

EFFECT OF C-C BONDS POLARIZATION ON SP² CLUSTERS SIZE IN A-CN_x THIN FILMS

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Abstract

In this paper we show that, in a-CN_x thin films, the nonlinear relationship between the charge effect resulted during XPS surface analysis and the C(sp³)-N bonds concentration is a direct result of the C-C bonds polarization. We found that the charge effect coefficient relates to both the number of C(sp³)-N bonds and the number of dipoles resulting from C-C bonds polarization. In addition, the results showed that the C-C bonds polarization is the main reason for the clustering processes.

Keywords: Carbon nitride, laser deposition, X-ray photo-electron spectroscopy, charge effect

Introduction

Amorphous carbon nitride thin films (a-CN_x) have the attention of the scientific community (Kayed, 2010; Abdullahi *et al.*, 2016; Hellgren *et al.*, 2016) because they have very important properties. It must be noted here that, it was thought that CN_x have important properties, a statement that need to be relativized and differentiated considering that many aspects of this original belief must be questioned and revised (Neuville, 2019). CN_x can have much different properties, according how much graphitic or more diamond like they can be, how the nitrogen is incorporated in the material, either in form of N, N⁺, or merely N⁺², and at which concentration and at which temperature and pressure the deposition process is operated. Recalling the flaw of the theory of Liu and Cohen predicting some much superior hardness of β-C₃N₄ than diamond with some quantum mechanical calculation ignoring in fact the very low binding energy of CN (~3.16 eV) and size in comparison to C-C in diamond and harder ta-C. On the other hand, considering the mechanical and tribological properties of CN_x to be observed for

instance that relatively soft CN_x (~6GPa), with much reduced content of sp³. Where atomic N is introduced in the material in substitution to carbon atoms (verified with NMR by Holloway *et al.*), has high elasticity and considering that wear rates are proportional to f.H/E (if no delamination is to be considered for different other adhesion, contamination and interfacial stress reasons), They have been used for hard disc tribological coatings.

With regard to the optical properties, band gap of CN_x materials can be adapted with the N content. This is particularly important for instance for achieving better photocatalytic effects for hydrogen production from water. However, this is to be combined with other properties important to be achieved such as thermal and chemical stability and electric conductivity. The model proposed by Rodil *et al.* (2001) for the bandgap of CN_x, does not consider the diamond like atomic rearrangement towards harder N doped ta-C and to N doped diamond.

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In many cases, the carbon-carbon bonds polarization hypothesis is used to interpret the results of some spectral measurements (Aono *et al.*, 2016). For example, this hypothesis was used to explain the mechanism of the formation of the (1,000-1,800) cm^{-1} feature in FT-IR spectra of a-CN_x films (Lejeune *et al.*, 2001). Also, this hypothesis is used when studying the optical band gap of amorphous carbon nitride thin films (Rodil *et al.*, 2003). Primarily, C-C bonds polarization theory is based on that, these bonds becoming IR active by the nitrogen incorporation into the graphitic rings which cause symmetry break of the C(sp^2)-C bonds (Hayashi *et al.*, 2001). The presence of C sp^2 hexagonal ring cluster is indicated with the sharpness of the G band (nominally at $\sim 1,580\text{ cm}^{-1}$) and with which some internal stress shift can be determined. The presence of C sp^3 cluster is documented with a band/peak at nominally $\sim 1,330\text{ cm}^{-1}$ (with eventually added stress shift). All this can be confirmed with the sp^2/sp^3 ratio that can be obtained with Auger carbon band distribution of the XPS.

In X-ray photoelectron spectroscopy (XPS), charge effect phenomenon is produced by the interaction between the generated X-rays and the sample during the characterization of low conductivity materials. In the case of conductive materials, the samples are grounded and this leads to no surface charge is arise on the samples surfaces. In the case of insulate materials, grounding becomes useless, so the surfaces of the samples become charged. The surface charge leads to a decrease in the kinetic energy of the electrons released from the sample, leading to a specific shift in the peaks positions of all elements from the expected locations. The peak shift (charge effect coefficient) has a negative effects on the XPS measurements, therefore, a correction factor must be added to obtain the actual locations of the peaks.

In this paper, we present a detailed analysis of experimental equations obtained in previous work (Kayed, 2018) which describe the relationship between the charge effect coefficient and C(sp^3)-N bonds concentration in amorphous carbon nitride thin films.

Materials and Methods

Sample Preparation

Carbon nitride thin films were synthesized using pulsed laser deposition (PLD) system. The films were deposited on non-heated polished n-type Si (100). Part of the samples were deposited in an atmosphere of pure nitrogen molecular gas (purity 99.999%). The other part were deposited in a

nitrogen plasma afterglow (NPA) by using Microwave SAIREM (GMP 20 KEDS) at transmitted power $P = 1,000\text{ W}$. The deposition was performed in N₂/ NPA with pressures varied in the range from 10-1,000 Pa. More details about the deposition procedures are explained in our previous works (Alkhawwam *et al.*, 2002; Alkhawwam *et al.*, 2011; Kayed, 2018).

Sample Characterization

Raman Analysis

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}).

SEM Analysis

The SEM photos was recorded by using a JEOL-type JSM 6400F scanning electron microscopy

XPS Analysis

The chemical composition of our films were measured by using a LEYBOLD LHS11 MCP- XPS spectroscopy where, carbon nitride thin films were irradiated by X-ray radiation emission from Mg $K\alpha$ X-ray gun with a photon energy of 1,253.6 eV. This gun was operated at $P = 120\text{ W}$ with high voltage $12\text{ V} = \text{kV}$ and a current emission $A = 10\text{ mA}$. The irradiation operations were performed under a vacuum condition ($\approx 10^{-8}\text{ Pa}$). As a result of irradiation process, XPS curves were obtained, which were used to determine the ratio of the bands C(sp^2)-C, C(sp^3)-N and C(sp^2)-N (Kayed, 2018). In addition, these spectra were used to calculate the charge effect coefficient (E). The method for calculating this coefficient was discussed in a previous work (Kayed, 2018).

Results and Discussion

A detailed description of the spectra obtained by XPS spectroscopy in addition to a detailed explanation of the method of calculating the charge effect coefficient (E) are mentioned in the previous works (Kayed, 2018; Kayed, 2019).

According to our previous papers (Kayed, 2018 and Kayed, 2019), the microstructure of each films was determined as shown in the Table 1. Table1 also contains A_D/A_G ratio, E (the charge effect coefficient) and BE (the C(sp^3)-N binding energy) of all prepared samples.

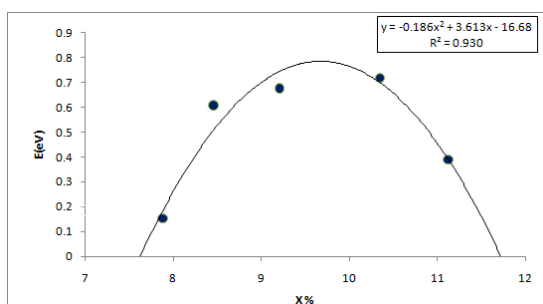
In each sample, the C-C(sp^3) bonding ratio ($X\% = [C-N(sp^3)]\%$) has been calculated by multiplying the relative area (S) corresponding to C-C(sp^3) bond (corresponding C1s spectral line) with the total carbon ratio in the thin film (C%). Table 2

Table 1. The N₂/nitrogen plasma pressure, microstructure, A_D/A_G ratio, E (the charge effect coefficient) and BE (the C(sp³)-N binding energy) of all prepared samples

	Sample code	P (Pa)	Micro structure	A _D /A _G	BE (eV)	E (eV) =BE-284.6
Series A	A	10	Hexagonal rings structure	2.731	285.206	0.6
	B	100	Hexagonal rings structure	2.425	284.987	0.4
	C	300	Hexagonal rings structure	1.451	285.318	0.7
	D	500	Hexagonal rings structure	3.348	284.752	0.1
	E	1000	Chains structure	1.457	284.782	0.2
Series B	F	10	Hexagonal rings structure	2.012	285.275	0.7
	G	100	Chains structure	2.802	285.454	0.8
	H	300	Chains structure	0.961	286.198	1.6
	I	500	Chains structure	0.414	286.18	1.6
	J	1000	Chains structure	2.205	285.771	1.2

Table 2. The values of the parameters S, C%, and X for each sample

	Sample code	S	C%	X%
Series A	A	0.1232	68.7	8.461
	B	0.1722	64.6	11.124
	C	0.1509	68.6	10.350
	D	0.0987	79.9	7.885
	E	0.0898	78.1	7.016
Series B	F	0.1346	68.4	9.208
	G	0.1206	71.8	8.662
	H	0.1916	61.9	11.862
	I	0.2228	51.7	11.519
	J	0.1693	56.5	9.563

**Figure 1.** The E coefficient as a function of X (the C(sp³)-N bonds concentration) in the case of hexagonal sp² rings structures

contains the values of the parameters involved in the X% calculation process for each sample.

In this paper, the synthesized thin films classified only according to the micro structure without taking the synthesis method into account. Samples are distributed in two groups, the first one includes samples with sp² hexagonal rings structure and the second one includes samples with sp² chains structure.

Figure 1 illustrate the E coefficient as a function of X (the C(sp³)-N bonds concentration) in the case of hexagonal sp² rings structures. It is clear that there is nonlinearity in the relationship between E and X due to the mutual effects of the chemical

bonds in the film. We used the Excel program to find the equation of the curve shown in this Figure. The resulting equation is:

$$E = 3.613 X - 0.186 X^2 - 16.68 \quad (1)$$

This equation consists of three terms and we will discuss each term separately:

(I) The first term (E1 = 3.613 X): This term is positive and proportional to the C(sp³)-N bonds concentration and represents the increase in charge effect coefficient (E) as a result of the reduction of the electrical conductivity of the film caused by the formation of the C(sp³)-N bonds. This is related to the fact that, in the a-CN thin films, the conductivity is significantly affected by the π electron delocalization in C(sp²)-C bonds, therefore, replacing these bonds with C(sp³)-N bonds will greatly affect the electrical properties of the film.

(II) The second term (E1 = -0.186 X²): This term is negative and proportional to the square of the C(sp³)-N bonds concentration and represents a decrease in charge effect coefficient (E) which in turn reflects a specific increase in the electrical conductivity of the film. The appearance of this term can be interpreted as follows: We assume that each bond of type C(sp³)-N causes polarization of one bond of type C-C. Accordingly, x² expresses the number of dipoles formed by all possible combinations of all poles generated by the induced polarization in the grain (for example, the polarization of only two bonds will lead to the formation of four dipoles). The formation of these dipoles will lead to a decrease in the electrical conductivity of the film and thus a decrease in the charge effect coefficient.

(III) The third term (-16.68): This term is constant, negative and represents the shift from the reference value (284.6eV) in the case of the absence of the C(sp³)-N bonds.

Based on above discussion Equation (1) can be written in the form:

$$E = E_1 + E_2 + E_3 \quad (2)$$

By differentiation we get:

$$dE/dx = dE_1/dx + dE_2/dx \quad (3)$$

The rate of change of the term E_1 is constant while E_2 increases in absolute value as X increases. At curve maxima (the equilibrium point) E is zero and $dE_1/dx = -dE_2/dx$.

In the left part of the curve we have $dE_1/dx > |dE_2/dx|$. This means that as the number of $C(sp^3)$ -N bonds increases, the electrical conductivity of the film decreases, despite the increase in the number of dipoles. Decreased electrical conductivity impedes the interaction between the dipoles and prevents them from configuration in larger clusters. Therefore, in this part of the curve the clusters size decreases as the number of $C(sp^3)$ -N bonds increases. This behavior continues until reaching the curve maxima. In this point, any increase in $C(sp^3)$ -N bonds concentration will result in a transition to the right part of the curve where $dE_1/dx < dE_2/dx$. Here the characteristics of the medium change where it becomes more electrically conductive and this feature is enhanced as the concentration of $C(sp^3)$ -N bonds increases. These conditions allow for increased interaction between the increasing dipoles, leading to their configuration in larger clusters with a higher degree of disorder.

Figure 2 illustrate the E coefficient as a function of X (the $C(sp^3)$ -N bonds concentration) in the case of sp^2 chains structures. In this case, the curve equation is:

$$E = 1.035 X - 0.039 X^2 - 5.156 \quad (4)$$

This equation also contain three terms: $E_1 = 1.035 X$, $E_2 = -0.039 X^2$ and $E_3 = -5.156$.

These terms have the same meanings as those in Equation 1.

In this Figure we notice that the E_{max} is bigger than that in Figure 1. The reason for this is that in this case the reaction mechanism depends on the

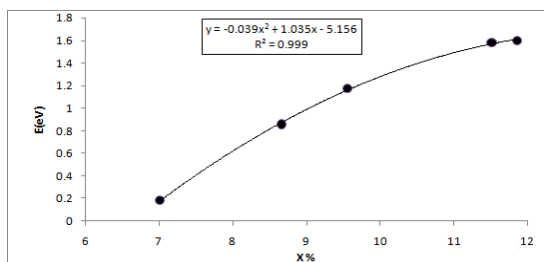


Figure 2. The E coefficient as a function of X (the $C(sp^3)$ -N bonds concentration) in the case of sp^2 chains structures

presence of $C(sp^2)$ -N bonds not on the sp^2 clusters size (Kayed, 2018). The existence of an abundance of $C(sp^2)$ -N bonds in the carbon chains structure prevents the dipole dipole long range interaction between the $C(sp^2)$ -C and $C(sp^3)$ -N bonds (Kayed, 2018). This behavior leads to a significant reduction in the absolute value of the rate of change of the term E_2 . We can conclude from this that the average dipole moment resulting from the induced polarization of C-C bonds in the case of chains structure has a lower value compared to the case of ring structure.

All the mechanisms reviewed above are consistent with our empirical results presented in our previous work (Kayed, 2018) and is an interpretation of these results.

In fact, an atomic rearrangement can be produce with many different effects, either in favor of sp^2 substructures with thermal activation energy (lower than the optoelectronic gap of some possible metastable final state), or in favor of metastable sp^3 substructure with quantum electronic activation (higher than the optoelectronic gap). In our case, there is no clear effect of these factors. Evidence for this is that the curves drawn in the Figures 1 and 2 indicate the regularity of the relationship between the coefficient and the $C(sp^3)$ -N bonds concentration. If there are other obvious effects added to the polarization effect, the experimental points will be distributed irregularly.

Figure 3 contains the charge effect coefficient E as a function of the ratio M . The ratio M represents the number of nitrogen atoms bonded to carbon due to sp^3 -hybrid to the total number of nitrogen atoms bonded with carbon atoms sp^2 and sp^3 hybrids:

$$M = [N-C(sp^3)]/[N-C(sp^3) + N-C(sp^2)] \quad (5)$$

We notice that there is a linear relationship between E and M . The linear relationship includes the points belong to all samples that have chains structure in addition to the samples that have hexagonal rings structure with small clusters size. These samples have poor polarization of the bond

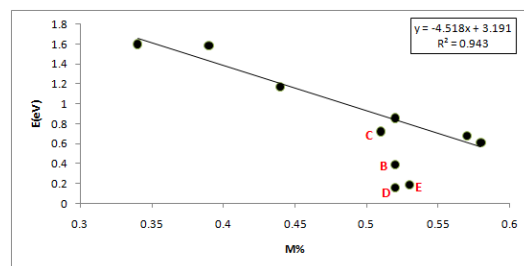


Figure 3. The E coefficient as a function of the ratio M

C-C, so we conclude that: In the cases where the C-C bond polarization is weak, the charge effect coefficient is proportional to the relative concentration of the N-C (sp^3) bonds. The rest of the points (C, B, D, E) that are not located on the straight line belong to the samples that have hexagonal rings structure with larger clusters size. The clusters size increases as the distance from the straight line increases (Figure 4). The significant polarization of C-C bonds in these samples appears as an additional influencing factor that eliminates the linearity of the relationship between E and M in Figure 3. Consequently, the increased clusters size in the samples D and E is a direct result of the high polarization of the C-C bonds in these samples.

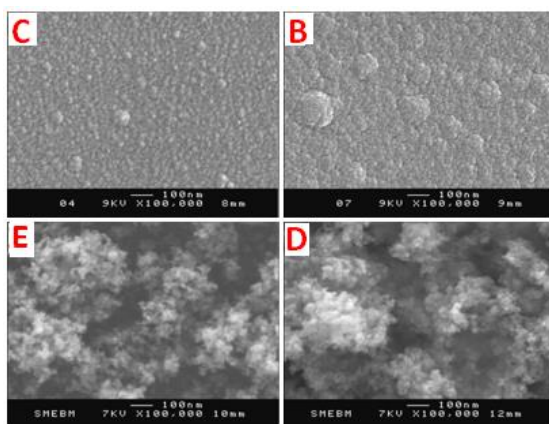


Figure 4. The SEM images of the samples belonging to the points located below the straight line in Figure 3 (The images were arranged according to the increasing the distance from the straight line)

In SEM images (Figure 4), we can see the non-homogeneous structure showing different local juxtaposed substructures. When discussing about formation of clusters, it must be differentiated the formation of Csp^3 crystallites and of Csp^3 disordered more or less amorphous substructures from Csp^2 graphenic clusters (Neuville, 2014). CN bonds can be formed especially if nitrogen is well dissociated in the laser focus and which can be incorporated in form of atomic N. Enhanced Csp^3 concentration can be obtained with the recombination of atomic N to molecular N_2 and with higher electric polarization. With enhanced Csp^3 concentration, more Csp^3 -N bonds can be formed, and is more insulating than with Csp^2 material. There is here a cumulated effect.

Finally, it must be noted that, reasoning on effect of C-C polarization on cluster growth and size might be maintained in considering that in fact sp^3 clusters -instead of sp^2 clusters- are formed. However, this will depend on temperature (at higher

temperature formed Csp^3 cluster can be degraded to Csp^2 cluster) and on the amount of incorporated dissociated N (at low N concentration, formation of Csp^3 substructure will be unlike, because less N_2 recombination will occur). Especially considering that with used laser, reduced activation, dissociation, and ionization will be produced in the evaporated material, and that more diamond like material cannot be produced without the high N_2 chemical recombination energy release.

Conclusions

This work is a continuation of previous work (Kayed, 2018), and aims to provide empirical evidence on the polarization of the C-C bonds due to nitrogen incorporation into carbon nitride thin films. Our results show that the E coefficient relates to both the number of C(sp^3)-N bonds and the number of dipoles resulting from C-C bonds polarization and. We found that the C-C bonds polarization is the main reason for the clustering. In addition, we found that, in the cases where the C-C bond polarization is weak the charge effect coefficient is proportional to the relative concentration of the N-C (sp^3) bonds.

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References

- Abdullahi, Y.Z., Yoon, T.L., Halim, M.M., R. Hashim, M., and Lim, T.L. (2016). Mechanical and electronic properties of graphitic carbon nitride sheet: First-principles calculations. *Solid State Commu.*, 248:144-150.
- Alkhawwam, A., Abdallaha, B., Kayed, K., and Alshoufi, K. (2011). Effect of nitrogen plasma afterglow on amorphous carbon nitride thin films deposited by laser ablation. *Acta Phys. Pol. A.*, 120:545-551.
- Alkhawwam, A., Jama, C., Goudmand, P., Dessaux, O., El Achari, A.M Dhamelin court, P., and Patrat, G. (2002). *Thin Solid Films.*, 408:15-25.
- Aono, M., Takeno, T., and Takagi, T. (2016). Structural, electrical, and optical properties of amorphous carbon nitride films prepared using a hybrid deposition technique. *Diam. Relat. Mater.*, 63:120-124.
- Hayashi, Y., Yu, G., Rahman, M.M., Krishna, K.M., Soga, T., Jimbo, T., and Umeno, M. (2001) Spectroscopic properties of nitrogen doped hydrogenated amorphous carbon films grown by radio frequency plasma-enhanced chemical vapor deposition. *J. Appl. Phys.*, 89:7,924-7,931.
- Hellgren, N., Haasch, R., Schmidt, S., Hultman, L., and Petrov, I. (2016). Interpretation of X-ray photoelectron spectra of

- carbon-nitride thin films: new insights from in situ XPS. *Carbon* 108:242–252.
- Kayed, K. (2010). *Synthesis and Properties of Carbon Nitride and Boron Nitride Thin Films Prepared by Different Techniques*, [Ph.D. thesis]. Damascus, Syria: Damascus University, 156p.
- Kayed, K. (2018). Effect of nitrogen plasma afterglow on the (1,000-1,800) cm^{-1} band in FT-IR spectra of amorphous carbon nitride thin films. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy.*, 190:253-258.
- Kayed, K. (2018). Effect of nitrogen plasma afterglow on the surface charge effect resulted during XPS surface analysis of amorphous carbon nitride thin films. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy.*, 199: 242-247.
- Kayed, K. (2019). The influence of nitrogen pressure on the structure of a-cnx thin films prepared by pld method. *Int. J. Nanoelectron. Mater.*, 12:19-24.
- Kayed, K. (2019). The optical band gap in amorphous carbon nitride thin films: Effect of sp^2 hybridized C atoms configurations. *Fullerenes, Nanotubes and Carbon Nanostructures.*, 27:796–802.
- Lejeune, M., Durand Drouhin, O., Zellama, K., and Benlahsen, M. (2001). Structure and optical properties of carbon nitride films deposited by magnetron sputtering. *Solid State Commun.*, 120:337-342.
- Neuville, S. (2014). *Carbon structure analysis with differentiated Raman spectroscopy*. Lambert Academic Press, CUISY, Paris: 169p.
- Neuville, S. (2019). Selective Carbon Material Engineering for Improved EMS and NEMS. *Micromachines.*, 10:539-581.
- Rodil, S.E., Ferrari, A.C., Robertson, J., and Milne, W.L. (2001). Raman and infrared modes of hydrogenated amorphous carbon nitride. *J. Appl. Phys.*, 89:5,425-5,430.
- Rodil, S.E., Muhl, S., Maca, S., and Ferrari, A.C. (2003). Optical gap in carbon nitride films. *Thin Solid Films.*, 433:119-125.