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Roughening aspects of room temperature vapor deposited oligomer thin films onto Si substrates

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Abstract

Growth front scaling aspects are investigated for poly-(*p*-phenylene–vinylene)-type oligomer thin films vapor-deposited onto silicon substrates at room temperature. For a film thickness d in the range from 15 to 300 nm, commonly used in optoelectronic devices, measurements of the correlation function by atomic force microscopy yields roughness exponents in the range $H = 0.45 \pm 0.04$, and an rms roughness amplitude which evolves with film thickness as a power law $\sigma \propto d^{\beta}$ with $\beta = 0.28 \pm 0.05$. The non-Gaussian height distribution and the measured scaling exponents (H and β) suggest a roughening mechanism close to that described by the Kardar–Parisi–Zhang scenario which is characteristic of non-surface diffussive growth processes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Growth; Surface roughening; Silicon

1. Introduction

Surface roughness scaling characteristics in thin films grown under non-equilibrium conditions has attracted considerable interest from a fundamental and an application point of view [1–5]. During recent years there has been an increasing technological interest in organic thin films, either polymers or oligomers, as the active layer in molecular devices such as light emitting diodes, photovoltaic devices and field effect transistors [2,6]. Injection, transport and recombination of charge carriers depend among other parameters on molecular packing, grain boundaries and roughness along the formed interfaces [7,8]. As a result, control of the film morphology is of primary concern for the optimization of electro-optical properties of organic-based photonic devices [6].

Up to now, only limited research has been concentrated on growth properties of organic thin films showing the possibility of various scaling relations controlling their growth morphology [3–5]. These studies have shown that the rms roughness amplitude σ evolves with film thickness as a power law $\sigma \propto d^{\beta}$ with β the growth exponent in the range $0.25 < \beta < 1$, and a roughness exponent H in the range of $H > 0.6$ [3–5]. The latter quantifies the degree of surface irregularity at short length scales ($<\xi$; with ξ the in-plane roughness

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correlation length [1]). For plasma polymer films [3], the scaling exponents $0.9 < H \leqslant 1$ and $0.6 < \beta \leqslant 1$ were measured. The evolution of roughness of a 100 nm thick T6 (sexithienyl) oligomer film [4], with increasing substrate temperature (25–250 °C) during deposition, was associated with a decreasing roughness exponent from $H = 1$ to $H = 0.7$. Finally, the growth of vapor deposited-polymerized linear poly(*p*-xylene) films [5] revealed the scaling exponents $H \approx 0.7$, $\beta \approx 0.25$, and $z = 3.2$ ($\xi \sim d^{1/z}$) which were consistent with a roughening model due to monomer bulk diffusion [5].

The former studies of oligomer and polymer films have clearly pointed out the importance of structural organization at higher levels [6,9–12]. In the present study we examine the scaling aspects of the growth front of oligomer van der Waals thin films [6] grown by vapor deposition on SiO_2 substrates held at room temperature (RT). It is shown that the surface roughening mechanism to be close to that described by the Kardar–Parisi–Zhang (KPZ) model which is characteristic of non-surface diffussive growth processes [1,13].

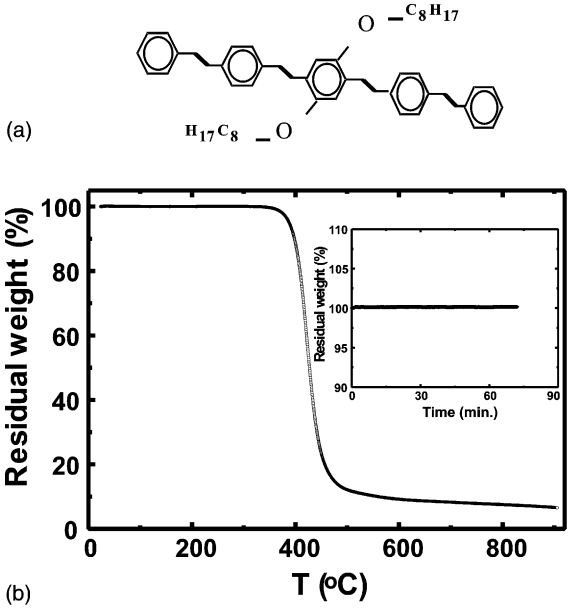

Fig. 1. (a) Chemical structure of the Ooct-OPV5, (b) thermogravimetric analysis for an Ooct-OPV5 specimen. The inset shows an isothermal for the temperature (230 °C) and the heating time (<45 min) used in our deposition experiments.

2. Experimental procedure

The five-ring poly-(*p*-phenylene–vinylene)-type oligomer 2,5-di-*n*-octyloxy-1,4-bis(4′-(styryl)styryl)-benzene (Ooct-OPV5; which is shown in Fig. 1a) is synthesized from solution, and its molecule exhibits a characteristic length of 2.9 nm [11]. The vacuum deposition system consisted of a bell-jar-type deposition chamber where the molecules sublimate at $\sim$230 °C, and then as a whole it condenses on the SiO_2 substrate (cleaned ultrasonically in a three-step procedure using xylene, 2-propanole and ethanol) held at RT. The base pressure in the deposition chamber was $\sim 10^{-8}$ mbar, while typically during deposition it was $\sim 10^{-7}$ mbar. During deposition the film thickness was monitored using a quartz crystal microbalance and an average growth rate of $\approx$0.12 nm/sec. Finally, as Fig. 1b indicates, thermogravimetric analysis measurements (Perkin–Elmer TGA 7) [10] showed that the molecule remains stable for temperatures up to $\sim$350 °C. An additional isothermal scan for the temperature and the heating time used for the deposition of the thickest films in our experiments verifies the latter (Fig. 1b, inset). Furthermore, after TGA analysis the color of the samples remained unchanged. Therefore, molecule fragmentation during evaporation can be excluded in the present experiments.

The film surface morphology was measured using an AFM (Digital Instruments Nanoscope IIIa) in tapping mode [12] to avoid any damage of the film surface (Fig. 1). The Si tips featured a radius $\leqslant 10$ nm, and a top angle $\leqslant 10°$, while 512×512 pixels were used during AFM imaging. Moreover, AFM analysis yielded a substrate rms roughness amplitude of $\sim$0.3 nm, which is much smaller than that of the oligomer film surfaces. Comparison with three samples prepared under identical conditions yielded roughness parameters (H, ξ, σ) within the indicated error bars. For each film thickness, the data of the height–height difference correlation function $g(\mathbf{r}) = \langle [h(\mathbf{r}) - h(\mathbf{0})]^2 \rangle$ data from five AFM topography images (acquired at different locations on the film surface) were averaged. $h(\mathbf{r})$ is the surface height at lateral position $\mathbf{r}$ $[= (x, y)]$ on the surface relative to the mean surface height, and the notation $\langle \cdots \rangle$ means an ensemble average. The calculation of $g(\mathbf{r})$ requires the use of a scan size at least 10 times larger than the significantly large cluster sizes seen in the AFM images in order to capture all of the necessary lateral roughness wavelengths [13].

3. Results and discussion

The height distribution *P(h)* shows deviations from the best Gaussian fit especially in the negative tail. To quantify further this point we calculated the skewness $S = \int h^3[P(h)/\int P(h)\mathrm{d}h]\mathrm{d}h/\sigma^3$, which is a measure of the symmetry of a distribution around a reference surface level. For a Gaussian distribution $S = 0$, while for the present case (i.e. Fig. 2) we obtain $0.2 < S < 0.5$ in agreement with the more pronounced positive tail of *P(h)*. Also for other film thickness we obtain $S > 0$, indicating violation of the $h \to -h$ symmetry during growth. The latter implies the presence of a non-linearity that leads to growth dependence on the local surface inclination [14].

Furthermore, the self-affine scaling hypothesis requires that

$$g(\mathbf{r}) = Ar^{2H} \quad \text{for } r \ll \xi \tag{1a}$$

$$g(\mathbf{r}) = 2\sigma^2 \quad \text{for } r \gg \xi \tag{1b}$$

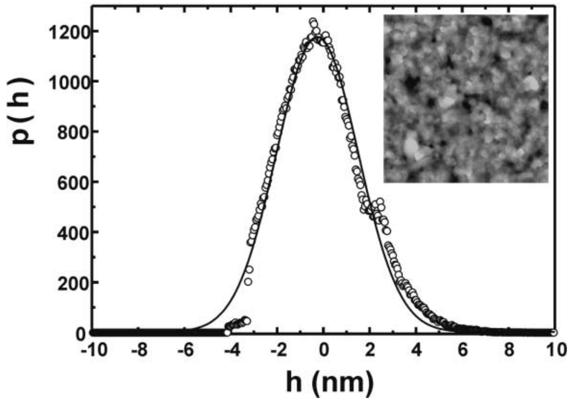

Fig. 2. Height distribution with the best fit to a Gaussian for the film of thickness $d = 50$ nm shown in the inset (scan size 2000 nm).

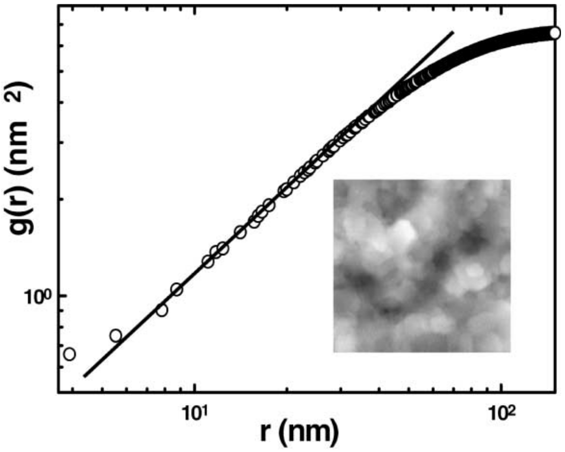

Fig. 3. Height–height difference correlation function $g(\mathbf{r})$ vs. the in-plane distance r (scan size L used to calculate $g(\mathbf{r})$ is 2000 nm ($>\xi$) for film of thickness $d = 50$ nm (Fig. 2). The rms roughness amplitude is $\sigma = 1.8$ nm. The correlation length is $\xi = 69.5$ nm and compares with observed cluster sizes. Linear fit at small length yields the roughness exponent $H = 0.44 \pm 0.02$. The inset shows an AFM image of small scan size 500 nm.

with A: constant ($A \approx \sigma/\xi^H$) [13]. The roughness exponent H describes the degree of surface irregularity at short roughness wavelengths ($r \ll \xi$) such that as H decreases the surface becomes more irregular (jagged) [1]. The saturation regime of $g(\mathbf{r})$ yields σ, and the log–log plot at short length scales yields the roughness exponent H (Fig. 3). The in-plane roughness correlation is determined from the intersection of the power-law line and the saturation line that yields $\xi = (2\sigma^2/A)^{1/2H}$. Since $\xi \gg 2.9$ nm (molecule length), significant lateral correlation develop during growth.

From the experimental data in Fig. 4 (inset), the roughness exponent is in the range $H = 0.45 \pm 0.04$ (for the thickness range $15 \leqslant d \leqslant 300$ nm which is used in oligomer-based devices [6,11]). The measured roughness exponents $H(< 0.5)$ are well below of any prediction of surface diffusion relaxation mechanism ($0.66 \leqslant H \leqslant 1$) of the deposited molecules [15,16]. On the other hand, the KPZ type of growth [14], where the dominant relaxation mechanisms are desorption or vacancy formation, leads to the prediction of a roughness exponent $H \approx 0.4$ [1,17] which is indeed much closer to the measured values. Due to finite tip size

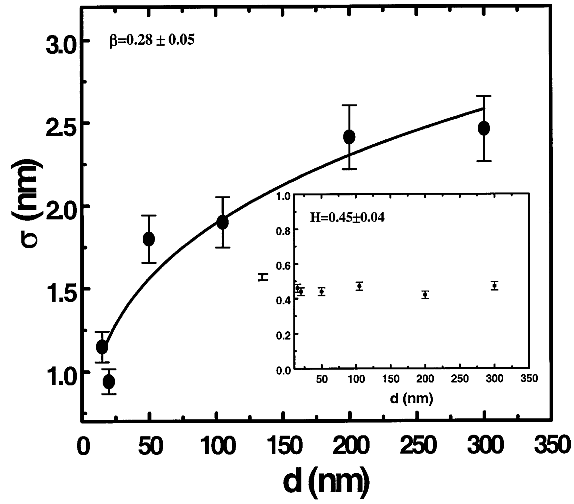

Fig. 4. Roughness amplitude σ vs. the film thickness d which grows with an exponent $\beta = 0.28 \pm 0.05$ as the fit yields. The inset shows the roughness exponent H vs. film thickness d. An average value is estimated to be $H = 0.45 \pm 0.04$.

effects the actual roughness exponent could be closer to the value $H \approx 0.4$ [18]. Roughness exponents $H \leqslant 0.3$ have been measured recently also on T6 oligomer films, without however addressing any further growth aspects such as the development of out-of-plane correlation as quantified by the growth exponent β [19]. Indeed, measurements of the growth exponent β from the rms roughness amplitude σ vs. film thickness d ($\sigma \propto \mathrm{d}^{\beta}$; Fig. 4) yields $\beta = 0.28 \pm 0.05$ which is within the predictions of the KPZ scenario for 2+1 dimensional growth with $\beta \approx 0.25$ [1,18].

The KPZ growth model reads of the form

$$\partial h/\partial t = v\nabla^2 h + b(\nabla h)^2 + n(\mathbf{r}, t) \tag{2}$$

with $n(\mathbf{r}, t)$ random white Gaussian noise ($\langle n(\mathbf{r}, t) n(\mathbf{r}', t')\rangle = 2D\delta^2(\mathbf{r} - \mathbf{r}')\delta(t - t')$ with D the noise amplitude) due to the deposition process, and v a coefficient associated with the surface relaxation mechanism (desorption or vacancy formation). The non-linear term $b(\nabla h)^2$ (with b being proportional to the growth velocity perpendicular to the surface) leads to the $h \rightarrow -h$ symmetry breaking. By itself, the non-linear term in the KPZ equation will convert a surface consisting of rounded hills into a surface of plateaus separated by narrow, step-sided canyons [1]. Such an effect appears to be consistent with the AFM topology images as can be seen clearly in Figs. 2 and 3. Formation of fine nanosize ($\leqslant 100$ nm, Fig. 3 inset) domains (plateaus) oriented almost randomly out-of-plane (with respect to the substrate) occurs, and being separated by deeper groove networks.

4. Conclusions

The growth front roughening of vapor-deposited oligomer thin films (Ooct-OPV5) on silicon-oxide substrates at RT appears to follow scaling behavior close to the KPZ model (assuming white Gaussian noise due to deposition process). This is supported by the roughness exponents $H = 0.45 \pm 0.04$, the growth exponent $\beta = 0.28 \pm 0.05$, as well as by the breakdown of the $h \rightarrow -h$ symmetry of the height distribution during growth. Further studies are in progress, concentrating on the effect of substrate temperature on the oligomer surface morphology.

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