Advanced Materials Research *Online: 2014-02-13*
ISSN: 1662-8985, Vol. 895, pp 407-410
doi:10.4028/www.scientific.net/AMR.895.407
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Fractal Analysis of Morphological Image of Organic phthalocyanine tetrasulfonic acid tetrasodium (TsNiPc) Film

Y.L. Kong[a], S.V. Muniandy, M.S. Fakir and K. Sulaiman

Department of Physics, University of Malaya, 50603 Kuala Lumpur, Malaysia

[a]kongyeolee@gmail.com

Keywords: Locally self-similar processes; Morphology; Fractal dimension; Power spectral density

Abstract

Surface morphology of thin films can be efficiently characterized using power spectral density method. Spectral based parameters from surface models can then be linked to electrical conductivity of thin films used for fabricating organic photovoltaic devices. In this study, the surface morphologies of the organic thin films phthalocyanine tetrasulfonic acid tetrasodium (TsNiPc) are investigated using atomic force microscopy. The thin film samples are imaged at 40-minutes and 120-minutes after the solvent treatment. The spectral exponent β is determined from the slope of PSD log-log plot and the fractal dimension D of each film is calculated based on fractal relation $\beta = 8 - 2D$. The relationship between surface roughness and fractal dimension with respect to electrical properties of thin film is discussed.

1. Introduction

Nanostructure morphologies reveal important information of materials properties such as charge carrier mobility, optical absorption and mechanical quality. Fractal geometry provides a powerful tool to analyze signals in different applications, such as medical imaging, biomaterials surfaces, geographical image analysis and other fields [1,2]. Its efficiency has been demonstrated in classification and segmentation experiments, where it was used as an additional texture parameter [3]. Fractal texture analysis provides useful surface descriptors that serve as alternative measures of surface roughness and heterogeneity. There are a number of fractal stochastic models such as the fractional Brownian motion [4] and generalized Cauchy models [5] that are widely used in the modeling of material surfaces and their characteristics parameters such the Hurst exponent (and fractal dimension) can be linked to material properties.

2. Experiment

In this study, we used organic phthalocyanine tetrasulfonic acid tetrasodium salt (TsNiPc) as the solution and commercially available glass slides as the substrates [6,7]. The glass slides are subsequently cleaned using acetone, isopropyl alcohol and de-ionized water for purification purpose. The TsNiPc powder had been dissolved in de-ionized water to prepare the TsNiPc solution with a concentration of 35mg/ml. As measured by a surface profiler meter, 100 nm thick TsNiPc films are coated onto the glass substrate using spin coating technique. The spin-coated TsNiPc layer is then annealed to 140°C for drying process to remove the water content. A poor solvent such as chloroform is chosen due to its very low solubility of TsNiPc powder. The thin films are then immersed in the chloroform solvent for 40 and 120 minutes. Nano fibers with a diameter not more

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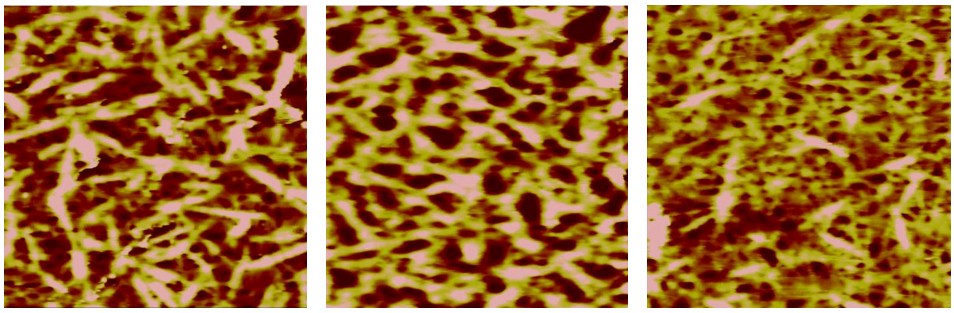
than 200 nm are formed from the solvent treatment. The thin films are thereafter carefully dried out under ambient conditions for further morphology analysis. The effect of immersion duration on the morphology and charge carriers' mobility are also investigated by incorporating the TsNiPc films with tris(8-hydroxyquinolinato) aluminum (Alq3) on the electrical properties. It has reported that there is a significant increase in the exciton generation at the interface layer of the treated films. The thin film samples are then imaged for the surface roughness (RMS) results. The scan size of the thin films is 10 μm× 10 μm, with the data scaled to a height of 100 nm. Five processed images of 400 ×400 pixels for each stage are sampled from the parent images.



(a) (b) (c)

Figure 1. AFM images of (a) untreated film, (b) 40 minutes and (c) 120 minutes solvent treated.

For untreated film, the elongated grain shape of nano fibers exhibit distinctive features. Due to the porosity of the exposed surface of the film, immersion in a poor solvent allows the solvent molecules to absorb and penetrate into the TsNiPc film. As immersion time increases, the formation of similar sized cluster nano fibers is obviously observed at the 40-minutes film, causing the interval distances between the grains to decrease. Film at 40-minutes has formed relatively bigger grain sizes compared to the other film due to the surface mobility of the adatoms in the nucleation stages of the film growth [8]. The film at 120-minutes has lower intrinsic film roughness and lateral features as compared to 40-minutes. The excessive solvent treatment time is causing the exposed surface of the film started to etch and therefore smoothen the surface of the film gradually.

3. Fractal Surface Analysis

Power spectral density (PSD) is defined as the square of the Fourier transform of the surface image $z(x, y)$ (in gray scale), namely [9]

$$P(f_x, f_y) = \frac{1}{MN}\left|\int_{-M/2}^{M/2}\int_{-N/2}^{N/2} z(x,y)e^{-j2\pi(xf_x+yf_x)}dxdy\right|^2 \quad (1)$$

where M, N are the scan length (or image size) in x and y directions; and f_x, f_y are the spatial frequencies for x and y directions, respectively. By assuming isotropy, the two-dimensional PSD, $P(f_x, f_y)$ can be reduced to one-dimensional $P(f)$, where $f = (f_x^2 + f_y^2)^{1/2}$. For image samples used in this study, the PSD for thin films show Lorentzian-type characteristics with plateau in lower spatial frequency region and a power-law roll-off in high spatial frequency region. Fractal scaling is attributed to power-law scaling behavior in the log-log plot, namely $P(f) \sim f^{-\beta}$ where β is the spectral exponent. Using a fractal stochastic model such as fractional Brownian motion of Hurst

parameter H, one can write $\beta = 2H + 2$, where $0 < H < 1$. Based on theory of fractal geometry, the fractal dimension D of a surface is given by $D = 3 - H$. Fractal Hurst exponent H or fractal dimension is a useful descriptor of complex surfaces. For example, extremely rough surface would give $D \sim 3$, while a marginal (smooth) surface has $D \sim 2$. Meanwhile, a Brownian fractal surface gives a unique $D = 2.5$ (or $H = 0.5$).

4. Results & Discussion

The PSD plot for the untreated and solvent treated films are shown in Figure 2. The fractal dimension of each sample is determined from the slope of the linear scaling regime of the log-log plot. The fractal dimension for untreated film is 2.41±0.02, while fractal dimension of the films treated with solvent for 40minutes and 120 minutes are 2.45±0.01 and 2.38±0.02, respectively.

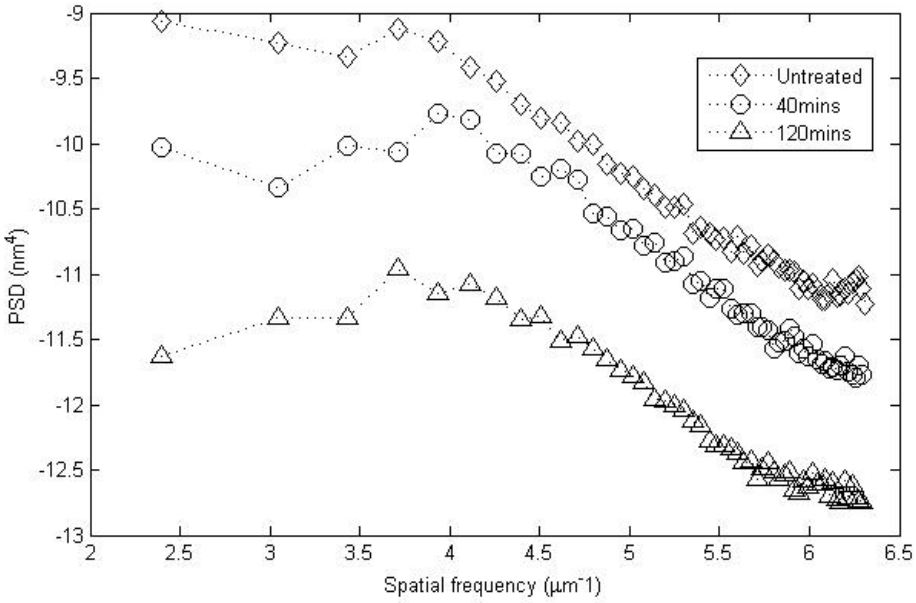


Figure 2. PSD plots of the surface images for untreated and solvent treated films.

The PSD spectrum shows that all the TsNiPc films exhibit fractal scaling behavior at higher spatial frequencies. This analysis concludes that the formation of the nano fibers is controlled by the immersion time, and a surface morphology with higher fractal dimension is demonstrating a significant increase in the exciton generation at the interface layer. The best exciton generation can be achieved when the nano fibers starts to etch at optimum time which can be predicted through this analysis.

5. Conclusion

In this study we have shown that fractal analysis can be useful for characterizing variation in surface roughness in organic thin film during solvent etching. Thin films exposed to solvent for longer duration are smoother and thus expected to have lower height fluctuation or RMS value. Higher electrical conductivity across interfaces is expected for thin film surfaces with higher fractal dimension.

Acknowledgements

The authors thank Malaysian Ministry of Higher Education (MOHE) for financial support under the Long Term Research Grant Scheme (LRGS) with grant number LR003-2011A. And thanks to KBU International College Malaysia for providing the conference and travel support.

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