

Kinetic roughening in polymer thin film growth

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Abstract

Kinetic roughening is revisited in the context of polymer thin film growth by vapor deposition using the simplest toy model of chemical vapor deposition polymerization (CVDP) growth, which was employed in [J. Stat. Mech. (2009) P02031]. As the ratio of monomer diffusion rate D to the deposition flux F of monomers ($G = D/F$) increases, dynamic scaling of the CVDP growth is investigated in (1+1) and (2+1) dimensions. Measuring the surface width (height fluctuations) and the q -th order moments of height-height correlation function, it is observed that anomalous scaling behavior and multifractality exist. In order to speculate the origin of such anomalies, the following two scenarios are suggested and tested: One is that the cosine flux of incident monomers (random angle deposition) is essential in anomalous kinetic roughening phenomena and the other is that the multi-affine structure of CVDP growing surfaces is attributed to the non-local shadowing effect caused by the cosine flux of incident monomers, which yields the power-law distribution of steps. Based on the comparison of the ballistic deposition model with some modification of noise, namely the power-law distribution of noise, it is numerically confirmed that two scenarios turn to be true. This implies that dynamic scaling of the CVDP growth depends not only on what value is used for the ratio of monomer diffusion rate to deposition flux (G) but also on what kind of intrinsic and extrinsic noise exists.

Keywords: kinetic roughening, thin film growth, chemical vapor deposition polymerization, anomalous scaling, multifractality, cosine flux, shadowing effect, ballistic deposition, noise

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1. Introduction

In the growth of thin films and multilayers, kinetic roughening and dynamic scaling have been of considerable interest [1, 2] by the demand for smooth or regularly structured surfaces and interfaces for miniaturized functional films in science and technology. There are lots of theoretical and experimental studies available for the growth of metal/semiconductor films by molecular beam epitaxy (MBE), which reveal the occurrence of scaling exponents corresponding to a few universality classes with minimal toy models and reasonable theories. While polymer thin films and growing mechanisms become technologically important in many aspects, such as molecular devices and microelectronic interconnects [3], only few systematic studies are available as pioneering works [4, 5, 6]. Chemical vapor deposition polymerization (CVDP) is one of the popular and useful techniques for polymer thin film growth since it well describes the process of coating with poly (p -xylylene)(PPX), also known by the trade name Parylene [7].

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The growth mechanism of CVDP is quite distinguishable from that of the ordinary physical vapor deposition (PVD), in the sense that a deposited monomer cannot be stable until it finds either an active end of the already formed polymers or another monomer to be an oligomer. While the ratio of monomer diffusion rate (coefficient) D to the deposition flux F of incident monomer depends on temperature in the corresponding experimental setup, the basic mechanism of CVDP are more or less universal as follows: A hot monomer in the gas phase deposits by a random angle (kind of random walk) on the cold substrate, reacts to form a high molecular weight as an oligomer (the basic unit of polymer), and becomes a part of the polymer consisting of the body (bulk) part and two active ends (boundaries). In order to mimic the CVDP growth process, some modification is needed in the well-known MBE-type growth model, so-called the ballistic deposition (BD) model [1, 8]. Kinetic roughening in $(d+1)$ dimensions, where d is the substrate dimension. The main purpose of this paper is to provide a guideline for the CVDP growth model study as well as some explanation of recent experimental data from the growth of polymer thin films in $(2+1)$ dimensions.

This paper is organized as follows: Section 2 describes the minimal toy model of CVDP growth in $d = 1, 2$ and define major physical quantities to investigate kinetic roughening and dynamic scaling. In section 3, updated numerical results are presented as well as the brief review of the earlier model studies in $(1+1)$ dimensions. Finally, the physical origin of anomalous scaling behaviors and multifractality is discussed, compared with the modification of the BD model in section 4 with closing remarks and outlook for $(2+1)$ dimensional CVDP growth in both model studies and experiments.

2. Model

A simple toy for CVDP thin film growth was first proposed by Bowie and Zhao [9] in a $(1+1)$ -dimensional lattice with L sites, where periodic boundary conditions are employed in a spatial direction, x . Later, the coalescence process of polymers was added to the original model in [10]. During the CVDP process, each monomer transports in the vacuum, which is very similar to the conventional PVD/MBE growth process for the metal/semiconductor thin film growth [1]. One big difference between two processes occurs in the nucleation and cluster/polymer propagation after the hot monomer is condensed either on the cold substrate or on the film surface. While in the PVD/MBE process each monomer is stable once it attaches to the nearest neighbors of any nucleated sites, so that the films get dense and compact as monomer diffusion increases, in the CVDP process it becomes stable only either when it reaches one of two active ends of a polymer chain or when it meets another monomer, so that the film gets rough as the monomer-diffusion rate increases since it occurs along polymer bodies. Moreover, surface diffusion, edge diffusion, step barrier effect are relevant to the PVD/MBE case, but intermolecular interaction and chain relaxation are more relevant to in the CVDP case besides monomer diffusion. Summing up major and minor differences, some distinct dynamic behaviors must exist in the CVDP film morphology.

Dynamic rules and updates

For simplicity, the chain relaxation of polymers is omitted and only the following five processes are taken as studied in [10] (see also Figure 1).

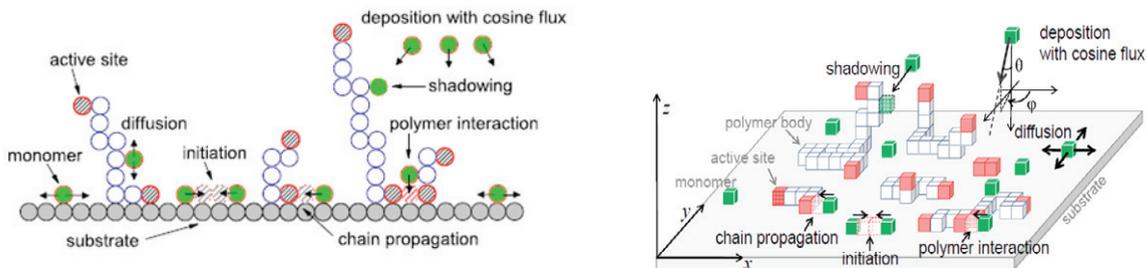


Figure 1: Five dynamic rules are illustrated as solid/green symbols (\circ in the left panel for $d = 1$ and \square in the right panel for $d = 2$) for monomers, open symbols with thin lines for polymer bodies, and patterned/red symbols with thick lines for active ends.

At each **deposition** step, a monomer is activated into the system with a random angle of incidence θ to the vertical direction from $\cos(\theta)$, not a collimated flux, which is called as a *cosine flux* [11] with the deposition rate F , the number of incident monomers per site for unit time. Before activated monomers are stabilized, an incident monomer deposited onto the polymer body sides or substrate randomly wanders from one site to another site along the polymer bodies or substrate with **diffusion** coefficient D , where D is the number of hops per monomer for unit time. The surface growth is controlled by the ratio of the diffusion coefficient to the deposition flux, $G = D/F$. Without loss of generality, $F = 1$ is set, such that $G = D$ from now on. When two monomers are met on substrate or polymer bodies, they form a dimer as a polymer seed (oligomer), called as **nucleation** (initiation). In contrast to the PVD/MBE growth where atoms can attach to the nearest neighbors of the nucleated sites, in the CVDP growth the stabilization reaction occurs only at the active ends of a polymer chain, so-called active sites. Such active bonding in the CVDP growth is a key ingredient as well as the cosine flux for monomer deposition. When a monomer reaches one of the active ends of a polymer, it is stabilized as part of the polymer and at the same time it becomes the active end of the polymer, called as **chain propagation**. In the process of the chain propagation, it is possible that an active end of polymer meets that of another polymer. Then two polymers are merged into one long polymer, namely **coalescence** (polymer interaction). It is noted here that, any polymer loop is not allowed. If one active end of a polymer meets the other side active end of itself, two active ends cannot merge into a stabilized polymer loop and such a try is rejected.

In order to determine the universality class of kinetic roughening, the following three physical quantities are defined and measured in the context of dynamic scaling with finite systems:

- Surface roughness (global):

$$W(L, t) \equiv \sqrt{\frac{1}{L} \sum_i^L [h(i, t) - \bar{h}(t)]^2} = L^{\alpha_g} f(t/L^{z_g}),$$

which is the root-mean-square (RMS) of height fluctuations with the global growth exponent, $\beta_g = \alpha_g/z_g$. Here $\bar{x} \equiv \frac{1}{y} \sum_{i=1}^y x(i)$.

- The q -th order moments of height-height correlation function (local) :

$$C_q(r, t : L) \equiv \frac{1}{L-r} \sum_{r=1}^{L-r} |h(i+r, t) - h(i, t)|^q = r^{q\alpha_l} g(t/L^{z_l}),$$

the local growth exponent, $\beta_l = \alpha_l/z_l$.

- RMS of step fluctuations:

$$M(L, t) \equiv \sqrt{\frac{1}{L-1} \sum_i^{L-1} [m(i, t) - \bar{m}(t)]^2} = L^\kappa s(t/L^z),$$

where $m(i) = h(i+1) - h(i)$ and the nonzero value of κ means $\alpha_g \neq \alpha_l$.

Table 1: Summary of roughness exponents and dynamic exponents for various G in (1+1) dimensions with the cosine flux. Note that the vertically collimated flux gives almost the same set of exponents as the ordinary BD model: $\alpha_g = \alpha_l = 0.5$, and $z_g = z_l = 1.5$.

G	α_g	α_l	z_g	z_l
10	0.89(1)	0.50(2)	1.27(1)	1.27(2)
10 ³	0.87(1)	0.47(2)	1.16(1)	1.27(2)
10 ⁵	0.72(1)	0.48(2)	0.81(1)	1.32(2)

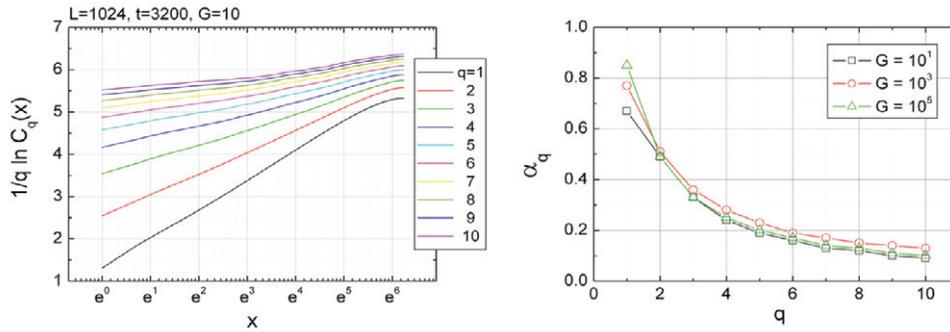


Figure 2: Multifractality is found in (1+1) dimensions, where $x = r$ (the distance between two sites) in the left panel.

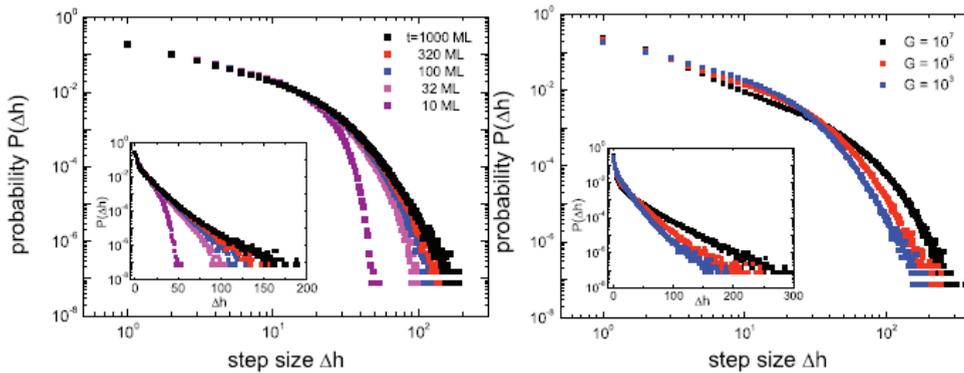


Figure 3: The distribution of steps in (2+1) dimensions is plotted as G varies, where $\Delta h = m$ (height difference between two consecutive sites).

3. Numerical results

The CVDP growth is numerically tested in terms of random sequential (continuous time) updating with the deposition probability of an incident monomer, $P_F = \frac{FL}{DN_m + FL}$, and the diffusion probability of an ad-monomer, $P_D = 1 - P_F = \frac{DN_m}{DN_m + FL}$, respectively. Here N_m is the number of ad-monomers and L is the system size. These probabilities can be also written by the ratio of monomer diffusion to deposition flux ($G = D/F$), and the ad-monomer density ($\rho_m = N_m/L$): $P_F = \frac{1}{G\rho_m + 1}$, and $P_D = \frac{G\rho_m}{G\rho_m + 1}$. The detailed procedure can be found in the earlier works [10, 12].

The surface width $W(L, t)$ in the CVDP growth as G varies shows clearly three regimes as L increases, initial growth, CVDP film growth, and saturation. Compared to the conventional surface growth, it exhibits anomalous dynamic scaling after about few monolayers (ML), irrespectively of system sizes. It also undergoes some unusual behavior before $W(L, t)$ saturates to W_{sat} due to the finite-size effect, which gives the hint of the global scaling behavior of CVDP film growth. To investigate its local scaling behavior, the two-point height difference correlation function is measured at $q = 2$, whose exponents are compared with those from the surface width. If $\alpha_g \neq \alpha_l$, the growth exhibits anomalous scaling behaviors, which requires some careful multi-affine/fractal analysis with a wide range of q values.

As G increases, the initial growth regime gets extended while at the real scaling regime by the CVDP growth, the effective growth exponent β becomes all the same as $\beta \approx 0.5 (\neq \alpha_g/z_g)$, irrespectively of the value of G . Until a polymer forms, the effect of the cosine flux is negligible and the monomer diffusion is dominant, explaining the first decay in the density profile. Some qualitative behaviors seem to be similar for all three cases of G , but its quantitative behavior quite depends on the value of G , see Table 1. It is noted that the growth exponent β is different from either α_g/z_g or α_l/z_l , which make data collapse somehow ugly (see [10]).

The argument that anomalous kinetic roughening in (1+1)-dimensional CVDP growth is attributable to the instability by the non-local shadowing effect related to active bonding in polymerization is proven by clear power-law step distributions in [10]. Such anomalies are also checked by the multi-affine/fractal analysis with the q -th moment of height-height correlation function (see Figure 2). This kind of interesting phenomena can be also found in the (1+1)-dimensional BD model with power-law noise [8], where the step distribution is also power-law, yielding $\kappa \neq 0$.

To explain recent experimental results by Lee and the co-workers [6, 14] for the growth of PPX-C films and its submonolayer regime behavior, the extended version of the model is considered as the modification of the earlier study by Zhao and his co-workers [15] in the sub-monolayer regime, where the multi-layer growth is allowed with the coalescence process of polymers, the (2+1)-dimensional model study becomes more realistic [16]. The preliminary results of dynamic scaling seems to be somewhat different from those in the (1+1)-dimensional model (see Figure 3: not power-law but exponential). However, it also exhibits anomalous scaling behavior in kinetic roughening with multifractality, similar to experimental results.

4. Remarks and outlook

In order to discuss the origin of the valley filling regime in experimental results, it might be necessary to consider some new dynamics, such as chain relaxations or flexibility, which was previous ignored. Polymer properties of CVDP growth would be another key to its universality class. The polymer interaction becomes relevant after polymers grow enough to be comparable with the typical length as shown in the (1+1)-dimensional version [10].

Based on the careful and detail analysis of (2+1)-dimensional model studies [16], it is found that dynamic scaling of the CVDP growth depends not only on what value is used for the ratio of monomer diffusion rate to deposition flux (G) but also on what kind of intrinsic and extrinsic noise exists by the non-local shadowing caused by the cosine flux.

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