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# Growth dynamics of ZnPc and TiOPc thin films: Effect of crystallinity on anomalous scaling behavior

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ABSTRACT

The surface morphology evolution and scaling behavior of zinc phthalocyanine (ZnPc) and titanyl phthalocyanine (TiOPc) thin films have been studied using atomic force microscopy, X-ray diffraction and height difference correlation function analysis. In contrast to the large growth exponent ($\beta$) values and anomalous scaling behavior previously reported for other crystalline molecular thin films, significantly small $\beta$ and anomaly values were observed for amorphous TiOPc thin films. The relatively small anomaly value of ZnPc thin films, though larger than that of TiOPc thin films, is also rationalized by the lack of crystallographic ordering at the initial stage of growth.

## 1. Introduction

In the last decades organic semiconductors have attracted increasing attention for their potential in a wide range of device applications [1–3]. Within a large number of organic semiconductors, phthalocyanines (Pcs) are a particularly important class of material finding use in a variety of optoelectronic devices such as photovoltaic cells and organic light emitting diodes due to their favorable physical properties such as thermal and chemical stability, well-ordered thin film growth and wide absorption band at the optical region [3–5]. These devices often require the formation of molecular heterostructures comprising several layers of different organic materials and the organic–organic interface morphology is known to play a crucial role in the device performance [6]. The growth behavior and resulting surface morphology evolution of molecular thin films, however, remains poorly understood.

Recent several studies reported two unique characteristics of the growth behavior of molecular thin films compared to inorganic and metallic thin films [7–9]. One is the large value of the growth exponent ($\beta$), which means rapid surface roughening during the deposition and the other is the pronounced upward growth of crystalline mounds and consequent significant deviation from conventional scaling laws. In the case of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) thin films in which the molecules adopt a layered configuration with their molecular planes parallel to the substrate, for example, showed the largest deviation from the conventional scaling laws. The reason was suggested that the surface-parallel configuration of PTCDA molecules cannot be maintained at the step edges when the impinging molecule moves down to the lower layer leading to a significant decrease in the $\pi$–$\pi$ interaction between interlayer molecules and hence large step edge barriers [8]. For the $C_{60}$ thin films characteristic of relatively isotropic molecular structure, however, much smaller deviation was observed [9]. This implies that the large $\beta$ values and anomalous scaling behavior for the molecular thin film systems are likely a consequence of intrinsic anisotropy of the molecular structure. In this paper, we present the results of the surface morphology evolution and growth behavior of two Pc, zinc phthalocyanine (ZnPc) and titanyl phthalocyanine (TiOPc) (Fig. 1), thin films with different crystallographic ordering and show how the crystallinity of the Pc films affect on the molecular thin film growth behavior.

## 2. Experimental

ZnPc and TiOPc thin films were grown in an ultrahigh vacuum organic molecular beam deposition (OMBD) chamber with a base pressure of $\sim 2 \times 10^{-8}$ torr. Commercially available ZnPc (Aldrich Chemical, 97%) and TiOPc (Aldrich Chemical, 95%) powder was outgassed thoroughly in the vacuum chamber for 15–20 h before growth and sublimed from a miniature effusion cell onto well cleaned glass substrates held at room temperature. The cell temperature was 390 °C and 405 °C for ZnPc and TiOPc respectively, which corresponds to a growth rate of ~0.6 Å/s determined by a quartz crystal microbalance (QCM) positioned near the substrate. *Ex-situ* surface morphology analyses at different film thicknesses (200–4000 Å) were performed using tapping mode atomic force microscopy (AFM)

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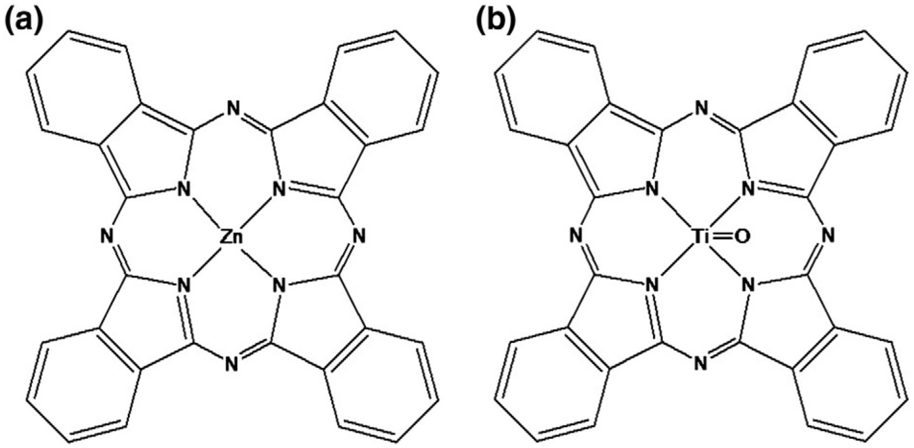

**Fig. 1.** Molecular structures of (a) ZnPc and (b) TiOPc.

(SII SPA400). Structural characterizations of the thin films were carried out using an X-ray diffractometer (XRD) (Philips PW1827).

## 3. Results and discussion

Representative AFM images of ZnPc and TiOPc thin films with various thicknesses ($D$) are shown in Fig. 2a–c, d–f respectively. All images were taken with the same scan area of 1 μm × 1 μm. In both molecular thin film systems, surface roughness and lateral size of the crystallites increase as film grows, similar to other molecular thin film systems. More quantitative comparison was carried out using height difference correlation function (HDCF) analysis [10]. The roughness scaling follows simple power laws characterized by the roughness ($\alpha$), growth ($\beta$) and dynamic ($z$) exponents, which can be determined from the mean-square surface fluctuation, $g(R)$,

$$\begin{aligned} g(R) &= \left\langle [h(x,y) - h(x',y')]^2 \right\rangle \\ R &= \sqrt{(x-x')^2 + (y-y')^2} \end{aligned} \tag{1}$$

The average is taken over all pairs of points $(x,y)$ and $(x',y')$ separated laterally by the length, $R$. Two distinct regimes can be identified depending on the relative magnitudes of $R$ and the correlation length, $\xi$; $g(R) \propto R^{2\alpha}$ for $R \ll \xi$, and $g(R) = 2\sigma^2$ for $R \gg \xi$, with $\sigma$ the mean-square

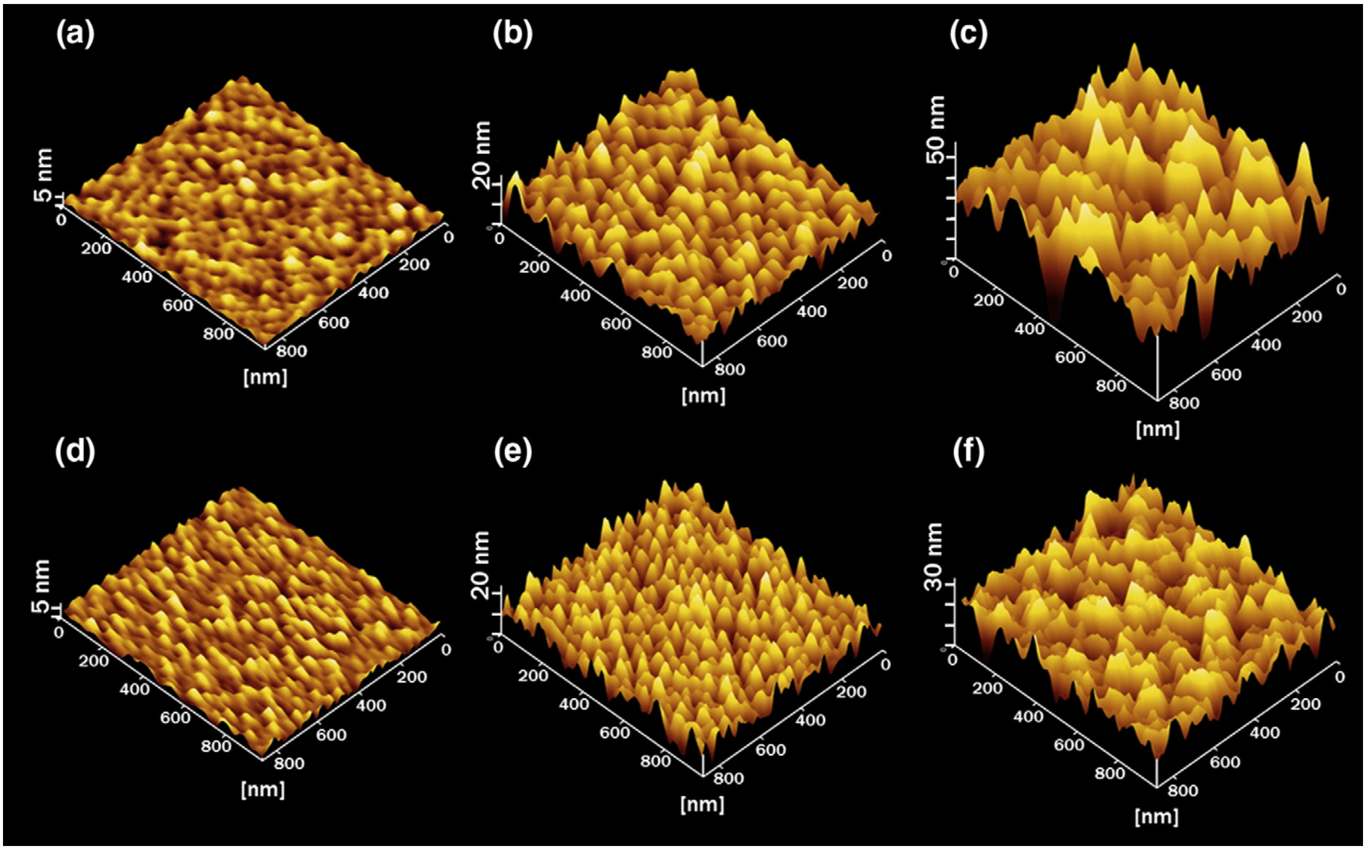

**Fig. 2.** Representative AFM images for ZnPc thin films deposited on glass substrates with various thicknesses, $D$, of (a) 301 Å, (b) 917 Å and (c) 2151 Å, and for TiOPc thin films with $D$ of (d) 227 Å, (e) 940 Å and (f) 2406 Å.