International Journal of Nanoelectronics and Materials
Volume 12, No. 1, Jan 2019 [19-24]

The Influence of Nitrogen Pressure on the Structure of a-CN_x Thin Films Prepared by PLD Method

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Received 1 February 2018, Revised 4 July 2018, Accepted 11 July 2018

ABSTRACT

The structure of amorphous CN_X thin films has a variety of chemical bond, and studies on these bonds ratios are very important because these ratios determine the appropriate technical use of these films. Therefore, this paper aim to investigate the relation between the conditions of preparation (deposition pressure) of a-CN_x thin films prepared using PLD (Pulsed Laser Deposition) method and the film's structure. Results shown that the deposition pressure variation does not affect the concentration in the same manner for all bonds in the film. Moreover, the sp^2 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_X thin films are characterized by a mix of CN bonds with different patterns of sp^2 and sp^3 hybridization. These thin films characteristics depend mainly on the percentage of these hybridizations [1-2]. The importance of the amorphous phase arises because synthesizing of Cubic-C_3N_4 phase requires applying high degrees of heat, which is not applicable for most applications. Alternatively, amorphous CN_X thin films with high content of CN bonds with SP^3 hybridization can be produced instead since it have similar characteristics to the Cubic-C_3N_4. Besides that, the amorphous CN_X thin films does not requires high degrees of heat, instead it can be prepared at the room temperature [1-2].

Amorphous carbon (a-C) and amorphous CN_X thin films (a-CN_x) garner the attention of the scientific community [1-9] because they have very important structural properties , such as high elasticity, low friction coefficient, significant optical properties, and for its biocompatibility features. [4, 6-9]. Moreover, these thin 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-CNx 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/ λ = 1064 nm, laser flounce = 12.8 J cm^{-}

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2). Five samples of carbon nitride thin films were prepared in an environment of pure nitrogen (purity 99.999%). The nitrogen (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 cm^{-1}). The chemical composition of the films were measured by using a LEYBOLD LHS11 MCP- XPS spectroscopy. The SEM photos was 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]. Figure 1 plots XPS spectrum of the sample prepared using pressure of 100 Pa. In this figure, the peaks C1s, O1s and N1s were distinguished.

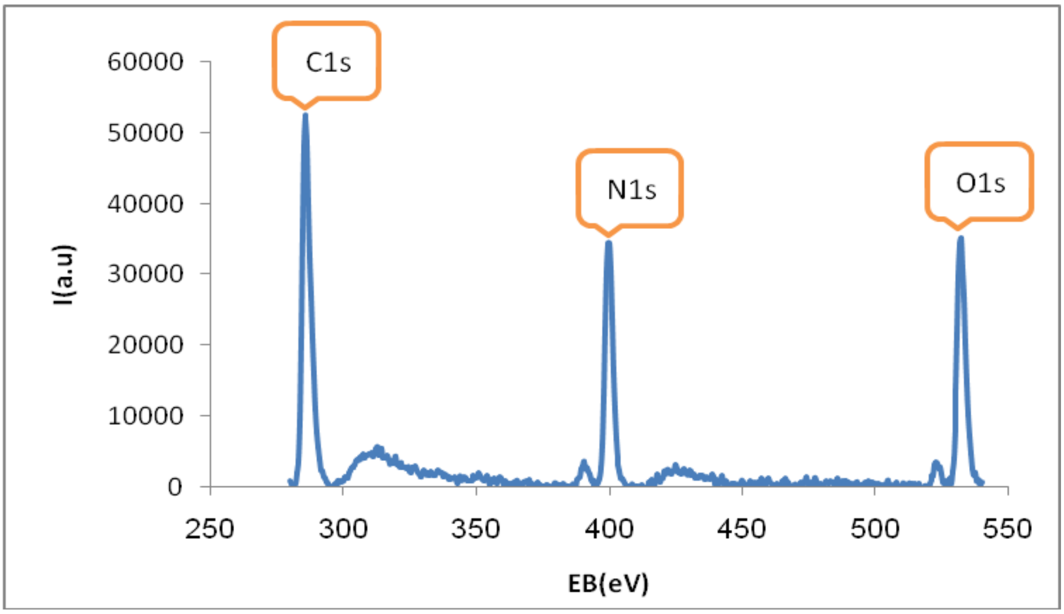

Figure 1. XPS spectrum of the sample prepared using nitrogen pressure of 100 Pa.

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.

Figure 2 shows the concentration of C(sp^2)-C bonds as a functions of deposition pressure. As the pressure increases, the concentration of C(sp^2)-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^3)-N bonds (refer Fig. 3).

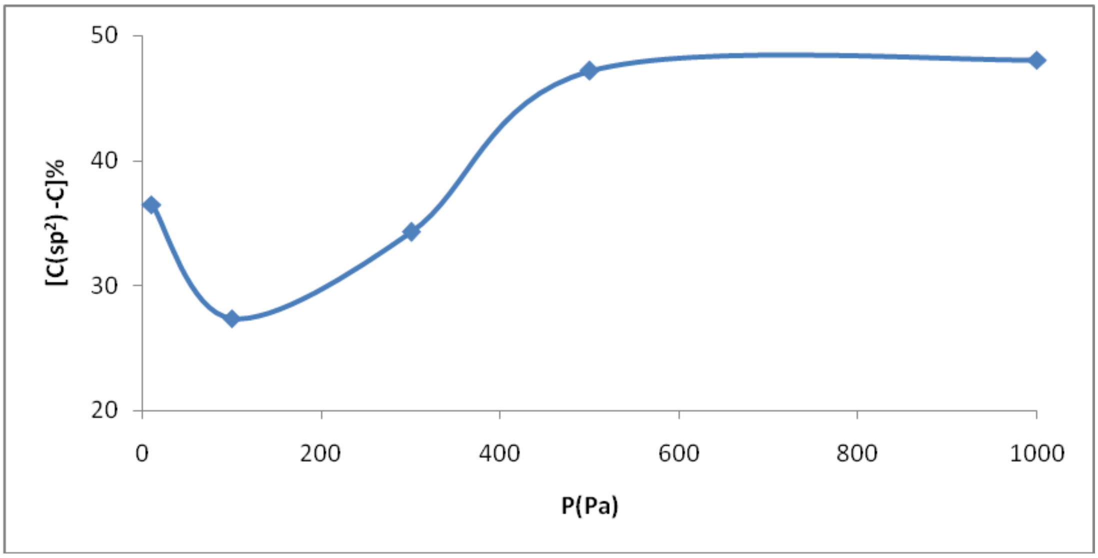

Figure 2. The concentration of C(sp^2)-C bonds as a function of deposition pressure.

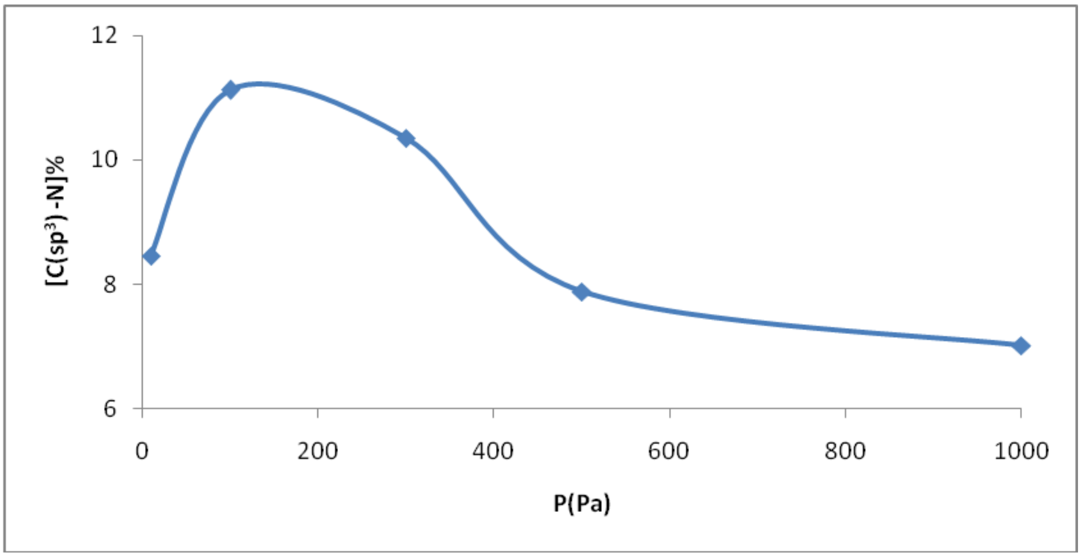

Figure 3. The concentration of C(sp^3)-N bonds as a function of deposition pressure.

There is no specific behavior in the case of C(sp^2)-N bonds (Figure 4), where the concentration swings around an average value (approximately 21%). The decreasing concentration of C(sp^2)-N and C(sp^3)-N bonds indicate that the nitrogen content in the films decreases when pressure increases.

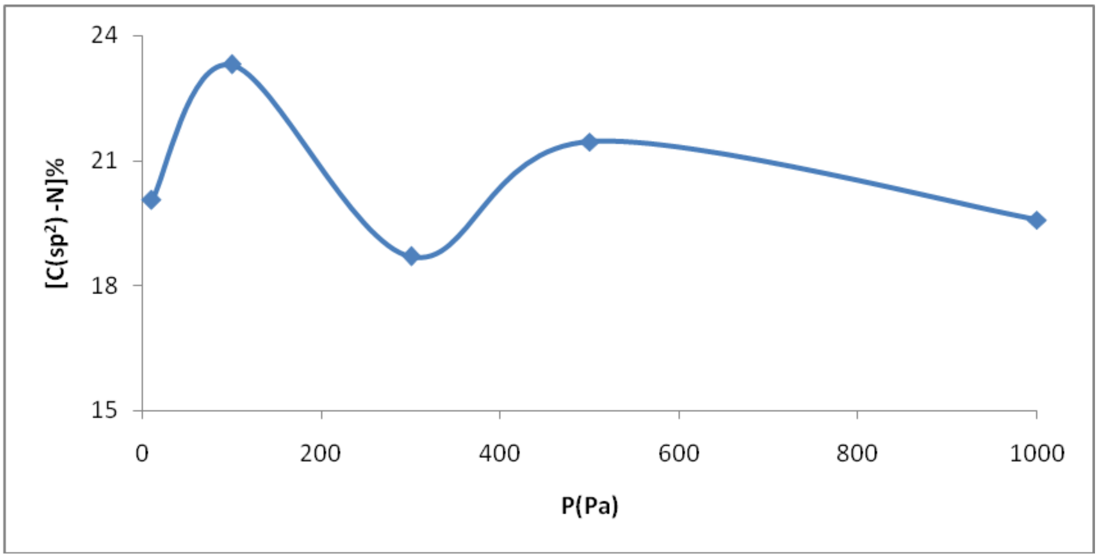

Figure 4. The concentration of C(sp^2)-N bonds as a function of deposition pressure.

Results obtained from previous plot in Figure 2 until Figure 4 imply that the use of high pressures is not beneficial to the forming of each of the N–C (sp^2) or N–C (sp^3) 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.

Comparison between the electron microscopy images (Figure 5) shows that the sp^2 clusters size increases with increasing C(sp^2)-N bonds concentration and decreases with the decreasing of these bonds. This result indicates that the C(sp^2)-N bonds contribute to the formation of sp^{2}different configurations (hexagonal rings or chains).

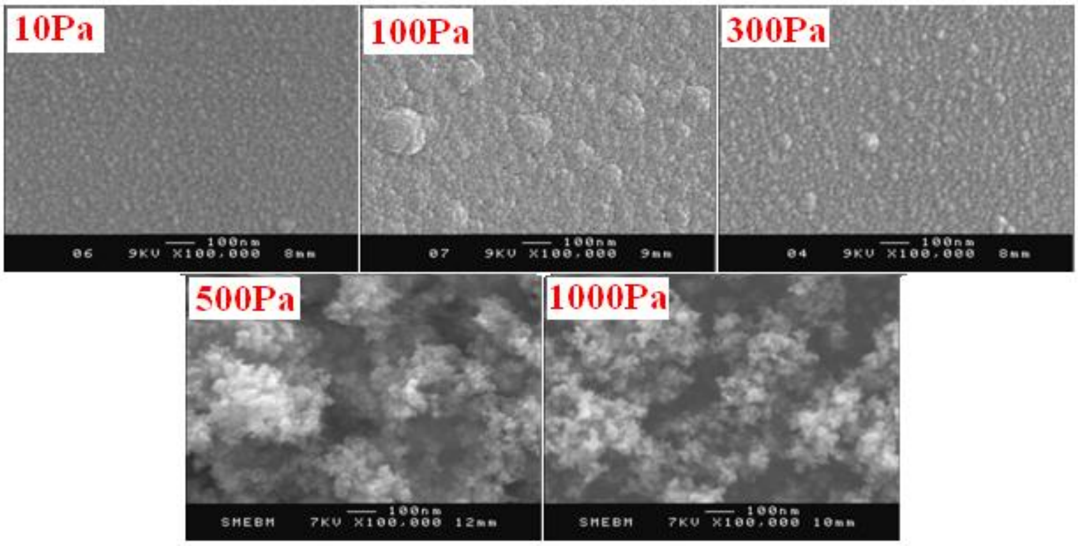

Figure 5. SEM photos of the prepared films.

Figure 6 illustrates the order degree A_D/A_G as a function of nitrogen pressure. 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. Oppositely, as the ratio A_D/A_G increases, the order phase (chains) ratio decreases.

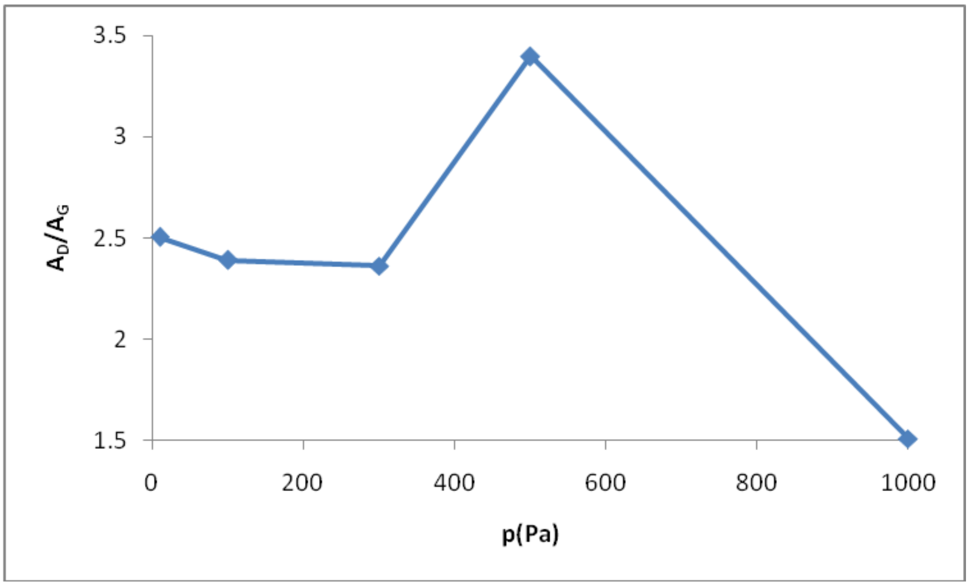

Figure 6. The order degree as a function of deposition pressure.

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. The C (sp^2)-N bonds was found to have contributed 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 the ratio of chains number to hexagonal rings number is sensitive to the numerical value of the applied pressure.

ACKNOWLEDGMENTS

We would like to thank the Director General of Syrian Atomic Energy Professor I. Othman, commission for encouragement and support; and Dr. A. Alkhawwam, and Dr. B. Abdallah for assistance.

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