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## Vibrational and optical properties of carbon nitride films prepared by reactive magnetron sputtering

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**Abstract.** Carbon nitride films were prepared by reactive magnetron sputtering of a graphite target in a nitrogen atmosphere at different pressures and temperatures. The films were characterized by infrared, Raman and ultraviolet–visible spectroscopies, as well as by ellipsometry. We obtained hydrogen-free dark films when a negative bias was applied to the substrates; the samples prepared at room temperature without bias were soft and hydrogen could be detected in their infrared spectra. The most prominent features, between 1000 and 1700  $\text{cm}^{-1}$ , in both the Raman and infrared spectra were modelled using two Gaussian curves. As the nitrogen content was varied, the ratio between their areas followed opposite trends in the Raman and the infrared spectra. The presence of hydrogen caused the main feature to absorb more strongly at lower frequencies but did not alter the trend. The presence of six and five membered heteroaromatic rings is suggested to explain the increase of the infrared vibrations associated with double conjugated double bonds. The index of refraction can be correlated with features in the infrared spectra, suggesting that its value increases as the number of carbon and nitrogen double bonds increases. Ion bombardment reduces nitrogen incorporation; it is responsible for the densification of the films and the introduction of several defects that make films prepared under bias more absorbing in the low energy region.

### 1. Introduction

Unlike the cases of diamond and cubic boron nitride a clear vibrational spectrum signature for carbon nitride (CN) with the desired properties of low compressibility and high hardness has not been established. Although several hard phases have been predicted [1, 2], none has unequivocally been identified by Raman or infrared techniques. This may be because very little crystalline material has been produced, but also because our understanding of amorphous and crystalline CN materials is still limited. As analysis techniques Raman and infrared spectroscopies are relatively accessible, non-destructive, fast and can be applied on films deposited on different kind of substrate. Therefore, it is important to further study the spectra of a variety of CN alloys and to relate these with production processes, and other film properties, to easily identify potentially useful material.

In this paper we report a quantitative investigation of Raman and infrared spectra from soft and hard CN alloy films prepared by magnetron sputtering. We have compared these spectra

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with the preparation conditions, as well as with the measured composition, index of refraction and absorption in the visible–ultraviolet region. We have found that the films have an  $sp^2$  bonded phase, whose features can be observed in the Raman. However, these Raman modes in the infrared [3] are eclipsed by the vibrational bands related to the presence of hydrogen in the films and to single and double CN bonds. Soft films have an infrared spectrum that has the most intense absorption in the  $1500\text{--}1700\text{ cm}^{-1}$  region and sharper Raman features. Additionally, hard hydrogen-free films have optical properties that can be related to the intensity and position of several features present in the infrared spectra; they are also less transparent in the low energy region than soft films.

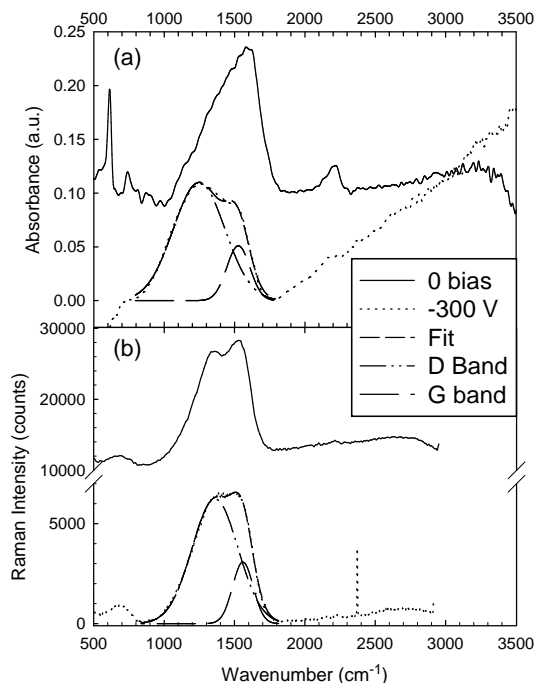
## 2. Experimental details

Films were produced in a stainless steel magnetron sputtering reactor with a graphite target (99.99% pure) 4 inches in diameter, using a direct current (d.c.) power supply to create the plasma. Nitrogen ( $N_2$ , 99.999% pure) was used as the sputtering and reactive gas. The substrates, placed 4 cm below the target, were heated to temperatures of up to  $530\text{ }^\circ\text{C}$ ; in some runs no external heating was used. To avoid contamination a load-lock was used to introduce and withdraw the samples. The substrate holder could be biased with respect to ground from 0 to  $-400$  volts. The base pressure was always  $<4 \times 10^{-6}$  Torr; the working pressure was varied from 10 to 40 mTorr. The plasma current used was 0.2 amperes, giving sputtering a power of 100 to 125 watts. Substrates were polished (100) crystalline silicon wafers, and prior to deposition they were cleaned in ultrasonic baths of acetone and propanol. To ensure good thermal contact silver paint was used to join the silicon to the substrate heater transfer plate.

Vibrational spectra were obtained with the aid of a Nicolet 205 Fourier transform infrared (FTIR) spectrometer and a Dilor LabRam fast analytical Raman microprobe spectrometer using a laser with a wavelength of 632.8 nm as the excitation signal. In the FTIR experiments 32 scans over the  $400$  to  $4000\text{ cm}^{-1}$  region were averaged; the Raman spectra were collected for 30 seconds in a range from  $500$  to  $3000\text{ cm}^{-1}$ . Composition analysis was carried out using energy dispersion spectroscopy (EDS) on a Leica-Cambridge scanning electron microscope, and by Rutherford backscattering spectroscopy (RBS) in a Van de Graaf accelerator using 1.95 MeV alpha particles [4]. For the EDS measurements melamine ( $C_3N_6H_6$ ) and sodium cyanide, 99.9% pure, were used as standards. The nitrogen fraction was calculated considering as unity the sum of the number of nitrogen and carbon atoms. The nitrogen fraction found by RBS was smaller than that of the EDS by about 5%. In earlier work we found experimentally that the nitrogen content can be increased using higher pressures, or reduced by increasing temperature [4]. To determine the index of refraction a Gartner ellipsometer equipped with a 632.8 nm wavelength laser was used. Visible and ultraviolet (UV) reflection spectroscopy was performed in a Shimadzu 260-UV spectrophotometer in the 300 to 800 nm range.

## 3. Experimental results

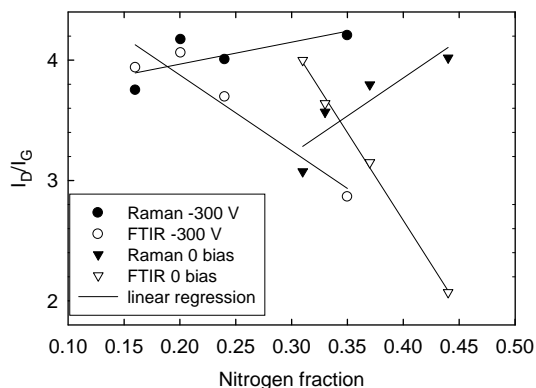
Infrared (ir) and Raman spectra from two samples are shown in figures 1(a) and (b) respectively. One sample was prepared without bias, at room temperature and at 40 mTorr, the other with a  $-300$  volts bias, 20 mTorr and at a deposition temperature of  $250\text{ }^\circ\text{C}$ . The former was easy to scratch with metal tweezers; the latter could not be scratched by the same method. Bands due to the stretching of C–H ( $2900\text{ cm}^{-1}$ ) and N–H (shoulder at  $3300\text{--}3400\text{ cm}^{-1}$ ) bonds [5] are observed in the ir spectrum of the sample prepared without bias, indicating that hydrogen was incorporated in this film; this may come from desorbed water vapour [6]. The existence of C–H



**Figure 1.** Infrared (a) and Raman (b) spectra of two samples. The continuous lines in both spectra correspond to a sample prepared with no applied bias, at 40 mTorr and at room temperature; the dotted lines correspond to a sample prepared applying  $-300$  volts to the substrate holder, 20 mTorr and at  $250^{\circ}\text{C}$ . The fitting has only been done on the spectra of the biased sample through two Gaussian curves, the D and G bands, shown in each figure.

bonds is confirmed by a weak photoluminescence signal, typical of soft polymer-like a-C:H [7], present in the unbiased films. The ir spectrum from the sample prepared under bias shows a steady increase on absorption at higher energies; such behaviour was common to all samples prepared under bias. All the spectra have features in three regions: near  $700\text{ cm}^{-1}$ , from  $900$  to  $1800\text{ cm}^{-1}$  and in the vicinity of  $2200\text{ cm}^{-1}$ . The first band is related to ring deformation modes, and, in contrast to the report of Raman spectra of amorphous carbon (a-C) [8], this feature is observed even in the sample containing hydrogen, although it is relatively weak. The second and more intense feature will be discussed in detail later. The third feature is composed of two bands in the ir spectra, but is very weak in the Raman with a peak at  $2220\text{ cm}^{-1}$ . This suggests the existence of two groups, one a nitrile group which is active both in the infrared and Raman spectra, and the other a carbodiimide or another heterocumulene group whose asymmetric (out-of-phase) modes are rather active in the infrared but very weak in the Raman [5]. Second order bands were observed in the Raman spectra peaking around  $2750\text{ cm}^{-1}$ .

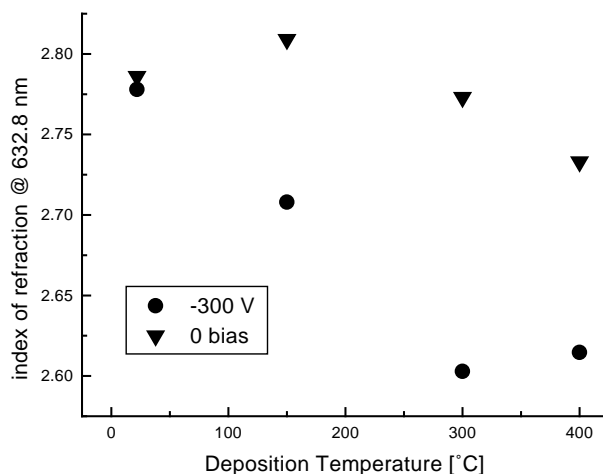
In Raman spectra of the carbonaceous materials the most intense feature,  $900$  to  $1800\text{ cm}^{-1}$ , has been deconvoluted into two bands: the lower energy one is called the D band and the higher energy one the G band [8]; the latter related to the main mode of crystalline graphite, the former related to the finite size of the graphitic domains. In CN materials it has been claimed that these bands become active in the infrared due to the breaking of symmetry in graphitic rings by means of nitrogen incorporation [3]. Moreover it has been claimed that it is possible to perform Raman analysis in the infrared [3, 9], by deconvoluting this main feature into two Gaussian curves. A careful inspection of figure 1 leads us to doubt this possibility. The Raman



**Figure 2.** The intensity ratio ( $I_D/I_G$ ) as a function of the nitrogen fraction present in the films prepared with a  $-300$  volts bias (circles) and without any bias (triangles), under 20 mTorr  $N_2$  pressure, 110 watts of sputtering power and at four different temperatures. The nitrogen content was determined by the deposition temperature in each case. The higher nitrogen concentration corresponds to films prepared without external substrate heating; as the temperature was increased to 150, 300 and 400 °C the nitrogen fraction was monotonically smaller in both cases. The filled symbols correspond to the values calculated after the fit of Raman spectra; the empty symbols correspond to the values calculated after the fit of FTIR spectra. The lines are minimum square fits to every set of data.

spectra show a similar shape in the main feature, with sharper features in the spectrum of the soft sample, but both resembling that observed in Raman spectra of a-C. However, in the infrared spectrum from the sample prepared without bias this feature is asymmetric towards higher energies, peaking at around  $1600\text{ cm}^{-1}$ , and for the sample prepared with bias the feature tends towards lower energies and peaks around  $1250\text{ cm}^{-1}$ . This particular difference could be explained by the presence of hydrogen linked to carbon and nitrogen atoms, since the scissoring modes of these bonds should be active in the  $1550\text{--}1650\text{ cm}^{-1}$  region [5], hence causing the main feature in the hydrogenated sample spectrum to peak at higher wavenumbers. The main feature is also wider in the infrared spectra than in the Raman spectra; this is clearly illustrated when two Gaussian curves are fitted to this feature as in figure 1 (this is shown for only one sample for the sake of clarity). The band at lower wavenumbers, or D band, is rather more distinct from one spectrum to the other; in the infrared it has its centre at a smaller wavenumbers and it is also wider. The differences in the centre positions and the band widths are larger than the experimental and fitting errors. A better fit for this infrared spectrum is achieved if three Gaussians are used, being centred at  $1142$ ,  $1361$  and  $1542\text{ cm}^{-1}$ . The latter two are close to the centres of the Gaussian Raman peaks. The Gaussian at  $1142\text{ cm}^{-1}$  may correspond to single C–N bonds which are expected in that region [10, 11].

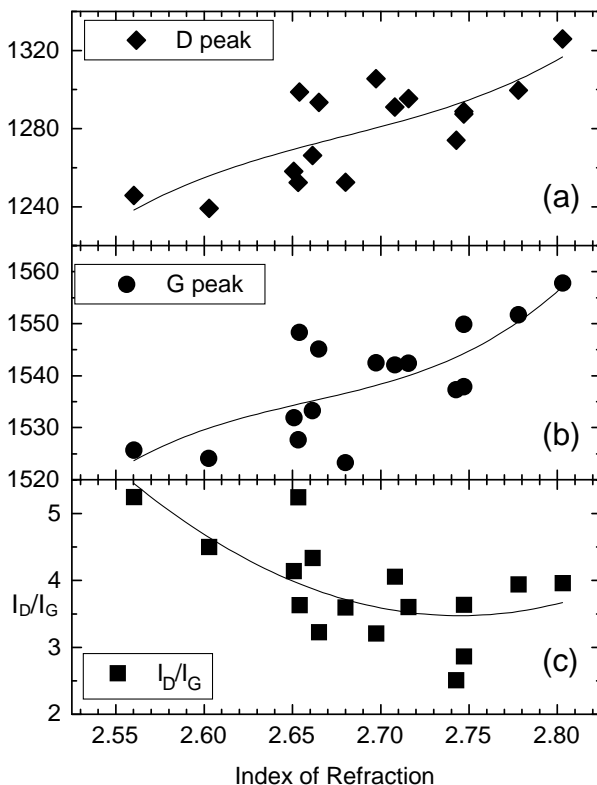
It is likely that hydrogen and CN bonds will affect mainly the ir spectra, masking the presence of the ir activated Raman modes [3]. The strength of these effects will determine whether the Raman modes, that become active in the ir spectra, can be used to perform structural studies by using FTIR techniques. If this is possible, then the behaviour of the Raman D and G bands should be similar to D and G bands fitted to the main feature in the ir spectra. To test this hypothesis we have performed a numerical analysis on the main feature of both vibrational spectra, fitting the two bands in each case and identifying them as described above. We have then plotted the  $I_D/I_G$  ratio (defined as the D band area divided by the G band area) for both the Raman and the FTIR spectra, as a function of the film nitrogen content in figure 2. The content was modified by varying the deposition temperature, as we have found that nitrogen



**Figure 3.** Index of refraction of CN films as a function of temperature for samples prepared under the following conditions:  $N_2$  pressure = 20 mTorr, sputtering power = 110 watts. That is, they correspond to the same samples used to derive the data depicted in figure 2.

content tends to diminish with rising temperature [4]. The Raman  $I_D/I_G$  ratio increases with increasing nitrogen content while the infrared  $I_D/I_G$  ratio actually diminishes. Furthermore, even though increased ion bombardment tends to increase the magnitude of this ratio for both methods, it does not alter the above mentioned trend. Other work on sputtered CN films has reported similar trends in Raman studies [12], and quantitative infrared analyses [9, 13] have also shown that the ir  $I_D/I_G$  ratio diminishes with nitrogen incorporation. We have also found that as the nitrogen content is increased, the width of the Raman G band diminishes noticeably, for both biased and unbiased samples, while that of the ir G band seems to decrease only slightly. Differences in the preparation conditions should introduce changes in the structure of the films and hence in the  $I_D/I_G$  ratio [8]. However, the trends are different in the Raman and ir cases, implying that the activation of the Raman modes in the infrared [3] is limited and too weak to be able to perform ‘Raman in the infrared’.

From figures 1 and 2 we can see that the presence of hydrogen strongly affects the ir spectrum as well as altering the mechanical and optical properties [14]; however a more detailed analysis on hydrogen effects will be published elsewhere. Nevertheless, we have found that the optical properties of the unhydrogenated samples prepared under bias are related to their infrared characteristics. We studied with the ellipsometer the samples whose  $I_D/I_G$  ratios are depicted in figure 2; the values of their index of refraction as a function of deposition temperature appear in figure 3. Comparing both figures one realizes that there might be a relationship between the vibrational properties in the ir and the refractive index in the case of the samples prepared under bias. So, for all the films prepared applying a negative bias to the substrate (–200 to –400 volts), at different temperatures (room temperature to 400 °C) and pressures (10 to 40 mTorr), we have plotted in figure 4 the position of the ir D and G peaks, as well as the ir  $I_D/I_G$  ratio as a function of the index of refraction. If we assume that the main ir feature depends mostly on the number of single and double nitrogen bonds (with the vibrations of the former present at the low energy side and those of the later at the high energy side), then the trends observed in the plots suggest that, regardless of the preparation conditions, there is a concurrent formation of double bonds and an increase in the refractive index. That in the biased samples’ infrared spectra the increasing absorption

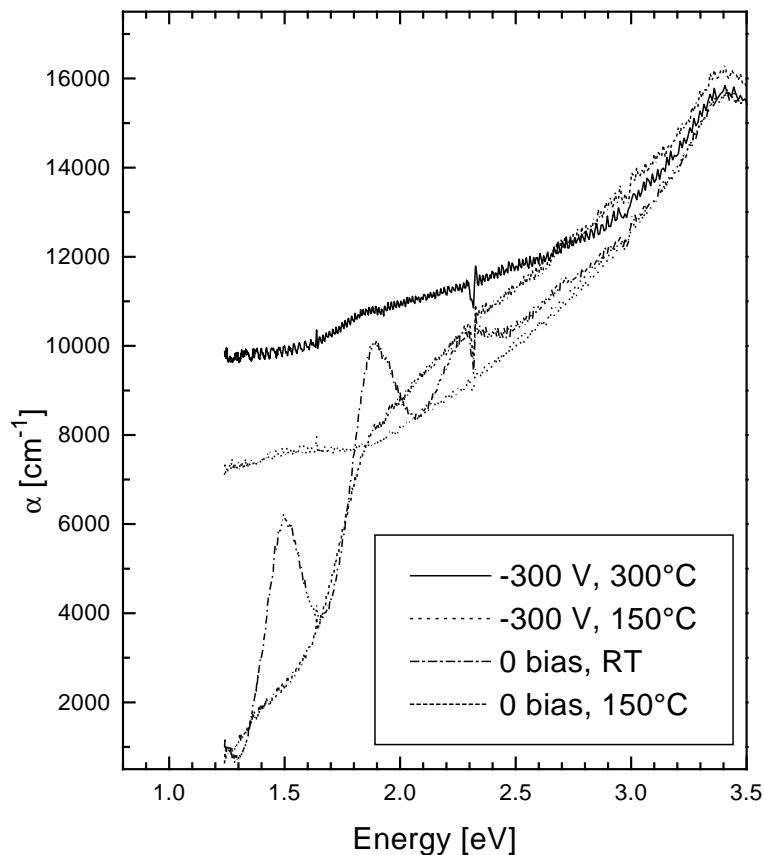


**Figure 4.** Relation between the parameters used in the fitting of Gaussian curves to the FTIR spectra and the index of refraction of samples prepared applying a negative bias to the substrates. The position of the D band centre (a) and that of the G band centre (b) are given in wavenumbers ( $\text{cm}^{-1}$ ), the  $I_D/I_G$  ratio (c) and the index of refraction are dimensionless. The lines are only a guide to the eye.

at  $1400\text{--}1700\text{ cm}^{-1}$  region is not due to the activation of C–H and N–H bending modes, but rather to the activity of conjugated double bonds, is suggested by two facts: (a) the presence of hydrogen would diminish the density and hence the refractive index but the opposite is observed, (b) the absence of stretching vibrations related to hydrogen containing groups in the spectra.

In fact, the bombarded material is less porous than the soft films: the proof was found after exposing the films to air; those prepared without bias did show an evolution of the ir absorption bands above  $3000\text{ cm}^{-1}$ , suggesting the incorporation—and possible reaction—of water [15], which leads to hydrogen bond formation. The films prepared under bias showed a little or no evolution of these bands, indicating that they had a smaller porosity through which water could be introduced in the material.

In figure 5 unaveraged absorption spectra are presented for four samples prepared under different conditions. The data were obtained from UV–vis reflectance spectroscopy, and are plotted in the most common pattern,  $\alpha$  as a function of energy, where  $E$  is the energy in electron volts and  $\alpha$  is the absorption coefficient in  $\text{cm}^{-1}$ . The data were not averaged to demonstrate the existence of interference fringes, but this does not affect the trend of the curves. This type of graph may yield information to construct a Tauc plot, where straight lines are then used



**Figure 5.** Absorption plots obtained from the unaveraged values obtained by UV–vis reflection spectroscopy of four CN samples. All the samples were prepared at a deposition pressure of 20 mTorr, at a sputtering power of 110 watts; other specific conditions are depicted in the legend.

to calculate the optical gap of some amorphous semiconductors [16]; in our case, no straight line could be fitted with confidence, implying mainly that the joint density of states is not parabolic. A clear difference can be observed in figure 5 between films prepared with and without substrate bias: the former produce absorption tails that extend to rather low energies, the latter are more transparent in the near infrared, as can be seen in the down-turn of the curves just below the visible range. The absorption tails observed in the layers prepared under bias might be responsible for the increasing absorbance in the FTIR spectra of these samples at higher wavenumbers. Notice also the presence of a band peaking near 3.4 eV. A similar peaking of the extinction coefficient was observed by Friederich *et al* [13], who only concluded that it was not caused by surface scattering; we ascribe it to  $n \rightarrow \pi^*$  transitions, originating from the nitrogen lone electron pair into the antibonding levels of the highly conjugated system of N-containing heteroaromatic rings.

#### 4. Discussion

The dissimilar behaviour of the observed  $900\text{--}1800\text{ cm}^{-1}$  feature in the Raman and the infrared spectra obviously stems from the fact that the activation of Raman modes in the infrared is



incapable of explaining all the ir active vibrations present in such a range; this fact has been noted already by Schwan *et al* [17] but no proof was given. The observed phenomena may be accounted for by several factors. Let us first consider the model more commonly used to explain the Raman spectra of a-CN and a-C. Raman spectra are expected to depend mainly on the  $sp^2$  bonded structures of carbonaceous materials [14, 18]; stress has been directly related to the width of the Raman G band in a-C and a-C:H [19]; nitrogen is expected to reduce connectivity and  $sp^3$  bonding in CN materials [20], as well as to form nitriles and other linear  $\pi$ -electron-rich compounds [6], which can produce heteroaromatic rings [21]. The increase of the ir G band intensity with nitrogen incorporation suggests that more CN double bonds are formed since this ir band is located at the same wavenumber range as the aryl C=N bonds [5] and conjugated C=N bonds in rings [21]. Thus the loss of connectivity might be through the formation of rings with  $-N=C$  bonds in them (pyridine-like); this would reduce the chemical links between them and the rest of the atomic network, and in this way diminish the stress transmitted from the highly fourfold and threefold coordinated regions. The result would be a reduction of the Raman G width, and would also allow vibrations from small groups of flat rings, of which the Raman D band is a consequence [14], and hence increase the D band area and the Raman  $I_D/I_G$  ratio. This explanation would be acceptable but we also have to consider the effects of bombardment in our films.

Bombardment, enhanced to a certain extent by the application of a negative bias to the substrate, is a key factor on the structure and composition of the films; it tends to reduce nitrogen incorporation, introduce optically active centres and induce greater Raman and ir  $I_D/I_G$  ratios (figures 2 and 4). It probably increases the films' density as well as introducing disorder in the atomic network, by the formation of bonds that increase crosslinking, probably through the development of some  $sp^3$  bonds (see below).

Obviously a question arises: if bombardment reduces nitrogen content but at the same time increases the Raman  $I_D/I_G$  ratio, how is it possible that a larger N content is reflected in a larger Raman  $I_D/I_G$  ratio as well? According to the graphite-like model, the D peak can grow in intensity when there are more or larger graphitic clusters [22]. It is tempting to think that the effect of nitrogen incorporation is to produce bigger clusters, and that ion bombardment has the effect of inducing the formation of a greater number of clusters. However, on the one hand nitrogen atoms reduce connectivity through the formation of digonal configurations which make ring fusing difficult; on the other hand, trigonal nitrogen in flat hexagonal clusters is very unstable [23, 24] as is the ladder structure proposed for paracyanogen [15]; so it is very unlikely that a larger nitrogen content would produce large graphitic clusters. To think that ion bombardment is the phenomenon that produces larger clusters is contrary to experience, as larger graphitic clusters would imply softer films, but we have found the opposite: bombardment makes them harder. Besides, the graphitic-like structure model, which explains the vibrational spectra of a-C as the more or less broadened density of vibrational states of disordered graphite, has been questioned by several authors [8, 19], considering that the modes present around  $1350\text{ cm}^{-1}$  do not necessarily originate from a maximum in the density of states of crystalline graphite like in ion-irradiated pyrolytic graphite [25]. The answer to such larger Raman  $I_D/I_G$  ratios is probably related to the fact that different structures, which nevertheless have bonds with similar force constants, give rise to vibrations in the vicinity of the D band. Upon these considerations, we feel then that it is necessary to look to other structures and models to explain the vibrational properties of a-CN.

We will suggest some structures that might exist in sputtered a-CN and that have vibrational modes below  $1580\text{ cm}^{-1}$  in the Raman spectra, which are then unlikely to contribute to the Raman G peak: the symmetrical (in-phase) modes of double cumulated groups which are present in the material [5].

The presence of nitriles and double cumulated groups suggest that they could be involved in the formation of heterocycles, through cyclization and cycloaddition reactions [26], giving place to six and five membered rings. These rings are found in fullerenes; fullerene-like structures have been observed in sputtered hydrogenated and unhydrogenated a-CN [27, 28]. Structures containing five membered rings such as pyrrole and imidazole have been observed in sputtered material by nuclear magnetic resonance [29] and bent structures, composed of five and six membered rings, linked one from each other by  $sp^3$  bonds, have also been proposed [28]. For example polypyrrole Raman spectra have strong bands at around 1350 and 1600  $cm^{-1}$  [30];  $C_{60}$  has its most intense band Raman band at 1469  $cm^{-1}$  [31]. It is then likely that these kinds of structure contribute to the increase in the scattering frequencies near the Raman D-band, as well as increasing the bond conjugation, which is reflected in a larger absorption near or at the ir G-band.

Another possibility for the increase of the D band upon bombardment is a true disorder band: there is evidence that the Raman band originated by the existence of edges in graphitic crystals, the so called Raman D-band, is different from the one present in material produced by ion irradiation of the crystals; this band, called by Comapagnini *et al* the D'-band, nevertheless lies very close to the first [32] and is ascribed to disordered structures. What these disordered structures would look like is still controversial, but they probably are very different from the almost flat, hexagonal, graphite-like structures that have been assumed to be mainly responsible for the vibrational states in a-CN [33]. Theoretical models in a-C suggest that they might not have flat rings at all but more  $sp^3$  bonds [34], facts that would agree with having fewer double conjugated bonds, hence a less intense ir G-band, as well as an increased hardness. The ir G band in a-CN could then be related more to C=N bonds and the ir D band with nitrogen single bonds in an  $sp^2$  trigonal configuration ( $>N-$ ) but not as a part of hexagonal rings. Support for this interpretation comes from chemists who have synthesized—using equilibrium methods [11, 35]—mainly  $sp^2$ -bonded CN solids with a high content of nitrogen in a trigonal position. These materials have infrared spectra whose strongest features span from 700 to 1650  $cm^{-1}$  and peak between 1100 and 1320  $cm^{-1}$ . Notice that trigonal nitrogen may increase connectivity in the atomic network, as compared with digonal  $sp^2$  nitrogen ( $-N=$ ).

We will now discuss the absorption spectra in the UV-visible-near infrared range. The optical absorption in a-C is considered to be controlled by the distortion of the rings, rather than their number, in the average graphitic cluster [7, 34]. By diminishing the stress acting on the rings, and hence the distortion they are subject to, one would expect an increase in the optical transparency. The fact that samples prepared without bias are more transparent in the near- and mid-infrared is probably related to the fact that less stress is built into these layers due to reduced bombardment. According to Lee *et al* [34], in a-C not only stressed rings give place to states in the gap, near the Fermi level, but also other  $sp^2$  bonded configurations which are linked to  $sp^3$  hybridized sites; in a-CN the  $sp^2$  bonds can obviously be either C=C or C=N. That the films prepared under bias have less nitrogen, are harder and absorb more at lower energies (say below 1.8 eV) could be accounted for by the fact that more carbon is driven to  $sp^3$  hybridization by effects of bombardment affecting neighbouring double bonds and introducing such electronic states.

The transitions from the nitrogen lone pair of electrons gives support to the presence of digonal  $sp^2$  bonded nitrogen, which has its lone pair in the same plane as the single and double bond. Also  $sp$  bonded nitrogen has a lone pair, but, as the nitrile ir and Raman signals are relatively weak, we do not expect to have a large contribution from such atoms.

More theoretical and experimental work needs to be done in order to elucidate the exact nature of the CN materials which have large Raman and ir  $I_D/I_G$  ratios, considerable hardness and are less transparent in the visible and near infrared.

## 5. Conclusions

Carbon nitride films have been produced by d.c. magnetron sputtering on silicon substrates. Films produced without bombardment are softer, more porous and contain hydrogen. Films produced under bias are less porous, have less nitrogen and their refractive index relates to the ir absorption shape in the 1000–1800  $\text{cm}^{-1}$  region, suggesting a larger index of refraction is related to the existence of a greater number of conjugated double bonds. Nevertheless for both kinds of material the  $I_D/I_G$  ratios follow different patterns in the infrared and the Raman spectra, suggesting that in neither kind of film is the activation of Raman modes in the infrared very strong. The increase of the Raman  $I_D/I_G$  ratio with both increasing nitrogen content and bombardment, which reduces the incorporation of nitrogen in the films, indicates that different structures can be responsible for a more intense scattering in the 1200–1500  $\text{cm}^{-1}$  region.

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