Digest Journal of Nanomaterials and Biostructures Vol. 7, No. 4, October-December 2012, p. 1481 - 1490

FABRICATION AND CHARACTERIZATION OF THIN POLYANILINE FILMS OBTAINED BY GLANCING ANGLE DEPOSITION (GLAD) TECHNIQUE

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In this manuscript we present interesting scientific results following the physical characterization of thin polyaniline polymer films achieved by means of Glancing Angle Deposition (GLAD) method. Aniline monomer was used as precursor in a cold plasma polymerization chamber and the resulting thin films were investigated by various physical techniques (Atomic Force Microscopy - AFM and Scanning Electron Microscopy - SEM), while also considering their conductive electrical properties.

(Received August 17, 2012; Accepted September 26, 2012)

Keywords: Plasma polymerization, GLAD technique, Aniline, Thin polymer films, Four points measurements

1. Introduction

Glancing Angle Deposition (GLAD) technique is an extension to the oblique angle deposition method, where the substrate position can be changed during the polymer film deposition. GLAD is a widely used and versatile technique for the fabrication of thin polymer films. It involves the dynamic control of the substrate tilt angle and rotation parameters with respect to the incoming vapor direction, allowing the control and manipulation of the morphology and physical properties at the nanometer scale for the deposited thin polymer film [1,2].

At the foundation of GLAD stands the ballistic shadow effect that occurs only when a flux of vaporized atoms or molecules reach the substrate, tilted at an oblique angle with respect to the flow direction. Ballistic shadowing is the key for GLAD - based thin film engineering. Such shadowing is only possible if the incoming vapor flux is well collimated. If there is a large angular spread for the incoming vapor flow, then the shadows will be poorly defined [3].

During this type of oblique deposition, the surface topology is molded by ballistic shadowing. The arrival of vapor flux and formation of film nuclei is nevertheless a random process. The nuclei grow into columns and develop shadows. The columns and shadows will also have a size distribution. Narrow angle distribution of the incoming flow of particles is required in the GLAD technique. If the angle distribution of the flux is excessively wide, the incoming particles will be able eventually to fill in the voids and cancel the columns growth.

As the nuclei grow, more incoming vapor flux will further aid to deposit on top of them. This self-reinforcing behavior helps in building isolated columns, in the case of adatom surface mobility being low. The growth of GLAD columns depends on many physical parameters such as the shadowing level between columns, deposition rate, deposition temperature, deposition pressure, vacuum level and composition, substrate type and morphology, substrate preparation and preferred crystallinity of the deposited material.

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The GLAD technique has been so far used with success for manufacturing optical filters, films with enhanced planar birefringence, high capacitance films and was employed in a multitude of other applications [4-6]. However, the method was not a lot exploited with the purpose of enhancing the response of active or functional materials [7-9].

In this paper we present an experimental analysis showing the influence of the deposition angle in Glancing Angle Deposition technique on the polyaniline thin films properties. By GLAD polymerization method we obtain an interesting striped aligned material, which can have multiple applications in the field of electro-optical devices, medical applications, biofuel cells or materials for supercapacitor electrodes.

2. Experimental details

For the cold plasma polymerization we employed a plasma reactor that was coupled to a vacuum system line (Figure 1). A controlled flux of monomer vapor flow was established in the plasma chamber in the proximity of the substrate holder, between the active anode and cathode elements. Electrons emitted by the surface of the cathode are accelerated into the applied electric field of the anode-cathode system and generate excited monomer molecules while en route to the substrate.

Si substrates (100) with type p conductivity and 10^2 Ωcm resistivity were oriented at different incident angles with respect to the vapor flux direction (70°, 90°,120°) and revolved at 20 rpm. We used aniline (C_6H_7N) as the primary monomer (Fluka, 99,0 % purity).

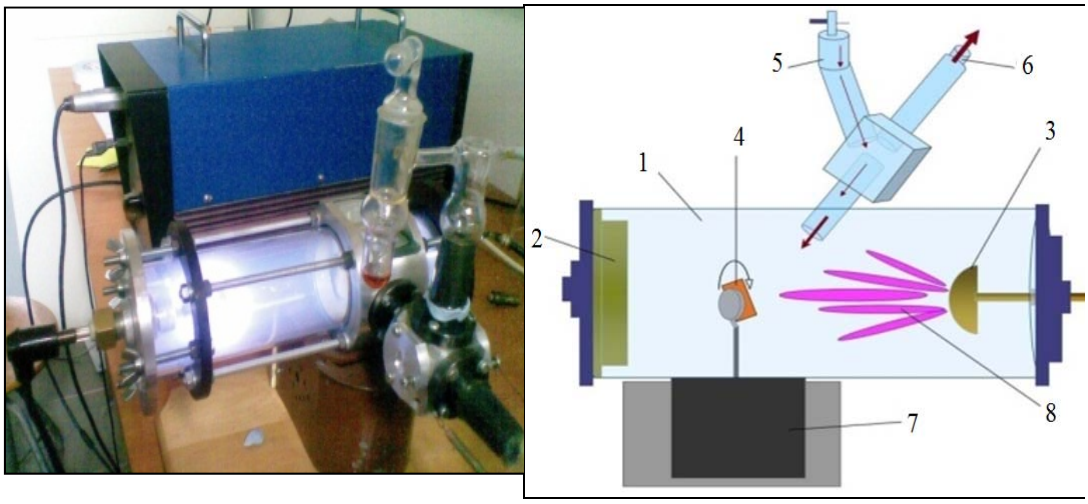


Fig. 1. Experimental setup. (Left) Picture of a discharge in the cold plasma GLAD reactor. (Right) Diagram showing the main parts inside the plasma reactor : 1-reaction chamber; 2- cathode; 3- anode; 4- rotating substrate; 5- monomer injection chamber and flux; 6- vacuum system; 7- motor for substrate rotation; 8- plasma discharge flux.

The obtained thin films were characterized by Atomic Force Microscopy (AFM) and the conductivity of the films was determined by 4-points electrical measurements. The AFM morphology measurements were performed with a NTegra Prima class instrument, while the electrical conductivities were measured with a Keithley model 2400 Series Sourcemeter of I-V characteristics instrument, in a 4-points setup configuration.

The cross sections of the films were investigated by means of a Scanning Electron Microscope (SEM - TESCAN VEGA XM) operated at 30 kV accelerating voltage and 10 μA emission current.

3. Results and discussions

3.1. Morphology of films. AFM and SEM results.

The characteristics of the thin polymer film samples such as surface morphology and roughness were studied by non-contact mode AFM. Geometric shadowing (due to the substrate tilt) and low adatom mobility leads generally to the appearance of surface nanostructures having moderate to high porosity.

Fig. 2 shows the AFM measurements for three discrete thin polymer films achieved in various tilt angles conditions (70°, 90° and 120° respectively), at a rotational speed ω=20 rpm. Experimental parameters employed for the GLAD thin film deposition are presented in Table 1.

Table 1. GLAD deposition parameters.

Sample	Deposition time (s)	Pressure (torr)	Deposition angle (α)
1	60	7.8×10^{-2}	120°
2	60	7.8×10^{-2}	90°
3	60	7.8×10^{-2}	70°

Figure 2 and Figure 3 show typical AFM topographical images for the considered three polyaniline thin film samples deposited on Si substrates. The scan areas are 10 μm x10 μm and 1 μm x1 μm respectively (Figure 3).

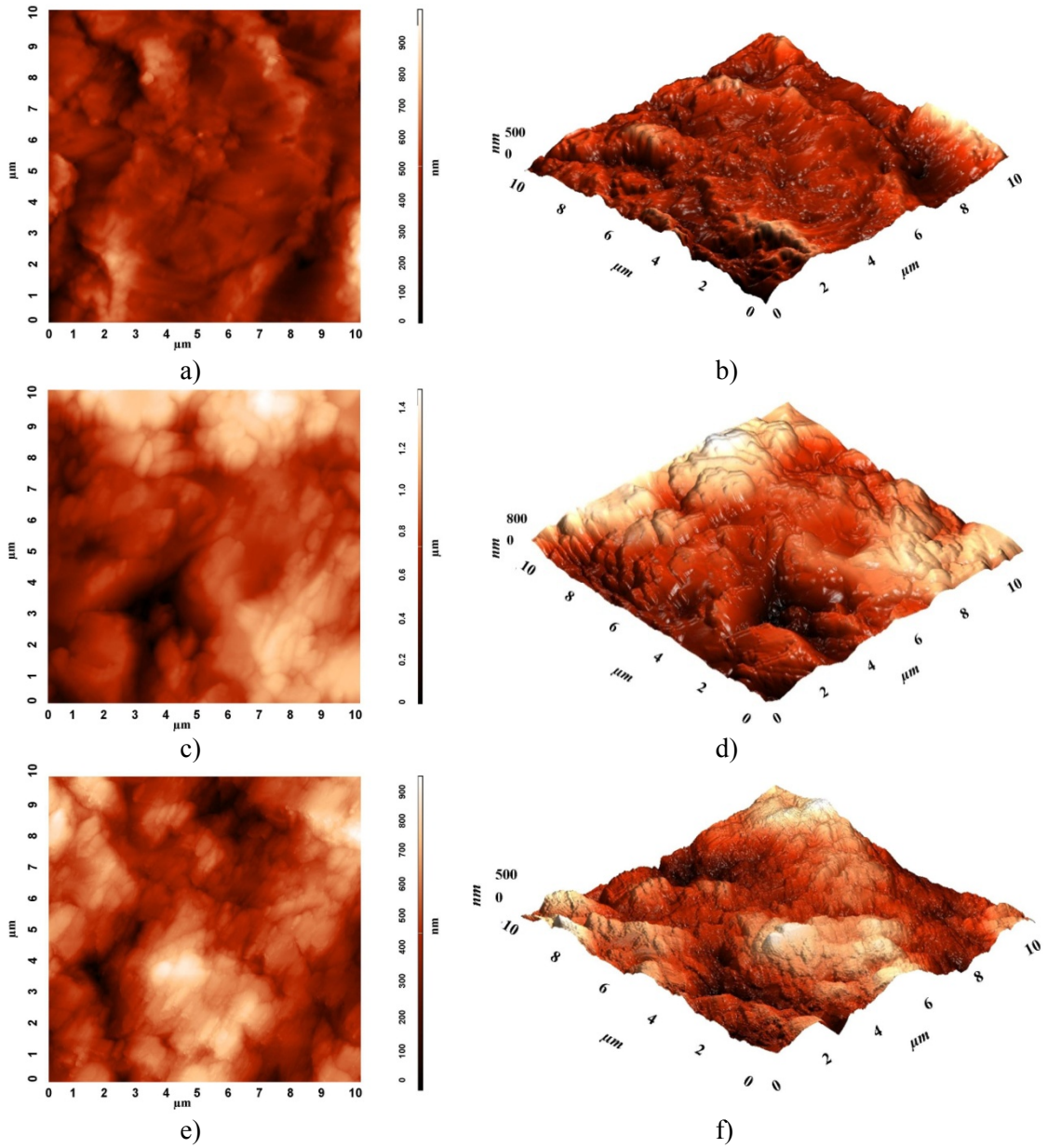


Fig. 2. 2D and 3D non-contact mode AFM scan representations of thin polyaniline films obtained by GLAD plasma polymerization technique (10 µm x10 µm image size). (a,b) Sample 1. (c,d) Sample 2. (e,f) Sample 3.

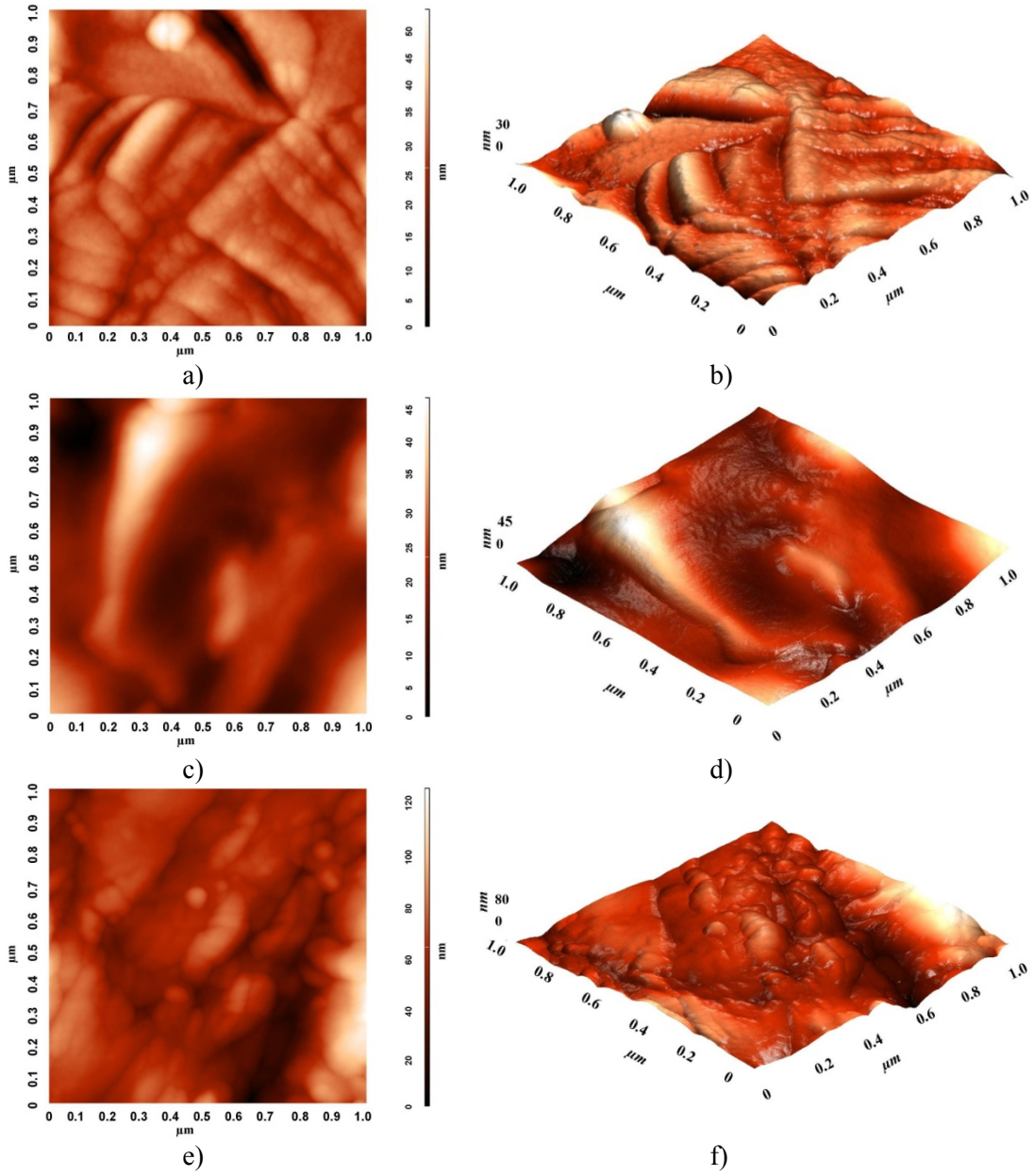


Fig. 3. 2D and 3D non-contact mode AFM scan representations of thin polyaniline films obtained by GLAD plasma polymerization technique (1 µm x 1 µm image size). (a,b) Sample 1. (c,d) Sample 2. (e,f) Sample 3.

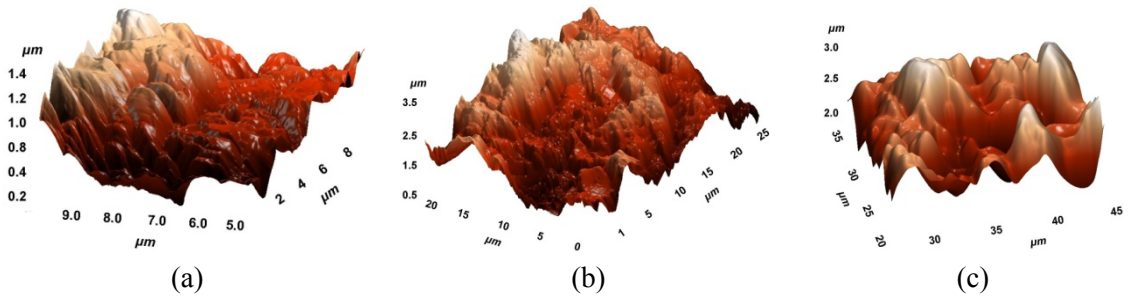
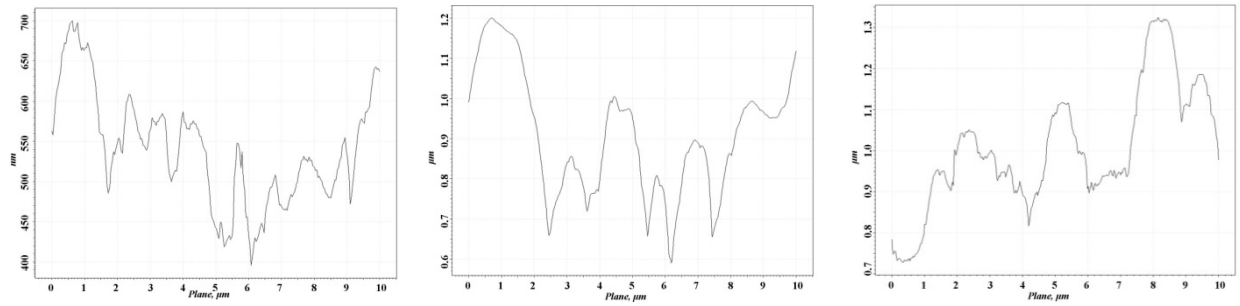


Fig. 4. Non contact AFM images of the polymer columns obtained via the GLAD technique. (a)Sample 1; (b)Sample 2 and (c) Sample 3.

In Fig. 4 we present the 3D AFM topographical images for the obtained samples. Some columnar growth can be observed, depending on the angle of incidence for the Si substrate. With increasing angle of incidence we can obtain higher tilt angle for the polymer columns. During the formation process of the columns there is an intra-columnar increase of the film, development that leads to the formation of aligned polymer stripes.

The quantitative values for the root-mean-square (RMS) roughness have been obtained through conducting sectional analysis (by using the built-it software of the AFM instrument).

Samples prepared in the range 70° - 120° tilt angles exhibit the increase in the RMS value for roughness from 200 to 250 nm, when measured on 10 μm^2 area AFM scans, as shown in figure 5 and table 2. The investigated polymer samples were 5 µm thick.



(a) (b) (c)

Fig. 5. RMS surface Roughness for : (a) Sample 1, (b) Sample 2, (c) Sample 3.

Table 2. Root Mean Square Roughness values for Samples 1, 2 and 3.

Sample	Root Mean Square (RMS) Roughness (nm)
1	247,334 nm
2	209,356 nm
3	201,378 nm

The roughness value of the polymer thin films increases with increasing value of the deposition angle (Figure 6).

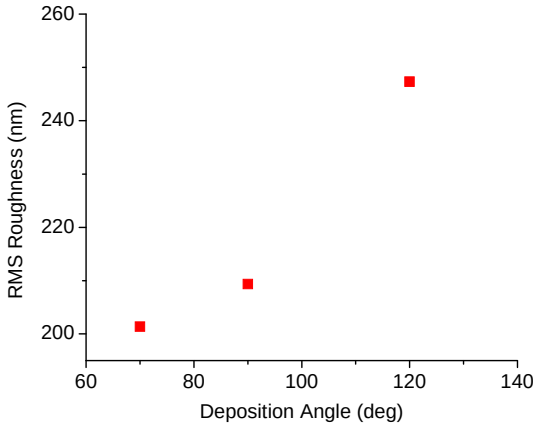


Fig. 6. Roughness Root Mean Square value dependence on the deposition angle for the three polymer films.

Fig. 7 presents the AFM 2D and 3D image scans at 300 nm x 300 nm resolution of Sample 2 (90° incident angle). Increased column diameter is about 50 nm.

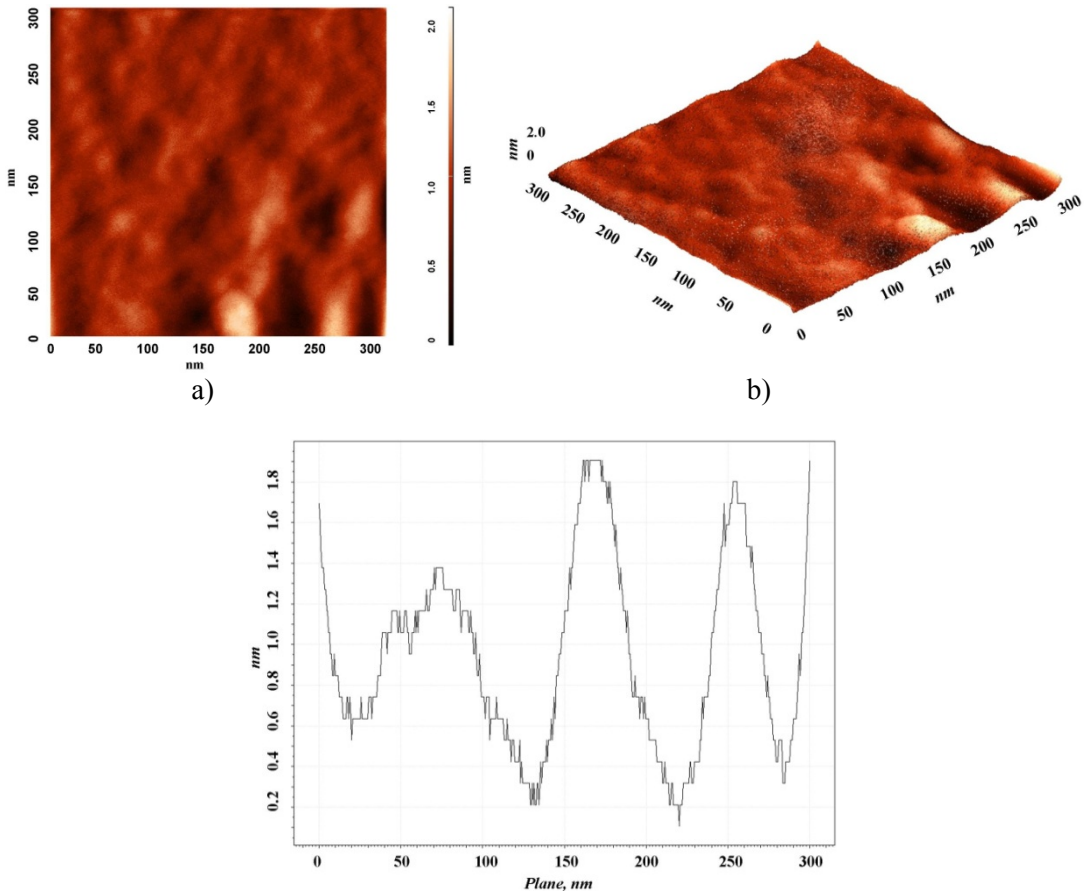


Fig. 7. AFM measurements of Sample 2. (a) 2D and (b) 3D representations of the 300 x 300 nm surface scans. (c) Columns profiles and height representation.

The cross sections of the polyaniline films were also investigated by means of a scanning electron microscope (TESCAN VEGA XM) operated at 30 kV accelerating voltage and 10 μA emission current (Fig. 8).

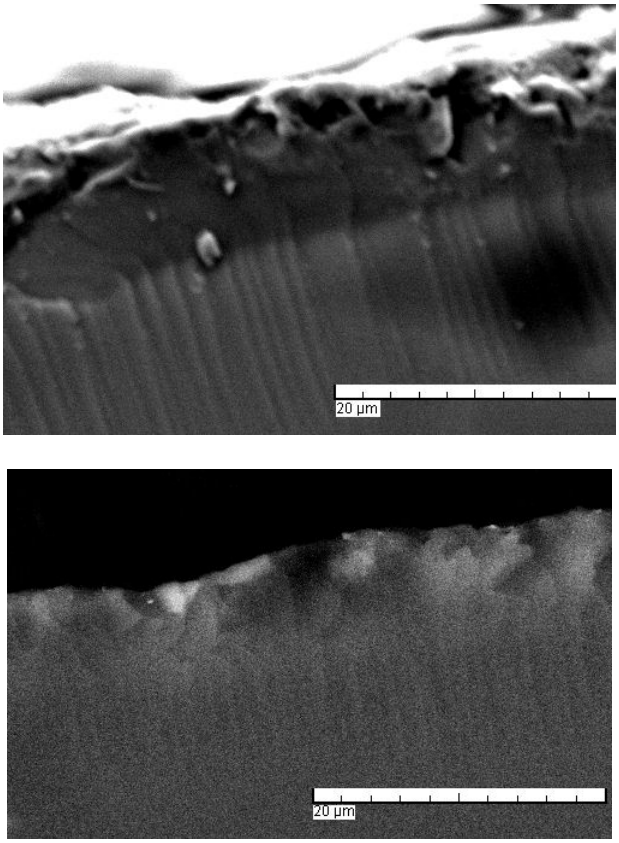


Fig. 8. Scanning Electron Microscopy (SEM) image for (top) Sample 1 and (bottom) Sample 2.

SEM measurements confirmed the columnar growth pattern in the form of aligned polymer strips.

3.2. Electrical resistivity and conductivity measurements.

The four-point collinear probe method was employed for measuring the resistivity for the obtained polyaniline thin films. Figure 9 shows the electrical probe arrangement consisting of a current source and a voltmeter.

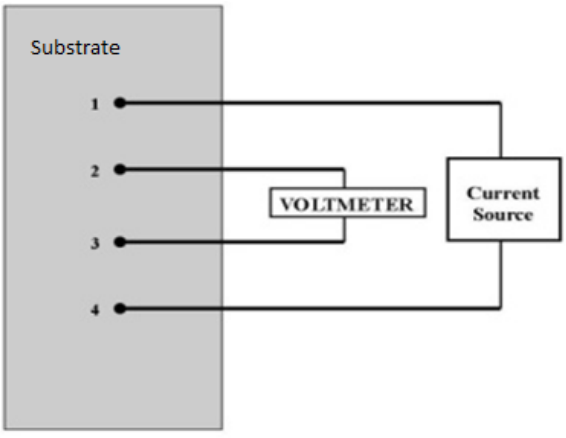


Fig. 9. Four-Points Collinear Probe Resistivity Configuration.

Obtained experimental results are shown in Table 3.

Table 3. Four-Points experimental data for the three polymer samples.

Sample	V_{14} (V)	I_{14} (A)	V_{23} (V)
1	1	6×10^{-8}	0.142
2	1	7.4×10^{-8}	0.170
3	1	9×10^{-8}	0.205

The volume resistivity (ρ) is calculated as follows:

$$\rho = \frac{\pi}{\ln 2} \times \frac{V}{I} \times h$$

where: V is the measured voltage, I is the source current and h is the sample thickness.

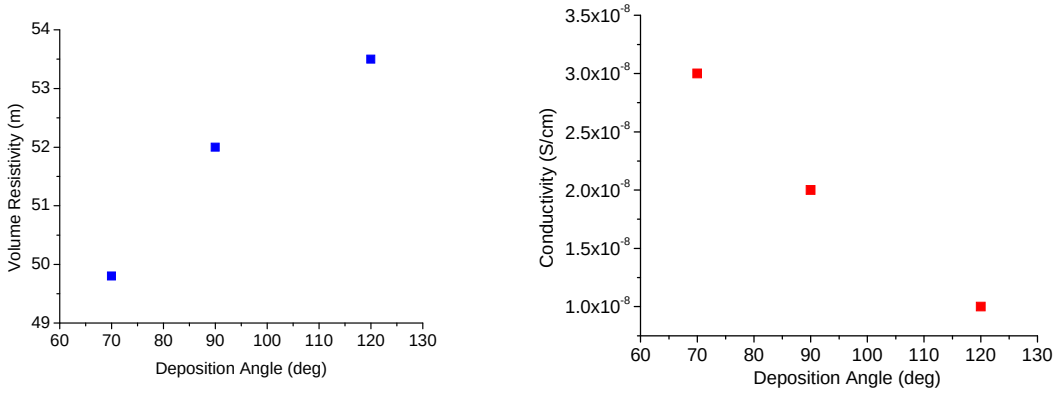
In table 4 we present the volume resistivity and conductivity results for the considered polyaniline samples.

Sample	Volume resistivity (Ωm)	Conductivity (S/cm)
1	53.5	1.87×10^{-8}
2	52.0	1.92×10^{-8}
3	49.8	2.00×10^{-8}

Table 4. Volume resistivity and conductivity data for Samples 1, 2 and 3.

The obtained results for the electrical conductivity of our thin films are comparable with reported values in scientific literature for plasma polymerized polyaniline.

The volume resistivity increases while the conductivity decreases with increasing angle of vapor deposition, as shown in Figure 10.



a) b)

Fig. 10. (a) The volume resistivity and (b) electrical conductivity dependence on the deposition tilt angle value.

4. Conclusions

In this paper we obtained and characterized thin polyaniline films achieved via cold plasma Glancing Angle Deposition technique. Atomic force microscopy measurements show that GLAD is an effective method in producing high quality structured thin films. We report the influence of the substrate deposition angle on the thin films physical properties. The roughness for

the obtained polymer films increases with increasing of the deposition angle. Growth models the thin films and results is a columnar pattern arranged in stripes along the substrate. The electrical conductivity measurements show a decrease in the mean value with increasing deposition angle. The obtained polymer material could be used in medical application arena as one-dimensional or directional preferred support growth for tissue, in biofuel cells, electro-optical devices or as material for supercapacitor electrodes. Further researches in the area of plasma opto-electronic polymer thin films are mainly focused on specific surface modifications and functionalization for achieving desired surface properties (e.g., environmental stability, biocompatibility, adhesion, low or high surface energy etc).

Acknowledgments

The work was supported by the Sectorial Operational Programme for Human Resources Development 2007-2013, co-financed by the European Social Found, under the projects numbers POSDRU/88/1.5/S/56668 and POSDRU/89/1.5/S/60746. The research work was also supported from the Romanian National projects UEFISCDI: PD nr.15/2010, TE 225-96/2010 and ID-PCE-2011/3/1007.

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