

# Amorphous hydrogenated carbon-nitride films prepared by RF-PECVD in methane–nitrogen atmospheres

E.F. Motta\*, I. Pereyra

*Departamento de Engenharia de Sistemas Eletrônicos, Escola Politécnica, Universidade de São Paulo,  
CP: 61548 CEP: 05424-970, São Paulo, SP, Brazil*

Available online 8 May 2004

## Abstract

In this work, films are deposited by PECVD-RF plasma using a gas mixture of CH<sub>4</sub>, N<sub>2</sub> and He or Ar. The Ar/CH<sub>4</sub> and He/CH<sub>4</sub> ratio is kept constant, while the nitrogen flow is allowed to vary. The samples were arranged in the anode plate as well as in the cathode plate. The effect of nitrogen addition on the films optical and structural properties of the films was analyzed by FTIR spectroscopy, UV–VIS–NIR spectroscopy, profilometry, ellipsometry and RBS. The intensities of the C=N (1600 cm<sup>-1</sup>), C=N (2300 cm<sup>-1</sup>) and NH (3250 cm<sup>-1</sup>) absorption bands, in the IR spectra, increase with the N<sub>2</sub>/CH<sub>4</sub> flow ratio. Samples deposited in the grounded electrode, show a decrease in the CH<sub>n</sub> stretching band for increasing N<sub>2</sub>/CH<sub>4</sub> flow ratio, while the NH absorption band increases, indicating that hydrogen is preferentially bonded to nitrogen. The C=N absorption increases for increasing N/C ratio; indicating that a nitrile phase is also formed. For the samples deposited in the powered electrode (Fig. 5), the CNH absorption band (1000–1700 cm<sup>-1</sup>) is much larger than the other bands (CH<sub>n</sub> and NH). The increasing signal in the 1000–1300 cm<sup>-1</sup> region suggests an increase in nitrogen bonding with sp<sup>3</sup> C. The C=N absorption is very small compared with the samples deposited in the grounded electrode. This behavior could be attributed to the increase in the methane and nitrogen radicals caused by stronger ion bombardment in the active electrode.

© 2004 Elsevier B.V. All rights reserved.

PACS: 81.15.-z; 81.05.-t

## 1. Introduction

In the last few years there has been an increasing interest in the study of nitrogen incorporation into hard amorphous hydrogenated carbon (a-C:H) films. Research into the search for proposed β-C<sub>3</sub>N<sub>4</sub> phase, which is predicted to be harder than diamond, was initiated by Liu and Cohen [1]. As a result of the nitrogen incorporation into carbon films it was found that both optical and the electrical properties [2,3], as well as the mechanical properties of the material can be modified. The mechanical properties are mainly controlled by the fraction of sp<sup>3</sup> bonded carbon, forming the skeleton of the material, the optical and electrical properties are determined by clustering of the sp<sup>2</sup> sites (rings or chains) and by the hydrogen content which decreases the connectivity of the sp<sup>3</sup>, forming termination CH<sub>n</sub> groups,

therefore lowering the hardness of the material [4,5]. Conventional plasma deposition processes result in films where, both the H content and the sp<sup>3</sup> fraction decrease with increasing ion energy, so that films are polymer-like at low ion energy and graphite-like at high ion energy. For low nitrogen content (up to 20%) the films retain their diamond like properties, however as the N/C atomic ratio increases, a polymer-like material is formed, with —C=N— structures and terminating C=N and NH groups that decrease the connectivity of the network [6].

Among the deposition processes reported, plasma-enhanced chemical vapor deposition (PECVD) possess the benefits of uniform large area deposition and easy handling, although promising results of the formation of crystalline β-C<sub>3</sub>N<sub>4</sub> has been reported by using a great variety of high energy input processes [7]. Smith et al. [8] reported that an RF parallel plate reactor design with the substrate mounted on the driven electrodes is the preferred choice for PECVD deposition. This configuration is employed to maximize energetic ion flux at the

\* Corresponding author.

E-mail address: [emotta@lme.usp.br](mailto:emotta@lme.usp.br) (E.F. Motta).

substrate during the films growth process. They found that driving the powered electrode with dual frequency power and introducing nitrogen into the gas mixture, they could produce films with DLC characteristics at conditions that would otherwise yield polymeric depositions.

In this paper we discuss the results on the growth behavior, chemical composition, bonding structure and optical properties of the a-C:H:N films deposited by the conventional radio frequency PECVD technique from methane (CH<sub>4</sub>), argon (Ar), helium (He) and nitrogen (N<sub>2</sub>) mixtures at temperatures lower than 100 °C. The films were characterized by Fourier transform infrared spectroscopy (FTIR), optical absorption and RBS technique due to the efficacy of these techniques for studying the chemical bonding in the films as well as the structure of the material [8–10], allowing to investigate the chemical composition, the N incorporation modes and the nature of the bonding between C atoms.

## 2. Experimental

The films were deposited in a standard 13.56 MHz RF-PECVD in a capacitively coupled reactor in diode configuration, from appropriated gaseous mixtures of methane (CH<sub>4</sub>), nitrogen (N<sub>2</sub>) and helium (He) or argon (Ar). The gas flow was controlled by mass flow controllers and the deposition pressure is monitored by a capacitance manometer (Baratron type) [9,11]. Films with different nitrogen and carbon contents were obtained fixing the methane and noble gas flows and varying the nitrogen flow. The samples were placed in both electrodes (grounded and powered) in order to analyze the effect of the ion bombardment on films properties. All the samples studied were deposited at 100 °C. The RF power was also kept at 250 W in order to obtain high deposition rates. The deposition pressure was kept at 250 mTorr. The deposition conditions for all the studied samples are listed in Table 1.

The refractive index of the deposited films was measured by ellipsometry in a Rudolph Research Auto E1 instrument, having a He–Ne laser (632.8 nm) as light source. The measurements were carried out at different points of the films in order to determine the standard deviation of the measured parameter along the sample. A (FTS-40 BIORAD) Fourier-transform infrared spectrometer was employed to analyze the chemical bonding

within the material and to give insight into their composition and structure. The detection limit of this equipment is given by an integrated area of  $\sim 2.5 \text{ cm}^{-1}$  with resolution of  $2 \text{ cm}^{-1}$ . Furthermore, the optical gaps of the samples were determined through optical absorption measurements performed in a UV–VIS–NIR Varian (model CARY-500) spectrometer. Finally, the amount of C and N atoms per unit area ( $\text{atoms cm}^{-2}$ ) were obtained by Rutherford backscattering spectroscopy (RBS) experiments done at LAMFI/USP, São Paulo, using a He<sup>+</sup> beam with an energy  $E = 2.4 \text{ MeV}$ .

The samples produced in the former system were deposited onto p-type, (100) single-crystalline silicon substrates in the 7–13  $\Omega\text{cm}$  resistivity range for ellipsometry and Fourier-transform infrared spectroscopy (FTIR) characterization. For the RBS measurements the films were deposited onto ultra-dense amorphous carbon, and for optical absorption, Corning glass substrate were utilized.

## 3. Results and discussion

In Fig. 1 the deposition rate for films deposited on both the grounded and the powered electrodes with CH<sub>4</sub> flow fixed at 3.3, 10 and 30 sccm and varying N<sub>2</sub> flow are shown. 75 sccm of He or Ar were added to the gaseous mixture to help in the break of the CH<sub>4</sub> molecules. It can be verified that the deposition rate tends to decrease for increasing nitrogen flow. The deposited samples using Ar in the gaseous mixture exhibit a smaller deposition rate, than those deposited with He. It was observed a decrease in deposition rate for increasing N<sub>2</sub> flow that could be attributed to the decrease in CH<sub>n</sub> radicals in the plasma provoked by the excess of N<sub>2</sub>, also there is a chemical sputtering of the growing surface induced by the N<sub>2</sub><sup>+</sup> bombardment [6,11]. Fig. 1(b) does not show data for samples deposited with Ar because no films deposition occurred in these conditions. This can be due to the intense N<sub>2</sub><sup>+</sup> and Ar<sup>+</sup> ions bombardment of the sample at the powered electrode. In the case of He diluted gaseous mixtures a decrease in the corrosion effect is observed. This can be a result of the less aggressive sputter etch of He compared to Ar and to the increased chemical reactivity of the plasma, due to the increase in CH<sub>n</sub> radicals, induced by He<sup>+</sup>, favoring the deposition process in opposition to the etching process.

Table 1  
Deposition conditions of the samples studied

CH <sub>4</sub> flow (sccm)	He flow (sccm)	N <sub>2</sub> flow (sccm)	Pressure (mTorr)	RF-power (W)	Temperature (°C)
3.3	25	50–125	250	250	100
10.0	75	1–10			
30.0	75	5–15			

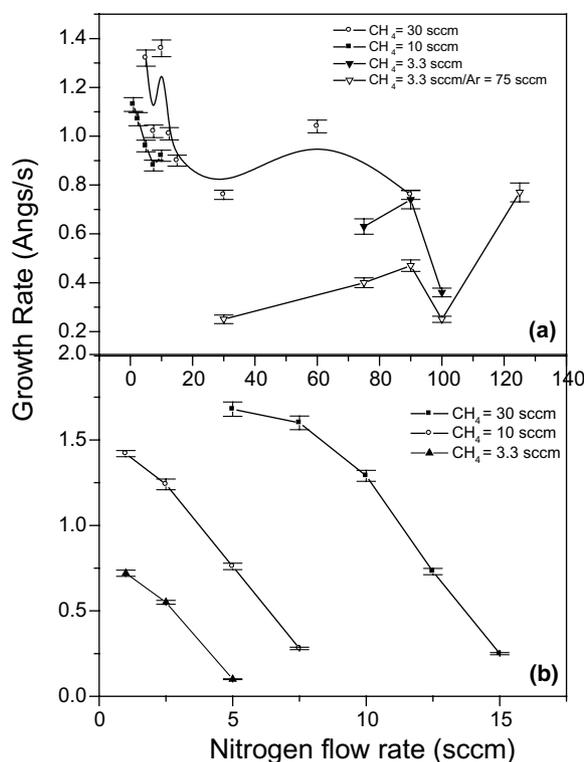


Fig. 1. Deposition rate as a function of the  $N_2$  flow ratio by four different  $CH_4$  flow, deposited on both the grounded (a) and the powered (b) electrodes.

Fig. 2 shows the N/C atomic ratio in the solid phase as a function of nitrogen to methane flow ratio ( $N_2/CH_4$ ), obtained by RBS experiments. An increase in the nitrogen incorporation for increasing  $N_2/CH_4$  ratios is observed which saturates for higher  $N_2/CH_4$  ratios. Similar results have been reported for material grown in FCVA system [4] and Electron Cyclotron Wave Resonance [5]. The maximum N/C value obtained is well below the 1.33 expected for theoretical  $C_3N_4$  [3,5]. The saturation trend represents one of the major difficulties for obtaining carbon nitride films. The samples deposited in the powered electrode present larger nitrogen incorporation than samples deposited in the grounded electrode.

The refractive index and the optical gap, obtained by the Tauc extrapolation technique from the optical absorption data for the films, reported in Table 2, show that: the refraction index as well as the optical gap re-

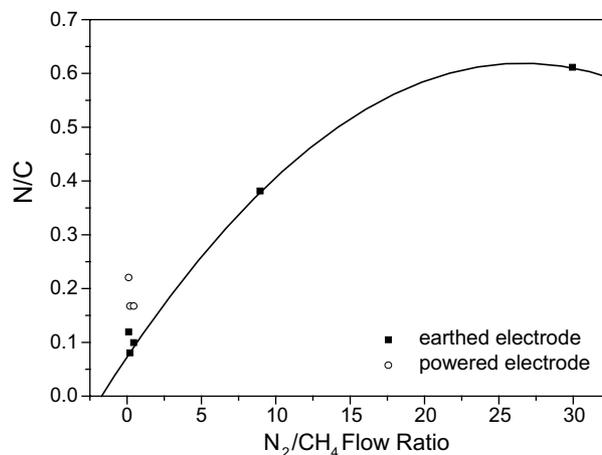


Fig. 2. The N/C atomic ratio in the solid phase as a function of nitrogen to methane flow ratio ( $N_2/CH_4$ ), obtained by RBS experiments.

mains almost constant for increasing nitrogen flow, indicating apparently that the structure of the material is not affected by the  $N_2$  flow. However, the refraction index increases and the optical gap decreases for increasing  $CH_4$  flow, which can be interpreted as due to an increase in  $sp^2$  carbon configuration.

The infrared spectra for some samples are shown in Fig. 3 (grounded electrode) and Fig. 4 (powered electrode) for different  $N_2/CH_4$  flow ratios. The spectra show the following absorption bands: The C–N ( $1020\text{--}1280\text{ cm}^{-1}$ ), C=N groups ( $1610\text{--}1660\text{ cm}^{-1}$ ), NH bending ( $1590\text{--}1640\text{ cm}^{-1}$ ),  $NH_2$  bending ( $1555\text{--}1590\text{ cm}^{-1}$ ),  $CH_n$  bending ( $1350\text{--}1450\text{ cm}^{-1}$ ), C=C bonds ( $1300\text{--}1500\text{ cm}^{-1}$ ), C=N stretching band at  $2200\text{ cm}^{-1}$ , the  $CH_n$  stretching band at  $2800\text{--}3000\text{ cm}^{-1}$  and NH absorption band at  $3300\text{--}3500\text{ cm}^{-1}$  [12–18]. Samples deposited in the grounded electrode, show a decrease in the  $CH_n$  stretching band for increasing  $N_2/CH_4$  flow ratio, while the NH absorption bond increases, indicating that hydrogen is preferentially bonded to nitrogen. The C=N absorption increases for increasing N/C ratio; indicating that a nitrile phase is also formed. Finally, a decrease in the C–N and  $CH_n$  bending together with an increase in the related C=N bonds with the increasing nitrogen flow is observed, indicating that nitrogen in large amounts facilitates the CN double bond in detriment of the other ones.

Table 2

The refractive index and the optical gap, obtained by the Tauc extrapolation technique from the optical absorption data for the films, prepared with He added to the gaseous mixture

Samples	CH <sub>4</sub> flow = 3.3 sccm		CH <sub>4</sub> flow = 10 sccm		CH <sub>4</sub> flow = 30 sccm	
	Powered electrode	Grounded electrode	Powered electrode	Grounded electrode	Powered electrode	Grounded electrode
Refractive index	–	1.93	2.2	1.86	2.55	1.66
Tauc gap (eV)	–	3.1	2.0	2.5	1.9	2.2

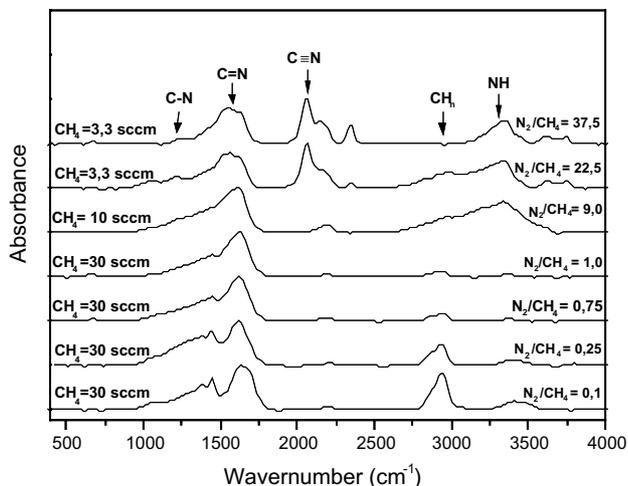


Fig. 3. Normalized absorption FTIR spectra taken from films with increasing  $N_2/CH_4$  ratio for samples deposited in the grounded electrode.

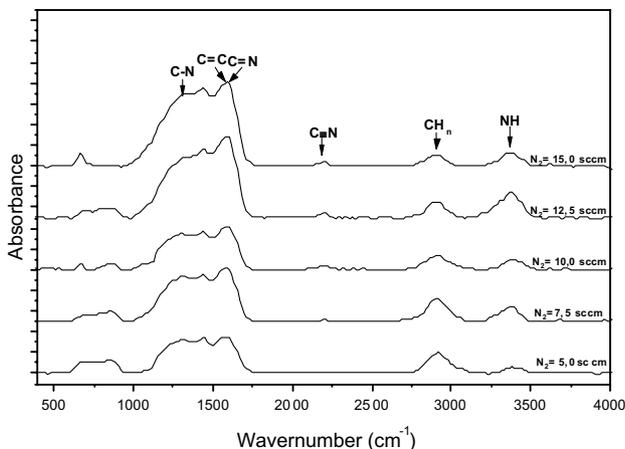


Fig. 4. Normalized absorption FTIR spectra taken from films with increasing  $N_2$  flow for samples deposited in the powered electrode with  $CH_4$  flow of the 30 sccm and He flow of the 75 sccm.

For the samples deposited in the powered electrode (Fig. 4), the CNH absorption band ( $1000\text{--}1700\text{ cm}^{-1}$ ) is much larger than the other bands ( $CH_n$  and NH). The increasing signal in the  $1000\text{--}1300\text{ cm}^{-1}$  region suggests an increase in nitrogen bonding with  $sp^3$  C. The C=N absorption is very small compared with the samples deposited in the grounded electrode. This behavior could be attributed to the increase in the methane and nitrogen radicals provoked by stronger ion bombardment in the active electrode. The obtained results are in accordance to the most recent results in the literature [19,20]. Even more our PECVD samples deposited in the powered electrode resemble samples deposited by reactive magnetron sputtering [17,21,22], presenting larger  $\beta\text{-C}_3\text{N}_4$  fraction than reported PECVD samples.

#### 4. Conclusion

In this work we studied the process of deposition of a-C:H:N films by RF-PECVD from methane ( $CH_4$ ), nitrogen ( $N_2$ ) and argon (Ar) or helium (He) gaseous mixtures. The obtained results for the deposition rate showed a decrease with increasing  $N_2$  flow, which is related with the etching provoked by the  $N_2^+$  ion. It is also shown, that He increases the chemical reactions in the plasma, favoring the deposition process in opposition to the corrosion process. The FTIR spectra revealed that the samples deposited in the powered electrode present a CNH absorption band ( $1000\text{--}1700\text{ cm}^{-1}$ ) much larger than the other bands ( $CH_n$  and NH) and also, the obtained films present a larger concentration of N- $sp^3$  C which is attributed to the intense ion bombardment in the powered electrode.

#### Acknowledgements

The authors acknowledge Dr Manfredo Tabacnicks, from Institute Physics at University of São Paulo, Brazil, by the RBS measurements. The acknowledge are also due to the Brazilian Government agencies CNPq, proc #140370/00-5, and FAPESP, proc. #00/100273-3, for financial support.

#### References

- [1] A.Y. Liu, M.L. Cohen, *Science* 245 (1989).
- [2] J.H. Haufman, S. Metin, *Phys. Rev. B* 39 (1989) 13053.
- [3] O. Amir, R. Kalish, *J. Appl. Phys.* 70 (1991) 4958.
- [4] Y. Catherine, in: R.E. Clausing (Ed.), *Diamond and Diamond-like films*, vol. 266, NATO Advance Study Institute, Ser. B, Plenum, New York, 1991, p. 193.
- [5] J.R. Shi, J.P. Wang, A.T.S. Wee, C.B. Yeo, C.T. Cheng, M. Ueda, S. Tomioka, J. Ohsako, *J. Appl. Phys.* 92 (10) (2002) 5966.
- [6] S.E. Rodil, N.A. Morrison, J. Robertson, W.I. Milne, *Phys. Status Solidi A* 174 (1999) 25.
- [7] J.L. He, W.L. Chang, *Thin Solid Films* 312 (1998) 86.
- [8] S.M. Smith, S.A. Voigh, H. Tompkins, A. Hooper, A.A. Talin, J. Vella, *Thin Solid Films* 398&399 (2001) 163.
- [9] M.N.P. Carreño, J.P. Bottechia, I. Pereyra, *Thin Solid Films* 308&309 (1997) 219.
- [10] S. Muhl, J.M. Méndez, *Diam. Relat. Mater.* 8 (1999) 1809.
- [11] J. Vilcarromeno, M.N.P. Carreño, I. Pereyra, *Thin Solids Films* 373 (2000) 273.
- [12] P. Hammer, M.A. Baker, C. Lenardi, W. Gissler, *Thin Solid Films* 290&291 (1996) 107.
- [13] D.F. Franceschini, F.L. Freire Jr., C.A. Achete, G. Marioto, *Diam. Relat. Mater.* 5 (1996) 471.
- [14] M.R. Wixom, *J. Am. Ceram. Soc.* 73 (1990) 1973.
- [15] J.M. Méndez, A. Gaona-Couto, E. Andrade, J.C. Pineda, E.P. Zavala, S. Muhl, *Nucl. Instr. and Meth. B* 136–138 (1998) 231.
- [16] D.F. Franceschini, F.L. Freire Jr., *Appl. Phys.* 60 (26) (1992) 3229.

- [17] J. Ju, Y. Xia, W. Zang, L. Wang, D. Tang, *J. Non-Cryst. Sol.* 278 (2000) 213.
- [18] Y. Togashi, Y. Hirohata, T. Hino, *Vacuum* 66 (2002) 391.
- [19] G. Yu, S.-H. Lee, J.-J. Lee, *Diam. Relat. Mater.* 11 (2002) 1633.
- [20] S.E. Rodil, A.C. Ferrari, J. Robertson, S. Muhl, *Thin Solid Films* 420&421 (2002) 122.
- [21] G. Fanchini, G. Messina, A. Paoletti, S.C. Ray, S. Santangelo, A. Tagliaferro, A. Tucciarone, *Surf. Coat. Technol.* 151&152 (2002) 257.
- [22] G. Fanchini, G. Messina, A. Paoletti, S.C. Ray, S. Santangelo, A. Tagliaferro, A. Tucciarone, *J. Appl. Phys.* 91 (3) (2002) 1155.