

## Optical gap in carbon nitride films

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### Abstract

In this paper we study the effect of introducing nitrogen into different carbon networks. Two kinds of carbon nitride films were deposited: (a) Using a DC-magnetron sputtering system  $sp^2$  bonded carbon nitride (a-CN) films were deposited and (b) Using a combination of filtered cathodic vacuum arc and a low-pressure  $N_2$  plasma source, N was introduced into  $sp^3$  carbon networks (ta-C), leading to the formation of a more dense CN film named ta-CN. For ta-CN films we found that the optical gap initially decreases as the N content and the  $sp^2$  fraction rises, but above a certain N quantity there is a level-off of the value, and the gap then remains constant despite further increases in the fraction and clustering of the  $sp^2$  phase. However, for a-CN films the optical gap increases with the nitrogen content. These two different trends are not easily explained using the same framework as that for carbon films, in which any decrease in the band gap is associated to an increase in the  $sp^2$  fraction or its clustering. Here we discuss the conditions that lead to high optical gap in  $sp^2$ -bonded carbon nitride samples, which are clearly not associated to the presence of any crystalline super-hard phase. We also compared other differences in properties observed between the two films, such as deposition rate, infrared and Raman spectra.

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### 1. Introduction

The prediction of Liu and Cohen [1,2] of a crystalline  $C_3N_4$  phase with a bulk modulus, hardness and optical gap similar to diamond has led to considerable research on carbon nitrides. Despite these efforts, there has been no agreed success on the synthesis of crystalline  $C_3N_4$  [3,4]. Many of the experiments produced instead amorphous carbon nitrides (a-CN<sub>x</sub>), with nitrogen contents ranging from zero to 40–50 at.%, which are of interest in their own right. They show promising tribological properties [5] and indeed amorphous carbon nitride is presently used as a protective coating for many hard disks and read heads [6,7]. Similarly, there are interesting applications as gas sensors [8] and IR detectors [9].

It is therefore important to understand and identify the carbon–nitrogen bonding and the range of film properties that can be achieved as a function of the nitrogen content. Non-nitrogenated amorphous carbon films have been extensively studied and good correla-

tions between film properties such as, optical gap or hardness and the bonding properties such as  $sp^2/sp^3$  fraction and hydrogen content have been obtained [10,11]. There is also a good body of information about the effect of the deposition parameters on the film properties [10]. In the case of carbon nitride compounds most of the efforts have been concentrated on trying to obtain the crystalline super-hard phase and, despite the huge number of published papers, there is no clear correlation between the film properties and the structural or bonding characteristics. One of the parameters that has not been studied in detail is the optical gap. In carbon films, on the other hand, it is very well established that the gap is controlled by the  $\pi$  electron delocalization, not only in ordered rings, but also in the whole  $sp^2$  phase.

The optical gaps in the published works on carbon nitride films (having any  $sp^2$  fraction) ranges between 0 and 3 eV but the reasons for such a spread are not clear. For hydrogenated carbon nitride films (a-CNH) a small decrease of the optical gap is observed as the nitrogen content increases [12–15]. The decrease is greater when N is introduced into hard a-C:H films than

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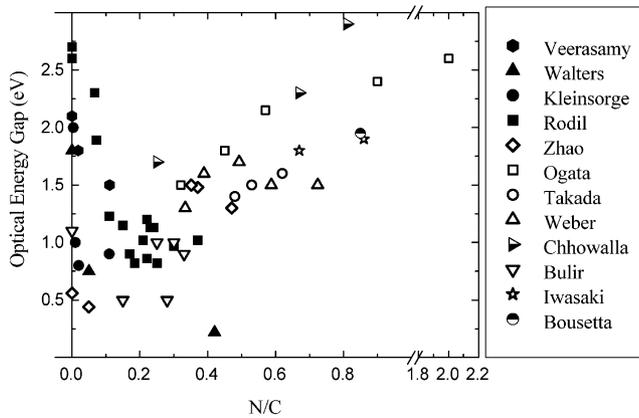


Fig. 1. Experimental variation of the optical gap (Tauc values) with nitrogen content of carbon nitride films.

in polymeric a-C:H films [12,13], with decreases in Tauc values between 2 and 1.2 eV, respectively. The decrease of the gap with nitrogen incorporation is related to the increase in the size of the  $sp^2$  clusters, because nitrogen acts as a bridging atom between clusters [16]. This has been confirmed by relating the decrease in the optical gap with the increase of the  $I(D)/I(G)$  ratio in the visible Raman spectra, since this is an indication of clustering of the  $sp^2$  phase [17–19]. However, as the nitrogen content is further increased most of the network becomes terminated by NH or  $CNsp^1$  bonds limiting the cluster size increase and in consequence the decrease in the optical gap [17]. A similar situation exists for highly polymeric a-C:N:H films, such as samples deposited in the anode [13] or at low ion energies [20], where wide band gaps are observed ( $>2$  eV). For the non-hydrogenated carbon nitride films (a-CN) the gaps have no direct correlation with the  $sp^2$  fraction [21] nor the N%; in some cases the optical energy gap decreases as the nitrogen content increases [22–26] and even semi-metallic [27,28] behavior has been observed, while in other reports the trend is exactly the opposite [29–35], as can be seen in Fig. 1, which is a collection of the gaps reported by different authors. Fig. 1 indicates that above a certain nitrogen concentration the optical gap again widens.

Another important reason to clarify the mechanisms determining the trends in the optical gap of CN films is that the gap increment observed in the right part of Fig. 1 is usually interpreted assuming that small  $C_3N_4$  crystallites have been obtained [36]. However, we show in this paper that there might be different explanations for the wide band-gap of CN films.

In this paper we compare the film properties and the growth of films with increasing gap (a-CN) with those of a decreasing gap (ta-CN) as a function of the nitrogen content. The aim of the paper is to look for plausible explanations for the different trends and therefore arrive

at some understanding of the mechanism controlling the optical gap in carbon nitride films.

## 2. Experimental

### 2.1. ta-CN samples

Nitrogen incorporation into highly tetrahedral carbon films (ta-C) was carried out using a double ion beam technique. The carbon ion source consists of a single bend filtered cathodic vacuum arc, FCVA. The average ion self-energy of the C ions is 25–30 eV, which is sufficiently high to produce ta-C films with 85%  $sp^3$  bonding so no substrate bias was used. The nitrogen ion beam is produced by a high-density plasma source called electron cyclotron wave resonance source (ECWR) [37]. The ECWR source operates at low pressure and provides a nitrogen ion beam with a high degree of dissociation, in which the  $N^+/N_2^+$  ratio depends on the operation parameters [20]. The energy of the ions was varied between 60 and 100 eV, sufficient to cause subplantation, but not too high to result in chemical sputtering which has been proven to be a cause of reduced N incorporation [37]. The ta-CN<sub>x</sub> films with different N concentrations were deposited by changing the relative position of the substrate holder with respect to the sources and therefore the C to N ion flux impinging on the substrate. The chamber pressure was maintained below  $5 \times 10^{-2}$  Pa to avoid loss of ionisation of the C ion flux.

### 2.2. a-CN Samples

In contrast to the previous deposition system, the sputtering system operates at relative higher pressures ( $\sim$ Pa), producing graphitic-like a-C films. Carbon nitride films were produced in a DC magnetron sputtering system (DC-MS) attached to a high vacuum chamber (base pressure  $1 \times 10^{-4}$  Pa). Prior to sputtering, the substrates were cleaned using an Argon plasma for 10 min, with a shutter to prevent deposition. After the cleaning the Ar was substituted by 20 sccm total flow of Ar/N<sub>2</sub> gas, the gas pressure was 8 Pa and the current 0.2 A. Films with different nitrogen concentrations were deposited by setting the percentage of nitrogen gas in the mixture to 0, 25, 50, 75 and 100%.

### 2.3. Film characterization

The N–C composition ratio and the C- $sp^3$  content, were determined by electron energy loss spectroscopy (EELS) as described elsewhere [21].

The optical gap was obtained for films deposited on Corning glass by transmission and reflection measurements using an ATI-Unicam UV2-200 spectrometer in the range 300–1100 nm. For the case of homogeneous

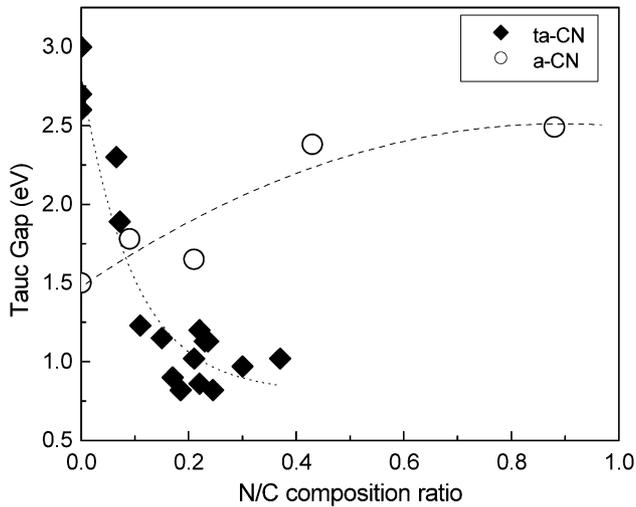


Fig. 2. Tauc optical gap of ta-CN and a-CN films as a function of the N/C composition ratio. The line is a guide for the eyes.

materials and smooth surfaces, in which scattering losses are negligible, traditional expressions for  $n$  and  $k$  for a thin film on a thick non-absorbing substrate can be obtained using the Fresnel transmission and reflection coefficients for normal incidence. The absorption coefficient  $\alpha$  is then obtained by the dispersion relation of the extinction coefficient ( $k$ ), as  $\alpha = \frac{4\pi k}{\lambda}$ , where  $\lambda$  is the wavelength. The Tauc gap is then estimated according to the Tauc's relation [38].

$$E\alpha(E) = A(E - E_{\text{Tauc}}) \quad (1)$$

Where  $E$  is the energy of the incident light and  $E_{\text{Tauc}}$  is the estimate of the optical band gap and  $A$  is a constant. Therefore,  $E_{\text{Tauc}}$  can be found by plotting the variation of  $\sqrt{\alpha E}$  against  $E$  and then performing a linear extrapolation to the  $x$ -axis.

The IR spectra were measured with a Nicolet205 Fourier transform infrared spectrometer.

Unpolarized Raman spectra were recorded at back-scattering geometry using two Renishaw spectrometers adapted to work at with excitation wavelengths of 514.5 and 244 nm, respectively.

### 3. Results

Fig. 2 shows the Tauc gap of both ta-CN and a-CN samples as a function of the N/C composition ratio. For the ta-CN samples the optical gap falls sharply from more than 2.5 eV to approximately 1 eV (N/C approx. 0.15) and then remains almost constant for further nitrogen incorporation. Whereas the optical gap of the a-CN film increases gradually from 1.5 to 2.4 eV as the N/C ratio increases close to 1.

Fig. 3 shows that there is also a strong difference in the film growth for the two types of films. It can be seen that the deposition rates as a function of the N/C composition ratio are very different. The inset in Fig. 3 is included to show that the increased deposition rate is a common result in the DC-MS system used. A similar trend was obtained independently of the power applied

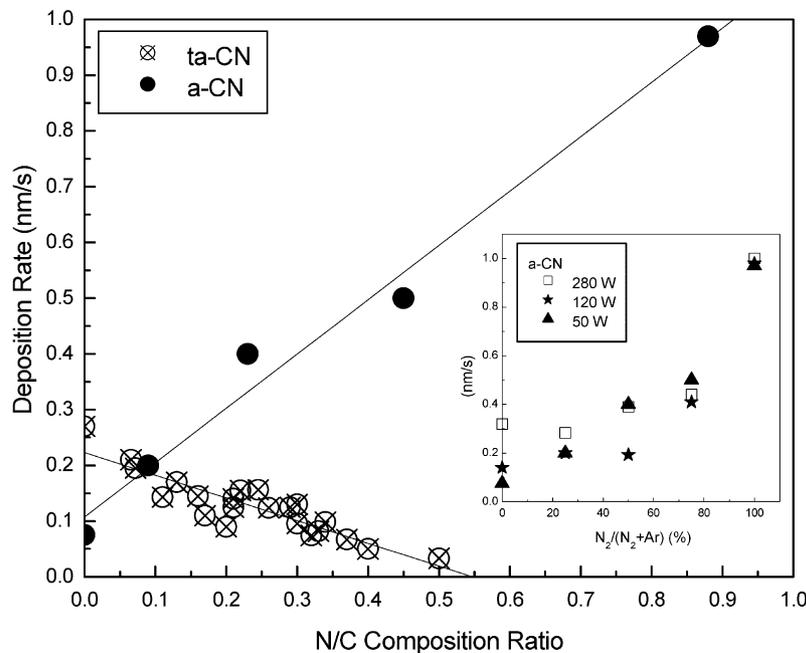


Fig. 3. Difference in the deposition rate within the arc-deposited ta-CN and sputtering a-CN films as the nitrogen content increases. The inset shows that the increasing deposition rate of the a-CN films is valid for different power.

to the cathode, while most other systems show a lower deposition rate as the nitrogen fraction in the gas phase increases. This variation is probably related to our sputtering system/target geometry.

Fig. 4a,b presents the Raman spectra of both ta-CN and a-CN films, respectively. The main difference is the strong photoluminescence background obtained for the a-CN films. The Raman spectra of the carbon nitride films were analyzed in a similar manner as that used for carbon films [17]. The G mode is due to the stretching vibration of any pair of  $sp^2$  atoms in both chains and rings, whereas the D mode is related to the breathing vibration of  $sp^2$  sites only in rings [39]. Thus, an increase in  $I(D)/I(G)$  is ascribed to an increase in the number and/or in the size of  $sp^2$  clusters. The Raman spectra were simulated using a Breit–Wigner–Fano (BWF) line shape for the G peak and a Lorentzian for the D peak [39]. From that, the intensity ratio of the D and G peaks heights,  $I(D)/I(G)$ , were determined. This is an important parameter since it has been shown that there is a correlation with the optical gap in a-C films according to the equation [10,39,40]

$$I(D)/I(G) \approx \frac{1}{(gap)^2} \quad (2)$$

The fitting results for the ta-CN films can be seen in Fig. 5, a similar trend was obtained for 514.5 and 244 nm excitation wavelengths. The data show that the introduction of nitrogen directly induces clustering of the  $sp^2$  phase. The fact that equation 2 is not obeyed by films with N/C ratios higher than 0.15 is a clear indication that the mechanism controlling the gap in CN

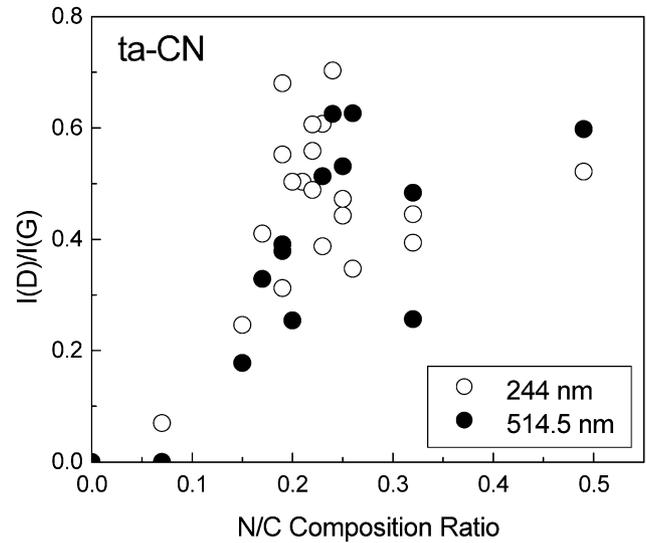


Fig. 5. Fitting results of the  $I(D)/I(G)$  ratio of the ta-CN films measured at two different laser wavelengths.

films is different than for a-C films. A similar plot was not obtained for the a-CN films due to the difficulty in simulating the PL background.

The infra-red (IR) spectra of ta-CN and a-CN films are shown in Fig. 6a,b, respectively. The IR spectra of CN show four main absorption bands. A weak sharp band is observed approximately  $2200\text{ cm}^{-1}$  due to CN  $sp^1$  bonds. Secondly, a broad band between  $1000$  and  $2000\text{ cm}^{-1}$ . It is usually stated that the effect of nitrogen into carbon films is to break the symmetry of the  $sp^2$  carbon bonds making the Raman ‘G’ (graphitic) and ‘D’ (disorder) modes IR active, so the broad band

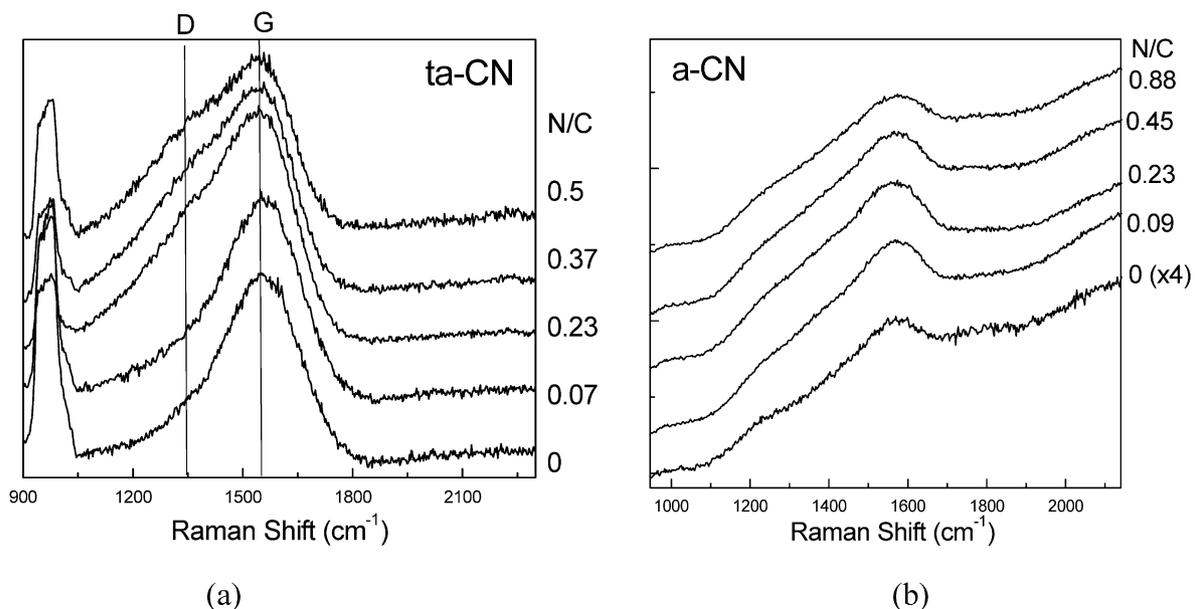


Fig. 4. Raman spectra for (a) ta-CN films and (b) a-CN films with different N/C composition ratios.

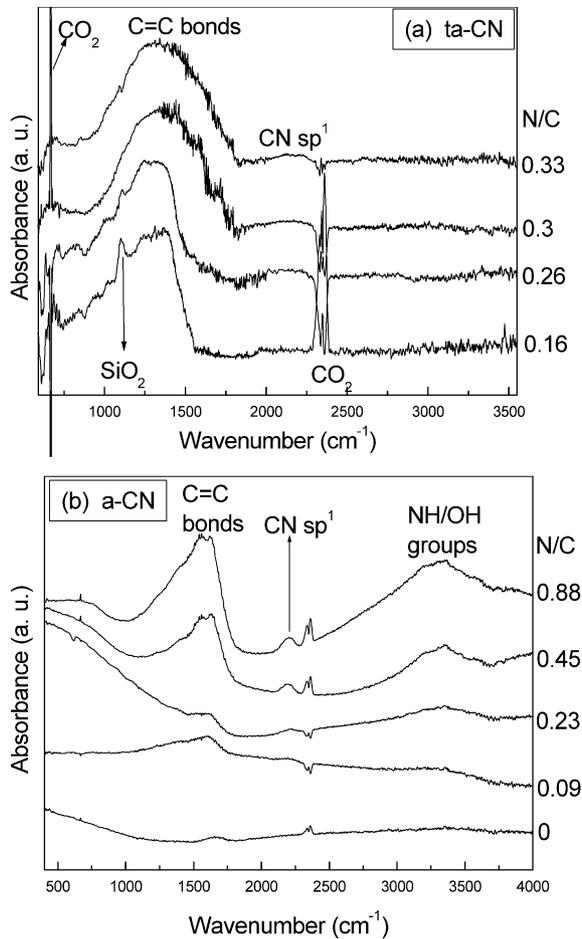


Fig. 6. Infrared spectra for (a) ta-CN and (b) a-CN films with different nitrogen contents. The main bands and its interpretation is shown in the graph.

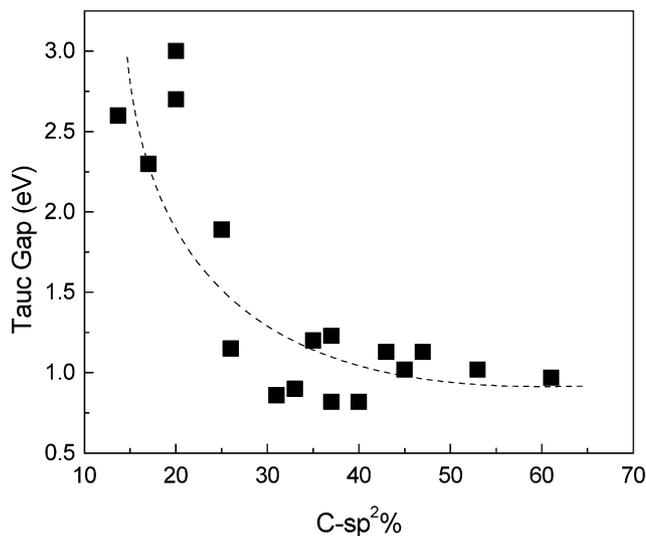


Fig. 7. Relationship between Tauc optical gap and the C-sp<sup>2</sup> fraction for the ta-CN films. The line is a guide only. Note that for C-sp<sup>2</sup> fractions above 20%, the gap becomes almost independent of the sp<sup>2</sup> fraction.

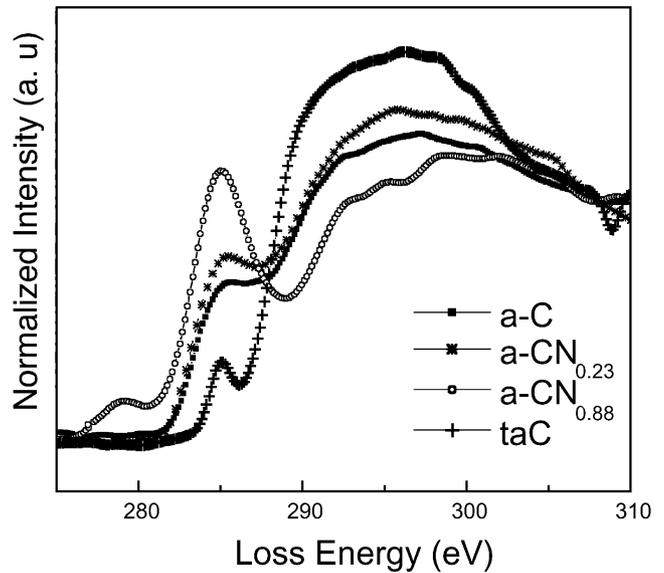


Fig. 8. High-loss-electron-energy-spectra, showing the broad  $\pi$  bands obtained for the sputtered a-CN samples in comparison with a non-nitrogenated ta-C film. The intensity ratio between the  $\pi$  and  $\sigma$  bands in the spectra indicates a high sp<sup>2</sup> fraction for the a-CN samples.

between 1000–2000  $\text{cm}^{-1}$  is similar in both IR and Raman spectra [41]. However, we have previously [42] shown that nitrogen is not necessary to have significant IR activity in the 1000–2000  $\text{cm}^{-1}$  region and that this band is due to the presence of a system of conjugated C=N/C=C bonds and the subsequent delocalization, even in small domains, of the  $\pi$  electrons. Finally, carbon–hydrogen functional groups ( $\text{CH}_x$ ) appear approximately 2800–3100  $\text{cm}^{-1}$  and NH/OH groups give rise to stretching vibrations at 3000 and 3400  $\text{cm}^{-1}$  like in hydrogenated CN samples.

The presence of the band due to NH/OH vibrations for the a-CN samples deserves special attention. Since hydrogen was not intentionally introduced during the deposition, this band is a consequence of water absorption from the environment [43]. Water is mainly incorporated through the formation of hydrogen bonds either between H and N (N–H...O) or between H and O (O–H...N) producing a broad IR signal, which can extend from 2000  $\text{cm}^{-1}$  to 3600  $\text{cm}^{-1}$ . Obviously, poor vacuum conditions during deposition can also lead to moisture contamination and then clear NH or OH bands are observed. However, in this case we placed special attention to have a good vacuum before starting deposition. A high porosity is a requisite for the formation of hydrogen bonding, since it is a long directional bond that needs sufficient space to be accommodated [44]. Therefore the presence of this band in the IR spectra of the a-CN films suggests the formation of a porous film.

Finally, Fig. 7 shows that the Tauc's gap in ta-CN films is independent of the C-sp<sup>2</sup> fraction for values above 20%. The equivalent plot for the sputtered CN

films could not be obtained due to the broad  $\pi$  bands in the EELS spectra, as shown in Fig. 8, which makes the  $sp^2$  calculation inaccurate. Nevertheless, the  $sp^2$  fraction estimated for the high nitrogenated samples exceeds 100%, which is an indicative of the different  $\pi$ -bonding configurations, such as C=C, C=N and CN  $sp^1$ .

#### 4. Discussion

Because the bonding in a-CN films consists of non-interacting  $\pi$  and  $\sigma$  bonds in a similar way as in a-C films, the electronic and optical properties should also be controlled by the  $\pi$  bonding that lies closest to the Fermi Level. Therefore, similar trends in the optical gap, as the observed for a-C, as a function of the  $sp^2$  fraction and ordering are expected for a-CN. However, Fig. 7 and Fig. 5 clearly show that above a certain nitrogen concentration, the optical gap of CN films becomes independent of both the  $sp^2$  fraction and the  $I(D)/I(G)$  ratio, i.e. the clustering of the  $sp^2$  phase.

The reason for the level-off of the optical gap in these ta-CN<sub>x</sub> films or the increasing gap for the a-CN samples is not easy to explain in terms of the properties of amorphous carbon films. The results suggest a different mechanism in CN compounds that counteracts the effect of the increasing  $sp^2$  bonding.

There are at least two possible mechanisms that we can propose.

1. Localization of the  $\pi$  electrons due to the heteropolar bonding.
2. The high porosity of the CN samples.

Firstly, the localization of the  $\pi$  electrons in highly  $sp^2$ -bonded system has been observed for paracyanogen-like films [45,46] and for aromatic heterocycles [47]. There are two polymers made of cyanogen, (CN)<sub>2</sub>, one is polycyanogen, which is a polymer with a backbone of  $-C=N-$  units and a pendant nitrile on the carbon. The other is paracyanogen, discovered by Gay-Lussac in 1816 whose properties are well known, but not its precise structure. Cuomo [44] and Maya [45], independently, showed that paracyanogen-like films having a 1:1 stoichiometry can be produced by sputtering methods. The films are insulating, even though IR and nuclear magnetic resonance indicate the presence of  $sp^2$  carbon in the form of C=N- moieties and a few nitriles. Thus, Maya [45] suggested that the structure of paracyanogen was mainly made of  $sp^2$  carbon in a disordered structure incorporating nitrogen but without an extended delocalized  $\pi$  electron system. However, the  $sp^2$  phase can form isolated domains of conjugation.

The second mechanism proposed is that the film porosity might be affecting the optical gap in a similar fashion than for porous silicon films [48] or porous III-V materials [49]. However, this is a subject that needs

more research from both the theoretical and experimental point of view. Theory is necessary to see if the mechanisms affecting the gap in crystalline-porous materials may or may not be applicable to these amorphous materials. Experimentally, it is necessary to measure the porosity of the a-CN films to correlate it with the measured optical gap.

#### 5. Conclusions

Vibrational and bonding properties of ta-CN and a-CN films with different nitrogen contents were analyzed and correlated to the optical gap of such films. We observed that nitrogen in highly  $sp^3$ -bonded carbon films increases the  $sp^2$  fraction by forming C=N bonds and also induces clustering of the  $sp^2$  phase. The optical gap decreases sharply at low N% and then remains constant, independent of the  $sp^2$  fraction and the degree of clustering. For highly  $sp^2$ -bonded carbon nitride films (paracyanogen-like) the optical gap increases with the N/C composition ratio. Therefore, we conclude that the variation of the optical gap of highly nitrogenated carbon nitride films cannot be explained in the same context as for a-C films.

We have presented two possible explanations for the observed results:

1. As the nitrogen content increases there is a localization of the  $\pi$  electrons due to the partially ionic character of the CN bonding, and as such the effect of increasing the  $sp^2$  fraction in the optical gap is not the same than for the case of a-C films.
2. Higher nitrogen content increases the film porosity, with this effect observed in the IR spectra as a strong water absorption signal. This is possibly responsible for the strong luminescence of the films. Furthermore, there might be a porosity-induced modification of the absorption spectra in a similar manner to that observed for porous silicon.

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