Kinetic Roughening in Polymer Film Growth by Vapor Deposition

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The growth front roughness of linear poly(p-xylylene) films grown by vapor deposition polymerization has been investigated using atomic force microscopy. The interface width w increases as a power law of film thickness d, $w \sim d^{\beta}$, with $\beta = 0.25 \pm 0.03$, and the lateral correlation length ξ grows as $\xi \sim d^{1/z}$, with $1/z = 0.31 \pm 0.02$. This novel scaling behavior is interpreted as the result of monomer bulk diffusion, and belongs to a new universality class that has not been discussed previously.

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Thin films grown under nonequilibrium conditions often show scaling behaviors and have attracted considerable interest [1–3]. The major efforts have been focused on the study of the growth of metal and semiconductor thin films [1–3]. Recently there is growing technological interest in polymer thin films for molecular devices and microelectronic interconnects [4,5]. So far, only a few works have been done on polymer thin films [6,7]. These pioneering works show that various scaling behaviors can also exist for thin polymer films. Most polymer film growth is quite complex, and the results are not trivial to interpret when compared to those of metal and semiconductor growth processes. In the present study we examine the roughness evolution of a simple polymer growth system, -(C_8H_{10})-, called p-xylylene [8–10]. The coating process is best described as vapor deposition polymerization (VDP), in which the monomer from the gas phase condenses on the substrate and reacts to form high molecular weight, linear poly(p-xylylene) (PPX), also known by the trade name Parylene. It was suggested that both the surface condensation and bulk diffusion of monomers occur in a VDP process [8–10]. The monomer can be consumed by two chemical reactions: initiation, in which new polymer molecules (chains) are generated, and propagation, in which existing polymer molecules are extended to higher molecular weight.

The monomer transport in the vacuum during the VDP process is very much like the conventional physical vapor deposition (PVD) process such as molecular beam epitaxy (MBE) process for metals or semiconductors, in which atoms or molecules condense from the gas phase onto the substrate. The differences between VDP and PVD lie in the nucleation and growth processes after the monomer is condensed on the substrate. In the PVD processes, atoms can attach to the nearest neighbors of the nucleated sites, making the films dense and compact. The surface dynamics, such as surface diffusion, edge diffusion, step barrier effects, etc. can affect the growth. For the VDP process, the reaction occurs only at the ends of a polymer chain. Surface diffusion, intermolecular interaction, and chain relaxation can occur during growth. The latter two processes are very different from the atomistic processes of PVD, and should give a distinct dynamic behavior for the VDP film morphology. In this Letter, we present our experimental study of the growth of Parylene films by VDP. A new scaling relation is found in this system, and can be explained by a bulk diffusion mechanism.

The vacuum deposition system consists of a sublimation furnace, a pyrolysis furnace, and a bell-jar-type deposition chamber. A detailed description of the experimental setup can be found elsewhere [5]. During the VDP process, the dimer molecules sublime at 155 °C and then pyrolize into monomer units at 665 °C. The monomer units condense and polymerize on a Si wafer at room temperature. The base pressure in the deposition chamber is high at 10^{-6} Torr. The pressure during deposition is typically in the low-mTorr range. During the growth, a differentially pumped quadrupole mass spectrometer was used to analyze the gas phase chemistry during each deposition. For each run, the growth always started on a fresh Si wafer and then proceeded without interruption for a predetermined time. After deposition, the film thickness was measured using ellipsometry, and the growth rate was extracted from the slope of the thickness versus growth time plot. By varying the deposition pressure P from 2 mTorr to 7 mTorr, the growth rate R increased linearly from 1.95 ± 0.03 to 13.9 ± 0.1 nm/min.

The surface morphology was measured using contact-mode AFM (atomic force microscopy) (Park Scientific Auto CP). The radius of the Si tip is about 10 nm, and the side angle is about 10°. Repeated scans with a small force set point (= 1 nN) were carried out in order to ensure no obvious distortion caused by tip-sample interaction. Representative surface morphologies are shown in Fig. 1 for growth times of $t = 10$, 40, and 90 min at 5 mTorr. With the increase of growth time, the overall surface features enlarge, and the gray scale range increases. The quantitative information of the surface morphology can be extracted from the equal-time height-height correlation function $H(\mathbf{r}, t)$, defined as $H(\mathbf{r}) = \langle [h(\mathbf{r}) - h(\mathbf{0})]^2 \rangle$. Here $h(\mathbf{r})$ is the surface height at position $\mathbf{r}$ $[= (x, y)]$ on the surface relative to the mean surface height. The notation $\langle \cdots \rangle$ means a statistical average. The scaling hypothesis requires that $H(r) = \rho^2 r^{2\alpha}$ for $r \ll \xi$ and

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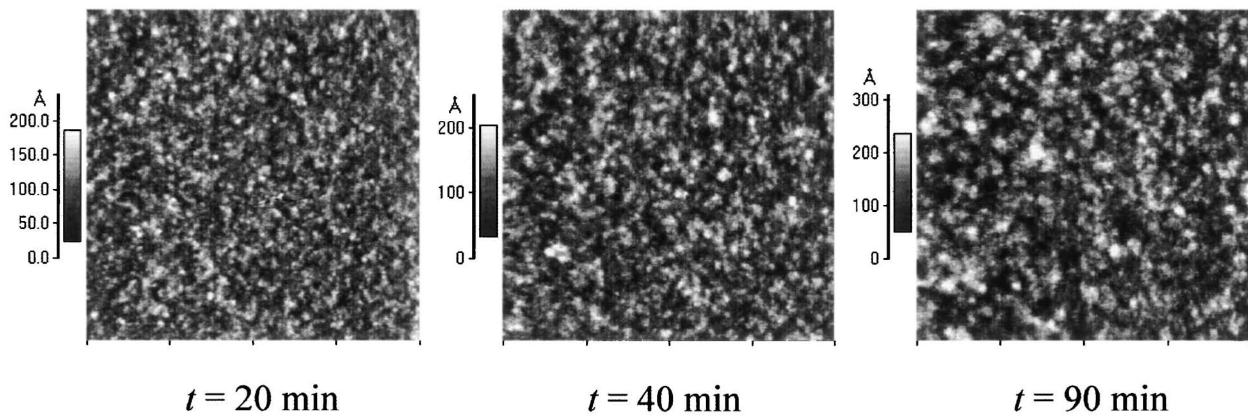

FIG. 1. Some representative surface morphologies ($4 \times 4\ \mu m^2$) measured by AFM for growth times of $t = 10$, 40, and 90 min at the growth rate $R = 9.5$ nm/min.

$H(r) = 2w^2$ for $r \gg \xi$ [1–3]. Here ρ is the average local slope, ξ is the lateral correlation length, w is the interface width or rms roughness, and α is the roughness exponent, which describes the surface fractality.

In Fig. 2 we plot $H(r, t)$ in log-log scale for $R = 5.5$, 9.5, and 13.9 nm/min. Clearly the overall behaviors of the height-height correlation function for the three different growth rates are similar: at small lateral length, the height-height correlation functions do not overlap each other, which implies that the growth is not stationary, i.e., the local slope is a function of growth time [11]. The roughness exponent values are equal within the experimental errors: $\alpha = 0.74 \pm 0.06, 0.70 \pm 0.05$, and 0.72 ± 0.03 for $R = 5.5$, 9.5, and 13.9 nm/min, respectively. The average roughness exponent from all different growth rates is 0.72 ± 0.05. However, if one considers the tip effect, the roughness exponent could be between 0.5 to 0.7 [12]. The average local slope ρ of the surface can also be extracted from the small-r behavior of the height-height correlation function. Figure 3 plots the local slope ρ as a function of film thickness for $R = 5.5$ and 13.9 nm/min. It increases with the film thickness as a power law. Because of the large statistical error in the fitting, the power is around 0.10–0.30. The interface width w and the lateral correlation length ξ versus film thickness d for various growth rates are plotted in Fig. 4.

For different growth rates, the log-log plots of w versus d are almost parallel, and, for the same thickness d, the higher the growth rate R, the larger the w value. The

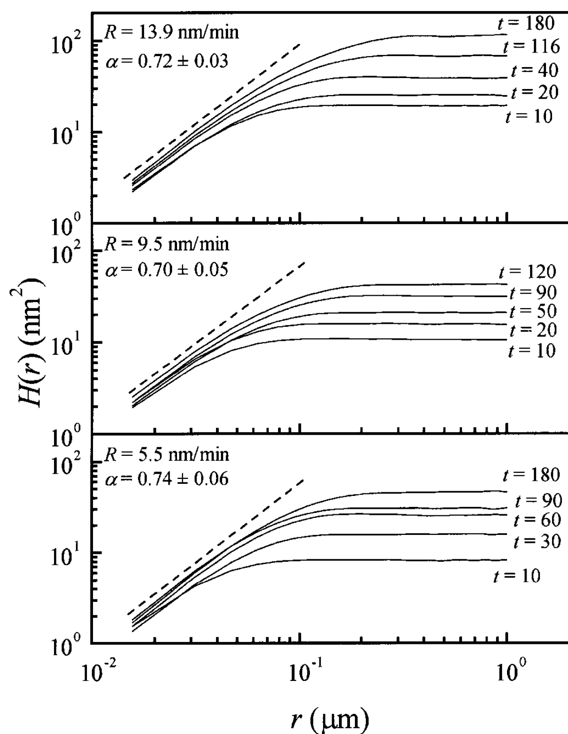

FIG. 2. The equal-time height-height correlation function $H(r, t)$ as a function of the distance r plotted in log-log scale for $R = 5.5$, 9.5, and 13.9 nm/min, respectively. Each $H(r, t)$ within the short-range spatial scaling regime gives the same α value. Time labels are in minutes.

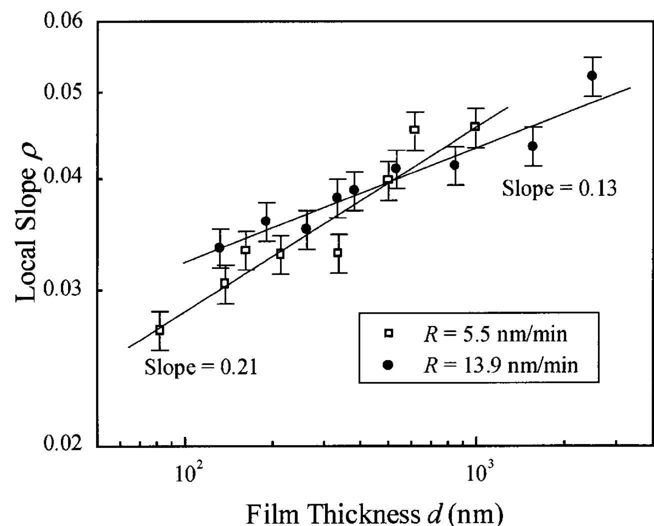

FIG. 3. The log-log plot of the local slope ρ versus film thickness d for $R = 5.5 \pm 0.1$ and 13.9 ± 0.1 nm/min.

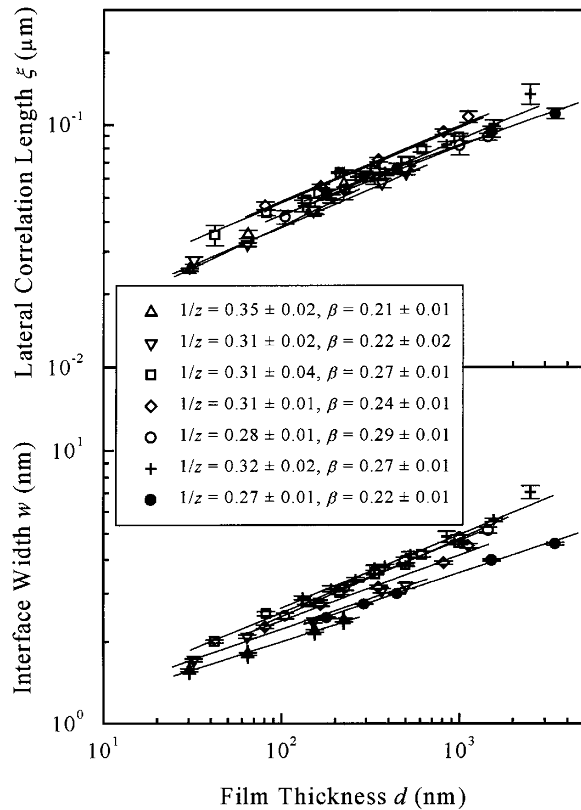

FIG. 4. The interface width w and the lateral correlation length ξ versus film thickness d for different growth rates and substrate temperatures are plotted in log-log scale (△: $P = 2$ mTorr, $R = 1.95 \pm 0.03$ nm/min; ▽: $P = 3$ mTorr, $R = 4.32 \pm 0.06$ nm/min; □: $P = 4$ mTorr, $R = 5.5 \pm 0.1$ nm/min; ◇: $P = 5$ mTorr, $R = 9.5 \pm 0.1$ nm/min, ○: $P = 6$ mTorr, $R = 11.9 \pm 0.4$ nm/min; +: $P = 7$ mTorr, $R = 13.9 \pm 0.1$ nm/min, all for $T = 20\,^\circ$C; and ●: $P = 7$ mTorr, $R = 53.3 \pm 0.6$ nm/min for $T = -30°$). For different growth rates, the log-log plots are almost parallel, indicating the same scaling property.

average growth exponent is $\beta = 0.25 \pm 0.03$. In order to determine ξ accurately, we calculated the two-dimensional autocorrelation function $C(\mathbf{r}) = \langle h(\mathbf{r})h(\mathbf{0})\rangle$ for each AFM image, and use the quadrant circularly averaged autocorrelation function $C_c(r)$ to determine ξ by the relation $C_c(\xi) = C_c(0)/e$. The log-log plots of ξ versus d for different growth rates are also almost parallel. The average dynamic exponent obtained is $1/z = 0.31 \pm 0.02$. The data for different growth rate tend to overlap each other. This suggests that the vertical roughness and the lateral correlation length of the film growth are independent of the growth rate.

A similar set of experiments was performed at a substrate temperature of $-30\,^\circ$C and $P = 7$ mTorr. The growth rate was 53.3 nm/min, and the growth gave a similar scaling behavior: $\alpha = 0.70 \pm 0.02$, $\beta = 0.22 \pm 0.01$, and $1/z = 0.27 \pm 0.01$ (see Fig. 4).

Our experimental results show that the scaling behaviors of the growth front do not change for growth rate spanning almost 1 order of magnitude. Of the known theoretical results for dynamic roughening, only the MBE nonlinear surface diffusion dynamics proposed by Lai and Das Sarma gives similar results: $\alpha = 2/3$, $\beta = 1/5$, and $1/z = 3/10$ [13]. However, this MBE model predicts stationary growth with a constant local slope, which was not observed in our experiment. As we discussed in the introduction, the chain relaxation and size of the molecule limit the surface relaxation for a polymer surface, and one would expect a very different roughening mechanism. Since an important mechanism of the VDP process is monomer bulk diffusion [8–10], the monomer concentration in the film is not uniform, and we need to consider the effect of bulk diffusion on the morphology evolution. We use the quasiequilibrium approach describing by [14]

$$\nabla^2 u(\mathbf{r}, z) = 0, \tag{1}$$

where $u(\mathbf{r}, z)$ is the chemical potential in the film. The boundary conditions are

$$u(\mathbf{r}, z = 0) = u_0, \tag{2}$$

$$u(\mathbf{r}, z = d + h) = u_1 - \nu \nabla_{\mathbf{r}}^2 h, \tag{3}$$

where ν is a term proportional to the surface tension. We assume that the chemical potential at the film/substrate interface $z = 0$ is a constant, and that the chemical potential at the growth front $z = d + h$ is determined by the Gibbs-Thompson relation [14]. After applying the boundary perturbation method, the solution of Eq. (1) has the form

$$\begin{aligned} u(\mathbf{r}, z) \approx u_0 + (u_1 - u_0)\frac{z}{d} &+ \int \left(\nu k^2 - \frac{u_1 - u_0}{d}\right) \\ &\times \frac{\sinh(kz)}{\sinh(kd)} \tilde{h}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{k}, \end{aligned} \tag{4}$$

where $\tilde{h}(\mathbf{k})$ is the Fourier transform of $h(\mathbf{r})$. The flux of atoms along the z direction is given by

$$j_z = -\frac{D_B c}{k_B T}\frac{\partial u}{\partial z}. \tag{5}$$

Assuming $u_1 \approx u_0$, and from the continuum equation $\frac{\partial h}{\partial t} = \Omega_0 j_z + \eta(\mathbf{r}, t)$, the change of the surface morphology due to bulk diffusion can be written (in Fourier space) as

$$\frac{\partial \tilde{h}(\mathbf{k}, t)}{\partial t} \approx -\gamma \frac{\cosh(kd)}{\sinh(kd)} k^3 \tilde{h}(\mathbf{k}, t) + \Theta(\mathbf{k}, t), \tag{6}$$

where $\gamma = \Omega_0 \nu \frac{D_B c}{k_B T}$, Ω_0 is the volume, D_B is the bulk diffusion coefficient, c is the bulk monomer concentration, k_B is Boltzmann's constant, $d = Rt$, and $\Theta(\mathbf{k}, t)$ is the Fourier transform of the noise $\eta(\mathbf{r}, t)$. The power spectrum can be written as

$$P(\mathbf{k}, t) = \langle |\tilde{h}(\mathbf{k}, t)|^2 \rangle = \int_0^t \left[\frac{\sinh(kRt)}{\sinh(kRt')}\right]^{2\gamma k^2/R} dt'. \tag{7}$$

A simple asymptotic calculation shows that, for very large k, Eq. (7) gives $P(k) \propto k^{-3}$. Thus, $\alpha = 0.5$. The

numerical integration of Eq. (7) gives $1/z = 0.3$, and $\beta = 0.2$, which is consistent with our experimental results. If surface diffusion contributes to the local smoothing, Eq. (6) can be rewritten as

$$\frac{\partial \tilde{h}}{\partial t} \approx -\gamma \frac{\cosh(kd)}{\sinh(kd)} k^3 \tilde{h}(\mathbf{k}) - \kappa k^4 \tilde{h}(\mathbf{k}) + \Theta(\mathbf{k}, t), \tag{8}$$

and the power spectrum becomes

$$P(\mathbf{k}, t) = \int_0^t \left[\frac{\sinh(kRt)}{\sinh(kRt')}\right]^{2\gamma k^2/R} \times \exp[-2\kappa k^4 (t - t')]\, dt'. \tag{9}$$

At large k, the asymptotic behavior of the power spectrum becomes $P(k) \propto 1/(\gamma k^3 + \kappa k^4)$. In this case the roughness exponent is not well defined, and at very large k the roughness exponent α eventually approaches 1, which is not consistent with the experimental results.

In summary, we reported our study of the dynamic scaling properties of Parylene films grown by vapor deposition polymerization. The roughening behavior was shown to belong to a novel universality class involving a bulk diffusion mechanism. At room temperature for various growth rates, the growth is nonstationary. The growth exponents, dynamic exponents, and roughness exponents are $\beta = 0.25 \pm 0.03$, $1/z = 0.31 \pm 0.02$, and $\alpha = 0.72 \pm 0.05$, respectively.

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