INFLUENCE OF THE KEY DEPOSITION CONTROL PARAMETERS ON THE STRUCTURE OF THIN FILMS IN A DIRECT CURRENT COLD PLASMA REACTOR FOR PHOTONICS APPLICATIONS

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Plasma polymerization is a method that uses plasma to initiate and sustain a polymerization process, the polymer being deposited and grown on a substrate. The main advantage of this method, over the classical one, is that the obtained thin films are highly cross-linked and adhere well to the substrate surface. For this study we deposited and characterized polyaniline thin films by means of Direct Current (DC) plasma polymerization technique, in a variable geometry reactor, under different experimental conditions. The samples were analyzed by Scanning Electron Microscopy (SEM) and Fourier Transformer Infrared Spectroscopy (FTIR). We investigated the influence of various experimental parameters such as: substrate distance from the monomer injection nozzle, monomer flight time through the plasma, substrate inclination to the incident vapors and monomer temperature at injection point, on the structural and morphological parameters of the resulted aniline thin films and the different results were correlated to these important deposition control parameters.

1. Introduction

Plasma polymerization under vacuum conditions offers some advantages over the classical method of polymerization. By using a plasma source to initiate and maintain the process, the obtained polymers are well ramified and reticular while presenting some specific proprieties. One of the most important advantages when using this method is the possibility of growing the polymer thin film up to the required thickness directly on the desired substrate [1-5]. In air, at atmospheric pressure, in corona discharges [6, 7], it was showed the possibility of thin polymer layers generation starting from liquid film precursors placed on the anode surface. Their structural [8,9] and morphological properties due to their deposition procedure, can determine the use of these polymers like inter-layers for an improved adherence of the coatings [10].

The present work is an investigation of the plasma polymerization technique under vacuum conditions, by employing a custom designed plasma reactor, while in-situ modifying the proprieties of the polymeric film during the deposition process. The variable geometry of the DC plasma polymerization reactor was conceived in such a way that every important physical control parameter may be modified in order to obtain thin films with different properties. The electrodes have different shapes and the distance between them may be changed, as a consequence the positive column's length of the discharge being altered. Therefore, we can obtain different flight times of the monomer molecules through the plasma field [11]. Ions created by the discharge starts to bombard the monomer that is inserted into the reaction chamber and the resulted fragments start to polymerize into a thin film that grows on the bottom substrate. The substrate manipulator may be rotated inside the reactor chamber, comparable to the GLAD deposition technique [12-14]. To achieve self-shadowing, the movement of the substrate inside the chamber during the deposition

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has to be well controlled, sometimes with very high angles respective to the incident monomer vapor direction [15.16]. The temperature is another important physical parameter for the plasma deposition [17] that will be considered in our experiment. The possibility to well manage a deposition and be able to fine tune the properties of a polymeric thin film represents a great challenge in the field and the successful understanding of these phenomena could bring improvements to many other inter-connected research branches such as condensed matter physics [18,19] , molecular dynamics and simulations [20-26] , optics and photonics [27,28], nanotechnologies [29,30] etc.

2. Experimental setup

The reactor is formed by two plane-parallel electrodes: an anode through which the monomer is injected and a cathode on which the substrate is positioned and can be manipulated by means of a six servo-mechanisms controllers with a custom-made software in order to ensures precise positioning and movement during deposition.
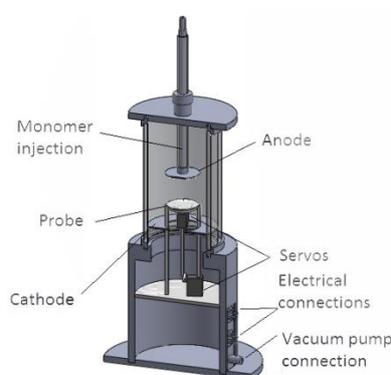
Fig.1 Transversal view of the DC plasma polymerization reactor[2].

In Fig. 1, a schematic section view of the reactor shows its main components. The monomer is injected through a pipe at the top of the device and centered on the anode. When the vapors reach the interior of the reactor, the voltage applied (~ 1000V) between the anode and cathode produces a breakdown and the monomers are bombarded by ions inside the positive column. The fragmented monomers begin to polymerize and deposit on the bottom substrate [8, 11].
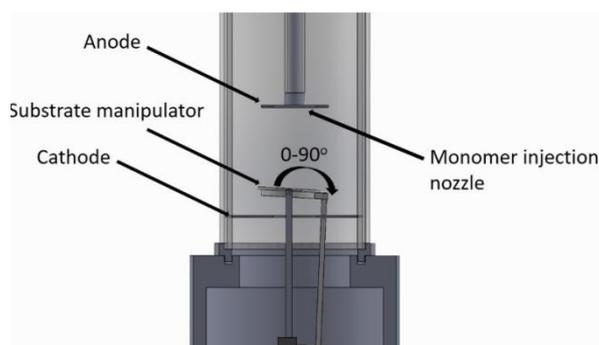
Fig. 2 Section view of reactor polymerization chamber[4].

The most important aspect in GLAD deposition is the substrate position and its inclination angle in relation with the incident flux of vapors. As shown in figure 2, the substrate stance may be

tuned inside the chamber by means of a 5-axis robotic arm, adjustable from 0 to 90° and rotated to over 1000 rpm, depending on the desired structural and morphological proprieties [11,31,32].

3. Experiment and Results

The emission spectra of the discharge was acquired by means of a Oceans Optics USB 4000 Spectrometer in the spectral range of 200-1100 nm, with a resolution of 0.1 nm. Three main spectra were measured for 10 mA, 20 mA and 30 mA values of the discharge current. The obtained spectral lines of the glow discharge with monomer vapors injected are presented in Fig. 3.
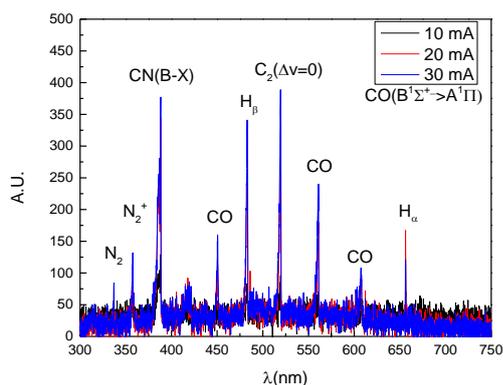
Fig. 3. Optical emission spectra of the DC glow discharge while injecting the aniline monomer.

The spectral line intensities increase with the discharge current value. This is due to the fact that more monomer bonds get bombarded by the plasma constituents. After analyzing the spectra with a custom made software [33] that determines the energy of the ions and electrons, we concluded that the bulk plasma have not sufficient energy to break the aromatic rings. However, according to the Electron Energy Distribution Function (EEDF), some fast electrons can reach 6 eV, sufficient to break the double C=C bonds [34].

In order to resolve parameters that influence the properties of the polymeric films, 9 different polyaniline layers were deposited on Ti substrates, by varying the distance between the anode and the substrate (resulting monomer flight time changes), temperature of the injected monomer and the angle of the substrate relatively to the incident flux of the monomer vapors. The parameters and various conditions used for obtaining the polymeric films are shown in Table 1.

Table 1. Deposition conditions of the thin polymer films.

	P1	P2	P3	P4	P5	P6	P7	P8	P9
Deposition time (min)	10	10	10	10	10	10	10	10	10
Voltage (V)	1000	1350	1300	1200	1200	1200	1350	1600	1600
Current (mA)	20	20	20	20	20	20	30	30	30
Inclination angle (degrees)	45	45	88	45	45	88	88	45	88
Anode – substrate distance (cm)	12	12	12	8	8	8	8	8	8
Pressure (10^{-1} torr)	4,2	3,3	3,2	2,6	2,7	3.0	2,6	4.4	4.4
Temperature (^{o}C)	20	50	50	20	50	50	20	50	50

3.1. FT-IR analysis

FT-IR analysis was performed on the obtained films. Because the films do not have the same thickness, due to variations in their orientation and positioning during the deposition process, the transmittance value changes from sample to sample (Fig.4) .
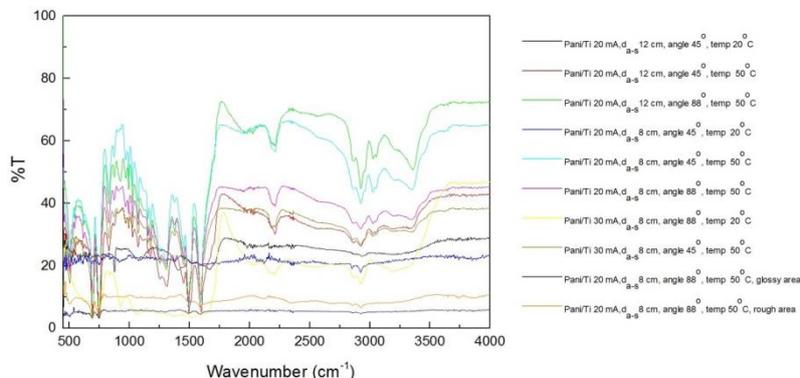
Fig. 4. FT-IR spectra of the obtained polyaniline samples.

The spectra were normalized and paired up, in order to determine the influence of the different deposition parameters.
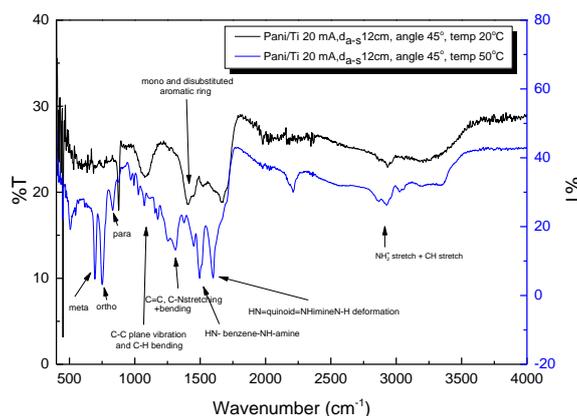
Fig. 5. FTIR spectra of the P1 and P2 samples obtained in the experimental conditions presented in Table 1 Comparison between samples (12 cm distance between electrodes, 45° deposition angle, but at different monomer temperatures -20 and 50 °C respectively).

Fig. 5 shows the characteristic IR bands for polyaniline polymers. The C-C meta (694 nm), ortho (751 nm) and para (831 nm) substitutions as well as the C-C and C-H bending vibrations are evidenced. The C=C, C-N stretching and bending vibrational bands, and those specific to HN-benzoid ring, respectively HN-amine group and HN-quinoid ring are also identified [35].
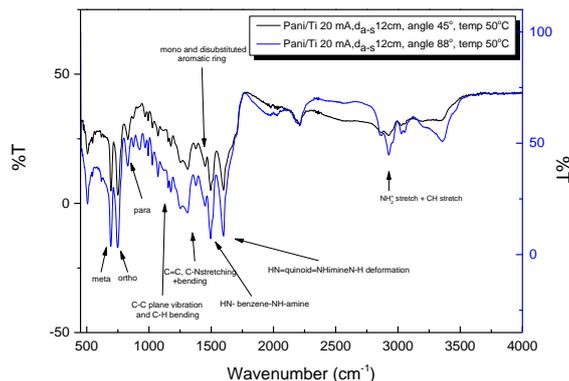
Fig. 6. FT-IR spectra characteristic to P2 and P3 samples.

In Figure 6 are presented the spectra obtained after the analysis of the sample generated in the following conditions: discharge current 20 mA, a distance between the anode (point of injection) and substrate of about 12 cm, a temperature of 50^0C and inclination angle of 45^0 respectively 88^0. The intensity of the IR bands specific to NH_2^+ stretching and CH bonds deformation vibrations increase with the inclination angle of the cathode related to the anode [34, 35].
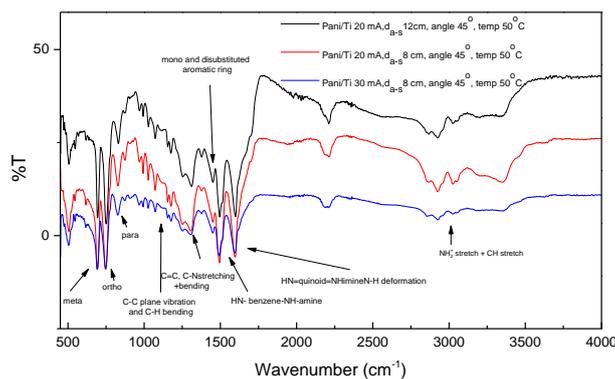
Fig. 7. FT-IR spectra of the P2, P5 and P8 samples.

In Figure 7 are presented the IR spectra obtained for different distances between the anode and the substrate but for the same inclination angles. It can be observed that the IR bands characteristic to polyaniline layers are similar.
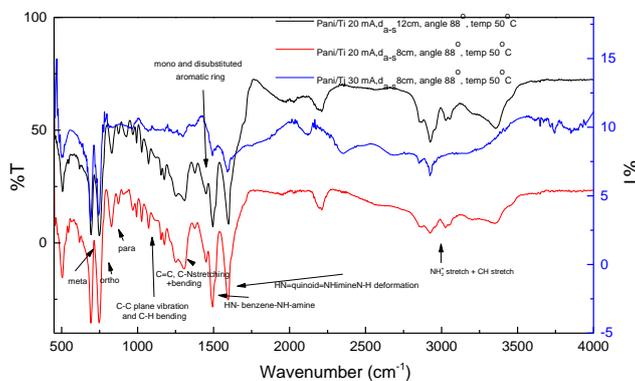
Fig. 8. FT-IR spectra of the P3, P6 and P9 samples.

For the samples deposited at 88°, respectively 45^0 angle and 20 mA, there are no major differences observed in the IR spectra (Fig.8).

Comparing these spectra with those deposited at a 30 mA discharge current, we observe some other peaks, compared to those specific for C=C and C-N stretching and bending bond vibrations, respectively para, mono and di-substituted aromatic ring namely those specific to HN-benzoid ring, HN-amine group and HN-quinoid ring [16].

The sample P9 deposited in the following conditions: 30 mA, 8 cm from anode, 88° angle and 50^oC temperature presents two different surface morphologies.

These particular areas, have a smooth respectively a rough texture. However, the FT-IR spectra do not show any major differences between them. Morphological analysis reveal the structures formed on the surface of the samples.
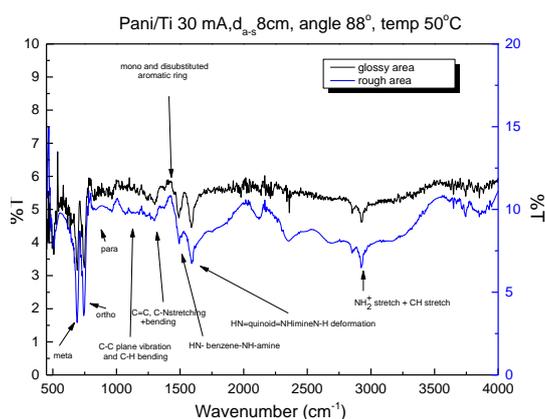
Fig. 9. FT-IR spectra of two distinct regions in the sample P9.

3.2. SEM imaging

Scanning electron microscopy imaging shows how the different deposition parameters influence the morphology of the resulting thin polymer films. While in the case of P2, P3, P5, P6 and P8 samples the images present uniform and smooth surfaces, samples P4 and P7 evidence uneven and porous structures.
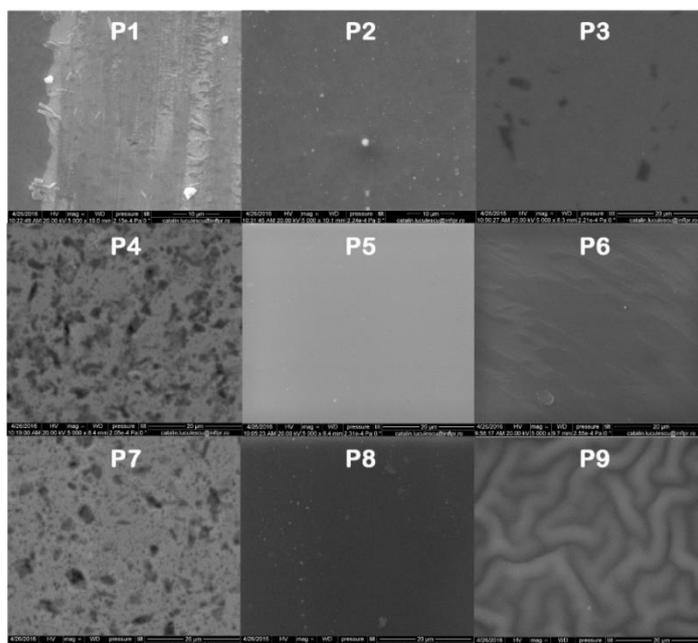
Fig. 10. SEM images of the P1-P9 plasma deposited polymeric samples.

The surface of the P9 sample presents two different kinds of surfaces, one smooth region and another one containing worm-like structures. FT-IR results for this sample sustain that both the smooth and the rough area have the same structural composition. The worm-like formations are uniformly distributed on a relatively large surface with macroscopic, ~1 cm^2, dimension. Extensive tests have shown that these strange formations only appear in the deposition conditions where the substrate is at an oblique angle from the incoming vapor flux and where the temperature of the monomer is over 40°. This is one very important aspect of our research study.

4. Conclusions

The use of a custom made configurable plasma polymerization reactor offers the possibility of creating thin polyaniline films with specific structural and morphological proprieties obtained by varying the key deposition parameters namely the inclination angle between the anode and the substrate. Important aspects such as the DC current, fine positioning and control of the substrate orientation make way in growing a variety of structured polymeric films. We have successfully demonstrated that by changing the injection temperature of the monomer, the distance between the electrodes, the angle between the substrate and the direction of the incident monomer vapors, various physical and chemical properties of the polymeric films can be modified as result from the FT-IR and SEM. The possibility to well manage a small sized material fabrication and be capable to fine tune the properties of a polymeric thin film represents a great challenge in the field and the good understanding of these effects and particular phenomena could bring improvements to many other inter-connected research domains such as condensed matter physics, surfaces and interactions, small scale molecular dynamics and simulations, optics and photonics, nanotechnologies and others.

References

[1] H. Biederman, D. Slavı´nska, Surface and Coatings Technology **125**, 371 (2000).
[2] Miroslava Trchová, Jaroslav Stejskal, Pure Appl. Chem. **83**, 1803 (2011).
[3] H. Yasuda, Plasma Polymers, Academic Press, New York, (1989).
[4] A.L. Alexe-Ionescu ,A. Th. Ionescu , E. S. Barna , V. Barna , N. Scaramuzza , J. Phys. Chem. B **108**, 8894 (2004).
[5] A.-L. Alexe-Ionescu, A. Th. Ionescu, E. S. Barna, V. Barna, N. Scaramuzza, Appl. Phys. Lett. **84**, 40 (2004).
[6] A. Groza, A. Surmeian, C. Diplasu, C. Luculescu, P. Chapon, A. Tempez, M. Ganciu, Surface and Coatings Technology **212**, 145 (2012).
[7] A. Groza, Romanian Reports in Physics 64, Supplement S, 1227 (2012).
[8] A. Groza, A.Surmeian, Journal of Nanomaterials 2015 (2015) .
[9] C. L. Popa, A. Groza, P. Chapon, C. S. Ciobanu, R. V. Ghita, R. Trusca, M. Ganciu, D. Predoi, Journal of Nanomaterials 2015 (2015).
[10] A. Groza, C.S. Ciobanu, C.L. Popa, S.L. Iconaru, P. Chapon, C. Luculescu, M. Ganciu, D. Predoi, Polymers **8**, 131 (2016).
[11] B. Butoi, C. Berezovski, D. Staicu, R. Berezovski, A. M. Marin, E.S. Barna, J. Optoelectron. Adv. M. **16**(9-10), 1212 (2014).
[12] M. M. Hawkeye, M. T. Taschuk, M. J. Brett, Glancing Angle Deposition of Thin Films: Engineering the Nanoscale, Wiley Series, New York (2014).
[13] M. M. Hawkeye, M. J. Brett, J. Vac. Sci. Technol. A **25**, 1317 (2007).

1382

[14] K. Robbie, J. C. Sit and M. J. Brett, J. Vac. Sci. Technol. B **16**, 1115 (1998).
[15] E. I. Toader, V. Covlea, Graham W.G., Steen P.G., Rev. Sci. Instrum. **75**, 382 (2004).
[16] E. I. Toader, V. Covlea, W G Graham, Plasma Sources Science Technol. **15**, 288 (2006).
[17] C. Miron, D. Nedelcu, Materiale Plastice **41**(4), 215 (2004).
[18] C Miron, Revista De Chimie-Bucharest, **59** (2), 181 (2008).
[19] C. Berlic, M. Moisescu, V. Barna, Digest Journal of Nanomaterials and Biostructures,
    7(4), 1401-1412, (2012).
[20] C Miron, F Simion, Materiale Plastice **41**(3), 185 (2004).
[21] C. Berlic, V. Barna, Molecular Crystals & Liquid Crystals, **549**(1), 140 (2011).
[22] C. Berlic, V. Barna, Optics Express, **18**(23), 23646 (2010).
[23] C. Berlic, V. Barna, Digest Journal of Nanomaterials and Biostructures, **11**(1), 159 (2016).
[24] C. Berlic, L. Constantinescu, Revista de Chimie, **55**(11), 910 (2004).
[25] C. Berlic, V. Barna, B. Manolescu Digest Journal of Nanomaterials and Biostructures,
    10(4), 1365 (2015).
[26] N. Scaramuzza , C. Berlic ,E.S. Barna , G. Strangi ,V. Barna, and A. Th. Ionescu , J. Phys.
    Chem. B, **108**(10), 32070 (2004).
[27] Barna V, et al. Opt Express., **14** (7), 2695 (2006).
[28] S. Ferjani, L. Sorriso-Valvo, A.o De Luca, V. Barna, R. De Marco, and G. Strangi Phys. Rev.
    E **78**, 011707 (2008).
[29] Lee JH, Atherton TJ, Barna V, De Luca A, Bruno E, Petschek RG, Rosenblatt C., Rev Lett.
    24, 102(16) (2009).
[30] M. Infusino, A. De Luca, V. Barna, R. Caputo, and C. Umeton, Optics Express,
    20(21), 23138 (2012).
[31] Y.-P. Zhao, D.-X. Ye, G.-C. Wang, T.-M. Lu, Proc. of SPIE 5219 (2003).
[32] M.O. Jensen, M.J. Brett, Appl. Phys. A **80**, 763 (2005).
[33] F. I. Iova, M. Băzăvan, Fl. Iova, Rom. Rep. Phys., **55**, 697 (2003).
[34] M. G. Olayo, J. Morales, G. J. Cruz, R. Olayo, E. Ordonez, S. R. Barocio, Journal of Polymer
    Science: Part B: Polymer Physics, 39 175–183 (2001) .
[35] C. Nastase, F. Nastase, A. Dumitru, M. Ionescu, I.Stamatin, Composites: Part A
    36, 481 (2005).