

Modification of Plasma Polymer Films by Ion Implantation

Deborah Cristina Ribeiro dos Santos^a, Rita de Cássia Cipriano Rangel^a, Rogério Pinto Mota^a, Nilson Cristino da Cruz^b, Wido Herwig Schreiner^c, Elidiane Cipriano Rangel^{b*}

^aLaboratório de Plasmas, Departamento de Física e Química,
UNESP, 12516-410 Guaratinguetá - SP

^bGrupo de Plasmas Tecnológicos, UNESP, 18087-180 Sorocaba - SP

^cLaboratório de Superfícies e Interfaces, Departamento de Física,
UFPR, 81531-990 Curitiba - PR

Received: January 29, 2003; Revised: April 26, 2004

In this work, thin polymer films were prepared from acetylene and argon radiofrequency (13.56 MHz, 80 W) glow discharges. Post-deposition treatment was performed by plasma immersion ion implantation in nitrogen or helium glow discharges (13.56 MHz, 70 W). In these cases, samples were biased with 25 kV negative pulses. Exposure time to the bombardment plasma, t , ranged from 900 to 7200 s. Chemical composition of the film surfaces was investigated by X-ray Photoelectron Spectroscopy and the resistance to oxidation by the etching process, in reactive oxygen plasmas. Oxygen and nitrogen were detected in all the samples. While the concentration of the former continuously changed with t , that of N kept practically constant in small proportions. The film is predominantly formed by sp^3 states, but the proportion of sp^3 hybridization slightly increased with t . The etching rate dropped under certain conditions of nitrogen bombardment whereas helium implantation has not significantly improved it. These results are ascribed to the crosslinking degree of the polymeric chains, ruled by the total amount of energy delivered to the film.

Keywords: plasma polymer, plasma immersion ion implantation, XPS, etching rate

1. Introduction

Polymer films with a great variety of physical and chemical properties can be deposited by plasma polymerization. Through the adjustment of the deposition conditions (plasma composition, pressure, excitation frequency, power, etc), materials with high degree of uniformity, homogeneity and stability can be obtained. They are generally applied as coatings for metals, conventional polymers, ceramics, woods, to change chemical, electrical, optical and biological properties^{1,2}.

Another way to modify the characteristics of plasma polymer films is through post deposition treatments. Amongst several techniques, ion beam implantation represents a very effective way of tailoring the properties of polymers to match the requirements of practical applications³⁻⁵. However, such technique is complex and expensive.

Plasma immersion ion implantation, *PIII*, is a low cost technique, which enables ion implantation of pieces with complex shapes while keeping the efficiency of conventional

beam implantation⁶. In the *PIII*, samples immersed in reactive or noble gas plasmas are biased with high voltage negative pulses. Positive ions from the plasma are attracted and implanted in the target. The mechanisms of ion energy dissipation induce structural and chemical modifications. Essentially, the degree of such modifications depends on the total energy delivered to the sample.

In this work, plasma polymerized acetylene films, *PPA*, were treated by *PIII*. An investigation was carried out on the effect of the exposure time t , and ion mass on the chemical composition and etching rate of the polymers.

2. Materials and Methods

Films were prepared from acetylene and argon radiofrequency, *RF*, plasmas (13.56 MHz, 80 W) in a cylindrical stainless steel reactor fitted with two parallel plate electrodes. The upper electrode is connected to an *RF* power supply and the other, used as substrate holder, is grounded.

*e-mail: elidiane@sorocaba.unesp.br

Article presented at the XV CBECIMAT, Natal - RN, November/2002

Total gas pressure was 12.7 Pa (93% Ar) and deposition time was 1200 s. The average thickness of the films was 50 nm.

Samples were then submitted to nitrogen or helium *PIII*, using the same equipment described before. In this case, however, the sample holder was biased with high voltage negative pulses (25 kV, 30 Hz, 1.3×10^{-7} s). The gas pressure and *RF* power were 1.3 Pa and 70 W, respectively. *PIII* base pressure was 0.4 Pa and exposure time varied from 900 to 7200 s.

The chemical composition of the film surfaces was investigated by X-ray Photoelectron Spectroscopy in a VG ESCA 3000 system. Base pressure was 2×10^{-8} Pa and no attempt was made to remove surface contaminants. The spectra were collected using MgK α radiation and the overall energy resolution was approximately of 0.8 eV. The C1s peak (284.6 eV) was taken as reference for the energy calibration of the other species. The high-resolution peaks were deconvoluted into their components, using a Gaussian profile with linear base. Polished silicon was employed as substrate in this case.

To investigate the etching rate, *R*, samples were exposed to *RF* oxygen plasmas (50 W, 1.3 Pa) in the same experimental system used for film deposition and treatment. A glass mask was applied to protect part of the film surface from the chemical attack, generating a step between the covered and etched region. With the aid of a Veeco Dektak 3 profilometer, the step height, *h*, was measured and *R* evaluated through the following expression:

$$R = h / \sigma$$

where σ is the exposure time to the etching plasma, equal to 1800 s in this work. For such analysis, samples were prepared onto microscope glass plates.

3. Results and Discussions

XPS analysis revealed the presence of C, O and N in all the samples. Oxygen incorporation can be explained by the presence of free radicals or dangling bonds in the polymeric structure⁷. High concentrations of such species are normally encountered in plasma polymer films as well as in those treated by plasma techniques^{1,5}. Furthermore, residual atmosphere in the reactor during the deposition can account for N and O incorporation⁷.

The C 1s spectra of the films bombarded for different times with nitrogen or helium ions are depicted in Fig. 1. For comparison, the spectra of the as-deposited sample is also shown ($t = 0$ s).

The highest component of the C 1s envelope is centered at 284.6 eV and is related to C-C and C-H bonds in the sp^2 coordination. The peaks at 286.1, 287.5 and 288.9 eV are respectively attributed to C-O (sp^2), C=O (sp^3) and O-C=O

(sp^3) groups. As can be observed there is variation in the shape of the C 1s peak as *t* increases. The intensity of the lines related to O-containing groups grows continuously resulting in a shoulder ($t = 900$ s) and finally in a well defined secondary peak ($t = 3600$ s).

From N 1s and O 1s high-resolution spectra, O/C and N/C atomic ratios were evaluated. The results are presented in Fig. 2. As a general trend, O/C increases after implantation, but the growth rate depends on the exposure time and ion species. At this point, it is interesting to take into consideration some phenomena taking place in polymers during the bombardment.

The deposition of energy in polymers promotes, amongst other processes, bond breakage with emission of atomic and molecular species³. It was verified that H groups are preferentially lost since they constitute side groups or chain termination in polymers⁶. Once H is a weakly bonded species, just its progressive emission enhances the medium strength of the structure. Moreover, it induces dangling bonds, which are unstable species and tend to be vanished through chain unsaturation and crosslinking.

Consumption of radicals through these processes depends on a number of factors, including their concentration, separation and chain mobility. The more radicals are generated, the higher is the probability of recombination and then of crosslinking and unsaturation. Structure strength

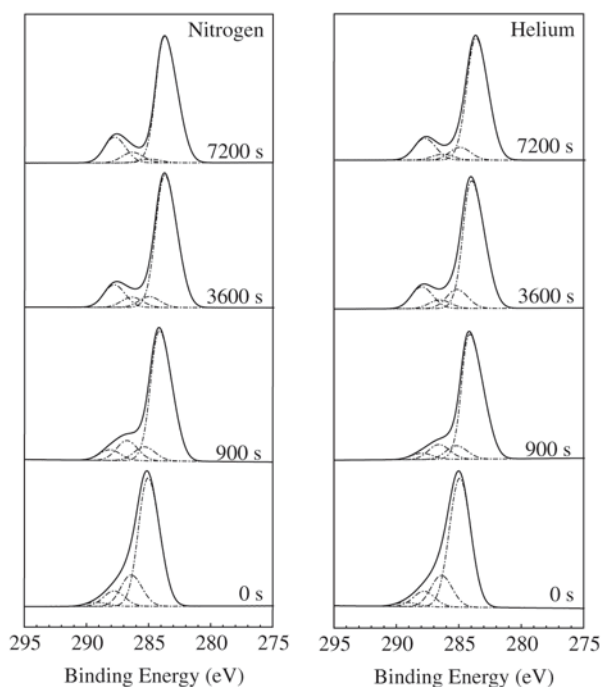


Figure 1. C 1s XPS spectra of PPA films bombarded with helium or nitrogen ions for different times.

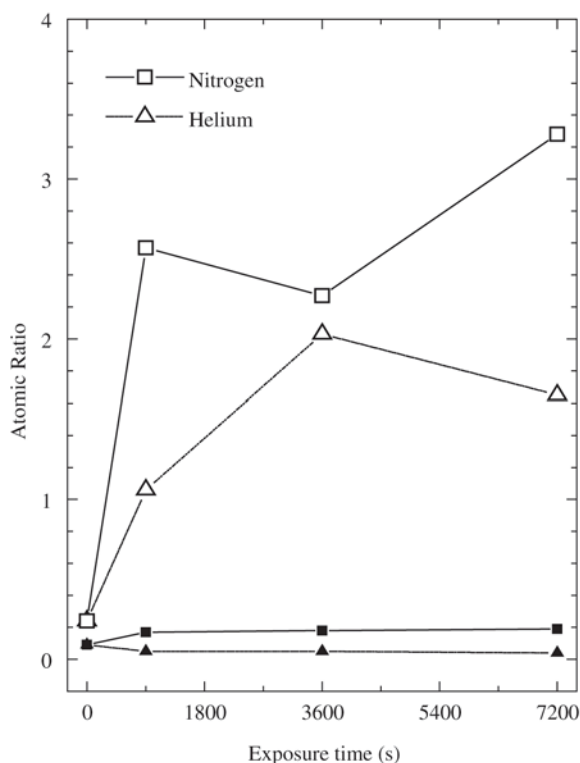


Figure 2. O/C (open symbols) and N/C (solid symbols) atomic ratios as a function of t in nitrogen or helium bombarded films.

is strongly affected by these processes.

Thus, the concentration of residual radicals left in the film treated, called here residual radicals, is a balance between their production and consumption. As mentioned before, they are responsible for atmospheric O incorporation into the structure¹. It has been proved in earlier studies (by Spin Paramagnetic Resonance) that the intensity of the ion bombardment rules the proportion of residual radicals and then of oxygen in plasma polymer films⁸. Therefore, variations in O/C can be taken as an indicator of the concentration of residual radicals in the film.

Analyzing the behavior of O/C in the sample exposed to nitrogen *PIII*, it can be stated that the concentration of residual radicals is practically the same in the 900 and 3600 s bombarded samples. Thus, the extra amount of radicals produced in the film treated for 3600 s is certainly being consumed by chain crosslinking and unsaturation.

The final increase in O/C suggests that, for the longest bombardment time, the connectivity of the backbones is no longer improved. As the bombardment proceeds, polymeric chains crosslink, turning the structure rigid⁹. Polymer mobility is essential to the crosslinking process and then, if further bombardment is performed, new radicals are gener-

ated but recombination is hindered by the immobile structure. In this case dangling bonds are generated and are not re-established. Radicals keep active and the solid prone to oxidation as the sample is exposed to the atmosphere.

From the data presented in Fig. 2 it can also be observed that the rate of modification is slower in samples bombarded with helium ions. In this case, the final increase in O/C (observed in the graph of nitrogen treated samples) is not detected in the whole range of exposure time investigated. This result can be ascribed to the different mechanisms of helium and nitrogen energy dissipation. According to estimations with the TRIM (TRansport of Ions in Matter) code³, for the same treatment time and energy, the degree of ionization produced by helium is sensibly lower than that induced by nitrogen. Therefore, the concentration of free radicals and consequently the modifications promoted in the material properties are smaller.

The proportion of nitrogen in the samples is very low, as revealed by the magnitude of N/C (Fig. 2). The small decline in this ratio after helium treatment indicates that N incorporation took place only during the deposition process (residual nitrogen in the reactor) and it is lost during the bombardment.

In the case of nitrogen implanted films, N/C is higher than in the as-deposited sample. From the invariance of N/C in the implanted films, it can be said that the concentration of nitrogen in the surface is independent of the exposure time or, equivalently, of the ion dose. The explanation for that lies on the fact that, at the energy employed in this work, implanted ions reach deeper regions (120 nm for N⁺) lying in the substrate and not in the body of the film (~ 50 nm thick). Only small concentrations of low energy nitrogen of the plasma are incorporated in shallower layers, accounting for the higher N/C values.

Figure 3 and its insert show the proportion of sp³ and sp² coordination in the films as a function of t . These results were evaluated from XPS data according to the method proposed by Nuzzo¹⁰. While the proportion of sp³ bonds (insert) increases, the concentration of sp² states decreases. This trend is more pronounced in films bombarded with nitrogen ions. It is worthwhile mentioning, however, that the bombarded layer is predominantly formed by sp² states, with no pure sp² or sp³ regions^{9,11,12}.

It has been reported that nitrogen incorporation in the surface of amorphous carbon films enhances the proportion of sp³ hybridization¹². In addition to the chemical effect, the deposition of low energy (~ 100 eV) through ionic collisions is known to promote sp³ bonds in such materials¹¹. Thus it can be concluded that the treated surface is composed of a three-dimensionally connected, crosslinked and amorphous structure in which carbon atoms co-exist in the tetrahedral (sp³) and trigonal (sp²) forms.

Figure 4 shows the etching rate of the films, R , as a func-

tion of the treatment time with helium or nitrogen ions. R grows in the sample bombarded with helium for 900 s and it keeps practically unchanged in the 900 s nitrogen bombarded film. Further increasing t promotes reduction of R for both ionic species. This trend is again reversed into growth in the film bombarded with nitrogen for 7200 s.

To interpret these results it should be considered that in polymers, the removal of C-containing groups is strongly dependent on connectivity of the carbon backbone⁹. The increase in R (helium treatment) suggests that the crosslinking degree is smaller than in the as-deposited film. For lighter ions, ionization power is lower. Small concentrations of sparsely distributed radicals are generated in a way that, crosslinking is not effective. Instead, connections initially existent are broken and are not restored. In this case, the implantation effect is of degradation.

In the samples bombarded with nitrogen, however, the generation and recombination of pendant bonds are more frequent, improving the connectivity of the carbon network. Hence, the structure strength increases and the etching rate decreases. The enhancement of R in the sample bombarded for 7200 s suggests that there is saturation and the implan-

tation effect is again converted into degradation. This feature is attributed to the increase in the structure rigidity inhibiting more crosslinking. The same behavior, however, was not observed in the samples bombarded with helium. As discussed before, the modifications produced by helium ions are less intense due to their lower ionizing power.

Finally, comparing the etching rates of the as-deposited and helium bombarded films, it can be concluded that, under the conditions employed in this work, helium bombardment was not effective to improve the oxidation resistance of the films. On the other hand, nitrogen P_{III} ($t = 3600$ s) reduced R to a half of its initial value, corroborating the idea that the crosslinking degree is higher in such samples. These results are in agreement with the O/C behavior and with the interpretation proposed for the free radical concentration in the films.

4. Conclusions

In this work, it was verified that surface chemical composition of PPA is dependent on the exposure time to the P_{III} as well as on the mass of the implanted species. There was variation in the concentration of O in the films with t .

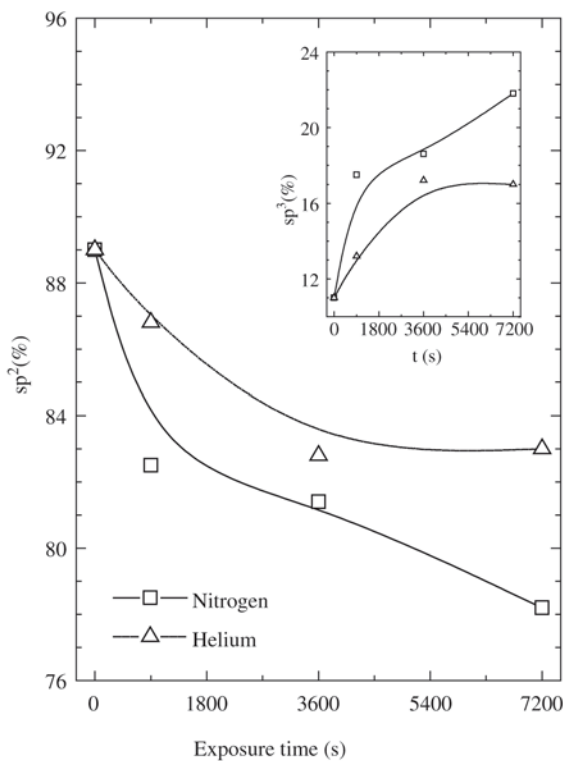


Figure 3. Proportion of sp^2 C bonds in the films as a function of the treatment time. The insert plot shows the proportion of sp^3 coordination.

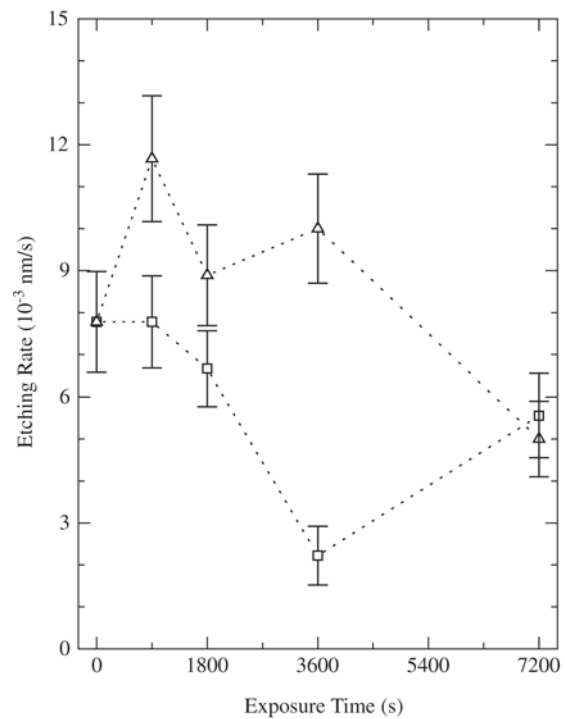


Figure 4. Etching rate of films implanted with nitrogen or helium ions as a function of t .

This was ascribed to changes in the concentration of residual radicals left in the film after the treatment.

Results revealed that bombarded layer is predominantly composed by sp^2 carbon hybridization and that crosslinking and unsaturation degree increased under moderate nitrogen bombardment. Saturation occurred only in the highest time nitrogen treated sample. On the other hand, helium treatments do not significantly enhanced crosslinking. As a consequence, oxidation resistance was not improved but it demonstrated almost 100% of improvement as the bombardment was performed with nitrogen for medium exposure times.

In a general way, the modifications induced by nitrogen were more pronounced than that induced by helium. These results were ascribed to the different mechanisms of helium and nitrogen energy dissipation into the sample.

Acknowledgements

The authors would like to thank Brazilian agencies FAPESP and CAPES for financial support and Professor Mário Antonio Bica de Moraes, from IFGW of State University of Campinas (UNICAMP) for the thickness measurements.

References

1. Yasuda, H. *Plasma Polymerization*, Academic Press, N.Y., 1985.
2. Borucki, S.V.; Achete, C.A.; Jacob, W. *Surface and Coating Technology*, v. 138, p. 256-263, 2001.
3. Lee, E.H.; Rao, G.R.; Mansur, L.K. *TRIP*, v. 4, n. 7, July 1996.
4. Rangel, E.C.; Cruz, N.C.; Moraes, M.A.B. de; Lepienski, C.M. *Surface and Coating Technology*, v. 127, p. 93-98, 2000.
5. Hutchings, R.; Short, K.T.; Tendys, J. *Surface and Coating Technology*, v. 83 p. 243-249, 1996.
6. Dong, H.; Bell, T. *Surface and Coating Technology*, v. 111, p. 29-40, 1999.
7. Durrant, S.F.; Baranauskas, V.; Peterlevitz, A.; Li, B.B.; Tosin, M.C.; Rangel, E.C.; Wang, J.; Castro, S.G.; Moraes, M.A.B. de *thin Solid Films*, v. 355-356 p. 184-188, 1999.
8. Rangel, E.C. in "Implantação Iônica em Filmes Finos Depositados por PECVD" PhD Thesis, State University of Campinas - UNICAMP, ch. 4.1, Campinas, SP, 1999.
9. Lee, E.H. in: M.K. Ghosh, L.K. Mittal (Eds), *Polyimides: Fundamentals and Applications*, p. 471, New York 1996.
10. Jackson, S.T.; Nuzzo, R.G. *Applied Surface Science* v. 90, p. 195-203, 1995.
11. He, X.M.; Bardeau, J.F.; Walter, K.C.; Nastasi, M. *J. Vac. Sci. Technol.*, v. 17, n. 5, p. 2525-2530, 1999.
12. Lu, W.; Komvopoulos, K. *Journal of Applied Physics* v. 85, n. 5, p. 2642-2651, 1999.