

## Physical Properties of Reactively Sputter-Deposited C-N Thin Films

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**Abstract:** The aim of this work was to prepare and study amorphous carbon nitride (CN<sub>x</sub>) films. Films were deposited by reactive magnetron radiofrequency (RF) sputtering from graphite target in argon and nitrogen mixture discharge at room temperature. The ratio of the gas flow rate was varied from 0.1 to 1. Deposited films were found to be amorphous. Highest Nitrogen concentration achieved was 42 atomic percent which is very rare and therefore, the highest nitrogen to carbon atomic ratio was 0.76. The incorporation of nitrogen promoted the clustering of diamond-like sites at the expense of graphitic sites leading to a decrease in disorder. The film surface became rougher with the increase nitrogen concentration. Films were optically transparent in the 200-900 nm wavelength range with a wide gap varying between 3.59 and 3.63 eV. There was an increase in resistivity from 15 to  $87.4 \times 10^{-3} \Omega \cdot \text{cm}$  for  $\alpha\text{-CN}_x$  thin films for  $0.1 < R_F < 0.8$  and a less decrease for  $R_F > 0.8$ . Pore size increased in the films, but had little influence on band gaps. On the other hand, increased pore size reduced electrical interaction between particles by increasing resistivity.

**Keywords:** carbon nitride, reactive magnetron RF sputtering, structural properties, optical properties.

### 1. INTRODUCTION

Quite recently, considerable attention has been paid to carbon nitride thin films. The observed properties have provided evidence for potential use in optoelectronic devices such as electroluminescence devices and photovoltaic solar cells [1]. In this regard, the optical characteristics of these films have attracted a lot of interest [2].

What we know about carbon-rich carbon nitride films is largely based upon empirical study carried out by Liu and Cohen in the 1990s [3]. In fact, they predicted the development of a  $\beta\text{-C}_3\text{N}_4$  structure with properties comparable to those of diamond. Indeed, this structure is not yet well evidenced, despite several publications on this subject.

Carbon nitride films have been studied as hard protective coating materials for rigid magnetic storage disks and as long-life charge stripper foils for tandem accelerators [4]. Carbon nitride films, in particular, may be utilized as antireflection coating for c-Si solar cells given to their indirect band gap, high thermal stability, great mechanical strength, high transmission, and low reflectivity, as well as their ease of manufacturing using reactive magnetron sputtering [5].

This study aims to enrich this growing area of

research by showing an important contribution.

In this paper, a technique that improves the formation of amorphous carbon nitride thin films, deposited by reactive radio-frequency magnetron sputtering under different nitrogen flow rate, has been presented. However very few publication, can be found in the literature, that discuss this method especially on carbon nitride thin films. Magnetron sputtering has become the process of choice for the deposition of a wide range of industrially important coatings and it is preferred for industrial applications because of its simplicity and its use for deposition of many materials [6-8].

The magnetron source developed in the 1970s represents a significant advance in the efficiency of sputter tooling. The magnetron uses strong magnetic fields which usually come from permanent magnets, to keep secondary electrons confined spatially close to the target surface. By confining the secondary electrons near the surface of the target, its residence time in the plasma is much longer, leading to higher ionization of the plasma particles of sputter steam, thicker plasma, higher plasma currents and deposition speeds.

In a magnetron sputter source, the high electrical field resulting from the fall potential of the cathode Accelerates secondary electrons in a

normal direction to the target surface. The configuration of the magnetic field is specifically developed so that the parallel field lines to the target surface, resulting in an ExB drift forces applied on the secondary electrons. The electrons are therefore confined to spiral motion drift orbits parallel to the target surface, resulting in additional collisional ionization of the sputter-gas atoms and higher overall plasma currents [9].

Reactive sputtering can be used to deposit films at room temperature; essential for optical and electronic structures. This method consists to deposit materials by adding gas to the sputtering chamber. The carbon nitride films can be produced by reactive sputtering using argon-nitrogen plasma. Despite all existing synthesis techniques, films with high nitrogen content are not easily achievable. Reports indicate that nitrogen rates exceeding 40 at. % are uncommon [10, 11]. In addition, most of the efforts result mainly in amorphous microstructures or even sometimes nano-sized crystalline clusters embedded in the amorphous matrix [12, 13].

## 2. EXPERIMENTAL PROCEDURES

### 2.1. Film Deposition

Reactive magnetron radiofrequency sputtering method was used to deposit carbon nitride thin films using Alcatel SCM 450 sputtering apparatus at 13.56 MHz frequency in different argon-nitrogen gas atmospheres at room temperature. In our work, the deposition process takes place in a vacuum chamber where the target and substrate are placed. A commercial graphite target of 99.999% purity, 100 mm diameter and 6 mm thickness was used. Before the deposition, the sputtering chamber was evacuated down to  $10^{-6}$  mbar, the plasma power has been set at 100 W and the deposition pressure was fixed at  $10^{-2}$  mbar. The deposits were made over a period of 15 min, at room temperature and the ratio of the gas flow rate  $R_F = F_{N_2}/(F_{Ar} + F_{N_2})$  varies between 0.1 and 1, where  $F_{N_2}$  and  $F_{Ar}$  are the flows of nitrogen and argon, respectively. The target's distance from the substrate was set at 122 mm.

Thin films were deposited on various substrates: silicon for thickness, optical and Atomic Force Microscopy (AFM) characterizations, silicon wafer for Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) measurements,

quartz for Electron Spin Resonance (ESR) and finally vitreous carbon for Rutherford backscattering spectrometry (RBS).

### 2.2. Characterization of Films

The structure of prepared samples was investigated using an X'Pert PRO X-ray diffractometer with a Cu  $K_{\alpha}$  anticathode and X'Celerator linear detector. The detector's scanning angle was varied between  $10^{\circ}$  and  $60^{\circ}$  with a step size of  $0.0017^{\circ}$ . The thicknesses of the deposited layers were measured with a DEKTAK 150 profiler. In this apparatus, the surface to be studied is scanned by a diamond tip; the probe has a lateral deflection of 4 nm and a vertical resolution of 5 nm.

Rutherford backscattering (RBS) with 2 MeV alpha particles and 15 nA current intensity was used to examine the layer composition; a charge of  $10 \mu\text{C}$  was collected at  $165^{\circ}$  detection angle. There is no overlapping in the RBS signal of the graphite substrate, which appears at a lower energy than the constituents of the film. We should mention that RBS is a restricted approach, with a depth resolution of about 5 to 10 nm. As a result, this method is unsuitable for studying materials in very thin layers, and it involves some errors.

The experimental spectra are processed using the SIMNRA simulation program [14]. For a better fit of the theoretical one to the experimental spectrum, the thin film can be subdivided into sub-layers parallel to the surface, of adjusted thickness and composition.

Film roughness was determined by Atomic Force Microscopy using Asylum MFP-3D AFM apparatus. The bonding structure was evaluated by a thermo Nicolet 5700 Fourier Transform Infra-red (FTIR) spectrometer in the range  $400\text{-}4000 \text{ cm}^{-1}$  with  $4 \text{ cm}^{-1}$  resolution. After subtracting a linear background, the FTIR spectra were fitted with Gaussian functions to determine the contributions of important band.

Electron Spin Resonance (ESR) measurements of films deposited on quartz substrates were carried out using a Bruker EMX ESR spectrometer, with a microwave frequency of 9.653 GHz (X-band) and a microwave power of 6.35 mW with a modulation amplitude of  $g = (2.0036 \pm 0.0002)$ , at a frequency of 100 kHz. The data were recorded and then simulated using Bruker WIN-EPR and SIMFONIA software, respectively.

Optical gap and Urbach energy were extracted from transmittance spectra obtained from a UV-Vis Perkin-Elmer spectrophotometer in the wavelength range extending from the region of the near-infrared (1100 nm) to the ultraviolet (200 nm).

### 3. RESULTS AND DISCUSSION

In this study, the abbreviation a-CN<sub>x</sub> will be used to refer to amorphous carbon nitride films; with x is N/C atomic ratio.

#### 3.1. Structural Properties

Initially, the X-Ray Diffraction investigation reveals that the spectrum, as shown in Figure 1, avoids sharp peaks, suggesting that the films are amorphous in nature. For practical applications, amorphous carbon films are very significant, for example, in the application of magnetic thin film recording disk overcoat [15] and for solar cell devices [16]. The great majority of the deposits have been found to be amorphous [17].

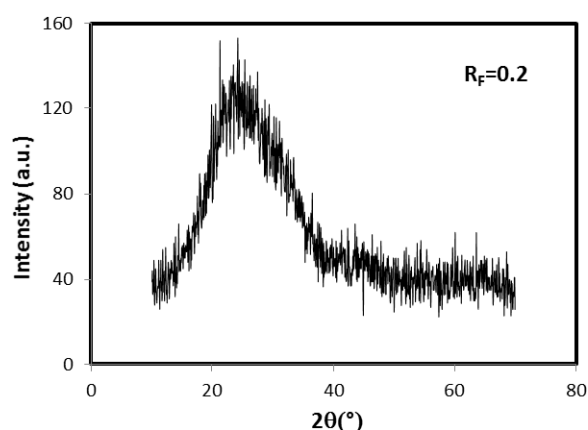


Fig. 1. XRD Spectrum of a-CN<sub>x</sub> for R<sub>F</sub>= 0.2

The thickness measurements allowed us to calculate the deposition rate of the layers. The deposition rate is a very good parameter to follow the evolution of the deposition process and to predict the nature of the deposited material.

As shown in Figure 2, two different areas can be defined. Initially, the deposition rate of the thin layers of a-CN<sub>x</sub> increases with the increase of gas flow rate R<sub>F</sub>. Indeed, values ranging from about 1.8 to 11.7 nm min<sup>-1</sup> were obtained when the gas flow rate R<sub>F</sub> was varied from 0.1 to 1. This can be explained by the fact that the increase in the amount of incident argon ions leads to a greater number of sputtered carbon atoms and thus to an increase in the growth rate. Then, with the

increase of the nitrogen content in the plasma, we note a very slight increase of the deposition rate until a "critical" level. After this critical composition value, there is a minor decrease in the deposition rate, whatever the amount of argon initially introduced. This behavior is the consequence of the change of pulverization mode. It results from the modification of the target surface which causes the variation of the sputtering efficiency and thus of the deposition rate. This result is in agreement with previous studies [18, 19].

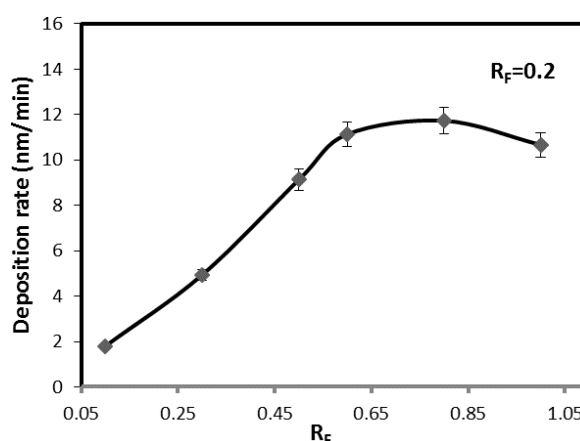


Fig. 2. Deposition rate of a-CN<sub>x</sub> as a function of R<sub>F</sub>

This work focuses specifically on the so-called "chemical" magnetron sputtering mechanism, particularly in the case of carbon-rich materials, because there is a variation between the binding energy of the reactive gas and the sputtered atoms [3]. If a target is bombarded with chemically reactive species, chemical effects must be taken into account. In this case, two opposite reactions can occur:

Chemical reactions between target atoms and reactive gas can form "CN<sup>+</sup>, C<sub>2</sub>N<sub>2</sub><sup>+</sup>..." species that are weakly bounded to the surface and easily sputtered. This results in an increase in the sputtering efficiency. Otherwise, the newly formed compounds may have strong bonds with the target atoms and, therefore, a higher surface binding energy, resulting in a decrease of sputtering rate [8]. In general, the sputtering intensity of the elements decreases considerably when compounds form on the target due to the lower sputtering yield of the relative compounds. This was nevertheless not the case in the reactive sputtering of carbon nitride films. As nitrogen gas was incorporated into the sputtering atmosphere,

reactive nitrogen ions, atoms and molecules were formed and reacted on the target, in the discharge and on the substrate surface with carbon atoms. It can be suggested that the higher partial nitrogen pressure caused a higher nitrogen flux to the substrate, leading to the formation of carbon nitride films [20]. On the other hand, we suggest that target atoms are removed from the surface by collisions between projectiles and/or recoil of produced atoms and the atoms in the near-surface layers of the target material, resulting in a decrease in sputtering efficiency.

Figure 3a, shows a typical experimental RBS spectrum and the corresponding simulation for  $R_F=1$ . As can be seen from Figure 3b, RBS results give the composition variation of thin films deposited in different gas mixtures. By increasing  $R_F$  from 0.1 to 0.6, the N content in the films increases from 0 to 42 at. %. After this, and when  $R_F$  increases beyond the value of 0.6, the N content decreases. Many approaches include interactions between nitrogen ions and carbon surfaces. Nitrogen is known to create chemical

bonds with carbon atoms during ion bombardment, to generate volatile compounds. It was proposed that chemical sputtering was responsible for the observed nitrogen content limitations and the growth rate of carbon nitride films. Subsequently, CN and  $C_2N_2$  molecules with optical emission spectroscopy and mass spectrometry were detected by a number of research groups, confirming the importance of chemical sputtering for the growth of carbon nitride films [21,22]. We also find that traces of oxygen ( $O < 3$  at. %) are present in the films deposited under argon-nitrogen plasma. We attribute this result to the presence of residual gases (oxygen, water vapor) in the deposition chamber and to the high reactivity of oxygen.

The nitrogen to carbon atomic ratio in a-CN<sub>x</sub> films was determined as shown in Fig. 3c the incorporated nitrogen atoms in a-CN<sub>x</sub> films were chemically bonded to carbon. N/C ratio was increased from 0.53 to 0.76 when  $R_F$  increases from 0.2 to 0.6, this was due to the impact of the increased amount of graphite receiving nitrogen.

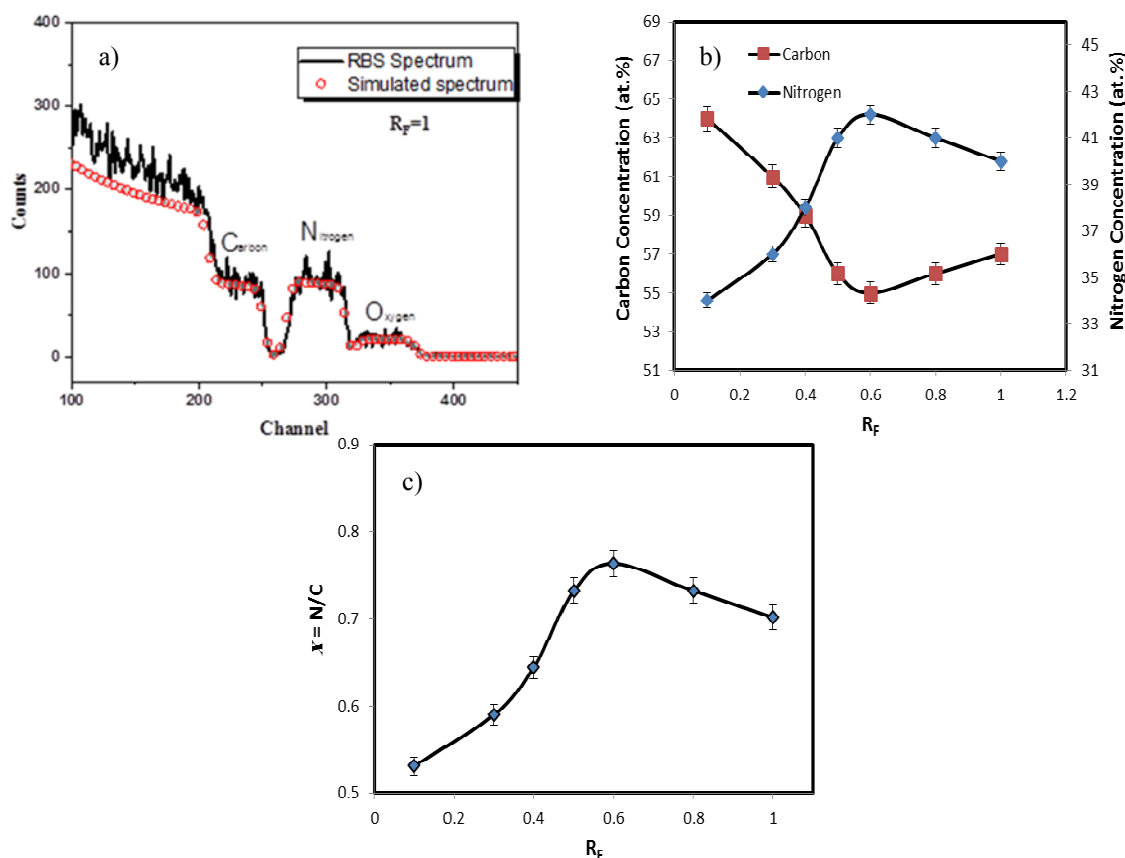


Fig. 3. a) Experimental and simulated RBS spectrum for  $R_F=1$  b) Composition of a-CN<sub>x</sub> films as a function of  $R_F$  c) Ratio of the number of nitrogen and carbon atoms in a-CN<sub>x</sub> films.

Then, the nitrogen carbon ratio decreased from 0.76 to 0.70 with the increase of  $R_F$  from 0.6 to 1. It is noted that in a previous study, the ratio was 0.75 but with deposition on substrates heated at 100°C [23]. A previous study found that calculated N/C ratios ranged between 1 and 1.3, but because silicon substrates were employed, it was unable to confirm whether this element was incorporated in the film [24].

ESR measurements afford information about the existence of unpaired electrons, as well as quantities, type, nature, surrounding environment, and behavior.

A typical ESR spectrum is shown in Figure 4 for  $R_F=0.4$ . We saw clearly that the line shape is close to Lorentzian as it is generally the case of amorphous materials.

The spin density  $D_S$  and the peak-to-peak line width  $\Delta H_{PP}$ , derived from ESR analysis for different  $R_F$  values are presented in Table I. The obtained spin density is in the order of  $10^{17} \text{ cm}^{-3}$ , however, the spin density observed in previous studies is estimated in the order of  $10^{16} \text{ cm}^{-3}$  [25, 26]. When  $R_F$  increases, the spin density tends to be similar suggesting that the structures are more alike, this is due to an ordering of the  $sp^2$  structures and less dangling bonds [27]. One can notice that spin density in some diamond like carbon (DLC) films is about  $10^{20} \text{ cm}^{-3}$  [28].

The average g-value, which reflects the orbit level occupied by the electron, is  $\sim 2.001$  for the different deposited films. As reported by Suter et al. [29], the g value varied between 2.0034 and 2.0035.

Surface topography can be explored using Atomic Force Microscopy (AFM) with near-atomic

resolution. It can measure the surface roughness of samples down to the Angström level. As shown in figure 5, 2D and 3D AFM image reveal the morphology of the materials in a total surface area of  $5\mu\text{m} \times 5\mu\text{m}$ . It is apparent that both surface roughness and surface morphology modifications are depending on the  $R_F$  variation.

Like films ( $sp^3$ ), graphitic films ( $sp^2$ ), and polymeric films ( $sp^1$ ) can be described.

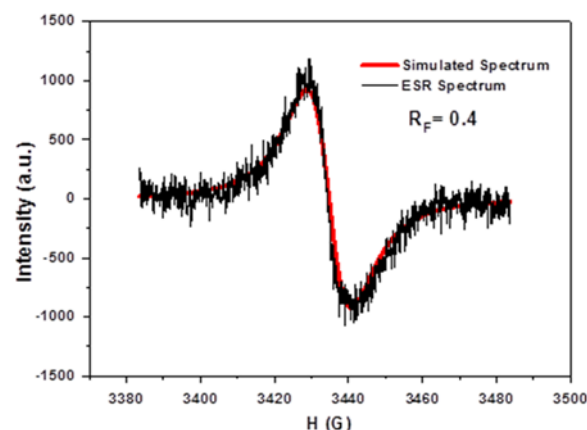


Fig. 4. ESR spectra of a-CN<sub>x</sub> thin films for  $R_F=0.4$  owing

Figure 6a presents the infrared spectra of the different deposits in the range  $500\text{-}3500 \text{ cm}^{-1}$ . Three bands can be identified: the first one at  $620 \text{ cm}^{-1}$  typical of the Si (100) substrate surface, the second one at  $730 \text{ cm}^{-1}$  corresponding to Si-C vibration mode. The second order vibration mode of silicon is observed at  $1120 \text{ cm}^{-1}$ . The elongation vibrations of the CC and CN bonds are observed in this range [32]. FTIR absorption spectra are shown in Figure 6.a for  $R_F=1$ .

Table 1. The spin density  $D_S$  and the peak-to-peak line width  $\Delta H_{PP}$ :

$R_F$	g (G)	$\Delta H_{pp}$ (G)	$D_S(10^{17}\text{cm}^{-3})$
0.2	2.000	15	5.16
0.4	2.002	15	5.23
0.6	2.001	15	5.21
0.8	2.000	12	4.20
1	2.002	9	5.61

Table 2. The variation of thickness, roughness and pore size of films for different  $R_F$  ratios.

$R_F$	Thickness (nm)	RMS (nm)	Pore size (nm)
0.1	27±10	0.917	2.996
0.3	74±10	-	-
0.5	137±10	1.030	6.184
0.6	167±10	-	-
0.8	176±10	13.82	32.448
1	160±10	-	-



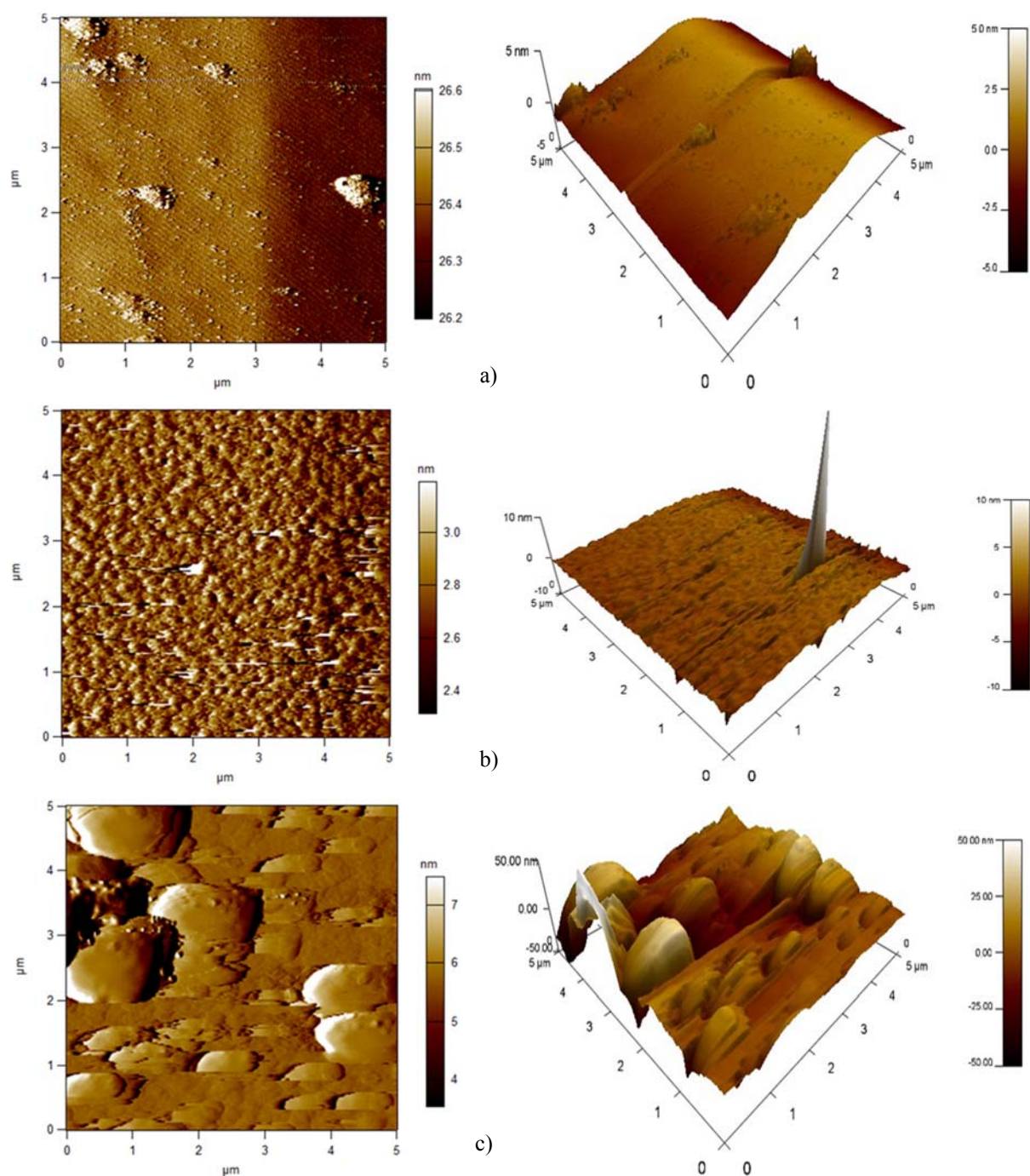


Fig. 5. 2D and 3D AFM topographic images of a-CN<sub>x</sub> thin films for (a) R<sub>F</sub> = 0.1, 0.3, and 0.8

As can be seen from Figure 6b, the intensities of the peaks at 1323 cm<sup>-1</sup> and 1403 cm<sup>-1</sup> are attributed to the C-N and the C=N symmetric stretching bonds respectively. It can be said that the C-N and C=N bonds behave in opposite behaviors and always pass through an extremum. The obtained results agree with those of Teter et al. [33], the C=N frequency is found below 1500 cm<sup>-1</sup>.

A narrowing of the D-peak at 1456.2 cm<sup>-1</sup> is observed with the increase of R<sub>F</sub>. This is attributed to the decrease of graphitic disorder and an ordering of the sp<sup>2</sup> structure [34]. One can also notice an increase of the intensity of the G-peak at 1595.9 cm<sup>-1</sup> with the increase of R<sub>F</sub> which is attributed to the graphitic vibrations of C=C. There is a great interest in estimating structural disorder due to sp<sup>2</sup>(C) sites. The evolution of the

$I_D/I_G$  intensities ratio of the peaks attributed respectively to D and G bands is shown in Figure 6c. It was known that the  $(I_D/I_G)$  parameter is sensitive to the degree of structural order; the more ordered, the structure of the material, the more this parameter decreases, and vice versa. According to the literature, disorder increases with decreasing size of  $sp^2$  sites.

These sites are formed because of the bond breakdown that occurs during ion bombardment when deposition takes place. Nitrogen atoms present in the plasma create substitutional bonds when bond cleavage occurs at the surface of the layers, which reduces the  $sp^2$  sites and their size [35].

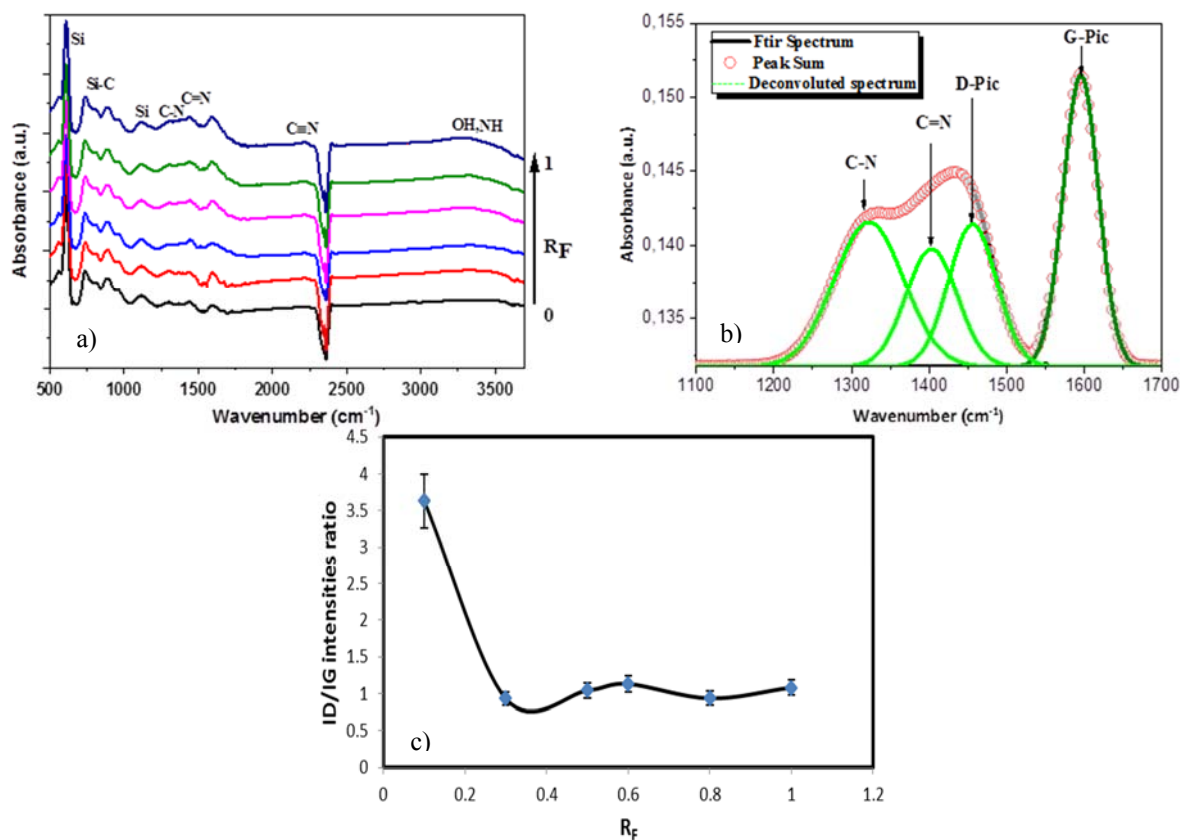
The decrease in the  $(I_D/I_G)$  ratio was observed for  $R_F$  values from 0.3 to 0.92, then it stabilises around 1, for  $R_F > 0.3$ . In [36] it was shown that the decrease in the  $(I_D/I_G)$  ratio leads to a presence of  $sp^2$  sites.

There is also a low-intensity absorption region at about  $2300\text{ cm}^{-1}$ , which can be associated to the presence of cyano group ( $C\equiv N$ ) such as  $-C\equiv N$ ,

$-N\equiv C$  and  $-C=N-$  bonds [37]. The presence of this absorption region allows us to confirm that the nitrogen is bounded to the carbon in the deposited layers, making the structure harder [38, 39]. According to Riedel et al. and Patai [40, 41], at high nitrogen concentration, a peak at about  $2200\text{ cm}^{-1}$  is frequently observed and is thought to be associated to CN.

The CN denotes the amount of  $sp^1$  carbon in the films. This type of bonding generates bond-terminating sites, leading to a lack of connectiveness and a less densely packed structure in the films.

There is a low intensity absorption region at  $3300\text{ cm}^{-1}$ , that can be associated with the OH or NH bond, suggesting low contamination inside the chamber or by the ambient air as soon as the deposits are extracted from the chamber [42]. Several studies have found D and G peaks in FTIR spectra. However, they demonstrated that the position of the D and G peaks can vary depending on the experimental conditions [43-45].



**Fig. 6.** a) FTIR absorption spectra of  $a-CN_x$  thin films for different  $R_F$  values b) Deconvolution of FTIR absorption spectrum of  $a-CN_x$  thin films in  $1200-1700\text{ cm}^{-1}$  zone for  $R_F = 1$  c)  $(I_D/I_G)$  intensities ratio of the Infrared D and G bands of the  $a-CN_x$  thin films as a function of different values of  $R_F$ .

### 3.2. Optical Measurement

The dependence between the photon energy and the optical absorption coefficient ( $\alpha$ ) for deposited films is expressed according to Tauc's law [46], by the relation 1:

$$(\alpha h\nu)^{1/n} = \beta(h\nu - E_g) \quad (1)$$

$\beta$  is a constant,  $E_g$  is the optical gap [eV], and  $h\nu$  is the photon energy,  $n$  is a factor that depends on the transition mode [47, 48]. According to Tauc's law, the variation in the absorption coefficient can be divided into three distinct regions:

- 1) A region of low absorption ( $\alpha < 1 \text{ cm}^{-1}$ ) in which absorption is due to defects and impurities present in the film.
- 2) A region in which the variation in absorption is due to states in the band tail, for  $1 \text{ cm}^{-1} < \alpha < 104 \text{ cm}^{-1}$ .
- 3) A region of high absorption ( $\alpha > 104 \text{ cm}^{-1}$ ). This region corresponds to the optical transitions between the valence band and the conduction band. These transitions are responsible for the absorption front at above  $\lambda = 303 \text{ nm}$  [49].

In the visible range, the spectra show good transparency for  $R_F < 0.5$ . On the other hand, for  $R_F > 0.5$ , the deposited layers show the lowest transmittance (Figure 7a).

Comparing these results with the AFM analysis, one can say, the higher the surface roughness, the lower the transmittance. We, therefore, observe that the transmission of the films decreases in the visible range if  $R_F$  increases.

For amorphous materials, the indirect transition is acceptable according to Tauc's law. Therefore, we take  $n = 2$  for our layers and we will have the relation 2:

$$(\alpha h\nu)^{1/2} = \beta(h\nu - E_g) \quad (2)$$

By extrapolating the linear part of  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  plot to the x-axis, the value of  $E_g$  can be obtained, as shown in Figure 7b.

The parameter that characterizes the material disorder is Urbach's tail energy.

According to Urbach's law, the expression of the absorption coefficient is given by the relation 3:

$$\alpha = \beta \exp(h\nu/E_u) \quad (3)$$

By plotting  $\ln(\alpha)$  against  $(h\nu)$  in Figure 7c, one can determine the value of  $E_u$  by the relation 4:

$$\ln \alpha = \ln \alpha_0 + h\nu/E_u \quad (4)$$

When the disorder becomes too pronounced (e.g., with the appearance of dangling bonds or

impurities in the material), the tails can become entangled. We will then define the notion of Urbach parameter ( $E_u$ ) which corresponds to transitions between the extended states of the valence band and the localized states of the conduction band.  $E_u$  being the width of the band tail which characterizes the disorder. Urbach energy  $E_u$  can also be interpreted as the band width of the states located in the band gap [50, 51].

The evolution of the optical gap  $E_g$  as a function of  $R_F$  is reported in Figure 7d. The values of  $E_g$  are in the range of 3.59 to 3.63 eV. These values show that our films have a wide gap and are transparent in the visible range. This result is promising with the aim of developing anti-reflection layers or transparent protective layers.

The variation in the optical gap  $E_g$  is negligible ( $3.63 - 3.59 = 0.04 \text{ eV}$ ) suggesting that the films are polymer-like carbon type (PLC), optimal for hemo-compatibility applications, with large optical gaps ( $> 2.6 \text{ eV}$ ) and low spin densities ( $10^{16} - 10^{17} \text{ cm}^{-3}$ ) [52]. It is clear that pore size has no effect on band gaps, as all films, regardless of pore size, have a band gap of about 3.6 eV. Different optical gap values (2-3.8 eV) [53, 54] and (3.2-4.3 eV) [55] have been registered by other authors.

These results suggested that the incorporation of nitrogen into the amorphous carbon enhances the optical band gap and this enhancement relies on the nature of C: N bond in the film. Moreover, it is consistent with previous works on  $\text{CN}_x$  films, in which the band gap was found to be significantly dependent on the  $I_D/I_G$  ratio as well as  $\text{sp}^2$  sites, as mentioned above [56, 57].

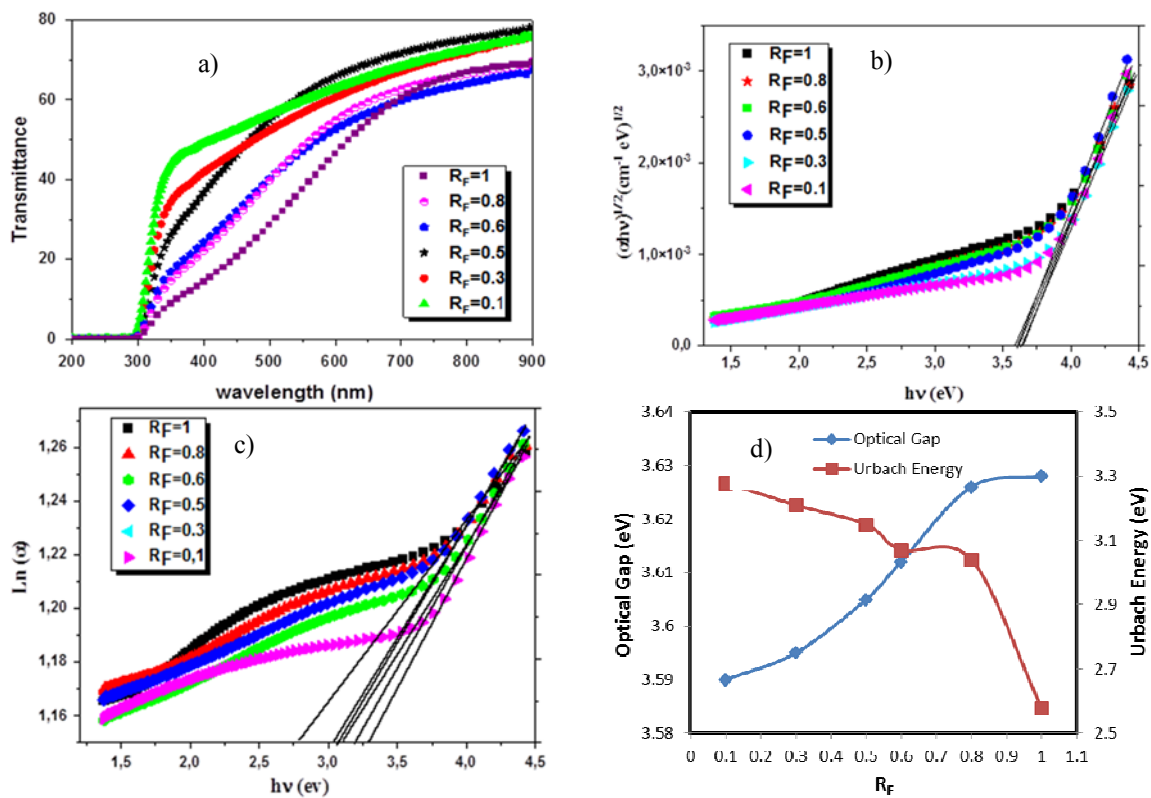
Let's remember that  $\text{sp}^3$  rich diamond has an optical gap equal to 5.5 eV and  $\text{sp}^2$  rich graphite has a zero optical gap, which allows us to predict that the deposited a- $\text{CN}_x$  films have a high hardness due to the presence of  $\text{sp}^3$  sites at the expense of  $\text{sp}^2$  sites [58, 59].

Fig. 7d also shows that as the nitrogen rate increases, less disorder in a- $\text{CN}_x$  thin films is observed. The decrease in  $\text{sp}^2$  sites and consequently the disorder has been studied and confirmed by infrared measurements as shown earlier in this study.

### 3.3. Electrical Measurement

The electrical properties were investigated by two-point probe method.



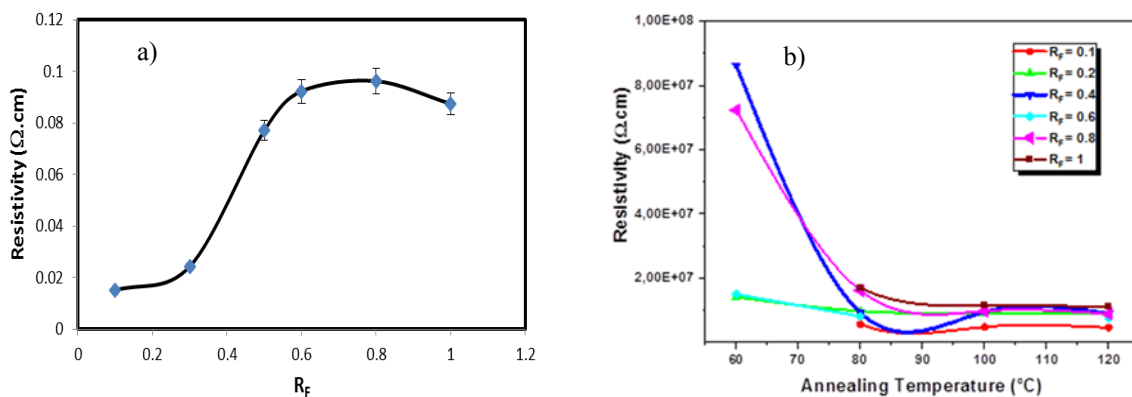


**Fig. 7.** a) Optical transmittance as a function of wavelength of a-CN<sub>x</sub> thin films for different values of R<sub>F</sub> b) Variation of  $(\alpha h\nu)^{1/2}$  with the photon energy ( $h\nu$ ) c) Variation of  $(\ln \alpha)$  with the photon energy ( $h\nu$ ) d) Variation of optical gap  $E_g$  and Urbach energy  $E_u$  as a function of different values of R<sub>F</sub>

The evolution of the resistivity of a-CN<sub>x</sub> thin films as a function of the ratio of the reactive gas flow rates R<sub>F</sub> is shown in Figure 8a. There is an increase in resistivity from 15 to  $87.4 \times 10^{-3} \Omega \cdot \text{cm}$  of a-CN<sub>x</sub> thin films for  $0.1 < R_F < 0.8$  and a less decrease for  $R_F > 0.8$ . This is because increasing the pore size reduces electrical interaction between particles. Note that the resistivity values are lower than those obtained in other studies, as shown in Table 3. The low resistivity of a-CN<sub>x</sub> films supports the development of electrical and

opto-electronic devices.

The film resistivity was measured under different temperatures ranging between 60 and 100°C. The obtained results show that the resistivity of a-CN<sub>x</sub> films is very sensitive to temperature. It decreases from  $9 \times 10^7$  to  $4 \times 10^6 \Omega \cdot \text{cm}$  when the temperature increases from 60 to 100°C then the resistivity still constant Figure 8b. The incorporation of nitrogen enhances carbon nitride films conductivity [60]. This gives the opportunity to their use in electrical devices.



**Fig. 8.** a) Resistivity of a-CN<sub>x</sub> thin films as a function of different values of R<sub>F</sub> b) Resistivity versus annealing temperature of a-CN<sub>x</sub> thin films deposited under different values of R<sub>F</sub>

**Table 3.** The obtained resistivity values compared to literature ones.

	Resistivity ( $\Omega \cdot \text{cm}$ ) at room temperature	Resistivity ( $\Omega \cdot \text{cm}$ ) from 60 to 120°C
This study	$15 \times 10^{-4}$ - $87.4 \times 10^{-3}$	$4 \times 10^6$ - $9 \times 10^7$
[35]	0.23-5.26	
[61]	$1 \times 10^7$ - $1 \times 10^{12}$	

#### 4. CONCLUSIONS

The objective of this work was to prepare and characterize amorphous carbon nitride (a-CN<sub>x</sub>) thin films. Films were deposited by reactive radio frequency sputtering of a graphite target under the atmosphere of argon and nitrogen at different concentrations at room temperature. The highest nitrogen content in films was estimated to 42 at. % which is very rare.

High-quality films with spin density in the order of  $10^{17} \text{ cm}^{-3}$  were achieved at ambient temperature, a very promising result that was reproducible and compatible with device quality. The spin density was similar, suggesting that the structures were alike.

The surface state study by AFM showed an increasingly rough surface with increasing nitrogen concentration. For  $R_F = 0.1$ , the surface was flat and then became rougher for  $R_F > 0.5$ .

Infrared spectroscopy measurement revealed that nitrogen atoms are embedded in the carbon bonding network with the presence of C-N, C=N and C≡N chemical bonds, as well as the D and G peaks, characteristic of the graphitic disorder in the layers and the graphitic vibrations of the C=C bonds. It was shown that the increase in the concentration of nitrogen, leads to a less disordered films.

The optical characterization showed good transparency in the visible range. The lowest value of the optical gap (3.59 eV) was obtained for  $R_F = 0.1$ , and the highest value (3.63 eV) for  $R_F = 1$ . These values show that deposited films have a wide band gap. The electrical conductivity was high compared to other studies. It was found that the increase in the pore size has minimal effect on band gaps. The increase in pore size, on the other hand, reduced the electrical resistivity.

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