Surface micromorphology characterization of PDI8-CN₂ thin films on H-Si by AFM analysis

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A nanoscale investigation of three-dimensional (3-D) surface micromorphology of archetypical N, N0- bis (n-etyl) x:y, dicyanoperylene- 3, 4:9, 10 bis (dicarboximide) (PDI8-CN₂) thin films on H-Si substrates, which are applicable in n-type semiconducting compounds, has been performed by using fractal analysis. In addition, surface texture characteristics of the PDI8-CN₂ thin films have been characterized by using atomic force microscopy (AFM) operated in tapping-mode in the air. These analyses revealed that all samples can be described well as fractal structures at nanometer scale and their three dimensional surface texture could be implemented in both graphical models and computer simulations.

Keywords: *perylene diimide derivatives; PDI8-CN₂ thin films; fractal analysis; surface micromorphology*

1. Introduction

In recent years, the development of n-type organic semiconductors based on perylene diimide (PDI) derivatives has attracted a lot of attention due to their potential applications in low-cost, large-area, and flexible electronic devices in commercially relevant products. Perylene diimides are directly bound to the basic atom with two cyano groups (C≡N) and are applied in organic field-effect transistors (OFETs) with high level of purity and reliability [1, 2]. Their usage in radio-frequency technologies, optoelectronic devices and sensors is significant [3–5].

Among the family of perylene diimide molecules, PDI8-CN₂ is the most studied compound with interesting applications, which is applied in n-type semiconducting compounds due

to its high electron mobility ranging from 0.01 to 0.1 cm²·V⁻¹·s⁻¹ and air stability [2, 6]. Despite the highest mobility of PDIF-CN₂, the main reason for choosing PDI8-CN₂ in this report is its poor sensitivity [7].

As observed recently in the AFM images of PDI8-CN₂ films on H-Si, ultrathin films are composed of complex three-dimensional (3D) connected domains, exhibiting a layered structure made of large monomolecular terraces. In addition, the nature of individual domains originates from a spiral growth around screw or half-loop dislocations and the crystalline domains coexist with regions covered by nanometric globular protrusions [1].

The objective of this work is to determine statistical and fractal characteristics of the PDI8-CN₂ thin films on H-Si samples evidenced by the AFM images.

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2. Experimental

Schottky junctions were prepared by vapor depositing PDI8-CN₂ (Polyera ActivInk N1200 by Polyera US) on hydrogen-terminated Si (1 0 0) (H-Si) substrates (10 × 5 × 0.5 mm³, n-type, 1–10 Ω·cm, wet etching in aqueous solution with dilute 5 % HF) in vacuum (base pressure < 10^{−6} Pa, deposition rate 1 nm/min, T_{substrate} = 100 °C) [8]. A quartz crystal microbalance was used to calibrate the nominal thickness d_{PDI}. The organic layer was thermally evaporated *ex situ* forming top-contact Au electrodes of ≈ 10 nm thickness using a shadow mask (area 1.8 mm²). The details of the measurements, Si ohmic back-contact, and Au grounding were published elsewhere [1, 9, 10].

2.1. Surface texture analysis from AFM images

The morphology of the PDI8-CN₂ films has been characterized by AFM (Solver P47-PRO by NT-MDT, Russia) operated in tapping-mode in the air (probes Olympus AC160TS) [1].

AFM images contain equally sampled height entries z(x,y) of the surface under study [11–13].

Spatial characteristics are derived from Areal Autocorrelation Function (AACF) [14]:

$$R_{xy} = \frac{\langle (z_{00}) - \langle z \rangle \cdot (z_{xy} - \langle z \rangle) \rangle}{S_q^2} \quad (1)$$

where: $\langle \dots \rangle$ is the mean operator, S_q –surface roughness (RMS), whereas xy – components of a vector of discrete spatial shift along the sides of the image. AACF decays with increasing lag and the ratio of two extreme decay lengths along various directions are used to define the anisotropy ratio S_{tr} that characterizes angular uniformity of the surface texture [15]:

$$0 < S_{tr} = \frac{\tau_{al}}{\tau_{a2}} \bigg|_{R=1 \rightarrow 0.2} \leq 1 \quad (2)$$

The Structure Function (SF) has been computed from angle-averaged AACF profile [15] and hence, fractal characteristics can be determined as follow:

$$S(\tau) = 2S_q^2(1 - R(\tau)) \quad (3)$$

Fig. 1. AFM images of the film under study taken at various scan lengths: (A) 4 × 4 μm, (B) 1 × 0.86 μm.

SF profiles obey allometric scaling law as a function of the spatial shift τ [16]:

$$S(\tau) = K\tau^{2(2-D)} \quad (4)$$

where: D – is the fractal dimension, and K – pseudo-topothesy. Beyond the threshold τ_c referred to the corner frequency, this allometric scaling breaks down and the SF asymptotically approaches $2S_q^2$ value.

Our previous studies demonstrated that the corner frequency can be used to estimate average seed diameter in the films composed of granular particles [17–19]. As a quick characterization tool, fractal analysis proved to be useful in studies of 3-D

Table 1. Surface texture characteristics of the samples under study: S_q – RMS surface roughness, S_{tr} – surface anisotropy ratio, D – fractal dimension, K – pseudo-topothesy, τ – corner frequency.

Sample	S_q [nm]	S_{tr}	D	K	τ_1 [nm]	D	K	τ_2 [nm]
A	5.02	0.39	2.24	0.019	52	2.42	0.078	260
B	4.41	0.56	2.38	0.095	57	2.61	0.596	210

surface texture of various structures from biomedical science [20–24] to nanotribology [25–29].

3. Results and Discussion

3.1. Fractal analysis

AFM images of the sample under investigation are shown in Fig. 1. The samples were probed with two different scan lengths: $4 \times 4 \mu\text{m}$ and $1 \times 0.86 \mu\text{m}$, respectively. Table 1 summarizes main spatial characteristics of these surfaces determined by both statistical and fractal measures.

Fig. 1 exhibits a structure of organic, polycrystalline semiconductor in the form of a series of elongated, semi-detached islands oriented axially with a small deviation to the main direction. Larger magnification (in Fig. 1B) has shown that each island is made of rhomboidal terraces 60–70 nm wide and 3–4 nm high. The edges of these terraces are found parallel, but inclined outwards. Previous works suggest that such a structure might be the result of a spiral growth around point defects on the surface of the substrate, but 3-dimensional maps of that sample presented in Fig. 2 do not agree with such conclusion. First of all, the edges of neighboring objects are of similar height, as marked with dotted lines in Fig. 2. We might conclude that these could be pieces of larger organic structures deposited on the silicon substrate at 100°C , which then split upon cooling to room temperature due to mechanical stress. Moreover, single protrusions can be seen in the AFM images. These protrusions are 1–2 nm high and are placed mostly on the edges of the terraces, and are homogeneously separated by 60–80 nm from each other.

Fractal characteristics presented in Table 1 demonstrate that the structures under study are made of two main spatial components of var-

ious scale-lengths, independent of magnification of AFM images. First-order arrangement consists of single 50–60 nm grains estimated by means of the corner frequency τ_1 , which appears comparable to the width of the terraces and the separation distance between protrusions. Low D_1 fractal dimension corresponds to the flat surface within the grains; hence, we might relate these grains to terraces. On the other hand, second-order pattern is associated to clusters with 200–260 nm diameters according to the corner frequency τ_2 . It is highly likely that the clusters are the agglomeration of the grains mentioned previously. Due to large anisotropy ratio S_{tr} , equal to 0.39, the above cluster size might be underestimated as an average value, since Fig. 1A clearly shows that the islands might grow up to 400–800 nm wide and several micrometers long. In addition, the surfaces of these agglomerates are much more developed according to fractal dimension D_2 .

3.2. Statistical analysis

The basic properties of the height values distribution on the samples surface (including its variance, skewness and kurtosis), computed according to [30] are shown in Table 2, for scanning square areas of $4 \mu\text{m} \times 4 \mu\text{m}$.

The surface stereometric measurements are useful in the assessment of quantitative parameters of surface geometrical structure [31–33].

The statistical properties of the individual points, belonging to the first-order statistical quantities, can be characterized with the height and slope distribution quantities (which belong to the first-order statistical quantities) and have been calculated as non-cumulative and cumulative according to [30]. The cumulative distributions are the integrals of densities with values in the

Fig. 2. Reconstruction of hypothetical surface topography features in the sample with $1 \times 0.86 \mu\text{m}$ scale length: (A) AFM image, (B-D) pseudo-3D views from various perspectives. Dotted lines mark various topographical features: lines (1–4, 6–7) that join edges of the same elevation in neighboring objects are possibly due to mechanical cracks of larger fragments of deposited organic semiconductor, line 5 is the steepest gradient for selected inter-grain path.

Table 2. Basic properties of the height values distribution (including its variance, skewness and kurtosis) of the surface samples, for scanning square areas of $4 \mu\text{m} \times 4 \mu\text{m}$.

The basic properties of the height values distribution	Ra (Sa) [nm]	Rms (Sq) [nm]	Skew (Ssk) [–]	Kurtosis (Sku) [–]	Inclination θ [°]	Inclination φ [°]
Values	3.93	5.02	–0.131	0.234	0.1	33.1

interval [0, 1].

The height and slope distribution functions for the analyzed samples in horizontal direction are shown in Fig. 3 and calculated as non-cumulative

and cumulative (where p is the corresponding quantity, height or slope; and abscissa is the tangent of the angle).

For a complete description of the surface prop-

Fig. 3. Height and slope distribution functions for the analyzed samples in horizontal direction, calculated as non-cumulative and cumulative (where p is the corresponding quantity, height or slope; and abscissa is the tangent of the angle).

erties, second-order statistical quantities conclude mutual relationship between two points on the surface using autocorrelation function and the power spectral density function [30].

The graphical representations of the analyzed samples of: a) the autocorrelation function (ACF), b) radial ACF, c) the power spectral density function (PSDF), and d) radial PSDF in horizontal direction can be seen in Fig. 4 based on the linear interpolation type.

4. Conclusions

In this study, the 3D surface texture of PDI8-CN₂ thin films on H-Si were studied using fractal analysis based on AFM images. The results confirm the relationship between samples processing parameters and 3D surface micromorphology expressed by fractal surface parameters. Topographical features can also be used to describe the local micro- and nano-levels of the microdomains in the samples that allow the control of interfacial boundary layers, which is crucial for

Fig. 4. Graphical representations of: a) ACF, b) radial ACF, c) PSDF, and d) radial PSDF, in horizontal direction based on the linear interpolation type.

nanotechnological applications. In addition, fractal analysis acts as a useful tool for understanding the underlying processes of physical mechanisms, as well as modern methods for analyzing composition, texture, and micromorphology on the micro- and nanometer level and provides greater quantitative information in comparison with conventional methods.

The fractal analysis can be used to acquire fractal characteristics for a dataset which may be a theoretical dataset or a pattern with more extensive applicability serving as a guidance and reference.

The basic properties of the height values distribution, including its variance, skewness and kurtosis,

computed according to [29] are defined as follows:

- RMS value of the height irregularities: this quantity is computed from data variance.
- Ra value of the height irregularities: this quantity is similar to RMS value with the only difference in exponent (power) within the data variance sum. As for the RMS this exponent is $q = 2$, the Ra value is computed with exponent $q = 1$ and absolute values of the data (zero mean).
- Height distribution skewness: computed from 3rd central moment of data values.
- Height distribution kurtosis: computed from 4th central moment of data values.

- Mean inclination of facets in area: computed by averaging normalized facet direction vectors.
- Variation, which is calculated as the integral of the absolute value of the local gradient.

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