

Infrared spectra of amorphous carbon based materials

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Abstract

The IR absorption in amorphous carbon and carbon nitride films is discussed in terms of a phenomenological model based on similar absorptions occurring in doped polyconjugated polymers. It is proposed that the strong IR absorption band observed in the $1800\text{--}900\text{ cm}^{-1}$ region arises from changes in the electronic structure in the micro-domains of the sp^2 clusters due to long and short range charge fluxes. These charge fluxes are enhanced by the increase in the Csp^2 fraction and/or the increase in the nitrogen content (with the subsequent formation of sp^2 and sp^1 sites) since both induce clustering of the sp^2 phase and delocalization of π electrons.

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In previous papers [1,2] we have discussed the infrared and Raman spectra of carbon nitride films produced under different deposition systems. Concerning the infrared spectra, four IR absorption spectra were presented that are characteristics of the spectra usually found in the literature (see Fig. 1). They present three main bands in the absorption spectra: band I corresponding to hydrogen related vibrations above 3000 cm^{-1} (NH, OH and CH), band II corresponding to cyanide groups or double conjugated NCN bonds and band III between 900 and 1800 cm^{-1} whose assignment is still controversial, and that will be called “the π -band” in the rest of this paper for reasons that will be clear later. In those papers [1,2], a series of arguments were presented to explain why the previous interpretations of the π -band are not reliable and a new model was proposed to explain the IR absorption in amorphous carbon-based films, including nitrogenated and non-nitrogenated a-C films. However, it seems that some key points were not clearly explained and further discussion is needed.

Firstly, the π -band cannot be interpreted simply as a convolution of molecular-like [3] C–N single bond ($1100\text{--}1300\text{ cm}^{-1}$) and CfN double bonds ($1500\text{--}1600\text{ cm}^{-1}$)

absorption bands for two main reasons. One is that two independent studies [4,5] have showed that under nitrogen isotopic substitution there was no shift of any part of the π -band. Although isotopic substitution studies are difficult to perform and the interpretation when broad convoluted bands are obtained is not always precise. The other reason is that in the $900\text{--}1800\text{ cm}^{-1}$ region of the spectra, the list of possible overlapping peaks which can form such a band is large, to mention some of these: carbon aromatic rings and double bond vibrations, CfO moieties, carboxyl-carbonates structures, bands due to nitrogen containing species, such as, pyridine-like or cyclic amides, tertiary nitrogen species, cyclic compound containing conjugated Cfc and CfN bonds, C–N-vibrations in heterocycles structures, C–H vibrations and the deformation vibrations of surface hydroxyl groups [6,7].

Secondly, there is no need to dope amorphous carbon with nitrogen in order to have an IR absorption band at the same wave-number region, as has been usually assumed. Pure carbon films show a non-negligible IR absorption band in the same region as the π -band [8,9].

Finally, the D- and G-like assignment of the π -band made by Kaufman et al. [4] based on the similar shape observed for Raman and IR spectra of some carbon nitride films is not a strong enough argument to assume that the vibrational modes detected with both systems are the same. Indeed, the Raman

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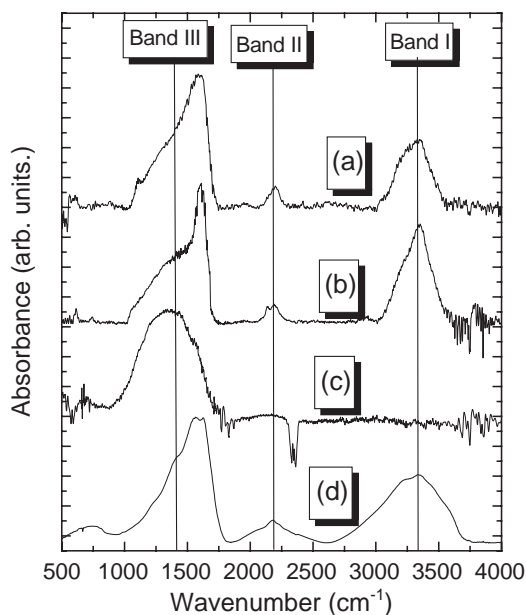


Fig. 1. Infrared spectra of different carbon nitride samples. (a) Hydrogenated carbon nitride film produce by electron cyclotron wave resonance plasma (ECWR) using C_2H_2 and N_2 . (b) Hydrogenated carbon nitride film produce by ECWR using CH_4 and N_2 . (c) Carbon nitride (taCN) sample produce by a combination of filtered cathodic vacuum arc (FCVA) and the ECWR as a nitrogen beam. (d) Sputtered carbon nitride sample.

shape depends on the excitation energy [10] and the IR and Raman spectra are not alike for all carbon nitride films [1,2], as assumed in Kaufman et al.'s paper.

It is however true that in disordered systems the lack of selection rules allows both IR and Raman spectroscopy to sense the complete vibrational density of states and therefore the spectra could look similar [11]. Infrared spectroscopy is associated with an absorption process. The absorption depends on the formation of an electric dipole by the vibrations. Raman spectra, on the other hand, are associated with a scattering process and are produced by the modulation of the electrical polarizability by vibrations. In a crystalline solid, the electromagnetic radiation practically couples to wavenumbers $k=0$. The basic difference between the IR and Raman spectra are associated with the difference of the symmetry which is described by a vector (dipole moment) for the absorption process and by a symmetrical tensor (Raman tensor) for the scattering. The selection rules are different and therefore, so are the spectra. However, in amorphous solids, the k vector is no longer a good quantum number. The crystalline selection rules are relaxed and from this point of view a similarity might be expected between the IR and Raman spectra. However, the intensity is modulated by different matrix elements and thus the spectra do not necessarily look alike. Indeed, in the case of tetrahedral amorphous carbon films, the IR absorption in the $400\text{--}4000\text{ cm}^{-1}$ region is negligible, while for more sp^2 bonded a-C films there is a strong absorption band centered around 1300 cm^{-1} , although the Raman active bands (D and G) are clearly seen for both type of films.

Hence, the questions that any model proposed to explain the IR spectra of the carbon nitride films must answer are:

- (1) Is there any relation between the IR active band of the sp^2 bonded amorphous carbon films and the π -band in a-CN?
- (2) Which are the IR active modes involved and which factors affect the IR absorption making the π -band more or less intense?

In the model that we propose [1,2], the answer to the first question is yes; there is a strong correlation among both bands and indeed the origin of the IR activity is the same in both systems. The answer to the second question is a little more complex, but basically the π electron density and their delocalization or mobility are the main factors that influence the IR intensity in the $900\text{--}1800\text{ cm}^{-1}$ region.

In the next part of the paper these suggestions will be explained in more detail, but before that there is another important point to the understanding of the origin and shape of the π -band that must be discussed. This is the effect of water adsorption on the IR spectra of a-CN films. One feature observed in a-CN films, and rarely in a-C, is the ability of the material to adsorb water from the environment. This chemisorbed water is clearly detected in the IR spectra in the high wavenumber region (3400 cm^{-1}) due to the stretching mode of hydroxyl groups (ν_{OH}), even for a-CN samples deposited under high vacuum conditions and without hydrogen [12,13]. The asymmetry of this band to lower wave numbers indicates the presence of strong hydrogen bonds [14], which is the most probable mechanism of water adsorption in a-CN films. Hydrogen bonding shifts the stretching vibrations to lower wavenumbers and broadens the IR bands, explaining the broad band observed in Fig. 1(d) that extends from 2000 cm^{-1} to 3600 cm^{-1} . A low density is a requisite for the formation of hydrogen bonding, since it is a long directional bond that needs sufficient space to be accommodated. Thus, the water adsorption is dependent on sample porosity and this will most probably influence the optical absorption (α) and in consequence the estimated optical gap [15], among other film properties. However, more specific studies are necessary to understand the extent of such effects. We consider that water adsorption also influences the IR absorption near 1600 cm^{-1} inducing the asymmetric shape of the π -band (as seen in Fig. 1(a), (b) and (d)) due to the effects of the bending mode (δ_{OH}) of water at 1630 cm^{-1} . In a previous paper [2] we showed that the asymmetric shape is not due to CH or NH bending modes by depositing isotopic substituted deuterated a-CDN samples and showing that the 1600 cm^{-1} peak was unaffected. Moreover, experimental observation of water adsorption on ultradispersed diamond (UDD) powders support the idea that adsorbed water induces both bending and stretching vibrational modes [16]. Infrared spectroscopy was used to study the adsorption and adsorption rates of water on the surface of UDD powders,

showing that after exposure to air the intensity of both ν_{OH} and δ_{OH} groups grows rapidly as a function of time. They found [16] that even at relatively low humidity (25–35% RH) the saturation point of adsorbed water was reached in a maximum of 150 min. Therefore, for the CN films that may adsorb water the only way to avoid the presence of hydroxyl groups in the IR spectra is to performed the IR in-situ in the deposition chamber, which is not the usual case. Most IR spectra for a-CN films in published papers were measured ex-situ after exposure to air for long periods. Thus, the vibrational modes of the adsorbed water may masked some of the fundamental vibrational modes of the a-CN film, probably leading to incorrect assignments. Now, as mentioned before water adsorption has not been documented for a-C films under normal deposition conditions (although porous carbon films might also adsorb water), but it is commonly seen in a-CN films. Thus, nitrogen doping somehow induces water adsorption, either because the interaction between nitrogen lone-pairs and hydroxyl groups is stronger or because nitrogen induces a higher porosity in the films with a subsequent increase in the surface area, or both. Analysis of ^{15}N and ^{13}C cross-polarization magic angle spinning and ^1H Nuclear Magnetic Resonance experiments on a-CN films confirms the presence of physisorbed water and suggest that water preferentially protonates nitrogen sites [17]. Furthermore, after many years studying a-CN films it has been shown that the saturation in the nitrogen content of a-CN films is due to the formation of N_2 molecules [18–20] which are more easily formed as the nitrogen content increases above a certain value. In carbon nitride films having a large number of terminating bonds such as NH or CNsp^1 the film density decreases showing an open interconnected void microstructure that allows the N_2 molecules to migrate more easily out of the films [19]. Whereas, for denser microstructures the N_2 remains trapped, decreasing the overall film density but not increasing the film porosity. This explains, why in Fig. 1(a), (b) and (d) we see a strong OH stretching absorption band, while in the more dense ta-CN film (Fig. 1(c)) no OH band is observed. Therefore, one initial point in the proposed model to explain the IR spectra of CN films is that the broad band in the fingerprint region has two components: one due to bending modes of water adsorption at higher wavenumbers ($>1600\text{ cm}^{-1}$) and the low-wavenumber component, the real π -band ($900\text{--}1600\text{ cm}^{-1}$) whose origin will be discussed in the next section.

Fig. 2 shows four different samples and the deconvolution of the broad band into two or three Gaussians, whose positions are shown in Table 1. In order to get a good fit it is necessary to introduce two Gaussians for the low-wavenumber component (π -band), however they will be treated as one broad vibrational mode, whose frequency is affected by the environment. It is important to notice that we are including a-C in Fig. 2 and that, after deconvolution of the OH bending mode, Gaussians 1 and 2 (shown in Table 1) are very similar for a-C and the nitrogenated samples. The

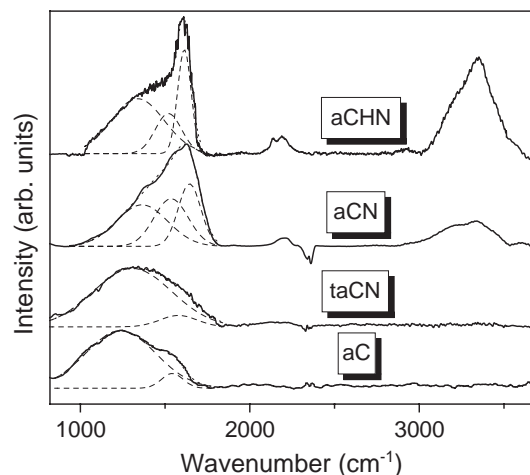


Fig. 2. Deconvolution of the band III using Gaussians for a-CHN, sputtered-aCN, ta-CN and a sputtered a-C sample.

differences in the positions and widths will be explained later.

Now that have identified that for many CN films water adsorption affects the IR spectra in both low and high wavenumbers, we can proceed to search for the origin of the π -band.

It is well known that amorphous carbon can be regarded as an heterogeneous material having sp^2 clusters embedded in a sp^3 matrix [21]. The sp^3 matrix controls the elastic constants of the films and the sp^2 sites define the electronic, optical and mechanical properties, depending on the sp^2 fraction, orientation and clustering [22]. Similarly, a-CN films show this heterogeneous microstructure with a higher degree of complexity due to the wider variety of bonding configurations [23]. The presence of sp^2 clusters is clearly evidenced by Raman spectroscopy through the increase of the relative D band intensity [24]. The characteristic of the sp^2 clusters is that they contain π states that interact between them forming large conjugated systems such as complex aromatic rings or long conjugated chains [21]. These conjugated systems have interesting vibrational properties that cannot be neglected. For the chemists it is known that some vibrational modes of molecules with conjugated π electron systems induce large infrared absorption, whose intensity can only be explained consistently in terms of long and short charge fluxes induced by a strong electron-phonon coupling [25]. Examples of these molecules include polyene chains, conjugated schiff bases, peptides and polycyclic aromatic hydrocarbons (radical cations of benzene, pentadienyl, heptacene, pentacene, naphthalene, perylene, biphenyl, pyrene, phenabtherene, etc.) [26–28]. In all these cases very intense infrared active vibration (IRAV) bands appear in the fingerprint region ($950\text{--}1700\text{ cm}^{-1}$, corresponding to the C–C stretches and the C–H in-plane bend modes) which are stronger for the charged or radical cations than for the neutral species. The intensity of these bands cannot be explained by static polarization of the relevant bonds, and hence some intricate interplay between

Table 1
Peak position of the Gaussian deconvolution shown in Fig. 2

Film	π -band		δ_{OH}
	Gaussian 1	Gaussian 2	Gaussian 3
a-CHN	1339	1520	1614
a-CN	1364	1536	1644
ta-CN	1307	1579	–
a-C	1238	1543	–

the vibrational and electronic motion is necessary for the generation of strong IR absorption. In the case of charged linear polyenes it has been shown that the strong IR bands are induced by the vibrations along the bond-alternation coordinate, in which adjacent $CfC/C-C$ or $CfN/C-C$ bonds in a conjugated chain stretch and contract alternately. In other words, infrared and Raman spectra of polyconjugated chain compounds show peculiar and characteristic features directly related to the efficiency of the π -electrons to delocalize along the quasi one-dimensional path of alternating double/single bonds and also with the different types of charged defects created upon chemical doping or photoexcitation [29]. In this case it was also demonstrated that the frequency of the IR band shifts to low wavenumber and the intensity increases as the conjugated chain becomes larger. On the other hand, for the polycyclic aromatic hydrocarbons the mechanism of charge fluxes is more complex, since electron–phonon interactions occurs at both long and short range. In order to determine the vibrational pattern and the associated IR absorption, it is necessary to calculate the details of the electronic structure of the particular polycyclic molecule or cluster [28].

The model that we proposed to explain the origin of the π -band is based on the presence of the sp^2 clusters found in a-C and a-CN films, which can be seen as conjugated systems. In these conjugated systems, either forming conjugated chains or aromatic rings, the electron–vibration interaction is responsible for the enhancement of the IR absorption in the fingerprint region. Due to the variety and distortion of the systems and, of course, to the effects of mutual interactions within the condensed matter, the IR spectra shows a broad band with strong IR intensity in the whole fingerprint region; the π -band. Thus, the π -band in a-C and a-CN films is a convolution of infrared active vibration bands of the conjugated systems formed by the clustering of sp^2 sites. Similarly, as with Raman the D peak is due to the breathing mode of different-size clusters and so the width of the peak is representative of the disorder in the sample. In the IR, the π -band is the result of the IRAV bands of different-size conjugated systems.

These IRAV bands depend on the efficiency of the π -electrons to delocalize and also on the different types of charged defects created upon chemical doping. Indeed, the electron–phonon coupling is stronger for doped or charged conjugated systems. Doping of the sp^2 clusters is provided when nitrogen is introduced, due to the extra charge of nitrogen atoms, and this explains the higher intensity of the

π -band in carbon nitride samples. Among the different bonding configurations of nitrogen in a carbon network there are two sp^2 doping sites: (1) nitrogen can substitute for carbon in a benzene ring forming a doped pyridine-like molecule and (2) with nitrogen forming a linear double bond unit and two σ bonds, with the fifth electron in an antibonding π^* state [30]. Nitrogen incorporation has additionally the effect of increasing the overall sp^2 fraction and clustering of the sp^2 sites, as demonstrated in many published work [31,32,23].

In previous papers, [1,2] we expressed the electron–phonon coupling through the well known equation

$$e^* = \sum_e \mu^{ge} \frac{\left\langle e \left| \frac{\partial H}{\partial Q_i} \right| g \right\rangle}{E_e - E_g}. \quad (1)$$

In which e^* is the IR effective charge, $\partial H/\partial Q_i$ is the electron phonon coupling term between the ground (g) and excited (e) states, Q_i is a normal mode, μ is the dipole moment and $E_e - E_g$ is the energy gap. The IR intensity is proportional to the square of the effective charge. Thus from Eq. (1) it follows that the IR intensity is in general higher for π -bonded systems than for σ -bonded systems since the π states have a smaller energy gap $E_e - E_g$ than the σ bonds and $\mu^{\pi\pi^*}$ increases with delocalization [25]. However, it is important to note that the energy gap in Eq. (1) refers to the energy gap of the conjugated system, which is not exactly the measured optical gap of the films [22].

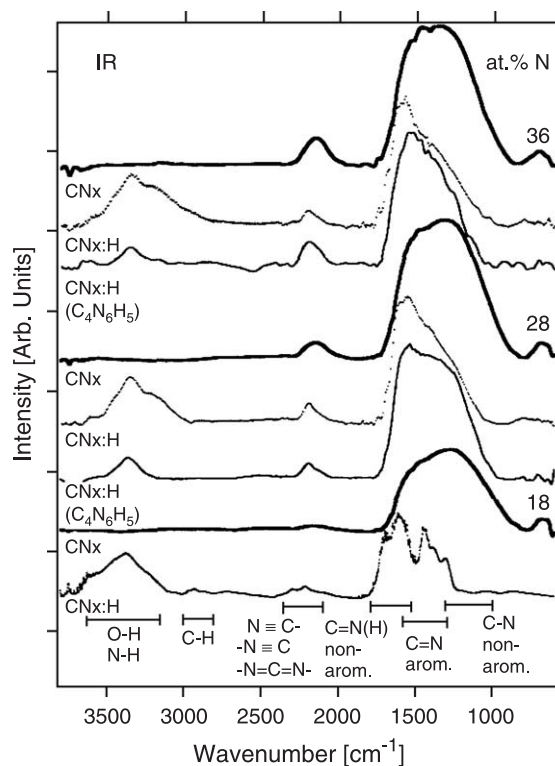


Fig. 3. Evolution of the IR spectra with increasing nitrogen content for a-CN and a-CNH films. Taken from [33].

As mentioned in the abstract this is a phenomenological model that explains qualitatively the origin of the π -band in both a-C and a-CN films and its relation with the sp^2 fraction, clustering, and π -electrons delocalization. However, theoretical calculations that support this model are required.

In the next section of the paper, some examples taken from the literature will be presented to give empirical support to the proposed model.

OH Adsorption

Fig. 3 was taken from Hammer et al. [33] paper. In this paper they prepared three different series of samples with various levels of N content: (a) Hydrogen-free a-CN by sputtering a graphite target with a N^+ beam, (b) Hydro-

genated a-CNH samples by introducing H_2 into the deposition chamber and (c) hydrogenated a-CNH samples by sputtering an azaadenine ($C_4N_6H_4$) target with Ar or N beam. The IR spectra from samples with the different nitrogen contents are shown and this clearly indicates that the π -band is asymmetric only for the samples having a strong OH stretching band. In their case the non-hydrogenated a-CN samples (a) are not porous because the sputtering is made by the aid of a nitrogen beam source that enhances ion bombardment during film growth, and no OH peaks are observed. However, for the hydrogenated samples, the formation of terminating CH, NH and $CNsp^1$ groups interrupts the network connectivity and favors the creation of voids allowing the subsequent OH adsorption.

In a more recent paper, Al Khawwam et al. [34] showed a good correlation between the sample porosity and the

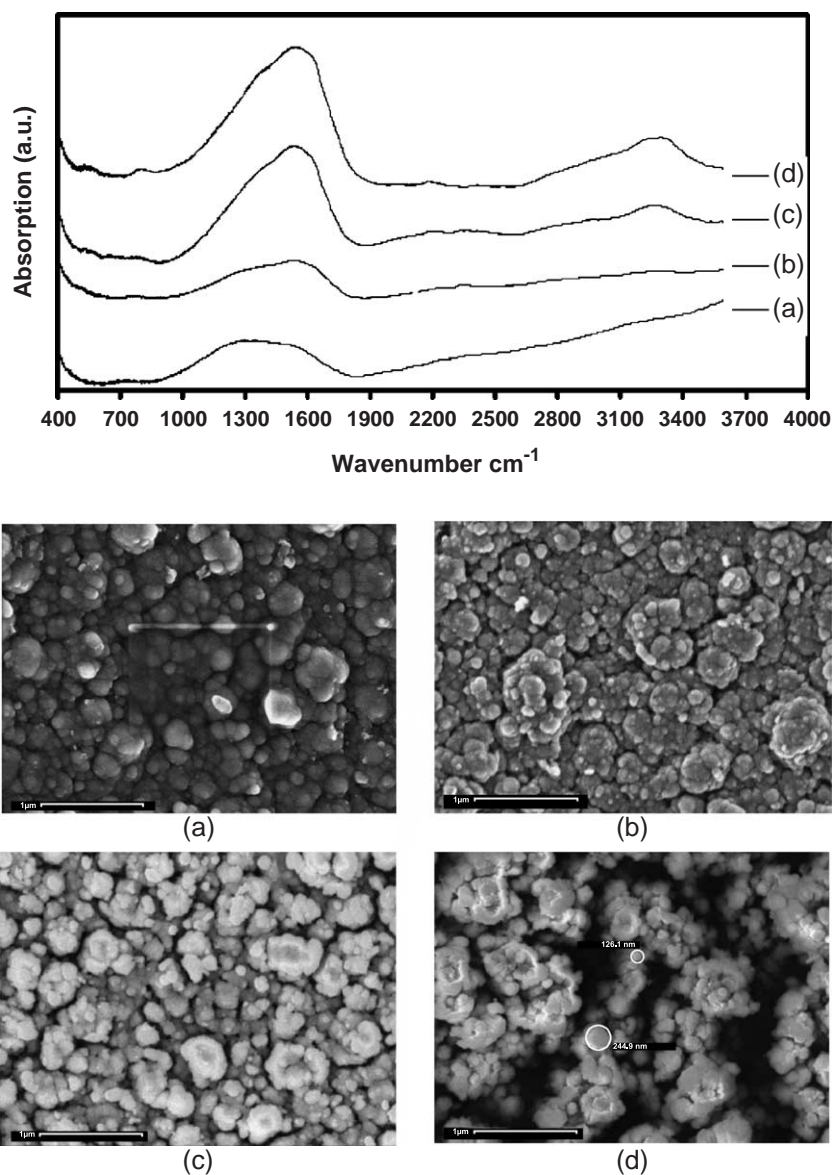


Fig. 4. FTIR absorption spectra and corresponding SEM pictures of the a-CN films deposited at different nitrogen pressures: (a) 4, (b) 100, (c) 300 and (d) 700 Pa. From [34]. The composition measured by XPS for each film was (a) $C_{77.4}N_{15.5}O_{7.1}$; (b) $C_{64.5}N_{30.3}O_{5.2}$; (c) $C_{61.5}N_{33.5}O_{5.3}$; (d) $C_{57.7}N_{34.6}O_{7.7}$.

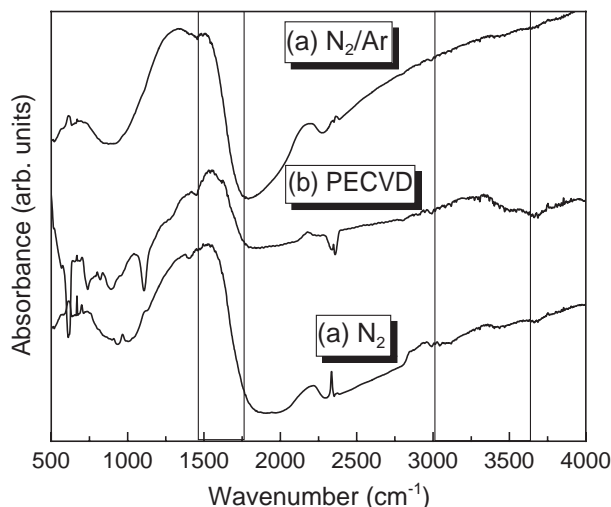


Fig. 5. Complete IR spectra of the samples shown in [35] and deposited under different conditions: (a) Magnetron sputtering using a mixture of Ar and N₂; (b) PECVD using CH₄ and N₂; (c) magnetron sputtering using only N₂ as the deposition gas. The composition measured by XPS was (a) C_{61.3}N_{37.5}O_{1.2}; (b) C_{47.3}N_{49.7}O_{3.0}; and (c) C_{57.7}N_{37.5}O_{2.5}.

variation in the IR absorption bands. Fig. 4 shows the IR spectra and the corresponding SEM pictures.

The films were prepared by CO₂ IR laser ablation of graphite in a remote nitrogen plasma atmosphere. By varying the nitrogen atmosphere, films with different microstructures were prepared. Films deposited at the lowest pressure had an IR absorption spectra with a π -band maximum near 1300 cm⁻¹, with nearly no OH absorption band and a compact microstructure. As the pressure was increased the π -band was more asymmetric with a maximum near 1600 cm⁻¹ and there was a strong OH absorption band and the SEM picture shows the increase in layer porosity.

Examples such as this are very common in the literature, although the interpretation given by the authors is not necessarily in agreement with that given in this paper. Ujvari et al. [35] also compare the IR absorption from CN samples deposited using different deposition systems. In paper [35] the IR spectra were plotted up to 2400 cm⁻¹. However, the authors kindly send me the complete spectra and these are shown in Fig. 5, in which again the effect of the OH adsorption is clearly seen. The stronger the OH stretching band, the more asymmetric is the broad band through 1600 cm⁻¹.

π -Electrons delocalization

The major implication of the model presented in this paper is that the IR intensity depends on the sp² fraction and π -electron delocalization. In [1] we showed that the integrated intensity of the whole 900–1800 cm⁻¹ band increases with the sp² fraction. We showed that for the ta-CN and ta-CHN samples the optical gap also decreased as the sp² fraction and the clustering increased, and so

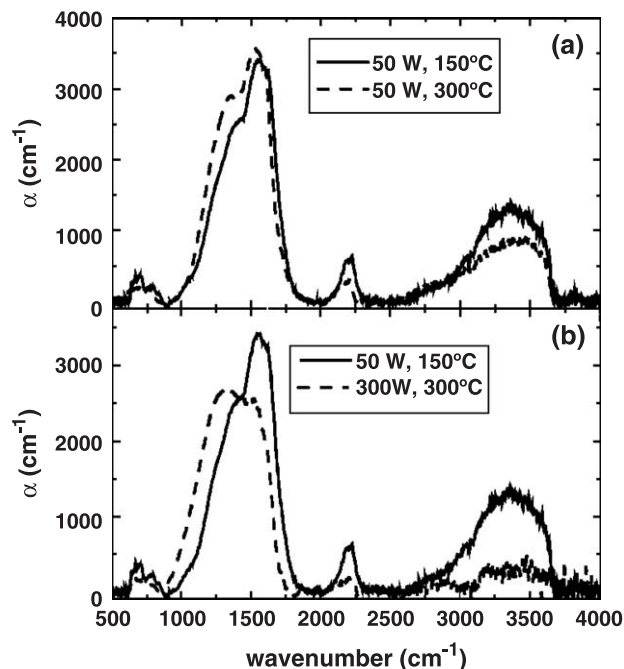


Fig. 6. Infrared spectra of a-CN samples deposited using magnetron sputtering at different substrate temperatures and power. Taken from [36].

accordingly the integrated IR intensity of the π -band was increased. A very nice correlation is also obtained by Lazar et al. [36] for sputtered CN films deposited at different substrate temperatures and power. They observed that the integrated IR absorption (1000–1800 cm⁻¹) increased with substrate temperature, while the room temperature conductivity and I_D/I_G ratio (i.e. clustering) increased and the optical gap decreased. This is an example of how the sp² clustering and subsequent π -electron delocalization induces an increase in the sample conductivity and a decrease in the optical gap, together with a greater IR intensity of the π -band.

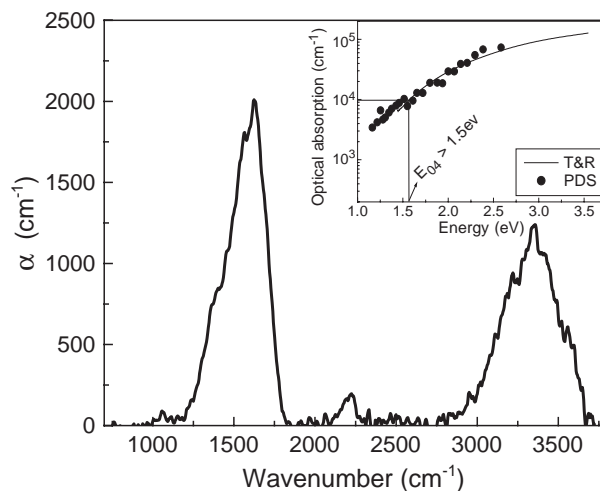


Fig. 7. FTIR Absorption spectra of sputtered a-CN films showing a high absorption for both the π -band and the OH band. The insert plots the optical absorption of the sample showing that the E₀₄ gap is about 1.5 eV.

The effect of OH absorption was also discussed; they observed that by increasing the deposition temperature or the RF power, the intensity of the bands at 3000–3800 cm^{-1} decrease significantly and nearly vanished for RF powers and temperatures higher than 150 W and 300 °C, respectively. Although not all the spectra are shown, the change in the asymmetry of the 1000–1800 cm^{-1} band between the 50 W–150 °C sample and the 300 W–300 °C sample clearly supports the arguments discussed in this paper (see Fig. 6b). This is a particularly good example because the sample porosity did not affect the optical or electrical measurements, as in the case of Al Khawwam et al. [34] where the resistivity was mainly controlled by the high porosity and loss of connectivity in the CN samples.

Therefore, one must be careful when using the IR absorption to say something about the optical or electrical properties of the CN films. The higher the IR absorption, the higher the conductivity should be and lower the optical gap, since the sp^2 clustering and π -electron delocalization have both increased. However, if the sample porosity has also increased, the measured optical and electrical properties are strongly influenced by the heterogeneous microstructure of the films, such that the sample could be considered as an effective medium composed of the “a-CN film plus voids”. Hence, the results do not reflect the microscopic features of the a-CN film, such as, sp^2 clustering and π -electron delocalization but the properties of the composed material. Fig. 7 shows an example of a sputtered CN sample with a strong π -band absorption. It is $\sim 100\%$ sp^2 bonded and the measured optical gap is about 1.5 eV. These high band gaps for sp^2 bonded carbon nitride films lead to another open question in the research about the physical properties of carbon nitride films. However, it has been determined that these wide gaps appear in films that show a strong OH absorption band [37,38] and therefore can be assumed to be associated with porous samples. It is not easy to determine the porosity in thin films, thus it is difficult to quantitatively correlate the porosity with the variation in the optical absorption.

Summarizing, the IR absorption of amorphous carbon and amorphous carbon nitride films can be explained considering the vibrational properties of the sp^2 clusters. The higher the sp^2 fraction and doping of the sp^2 clusters (or conjugated systems), the greater the π -electron delocalization which promotes charge fluxes within the clusters and thus intense IR active absorption bands. For amorphous carbon layers, the intensity of the broad absorption band increases with the sp^2 fraction since in the conjugated systems the π -electron delocalization enhances electron–phonon interactions. Experimentally, it has been demonstrated that when nitrogen is introduced into the carbon network, it increases the C- sp^2 fraction, (either by forming CfN or inducing CfC bond formation) and the clustering of the sp^2 phase, and this alone increases the intensity of the IRAV bands. Moreover, nitrogen can be considered as a dopant for the conjugated systems with the consequent

enhancement of the IR absorption in the 950–1600 cm^{-1} region. The vibrational modes correspond to C–C/C–N stretching modes whose intensity is enhanced by electron–phonon interactions. Thus their frequency and intensity depend on the specific electronic structure of the conjugated systems that constitute the sp^2 phase of the films.

The other important result of the analysis of the IR spectra from many different papers is that IR active bands due to OH adsorption (δ_{OH} around 1630 cm^{-1} and ν_{OH} around 3400 cm^{-1}) modify the absorption spectra of carbon nitride films and must be taken into account when studying the bonding characteristic of the films by IR spectroscopy.

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