Random Walk Model for the Growth of Monolayer in Dip Pen Nanolithography

H. Kim, S. Ha, and J. Jang
Department of Nanomaterials Engineering, Pusan National University, Miryang 627-706, Republic of Korea

E-mail: jkjang@pusan.ac.kr

Abstract. By using a simple random-walk model, we simulate the growth of a self-assembled monolayer (SAM) pattern generated in dip pen nanolithography (DPN). In this model, the SAM pattern grows mainly via the serial pushing of molecules deposited from the tip. We examine various SAM patterns, such as lines, crosses, and letters by changing the tip scan speed.

1. Introduction

Dip-pen nanolithography (DPN) emerged as a general tool to fabricate nanopatterns on various substrates, including metallic, insulating, and semiconducting substrates [1-3]. In DPN, an atomic force microscope (AFM) tip functions as a source for continuously creating nanodroplets of molecules that subsequently spread to form a self-assembled monolayer (SAM) on a substrate. The molecular transport from the tip to the substrate is mediated by the water meniscus which naturally forms between the tip and substrate under ambient conditions [4-6].

Little is known about the molecular mechanism and time scale of the SAM growth in DPN. In this respect, theory and modelling have proven to be useful [4, 7-10]. Given molecules are designed to chemisorb to the substrate, Jang et al.[8] proposed a diffusion model of DPN by assuming that molecules are irreversibly trapped once they reach the chemisorbing sites on the substrate. Molecules can diffuse on top of other molecules. This model fails to reproduce the dendritic SAM patterns observed in DPN using dodecylamine [11] or polyethylene glycol [12] on mica. Molecular dynamics (MD) simulation [7] showed that a SAM pattern mainly grows via the serial pushing mechanism (Figure 1a) in which a molecule in the upper layer (open circle in the second layer in the figure) pushes a molecule on the substrate out of its original position, and the molecule pushed out in turn pushes out another molecule nearby. Such a consecutive push propagates and reaches the periphery, and then the pushing stops. This serial pushing was taken to have a finite directional coherence length, $N_d$, defined as the number of consecutive pushing events which has the same direction (see Figure 1b). By simply varying $N_d$, this model can reproduce various SAM patterns, ranging from an isotropic to a dendritic pattern. The serial pushing model also captured the essential features of an MD simulation [10]. Previously, the serial pushing model was applied for the case where an AFM tip is fixed in position. However, the SAM patterns in DPN are generally made by moving the tip on a substrate. Then, the outcome of DPN depends on the moving speed of tip. Herein, we simulate various

To whom any correspondence should be addressed.
line-based SAM patterns and study how DPN is affected by the tip scan speed and the directional coherence length.

**Figure 1.** (a) Serial pushing model. A molecule (an open circle in the second layer) pushes the molecule below it (one of the open circles in the first layer), and the molecule pushed out in turn pushes its neighbor out of place. This pushing propagates (drawn as left arrows) toward the periphery of the monolayer until there is no molecule left to push out. (b) Schematic diagram for serial pushing events with the directional coherence length \( N_d \) of 3. The serial pushing changes its direction after every 3 consecutive pushing events.

2. Details of Model and Simulation

Random walk simulations are performed by using a three dimensional lattice and a discrete time step. The three dimensional lattice was constructed by vertically stacking two dimensional trigonal lattices. The lattice spacing of the trigonal lattice is identified as the distance between the nearest neighbor molecules in the SAM of octadecanethiol on a gold surface, \( l = 0.5385 \text{ nm} \) [7, 10]. Every molecule belonging to of the layers above the substrate executes a three dimensional random walk. If a random walk of such a molecule happens to be at the position of a molecule below it, this random walk is taken to push the molecule below out of place. Then the molecule pushed out in turn pushes its neighbor out of place. This push-induced movement laterally propagates toward the periphery until there are no molecules left to push out. This sequence of push-induced movements occurs without time delay. Unlike the molecules in the upper layers, a molecule on the bare surface is allowed to move only if it is pushed by one of its nearest neighbors, above or beside it.

If a molecule initially pushes out its neighboring molecule, the subsequent \((N_d - 1)\) movements take the same direction as the initial pushing direction. The direction of the \((N_d + 1)\) th molecular displacement becomes random, and then, the subsequent \((N_d - 1)\) movements are taken to occur in the same direction as the \((N_d + 1)\) th displacement. This series of push-induced movements continues until it stops at the periphery (where there are no molecules left to push out).

The time step of simulation \( \Delta t \) is set by following Jang et al [8]. Theory of diffusion shows \( \Delta t \) and \( l \) satisfy \( 4D\Delta t = l^2 \), where \( D \) is the diffusion constant of molecule. Here, estimating the value of \( D \) is rather tricky as \( D \) refers to the molecular diffusion on top of other molecules (not the surface diffusion on a bare surface). Previously, \( D \) was estimated for eicosanethiol in the context of the microcontact printing, as \( D = 7 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} \) [13]. Using this value of \( D \), we get \( \Delta t = 10.4 \text{ ns} \).

In the present work, the tip scan speed \( v \) is reported in terms of a dimensionless value, \( v^* \), defined as \( v^* = v/(l/\Delta t) \). For a slow tip scan speed, \( v^* < 1 \), the tip moves by \( l \) for every \( 1/v^* \) time steps. If
the displaced tip is not exactly at one of the lattice points, the tip position is taken to be at the lattice point nearest to the tip position. We consider three tip scan speeds, \( v^* = 0.25, 0.5, \) and 1.

Another parameter needed for the present simulation is the dripping rate of molecules from the tip, \( n^* \). Here, the dripping rate is reported in terms of a reduced rate, \( n^* = n \Delta t \), which represents the number of molecules dropped per simulation time step. Throughout the present work, \( n^* \) is fixed to be 5.

### 3. Results and Discussion

We first examine how the SAM patterns are affected by varying the directional coherence length of serial pushing. In Figure 2, we show cross patterns generated by using a tip scan speed \( v^* \) of 0.25. The horizontal line is drawn first and the vertical line next. As \( N_d \) varies as 0 (a), 10 (b), 20 (c), and 30 (d), the periphery of the cross SAM pattern becomes more rugged. Compared to the case where the tip is fixed in position, the effects of changing \( N_d \) are small. A dendritic pattern with self-replicating branches was found for high values of \( N_d \) in the case of a fixed tip. However, we did not find any dendritic pattern for a moving tip.

![Figure 2. Cross SAM patterns generated by scanning a tip. The \( N_d \) of serial pushing is varied as 0 (a), 10 (b), 20 (c), and 30 (d). The tip scan speed \( v^* \) and the molecular dripping rate \( n^* \) are fixed to be 0.25 and 5, respectively.](image)

We move on to study the effects of tip scan speed on the SAM patterns. By varying \( v^* \) as (a) 0.25, (b) 0.5, and 1 (c), we inspect the SAM line pattern (Figure 3). \( N_d \) is fixed to be 30 for all the cases. As the tip scans faster, the width of SAM line becomes narrow. Note also the SAM line pattern gets rougher in its periphery as the tip scans slower, even though the same \( N_d \) value was used for all the cases in Figure 3.

![Figure 3. The SAM lines patterned by using the tip scan speeds \( v^* \)s of 0.25 (a), 0.5 (b), and 1 (c). The directional coherence length (\( N_d \)) and the molecular dripping rate \( n^* \) are 30 and 5, respectively.](image)

### 4. Conclusion

The growth of a SAM pattern in dip-pen nanolithography was simulated by using a simple random walk model. In this model, a SAM pattern primarily grows via the serial pushing of molecules initiated
by molecules dropping from an AFM tip (source). This serial pushing is taken to have a finite length for its direction called directional coherence length. To model various SAM patterns made of lines, we have implemented the movement of tip in the present simulation. For these line-based SAM patterns, the tip scan speed plays a major role in determining the outcome of DPN. As the tip scan speed increases, the SAM patterns become narrower and less rugged in their peripheries. The effect of directional coherence length is relatively small compared to the case of a tip fixed in position.

References

[1] Piner R D, Zhu J, Xu F, Hong S and Mirkin C A 1999 "Dip-Pen" Nanolithography Science 283 661-3
[2] Mirkin C A 2007 The Power of the Pen: Development of Massively Parallel Dip-Pen Nanolithography ACS Nano 1 79-83
[3] Salaita K, Wang Y and Mirkin C A 2007 Applications of dip-pen nanolithography Nat Nano 2 145-55
[4] Kim H, Saha L C, Saha J K and Jang J 2010 Molecular simulation of the water meniscus in dip-pen nanolithography Scanning 32 2-8
[5] Rozhok S, Piner R and Mirkin C A 2002 Dip-Pen Nanolithography: What Controls Ink Transport? The Journal of Physical Chemistry B 107 751-7
[6] Giam L R, Wang Y and Mirkin C A 2009 Nanoscale Molecular Transport: The Case of Dip-Pen Nanolithography† The Journal of Physical Chemistry A 113 3779-82
[7] Heo D M, Yang M, Kim H, Saha L C and Jang J 2009 Tip Dependence of the Self-Assembly in Dip-Pen Nanolithography J. Phys. Chem. C 113 13813-8
[8] Jang J, Hong S, Schatz G C and Ratner M A 2001 Self-assembly of ink molecules in dip-pen nanolithography: A diffusion model J. Chem. Phys. 115 2721-9
[9] Kim H and Jang J 2009 Serial Pushing Model for the Self-Assembly in Dip-Pen Nanolithography J. Phys. Chem. A 113 4313-9
[10] Kim H, Schatz G C and Jang J 2010 Simplistic Model for the Dendritic Growth of a Monolayer in Dip Pen Nanolithography J. Phys. Chem. C 114 1922-7
[11] Manandhar P, Jang J, Schatz G C, Ratner M A and Hong S 2003 Anomalous Surface Diffusion in Nanoscale Direct Deposition Processes Physical Review Letters 90 115505
[12] Rivas-Cardona J A and Banerjee D 2007 Microfluidic device for delivery of multiple inks for dip pen nanolithography Journal of Micro/Nanolithography, MEMS, and MOEMS 6 033004
[13] Delamarche E, Schmid H, Bietsch A, Larsen N B, Rothuizen H, Michel B and Biebuyck H 1998 Transport Mechanisms of Alkanethiols during Microcontact Printing on Gold The Journal of Physical Chemistry B 102 3324-34

Acknowledgments

This study was supported by National Research Foundation Grants funded by the Korean Government (MEST) (No. 2011-0027445 and No. 2011-0027696). J.J. wishes to thank the Korea Institute of Science and Technology Information for the use of the PLSI supercomputing resources.