Anomalous Surface Diffusion in Nanoscale Direct Deposition Processes

P. Manandhar,[1] J. Jang,[2] G. C. Schatz,[2] M. A. Ratner,[2] and S. Hong[1,*]
[1]*Physics, MARTECH, and IMB, Florida State University, Tallahassee, Florida 32306*
[2]*Department of Chemistry, Northwestern University, Evanston, Illinois 60208*
(Received 4 October 2002; published 19 March 2003)

We report the first observation of anomalous diffusion in nanometer scale direct deposition processes utilizing dip-pen nanolithography (DPN). DPN permits quite general nanostructure patterns to be drawn on flat surfaces. Here we demonstrate experimentally, and discuss theoretically, the situation in which the molecular ink in DPN binds weakly to the surface. We observe, for the weak-binding case of 1-dodecylamine on mica, that anomalous diffusion occurs, leading to nearly fractal deposition patterns.

DOI: 10.1103/PhysRevLett.90.115505 PACS numbers: 81.16.Nd, 68.35.Fx, 81.16.Dn, 81.16.Rf

Surface diffusion has been drawing attention due to its scientific and technological importance in thin film growth, nanoscale molecular patterning, and biological applications [1,2]. Although the invention of scanning probe microscopy has allowed us to image nanostructures, most surface diffusion research has relied on bulk self-organization processes on solid substrates. The development of dip-pen nanolithography (DPN) has opened up new possibilities by allowing us to deposit organic molecules onto desired nanoscale surface regions [3]. In the DPN process, one uses an AFM (atomic force microscopy) tip to deposit organic molecules onto a specific area, and then the diffusion process is directly observed. However, until now, diffusion studies utilizing DPN have been limited to normal diffusion cases [3–6]. Herein, we report the first observation of anomalous diffusion in nanoscale direct deposition processes utilizing DPN. Specifically, we present an example of anomalous diffusion phenomena, e.g., anisotropic pattern growth, which cannot be explained by a random walk model. The possible impact of anomalous diffusion in molecular patterning applications is also discussed.

Jang *et al.* presented a theoretical model explaining DPN as a three-step process (Fig. 1) [4]: (1) molecular deposition; (2) lateral diffusion on a monolayer of molecules; (3) termination of diffusion by chemical binding to a substrate. With the assumption of a constant deposition rate, which has been confirmed by several experiments, Jang *et al.* successfully described the patterns generated in DPN by a random walk simulation. Sheehan *et al.* subsequently extended the diffusion model to explain the deposition process [5]. Weeks *et al.* presented a model including the water meniscus at the AFM tip/substrate junction [6]. In previous literature, the diffusing organic molecules on substrates are assumed noninteracting, and therefore their behavior is described by a 2D Fickian diffusion model. The effect of intermolecular interaction in the diffusing molecules other than the excluded volume effect [4] has not been reported.

The DPN procedure in this manuscript is similar to the previous method of creating "dot" patterns [3–7]. In this procedure, the molecule-coated AFM tip is held at a fixed position in contact with the substrate so that molecules diffuse out onto the substrate, forming dot patterns whose sizes depend on the contact time (Fig. 2).

The following are novel features of our experiment. Unlike previous DPN experiments, we use molecules with weak binding on the substrate: 1-dodecylamine (DDA) on mica. In the case of strong surface binding, the results are dominated by surface binding events, and the details of lateral diffusion do not show up. From a practical point of view, the amine terminal groups of DDA can be utilized to chemically dope carbon nanotubes [8]. The results of 1-octadecanethiol (ODT) and 16-mercaptohexadecanoic acid (MHA) on Au are also presented as examples of strong binding cases. Both molecules chemically bind to Au surfaces using thiol groups [3–6]. Second, to minimize residual solvent effects, we utilized a vapor deposition method to coat DDA on the AFM tip. Here, 200 mg

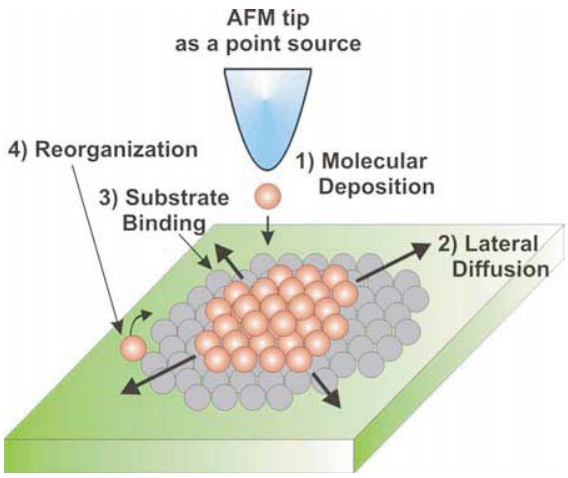

FIG. 1 (color online). DPN process with weak surface binding.

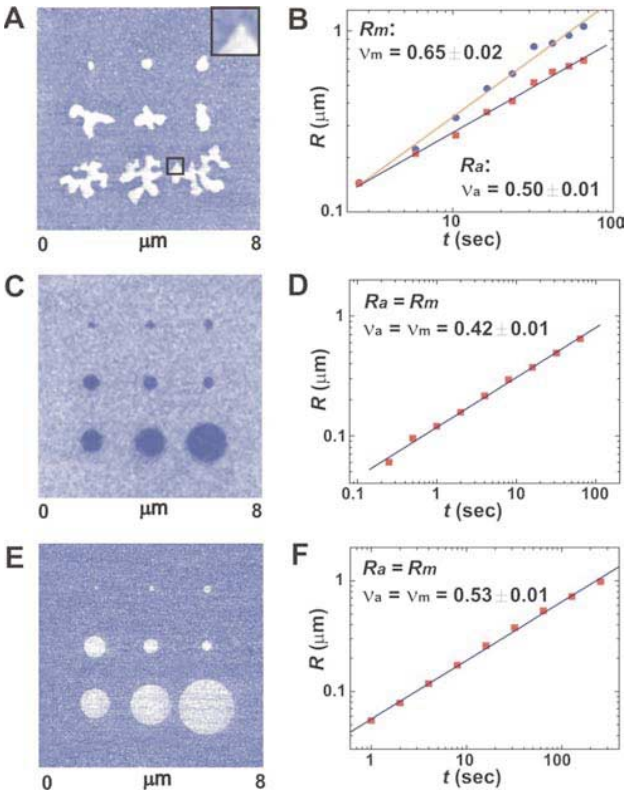

FIG. 2 (color online). Lateral force microscopy (LFM) images and scaling analysis of DDA on mica [(A) and (B)], ODT on Au [(C) and (D)], and MHA on Au [(E) and (F)]. The solid lines are least squares fits. The errors represent the statistical uncertainty of the fitting parameters.

of DDA is placed in a 15 ml tin can with an AFM tip, and the tin can is heated up to 60 °C for 20 min resulting in a thin DDA coating on the tip. When molecules are coated from solution, the coating usually contains residual solvent that may alter the diffusion properties. ODT is also coated via vapor deposition [3]. The results of MHA coated from 1 mM acetonitrile solution are presented for comparison. Finally, a stable molecular deposition rate is crucial for a scaling analysis. Ink depletion in the AFM tips can easily ruin the analysis. To minimize the effect, we repeated the same experiments twice. Whenever there was more than a 10% difference in pattern sizes in two successive experiments, the data were discarded.

Surprisingly, DDA shows anisotropic patterns that have not been observed in previous DPN experiments (Fig. 2). Repeated AFM imaging of DDA patterns does not change the shape of the patterns, implying that even though the binding of DDA to the mica surface is very weak the final DDA patterns are stable "solid" structures.

For analysis, we define two new parameters R_a and R_m for each dot pattern as follows: $R_a = (Area/\pi)^{0.5}$; $R_m = (maximum\ separation)/2$. The *area* of each pattern in the AFM images is measured to calculate R_a. R_m is measured from the maximum distance of molecules in the final patterns. In a short time period, R_a and R_m are found to be proportional to t^{ν}, where t is the tip contact time. ν_a and ν_m are obtained by fitting ($\log R$) vs ($\log t$) as plotted in Fig. 2.

ν_a represents the area growth rate of the patterns. Previous lattice imaging and etching experiments strongly suggest the uniform number density of molecules in DPN-generated dot patterns [3]. In this case, the area of the pattern is proportional to the number of deposited molecules, and ν_a represents the deposition rate of molecules. If DPN writing is stable, the deposition rate should be constant, resulting in $\nu_a \sim 0.5$. For an increasing or decreasing deposition rate, ν_a should be larger or smaller than 0.5, respectively. We find that DDA, ODT, and MHA show stable deposition rates with slight systematic variations. The increasing growth rate for MHA [$\nu_a = 0.53 \pm 0.01$ in Fig. 2(F)] is especially surprising. In the case of MHA, three consecutive data sets including a total of 27 patterns show similar values of ν_a (0.54, 0.52, and 0.53). One explanation for the MHA results is an increasing affinity of the MHA ink, which is presumably mixed with adsorbed water and residual solvent molecules, to the surface as the substrate is being covered by a hydrophilic monolayer of MHA. A similar effect has been observed in microscale pen and stamping experiments [9]. The MHA results suggest that, in addition to a simple random walk of molecules, it is necessary to include more complicated phenomena at the tip/surface junction such as the water meniscus to provide a general understanding of the DPN deposition process [6,10]. Another astonishing aspect is the constant deposition rate for DDA [$\nu_a \sim 0.5$ in Fig. 2(B)] even with its anisotropic patterns. This implies that the deposition step is relatively independent of the lateral diffusion process and, after proper considerations, one can achieve stable DPN writing even for weak-binding cases.

The circular patterns of ODT and MHA can be attributed to isotropic diffusion of the molecules followed by strong chemical binding onto the substrate [3,4]. If the molecules stop moving whenever they meet the bare substrate, the final pattern will be determined by the probability for molecules to reach the bare substrate. When the tip is an isotropic point source, the probability for each molecule to be captured on the bare substrate at a distance R from the AFM tip is isotropic, and it should be a decreasing function of R due to the increased time required to travel a longer distance. In this case, the final patterns are circular [4]. However, when the surface binding is weak, the final pattern is determined by interaction between the molecules, and it can be either circular or anisotropic. For DDA, this leads to an isotropic shape when the pattern is small, and then a more anisotropic pattern when it gets large [Fig. 2(A)]. Previously, Jang *et al.* demonstrated that the random walk of molecules followed by binding at the pattern edges does not result in

the fractal-like patterns seen for DDA [4]. Thus, the behavior for DDA can be called *anomalous*, as it cannot be explained by a simple random walk model.

To characterize the DDA patterns, we have defined a scaling parameter ν_D based on the function, $(Area) \sim (maximum\ separation)^{\nu_D}$. For example, filled circular patterns should have a ν_D of 2 because the maximum separation in a circle is its diameter. From the definitions of ν_a and ν_m, it follows that $\nu_D = 2\nu_a/\nu_m$. From the data in Fig. 2, we find that DDA growth shows ν_D of 1.53, while circular patterns of ODT and MHA on Au have ν_D of 2. ν_D can be a critical parameter to distinguish anomalous diffusion from normal diffusion. Even though we used freshly peeled mica surfaces, we also considered the possibility that the nonuniform patterns are due to randomly distributed surface defects that may hinder adhesion of the DDA molecules. However, nonuniform growth due to such surface defects should have a ν_D of 2: let us consider a nonuniform pattern that fills the circular area with a radius R. If the nonuniformity of the pattern is due to the randomly distributed surface defects which cover $x\%$ of the surface area, the total filled area A is $\pi R^2(1 - x/100)$. So, nonuniform patterns due to the surface defects should satisfy $A \sim R^2$ implying ν_D of 2. The analysis shows that not all anisotropic patterns represent anomalous diffusion, and the origin of DDA growth is not an effect from the substrate but instead reflects intermolecular interaction. This argument indicates that ν_D is an important parameter which allows us to identify anomalous diffusion.

One common model for the anomalous growth of bulk thin films is the *diffusion limited aggregation* (DLA) model, where particles diffuse towards a cluster (nucleation site) and are then captured when they hit it. The final pattern shows a fractal-like shape. Witten *et al.* have demonstrated that the density correlation function $C(r)$ of a finite size fractal follows a power law, $C(r) \sim r^{D-d}$, over distances from a few lattice spacings to the size of the cluster, where D and d are the fractal and Euclidean dimensions, respectively [11]. The values of D for the DLA models are 1.5 or 1.7 depending on the detailed assumptions used in the simulation [12,13]. Even though it is still not clear whether the DDA patterns have *self-similarity*, we can define another measure of pattern structure by explicitly calculating the density correlation function. In the AFM images, the density $\rho(\mathbf{r})$ is defined to be 1 for the molecule-filled pixels and 0 for others. The D is estimated by fitting $C(r)$ to the function, $C(r) \sim r^{D-d}$ with the Euclidean dimension $d = 2$ [11]. Applying this to large DDA patterns, we find a fractal dimension D of $\sim$1.5 [Fig. 3(A)]. This is almost identical to ν_D, and it is also close to that obtained for some DLA models [12]. However, the similarity with the DLA model needs to be viewed with caution as the underlying mechanism in the anomalous DPN process is, in fact, opposite to the DLA model. In the DPN process, new particles are initially placed only at the center of the cluster (nucleation site), and the particles travel on top of the cluster until they reach a binding site on the edge of the cluster. If the deposited particles in the DPN process behave in the same way as the particles in the DLA model, they are more likely to be captured before reaching the far end of the cluster, and the final pattern should be a filled circle as demonstrated by Jang *et al.* [4]. The fractal-like growth implies that the molecules deposited from the AFM tip tend to be captured at the far end of the patterns. This is a new situation that requires a direct deposition method such as DPN to be realized.

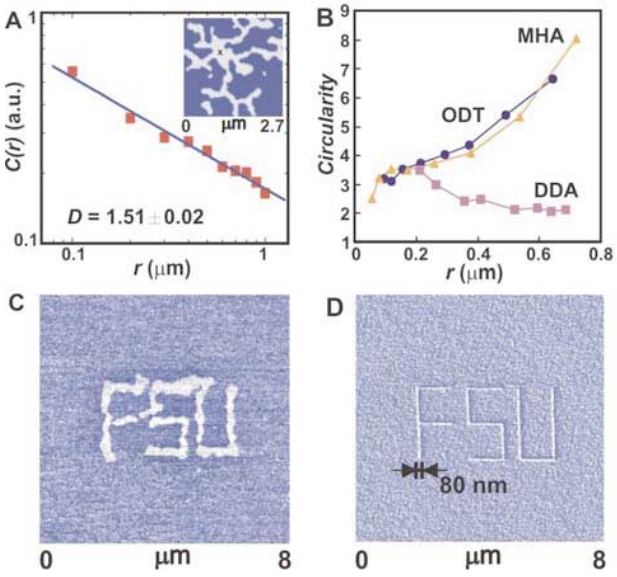

FIG. 3 (color online). (A) Density correlation function $C(r)$ for a large DDA pattern (inset) and the least square fit (solid line). The $C(r)$ scales as $C(r) \sim r^{-0.49\pm0.02}$ resulting in the fractal dimension D of $\sim$1.51. The position of the AFM tip during the DPN process is marked by "x" in the LFM picture. (B) Circularity measured from the results in Fig. 2. (C) DPN-generated DDA patterns showing anomalous diffusion effect. To generate the patterns, the molecule-coated AFM tip was moved along the line with a constant speed of $\sim$0.1 μm/s. (D) The normal diffusion case of MHA on Au (writing speed $\sim$0.2 μm/s).

One plausible explanation for the observed anomalous diffusion is rapid crystalline growth of DDA molecules on the mica surface. DDA is known to form high quality crystalline structures on mica [14]. Thus, when the pattern size is small (encompassing a small number of crystalline domains), the pattern remains more circular because of the isotropic velocity distribution of molecules coming from the AFM tip. When the pattern gets much larger than the domain size, then the diffusing molecules can sprout new crystalline domains at the edges of old domains, largely at random, leading to irregular patterns. Indeed, sharp triangular facets are often evident in the large patterns [inset of Fig. 2(A)]. The directions of the sides of the facets are not all identical, implying that

the pattern is divided into multiple domains with random directions. We can also observe small crystalline facets in the small patterns although it does not appear as clearly as in the large patterns because of the small dimensions and isotropic shapes of small scale patterns. Similar anomalous diffusion due to pattern growth in the preferred crystalline directions has been reported in bulk thin film growth [1]. In the supporting materials, we show that ODT deposition on mica results in $\nu_D \sim 2$ even with irregular pattern shapes, indicating that weak binding does not necessarily give anomalous diffusion [14].

One parameter of practical importance is the circularity $N \cong 1.3869(\mu_R/\sigma_R)^{0.4721}$, where μ_R and σ_R are the average radius and standard deviation, respectively, of edge points of the patterns [15]. We utilized AFM images in Fig. 2, and the edge points were detected by finding the pixels with 2 or 3 nearest pixels filled with molecules. Jang *et al.* demonstrated that normal diffusion should show increasing circularity with increasing radius of patterns [4] as we find for ODT and MHA [Fig. 3(B)]. However, DDA shows decreasing circularity which is another characteristic feature associated with anomalous diffusion. Even with anomalous diffusion, we can generate desired nanoscale patterns reliably [Fig. 3(C)]. However, the effect of anomalous diffusion is clearly visible in the final results. The pattern produced via normal diffusion is also presented for comparison [Fig. 3(D)]. The tool set in this manuscript allows one not only to characterize anomalous diffusion processes but also to find a solution for practical applications. For example, the circularity results of DDA deposition indicate that the effect of anomalous pattern growth becomes significant for large size patterns where the DDA molecules have to travel larger distances on the surface. One obvious solution is minimizing surface diffusion during pattern generation. In other words, to generate large size patterns, one should opt for moving the AFM tip to fill the area, rather than relying on the diffusion of DDA molecules on the surface.

In summary, we have presented the first systematic study of anomalous diffusion in nanoscale deposition processes. The experimental and analysis tools in the manuscript can be utilized to study general diffusion processes for organic molecules on solid surfaces. From a practical point of view, this result demonstrates that, after proper considerations, nanoscale direct deposition methods can be utilized to generate organic molecular patterns for very weak-binding cases. Weak binding is likely to be a common deposition motif, and it may already play an important role in the chemical doping of carbon nanotubes and biomolecules on inert surfaces. In addition, the development of nanoscale deposition methods raises a set of new scientific questions. What is the phase of the diffusing molecules? Do the patterns generated via nanoscale deposition have self-similar fractal properties as bulk thin films? If so, what are the dimension and mechanism? These are the issues we can address in the future utilizing the methods in the manuscript.

This project is supported by the AFOSR and NASA. Support for P. M. has been provided by the MARTECH at Florida State University. Support at Northwestern comes from the NSF Nanoscale Science and Engineering Center.

*To whom correspondence should be addressed.
Electronic address: shong@martech.fsu.edu

[1] T. Michely *et al.*, Phys. Rev. Lett. **70**, 3943 (1993); S. M. Oh *et al.*, Phys. Rev. Lett. **88**, 236102 (2002).
[2] E. Delamarche *et al.*, J. Phys. Chem. B **102**, 3324 (1998); M. Jaschke and H. J. Butt, Langmuir **11**, 1061 (1995); S. Xu, P. E. Laibinis, and G. Y. Liu, J. Am. Chem. Soc. **120**, 9356 (1998); V. Schmitt and F. Lequeux, Langmuir **14**, 283 (1998).
[3] R. Piner *et al.*, Science **283**, 661 (1999); S. Hong *et al.*, Science **286**, 523 (1999); D. Weinberger *et al.*, Adv. Mater. **12**, 1600 (2000); D. L. Wilson *et al.*, Proc. Natl. Acad. Sci. U.S.A. **98**, 13660 (2001); M. Zhang *et al.*, Nanotechnology **13**, 212 (2002); S. Rozhok *et al.*, J. Phys. Chem. B **107**, 751 (2003).
[4] J. Jang *et al.*, J. Chem. Phys. **115**, 2721 (2001).
[5] P. E. Sheehan and L. J. Whitman, Phys. Rev. Lett. **88**, 156104 (2002).
[6] B. L. Weeks *et al.*, Phys. Rev. Lett. **88**, 255505 (2002).
[7] The CP AFM (Digital Instruments) equipped with a close loop scanner and the DPN software (NanoInk) is placed in the glove box for the humidity control. The temperature is controlled by the resistive heaters attached on the AFM tip (Microlevel A, Digital Instruments) and sample holders. The humidity and temperature for the experiments are 55% and 29 °C, respectively.
[8] C. W. Zhou *et al.*, Science **290**, 1552 (2000).
[9] H. A. Biebuyck and G. M. Whitesides, Langmuir **10**, 4581 (1994); Y. Xia and G. M. Whitesides, J. Am. Chem. Soc. **117**, 3274 (1995).
[10] J. Jang, G. C. Schatz, and M. A. Ratner, J. Chem. Phys. **116**, 3875 (2002).
[11] T. A. Witten, Jr. and L. M. Sander, Phys. Rev. Lett. **47**, 1400 (1981).
[12] P. Meakin, Phys. Rev. Lett. **51**, 1119 (1983).
[13] P. Meakin, Phys. Rev. A **27**, 1495 (1983).
[14] See EPAPS Document No. E-PRLTAO-90-004309 for AFM microscopy images of bulk deposited 1-dodecylamine crystalline film and DPN-generated ODT patterns on mica surfaces. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.
[15] R. M. Haralick, IEEE Trans. Syst. Man. Cybern. **4**, 394 (1974).