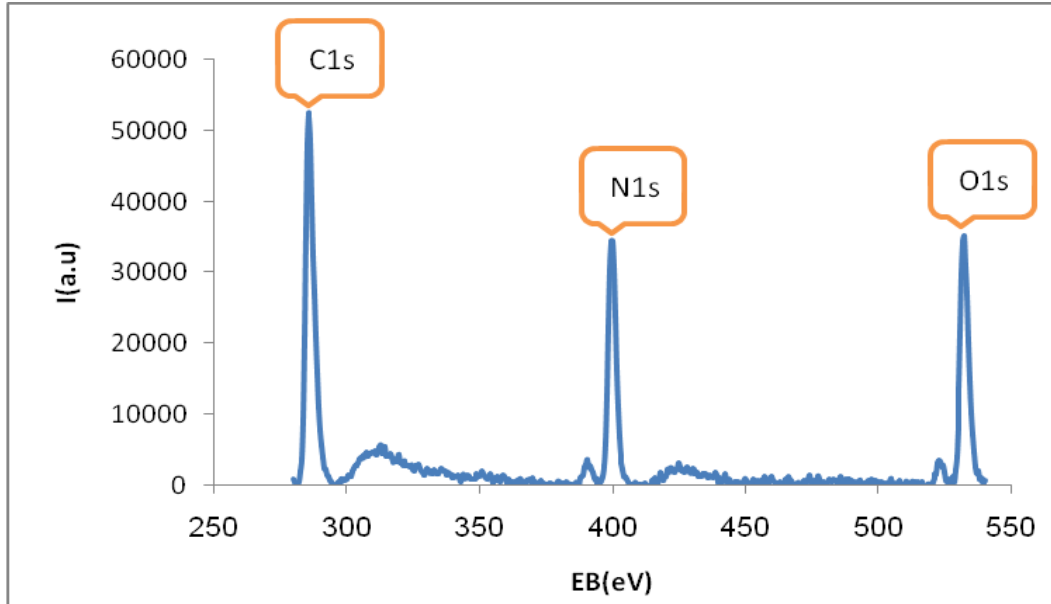


Fig. 1: XPS spectrum of the sample prepared using nitrogen pressure of 100 Pa.

$C(sp^2)$ -C,  $C(sp^2)$ -N and  $C(sp^3)$ -N bonding ratios have been calculated for all samples. The calculation was done using the method explained in our previous work [4]. Table 1 contains the  $C(sp^2)$ -C,  $C(sp^2)$ -N and  $C(sp^3)$ -N bonding ratios for all sample.

Table 1: The  $C(sp^2)$ -C,  $C(sp^3)$ -N and  $C(sp^2)$ -N bonding ratios for all samples.

Pressure (Pa)	[C-C( $sp^2$ )]	[C-N( $sp^2$ )]	[C-N( $sp^3$ )]
10	36.496	20.045	8.461
100	27.370	23.298	11.125
300	34.259	18.696	10.350
500	47.177	21.450	7.885
1000	48.052	19.573	7.016

What distinguishes our work from previous works [6, 8, 9] is that the deconvolution process of C1s core level spectra allows access to a specified number of peaks which in turn

allow calculation of the total concentrations of each bond not only the calculation of the relative areas of all peaks in C1s core level spectra.

Fig. 2 shows the concentration of C(sp<sup>2</sup>)-C bonds as a functions of deposition pressure. We notice that as pressure increases, the concentration of C(sp<sup>2</sup>)-C bonds decreases at low pressure (10–100 Pa) and increases when moving to higher pressures. An opposite behavior can be observed in the case of C(sp<sup>3</sup>)-N bonds (fig. 3).

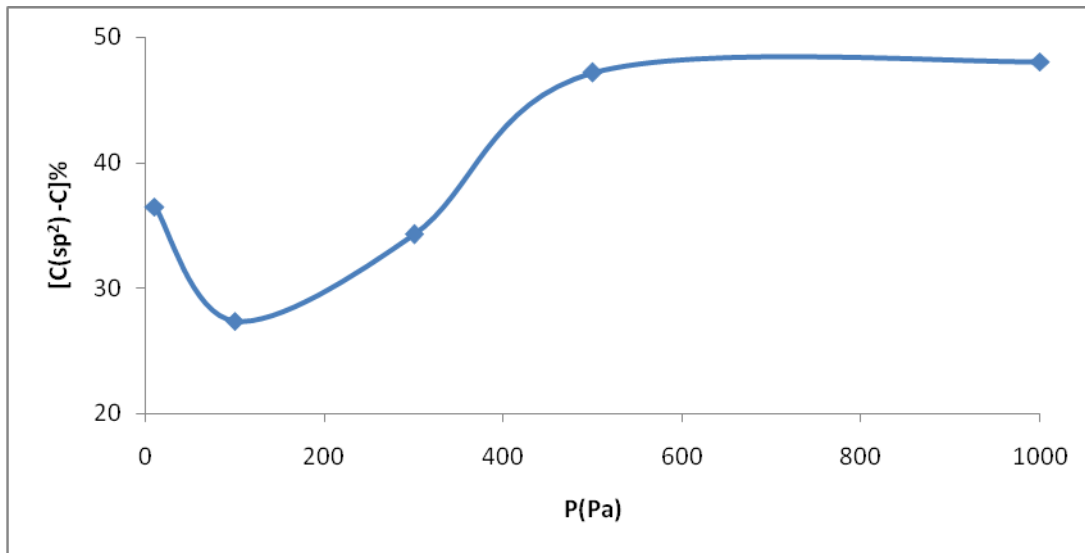


Fig. 2. The concentration of C(sp<sup>2</sup>)-C bonds as a functions of deposition pressure.

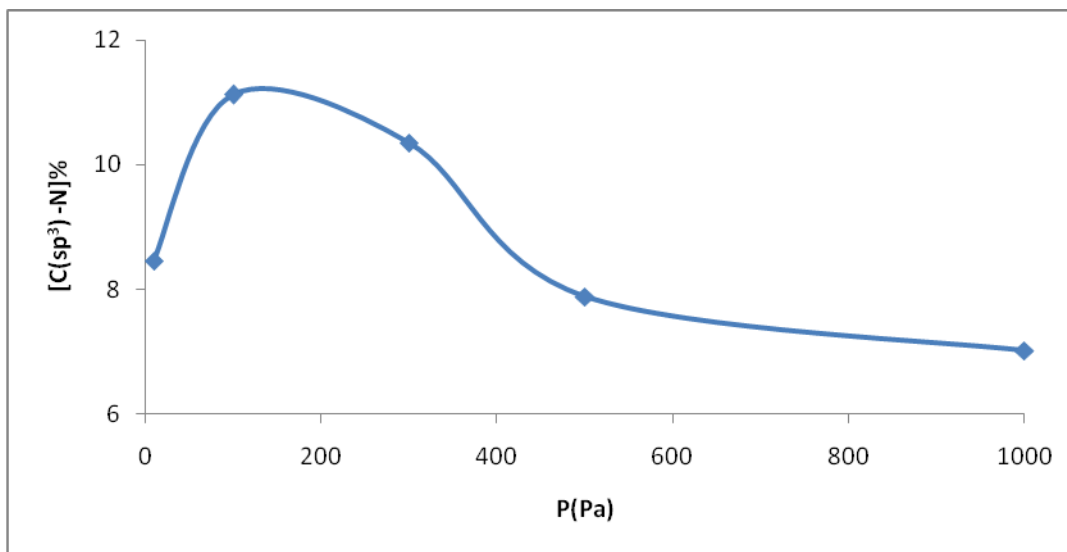


Fig. 3. The concentration of C(sp<sup>3</sup>)-N bonds as a functions of deposition pressure.

There is no specific behavior in the case of C(sp<sup>2</sup>)-N bonds (fig. 4), where we notice that the concentration swings around an average value (approximately 21%).

The decreased concentration of C(sp<sup>2</sup>)-N and C(sp<sup>3</sup>)-N bonds indicates that the nitrogen content in the films decrease when pressure increases.

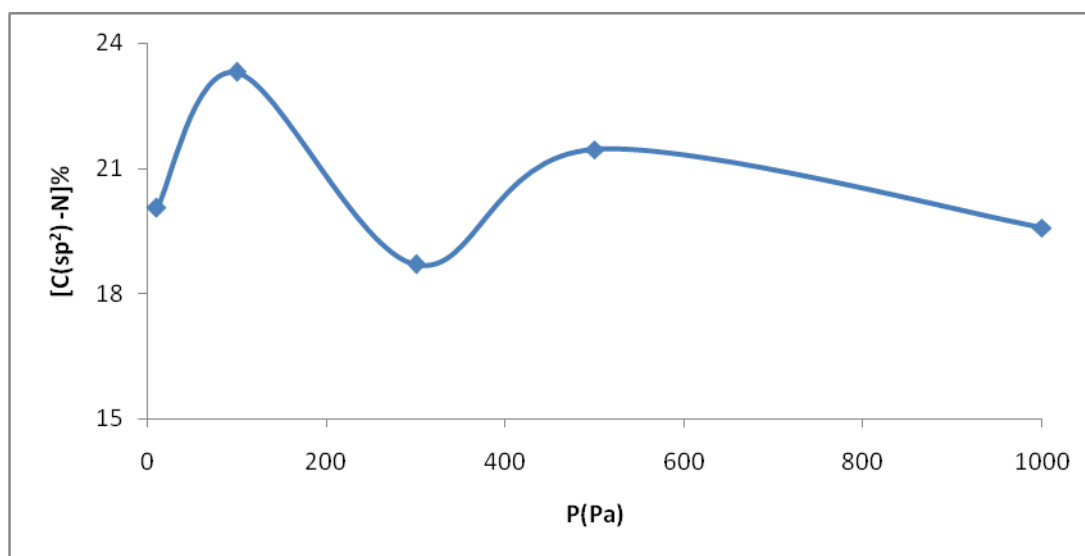


Fig. 4: The concentration of C(sp<sup>2</sup>)-N bonds as a functions of deposition pressure.

Results obtained from previous curves imply that the use of high pressures is not beneficial to the forming each of the N–C (sp<sup>2</sup>) or N–C (sp<sup>3</sup>) bonds in the films. This may be the result of the increased rate of inelastic collisions between ions in high pressures during the film growth process.

By comparison with electron microscopy images (fig. 5), one can notice that, the sp<sup>2</sup> clusters size increases with increasing C(sp<sup>2</sup>)-N bonds concentration and decreases with the decreasing of these bonds. This result indicates that the C(sp<sup>2</sup>)-N bonds contribute to the formation of sp<sup>2</sup> different configurations (hexagonal rings or chains).

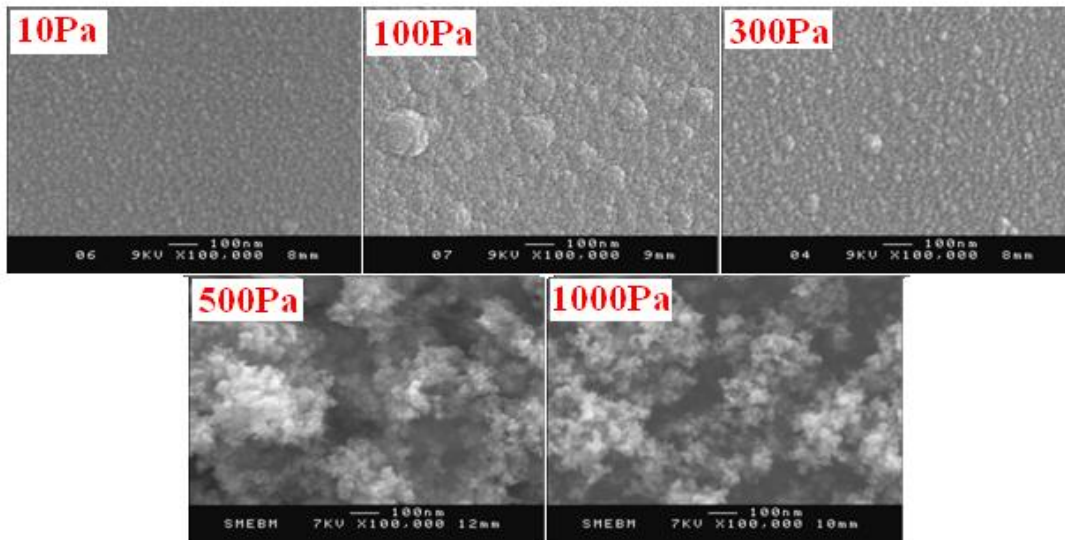


Fig. 5: SEM photos of the prepared films.

Fig. 6 illustrates the order degree  $A_D/A_G$  as a function of nitrogen pressure. We notice that, in general, the order degree decrease as the deposition pressure increase with the exception of the case of the sample prepared at 500 Pa. The ratio  $A_D/A_G$  decrease indicates that the order phase (chains) ratio is increased at the expense of the disorder phase (hexagonal rings) ratio. On the other hand, the increase in this ratio indicates exactly the opposite.

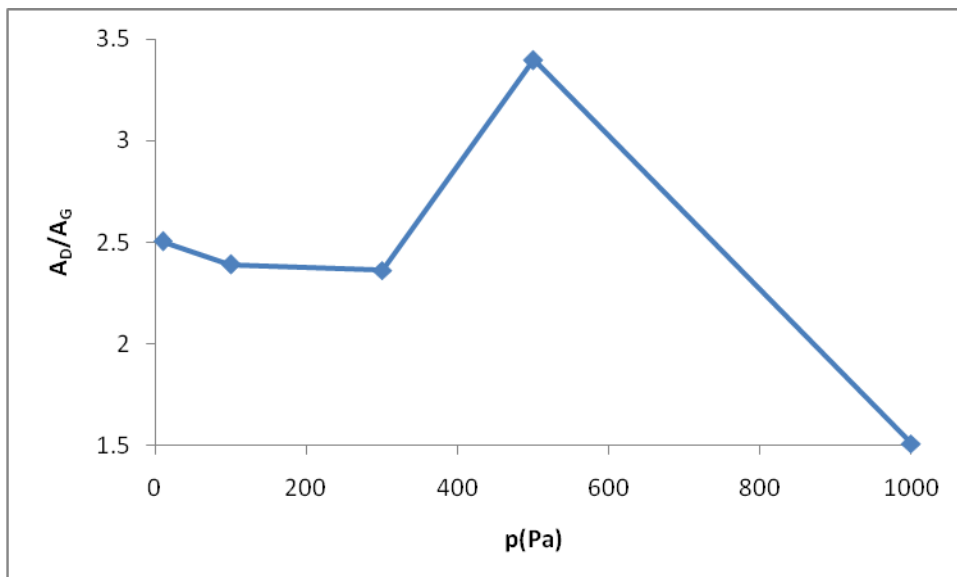


Fig. 6: The order degree as a function of deposition pressure.

#### 4. Conclusion

Amorphous  $CN_x$  thin films were deposited onto unheated silicon (100) and glass substrates using pulsed laser deposition of graphite tablets in  $N_2$  gas atmosphere. The samples were analyzed by XPS, Raman and SEM Spectroscopes. The results showed that the nitrogen ratio decrease as the deposition pressure increases. We found that the  $C(sp^2)$ -N bonds contribute to the formation of  $sp^2$  configurations (hexagonal rings or chains). It was found that the order degree decreases as the deposition pressure increase in the area of low pressure. There is no obvious relationship between order degree and deposition pressure in the case of higher pressure, where we found that, the ratio of chains number to hexagonal rings number is sensitive to the numerical value of the applied pressure.

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