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Published in:
Applied Physics Letters

DOI:
10.1063/1.1484250

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2002

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Tsamouras, D., & Palasantzas, G. (2002). Temperature dependence of the growth front roughening of oligomer films. Applied Physics Letters, 80(24), 4528 - 4530. DOI: 10.1063/1.1484250

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APPLIED PHYSICS LETTERS VOLUME 80, NUMBER 24 17 JUNE 2002

Temperature dependence of the growth front roughening of oligomer films

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(Received 6 February 2002; accepted for publication 11 April 2002)

Growth front roughening characteristics of vacuum deposited pentamer 2,5-di-*n*-octyloxy-1,4-bis[4-(styryl)styryl]-benzene oligomer thin films, onto silicon substrates, strongly depend on the substrate temperature in the range ~20 °C–100 °C. The measured roughness exponents H increase from $H \approx 0.4$ at low substrate temperatures where growth is dominated by vacancy formation, to $H \approx 0.7-0.8$ at elevated temperatures where diffusive growth takes place. Moreover, the root-mean-square roughness amplitude and the correlation length evolve with temperature closely as an Arrhenius process with activation barrier comparable to molecule transnational and rotational barriers on oligomer surfaces. © *2002 American Institute of Physics.*
[DOI: 10.1063/1.1484250]

The surface morphology of thin films grown under nonequilibrium conditions show, in many cases, scaling characteristics which are of strong technological interest in relation to electro-optical properties.[1–6] Such an interest in organic thin films (polymers or oligomers) stems from their utilization as the active layer in molecular devices (light-emitting diodes, solar cells, field-effect transistors, etc.).[2,7] At any rate, since charge transport is strongly correlated to electronic structure and self-organized structural order,[8,9] control of the film morphology is of primary interest for the optimization of the performance of such organic based devices.[7]

So far, only limited research has been concentrated on growth properties of organic films.[3–6] These studies have shown that the root-mean-square (rms) roughness amplitude σ evolves with film thickness d 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 $0.4 \leq H \leq 1$.[3–6] For plasma polymer films,[3] scaling exponents of $0.9 < H \leq 1$ and $0.6 < \beta \leq 1$ were measured. The evolution of roughness for a 100 nm thick sexithienyl oligomer film,[4] with increasing substrate temperature (25 °C–250 °C) during deposition, was associated with a decreasing roughness exponent from $H = 1$ to $H = 0.7$. The growth of vapor deposited-polymerized linear poly-xylene films[5] revealed the scaling exponents $H \approx 0.7$, $\beta \approx 0.25$, and $z = 3.2$ ($\xi \sim d^{1/z}$ with ξ as the roughness correlation length) which were consistent with monomer bulk diffusion.[5] Finally, room-temperature growth of the pentamer 2,5-di-*n*-octyloxy-1,4-bis[4′-(styryl)styryl]-benzene (Ooct-OPV5) onto Si/SiO_2 substrates,[6] respectively, yielded roughness and growth exponents $H = 0.45 \pm 0.04$ and $\beta = 0.28 \pm 0.05$, suggesting a roughening mechanism close to the Kardar–Parisi–Zhang (KPZ) model.[10,11]

In the present study, we investigate the temperature dependence of scaling aspects for Ooct-OPV5 oligomer thin films [Fig. 1(a)][12,13] grown by vapor deposition onto Si substrates, held at temperatures in the range 20 °C–100 °C and fixed thickness $d = 100$ nm.[14] During vacuum deposition, the molecules sublimate at ~230 °C, and then, as a whole, condense onto the Si substrate. The base chamber pressure was $\sim 10^{-8}$ mbar, while during deposition $\sim 10^{-7}$ mbar. Prior to deposition thermogravimetric analysis measurements (TGA) showed that the molecule remains stable for temperatures up to ~350 °C avoiding fragmentation during evaporation.[6,14]

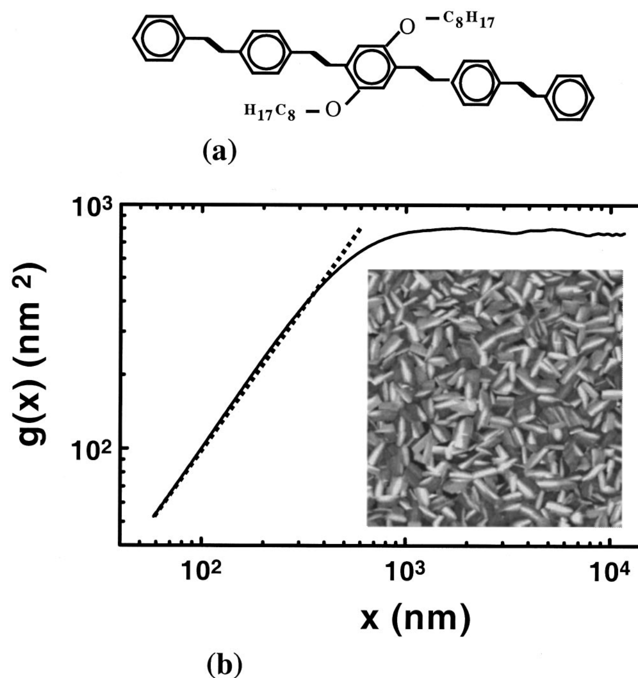

FIG. 1. (a) Chemical structure of the Ooct-OPV5. The five-ring poly(phenylenevinylene)-type molecule exhibits a length of ≈2.9 nm. (b) Correlation function $g(x)$ vs x for a film grown at 80 °C of substrate temperature (scan size: 30 000 nm). Linear fit (dotted line) at small length scales yields the roughness exponent $H = 0.73 \pm 0.04$.

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The film surface morphology was recorded using an atomic force microscope (AFM: Digital Instruments Nanoscope IIIa) in tapping mode to avoid any film damage.[15] The Si tips featured a radius $\leqslant 10$ nm and a top angle $\leqslant 10°$ while 512×512 pixels were used during imaging. AFM analysis yielded substrate rms roughness amplitude of ~ 0.3 nm that is much smaller than that of the oligomer surfaces. For each film, the correlation function $g(x) = \langle [h(x) - h(0)]^2 \rangle$ from five AFM images (acquired at different locations on the surface) were averaged [Fig. 1(b)]. $h(x)$ is the surface height at lateral position x on the surface relative to the mean surface height (along the fast scan direction).[16]

If the roughness follows the self-affine scaling hypothesis, then we have $g(x) = Ax^{2H}$ for $x \ll \xi$, and $g(x) = 2\sigma^2$ for $x \gg \xi$.[1,16] The roughness exponent H describes the degree of surface irregularity at short roughness wavelengths ($x \ll \xi$) such that as H decreases the surface becomes more irregular (jagged).[1,20] The saturation regime of $g(x)$ yields σ, and the slope of the linear fit in a log–log plot (at $x \ll \xi$) yields the roughness exponent H [Fig. 1(b)].[16] The intersection of the power-law and saturation lines yields the correlation length $\xi = (2\sigma^2/A)^{1/2H}$ that is much larger than the molecule length (≈ 2.9 nm).[13]

As Fig. 2 indicates, with increasing substrate temperature T from 40 °C to 100 °C, the film surface undergoes a morphology transition. Starting from a state where there is formation of fine nanosize domains (plateaus) oriented almost randomly out of plane [with respect to the substrate, Fig. 2(a)];[6] another state appears with elongated crystals of significant size [Fig. 2(c)]. Moreover, the normalized height distribution $P^*(h)$ $[\equiv P(h)/\int P(h)dh]$ shown in Fig. 3 is highly asymmetrical with positive Skeweness ($S = \int h^3 [P(h)/\int P(h)dh] dh/\sigma^3 > 0$; pronounced positive tail). Such a distribution asymmetry indicates violation of the $h \leftrightarrow -h$ symmetry during growth implying the presence of a nonlinearity and a growth dependence on the local surface inclination.[10,11]

The pyramidal configuration shown in Fig. 2(c) includes several large domains with similar orientation. It is most likely indicative of the presence of Schwoebel barriers at step edges that inhibit downhill surface diffusion of deposited molecules.[1] A more detailed profile analysis across the crystal terraces yields a step height of ≈ 1.5 nm. This value corresponds to the thickness of one molecular layer since it coincides with an earlier estimation for annealed Ooct-OPV5 films.[12,14] That was assumed to be the result of a particular molecular orientation, which was attributed to deformation due to adjustment of the c axis and/or the monoclinic angle. The high-temperature morphology of the Ooct-OPV5 film has to be seriously considered in optoelectronic device fabrication. This is because the growth of such large, highly oriented, crystalline domains is known to facilitate charge transport, and it always enhances the device performance especially when the optimum directional molecular features and film thickness have been determined.[17–19] The pyramidal pattern in Fig. 2(c) leads simultaneously to the formation of various pinholes within the film that can be responsible for deficient substrate coverage, resulting in direct contacts between two metal electrodes and consequently to short circuits. Therefore, a critical thickness minimum is required with respect to heat treatment.

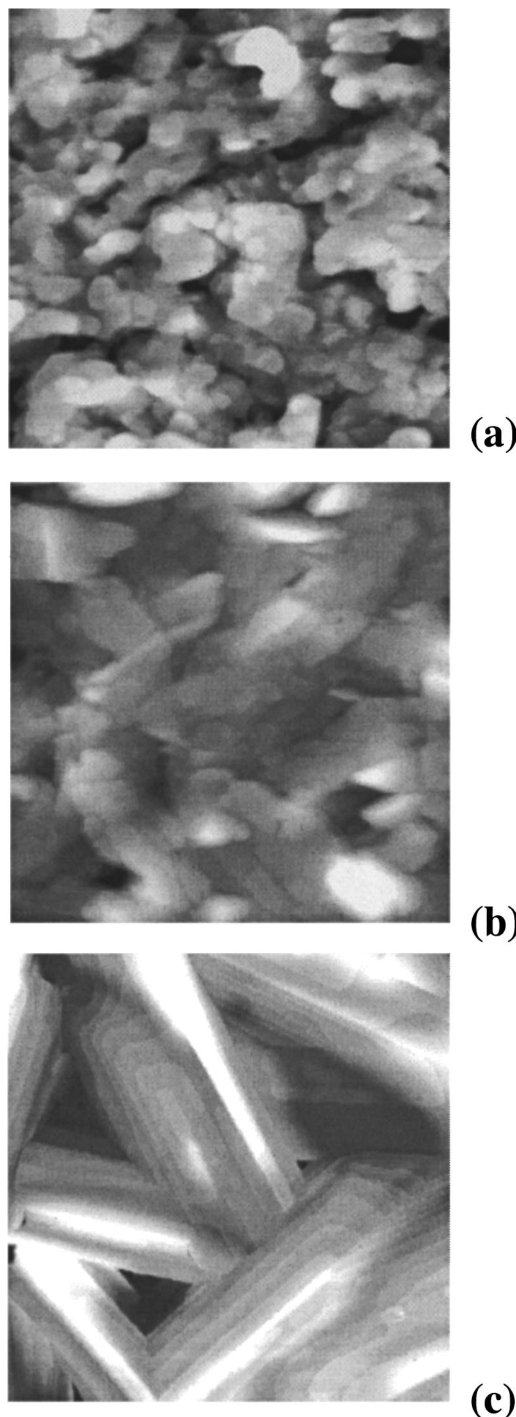

FIG. 2. AFM topography images for varying substrate temperature (a) 40 °C (scan size: 1500 nm), (b) 60 °C (scan size: 1500 nm), and (c) 100 °C (scan size 7500 nm).

The low-temperature morphology ($\leqslant 40$ °C) is indicative of KPZ growth driven by vacancy formation and it is characterized by roughness exponents $H \approx 0.4$ (Ref. 11) which is in close agreement with our earlier findings (Fig. 3; inset).[6] Due to finite tip size effects, the actual roughness exponent H could be closer to the value $H \approx 0.4$.[20] With increasing substrate temperature, the relaxation of incoming oligomers is strongly influenced by surface diffusion which is in agreement with the large roughness exponents ($H > 0.6$).[21] The

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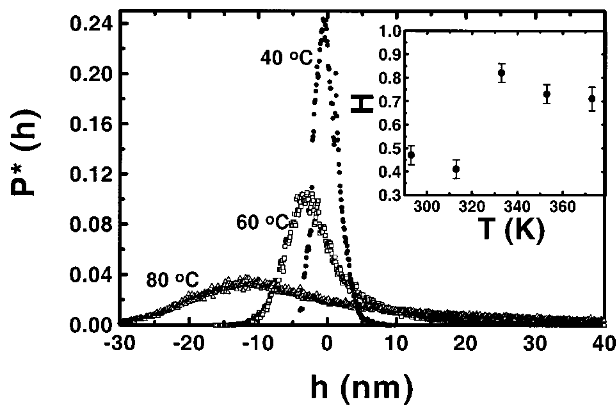

FIG. 3. Height–height distributions for films grown at three distinct substrate temperatures. The inset shows the various roughness exponents H obtained vs various substrate temperatures T (K).

different behavior with the $T6$ oligomer (H decreased with increased deposition temperature)[4] may be attributed to the absence in this molecule of the tails $O-C_8H_{17}$ [Fig. 1(a)] which influence local molecular ordering.[12] Furthermore, with increased temperature, both the rms roughness amplitude σ and the in-plane correlation length ξ increase closely following an Arrhenius behavior as $\sigma, \xi \propto \exp(-E_{\mathrm{Bar}}/K_B T)$ with activation barrier $E_{\mathrm{Bar}} = 0.37 \pm 0.07$ eV and K_B the Boltzmann constant (Fig. 4). The latter compares to molecule transnational and rotational barriers on oligomer surfaces.[4] Although a precise agreement is rather fortuitous, it encourages AFM analysis over a rather wide range of spatial length scales in order to elucidate microscopic growth mechanisms of organic thin films.

In conclusion, we investigated the temperature dependence of growth front scaling characteristics for Ooct-OPV5 thin films vapor deposited onto silicon substrates in the temperature range 20 °C–100 °C. The obtained roughness exponents H increase from $H \approx 0.4$ at low temperatures, where growth is dominated by vacancy formation, to $H = 0.7-0.8$ at elevated temperatures where diffusive film growth occurs. The activated increase in feature size (with activation energy comparable to transnational and rotational barriers on oligomer surfaces) and the skewed particle size distributions are also possibly consistent with a process of coalescence between small particles depending on mobility of molecules or small molecular clusters.

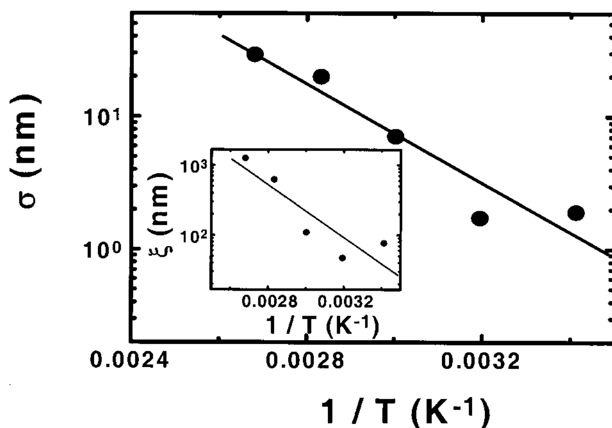

FIG. 4. Roughness amplitude vs inverse temperature $1/T$ with the linear fit yielding the activation barrier $E_{\mathrm{Bar}} = 0.33 \pm 0.08$ eV. The inset shows a similar plot for the in-plane roughness correlation length ξ vs $1/T$.

The authors would like to thank J. Wildeman for the synthesis of Ooct-OPV5. Financial support from EU [Marie Curie Individual Fellowship for one of the authors (D.T.) under Contract No. HPMF-CT-199900010] is also gratefully acknowledged.

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