Plasma-deposited a-C(N):H Films

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The growth behaviour, film structure and mechanical properties of plasma-deposited amorphous hydrogenated carbon-nitrogen films are shortly reviewed. The effect of nitrogen-containing gas addition to the deposition to the hydrocarbon atmospheres used is discussed, considering the modifications observed in the chemical composition growth kinetics, carbon atom hybridisation and chemical bonding arrangements of a-C(N):H films. The overall structure behaviour is correlated to the variation of the mechanical properties.

I Introduction

In the last ten years there has been a great interest in the study of plasma-deposited amorphous hydrogenated carbon-nitrogen (a-C(N):H) films. The main reason for the initial interest was the suggestion, by Liu and Cohen [1], that the hypothetical compound β-C_3N_4 would have mechanical properties similar to that of crystalline diamond. Since that suggestion, much work has been done on the search for carbon nitride synthesis, effort that was recently reviewed [2,3]. The aim of the work on plasma-deposited a-C(N):H was obviously not to produce crystalline carbon nitride, but to study the supposed beneficial effects of nitrogen incorporation on the mechanical, electrical and optical properties of a-C:H films.

The research on a-C(N):H films started even before Liu and Cohen's suggestion, with the study of nitrogen electronic doping of a-C:H films reported by Jones and Stewart [4]. After that, followed the pioneering works of Han and Feldman [5] and Amir and Kalish [6], mainly considering optical and electrical properties, and the work by Kaufman et al [7] on Infrared Spectroscopy of a-C(N):H films, which stated important structural effects of nitrogen incorporation into amorphous hydrogenated carbon films. Further research on the field showed that some aspects of the nitrogen incorporation process in a- C:H films place obstacles to the achievement of the expected benefits. The first one is the limited nitrogen uptake observed in a-C(N):H films. No more than about 20 at.% N could be achieved up to now in plasma deposited a-C(N):H films. The second one is that nitrogen incorporation results in a strong decrease in the sp^3 carbon atom fraction [8], which is the main responsible for a-C:H film rigidity. And finally the preferential bonding of hydrogen atoms to the nitrogen atoms, which makes difficult carbon-nitrogen extended network formation, and adds terminating groups to the amorphous network.

Despite such limitations, plasma-deposited a-C(N):H films were found to be used in a number of applications. The stress reduction induced by nitrogen incorporation [9] and consequent adhesion improvement, allowed the development of a-C(N):H antireflective coatings for Ge-based infrared detectors [10]. It was found also that nitrogen can electronically dope a-C:H films, and strongly decrease the defect density, enabling its use as a semiconductor material [11]. Nitrogen incorporation was found also to decrease the threshold electric field in electron-field emission process [12], making possible the use of a-C(N):H films as a overcoat on emission tips in flat-panel display devices [13].

In a simple way, hard a-C:H film structure may be pictured by an over-constrained random network composed by sp^3 and sp^2- hybridised carbon atoms and hydrogen atoms. This means that the mean coordination number of the atoms forming the network is greater than the ideal geometrical value [14]. This high degree of overconstraining in a-C:H films is due to the presence of a large fraction of sp^3 atoms, highly crosslinked, which results in the observed rigidity, as well as in the development of a high internal compressive stress due to chemical bond distortion. So, in the study of a-C(N):H films structure special attention must be paid to the structure changes that affect the network connectivity, such as chemical composition, carbon atom hybridisation, and chemical bonding scheme.

The processes involved in plasma deposition of amorphous hydrogenated carbon films are quite complex. Besides the hydrocarbon plasma chemistry details, each different species from the plasma interact with the growing layer in a different way [15]. At first, we have the positively charged ions, mainly the carbon-carrying ones, that are extracted from the plasma and

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accelerated towards the substrate by the negatively biased substrate electrode. They are the responsible, by energy deposition, for the activation of C-C bond formation, among other consequences. Carbon-carrying slow neutral radicals contribute manly to film growth itself, by sticking to dangling bonds at the film growing surface. Hydrogen fast ions and slow neutrals can be involved in dangling bond creation or saturation, among other processes. Nitrogen addition to the deposition atmosphere may, besides altering the plasma chemistry, also alter the surface process acting in the growing layer, as will be discussed in this paper.

The aim of the present work is to shortly review aspects concerned to the nitrogen incorporation process, film growth kinetics, and modification of a-C(N):H film structure and mechanical properties. No reference will be made on electrical or optical properties of a-C(N):H films. Further reference on this subject may be found in a number of papers [4,5,6,11,16,17]. In section II are discussed results on the effects of nitrogen-containing gas addition to the deposition atmosphere, on film chemical composition and growth kinetics. In section II, The main structural changes observed in a-C(N):H films, as determined by several characterisation techniques, are discussed in section III. In addition, the structure changes are related to the observed mechanical properties. Section III summarises the overall discussion.

II Chemical Composition and Growth Kinetics

Several plasma deposition methods were used in the study of a-C(N):H films. Most of the work was done on films deposited by conventional radio-frequency Plasma Enhanced Chemical Vapour Deposition (rf-PECVD) [18], in a hydrocarbon / nitrogen-containing gaseous mixture, with the substrate placed on the rf-biased electrode [19-22]. In this method the capacitive coupling of the rf power to the cathode allows the development of an averaged-in-time DC negative bias at the powered electrode, known as self-bias potential (V_B). The potential V_B extracts the ions in the plasma, and accelerate them towards the film growing surface. There were some reports on films deposited by the DC glow-discharge method [23], and also a variation of the rf flow-discharge, in which the substrate is placed in a negatively DC-biased electrode parallel and opposed to the rf- powered one [7].

In order to achieve higher plasma ionisation and dissociation, some authors used high density plasma sources to study a-C(N):H films. The Electron Cyclotron Resonance- Microwave (ECR-MW) plasma source [24,25], and the helical resonator plasma source [26] were used to generate a high density plasma, to ether with rf-biasing of the substrate electrode, in order to extract the ions from the plasma. A variation of the rf-glow-discharge method, in which a steady magnetic field is perpendicularly imposed to the rf-biased electrode surface, was used to deposit a-C(N):H films with a gaseous mixture largely diluted in helium [11]. Production of a-C(N):H films was also performed by using highly ionised plasma sources [27] or ion beam sources [28], in order to deposit or assist the deposition process . The effects of nitrogen-containing gas on the chemical composition of films deposited by several techniques, and precursor atmospheres may be viewed on Table 1. In this table are displayed the maximum nitrogen content and the hydrogen content range obtained for the whole variation of the nitrogen-containing gas partial pressure. For easier comparison of the results, the table also displays the deposition technique used and the main deposition parameters.

As shown in table 1, the maximum nitrogen uptakes are about 20 at %, and were obtained using acetylene - nitrogen atmospheres. On the other hand, results using other gas mixtures hardly reach 15 at. % nitrogen. Despite this dependence on the precursor gas, it seems that the maximum nitrogen content does not depend on the deposition technique used. It is interesting to note also that the maximum nitrogen uptake is not directly correlated to the nitrogen incorporation yield of the particular nitrogen-containing gases. It is easily seen by comparing results from references [9] and [20] in the table, which were obtained by using CH_4-N_2 and CH_4-NH_3 mixtures. Both works obtained about the same maximum nitrogen uptakes, despite the great differences in the nitrogen atomic fraction in the deposition atmosphere at the maximum nitrogen incorporation . Thus, process other then chemical reactivity may drive the nitrogen incorporation. In which concerns to the hydrogen content some authors report a continuously decreasing behaviour upon nitrogen incorporation, while others report a relatively insensitive behaviour, showing also different levels of hydrogen content.

The observed relatively low upper limit for the nitrogen content in a-C(N):H films has been ascribed to the strong decrease on the film deposition rate upon nitrogen precursor addition to the deposition atmosphere, as shown on Fig. 1. In this figure are shown plots of deposition rate against the nitrogen content, normalised to that of the nitrogen-free film, for several precursor gas mixtures [22]. All the plots show a clear decrease on the deposition rate against nitrogen content. In the figure, the deposition rate plots for CH_4-N_2 or NH_3, and C_2H_2-CH_3NH_2 gaseous mixtures seem to follow a very similar dependence with nitrogen content. This common dependence shows an about 13 at. % N apparent vanishing of deposition rate. On the other hand, the plot corresponding to the C_2H_2-N_2 mixture follows a clearly different dependence, showing the deposition rate fall at higher nitrogen contents, allowing the deposition of nitrogen-richer films.

Table 1. Chemical composition and deposition details for a-C(N):H films deposited by several techniques.

Ref.	Deposition method	Hydrocarbon	Nitrogen precursor (partial pressure range)	Substrate bias (-V)	Pressure (Pa)	Maximum N Content in the film (at.%)	H Content in the film
7	rf PECVD/DC bias	C_5H_{10}/Ar	N_2 (0-95%)	380	3.5	11	-
11	magnetic field enhanced rf PECVD	CH_4/He	N_2 (0-80%)	-	13	15	12-21
16	rf PECVD	C_2H_2	N_2 (0-70%)	-	7	20	30-38
9	rf PECVD	CH_4	N_2 (0-50%)	370	8	11	12-17
20	rf PECVD	CH_4	NH_3 (0-25%)	370	8	13	16-20
21	rf PECVD	C_2H_2	CH_3NH_2 (0-40%)	350	3	12	12-16
22	rf PECVD	C_2H_2	N_2 (0-90%)	300	3	22	11-13
23	DC PECVD	C_2H_2	N_2	500	20	14	19-37
29	rf PECVD	C_6H_6	N_2 (0-80%)	500	13	10	22-27
29	rf PECVD	C_6H_6	NH_3 (0-80%)	500	13	8	27
52	ECR-MW/rf bias	CH_4/Ar	N_2 (0-63%)	120	-	11	-

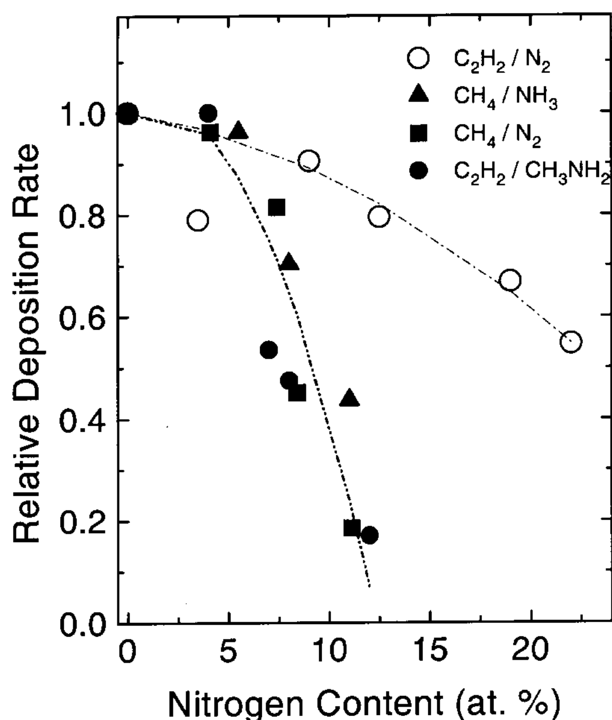

Figure 1. Variation of the relative deposition rate as a function of the nitrogen content in the film, for films deposited from CH_4-N_2 [9], CH_4-NH_3 [20], C_2H_2-CH_3CH_2 [21], and C_2H_2-N_2 mixtures [22].

Although data on plasma chemistry of hydrocarbon-nitrogen plasmas may be found on the literature [30,31], no clear connection is made with the film growth process. The changes observed in the optical emission spectra of hydrocarbon-N_2 mixtures are the increase in the CN and N-derived emission lines, in parallel with a decrease in the intensity of the CH emission lines [31]. Since these changes cannot by themselves be correlated with the film surface process, little information can be extracted from this kind of analysis.

Two factors were identified as being the cause for the observed strong decrease on the deposition rate [22]. The first one is the erosion of carbon atoms by energetic nitrogen ions like N_2+ that comes from the plasma. This effect was studied in detail by Hammer and Gissler [32]. They found that low- energy (150 eV) N_2^+ ion bombardment of a hydrogen-free amorphous carbon film resulted in carbon atom removal at rates as high as 0.5 C atom per N_2^+ ion, mainly as CN and C_2N_2 molecules. This process was identified as a chemical sputtering process, since the observed sputtering rate is far higher than that expected by physical sputtering process. A similar process was observed by Hong and Turban [33] when studying the etching process of a-C:H films by N_2 ECR plasmas. They found that rf-biased, previously grown a-C:H films were eroded by the N_2 plasma, being evolved in this process the same kind of fragments as the observed in N_2^+ ion bombardment of hydrogen-free carbon films. The second factor is the evaporation of N_2 molecules as a consequence of N-N bond formation. Since it is expected that nitrogen

and carbon atoms incorporation may show a disordered nature in a-C(N):H film growth, nitrogen evaporation is very likely to occur when the film nitrogen content increases.

Both factors were taken into account by Todorov et al [34] in order to model ion-beam deposited a-CN_x film growth, for a particular C/N ion arrival ratio. In this work, besides carbon atom chemical sputtering carbon removal by N+ ions and N_2 evaporation, the authors also included N atom sputtering by C^+ ions, within a Monte-Carlo simulation of the collision process following ion subsurface penetration. With this model they could fit results of the chemical composition depth profile, but no attempt was made to model deposition rates.

A simple statistical model for a-C(N):H films growth kinetics and nitrogen incorporation was recently proposed [35]. This model incorporates the main effects caused by the plasma nitrogenated species on the growth kinetics: The chemical sputtering of carbon atoms by nitrogen ions, and the evaporation of N_2 molecules. This was achieved by considering only two species arriving at the film surface with complimentary probabilities: a fully aggregating "C" species, representing carbon-carrying ions and radicals, and a "N" species, representing the N_2^+ ions extracted from the plasma. In the model, when a "N" species fall over a "C" atom in the deposit, the interaction between and incoming "N" species and the deposit is described by the interaction parameter q. This parameter represents the probability of a N atom to remove a C atom from the film, being $(1-q)$ the probability of aggregation of the "N" species. When a "N" species falls over another a N atom, both leave the deposit as an N_2 molecule. N atom removal by a "C" species was not considered, since for most a-C:H film deposition processes the main channel for material aggregation at the film surface is the sticking of carbon carrying slow radicals. By using an interaction parameter q equal to 0.25 (very close to the carbon removal rate reported in reference [19]), this model was found to fit very well the deposition rate results obtained from plasma deposition using acetylene-nitrogen mixtures reported in reference [22]. In addition, the obtained maximum nitrogen uptake as a function of the interaction parameter showed that no more than about 33 at .% N could be incorporated in a-C(N):H films, even considering no chemical sputtering but only N_2 evaporation. Moreover, no fit could be obtained for deposition rate experimental results from deposition atmospheres other than C_2H_2-N_2.

The lower nitrogen uptake associated with a sharper decrease on the deposition rate upon nitrogen shown on figure 1 (for the CH_4-N_2 or NH_3 and C_2H_2-CH_3NH_2 mixtures) was ascribed to the role of hydrogen in the deposition process [22]. According to Jacob [15], the main role of hydrogen in a- C:H film deposition at room temperature, is to saturate surface dangling bonds. So higher the hydrogen content in the deposition atmosphere, lower would be the surface sites available to film growth by slow radicals. Fig. 2 shows the hydrogen atomic fraction in the deposition atmosphere, as a function of the nitrogen precursor gas partial pressure, for the film deposition experiments shown on Fig. 1. The ranges shown correspond to the non-zero deposition rate range. It is easy to note that when using the C_2H_2-N_2 mixture, the deposition atmosphere hydrogen fraction is far lower than that shown by the other mixtures. Further improvement of the above discussed statistical model for a-C(N):H film growth incorporated such an effect, by blocking a fixed fraction of surface sites to film growth [36]. With this modification, the model was able to fit the two kinds of deposition rate curves shown in Fig. 1.

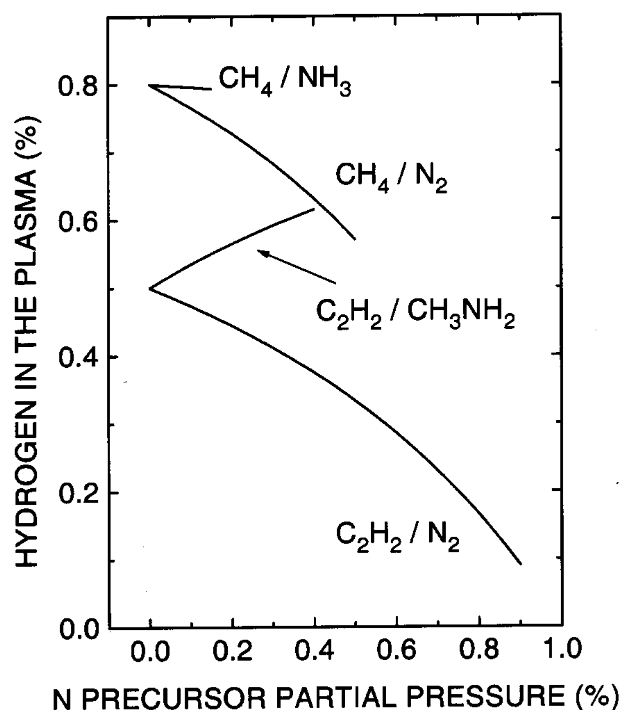

Figure 2. Hidrogen content in the deposition atmospheres, for the gaseous mixtures indicated in the plot, in de non-zero deposition rate range.

III Film structure and mechanical properties

As it was mentioned in the introduction, the main structural aspect concerning amorphous carbon films is the carbon atom hybridisation. The presence of a large fraction of sp^3 carbon atoms in a-C:H films, with a high cross-linking of the amorphous network, gives rise the rigidity shown by this films. So, the first concern in the study of the structure of a-C(N):H films should be the effects of nitrogen incorporation on the hybridisation

state of carbon atoms. Unfortunately there are only a few reports of such kind of analysis.

Seth and Babu [37] reported a study on the carbon sp^3 fraction of a-C(N):H films deposited from butadiene-nitrogen and butadiene-ammonia atmospheres, as determined by ^{13}C-NMR spectroscopy. They reported that nitrogen incorporation resulted in an increased C sp^3 fraction for ammonia-derived films, whereas not remarkable changes were found for nitrogen-derived films.

The above finding was not corroborated by later studies. Table 2 summarises results on the hybridisation state of carbon atoms in plasma deposited a-C(N):H films. There are shown results obtained by the comparison of the of the 1s-σ^* and 1s-π^* peaks of the C K-edge Electron Energy Loss (EELS)spectra of films deposited by rf-PECVD [8] (also shown in Fig. 3) and magnetically-enhanced rf-PECVD [11]. In addition, are also shown results obtained from the combination of the EELS spectra in the plasmon region and Auger Electron Spectra (AES) taken from films deposited by ECR-MW onto rf-biased substrates [24]. Together with the sp^3 fraction results, the deposition details are also shown.

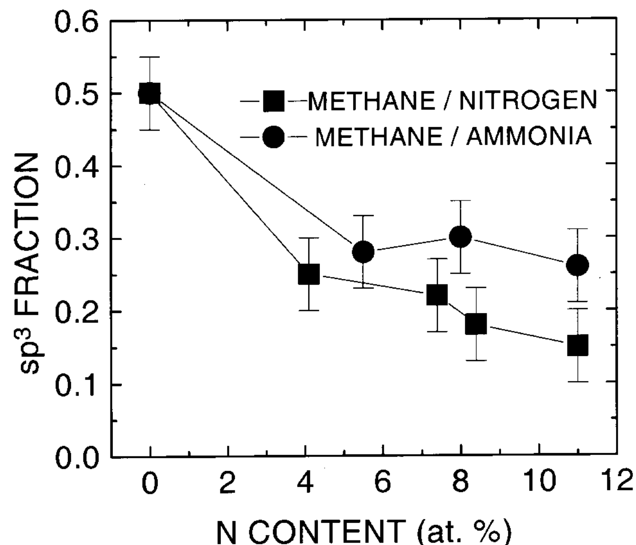

Figure 3. Variation of the C atom sp^3 fraction as a function of nitrogen content for films deposited CH_4-N_2 and CH_4-NH_3 mixtures (reference [8]).

Table 2. The sp^3 carbon atom fraction variation upon nitrogen incorporation.

Ref.	Deposition method	Maximum nitrogen content (at %)	sp^3 C atom fraction range (%)
8	rf-PECVD CH_4/NH_2	11	50-10
8	rf-PECVD CH_4/NH_3	11	50-25
24	ECR-MW CH_4/N_2	4.6	41-15
11	Magnetically enhanced PECVD $CH_4/N_2/He$	15	35-20

As displayed in table 2 nitrogen incorporation in all cases results in a decrease of the sp^3 C atom fraction upon nitrogen incorporation. No sensitivity on the nitrogen precursor gas was observed. Even the use of a high density plasma source could not avoid the sp^3 fraction decrease. This strong decrease in the carbon sp^3 fraction on the nitrogen content was also observed upon nitrogen content in highly tetrahedral amorphous carbon (t-a-C) films [38].

Raman spectroscopy can give complimentary information about sp^2 carbon atom arrangement on amorphous carbon films. As in a-C:H films, the main features of the Raman spectra of a-C(N):H films are the so-called D and G bands present in graphitic carbon materials. Information on sp^2 C atom structure is get from Raman spectra by the analysis of the integrated band intensity ratio I_D/I_G, and the peak positions and widths of the D and G bands, after spectra deconvolution by fitting two gaussian lines to it. Mariotto *et al.* [39] studied the Raman spectra of a-C(N):H films deposited by rf-PECVD in methane-nitrogen atmospheres. They found a continuous increase of the I_D/I_G band ratio upon nitrogen incorporation, and an increase of the G band peak position towards that of crystalline graphite. This behaviour was ascribed to an increase in the size or number of the graphitic clusters present in the film, in accordance with the interpretation stated by Dillon and co-workers [40], in the study of different kinds of amorphous carbons, heat-treated at increasing temperatures. Similar conclusions may be drawn by comparison to results reported by Tamor *et al.* [41], on the study of a-C(H) plasma-deposited films at several self-bias voltages.

Fig. 4 shows a typical variation of Raman spectra upon nitrogen incorporation into a-C:H films, showing spectra taken from films deposited by PECVD in

methane-ammonia atmospheres [20]. The main results of the fitting procedure (I_D/I_G ratio and the peak positions ω_G of the G band) are displayed on table 3 as functions of the nitrogen atomic fraction in the film. This table clearly shows the increase on I_D/I_G and Λ_G upon nitrogen incorporation. Raman spectra taken from a-C(N):H films deposited by different deposition techniques and precursor gas mixtures [42] always show this kind of behaviour.

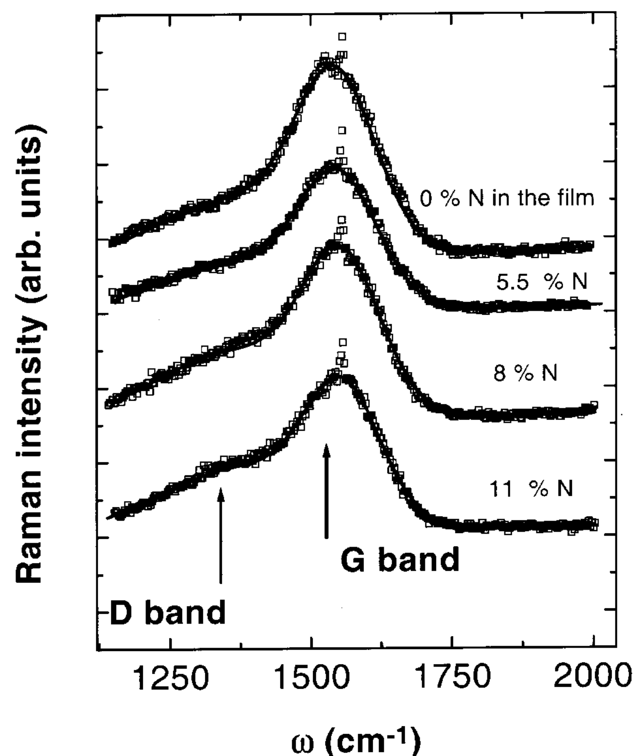

Figure 4. Raman spectra taken from films deposited using CH_4-NH_3 for several nitrogen contents (reference [20]).

Table 3. The Raman band intensity ratio I_D/I_G and G band peak position as functions of the nitrogen content in the film (Ref. 20).

Nitrogen content (at%)	I_D/I_G	ω_G (cm^{-1})
8	0.73	1545
5.5	0.83	1549
7.9	0.98	1555
11	1.07	1557

If we analyse Raman Spectroscopy results together with the above carbon atom hybridisation studies, one can say that nitrogen incorporation into a-C:H films may give rise to an increasing presence of clustered Sp^2 carbon atoms. Such structure modification would give rise to a decrease in the amorphous network connectivity, as suggested by Robertson [43].

Infrared (IR)Spectroscopy has been used to probe local chemical bonds configuration in a-C(N):H films. The main features on the IR spectra of the a-C(N):H films are the C-H band, at about 2925 cm^{-1}, the N-H stretching band, at about 3500 cm^{-1}, the $C \equiv N$ stretching band, at about and a broad band placed in the 1400-1600 cm^{-1} wave-number range. By comparing spectra taken from ^{14}N and ^{15}N-incorporated a-C:H films, Kaufman *et al.* [7] showed the this broad band is in fact an IR observation of the IR-forbidden Raman D and G bands. This is made possible by the symmetry breaking introduced by the presence of polar carbon - nitrogen bonds in the films. The presence of this band clearly shows that there are N atoms bonded to sp^2 carbon clusters in a-C(N):H films.

Fig. 5 shows a typical IR spectra evolution upon nitrogen incorporation into a-C:H films. The figure shows, besides the continuous increase in the Raman, NH, and CN band intensities, a continuous decrease in the CH band intensity, which almost vanishes for the higher nitrogen contents, showing that hydrogen preferentially bonds to nitrogen. As a number of works on a-C(N):H film deposition showed no sensitive variation of hydrogen content upon nitrogen incorporation, we may expect that most of the N atoms would be present as terminal bonds in the amorphous network. This is also the case for the $C \equiv N$ bonds. So, we may expect that nitrogen atoms, at least as a great part, must not be contributing to the network connectivity.

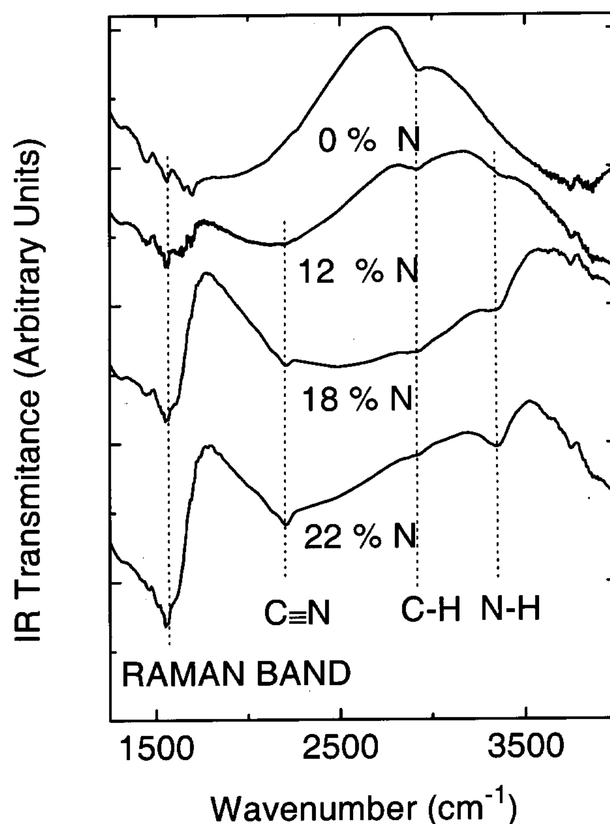

Figure 5. Infrared spectra taken fromfilms deposited using C_2H_2-N_2 mixtures, for several nitrogen contents (reference [22]).

Further support for this conclusion is given by a X-Ray Photo-Electron Spectroscopy (XPS) study on hydrogen incorporation into a-CN_x sputtered films [44]. The XPS results showed that hydrogen interrupts C-N bond formation, and also evidenciated preferential hydrogenation of N atoms.

This is also the case of the ^{13}C NMR spectroscopy study carried out by LaManna *et al.* [45] on a- C(N):H films deposited by rf-PECVD on the grounded electrode. Contrary to most NMR studies on amorphous carbon films, which in general show broad bands associated to sp^2 and sp^3-hibridized atoms, this study found very thin lines superimposed to the broad ones, which were associated to ordered structures. They could fit the obtained spectra to structures similar to nitrogen containing fused aromatic rings terminated by NH_2 groups. Such a structure is very similar to sp^2 carbon clusters bonded to mostly hydrogenated nitrogen atoms.

The formation of network-terminating bonds as a consequence of nitrogen incorporation found also parallel from other observations, not directly related to atomic or electronic structure. Dopler- broadening observation of positron annihilation in a-C(N):H films [46] showed that nitrogen incorporation increases the open volume fraction in the film, what we would expect from the breaking of network interconnections. Hydrogen thermal effusion studies showed, for the same nitrogen-incorporated films, low temperature (about 200°C) effusion peaks. As the compact a-C:H films usually shows only high temperature (about 600°C) hydrogen effusion peaks, the low temperature peaks present in a-C(N):H films were assigned to the presence of open voids in the film [47].

The influence of nitrogen incorporation on the structure modification of amorphous carbon films has also been subject for theoretical investigation. Although almost totally focused on hydrogen-free carbon-nitrogen materials, those works may give some insight to the discussion of hydrogen-containing films.

Weich *et al.* [48] reported a molecular dynamics simulation study on the formation of carbon- nitrogen solids. They studied the nitrogen incorporation on amorphous carbon within several density ranges, and found that the presence of nitrogen induces the continuous increase of the sp^2 C atom fraction in all the cases. Hu *et al.* [49] studied by semiempirical methods the nitrogen incorporation effects in carbon clusters formed by diamond cells, and found that for N contents greater than about 12 at. % a transition to the sp^2 state is likely to occur. Both findings at least support the possibility that the sp^2 C atom increase observed in a-C(N):H films may be due to a chemical bonding effect.

Another approach is to consider the effects of ion bombardment. It is well known that fast ionic species bombardment of film growing surface plays a key role in the formation of C atoms tetrahedral bonding. As it was discussed in session II, the incidence of carbon or nitrogen fast species over a film containing carbon and nitrogen, may give rise to chemical sputtering. As pointed out by Marton *et al.* [50], damage by ion impact may act as a source for trigonal bond formation in carbon-nitrogen films, and thus may be playing a role in a-C(N):H structure.

As discussed above, the structure of a-C(N):H films may be viewed as a over-constrained, stressed random network. So the measurcment of the intemal stress, besides being of practical interest, may give a diagnostics of the degree of overconstrainig, and thus of the connectivity of the amorphous network.

Nitrogen incorporation into a-C:H films result, as a general rule in the reduction of the internal stress [22,42,51]. Fig. 6 shows the internal compressive stress variation for three series of a-C(N):H films rf-PECVD-deposited from different gaseous mixtures [9,20,22]. The three curves show a clear stress decrease upon nitrogen incorporation, at least above a certain nitrogen content. This behaviour is in close correspondence to the above discussed structure changes in a-C(N):H films. The increase on the sp^2 fraction, the clustering of sp^2 carbon bonds, and the introduction of terminal sites in the network, all of them may contribute to the decrease of the number of constrains in the amorphous network, and thus to stress relaxation.

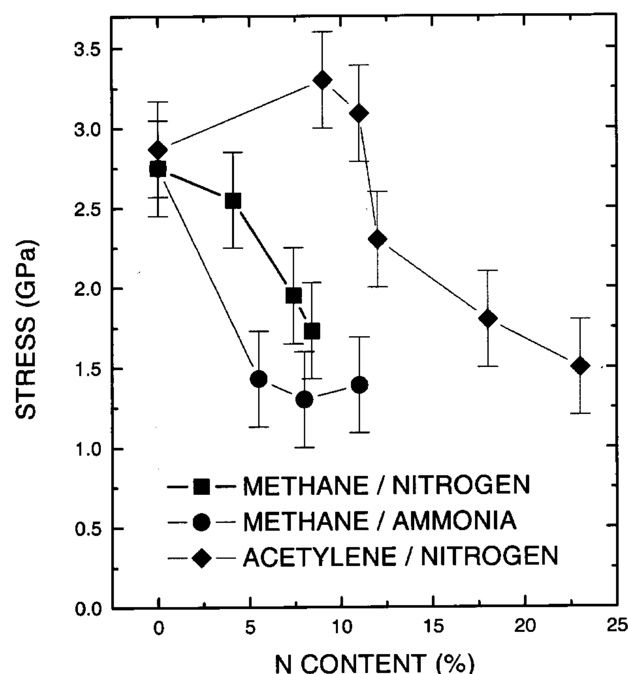

Figure 6. Variation of the internal compressive stress for films derived from CH_4-N_2, CH_4-NH_3 and C_2H_2-N_2 gaseous mixtures, as a function of nitrogen content.

But is also clear in the figure that the stress release is accomplished in different ways for each of the experiments shown. Two of them - the CH_4-N_2 and CH_4-NH_3

series - have shown almost the same C sp^2 fraction variation [8]. The difference observed in the their internal stress variation was ascribed to different variations in the hydrogen content of the two series of samples [9,22]. The hydrogen content may also explain the differentiated behaviour of the C_2H_2-N_2 series, which shows a relatively large nitrogen content range with no stress variation, and the lower hydrogen contents of the three series (See table 1).

Although the internal stress decrease has been always observed upon nitrogen incorporation in a-C(N):H films, the mechanical hardness has shown a spread in the observed behaviour. Some works reported no remarkable changes in the hardness upon nitrogen incorporation, at the same time that a strong decrease is observed in the internal stress [9,10,29]. Other ones reported continuous hardness decrease upon nitrogen incorporation [16,19], as it would be expected from a decreased network connectivity. Different hardness behaviours - constant or decreasing upon N incorporation - as the deposition parameters changed were also observed [16].

The reason for the observed discrepancies may be due to the different methods employed in the hardness measurements. Most of the first works on the mechanical properties of a-C(N):H properties used micro- indentation methods. In this methods, since the depth of indentation may be comparable to thin film thickness, the hardness values measured may be influenced by the substrate hardness, reducing the validity of the comparison between experiments.

More recent studies used nano-indentation techniques for hardness measurement of a-C(N):H films. In this case a hardness decrease has been always observed. This was the case of a-C(N):H films deposited by ECR-MW plasmas in CH_4-N_2 atmospheres reported by Chan *et al.* [52]. Hauert *et al.* observed the same behaviour for films deposited from pentadiene-nitrogen-argon mixtures by DC-biased rf-PECVD [53]. In this case, earlier micro-indentation hardness measurements have shown essentially constant hardness, in films deposited by the same technique and gaseous mixture [10]. Fig. 7 shows the hardness variation for a-C(N):H films rf-PECVD deposited in C_2H_2-N_2 atmospheres, plotted together with the stress variation [22]. The observed variation is rather step-like than a continuously decreasing one. But the hardness clearly falls when the stress show decreasing behaviour.

Atomic Force Microscopy was used to investigate the friction coefficient and surface roughness of a-C(N):H films obtained rf-plasma decomposition of CH_4-NH_3 mixtures [54]. The friction coefficient was found to be insensitive to nitrogen incorporation, being in the 0.2 range. The surface roughness was found to increase by a factor of two for a 11 at % nitrogen content. The roughness increase as upon nitrogen incorporation was also observed by Silva *et al.* [55], and seems to be related to the details of film growth kinetics [36]. In reference [36] a random deposition model for a-C(N):H film growth was used to calculate surface roughness values. A increasing behaviour was found for increasing nitrogen content, as a consequence between growth and the erosion driven by N_2^+ ion bombardment.

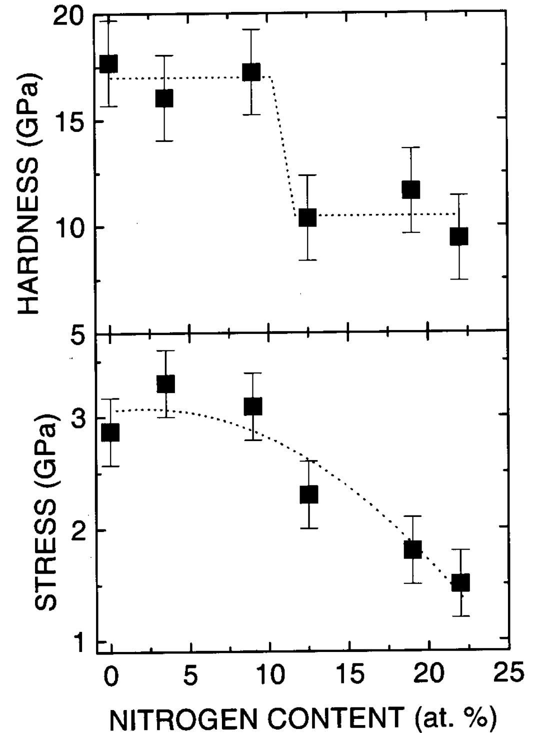

Figure 7. Variation of the nanohardness and internal compressive stress as functions of the nitrogen content (reference 22).

IV Summary

The chemical composition, growth kinetics, structure and mechanical composition changes on the nitrogen incorporation process are reviewed. With minor differences, a-C(N):H films deposited by several techniques, using a range of deposition parameters and precursor gas mixtures, showed the same overall behaviour.

Nitrogen incorporation in the deposition atmosphere cause severe decrease on the film deposition rate, which limits the maximum nitrogen uptake to about 20 at % N. The behaviour of the film growth kinetics seems to be driven by the competition between erosion (carbon atom chemical sputtering by N_2 fast ions and N_2 molecules evaporation) and aggregation processes, being modified by the changes in the hydrogen flux to the growing layer.

The main structure changes observed in a-C(N):H deposition, the decrease of the C atom sp fraction, clustering of the C sp^2 atoms, and preferential hydrogenation of the nitrogen atoms, all of them act in a way to decrease the network connectivity. As a consequence,

the mechanical properties of the films change drastically, as is shown by the strong decrease observed in the mechanical hardness and internal compressive stress. Besides the structure changes, the hydrogen content itself was found to alter the mechanical properties also.

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