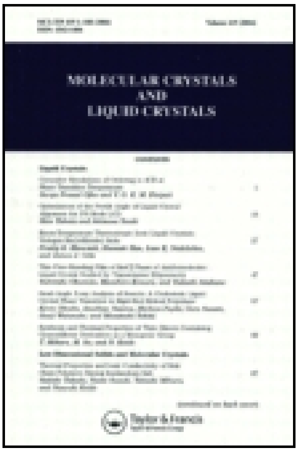

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Analysis of Polyaniline Films Using Atomic Force Microscopy

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This work presents a morphological study of polyaniline (PANI) films, chemically and electrochemically synthesised over ITO (Indium Tin Oxide covered glass) substratum using atomic force microscopy (AFM). From AFM images we calculate the fractal dimension of the polyaniline formed films using power spectral density (PSD) and the box counting method (roughness versus scale). As a result it is shown that the fractality obtained by PSD are in good agreement with box counting.

Keywords: polyaniline; atomic force microscopy; fractal; power spectral density; box counting

INTRODUCTION

It is well known that the electrical properties of conjugated polymers depend strongly on the film morphology. Since such polymers are candidates for active materials of a new class of electronic and optoelectronic devices, it is useful to control their morphology looking better device efficiencies. Therefore, the control of the morphology may improve such properties and, consequently, the

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efficiency of any derived devices. This work presents chemical and electrochemical synthesis of thin polyaniline (PANI) films and their characterisation by Atomic Force Microscopy (AFM). AFM images can be represented in the frequency domain by a Fourier Transform (FT) image[1]. From the FT, it is possible to derive the 2D power spectrum density[2]. From the PSD integral[3], it is obtained a curve whose characteristics indicates the self-affine character of the surface[4, 5]. If a linear PSD integral versus wavelength dependence is observed, at least in the part of the total PSD integral curve, the surface is self-affine in such part[6]. So, using the angular coefficient of this part of the curve, it is possible to calculate the fractal dimension of the surface[7]. Another way to obtain this fractal dimension is that of the roughness curve as function of the scale. From the angular coefficient of the inclined portion of the curve (α) it is possible to calculate the fractal dimension[8, 9]. Fitting the inclined and the horizontal portion of the curve, as well as calculating the intersection of then it is possible to find the characteristic length (ξ) of the surface which is related to the lateral character of the surface[10].

EXPERIMENTAL PROCEDURES

The electrochemical synthesis was accomplished in an aqueous solution of HCl using calomelan as reference electrode and platinum in form of helical thread as counter-electrode, and ITO (Indium Tin Oxide covered glass) as work electrode. The polyaniline was synthesised electrochemically in an aqueous solution of HCl 1M and aniline monomer in the initial concentration of 0,01 M and 0,05 M using cyclic voltametry method in the interval of 0,0 to 0,9 V versus SCE.

The chemically synthesised polyaniline was dissolved in N-methyl-2-pyrrolidone (NMP), 0,1 g of PANI in 100 ml of NMP, and stirred magnetically for 48 hours, and then filtered in paper filter and in 0,5 μm filter. The deposition over ITO substrate was accomplished using a micropipette that facilitates the leak of 5 μ litres on the substrate. After the casting procedure the sample was placed in an oven at 30°C for 72 hours to eliminate the solvent. The produced sample was, then, examined by optical microscopy to evaluate how uniform the deposited film was.

RESULTS AND DISCUSSION

AFM experiments were carried out using a Nanoscope IIIa (Digital Instruments) on contact mode, with a silicon nitride triangular shaped cantilever tip (0,06 N/m spring constant).

Figure 1 shows AFM images of electrochemically deposited PANI film for 1, 2 and 3 deposition cycles using solution concentrations of 0,01M. It is ease to note that the aggregates have a similar magnitude order for the samples cycled 1 time and three times. The sample cycled two times appear to be greater aggregates.

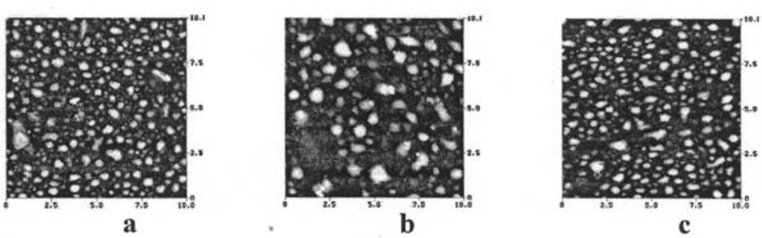

FIGURE 1 AFM images of electrochemically deposited PANI films for 1(a), 2(b) and 3(c) deposition cycles using solution concentrations of 0,01M.

Figure 2 shows AFM images of electrochemically deposited PANI film images for 1, 2 and 3 deposition cycles using solution concentrations of 0,05M. It is shown a degreasing tendency of the aggregate size from 1 cycle to 3 cycles. Figure 3 shows AFM image of chemically deposited PANI film.

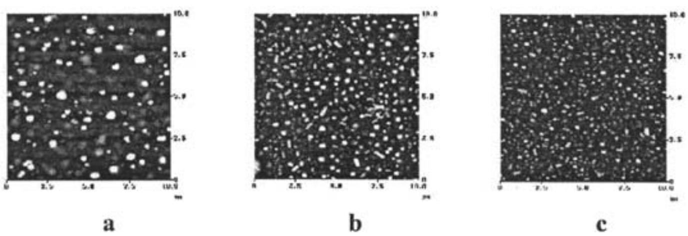

FIGURE 2 AFM images of electrochemically deposited PANI films for 1(a), 2(b) and 3(c) deposition cycles using solution concentrations of 0,05M.

Figure 3 shows AFM image of chemically deposited PANI film where the aggregate size are smaller than that produced by electrochemical deposition.

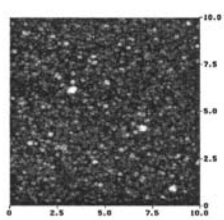

FIGURE 3 AFM image of chemically deposited PANI film.

The AFM images made possible to plot power spectrum density and power spectrum density integral versus wavelength as shown on figures 4 to 6. cycled surfaces. The power spectrum density integral was used to investigate the existence of fractal character in these surfaces. All of them showed the existence of a linear portion on an interval of the curve, indicating a fractal character in such interval. The calculated fractal dimension are shown on table 1.

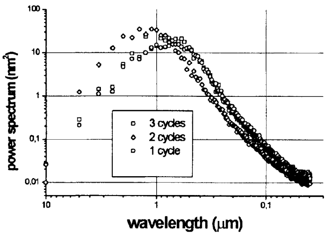

FIGURE 4 Power spectrum density of samples prepared by electrochemical process on 0,01M solution.

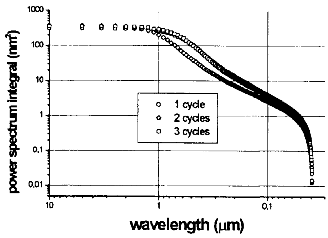

FIGURE 5 Power spectrum density integral of samples prepared by electrochemical process on 0,01M solution.

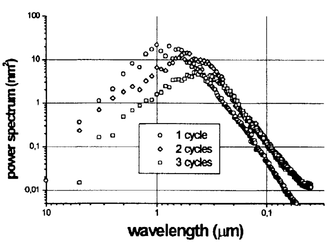

FIGURE 6 Power spectrum density of samples prepared by electrochemical process on 0,05M solution.

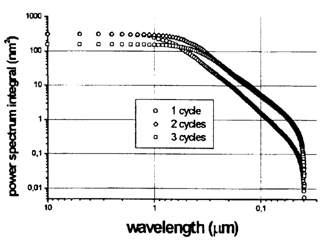

FIGURE 7 Power spectrum density integral of samples prepared by electrochemical process on 0,05M solution.

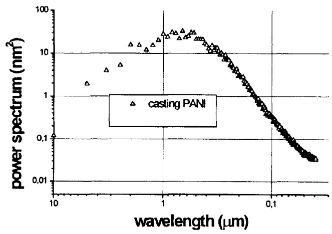

FIGURE 8 Power spectrum density of samples chemically prepared.

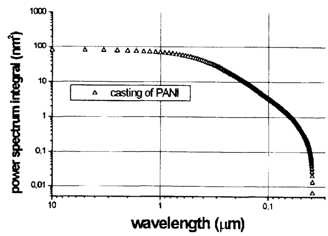

FIGURE 9 Power spectrum density integral of samples chemically prepared.

Table 1 – Fractal dimension calculated using power spectrum

Deposition Process			Fractal dimension D_{PSD}
Casting			2.61
Electrochemical	0,01M	1 cycle	2.54
		2 cycles	2.38
		3 cycles	2.26
	0,05M	1 cycle	2.26
		2 cycles	2.37
		3 cycles	2.34

Another way to calculate the fractal dimension of these surfaces is by the box counting method. The resulting plot of roughness versus scale (box counting) are shown on figure 10 to figure 12.

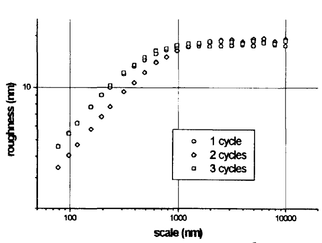

FIGURE 10 Box counting plot of samples prepared by electrochemical process on 0,01M solution.

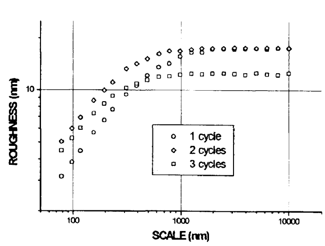

FIGURE 11 Box counting plot of samples prepared by electrochemical process on 0,05M solution.

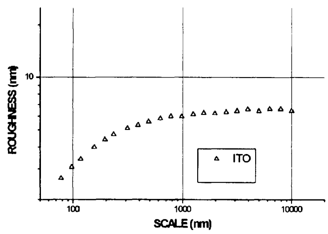

FIGURE 12 Box counting plot of PANI chemically prepared.

It can be observed from figures 10 to 12 that for the surfaces prepared electrochemicaly the roughness goes to about 20 nm while for the chemically deposited it stands at 6nm.

The angular coefficient of the inclined portion of the curve was used to calculate the fractal dimension of the surfaces On table 2 the results of fractal dimension calculations for samples prepared in 0,01 M solution the fractal dimension is about 2,2. For the surfaces prepared in 0,05 solutions the fractal dimension varies from 2,1 to 2,3. For the chemically prepared surface the fractal dimension is 2.45. Comparing these result with the corresponding images it can be seen that the fractal dimension can distinguish the surface character.

Table 2 – Fractal dimension calculated using box counting

Deposition Process			Fractal dimension D_α
Casting			2.45
Electrochemical	0,01M	1 cycle	2.27
		2 cycles	2.26
		3 cycles	2.25
	0,05M	1 cycle	2.18
		2 cycles	2.25
		3 cycles	2.32

It was fitted the inclined and horizontal portion of the box counting curves to calculate the characteristic length ξ for all the surfaces using the box counting graph. The characteristic length was taken from the intersection between the inclined and the horizontal portion of the curves on box counting graph. It results ranging from 450 to 700 nm for the surfaces grown on 0,01 M solution, from 300 to 550 for the surfaces grown on 0,05 M solution and about 270 nm for the chemically synthesised sample. Table 3 summarises these results. Comparing these with the AFM images we note that there is a strong relationship between the characteristic length and the lateral (clusters) aspects of the images.

Table 3

Deposition Process			Correlation Length ξ
Casting			270
Electrochemical	0,01M	1 cycle	450
		2 cycles	700
		3 cycles	500
	0,05M	1 cycle	550
		2 cycles	380
		3 cycles	300

CONCLUSION

From the results presented here, it is possible to conclude that AFM, in contact mode, is a good tool to study polyaniline surfaces deposited over ITO substrate. Power spectral density and power spectral density integral provide good quantitative results to verify the existence of fractal character in the surfaces and calculate the fractal dimension. From the box counting it is possible to extract two important quantitative parameters: the fractal dimension and the characteristic length. Despite the relative imprecision of the experimental method to obtain the fractality and the approximations of the theoretical models, the fractal dimension obtained by the roughness curve is in good agreement to that obtained by PSD.

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