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INFRARED ABSORPTION PROPERTIES OF AMORPHOUS CARBON FILMS

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It is presented a detailed investigation of the IR absorption properties for three types of amorphous carbon thin films: hydrogenated amorphous carbon (a-C:H), nitrogen containing hydrogenated amorphous carbon (a-C:H:N) and hydrogen free nitrogenated amorphous carbon (a-C:N). The 2900 cm^{-1} absorption peak, who shown the C-H bonds type and concentration, is used to study the sp^3/sp^2 bond proportion and the hydrogen concentration in films. The presence of the nitrogen is associated with a broad absorption band between 1700 and 1000 cm^{-1}.

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1. Introduction

Over the last two decades amorphous carbon films stimulated growing interest, both scientifically and technologically, by virtue of their unique combination of useful properties [1]. Despite the intensive research, much has yet to be learned about the structure of amorphous carbon films. Their physical properties are intimately correlated with the microstructure at both the atomic level and at intermediate level, where growth mode structures such as voids and columns come into play. It is now well known that the ability of carbon to form different bonding configurations is responsible for the wide range of properties of amorphous carbon films. In particular, the ratio of sp^3/sp^2 is often cited as the controlling factor for both the optical and the mechanical properties [2]. Due to sensitivity of infrared to carbon-hydrogen, carbon-nitrogen and carbon-carbon bonding, infrared spectroscopy has been widely used for structural investigation of hydrogenated and nitrogenated amorphous carbon films [3-5].

The 2900 cm^{-1} absorption peak, who is related to the C-H bonds type and concentration, is used to study the sp^2/sp^3 bond proportion and the hydrogen concentration in films [3]. The interpretation of the absorption IR spectra for nitrogen containing carbon films is not very clear yet. The problem is the broad band between 1700 and 1000 cm^{-1} which represents a superposition of several bond contributions. In the literature, three major assignments can be found for this band: (i) the Raman "G" and "D" bands becoming infrared active by the incorporation of nitrogen into the graphitic rings [6], (ii) various bending modes of CC, NC, CH and NH bonds [7,8] and (iii) a combination of the first two [5].

This paper is an attempt to clarify this problem, starting from the interpretation of IR absorption spectra for three different types of amorphous carbon films. We present a comparative study of the IR absorption spectra for hydrogenated amorphous carbon (a-C:H), nitrogen containing hydrogenated amorphous carbon (a-C:H:N) and hydrogen free nitrogenated amorphous carbon (a-C:N).

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2. Experimental

All films were obtained by magnetron sputtering technique, in radio frequency (RF) plasma from pure graphite target. a-C:H and a-C:H:N films were deposited using a home-built system [4,9] in Ar/CH_4 and Ar/CH_4/N_2 plasma, in a Bacau University laboratory. The unusual use of methane in the gas mixture in the sputtering process implies a combination of sputtering and CVD deposition. The amorphous carbon nitride films were prepared using pure nitrogen as sputtering gas in Amiens University laboratories [10].

The analysis of the different bondings was obtained from IR transmission measurements. To deduce the IR absorption coefficient α, a special care was devoted to the determination of the baseline (i.e. $\alpha = 0$), taking into account the interference fringes in the measured transmission spectra.

3. Results and discussion

We present in Fig. 1 the IR absorption spectra (i.e. α) obtained in the 700-4000 cm^{-1} range for three samples. The a-C:H sample was deposited using the following conditions: working gas Ar/CH_4 = 1/1, gas pressure 1.3 Pa, 70 W RF power, room temperature. For the a-C:H:N film only the gas composition was changed, the proportion between Ar and methane was maintained constant at 1/1 and the volumetric concentration of the nitrogen was 8 %. The a-C:N film was deposited using pure nitrogen as sputtering gas at 2 Pa gas pressure, 150 W RF power and 300 °C substrate temperature.

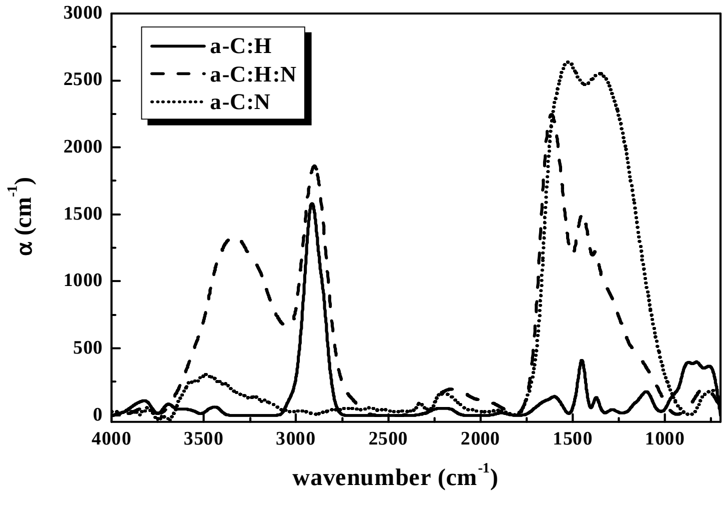

Fig. 1. IR absorption spectra (i.e. α) obtained in the 700-4000 cm^{-1} range for three samples: hydrogenated amorphous carbon (a-C:H), nitrogen containing hydrogenated amorphous carbon (a-C:H:N) and hydrogen free nitrogenated amorphous carbon (a-C:N).

The analysis of the whole absorption spectrum shows four major absorption bands. The first band, between 1000 and 1700 cm^{-1}, is dominated by the nitrogen-related absorption peaks. The second band, around 2200 cm^{-1} is assigned to the vibrations of CN bonds in configurations such as isocyanate (–C=N=O), isonitrile and nitrile [11]. The absorption band at 2800-3000 cm^{-1} is associated with C-H bonds [9], and the large band between 3000 and 3800 cm^{-1} can be related to the O-H and/or N-H vibrational modes [12].

Table 1. Major peak positions in the 1700-1000 cm^{-1} absorption band of hydrogenated carbon nitride films.

	Wavenumber (cm^{-1})	Assignment	Reference
1	1620-1650	C=C, C=N, NH$_x$	[13],[14],[15]
2	~1600	C=N, C=C	[14],[16]
3	1550-1570	Raman G, C=N	[5],[6],[13]
4	1500-1510	C-N, C=N, C=C	[8],[15]
5	1450	sp^3 CH$_x$	[14]
6	1360-1380	Raman D, CH$_3$, CC, C=N	[5],[6],[13],[14],[15]
7	1300-1350	sp^2 carbon, C-N, C=N	[8]
8	1220-1265	C-N (in C$_3$N$_4$), CC, C=N	[15],[17],[18],[19]
9	1020-1150	C-N (aliphatic), N-H	[15]

The broad band observed between 1700 and 1000 cm^{-1} for all nitrogenated samples evidently represents a superposition of several contributions. At a first glance, this broadband is composed of at least five components. For a possible assignment of the individual absorption bands to the corresponding bond configuration an analysis of the published data is necessary. Despite a large variation in the peaks positions and assignments, nine main bands can be identified (Table 1).

Not all these maxima can be found in the absorption spectrum for a given film. Each peak can be correlated with other peaks in the absorption spectrum or with the results of other experiments. For the nitrogen-containing films we carried out the deconvolution of the band into individual absorption peaks, according to the values presented in Table 1. The results are shown in Fig. 2 and in Table 2.

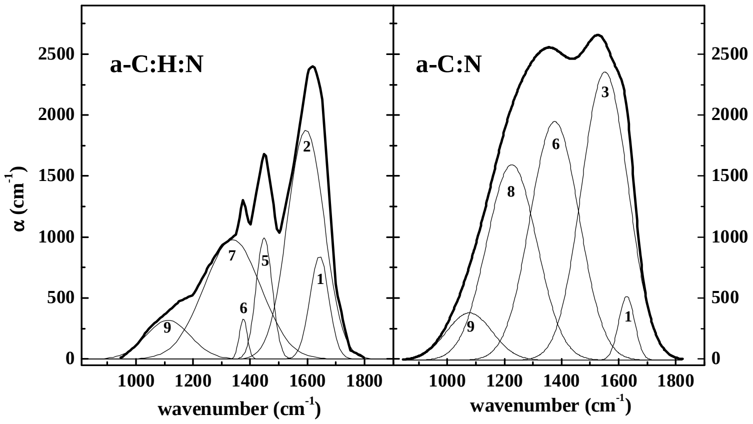

Fig. 2. The deconvolution of the 1000-1700 cm^{-1} absorption band of the nitrogen-containing films. The numbers are related to Table 1 peaks positions.

Table 2. Peak positions in the 1700-1000 cm^{-1} absorption band deconvolution of hydrogenated carbon nitride films.

	Predicted wavenumber (cm^{-1})	Obtained wavenumber (cm^{-1}) a-C:H:N	 a-C:N
1	1620-1650	1639.4	1628.2
2	~1600	1598.6	-
3	1550-1570	-	1551.8
4	1500-1510	-	-
5	1450	1448.4	-
6	1360-1380	1377.4	1376.0
7	1300-1350	1357.8	-
8	1220-1265	-	1225.8
9	1020-1150	1105.9	1077.1

The shape of the band and its deconvolution is very different for the two films, showing different properties. In first case, the 2900 cm^{-1} peak position and amplitude suggest large quantities of sp^3 bonded CH_2 and CH_3 groups, that implies the presence of the 1450 and 1370 cm^{-1} peaks [4]. The absence of the absorption at 3050 cm^{-1} offers evidence that sixhold aromatic structures are not major components in this polymeric films [20]. In these conditions, the influence of the Raman D (at 1360-1380 cm^{-1}) and Raman G (at 1550-1570 cm^{-1}) peaks can be neglected but the 1370 cm^{-1} feature still remains in deconvolution because of the CH_3 contribution, like in nitrogen-free film (Fig. 1). The absence of the 1450 cm^{-1} peak for a-C:N film confirms the allocation of this absorption band. On the other hand, the importance of the Raman D (at 1376 cm^{-1}) and Raman G (at 1552 cm^{-1}) peaks for this sample implies a dominant graphitic structure for the material. It is almost generally accepted the hypothesis that carbon-nitrogen bonding breaks the symmetry in *sp*^{2} domains and causes the C=C symmetric bonds to become IR active [21]. Moreover, it has been recently reported, for sputtered a-CN_x films, using FTIR, XPS, XANES and NMR measurements, that the 1000-1800 cm^{-1} absorption band must involve contributions from CN complexes in sp^2 domains [22]. In these conditions, the major contribution of the 1220-1265 cm^{-1} is from C=N and C-C bonds and not from sp^3 C-N in C_3N_4 structures. The presence of the C=C peak at 1600 cm^{-1} in nitrogen-free film suggests a similar position of the peak in the nitrogenated samples spectra, but the absence for hydrogen-free sample suggest an influence of the hydrogen.

The 2900 cm^{-1} absorption peak shows the C-H bonds type and concentration. The shape and position of the peak are similar for both hydrogen-containing samples, indicating a low variation of the proportion of sp^3 bonds. The evidence of the very high value of the sp^3 fraction is shown in Fig. 3 where it is presented the infrared absorption spectrum for the C-H stretching mode region for a-C:H and a-C:H:N samples. For a-C:H sample, the spectrum can be decomposed to seven Gaussian components, and for a-C:H:N film, to five bands. The positions of these components are in very good agreement with other results [23,24] and are summarized in Table 3. From the large difference between sp^3 peaks (3, 4 and 5 in Fig. 3) and sp^2 peaks (1 and 2 in Fig. 3) area we conclude that the type bonding of C adjacent to H is predominantly sp^3 [9].

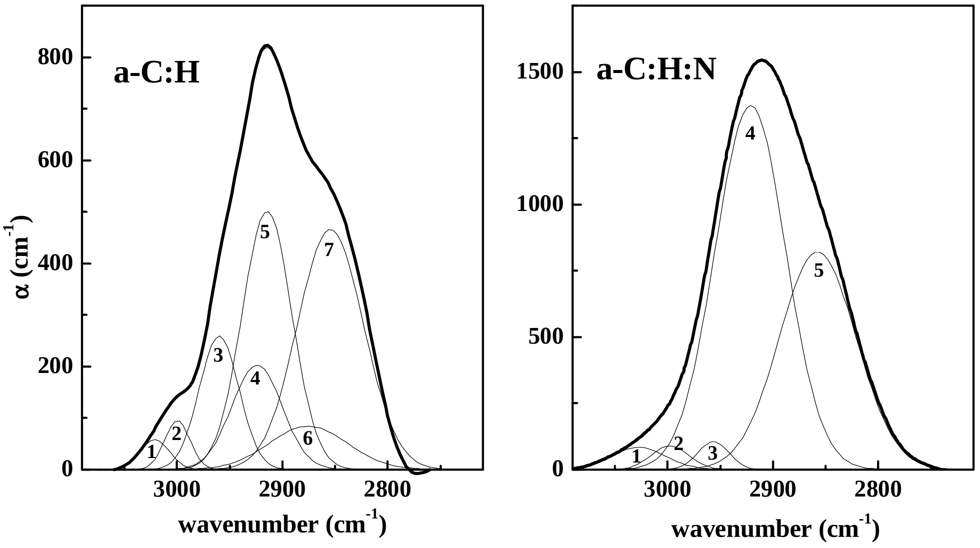

Fig. 3. The deconvolution of the 2900 cm^{-1} absorption band of the hydrogen-containing films. The numbers are related to Table 3 peaks positions.

The two deconvolutions show a great reduction of the amount of terminal sp^3 CH_3 group (peaks 3 and 6) for the a-C:H:N film. This implies an increase of the polymeric chain length. It is remarkable the increase of the intensity and width of the sp^3 peaks in the film containing nitrogen, compared to the film lacking nitrogen. This feature can be ascribed to the effect of nitrogen which induces the formation of sp^3 bonding in CH_3 and CH_2 groups, with a greater structural disordering of these groups.

All the nitrogenated films present a broad feature between 3700 and 3000 cm^{-1}, associated with N-H and O-H bonds [7]. The results of infrared absorption show additional bands due to O–H bond stretching modes, which are probably related to the contamination by oxygen and water. It is evident that the contamination is more advanced when the nitrogen is present.

Table 3. Obtained peaks positions in the 2900 cm^{-1} absorption band deconvolution of hydrogenated carbon films.

	Predicted wavenumber (cm^{-1})		Obtained wavenumber a-C:H	(cm^{-1}) a-C:H:N
1	3020	sp^2 CH_2 (olefinic)	3020.9	3027
2	3000	sp^2 CH (olefinic)	2999.6	2998
3	2960-2970	sp^3 CH_3 (asymmetrical)	2960.0	2956
4	2920-2925	sp^3 CH_2 (asymmetrical)	2924.1	2921
5	2915-2920	sp^3 CH	2914.6	
6	2865-2875	sp^3 CH_3 (symmetrical)	2875.3	-
7	2850-2855	sp^3 CH_2 (symmetrical)	2854.3	2858

4. Conclusions

The IR absorption spectrum can offer fast and valuable informations about film structure and composition. The decomposition of the absorption band indicates the graphitic/tetrahedral dominant character of the material. For the hydrogenated films, the 2900 cm^{-1} absorption band is very important and indicates the presence of carbon-hydrogen bonding. The broad absorption band situated in the range 1000-1700 cm^{-1} was associated to the presence of nitrogen. In a-C:H:N films it was demonstrated by deconvolution of the absorption band situated at 2900 cm^{-1} that the contribution of the sp^3 CH_2 group increases when nitrogen is present, thus proving the increase of the length of polymeric chains.

For a complete analysis, other investigation methods must be used: Raman spectroscopy, X-ray methods, nuclear methods. Despite all the interpretations, the IR absorption remains a fast and cheap method for a qualitative analysis of the amorphous carbon films, when the hydrogen and/or nitrogen is present.

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