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Direct current plasma polymerization reactor for thin duromer film deposition

B. BUTOI[a], C. BEREZOVSKI[a], D. STAICU[a], R. BEREZOVSKI[a], A. M. MARIN[b], E.S. BARNA[a*]
[a]*University of Bucharest, Faculty of Physics, PO Box Mg-11, 077125, Bucharest, Romania*
[b]*University of Medicine and Pharmacy "Carol Davila", No. 8 Eroilor Sanitari Blvd., Bucharest, Romania*

Plasma polymerization is a technique for obtaining thin polymer films on a substrate surface from organic monomers by means of plasma discharge. In glow discharge polymerization, the monomer structure is not retained, yet the original monomer molecules serve as a source of elements for the formation of larger molecules. Here we present a new model of variable geometry Direct Current (DC) plasma polymerization discharge reactor, demonstrating some clear advantages over the already existing devices. The way our reactor is built allows for dynamically changing all of the most important discharge parameters for the polymer deposition. By carefully adjusting these main quantities, one can obtain countless duromer thin film structural morphologies exhibiting interesting chemical and physical features.

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1. Introduction

Human produced plasma is commonly used in various areas, due to its important role in the processing of industrial materials, such as: engraving, removal, pulverization, thin film developing etc. In its true meaning, plasma may be defined as a cvasineutral electric system formed of particles which are charged and neutral, having collective behaviour, photons, and electromagnetic fields. Positive charged particles are atomic or molecular ions and the negative ones are, usually, electrons, or, in particular cases, they are both electrons and negative ions. The neutral particles are those atoms or molecules which may be found in a fundamental state or in different excited states [1-3].

Plasma contains a mix of particles with different masses and electrical charges. At first sight, by thermal point of view, plasma may be considered to be made up of two subsystems, one of electrons and one of the heavy particles (molecules, neutral atoms and ions), each of them being in thermal equilibrium. This is why ions and electrons can be characterized by their own temperatures: the ion temperature (T_i) and the electron temperature (T_e). In particular cases, other temperatures can characterize the particles in plasma. At the same time, the heavy particles in the plasma can be characterized by the temperature of the gas (T_g), the temperature of the excitation (T_{ex}), the temperature of the ionization (T_{ion}), the temperature of dissociation (T_d) and the temperature of radiation (T_r). [4-6]

The thermodynamic equilibrium in plasma is reached only if:

$$T_g = T_{ex} = T_{ion} = T_d = T_r = T_e \qquad (1)$$

The thermodynamic equilibrium cannot be reached since T_r at the external limits of the plasma is never equal to the value of T_r for the core region. Nevertheless, in certain conditions, a local thermodynamic equilibrium (LTE) can be achieved. Generally, in the low pressure plasmas, the stabilization condition of LTE is not fulfilled. For these types of plasma, the temperature of the electrons is the most important parameter [2-4,7,8].

Plasma polymerization technique makes use of plasma sources to generate a discharging gas that supplies the energy to activate or fragment a liquid or gas monomer (often containing a formation of vinyl) in order to start the polymerization process. Generally, the resulting polymers are very ramified, reticular and adhere very well to solid surfaces, unlike the usual polymers created by means of classical methods. Some of the main properties of the ramified polymers are considered elsewhere [9]. The greatest advantage offered by plasma polymerization is that polymers can be directly attached to the desired surface, while the chains are growing, reducing the number of steps necessary for other processes for covering (i.e. grafting). This is an important phase for covering surfaces from 1000 pm, to a thickness of hundreds of microns, with otherwise insoluble polymers [10]. The mechanism of plasma polymerization is very complex [2,3]. The energy of ionization of plasma, the ion precursor, free electrons, radicals and neutral fragmentations may be parts of the recombination of polymer remains in plasma, on the surface of a substrate. The process is highly dependent on the chemistry of the precursor, along with the main parameters for the plasma process, such as geometry of the discharging chamber, of the electrodes, the strength of the plasma, temperature, the vacuum level and the rate of injection for the monomer [11, 12].

It is known that, for the plasma polymerization of thin films, the results can be divergent from those obtained by means of classic polymerization techniques. This is due to the altered constituents of the plasma and way of interacting with the monomer. Properties of polymeric films in general and plasma obtained ones in particular are very different, covering a broad field of applications (films for improving adhesion, compatibility and molecular alignment at the interface, wear resistant films, thin films used in membrane separation processes, hydrophobic films for optical applications, thin films for controlling the electo-optical switching in liquid crystal cells, organo-metallic films for microelectronics, films used for biocompatible materials) [13-18].

In another category of plasma-organic compounds interactions one can include the surface plasma treatments. This technique changes the surface properties of a conventional polymer, with the purpose of generating polar groups, reactive species and crosslinking of the surface molecules, allowing to improve wettability, adhesion, wear resistance and chemical reactivity [19].

The goal is using plasma polymerization to obtain new types of thin duromer films (from chemical and physical points of view), which are later to be used as control substrates in liquid crystals cells with special all-around properties. Some of our group members have extensively investigated this highly interesting research field (theoretically and experimentally) [20-28]. Nevertheless, we wish to gain further understandings of these motivating interaction phenomena, by using a particular variable geometry direct current plasma reactor that we have designed and built in the group.

In the present, paper we present a plasma reactor specially built for room temperature plasma polymerization thin film depositions. The device has certain characteristics which are absolutely necessary for the formation and control of the polymer thin film deposition. The reactor works on continuous voltage, a necessary aspect, in order to be able to use the ions (which have temperature close to those of the chamber) in the polymerization process, without having to worry about thermal affects on the monomer. Important aspects of our reactor are the variable geometry of the electrodes, variable position of the substrate while discharging, but also flexible deposition angle. There is a huge influence of the angle of deposition on the topography of the resulting thin duromer film.

2. Experimental setup

The reactor built for plasma polymerization was designed to meet the following conditions:

- the chamber of the reactor must have a variable geometry;
- the injection of the monomer must be directly made in the plasma through the anode;
- to have the possibility for modifying the position of the probe substrate between the two electrodes;
- the sample substrate can be rotated (with a controlled frequency) during the deposition process.

Having a variable geometry for the reactor chamber is a very important aspect. Because in plasma live different constituents (electrons, ions, neutral particles), having different energies in certain regions of the discharge, it is very important that the geometry of the system can be modified. That is - in order to create a plasma with a shorter or longer discharge column which can be either striated or non-striated (allowing for changing the process parameters). Also, the position of the electrodes, their shape and built material (in our case the electrodes are made of duralumin), the volume of the chamber can be customized.

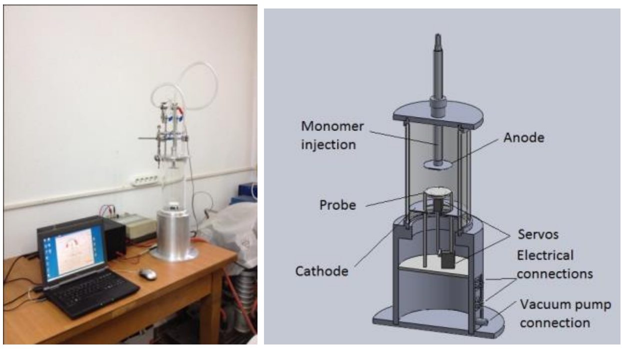


Fig. 1. DC plasma reactor used for plasma polymerization experiments.

The injection of monomer in the reactor takes place through a hole in the centre of the anode. This is necessary, in order to guarantee the symmetry conditions for a polymer deposition. By injecting the monomer in this way, it interacts with the ions through the positive column (a necessary process for the polymerization, because the temperature of the ions $T_{ion}<T_e$, thus breaking some bounds of the monomer). The gravitational force is somehow suppressed, despite the monomer being injected on the upper side of the probe. It does not drop so rapidly on the probe substrate, due to the applied electric field, and only after its interaction with the plasma glow discharge. A sketch of the main parts of the plasma reactor together with an actual picture of the device are presented in Fig. 1.

By modifying the probe substrate position in the chamber of the reactor emerges the possibility of employing different regions of the plasma discharge. A polymerization process taking place in the positive column (where ions are used) offers certain possibilities for the formation of a thin polymer film on the substrate, while an experiment in the negative region opens the chance to benefit from the electrons in the discharge. Because they have larger energies and temperatures than the ions, the electrons influence the polymer deposition in a different way. With our design, the probe can be placed either up to 1cm away from the anode (between the two electrodes), or up to 10cm under the cathode.

As an upgrade to the technique of Glancing Angle Deposition (GLAD) which implies a deposition at a certain chosen angle [29], besides the inclination of the probe from 0^0 to 90^0, the sample substrate has the possibility to rotate with a controlled frequency (between 1 and 1000 rpm) (Fig. 2).

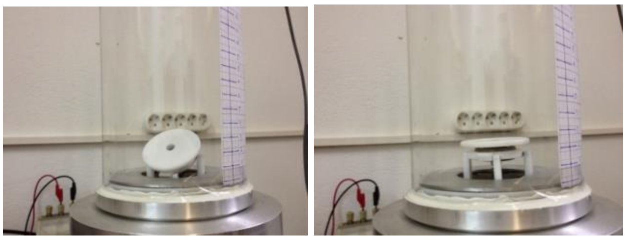


Fig. 2. Pictures of the plasma reactor showing different possible angle inclinations for the sample substrate inside the deposition chamber.

The main control parameters for the plasma discharge during deposition can be varied in our device as follows: applied voltage between 100 - 1500V, discharge current between 5 - 300 mA, in chamber vacuum pressure level between 10^{-1} - 10^3 torr. This is a very important aspect for the polymer deposition, since these parameters can highly influence the way the polymer develops, either in the plasma glow or on the surface of the probe substrate, and can also lead to different structural formations. For example, a high discharging current may destroy the monomer, breaking all of its chemical bounds. Correlated with the speed of the injection of the monomer, but also with the position of the substrate inside the reactor, it can be deduced what kind of deposition will be taking place, what structure it will adapt to. The position of the substrate is controlled with the help of two servomotors, which are computer controlled, in order to have a greater precision. The schematic representation of the reactor with all its components is presented in Fig. 3.

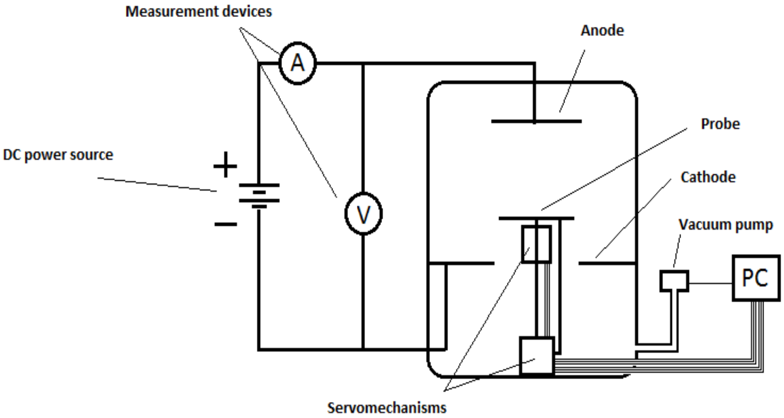


Fig. 3. Schematic representation of our DC plasma reactor including all its main parts.

3. Experimental Results and Discussions.

3.1 Optical characterization of plasma

The rotational structure of the emission spectra of molecular plasma is often not resolved, because in the process of controlling materials with plasma, the spectral devices with high power resolution are not being used. Therefore, in order to determine the parameters of plasma, it is necessary to create a deconvolution of these spectra. In our situation, the deconvolution was performed with a special software for fitting the experimental spectra [30].

The temperatures of rotational and vibrational modes were determined by applying a local thermodynamical equilibrium model with two temperatures, T_r and T_v. Procedures, algorithms, fitting and simulations of the spectra software were developed for the following molecular transitions: N_2(C $^3\Pi_u$ → B $^3\Pi_g$, the second positive system (SPS), N_2^+(B $^2\Sigma_u^+$ → X $^2\Sigma_g^+$), the first negative system (FNS).

The steps followed in the simulation of the spectra were:

a. The frequencies of the permitted transitions were calculated using of the following relations for N_2 and N_2^+ molecules:

$$\begin{aligned}\nu_R &= \nu_{v'v''} + \left[F_{v'}(J+1) - F_{v''}(J)\right]c \\ \nu_R &= \nu_{v'v''} + \left[F_{v'}(J) - F_{v''}(J)\right]c \\ \nu_P &= \nu_{v'v''} + \left[F_{v'}(J) - F_{v''}(J+1)\right]c\end{aligned} \tag{2}$$

where

$$\nu_{v'v''} = \nu_0 + \left[G(v') - G(v'')\right]c \tag{3}$$

The expression of the rotational constants B_v, D and the term of vibration, G, were calculated, taking into consideration the molecular constants:

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) \tag{4}$$

$$D = \frac{4B_e^3}{\omega_0^2} \tag{5}$$

$$G(\mathrm{v}) = \left[\left(\mathrm{v}+\frac{1}{2}\right) - \left(\mathrm{v}+\frac{1}{2}\right)^2 x_e + \left(\mathrm{v}+\frac{1}{2}\right)^3 y_e\right]\omega_e \tag{6}$$

For the N_2 and N_s^+, the rotational terms are:

$$F_\mathrm{v}(J) = B_\mathrm{v} J(J+1) - DJ^2(J+1)^2 \tag{7}$$

The intensity of a not broadened rotational line, which is part of the wave v’-v’’, is given by:

$$I(\nu_i) = const. \times \nu^4_{\mathrm{v'v''}} q_{\mathrm{v'v''}} \nu_i^4 s_{J'J''} e^{-\frac{hc}{k}\left[\frac{G(\mathrm{v'})}{T_\mathrm{v}} + \frac{F_{\mathrm{v'}}(J'c}{T_r}\right]} \tag{8}$$

Here, $S_{J'J''}$ is the Hoenl-London factor associated to the transition J’-J’’ and $q_{y'y''}$ is the Franck-Condon factor characteristic to the vibrational wave v’-v’’.

The width of the spectral lines is a parameter which must be separately taken into consideration, due to the fact that rotational structure is not resolved. The spectral lines are Doppler broadened, also due to the bumps in the plasma. In many cases as well, the width caused by the spectral device is larger than the one in the plasma lines. In the simulation of the spectrum, the instrument profile was approximated by a Gaussian profile. In this way, for a certain wavelength, the intensity in the simulated spectrum was obtained through suppression of the contribution of all the rotational spectral lines at the same wavelength. An example of a fitted spectrum is presented in Fig. 4.

$$I_{sim}(\nu) = const. \times \sum_i e^{-\left(2\frac{\nu-\nu_i}{\delta\nu}\sqrt{\ln 2}\right)^2} \nu^4_{\mathrm{v'v''}} q_{\mathrm{v'v''}} \nu_i^4 s_{J'J''} e^{-\frac{hc}{k}\left[\frac{G(\mathrm{v'})}{T_\mathrm{v}} + \frac{F_{\mathrm{v'}}(J'c}{T_r}\right]} \tag{9}$$

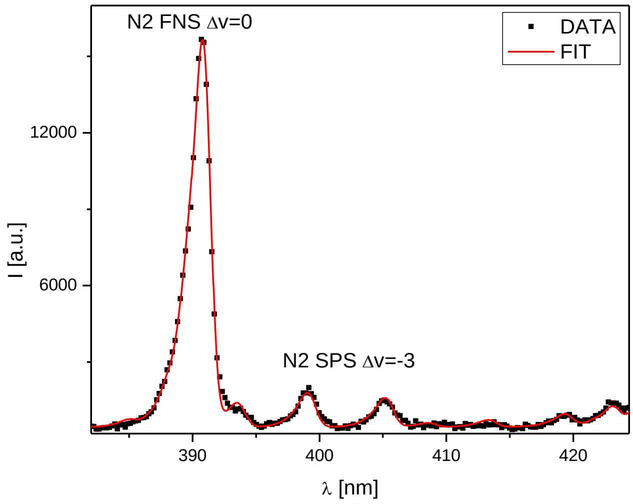
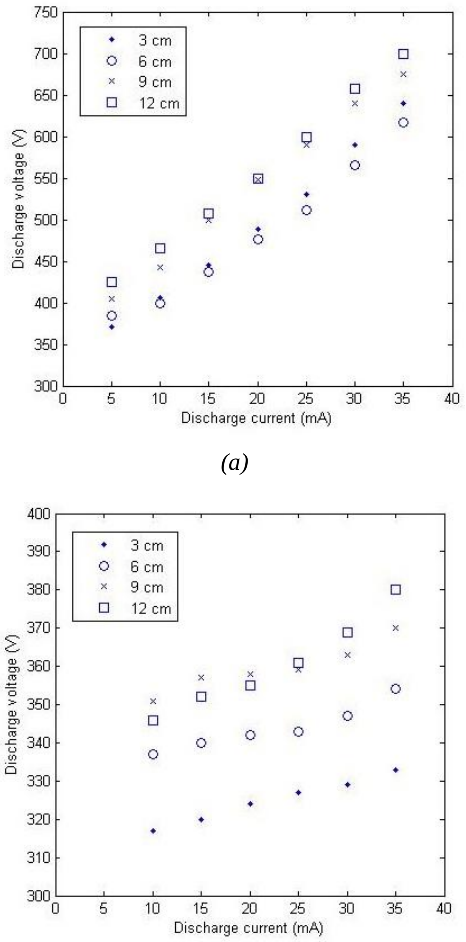


Fig. 4. Fitted spectrum for 20mA discharge.

3.2 Electrical characterization of plasma

Fig. 5 shows the volt-ampere characteristics of the reactor when using 0.1 torr and 1 torr of inside vacuum level, for different distances between the two discharge electrodes.



(a)

(b)

Fig. 5 The volt-ampere characteristics of our DC plasma reactor for various distances between the electrodes. The pressure inside the chamber was: (a) p = 0.1 torr and (b) p = 1 torr.

From these volt-ampere characteristics, we may notice that, in the stationary state and before the injection of the monomer in the discharging chamber, a slight rise in the voltage can lead to a relatively high rise of the discharging current.

In table 1 we present the temperatures for rotational and vibrational modes obtained from the fitting of the discharging spectrum: N_2^+ FNS sequence Δv=0 and N2 SPS sequences Δv=-2,-3. The fitting of the spectrum was done for the 360-410 nm wavelength region. Here, d is the distance between the two discharge electrodes.

Table 1. Rovibrational temperatures obtained from the fitting of the spectrum.

File	**T_r** N2 FNS $\Delta v=0$ [K]	95% ±confidence bounds [K]	**T_r** N2 SPS $\Delta v=-2,-3$ [K]	95% ±confidence bounds [K]	**T_v** N2 FNS $\Delta v=0$ [K]	95% ±confidence bounds [K]	**T_v** N2 SPS $\Delta v=-2$ [K]	95% ±confidence bounds [K]
d=5cm								
0p1torr20mA360V.txt	340	19	328	58	1750	188	4261	380
1p1torr20mA380V.txt	379	24	375	44	1799	224	4130	249
d=10 cm								
0p1torr20mA460V.txt	319	32	392	163	2105	320	5846	1526
1p1torr20mA420V.txt	367	20	371	65	1660	196	4357	409
d=15 cm								
0p1torr20mA450V.txt	329	34	383	143	1872	345	4895	1044
1torr20mApeste1kV.txt	349	35	378	60	1586	378	3890	307

After the fitting, for the discharging currents used in the deposition, the ion medium temperature is approximately 330 K, not much bigger than room temperature. So, there are no significant thermal phenomena that can perturb the monomer during the polymerization process.

5. Conclusions

Plasma polymerization has a lot of advantages when compared to classic polymerization techniques. In plasma polymerization processes, the monomer does not need to have a double bond, an aromatic structure or an unsaturated bond in order to be able to form polymers. Practically all the carbon (or silicon) compounds can be polymerized in plasma. Due to the high energies (compared to the binding energy of molecules) of the plasma species (electrons, ions, excited species) the modification of the initial structure of the monomer is expected and new compounds are obtained. In this manuscript we propose a new variable geometry model of device as a DC plasma polymerization discharge reactor, which shows some clear advantages over the already existing instruments. The way our reactor is built allows for carefully controlling and even dynamically changing all of the most important discharge parameters such as: pressure, distance between the electrodes, applied voltage and discharge current, temperature, sample substrate position within the reactor chamber and its inclination with respect to the vertical position (while even having the possibility to rotate the probe with different frequencies). By adjusting these main parameters one can obtain various duromer thin film structural morphologies exhibiting different chemical and physical features. The use of the ions from the positive column of discharge does not affect thermally the initial monomer flow. An important element is obtaining numerous structural types of polymers by changing the angle between the probe substrate and the monomer flow direction. In this way, layers of the same polymer can be achieved, having different morphologies and therefore presenting many possibilities in fabricating the subsequent liquid crystalline cells. The variety of obtainable plasma polymer layers can be increased if we mix the monomer with gases, which are typically used for modification processes. The result will be a modified plasma polymer layer, which combines the principal advantages of the plasma polymer with the functionality of a plasma modified surface. We also present and the volt-ampere characteristics for several distances between the two discharge electrodes and at different vacuum pressure levels.

The high demand of thin polymer films leads to the necessity of further investigating these fabrication and deposition methods and, additionally, to enhance the properties of the resulting materials for a broader field of employment and application.

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* Corresponding author: barna_emil@yahoo.com