

Height-Height Correlation Function to Determine Grain Size in Iron Phthalocyanine Thin Films

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Abstract. Quasi one-dimensional iron chains are formed in thermally evaporated iron phthalocyanine ($\text{FeC}_{32}\text{N}_8\text{H}_{16}$) thin films on silicon substrates. The chain length is modified by the deposition temperature during growth. Atomic force microscopy images show spherical grains at low deposition temperatures that become highly elongated at high deposition temperatures due to diffusion. The grain distributions are quantitatively characterized with a watershed-based segmentation algorithm and a height-height correlation function. The grain size distributions are found to be characteristically distinct for the α -phase and β -phase samples. The average effective grain size from the distribution is proportional to the correlation length found from the height-height correlation function and grows exponentially with deposition temperature. The long-range roughness and Hurst parameter increase only slightly with the deposition temperature.

1. Introduction

The surface morphology of organic thin films plays an important role in device fabrication. The grain boundaries and grain size of polycrystalline thin films can affect the performance of gas sensors, field-effect transistors, and photovoltaic devices.[1, 2, 3] Understanding the growth mechanism and the surface structure at the nanometer length scale would allow fabrication of devices with optimized performance characteristics. The growth of small molecules is different due to weaker van-der-Waals interactions and generally more complex as compared to inorganic atomic growth. In order to understand the growth mechanism, the polycrystalline surface of many materials is described with its grain size distribution, long-range roughness, the average grain size, and the short-range roughness. These parameters can also be modeled and so compared with theory.[4, 5]

Here, we extract the quantitative surface structure data to understand the growth process in metallo-organic thin films. The metallo-phthalocyanine molecule ($\text{M-C}_{32}\text{N}_8\text{H}_{16}$) is a planar molecule with four-fold symmetry and a metal ion at its center, see inset in Fig. 1(b). While iron phthalocyanine (FePc) grows similar to other low-Z metallo-phthalocyanine molecules, such as copper phthalocyanine, it is used here due to its ability to form quasi one-dimensional magnetic iron chains.[3, 6] The iron chain length effectively corresponds to the crystalline or grain size and can be controlled by deposition parameters including the substrate temperature. The surface parameters will be extracted from a watershed-based segmentation algorithm and a correlation function based on the atomic force microscopy (AFM) data. By measuring the AFM correlation length the average iron chain length is inferred.

2. Experiment

Thin films of iron phthalocyanine (FePc) were prepared via thermal evaporation. Silicon (100) substrates are used, because they are known to weakly interact with the molecule and lead to growth where the molecular plane is perpendicular to the substrate (edge-on growth). The substrates were cleaned via suspension in ultrasonic baths of acetone and methanol. Two substrates were mounted in the thermal evaporator for each deposition on a temperature-controlled holder that is allowed to rotate during deposition. The chamber's base pressure was $2 \cdot 10^{-6}$ torr and the substrates are preheated to about 200°C to remove water from the surface, while the organic material was outgassed for 12 - 24 hours before deposition. Commercially available FePc was pre-purified by the thermal gradient method. For the deposition FePc was heated to roughly 350°C for continuous sublimation. A steady sublimation rate of 2 nm/min was used for all depositions for a total film thickness of 80 ± 4 nm as monitored with an in-situ quartz crystal monitor. While the film thickness is kept constant, the deposition temperature is varied from room temperature to 230°C . Additional samples were used for the watershed-based segmentation algorithm analysis and the sample preparation procedure is discussed elsewhere.[7]

The FePc thickness was calibrated from Kiessing fringes in the Cu K_{α} x-ray diffraction spectrum. The spectrum shows a prominent (200) FePc peak at the 2θ angle of 6.8° . [7, 8] This angle corresponds to a lattice spacing of 1.3 nm and confirms that the molecules crystallize and tend to align edge-on with respect to the substrate. Since the x-ray peak width is only suggestive of the correlation length, AFM images are used instead.

The morphology of FePc thin films was studied utilizing AFM with a Digital Instruments Nanoscope MultiMode scanning probe microscope operated in tapping mode. A total of twelve samples were studied and for each sample two image sizes were taken: one $4\mu\text{m} \times 4\mu\text{m}$ image and one $1\mu\text{m} \times 1\mu\text{m}$ image. The AFM images were converted to a linear gray scale using WSxM software[9] and then processed with a Matlab code to generate the correlation functions, see Fig. 1. The statistics analysis was performed using a watershed-based segmentation algorithm.[10]

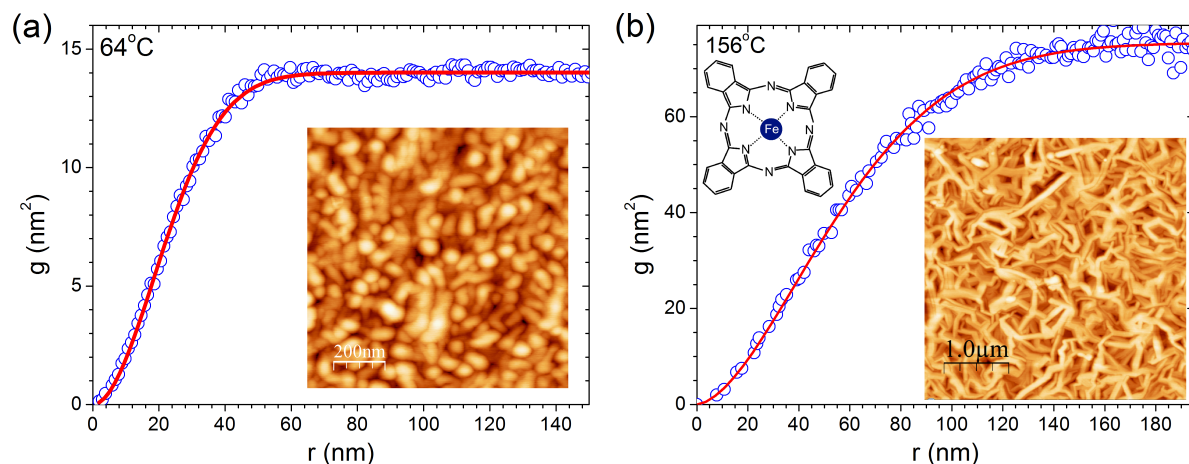


Figure 1. (Color online) The calculated height-height correlation functions (circles) according to Eq. 1 from their respective atomic force microscopy images for two iron phthalocyanine thin films. The continuous lines are best fits according to Eq. 2. The sample was deposited at (a) 64°C and (b) 156°C with equal thickness of 80 nm. The corresponding AFM image shown in the inset has a lateral size of (a) $1\mu\text{m}$ and (b) $4\mu\text{m}$, respectively. The inset shows the chemical structure of the iron phthalocyanine molecule.

3. Analysis and Results

The surface morphology of the iron phthalocyanine thin films is quantified with two methods. In the first method, a correlation function is used to determine the average grain size, film roughness, and short-range roughness. In the second method the grain size distribution is measured from several AFM images and the statistics are analyzed. The former characteristics are obtained from the Height-Height Correlation Function (HHCF)

$$g(r) = \langle [h(\vec{x}) - h(\vec{x} - \vec{r})]^2 \rangle, \quad (1)$$

where \vec{x} is a any specific point in the image and \vec{r} is a displacement vector. The average height difference between any two points separated by a distance r are described by the function $g(r)$. Phenomenologically the HHCF can be interpreted by

$$g'(r) = 2\sigma^2 \left[1 - e^{-\left(\frac{r}{\xi}\right)^{2\alpha}} \right], \quad (2)$$

where σ is the surface roughness, α is the Hurst parameter, and ξ is the correlation length.[11, 12] The Hurst parameter measures the short-range roughness; i.e. it describes the grain surface structure.[13] In order to fit the function $g'(r)$ to the HHCF data, only small values of r (<250 nm) are used due to the fact that the HHCF quickly reaches a saturation value, see Fig. 1. The saturation value corresponds to the long-range film roughness $g'(r) \sim 2\sigma^2$ with $r \gg \xi$. On the other hand, for values of $r \ll \xi$, Sinha et al.[14] found that Eq. 2 is not a good fit to the data and will overestimate the Hurst parameter. Instead a linear fit on a log-log plot is used to fit α , since $g'(r) \simeq Ar^{2\alpha}$, where A is a constant.

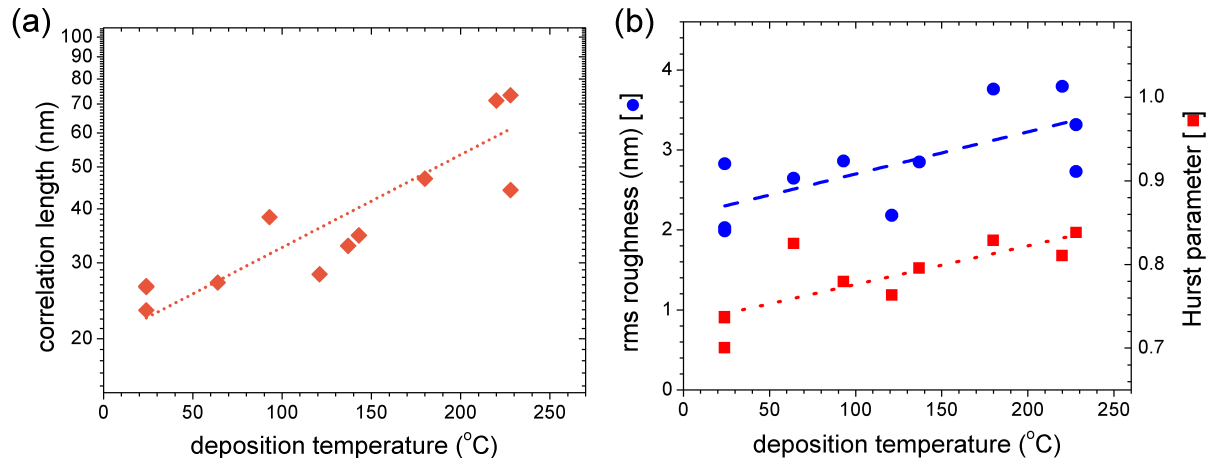


Figure 2. (Color online) (a) The correlation length ξ increases with the deposition temperature due to the increased diffusion. The dashed line is a fit to an exponential growth. (b) The rms roughness σ (circles) and the Hurst parameter α (squares) depend only weakly on the deposition temperature. Linear fits are drawn as guides to the eye.

The most common phases of FePc growth are the α - and β -phase.[15] Both have a characteristic herringbone structure but the phases differ in the angles made to adjacent molecular chains. When deposited onto substrates at temperatures lower than 200°C , FePc will assemble in the α -phase and otherwise in the β -phase. Moreover, as the substrate temperature is increased during deposition, the molecules tend to diffuse over longer distances and the grain size increases. For thin films deposited at room temperature, the correlation length ξ is 25 nm and increases to over 70 nm for samples deposited above 200°C , see Fig. 2(a). An exponential

fit illustrates the rapid increase. While the diffusion leads to strong growth of the grain size, it changes the long-range roughness σ only slightly, see Fig. 2(b). Using the smaller AFM images, the rms roughness σ increases from 2.2 – 3.2 nm. Equally, the Hurst parameter α , which characterizes the short-range roughness, increases only from 0.74 – 0.84. These three parameters describe the grain growth as a function of the deposition temperature.

Concurrent with the increase of the correlation length, the grain shape changes from circular to strongly elongated. The surface area of each grain can be approximated as an ellipsis with a defined minor and major axis with an area equal to that of the actual grain.[7] The circularity (axes ratio) decreases from 0.75 to 0.50 with deposition temperature. Since the grains are elongated, an effective grain diameter d_0 is defined by the total grain area $A = \pi(d_0/2)^2$. The comparison of the watershed-based segmentation algorithm that measures individual grains to the HHCF shows that there is a linear correlation between the average effective grain size diameter d_0 and the correlation length ξ . The proportionality factor is determined from a best fit: $d_0/\xi = 3.4$. Similarly, a factor of 2.8 was previously found for inorganic materials.[12]

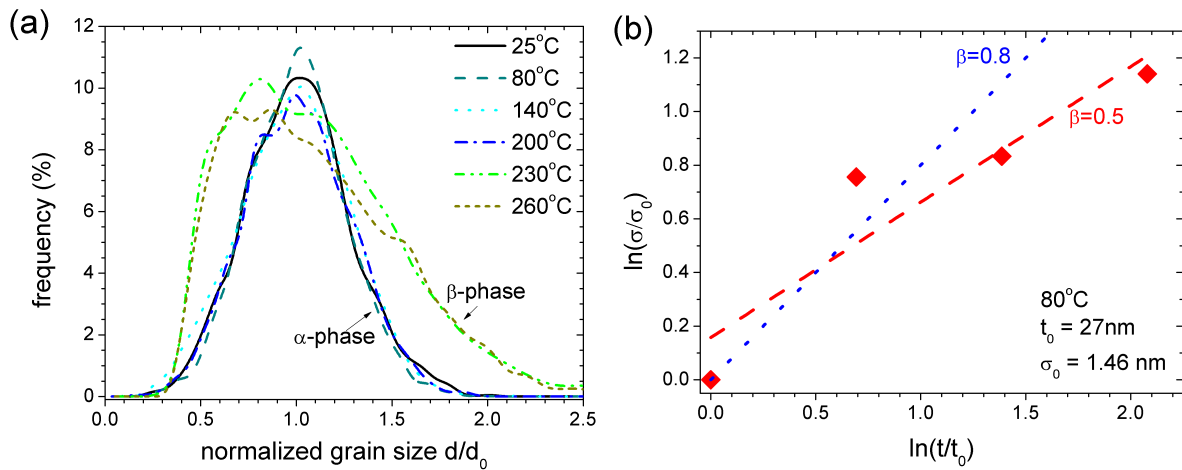


Figure 3. (Color online) (a) The effective grain diameter is determined from elliptical fits to individual grains of many AFM images using a watershed-based segmentation algorithm. The average effective grain diameter d_0 at a given deposition temperature is used as a scaling parameter. Samples with different deposition temperatures show two fundamentally distinct distributions. The α -phase FePc ($< 200^\circ\text{C}$) samples fit better to a Gaussian distribution, whereas the β -phase FePc ($> 200^\circ\text{C}$) samples fit better to a log-normal distribution. (b) From the sample thickness dependence t at fixed deposition temperature (80°C), the scaling exponent $\beta = 0.51 \pm 0.14$ is determined using a best fit (long dashes). As a guide to the eye, $\beta = 0.8$ is drawn (short dashes). The thickness is normalized by $t_0 = 27$ nm and the roughness by $\sigma_0 = 1.46$ nm corresponding to the parameters of the thinnest sample.

The watershed-based segmentation algorithm from many AFM images results in explicit grain size distribution functions shown in Fig. 3(a). Despite the strong growth of the average grain size, once the distribution is scaled by the average grain size d_0 , the curves collapse to two distinct distributions. At low deposition temperatures ($< 200^\circ\text{C}$) the distributions are similar to a Gaussian distribution and at high deposition temperatures ($> 200^\circ\text{C}$) the distribution can be easily fit to a lognormal distribution. These distinct differences in grain size distributions overlap with the documented α - to β -phase transition that occurs during the growth of the phthalocyanine molecule.[7, 16] Additionally, we observe round mounds at low temperatures and pin holes at high deposition temperatures. Rapid roughening and pin holes are generally attributed to energy barriers that appear at molecular steps on the surface. They are also

referred to as Ehrlich-Schwoebel energy barriers.[17, 18] Recently, evidence for such an energy barrier was found in organic thin films.[19] Rapid roughening is referred to the anomalous growth exponent in the power law of roughness σ versus thickness t , where $\sigma \sim t^\beta$. For a simple random deposition $\beta = 0.5$. [20] Specifically in samples of di-indenoperylene thin films good agreement between the experiment and the Ehrlich-Schwoebel growth model was found. In support of this, a growth scaling exponent of $\beta = 0.8$ was measured.[21] In the FePc thin films discussed here, the scaling exponent β is fit to four samples deposited at 80°C and found to be 0.51 ± 0.14 , see Fig. 3(b). As a comparison $\beta = 0.8$ is plotted in the same graph suggesting no or minimal rapid roughening occurs in the measured FePc samples.

4. Conclusion

Thermally evaporated iron phthalocyanine thin films were quantitatively characterized with a watershed-based segmentation algorithm and a correlation function. The grain size distributions revealed two distinct distributions coinciding with the α - and β -phase. This suggests that the grain size distribution may be fundamentally impacted by the underlying unit cell. An atomic force microscopy study of samples deposited at different temperatures allowing for differences in the diffusion during growth shows that while the grain size increases exponentially with deposition temperature, both long-range and short-range roughnesses grow only slowly. The formation of mounds, pin holes, and asymmetric grains suggests that there is an Ehrlich-Schwoebel-like energy barrier present that breaks the growth symmetry. Although the grains are strongly asymmetric, the measured growth scaling exponent was found to be close to the stochastic limit explained by a random deposition.

Acknowledgments

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