PHYSICAL REVIEW B **73**, 161305(R) (2006)

Anomalous scaling behavior and surface roughening in molecular thin-film deposition

S. Yim and T. S. Jones
Centre for Electronic Materials and Devices, Department of Chemistry, Imperial College London, London SW7 2AZ, United Kingdom
(Received 21 December 2005; revised manuscript received 3 March 2006; published 25 April 2006)

The thin film growth dynamics of a molecular semiconductor, free-base phthalocyanine (H_2Pc), deposited by organic molecular beam deposition, has been studied by atomic force microscopy (AFM) and height difference correlation function (HDCF) analysis. The measured dynamic scaling components ($\alpha_{loc}=0.61\pm0.12$, $\beta=1.02\pm0.08$, and $1/z=0.72\pm0.13$) are consistent with rapid surface roughening and anomalous scaling behavior. A detailed analysis of AFM images and simple growth models suggest that this behavior arises from the pronounced upward growth of crystalline H_2Pc mounds during the initial stages of thin film growth.

DOI: 10.1103/PhysRevB.73.161305 PACS number(s): 81.15.Hi, 68.37.Ps

The precise control of thin film deposition and surface morphology is a key requirement in many areas of materials science, in particular for applications in which complex multilayered structures are required. Consequently, the growth behavior of many thin-film systems has been studied extensively in recent years with particular focus on metals and inorganic semiconductor materials.[1,2] Significant advances in understanding have arisen primarily through the use of scanning probe microscopy measurements and the development of theoretical approaches to describe the growth dynamics and thin-film evolution. Scaling concepts have been particularly insightful for understanding key phenomena such as surface roughening.[3]

Thin films based on molecular semiconductors (often referred to as "small" molecules) are finding an increasing application in a number of (opto)electronic device applications, in particular organic light emitting diodes, photovoltaics, and field effect transistors.[4] These devices rely on the controlled deposition of molecular thin films and often require the formation of molecular heterostructures comprising several layers of different organic materials.[5] The organic-organic interface quality is crucially important in these multilayer heterostructures, however, the growth behavior of molecular semiconductors remains poorly understood and a more detailed understanding of the factors that control the film morphology is therefore of significant interest, both from a fundamental and technological perspective.

Molecules present a number of unique aspects that can have a strong influence on the thin-film growth properties, most notably their tendency to form large unit cells, the internal degrees of freedom, and (usually) van der Waals interaction potentials.[6] Two recent studies on perylene (Pe)[7] and diindenoperylene (DIP)[8] thin-film formation have highlighted the complex growth dynamics associated with molecular systems. In particular, Dürr *et al.*[8] determined the scaling exponents for DIP thin films grown on SiO_2. Although the measured exponents were largely consistent with those observed in many inorganic thin-film materials systems, the relatively large value for the growth exponent ($\beta=0.748$) suggested rapid roughening. This was rationalized by spatial inhomogeneities due to the presence of different tilt domains and grain boundaries.[8]

In this paper we show that the unique properties of molecular semiconductors can have an even more pronounced impact on the thin film growth behavior. We focus specifically on free-base phthalocyanine (H_2Pc), a member of a very important class of material (phthalocyanines) widely used in organic optoelectronic devices.[9,10] The results again suggest rapid surface roughening and anomalous scaling, however, in this case a steepening exponent considerably larger than previously reported for a molecular thin film materials system is obtained. While several cases of anomalous behavior have been reported for inorganic thin films,[11–13] the reasons are not fully understood, even for these simpler atomic based systems. From an analysis of simple growth models, we suggest that the anomalous behavior of H_2Pc thin films arises from the upward growth of crystalline mounds during the initial stages of film formation.

The films were grown in an organic molecular beam deposition (OMBD) chamber with a base pressure of $\sim2\times10^{-9}$ Torr. H_2Pc powder (Syn Tech, 99%) was outgassed for 15–20 h before growth and sublimed onto glass substrates (at room temperature) using a miniature effusion cell. The cell temperature was ~330 °C, which corresponds to a growth rate of ~5 Å s^{-1}, as determined by a quartz crystal microbalance (QCM) positioned near the substrate. *Ex situ* morphology analyses at different film thickness were performed using tapping mode AFM.

H_2Pc exists as the α polymorph when deposited at room temperature on weakly interacting substrates such as glass, characterized by a slightly tilted herringbone structure with the molecules stacked along the b axis (Fig. 1(a)).[14–16] AFM images of H_2Pc thin films of different thickness ($D=651-7440$ Å) are shown in Figs. 1(b)–1(f). The images were all taken with the same scan area of 3.5 μm $\times$ 3.5 μm, and in each case the morphology is characterized by spherical crystallites, a characteristic signature of α-H_2Pc films.[14,15]

The surface morphology of the films was analyzed using a height difference correlation function (HDCF) analysis.[3] For self-affine growth, in which the films preserve a similar morphology upon a change of magnification, and after the rescaling of the heights, the roughness scaling follows simple power laws characterized by the growth (β), roughness (α), and dynamic (z) scaling exponents.[8,16,17] These can be determined from the mean square surface fluctuation, $g(R)$, written as

 ©2006 The American Physical Society

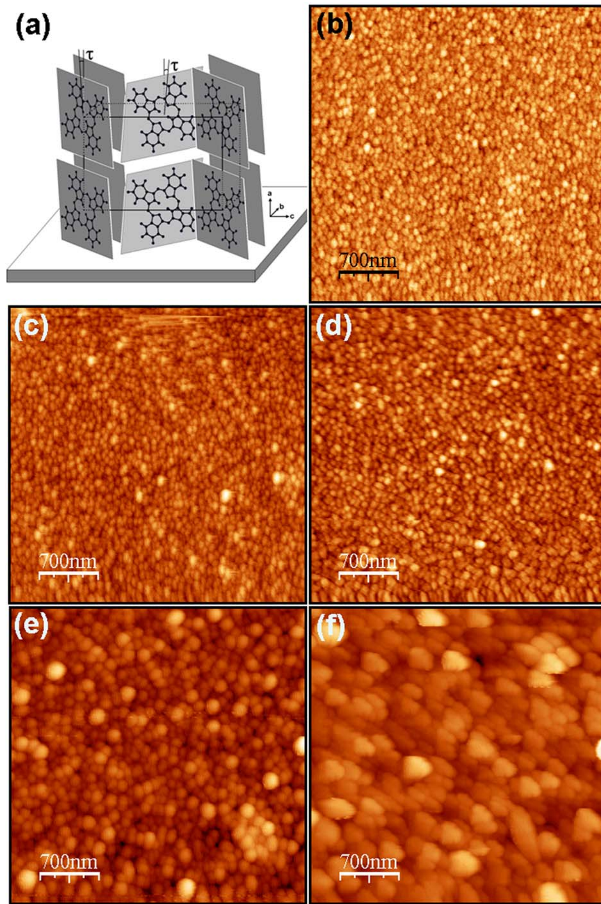

FIG. 1. (Color online) (a) Schematic of the structure of the H_2Pc α-herringbone unit cell; the molecular planes are slightly tilted with $\tau = \pm 8.6°$. (b)–(f) AFM images for H_2Pc thin films deposited on glass substrates with various thicknesses (D) of (b) 651 Å, (c) 930 Å, (d) 1628 Å, (e) 3720 Å, and (f) 7440 Å.

$$g(R) = \langle [h(x,y) - h(x',y')]^2 \rangle,$$

$$R = \sqrt{(x-x')^2 + (y-y')^2}. \quad (1)$$

The average is taken over all pairs of points (x,y) and (x',y') separated laterally by the length, R. There are two distinct regimes that depend on the relative magnitudes of R and the correlation length, ξ, i.e.,

$$g(R) \propto R^{2\alpha}, \quad \text{for R} \ll \xi, \quad (2a)$$

$$g(R) = 2\sigma^2, \quad \text{for R} \gg \xi, \quad (2b)$$

where σ is the mean-square surface roughness. The parameters σ and ξ are related to the film thickness, D, according to the power laws $\sigma \propto D^{\beta}$ and $\xi \propto D^{1/z}$. In many cases, the exponents α, β, and z are not independent and obey the scaling law, $1/z \cong \beta/\alpha$.[8,18–20] In recent years, however, several experiments for inorganic film growth have revealed that the scaling of the long (global) and short (local) length characteristic interface fluctuations can be substantially different,[21,22] and modified growth models with different roughness exponents at long (α) and short (α_{loc}) length scales have been proposed.[23–25] The local roughness exponent, α_{loc}, can be determined experimentally and the short length scales follow the so-called anomalous scaling *ansatz*:

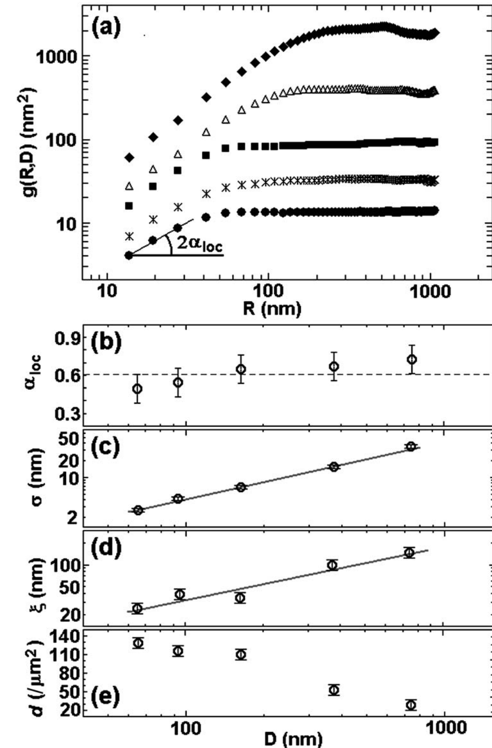

FIG. 2. (a) Plot of averaged $g(R,D)$ vs R for H_2Pc films with various D (●=651 Å, *=930 Å, ■=1628 Å, △=3720 Å, and ◆=7440 Å). Also shown are plots of (b) α_{loc}, (c) σ, (d) ξ, and (e) d as a function of film thickness, D. The horizontal dashed line in (c) denotes the average value of α_{loc}.

$$g(R,D) \propto R^{2\alpha_{loc}} \cdot D^{(\alpha-\alpha_{loc})/z}, \quad \text{for R} \ll \xi, \quad (3a)$$

$$g(R,D) = 2\sigma^2, \quad \text{for R} \gg \xi. \quad (3b)$$

Figure 2(a) shows a plot of $g(R,D)$ as a function of lateral distance, R, for different values of D. By fitting $g(R,D) \propto R^{2\alpha_{loc}} \cdot D^{(\alpha-\alpha_{loc})/z}$ to the correlated part, where $R \ll \xi$, an average value of $\alpha_{loc} = 0.61 \pm 0.12$ was determined [Fig. 2(b)] and used for the range of film thicknesses studied since it lies within the error range of the individual α_{loc} values, although α_{loc} does show a slight tendency to increase with D. The surface roughness values (σ) are plotted in Fig. 2(c) as a function of D, and this yields a β value of 1.02 ± 0.08. This β value is significantly larger than the values reported for most surface roughening mechanisms. Large β values (>0.5) have been reported for other organic thin film systems, e.g., DIP on SiO_2 ($\beta = 0.748$)[8] as well as plasma deposited polymers ($\beta = 0.70$).[19] The very large β value in our work suggests rapid roughening and is most likely to arise from the upright and slightly tilted orientation of the α-herringbone H_2Pc molecules on the glass substrates, as shown in Fig. 1(a). The correlation length, ξ, at each thickness was determined by fitting the HDCF to the following analytical function: $g(R) = 2\sigma^2 \tilde{g}(R/\xi)$, where $\tilde{g}(x) = 1 - \exp(-x^{2\alpha_{loc}})$.[26,27] Figure 2(d)

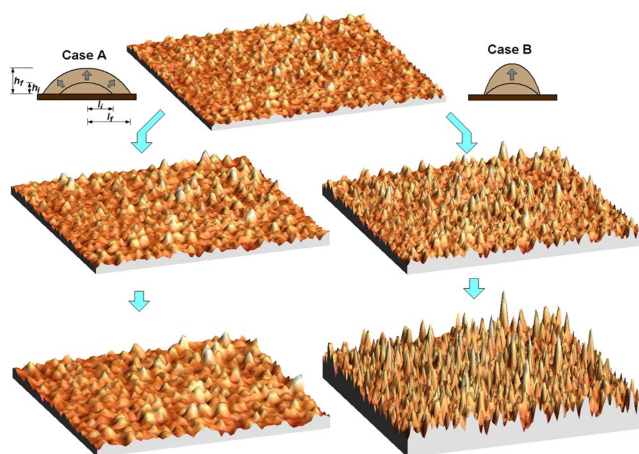

FIG. 3. (Color online) Schematic of the two growth models used for HDCF analysis. In case A, the mounds grow in every direction, whereas in B, they grow only in an upward direction. The starting surface is the same for both models.

shows a plot of ξ as a function of D and yields $1/z = 0.72 \pm 0.13$.

The conventional scaling laws can be modified by introducing a steepening exponent, λ, as $\beta = \alpha_{loc}/z + \lambda$. If $\lambda = 0$, then $\beta = \alpha_{loc}/z$, so that $\alpha = \alpha_{loc}$, which implies that the scaling is truly self-affine. For H_2Pc, the λ value of 0.58 is significantly larger than zero and/or the value reported for DIP thin film growth (=0.12),[8] suggesting a very pronounced anomalous scaling behavior. According to the growth models proposed by Ramasco *et al.*,[23] this scaling behavior corresponds to what is termed "intrinsic" anomalous scaling.

The AFM images in Fig. 1 show that the number of H_2Pc spherical crystallites shows little change with increasing D for thicknesses up to 1628 Å, while the z amplitude and roughness both increase. This is confirmed by Fig. 2(e), which is a plot of the experimentally determined density of islands (d) as a function of film thickness. For $D > 1628$ Å the crystallites undergo coalescence, and there is a significant decrease in d. The negligible change in density for $D < 1628$ Å is in contrast to previous reports of molecular thin film growth, for example, DIP, where the surface shows a terrace morphology and the number of islands decreases as the film thickness is increased.[8,28]

To understand the mechanism of H_2Pc film growth in greater detail, two simple growth models were simulated and then analyzed using the HDCF method. The starting configuration in both models was taken from the surface of the 1628 Å thick H_2Pc film (the top center in Fig. 3). In case A, the mounds were allowed to grow in every direction, hence the number of mounds decreases due to coalescence. We have found that the scaling behavior is strongly influenced by the relative logarithmic growth rates of the increase in lateral size (r_l) and height (r_h) of the mounds. Here r_l and r_h

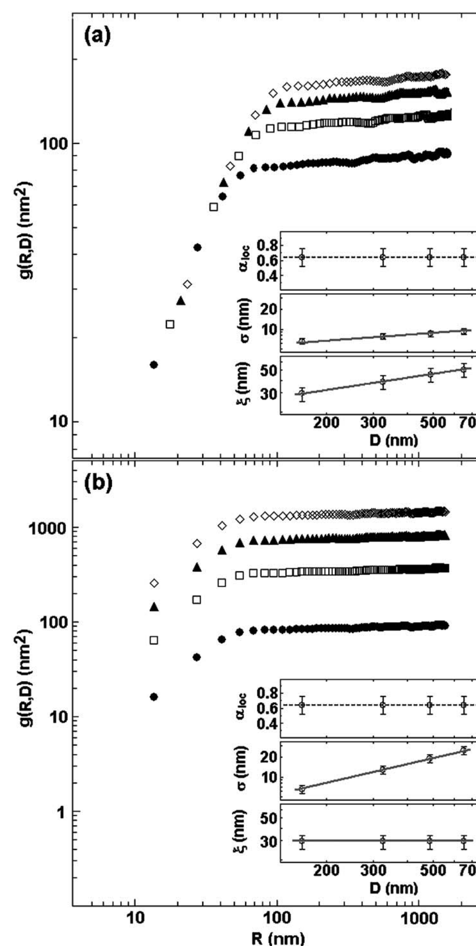

FIG. 4. Plots of averaged $g(R,D)$ vs R for growth models A (a) and B (b). The insets show the corresponding plots of α_{loc}, σ, and ξ as a function of D.

TABLE I. A summary of experimentally determined scaling exponents for several organic thin film systems, including H_2Pc/glass. The exponents determined from an analysis of the two simple growth models (Fig. 3) are also listed.

	α_{loc}	β	β/α_{loc}	$1/z$	Ref.
H_2Pc/glass	0.61±0.12	1.02±0.08	1.7±0.5	0.72±0.13	This work
DIP/SiO_2	0.684±0.06	0.748±0.05	1.09±0.19	0.92±0.2	8
PPX/Si	0.72±0.03	0.25±0.03	0.35±0.06	0.31±0.02	18
Plasma polymer	0.90±0.07	0.70±0.10	0.78±0.18	0.70±0.10	19
Perylene/glass	0.82±0.02	0.21±0.01	0.26±0.03		7
Model A	0.64±0.12	0.24±0.02	0.38±0.12	0.38±0.1	This work
Model B	0.64±0.12	1.00±0.08	1.6±0.3	0.00±0.1	This work

are defined by the ratio of the initial and final values of the mound dimensions, l_f/l_i and h_f/h_i, respectively (see the top left in Fig. 3). In case A, the growth of the mounds was simulated with $\log r_h/\log r_l=0.64$ ($=\alpha_{loc}$), yielding results that are most consistent with the conventional scaling laws (see later). In case B, the mounds only grow upward, and hence the number of mounds remain constant. In this case $\log r_h/\log r_l$ is infinite. The increase in the total volume of the mounds was set to be the same in both A and B.

HDCF analysis (see Table I) of case A yields average values for α_{loc}, β, and $1/z$ of 0.64 ± 0.12, 0.24 ± 0.02, and 0.38 ± 0.1, respectively [Fig. 4(a)]. The value for β/α_{loc} ($=0.38\pm0.12$) is therefore consistent with the $1/z$ value. In case B, however, dramatic differences in the ξ and $1/z$ values are apparent. The α_{loc} and β values are 0.64 ± 0.12 and 1.00 ± 0.08, respectively; hence the β/α_{loc} ratio is calculated to be 1.6 ± 0.3. The ξ value, however, does not change with respect to the film thickness; the $1/z$ value is zero and hence very different to β/α_{loc}. These simple models clearly represent two extremes in terms of growth behavior, however, the result obtained from the analysis of the upward growth model (B) suggests that many of the H_2Pc crystalline mounds in our experimentally investigated system grow in a similar manner and give rise to the significant experimental difference between β/α_{loc} and $1/z$.

Molecular semiconductors such as H_2Pc are bonded to each other by relatively weak van der Waals forces, which cause the impinging molecules to diffuse laterally across the surface and stop when they find an energetically stable position. The upward growth mechanism we suggest for H_2Pc suggests that the potential energy barrier at the edges of existing H_2Pc islands (the *Schwoebel barrier*[3]) is sufficiently large to prevent freshly deposited molecules from moving down to adjacent lower layers. This results in the anomalous scaling behavior and the large discrepancy in the experimentally determined values for $1/z$ and β/α_{loc}.

It is interesting to compare our results with those reported for DIP/SiO_2, in which rapid surface roughening was observed with a considerably smaller deviation from conventional scaling laws.[8] The DIP molecules adsorb in an upright orientation with a tilt angle $\phi\sim15°-20°$.[8] This tilted upright geometry is likely to result in a low *Schwoebel barrier*, giving rise to the observed terracelike morphology. By contrast, the H_2Pc films adopt a herringbone structure, consisting of molecules with two different types of orientation, where individual molecular planes are almost perpendicular to the substrate.[16] The less tilted geometry appears to hinder the sliding down of the molecules and is therefore consistent with the existence of a significant *Schwoebel barrier* at the island edge. The probability of sticking to existing molecules in the same layer compared to that of jumping down to a lower layer is therefore higher for H_2Pc than DIP. Theoretical calculations of the magnitude of the step edge barriers for these different molecular systems are clearly required in order to fully understand the role of intermolecular interactions in determining the thin film growth behaviour.

In conclusion, the growth dynamics of H_2Pc thin films has been studied using AFM and HDCF analysis. Anomalous scaling behavior is observed that can be rationalized by analysis of simple growth models which suggests that the H_2Pc islands grow upward as the film thickness increases without any significant change in number density. These results suggest that new theories are required in order to explain the growth behavior of molecular thin films and that it is important to consider the role of intermolecular interactions.

[1] J. Krug, Adv. Phys. **46**, 139 (1997).
[2] Z.-J. Liu, Y. G. Shen, L. P. He, and T. Fu, Appl. Surf. Sci. **226**, 371 (2004).
[3] A. L. Barabasi and H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, Cambridge, 1995).
[4] S. R. Forrest, Chem. Rev. (Washington, D.C.) **97**, 1793 (1997).
[5] F. Yang, M. Shtein, and S. R. Forrest, Nat. Mater. **4**, 37 (2004).
[6] F. Schreiber, Phys. Status Solidi A **201**, 1037 (2004).
[7] S. Zorba, L. Yan, N. J. Watkins, and Y. Gao, Appl. Phys. Lett. **81**, 5195 (2002).
[8] A. C. Dürr, F. Schreiber, K. A. Ritley, V. Kruppa, J. Krug, H. Dosch, and B. Struth, Phys. Rev. Lett. **90**, 016104 (2003).
[9] D. X. Wang, Y. Tanaka, M. Iizuka, S. Kuniyoshi, K. Kudo, and K. Tanaka, Jpn. J. Appl. Phys., Part 1 **38**, 256 (1999).
[10] P. Peumans, S. Uchida, and S. R. Forrest, Nature (London) **425**, 158 (2003).
[11] J. H. Jeffries, J.-K. Zuo, and M. M. Craig, Phys. Rev. Lett. **76**, 4931 (1996).
[12] S. Huo and W. Schwarzacher, Phys. Rev. Lett. **86**, 256 (2001).
[13] J. M. Lopez, M. Castro, and R. Gallego, Phys. Rev. Lett. **94**, 166103 (2005).
[14] S. Heutz, S. M. Bayliss, R. L. Middleton, G. Rumbles, and T. S. Jones, J. Phys. Chem. B **104**, 7124 (2000).
[15] S. Yim, S. Heutz, and T. S. Jones, J. Appl. Phys. **91**, 3632 (2002).
[16] S. Yim, S. Heutz, and T. S. Jones, Phys. Rev. B **67**, 165308 (2003).
[17] F. Biscarini, P. Samorí, O. Greco, and R. Zamboni, Phys. Rev. Lett. **78**, 2389 (1997).
[18] Y.-P. Zhao, J. B. Fortin, G. Bonvallet, G.-C. Wang, and T.-M. Lu, Phys. Rev. Lett. **85**, 3229 (2000).
[19] G. W. Collins, S. A. Letts, E. M. Fearon, R. L. McEachern, and T. P. Bernat, Phys. Rev. Lett. **73**, 708 (1994).
[20] G. Palasantzas and J. Krim, Phys. Rev. Lett. **73**, 3564 (1994).
[21] J. Soriano, J. J. Ramasco, M. A. Rodriguez, A. Hernandez-Machado, and J. Ortin, Phys. Rev. Lett. **89**, 026102 (2002).
[22] J. Santamaria, M. E. Gomez, J. L. Vicent, K. M. Krishnan, and I. K. Schuller, Phys. Rev. Lett. **89**, 190601 (2002).
[23] J. J. Ramasco, J. M. Lopez, and M. A. Rodriguez, Phys. Rev. Lett. **84**, 2199 (2000).
[24] J. M. Lopez, M. A. Rodriguez, and R. Cuerno, Phys. Rev. E **56**, 3993 (1997).
[25] J. M. Lopez and M. A. Rodriguez, Phys. Rev. E **54**, R2189 (1996).
[26] G. Palasantzas and J. Krim, Phys. Rev. B **48**, 2873 (1993).
[27] V. Holý, U. Pietsch, and T. Baumbach, *High-Resolution X-Ray Scattering From Thin Films and Multilayers* (Springer-Verlag, Berlin, 1999).
[28] A. C. Dürr, N. Koch, M. Kelsch, A. Rühm, J. Ghijsen, R. L. Johnson, J.-J. Pireaux, J. Schwartz, F. Schreiber, H. Dosch, and A. Kahn, Phys. Rev. B **68**, 115428 (2003).