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Dip Pen Nanolithography is a direct write process that creates nanoscale dots and lines. Models typically predict dot and line size via assumption of constant ink flow rate from tip to substrate. This is appropriate for dot writing. It is however well-known, though models rarely reflect, that the ink flow rate depends upon writing speed during line writing. Herein, we explain the physical phenomenon that governs line writing and use this to model tip-substrate diffusion in line writing. We accurately predict (i) the increase in flow rate with writing speed and (ii) line width within 12.5%. © *2010 American Institute of Physics*. [doi:10.1063/1.3454777]

Dip Pen Nanolithography[1–3] (DPN) is a nanofabrication process in which an "inked" tip is used to deliver ink molecules directly on to a substrate, thereby producing nanometer-scale features that are comprised of self-assembled monolayers (SAMs). A schematic of the DPN line writing process is shown in Fig. 1(a). When the tip is brought into contact with the substrate, a water meniscus forms and ink molecules diffuse from the tip onto the substrate surface. A stationary tip makes dots and a moving tip writes lines.

Ink transport is modeled as surface diffusion with the tip acting as an infinite ink reservoir and molecules treated as "trapped" when they encounter the substrate.[4–6] Thus, ink transport consists of diffusion of ink molecules over the pre-existing SAM and formation of an immobile SAM at the edge of the pre-existing layer. A salient point of this paper is that line writing models incorrectly use ink transfer rate information obtained from dot writing experiments. Our purpose here is to explain the difference in driving physical phenomena for dot and line writing and to incorporate the pertinent physics into a model that is unique to line writing. We show that (a) ink flow rate should increase with the tip velocity for a constant concentration source tip and (b) this approach predicts experimental results.

Experiments have shown that ink flow rate in a dot writing process is near-constant and independent of writing time.[4] As such, dot size and flow rate may be predicted by a one-time measurement of dot size for a given ink-substrate combination. Ink flow rate in a line writing process depends upon the (a) parameters that are important in dot writing[7,8] and (b) magnitude of the tip velocity. The effect of the later has a significant impact on line width. Its effect is not captured in dot-based models/experiments. As such, the methods and diffusion rates associated with dot models/experiments are not appropriate for use when predicting diffusion rates in line writing.

Specifically, the difference in line writing diffusion is that free substrate sites are continuously exposed as the tip moves forward. This leads to (i) an ink flow rate that is larger than exhibited in dot writing and (ii) demand for ink flow that changes as tip velocity changes. It is not appropriate to use a constant flow rate assumption (dot writing) in modeling variable flow rate problems (line writing).

The effect of the preceding, not the reasoning, is well known. Line width is not accurately predicted using a constant flow rate approach.[9,10] Accurate width prediction is obtained via polynomial fits of data[11] that function as an arbitrary "fix" that adjusts an incorrect approach to match relevant physics. DPN line writing is fundamentally a two-dimensional (2D) moving boundary diffusion problem, where the source (tip) and sink (edge of SAM) move with time. In the following, we show that line writing, and predictions of line width versus velocity, must be modeled as 2D surface diffusion from a moving, constant concentration source.

Consider an "inked" tip moving on the substrate surface with constant velocity, $\boldsymbol{V}$, parallel to the surface. We model the diffusion as concentration driven, 2D Fickian diffusion, from the tip to the line-edge boundary as follows:

$$\frac{\partial^2 C(x,y,t)}{\partial x^2} + \frac{\partial^2 C(x,y,t)}{\partial y^2} = \frac{1}{D_s}\frac{\partial C(x,y,t)}{\partial t}. \quad (1)$$

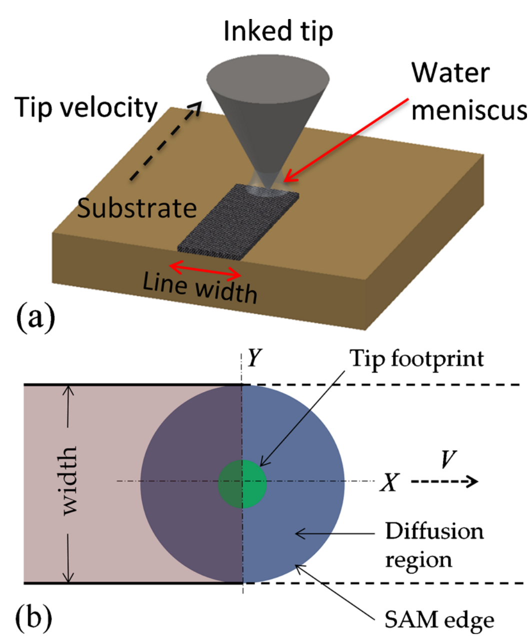

FIG. 1. (Color online) Schematic of DPN line writing. (a) A line is generated when ink deposits from a moving tip onto a substrate. (b) Top view of the substrate with the regions of ink diffusion where the (i) inner circle represents the tip footprint which has a constant ink concentration and (ii) outer circle is the edge of the SAM.

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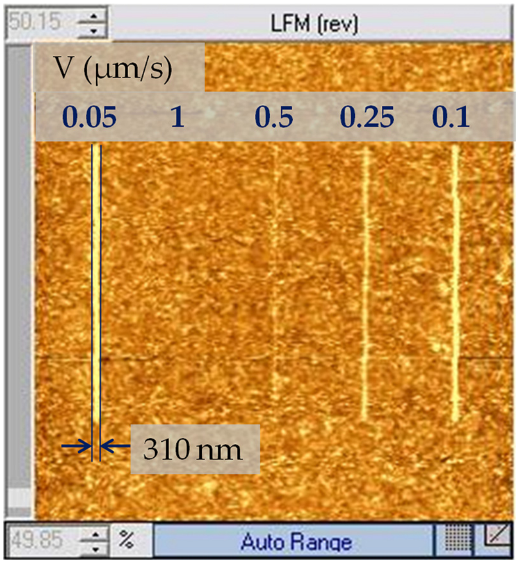

FIG. 2. (Color online) Lateral force microscopy scan of the lines written at a temperature of 23.5 °C and relative humidity of 30%. No line was observed at 1 μm/s indicating that the cut-off velocity was exceeded.

In Eq. (1), C is the surface ink concentration on the SAM layer, D_s is the ink diffusivity on the SAM and $\boldsymbol{V}$ is the tip velocity parallel to the x direction. The boundary conditions are as follows: (i) a constant, finite ink concentration at the tip, (ii) zero ink concentration at the SAM edge, and (iii) a mass balance at the SAM edge that is used to determine the rate of boundary growth.

We define the coordinate system, (ζ,η), that is centered at the moving tip. Coordinate transformations are obtained via $\zeta = x\text{-}Vt$ and $\eta = y$. Equation (1) may be rewritten as follows:

$$\frac{\partial^2 C(\zeta,\eta,t)}{\partial\zeta^2} + \frac{\partial^2 C(\zeta,\eta,t)}{\partial\eta^2} = -\frac{V}{D_s}\frac{\partial C(\zeta,\eta,t)}{\partial\zeta} + \frac{1}{D_s}\frac{\partial C(\zeta,\eta,t)}{\partial t}. \tag{2}$$

In practice, line writing is quasi-static when line width is uniform along the length of the line. Therefore, it is appropriate to neglect the time dependence term from Eq. (2). We nondimensionalize length variables via line width w, i.e., $X = \zeta/w$ and $Y = \eta/w$. Equation (2) then becomes as follows:

$$\frac{\partial^2 C(X,Y)}{\partial X^2} + \frac{\partial^2 C(X,Y)}{\partial Y^2} = -\frac{Vw}{D_s}\frac{\partial C(X,Y)}{\partial X}. \tag{3}$$

The relative scaling of the terms in Eq. (3) may be used to ascertain which are of practical import in line writing. The scale of Vw/D_s may be estimated from values used in typical DPN systems as follows: $w \sim 100$ nm, $V \sim 1$ μm/s, and $D_s \sim 10^{-9}$ m^2/s.[12] This yields the following:

$$\frac{Vw}{D_s} \sim 10^{-4} \ll 1.$$

Given $Vw/D_s \ll 1$, the RHS of Eq. (3) may be assumed small enough to be of little practical consequence. This is physically equivalent to assuming that mass convection due to tip motion has little impact upon the overall diffusion. Diffusion is therefore approximately described by the following:

$$\frac{\partial^2 C}{\partial X^2} + \frac{\partial^2 C}{\partial Y^2} = 0. \tag{4}$$

This equation essentially means that *for a given tip velocity*, the ink diffusion from a slow moving tip is the same as that from a stationary tip when viewed from the tip frame. When tip velocity changes, the diffusion rates will change, but the quasistatic transport of ink resembles dot writing when viewed in the tip's coordinate system. When an axisymmetric boundary condition is applied at the tip, Eq. (4) may be stated in cylindrical coordinates as follows:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C(r)}{\partial r}\right) = 0, \tag{5}$$

with $r^2 = \zeta^2 + \eta^2 = (x - Vt)^2 + y^2$ and following boundary conditions:

$$C = C_0 \ @ \ r = R,$$

$$C = 0 \ @ \ r = S.$$

Here S is the edge of the SAM and R is the tip footprint radius ($S > R$). A physical representation of the diffusion model is shown in Fig. 1(b). Diffusion of ink molecules from the moving tip of radius "R" leads to the formation of a "diffusion circle" of radius "S." As the circle moves with the tip, the line is generated on the substrate as the locus of this moving circle.

We solve Eq. (5) using the preceding boundary conditions as follows:

$$C = -C_0\frac{\ln(r/S)}{\ln(S/R)}. \tag{6}$$

The ink diffusion rate, J, from the tip is defined as follows:

$$J = -\left(2\pi r D_s \frac{\partial C}{\partial r}\right)\Big|_{r=R}. \tag{7}$$

Therefore, using Eqs. (6) and (7) as follows:

$$J = \frac{2\pi D_s C_0}{\ln(S/R)}. \tag{8}$$

As $y = (1/2)w$ at $\zeta = 0$ and $S^2 = \zeta^2 + y^2$, we know that $w = 2S$ and the rate of diffusion is as follows:

$$J = \frac{2\pi D_s C_0}{\ln(w/2R)}. \tag{9}$$

Although the SAM grows, when $\boldsymbol{V}$ is constant the size of the "diffusion circle" must be same at all tip positions along the line, and therefore constant with respect to the transformed coordinate system. This is expected as a time dependent "S" implies a time dependent flux from the tip, which is not possible in quasi-static line writing.

A first link between $\boldsymbol{V}$ and w is provided via mass conservation as follows:

$$\rho V w = J + 2\rho V R. \tag{10}$$

In Eq. (10) ρ is density of ink molecules in the ordered SAM structure, J is the ink flow rate that is solely due to diffusion, and the second term on RHS is the contribution due to direct ink deposition within the tip footprint. Thus, Eq. (10) represents the total ink flow rate to the line. By

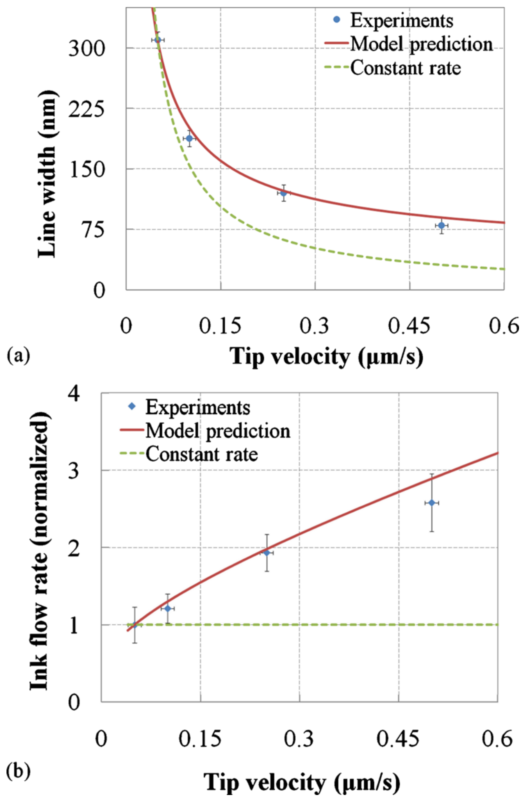

FIG. 3. (Color online) Comparison of model prediction to DPN experiments. (a) Line width vs tip velocity. (b) Total ink flow rate vs tip velocity. Experimental data points in the form $[V(\mu\mathrm{m/s})\ w(\mathrm{nm})]$ are as follows: [0.05 310], [0.1 188], [0.25 120], and [0.5 80]. Tip footprint radius R is 15 nm.

using Eqs. (9) and (10), we obtain a form that is useful in linking the controlling process parameters and material-specific constants as follows:

$$(w-2R)\ln\frac{w}{2R}=\frac{2\pi D_s C_0}{\rho V}. \quad (11)$$

16-mercaptohexadecanoic acid (MHA) ink and gold substrate [Au(111)] were used in a set of experiments that we compare to the results of Eq. (11). A lateral force microscopy scan of the written lines is shown in Fig. 2. For a full predictive capability, it is necessary to know the ink concentration at the tip. This cannot be measured; therefore it was inferred by comparing Eq. (11) to one data point. As the sensitivity of width to concentration $(\partial w/\partial C_0)$ drops with increase in tip velocity, the inferred concentration value is least sensitive to width measurement errors at low velocity $(V=0.05\ \mu\mathrm{m/s})$.

By inspecting Fig. 3(a), we see that line width decreases with increase in tip velocity. This trend had previously been interpreted as the consequence of constant ink flow rate. The total ink flow rate may be estimated from the line width and tip velocity via Eq. (10). From the experimental data in Fig. 3(b) it is clear that the ink flow rate must increase with tip velocity. When a constant flow rate approximation is used, Fig. 3(a) shows that estimated width is smaller than measured values; up to three times smaller at high tip velocities. Our model predicts the increase in flow rate with tip velocity and the line width with less than 12.5% error.

A likely source of the 12.5% error at high tip velocity is the assumption that the tip concentration is independent of tip velocity. During meniscus-mediated ink transport in DPN, the inked tip surface is not in direct contact with the substrate. Instead, ink dissolution at the tip-meniscus interface and transport across the meniscus adds extra resistance to ink transport. Therefore, the effective ink concentration at the substrate should decrease with ink flow rate, thereby pulling down the model prediction curves (Fig. 3) toward the experiments at high writing speeds. Thus, the next step for accurate feature size predictions is to link the line width to directly controlled parameters, such as amount of ink on the tip, by incorporating the ink dissolution,[10,13] and meniscus transport steps in the transport model.

In summary, the nature of surface diffusion in DPN line writing is fundamentally different from that in dot writing. As the tip moves, it is exposed to SAM free surface, thereby enabling faster diffusion at higher tip velocities. The constant flow rate approximation works well when predicting dot writing characteristics but is not appropriate for predicting the width of lines. Our model provides insight into the relationship between line width and tip velocity. The model width prediction matches within 12.5% of the measured values and shows the trend of increase in flow rate with tip velocity. This is an important first step in moving beyond empirical modeling and toward predictive modeling of DPN; which is essential if DPN is to be implemented in large-scale nano-manufacturing systems.[14,15]

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