# Diagnostic of an Allylamine Pulsed Plasma

L. Denis*, F. Renaux, J.-P. Dauchot, and M. Hecq, Université de Mons-Hainaut, Mons, Belgium

## ABSTRACT

In order to optimize the primary amine content in plasma polymer films, characterization of allylamine pulsed plasmas was preformed. The discharge was produced in an inductively coupled plasma reactor. Plasma diagnostic was carried out by optical emission spectroscopy as well as by mass spectrometry. The relative concentration of primary amines in the plasma polymer films was estimated by X-ray photoelectron spectroscopy by using as probe molecule the trifluoromethyl benzaldehyde (TFBA). Results reveal a preferential consumption of the primary amines in the films by increasing the pulse frequency. This trend can be underlined by the increase of both primary amines content and N/C atomic ratio measured in the plasma polymer films while primary amines density in the plasma decreases.

## INTRODUCTION

Non-equilibrium plasmas of organic compounds have shown to be a very attractive tool for the synthesis of polymer-like thin films. The process allows modifying the surface properties of a wide range of materials such as polymers, metals and glasses, without altering their intrinsic bulk properties [1]. Plasma polymer films can be used in a number of applications including the biocompatibility improvement of artificial materials [2], the immobilization of biomolecules [3], the modification of purification membranes [4], the conception of sensor devices [5], the synthesis of waterproof coatings [6], etc. However, the process reaction pathways are not completely understood, particularly in the pulsed plasma mode.

The majority of plasma polymerization studies deals with the use of radiofrequency discharges, and to a lesser extent microwave systems. At these frequencies, only electrons can follow the electric field oscillations. Consequently, the monomer molecules are activated in the plasma phase by fragmentation(s) through electron impact collisions. The diversity of reactions that take place during the process produces a large variety of chemical functions in the corresponding plasma polymer films. This is caused by the complex nature of the discharge which involves essentially (i) monomer fragmentation(s) in the plasma, (ii) chemical reactions between the surface active sites and reactive monomer species coming from the plasma, (iii) chemical bonds dissociation at the plasma-substrate interface, (iv) ablation reactions and (v) surface etching. Additionally, the plasma polymer films reveal a highly cross-linked structure.

For biomedical applications, the use of monofunctional organic thin films is required. It has been reported that improvements in the polymer films functional specificity can be obtained by performing plasma polymerization at low input power [7,8] or in the post-discharge region [9]. When low input power is used, the plasma polymer films show poorer substrate adhesion characteristics than films produced under high power conditions [10]. When placed in the post-discharge, the film deposition rate is reduced compared to deposition in the plasma and relatively poor thickness control is achieved [11]. As a consequence, the resulting plasma polymer films are less cross-linked due to bonds dissociation limitation at the plasma-substrate interface.

In contrast, pulsed plasma polymerization shows a high control degree over the film chemistry [12] and stability [13]. In this working mode, the plasma polymerization mechanisms proceed with reduced monomer fragmentation, reduced charged particles bombardments of the substrate surface, reduced vacuum UV effects, and reduced substrate heating. Moreover, the species created during the plasma-on phase can react at the substrate surface during the subsequent plasma-off phase and when the precursor contains polymerizable structures, conventional molecular polymerization can also contribute to the growth of plasma polymer films.

The plasma modulation is defined by the duty cycle ($\Delta$) which is the ratio between the plasma on-time and the pulse period (sum of the on-time and the off-time).

$$\Delta = \frac{\tau_{on}}{\tau_{on} + \tau_{off}} \qquad (1)$$

The average power ($P_{av}$) experienced by the substrate during the process is expressed as the product of the duty cycle by the input power ($P_{peak}$).

---

*SVC Student Presenter

50th Annual Technical Conference Proceedings (2007) ISSN 0737-5921

$$P_{av} = \frac{\tau_{on}}{\tau_{on} + \tau_{off}} \cdot P_{peak} \qquad (2)$$

Pulsed plasma polymerization has already proved its efficiency in producing films containing amine groups which are of particular interest in the biomedical field for subsequent molecules immobilization, cells adhesion and cells growth. Additionally, plasma polymer films synthesized from allylamine ($CH_2$=CH-$CH_2$-$NH_2$) have been reported to exhibit relatively good chemical stability to repeated autoclaving cycles and can thus be re-used [2]. However, to achieve the process control, a better understanding of the phenomena that governed the pulsed plasma polymerization is needed.

In this work, the pulsed plasma polymerization of allylamine was studied. The plasma composition was correlated to the films chemical composition in order to optimize the primary amines content in the corresponding plasma polymer films. The monomer flow rate, the working pressure, the input power, the duty cycle and thus the average power were kept constant while the pulse frequency was varied. The pulse frequency influences the species production kinetics in the plasma. For plasma diagnostic, optical emission spectroscopy and mass spectrometry measurements were performed in the substrate vicinity. The films characterization was focused on the relative primary amines quantification by x-ray photoelectron spectroscopy (XPS). For that purpose, a derivatization method with trifluoromethyl benzaldehyde (TFBA) was used [14].

## EXPERIMENTAL SET-UP

The discharges are generated by inductively coupled plasma in a cylinder stainless steel vacuum chamber 350 mm diameter and 450 mm high which is pumped to a residual pressure of $8.10^{-6}$ Torr by rotary and turbomolecular pumps connected in series (Figure 1). The water-cooled radiofrequency copper coil has a 150 mm internal diameter and an 8 mm tore thickness. It is placed inside the chamber 100 mm in front of the substrate. No copper contamination has been detected in the plasma polymer films because of capacitive discharge appearance. This phenomenon is due to coil covering by plasma polymer. A load-lock system allows transferring the substrate inside the reactor from atmosphere to high vacuum in few minutes. The introduction airlock is separated of the main chamber by a slide valve. The substrate holder is mounted on a transfer stick and the substrate kept at floating potential during film deposition. The 13.56 MHz plasma generator, combined with a matching box, delivers a maximal (peak) power of 1000 W. The plasma can be pulsed at frequency in the range of 1 Hz to 200 kHz. A full-range gauge allows controlling the residual pressure before film synthesis whereas the process pressure is given by a Baratron gauge and regulated at 20 mTorr by a throttle valve placed upstream the turbomolecular pump. The organic precursor inlet is placed in front of the substrate. A regulation system allows maintaining a constant monomer flow rate, fixed at 10 sccm during all the experiments. The input power is fixed at 200 W and the duty cycle at 30 % that give an average power of 60 W.

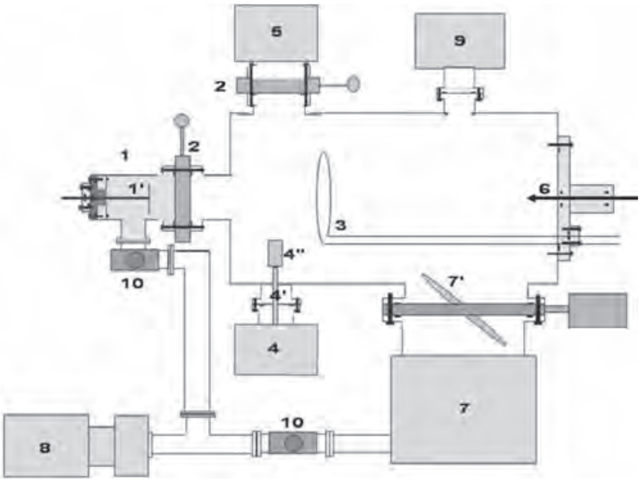

*Figure 1: Experimental set-up. 1: introduction airlock; 1': substrate holder; 2: slide valves; 3: water-cooled radiofrequency copper coil; 4: optical spectrometer; 4': optical fibre; 4": collimator network; 5: mass spectrometer; 6: organic precursor inlet; 7, 7': turbomolecular pump and throttle valve; 8: rotary pump; 9: Baratron gauge; 10: tap valves.*

The plasma light is collected by a quartz optical fiber after focalization with a lens. A collimator network protects the lens from plasma polymer covering. The optical fiber is connected to the spectrometer allowing studying emission lines/bands in the 200-1200 nm range.

During the experiments, the mass spectrometer samples the allylamine plasma through a 100-$\mu$m hole. The mass spectrometer can be configured to analyze the plasma neutral species or positive ions. In this work, only neutral species are studied as these are responsible of the film growth under the power conditions used. However, some studies have underlined the important role that ions can have during the deposition process when the input power is very low [8]. In order to avoid equipment contamination by plasma polymer deposit, the mass spectrometer can be isolated from the reactor through a slide valve. Differential pumping leads to a residual pressure of $5.10^{-9}$ Torr in the mass spectrometer chamber.

X-ray photoelectron data are collected by sample irradiation with the Al K$\alpha$ (1486.6 eV) monochromatic x-ray beam of 250 $\mu$m x 1000 $\mu$m. The pressure in the chamber analysis was typically $2.10^{-9}$ Torr. The photoemission angle was normal to the surface. Because of the insulating character of the plasma polymers, the surface charge effect was offset by using an electron flood gun. Elemental composition was deduced from photoelectron peak areas using photoionisation cross section calculated by Scofield and corrected by the escape depth dependence on the electron kinetic energy (assumed to have the form $\lambda = KE^{0.6}$) and by the analyzer transmission function of the spectrometer.

## RESULTS AND DISCUSSION

### Mass Spectrometry

The mass spectra are recorded in Residual Gas Analysis (RGA) mode. The neutral species generated in the plasma are ionized by electron impact (EI) prior to mass analysis in the spectrometer. The electron kinetic energy is fixed at 20 eV to allow all species ionization and to reduce fragmentations that take place in the ionization chamber. In this way, the mass spectra recorded with this procedure give a more accurate description of the plasma composition. Ten successive scans are considered with signals accumulation and average after each scan. The results are expressed in relative intensities to avoid global fluctuation effects of signals from an experiment to the other one.

In order to distinguish the chemical species produced by monomer fragmentation in the mass spectrometer from those created in the plasma, two mass spectra have been compared: one recorded in the plasma off-mode and another one obtained in the plasma on-mode at a pulse frequency of 600 Hz (Figure 2). The allylamine mass spectrum without plasma is mainly constituted by four peaks at m/z = 57, 56, 30 and 28 which can be readily assigned using the principles of conventional EI mass spectrometry. Then, when the plasma is on, a large number of additional peaks appear in the spectrum. The 57 m/z peak corresponds to the monomer and the 56 m/z peak to the loss of one hydrogen atom. Moreover, the 41 m/z peak can be assigned to the allylic radical while its complementary fragment, the primary amine of the monomer, is detected at 16 m/z. In this spectrum range, the very weak peak at m/z 14 corresponds to atomic nitrogen with a possible contribution of methylene radical, the 15 m/z peak is assigned to NH radical and the 17 m/z peak to the formation of ammonia as a result of recombination reactions that can occur during the process particularly during the plasma off-phase. Finally, the three peaks at m/z 26, 28 and 30 can be attributed to C=N radical, CH=NH radical and $CH_2$-$NH_2$ radical respectively. It is to notice that no mass has been detected under the 10 m/z ratio with the exception of atomic and molecular hydrogen respectively at m/z 1 and 2. Nevertheless, with the followed experimental protocol, the spectrum survey must start from this 10 m/z ratio to avoid saturation effect of the atomic hydrogen signal that automatically stopped the acquisition.

In order to study the pulse frequency effect on the plasma phase composition, four experimental conditions have been considered namely at 150 Hz, 300 Hz, 450 Hz and 600 Hz. Increasing the pulse frequency leads to lower pulse period and consequently, lower on- and off-time.

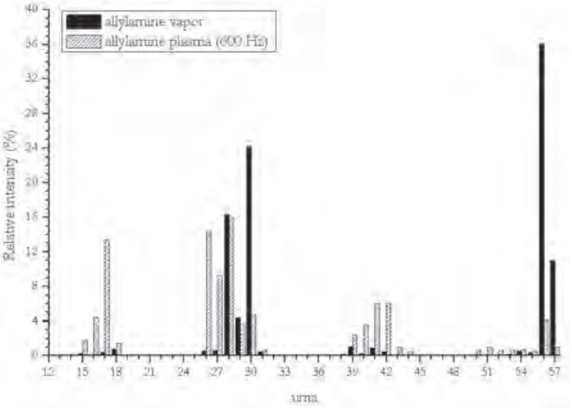

*Figure 2: Comparison of allylamine mass spectra with and without plasma. Both spectra are recorded with a pressure of 20 mTorr in the reactor.*

The mass spectra obtained for the two extreme pulse frequency are presented in Figure 3. It can be observed the enhancement in intensity of the signal at m/z 56, associated to the monomer, for increasing the pulse frequency; the intensity of the signals at 41 and 30 m/z follow the same trend. These fragments are direct by-products of the monomer which are generated by only one electronic collision. Theses results suggest that the considered species are better preserved in the plasma with higher pulse frequencies. This phenomenon is related to the on-time period decrease; for high frequency, the discharge is rapidly extinguished resulting in a less extensive fragmentation of heavy species than the one occurring when the pulse frequency is reduced. The intensity evolution of the fragments appearing at 26 and 28 m/z confirms this result. These species need several electronic collisions to be produced. Consequently, their increase with longer on-time, at low frequency, can effectively occur through a cascade process. This explains the production increase of unsaturated radicals in the plasma and thus the formation of chemical functions not related to the chemical group of the starting molecule.

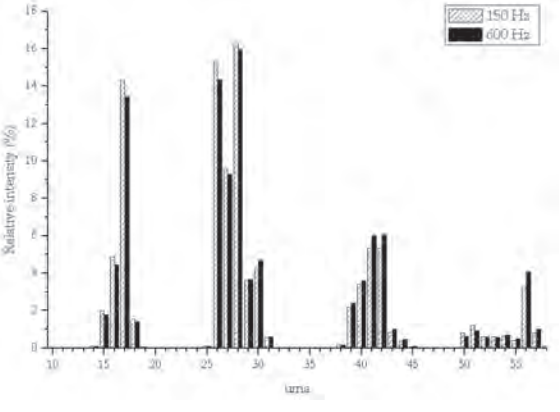

*Figure 3: Evolution of the plasma composition considering the extreme pulse frequencies studied namely 150 and 600 Hz.*

Low frequencies are also characterized by longer off-time which favors recombination reactions. The formation of ammonia is thought to be due to recombination reactions between $NH_2$ radical and hydrogen radical. Besides, the ammonia trend follows the primary amines one. It is important to note that the primary amine signal at 16 m/z has an unexpected evolution with the pulse frequency increase. As discussed before, for increasing the pulse frequency, the heavy species are better preserved, thus the primary amine should follow the allylic radical (41 m/z) trend, its complementary radical. Nevertheless, these fragments have an opposed evolution.

In order to better understand this phenomenon, the chemical analysis of the corresponding films was performed by XPS with focus on the primary amine relative quantification. For that purpose, the chemical derivatization method was carried out using trifluoromethyl benzaldehyde as probe molecule.

**X-ray Photoelectron Spectroscopy**

The XPS spectra recorded on the allylamine plasma polymer films are characterized by a main peak near 399 eV which testifies the presence of amines. However, the resolution of the XPS system used in this work (~0.6 eV) does not allow distinguishing primary amines from secondary and/or ternary amines due to the small chemical shift among them. This difficulty can be overcome using the chemical derivatization method. This latter consists of inducing a chemical reaction between a specific functional group present on the sample surface and a chemical reagent which contains at least one atom completely foreign to the ones in the plasma polymer films. Photoelectrons emitted from the new element can then be used to quantify the targeted chemical group. In this work, the chosen derivatization agent is the trifluoromethyl benzaldehyde (TFBA) [14]. The TFBA has the faculty to only react with the primary amines. This derivatization reaction introduces fluorine atoms on the primary amines sites of the films surface. The primary amines relative concentration, among all the nitrogenous groups, is derived as follows:

$$[NH_2] = \left( \frac{\frac{[F]}{3}}{[N]} \right) \times 100\% \qquad (3)$$

where [F] and [N] are respectively the relative atomic percentage in fluorine and nitrogen measured by X-ray photoelectron spectroscopy at the allylamine plasma polymers surface after the derivatization step.

The influence of the pulse frequency on the relative primary amine concentration is shown in Figure 4. It can be observed that the primary amine content in the plasma polymer films enhances as the pulse frequency increases. However, the primary amines signal in the mass spectra decreases for increasing pulse frequency. This trend can be explained by a preferential consumption of the plasma primary amines in the corresponding films when the pulse frequency is increased. To confirm this assumption, the N/C atomic ratio evolution is considered. As seen in Figure 4, a high pulse frequency favors the N/C ratio increase. Consequently, the atomic nitrogen percentage increase is more important than the carbon one. Nevertheless, increasing the pulse frequency was shown to promote heavy functionalized hydrocarbon species in the plasma phase due to reduction in fragmentation processes. As a result, if these fragments were responsible to the relative nitrogen content value in the plasma polymer films, the N/C ratio would stay at least constant and even decrease but this phenomenon is not observed in the present case. Therefore, it can be assumed that nitrogen content increase in the plasma polymer films is only due to an increase of the plasma primary amines consumption as the pulse frequency increases. These results allow clarifying the corresponding primary amine signal decrease noticed in the plasma-phase characterization.

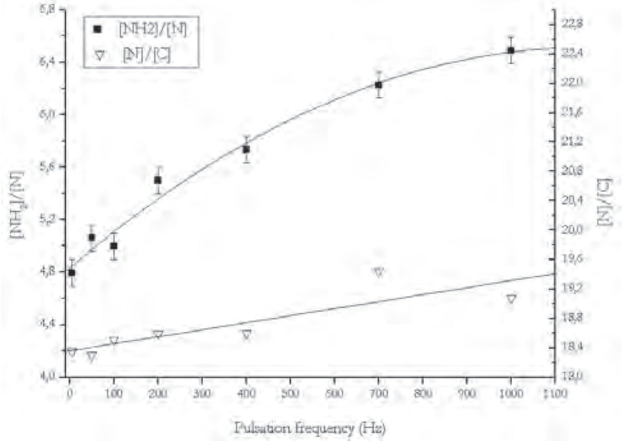

*Figure 4: Relative percentage of primary amines groups and N/C atomic ratio with regard to the pulse frequency.*

**Optical Emission Spectroscopy**

For optical emission spectroscopy measurements, the actinometric approach is used to provide semi-quantitative data about the relative density of the excited species in the fundamental state. For that purpose, few percents of argon are added in the discharges (3% in this work) [15]. According to this method, the intensity ratio between the studied specie line (or band) and the Ar line at 750.4 nm, is directly proportional to the studied specie relative density in the fundamental state in condition that first, the excitation of the radiative state is mainly due to direct electron collision on the specie ground state and second, that the radiative state destruction mainly proceeds by radiative emission [16]. In these conditions, it can be written:

$$\frac{I_X}{I_{Ar}} = k(X)\frac{[X]}{[Ar]} \tag{4}$$

where k(X) is a constant value for given plasma parameters, $I_X$ and $I_{Ar}$ are the intensity of the followed specie line (or band for molecular system) and argon line respectively and, [X] and [Ar] are the ground state relative density of the studied specie and argon respectively.

The spectral emissions of two key species (NH and H) in the organic precursor fragmentation have been followed. These are the NH band at 336.0 nm (v'=0, v"=0) which is part of the $A^3\Pi$-$X^3\Sigma$ system and the $H_\beta$ line at 486.1 nm corresponding to the $2p^2P^0$-$4d^2D$ system.

The actinometric ratio evolution of these two active species is plotted in Figure 5 as a function of the pulse frequency. A clear decrease of both fragments relative density in the fundamental state is observed. The reduction in plasma species fragmentation for increasing the pulse frequency, as shown by mass spectrometry measurements, explains the hydrogen radical trend. The atomic hydrogen being majority in the monomer and heavy fragments, its production is very sensitive to the plasma on-time. Consequently, at high frequency, and thus short plasma on-time, the fragmentation reactions resulting in hydrogen radical are reduced. The NH trend is similar to the hydrogen radical one. The NH actinometric ratio evolution is found to follow the $NH_x$ mass spectrometry signals decrease, underlining the preferential consumption of the primary amine groups in the corresponding plasma polymer films for increasing the pulse frequency.

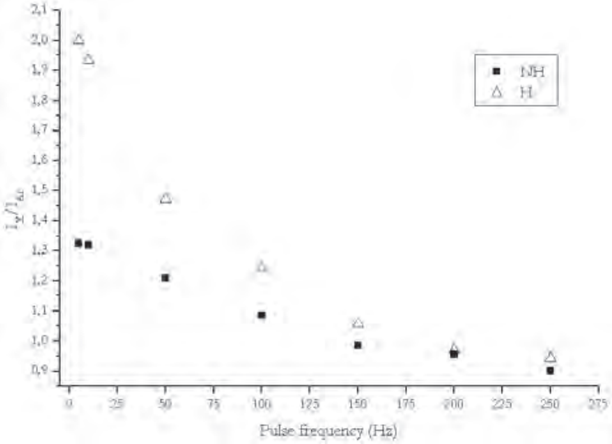

*Figure 5: Actinometric ratio ($I_X/I_{Ar}$) evolution of X=NH and X=H in the plasma for increasing the pulse frequency.*

## SUMMARY AND CONCLUSIONS

In order to improve the comprehension of the phenomena that govern the pulsed plasma polymerization of primary amines compounds, diagnostic of allylamine pulsed plasma as a function of the pulse frequency was preformed. The plasma-phase composition was correlated to the plasma polymer films composition with particular interest in the primary amines relative quantification. By mass spectrometry, a decrease in the organic precursor fragmentation for increasing the pulse frequency was found. In this case, heavy species are better preserved in the plasma. Primary amines are the complementary fragment of allylic radical, thus both should have the same trend for increasing the pulse frequency. However, the intensity of the m/z signal corresponding to primary amines decreases. This trend was explained by a preferential consumption of these chemical groups in the corresponding plasma polymer films by virtue of the increase in the primary amines concentration and the N/C ratio. The use of the actinometric method was validated by correlation of its results to the mass spectrometry ones. The $I_{NH}/I_{Ar}$ ratio follows the $NH_x$ mass spectrometry signal, which also underlines the $NH_2$ preferential consumption in the plasma polymer films for increasing the pulse frequency.

## ACKNOWLEDGEMENTS

The authors thank the “Fonds pour la formation à la Recherche dans l’Industrie et dans l’Agriculture” (F.R.I.A.) and the “Université de Mons-Hainaut” for their financial support.

## REFERENCES

1. H. Biederman and Y. Osada, *Plasma Technology 3: Plasma Polymerization Processes*, p. 4, Elsevier, Amsterdam, 1992.

2. A. Harsch, J. Calderon, R.B. Timmons and G.W. Gross, “Pulsed plasma deposition of allylamine on polysiloxane: a stable surface for neuronal cell adhesion,” *J. Neurosci. Methods*, 98, 135, 2000.

3. Z. Zhang, Q. Chen, W. Knoll, R. Foerch, R. Holcomb and D. Roitman, “Plasma polymer film structure and DNA probe immobilization,” *Macromolecules*, 36, 7689, 2003.

4. G. Pozniak, I. Gancarz, M. Bryjak and W. Tylus, “N-butylamine plasma modifying ultrafiltration polysulfone membranes,” *Desalination*, 146, 293, 2002.

5. A. Hiratsuka and I. Karube, “Plasma polymerized films for sensor devices,” *Electroanalysis*, 12(9), 695, 2000.

6. A. Taniguchi and K. Yasuda, "Waterproofing of carbon paper by plasma polymerization," *J. Appl. Polym. Sci.,* 100, 1748, 2006.

7. S. Candan, A.J. Beck, L. O'Toole, R.D. Short, A. Goodyear and N.St J. Braithwaite, "The role of ions in the continuous-wave plasma polymerisation of acrylic acid," *Phys. Chem. Chem. Phys.*, 1, 3117, 1999.

8. A.J. Beck, S. Candan, R.D. Short, A. Goodyear and N.St J. Braithwaite, "The role of ions in the plasma polymerization of allylamine," *J. Phys. Chem. B,* 105, 5730, 2001.

9. F. Fally, C. Doneux, J. Riga and J.J. Verbist, "Quantification of the functional groups present at the surface of plasma polymers deposited from propylamine, allylamine, and propargylamine," *J. Appl. Polym. Sci.,* 56, 597, 1995.

10. R. Förch, Z. Zhang, W. Knoll, "Soft plasma treated surfaces: tailoring of structure and properties for biomaterial applications," *Plasma Process. Polym.*, 2, 351, 2005.

11. H. Biederman and Y. Osada, *Plasma Technology 3: Plasma Polymerization Processes*, p. 39, Elsevier, Amsterdam, 1992.

12. C.R. Savage, R.B. Timmons and J.W. Lin, "Molecular control of surface film compositions via pulsed radio-frequency plasma deposition of perfluoropropylene oxide," *Chem. Mater.*, 3, 575, 1991.

13. H. Biederman, *Plasma Polymer Films*, p. 225, Imperial College Press, London, 2004.

14. A. Choukourov, H. Biederman, D. Slavinska, M. Trchova and A. Hollander, "The influence of pulse parameters on film composition during pulsed plasma polymerization of diaminocyclohexane," *Surf. Coat. Technol.,* 174-175, 863, 2003.

15. J.W. Coburn and M. Chen, "Optical emission spectroscopy of reactive plasmas: a method for correlating emission intensities to reactive particule density," *J. Appl. Phys.,* 51(6), 3134, 1980.

16. J. Henriques, S. Villeger, J. Levaton, J. Nagai, S. Santana, J. Amorim and A. Ricard, "Densities of N- and O-atoms in $N_2$-$O_2$ flowing glow discharges by actinometry," *Surf. Coat. Technol.*, 200, 814, 2005.