CHARACTERIZATION OF NITROGEN INCORPORATED CARBON FILMS DEPOSITED BY RF-GLOW-DISCHARGE USING ERD, RBS, NUCLEAR REACTOR, X-RAY DIFFRACTION AND INFRARED SPECTROSCOPY

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Abstract

We report a study on nitrogen incorporation into hard a-C: H thin films were deposited by RF self-bias glow-discharge in a CH_4-N_2 atmosphere, under several conditions of total pressure, N_2 partial pressure and measured self-bias. Elemental analysis of the obtained films was carried out by Nuclear Reaction Analysis, Rutherford Back-Scattering Spectroscopy and Elastic Recoil Detection. Film structure was studied by infrared spectroscopy and X-Ray diffraction. Results show that N_2 partial pressure is the major factor affecting nitrogen incorporation, not being detected any influence of the self-bias on nitrogen content. Infrared spectra show that nitrogen is effectively incorporated in the amorphous network.

Keywords: a-C: H; diamond-like carbon; ion beam analysis; infrared spectroscopy; glow-discharge.

INTRODUCTION

Amorphous hydrogenated carbon (a-C: H) films deposited by plasma decomposition of hydrocarbon gases may be quite hard, with hardness values often higher than that of silicon carbide [1], insulating and resistant against corrosion. These properties make hard a-C: H films a candidate for several applications, specially as protective coatings. The structure and properties of these films, mainly those deposited by self-bias glow-discharge, have been extensively studied under a wide range of deposition parameters [2-5]. These studies reported on a strong dependence of structure and chemical composition, as well as the mechanical, electrical and optical properties on deposition pressure and measured self-bias V_B.

Recently, there have been reports of the effects of nitrogen incorporation into a-C: H films [6-8]. It has been shown that nitrogen incorporation causes the reduction of the electrical resistivity [6] and of the optical band-gap width [7]. None of these works used a deposition process that can be clearly characterized as self-bias glow discharge. In this work we report on a study on the characterization of nitrogen-incorporated a-C: H films deposited by self-bias glow-discharge in CH_4-N_2 atmospheres, under several conditions of deposition pressure, measured self-bias and N_2 partial pressure.

EXPERIMENTAL

The nitrogen incorporated a-C: H films were deposited on undoped Si(100) substrates, which were mounted over the stainless steel cathode of a Varian RF(13.56 MHz) diode sputtering system. Three sets of films were produced, the first two at a constant self bias voltage of -370V, with N_2 concentration in the plasma ranging from 0 to 50%, at deposition pressure of 0.8 and 8 Pa. The third set was produced at a deposition pressure of 8 Pa and 25% nitrogen concentration in plasma, while varying the self-bias from -200 to -950 V. The thicknesses of the obtained films was determined by measuring the height of the step produced by the clamps used to fix the substrates on the electrode, with a Dektak IIA stylus profilometer.

Chemical analysis of the films was performed by MeV ion bean techniques. Hydrogen content was determined by Elastic Recoil Detection of protons using a 2.2 MeV, $^4He^+$ incident beam. Nitrogen content was determined by a $^{14}N(d, p)^{15}N$ nuclear reaction, excited by a 610 KeV deuteron beam. The presence of oxygen in the films was also checked by nuclear reaction analysis. Carbon content was

determined by Rutherford Back-Scattering Spectroscopy (RBS).

Film structure was studied by submitting the samples to FTIR spectroscopy and X-ray diffraction. Infrared spectroscopy was performed by a Perkin-Elmer 1700 FTIR spectrometer. X-ray diffraction analysis was made in a Rigaku goniometer coupled to a Phillips X-ray generator, using Mo K_α radiation.

RESULTS AND DISCUSSION

The deposition rate dependences on N_2 partial pressure in the plasma, and self bias V_B are shown in figure 1. In figure 1(a) the deposition rate is plotted against N_2 partial pressure, for films obtained at 0.8 and 8 Pa, with V_B fixed at -370V The two curves show a dramatic decrease in deposition rate upon increasing of N_2 partial pressure. This decrease cannot be attributed to a simple dilution effect, as it is suggested by comparison between deposition rate values obtained from films deposited with 0% N_2, which show a factor of two reductions in deposition rate for a ten-fold decrease of total pressure, although the addition of 50% N_2 in the plasma resulted in nearly vanishing the deposition rate. In figure 1(b) the deposition rate is plotted against the measured self-bias, for films obtained with 8 Pa and 25% N_2 in plasma. The curve shows a maximum for V_B equal to -800 V Such a behavior was previously reported for undoped a-C: H films and has been attributed to the onset of sputtering induced by the more energetic ions produced at higher self-bias values [2].

Concerning to the chemical composition, the films studied in this work were found to be oxygen-free as determined by nuclear reaction analysis, and heavy element-free as determined RBS. The hydrogen content of the films has found to be constant within experimental error, upon nitrogen incorporation and self-bias variation, as shown on table 1. The constant behaviour of the hydrogen content upon nitrogen incorporation is consistent with results reported by Kaufman et al [8] As expected, the nitrogen content was found to increase upon increasing N_2 partial pressure, as shown in figure 2(a). No changes on nitrogen content were found upon self-bias variation, as shown in figure 2(b).

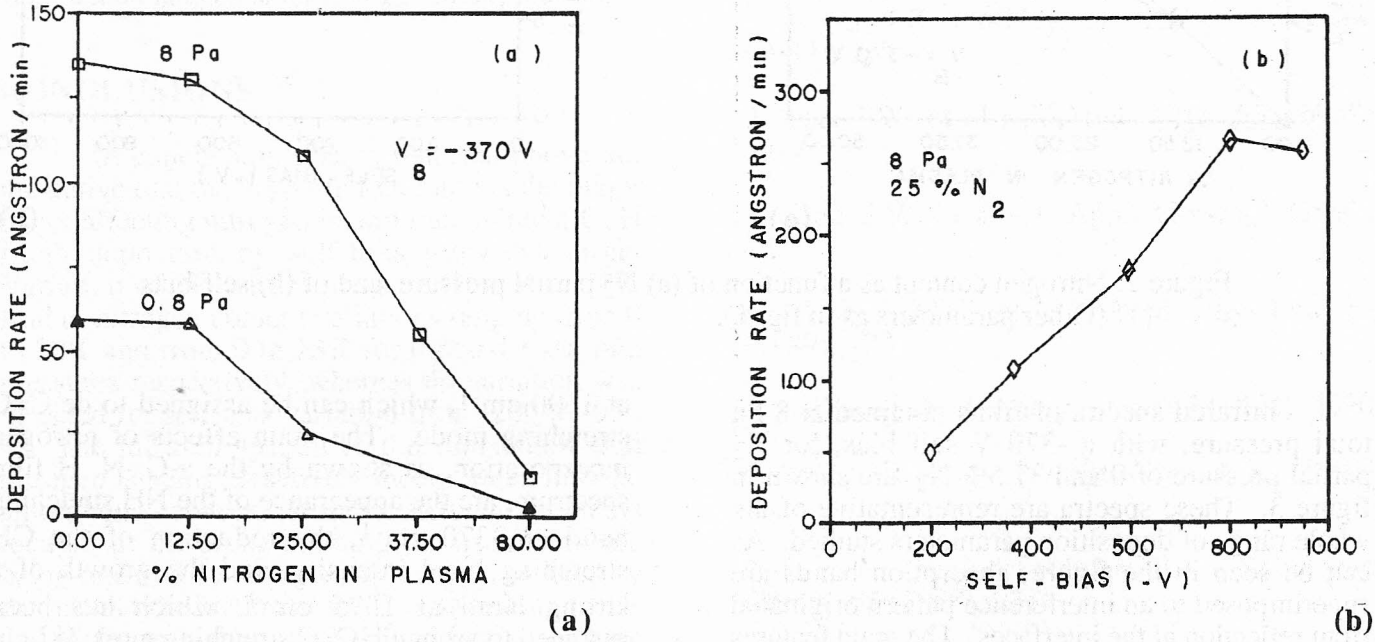

Figure 1. Deposition rate as a function of (a) N_2 partial pressure, with fixed V_B and total pressure, and of (b) V_B, with fixed total pressure and N_2 partial pressure.

Table 1. Hydrogen content determined by Elastic Recoil Detection
(I) Films deposited with fixed V_B, at total pressures indicated.
(II) Films deposited at 8 Pa total pressure and 25% N in plasma.

(I)			(II)	
$\%N_2$ in plasma	Hydrogen content (%)		self-bias (V)	Hydrogen content (%)
	(0.8 Pa)	(8 Pa)		
0	15.3	12.8	-200	-
12.5	13.7	15.8	-370	13.7
25.0	12.0	13.7	-600	17.13
37.5	-	12.0	-800	16.6
50.0	-	16.6	-950	16.3

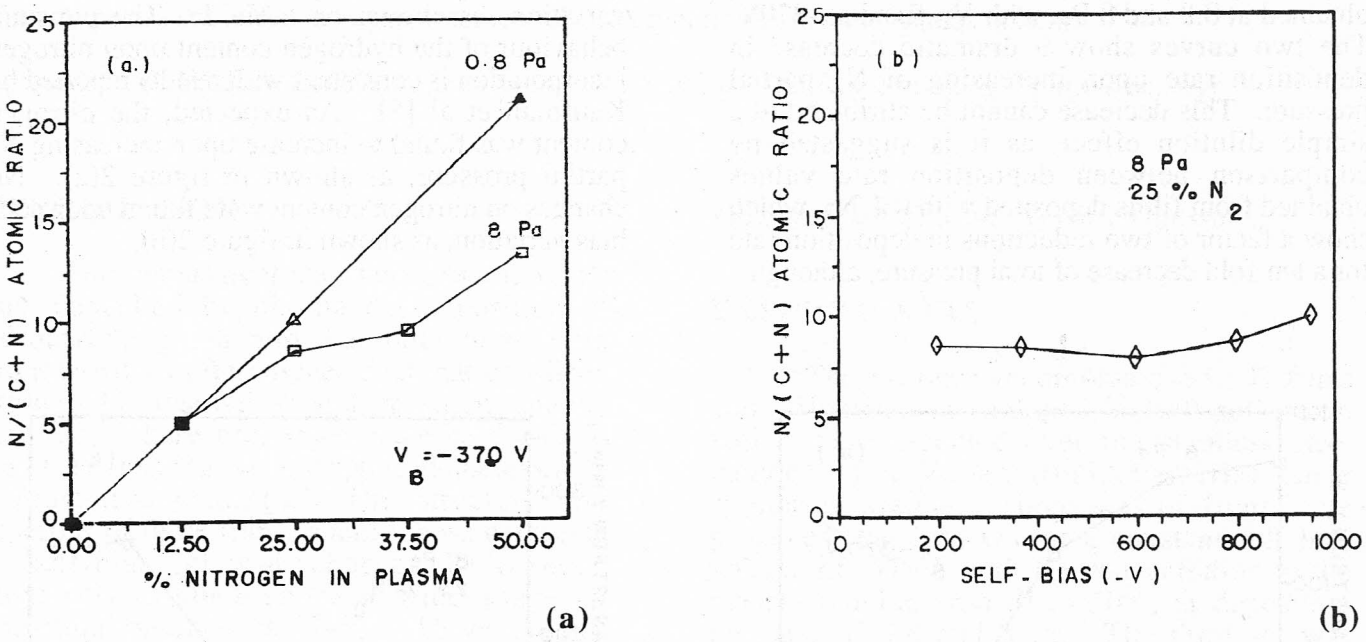

Figure 2. Nitrogen content as a function of (a) N_2 partial pressure, and of (b) self-bias. (Other parameters as in fig. 1).

Infrared spectra of films obtained at 8 Pa total pressure, with a -370 V self bias, for N_2 partial pressure of 0 and 37.5% N_2 are shown in figure 3. These spectra are representative of the whole range of deposition parameters studied. As can be seen in the figure, absorption bands are superimposed to an interference pattern originated from reflection at the interfaces. The main features of the pure a-C: H film spectrum are the C-H stretching (2920 cm^{-1}) and bending (1450 cm^{-1}) modes. This spectrum also displays a small band at 1600 cm^{-1}, which can be assigned to de C=C stretching mode. The main effects of nitrogen incorporation, as shown by the a-C, N: H film spectrum, are the appearance of the NH stretching band at 3370 cm^{-1}, the reduction of the CH stretching band intensity, and the growth of a strong band at 1575 cm^{-1}, which has been assigned to aromatic C=C stretching mode [8]. In reference [8] this band was correlated to an infrared observation of Raman vibrational modes characteristic of graphitic micro-domains, which

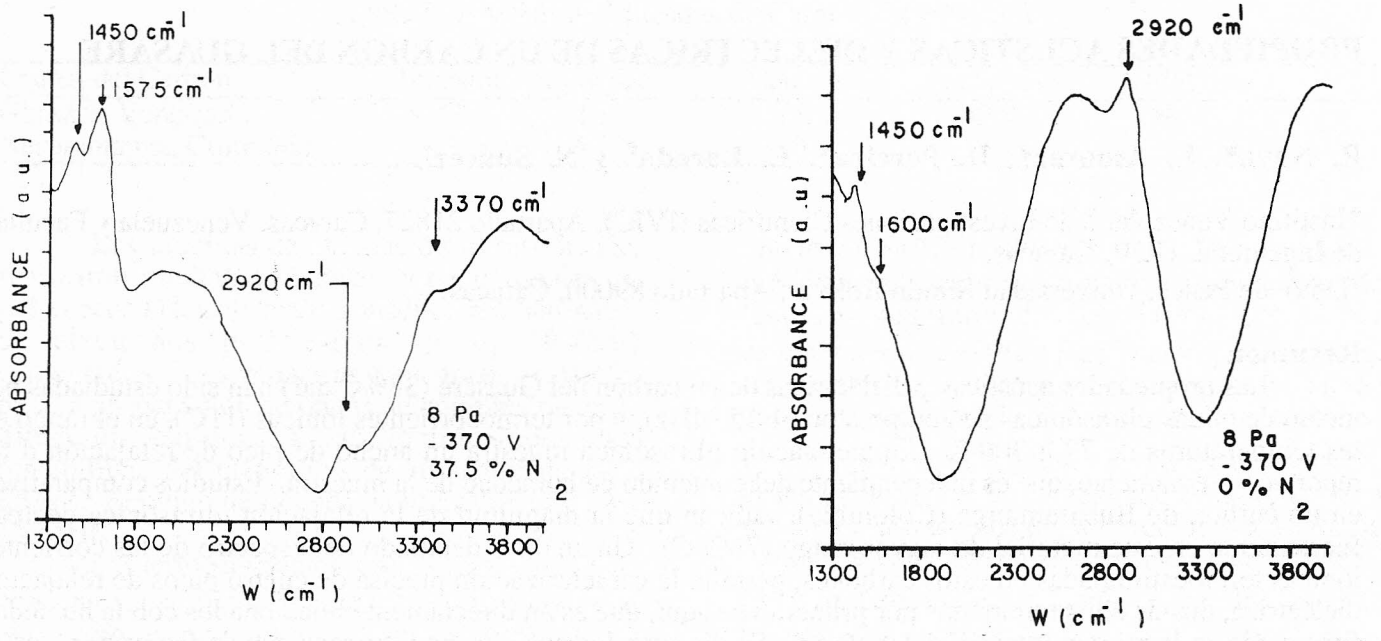

Figure 3. Infrared spectra of films deposited with 0 and 37.5 %N_2 partial pressures. (Other parameters indicated in figure).

was made possible by the symmetry breaking diffraction patterns taken from films obtained at 8 Pa total pressure, with -370 V self-bias and varying N_2 concentration, showed only diffuse bands characteristic of amorphous solids, with very small changes upon nitrogen incorporation.

CONCLUSIONS

In conclusion, results reported above are indicative that the N_2 partial pressure is the major factor affecting nitrogen incorporation into a-C: H films deposited by self-bias glow-discharge. Variation of N_2 partial pressure from 0 to 50% lead to nitrogen content variations ranging from 0 to 20% and from 0 to 13% for 0.8 and 8 Pa total pressures respectively, whereas no variation was detected for self-bias variation from -200 to -950 V. The infrared spectra of the films show that nitrogen is being effectively incorporated into the amorphous network. It seems that carbon atoms located at different bonding environments are being replaced by nitrogen, as it is evidenciated by the intensity reduction of the C-H stretching bands and by the growth of the N-H and C=C stretching bands.

Work on the determination of the mechanical properties and on Raman and Auger spectroscopy analysis of the films studied in this work is now in course.

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