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Characterization of the Dip Pen Nanolithography Process for Nanomanufacturing

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Dip pen nanolithography (DPN) is a flexible nanofabrication process for creating 2-D nanoscale features on a surface using an “inked” tip. Although a variety of ink-surface combinations can be used for creating 2-D nanofeatures using DPN, the process has not yet been characterized for high throughput and high quality manufacturing. Therefore, at present it is not possible to (i) predict whether fabricating a part is feasible within the constraints of the desired rate and quality and (ii) select/design equipment appropriate for the desired manufacturing goals. Herein, we have quantified the processing rate, tool life, and feature quality for DPN line writing by linking these manufacturing metrics to the process/system parameters. Based on this characterization, we found that (i) due to theoretical and practical constraints of current technology, the processing rate cannot be increased beyond about 20 times the typical rate of $\sim 1 \mu\text{m}^2/\text{min}$, (ii) tool life for accurate line writing is limited to 1–5 min, and (iii) sensitivity of line width to process parameters decreases with an increase in the writing speed. Thus, we conclude that for a high throughput and high quality system, we need (i) parallelization or process modification to improve throughput and (ii) accurate fixtures for rapid tool change. We also conclude that process control at high speed writing is less stringent than at low speed writing, thereby suggesting that DPN has a niche in high speed writing of narrow lines. [DOI: 10.1115/1.4004406]

Keywords: process limits, high throughput DPN, DPN tool life, DPN niche, process driven system design

1 Introduction

Tip based processes are a set of fabrication techniques that allow for transfer of mass or energy from a tip to a substrate surface with nanoscale resolution [1]. These processes enable the fabrication of a variety of nanoscale features with microscopy instruments such as an atomic force microscope or a scanning tunneling microscope. Several of these nano-enabled products have been shown to have widespread potential applications in the fields of biomedical diagnostics, sensing, and electronics [1,2]. High throughput and high quality manufacturing of the nanofeatures is a necessity for such applications. However, a lack of sufficient predictive process knowledge and appropriate manufacturing equipment makes it difficult to successfully scale-up these processes from the research laboratory to full scale manufacturing. Herein, we use dip pen nanolithography (DPN) as a case study to demonstrate (i) how a tip based process can be characterized for nanomanufacturing and (ii) how this process characterization can be used to identify the parameters for selecting/designing a system appropriate for high throughput and high quality manufacturing.

DPN is a tip based process that is used for transferring “ink” molecules directly from the tip on to a surface [3,4]. A schematic of the process is shown in Fig. 1. Ink molecules are transported via mass diffusion from the tip on to the surface. Features are formed on the surface via either chemisorption based self assembly or physisorption. Ink transport is mediated by the presence of the water meniscus that forms when the tip is brought in close proximity of the surface. The direct write mechanism of DPN makes it possible to use a variety of different ink-surface combinations. Alkanethiol ink and gold surface are among the most commonly

used ink-surface combinations for DPN. Many other combinations have also been successfully demonstrated; for example, silazane ink on semiconductor surfaces [5], gold particles on silicon surface [6], and biomolecular ink on metal and insulator surfaces [7,8]. As such, DPN is a flexible nanofabrication process for making 2-D nanoscale features with a variety of ink-surface combinations [9].

Although material flexibility in DPN has been extensively studied and developed, DPN is still underdeveloped and unsuitable for manufacturing. This is so because of (i) the ability to accurately predict process performance, (ii) the ability to predict and quantify the practical and theoretical process limits in terms of the feasible rates and qualities, and (iii) the ability to link process capabilities to the process/system parameters. This lack of process knowledge limits the ability to produce parts within the desired rate and quality. It also makes it difficult to evaluate whether metrology based systems are appropriate for high throughput and high quality manufacturing or there is a need for entirely new systems. Therefore, in order to develop DPN for nanomanufacturing, it is important to first develop accurate process models and then characterize the process for the manufacturing metrics.

Accurate process models are a prerequisite for manufacturing. Earlier, we have developed a model for DPN that accurately predicts feature sizes over a wide range of operating conditions [10]. Herein, we demonstrate how this model can be used to characterize DPN for manufacturing. To characterize the process, we have quantified the processing rate, tool life, and feature quality in terms of the process/system parameters. This has enabled us to quantify the theoretical and practical limits of throughput and quality. Based on the characterization, we have also identified the niche capabilities of the DPN process and have determined the design parameters for DPN equipment. This set of information can be subsequently used to (i) predict whether a part is feasible within the constraints of rate and quality and (ii) select/design the appropriate DPN equipment. Thus, process characterization would enable implementation of DPN in a high throughput and high quality nanomanufacturing system.

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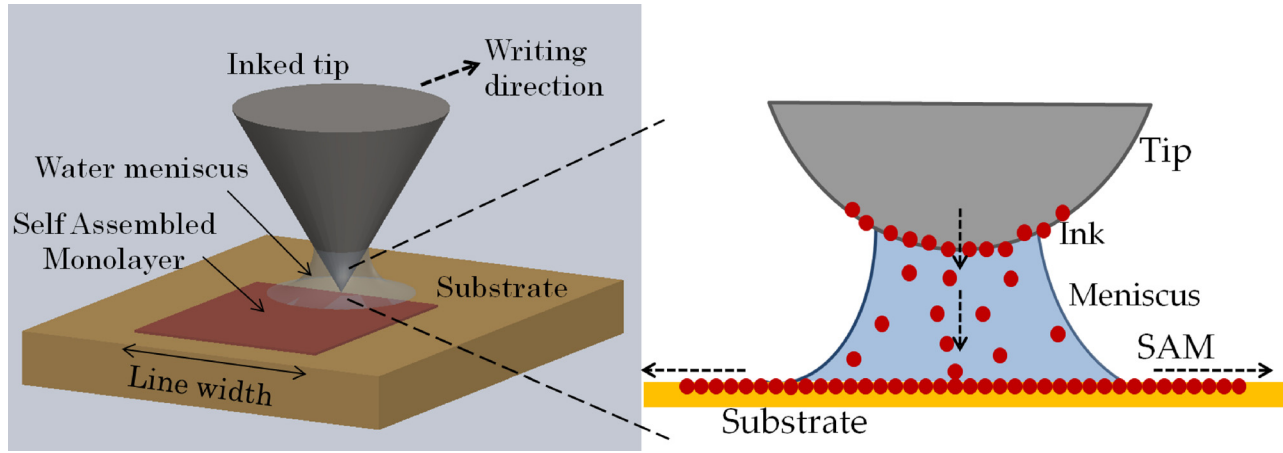


Fig. 1 Schematic of the dip pen nanolithography process

2 DPN Background

2.1 Nanofabrication With DPN. Dip pen nanolithography is a direct write process that allows for material transfer from an ink coated probe tip on to a surface. Writing nanoscale features with the probe tip is similar to writing with a dip pen. The process consists of (i) dipping the tip in a solution of the ink molecules, (ii) drying the tip, and then (iii) holding the tip in contact with the surface or dragging it on the surface. Dot features are formed with a stationary tip and line features are formed when the tip is moved on the surface. The DPN process relies on concentration driven diffusion for transport of ink molecules from the tip to the surface. This diffusion is usually mediated by a water meniscus that forms due to capillary condensation when the tip is brought in close proximity of the surface. Ink molecules spread out from the tip onto the substrate surface and form stable features on the surface via chemisorption based self assembly or physisorption. The shape and size of the self assembled monolayers (SAMs) are determined by the diffusion of ink molecules from the tip.

2.2 DPN Process Modeling. The primary goal of DPN process modeling is to predict the feature sizes based on the process parameters. Several empirical studies in the past have identified the relevant parameters that affect feature size [11–13]. It is known that ambient conditions such as relative humidity and temperature have an effect on dot diameter and line width. For dot writing, it has also been experimentally found by several researchers that the rate of ink transport is independent of writing time [14,15]. Therefore, dot diameters can be easily predicted via an empirical calibration of the tip [15]. This approach, however, does not work for line writing as the transport rate depends on the writing speed [13,16]. Therefore, in the past, we have developed and verified an analytical model to predict line width [10,17]. We briefly describe the process model here.

Ink transport in DPN can be separated into three distinct steps: (i) ink dissolution from the tip, (ii) ink diffusion across the meniscus, and (iii) ink transport on the substrate surface. These steps are schematically shown in Fig. 2. We developed individual models for the three steps and then combined them to generate a comprehensive transport model. We modeled ink dissolution at the tip as a first order chemical reaction. For the meniscus, we considered a simplified uniform cylinder of radius R and height L and modeled ink transport through it as 1-D Fick's diffusion. Finally, we modeled transport on the surface as 2-D surface diffusion from a moving source [17]. With these individual models, line width (w) is linked to the writing speed (V) in terms of other operating conditions as

$$a\rho V(w - 2R) \ln \frac{w}{2R} + b\rho Vw = N\alpha \quad (1)$$

In Eq. (1), ρ is the surface density of ink molecules in the SAM, R is the effective radius of the meniscus, N is the amount of ink molecules on the tip and α is the rate of ink detachment from the tip. The model parameters “ a ” and “ b ” are nondimensional numbers that are a combination of the ink properties and the meniscus geometry. Parameter a incorporates the effect of surface diffusion, whereas b incorporates the effect of meniscus diffusion. Model parameters in terms of the process parameters and material properties are shown in Table 1. We have verified this model against a set of experiments; details of the experiments and model verification are available elsewhere [10]. We used a silicon nitride tip to write lines of 16-mercaptohexadecanoic acid ink on evaporated gold-on-silicon (Au(111)) surface. The parameters corresponding to these experiments are summarized in Table 2.

2.3 DPN and Manufacturing. The DPN process model detailed in Sec. 2.2 can be used to predict the line width for a given set of writing speed and material properties. This model can also be used to characterize the DPN process for manufacturing. To do so, the manufacturing metrics of rate and quality should be defined and quantified in terms of the process parameters and the process outcome. In this section, we define the manufacturing metrics and then quantify them in Sec. 3.

2.3.1 Rate. Processing rate in DPN may be defined in two different yet equivalent ways. First, rate may be defined as the linear writing speed (V), i.e., the speed with which the tip is moved around on the substrate surface. Second, rate may also be defined in terms of the area coverage rate, which is determined by the rate of material transport from the tip to the surface. The area coverage rate (A) is given by

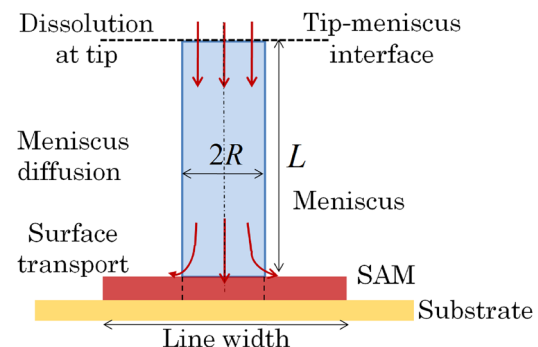


Fig. 2 Cross-sectional view of the meniscus depicting the three step ink transport model for DPN

Table 1 Parameters of the DPN process

Process parameters		Ink-surface properties	Model parameters
Ambient conditions	T : Temperature	E_d : Activation energy for ink detachment	$a = \frac{\beta}{2\pi D_s Z_l}$
	R_h : Relative humidity	E_a : Activation energy for ink re-attachment	$b = 1 + \frac{\beta}{D_l(\pi R^2)/L}$
		D_l : Ink diffusivity in meniscus	$\alpha = \nu e^{-E_d/kT}$
		D_s : Ink diffusivity on surface	$\beta = \pi R^2 \sqrt{\frac{kT}{2\pi m}} e^{-E_a/kT}$
Meniscus geometry	R : Radius	m : Mass of ink molecule	—
	L : Height	ν : Attempt frequency of ink detachment	—
		Z_l : Height of SAM	—

$$A = V_w \tag{2}$$

Although rate can be represented as either the linear writing speed or the area coverage rate, the two forms are equivalent because line width and writing speed are related by Eq. (1).

2.3.2 Tool Life. Processing in DPN occurs via mass transfer from a finite sized source, i.e., from the inked tip. As the amount of ink on the tip is limited, tip re-inking at regular intervals may be necessary. Tool life represents the writing time between subsequent tip re-inking. Tool life may be limited either by the total amount of ink on the tip (N) or by the effect of the change in N (δN) on the line width. If the tool life is comparable to the tool setup time, it may become an important consideration for the overall throughput.

2.3.3 Quality. Quality of the DPN process may be defined in terms of the resolution, feature size accuracy or process variation. Resolution refers to the smallest feature that can be reliably fabricated using the process; accuracy refers to the ability to produce features of the desired dimensions; and process variation refers to the variability in the dimensions of a feature during processing or across multiple parts. As resolution is frequently used for comparing tip based processes, DPN resolution has been extensively studied in the past [15]. However, models for predicting the feature size accuracy and process variations are not available. Therefore, we focus on accuracy and process variations based quality metrics. In Sec. 3.3, we demonstrate how one may use the process model to quantify these quality metrics for DPN.

3 DPN Characterization

3.1 Processing Rate. For implementing DPN in a high throughput system, it is important to identify (i) the parameters that can be used to increase the throughput and (ii) the theoretical and practical rate limits. As the ink transport rate increases with writing speed, increasing the writing speed is a straightforward technique for increasing the processing rate. However, writing speed can be increased only up to a cut-off limit. Beyond this limit, discontinuous lines are generated due to the rate limitation of the process. This cut-off speed determines the maximum operating speed for which the DPN equipment needs to be designed. This cut-off speed (V_c) is found to be $\sim 1 \mu\text{m/s}$ for the typical DPN writing conditions and is given by [10]

$$V_c = \frac{N\alpha}{2Rb\rho} \tag{3}$$

Although processing rate can be increased by increasing the writing speed, this technique is impractical when lines of a particular width are desired. This is so because line width varies inversely with the writing speed. For a set of writing conditions, the writing speed for a target width is determined by Eq. (1). Thus, practical means of increasing the throughput involve changes in other writing conditions such as the tip and meniscus geometry or the ink properties. For example, by increasing the ink diffusivity, it is possible to write a line of the same width but at a higher writing speed. Ink diffusivity can be increased either by selecting an appropriate ink of higher diffusivity or by increasing the ambient temperature. Equation (1), along with the definition of the parameters a and b , can be used to identify other process parameters that affect the rate.

In order to have an idea about the maximum writing speed that can be obtained by changing other writing conditions, one needs to quantify the theoretical and practical rate limits for all possible writing conditions. The effect of increase in the meniscus diffusivity (D_l) and the surface diffusivity (D_s) can be bounded by the hypothetical case when the diffusivities are high enough to be considered as infinite. Such high diffusivities may not be approachable in a real system due to the limited range of temperature control or nonexistent inks. Nevertheless, this analysis is helpful in bounding the rate within limits. By setting $D_l \rightarrow \infty$ and $D_s \rightarrow \infty$ in the definition of the parameters a and b (Table 1), we obtain: $a=0$ and $b=1$. These values of a and b can also be obtained by considering the limiting cases of other parameters that affect a and b and favor a high rate. These cases are: (i) perfectly irreversible ink detachment at the tip ($\beta \rightarrow 0$) and (ii) extremely short meniscus ($L \rightarrow 0$). Therefore, the effect of all the process parameters that indirectly affect the rate via a and b can be consolidated by considering the limiting case of $a=0$ and $b=1$. Equation (1) then reduces to

$$V_w = \frac{N\alpha}{\rho} \tag{4}$$

Thus, the area coverage rate (Eq. (2)) becomes constant and is limited by the tip condition, i.e., the amount of ink on the tip (N) and the ink detachment rate (α). This limit is shown in Fig. 3 in terms of the linear writing speed and corresponds to a constant area coverage rate of $2.0 \mu\text{m}^2/\text{min}$. A rate higher than this limit cannot be achieved by changing either the ink diffusivity or the meniscus geometry. Instead, rate can be increased only by increasing either N or α . The amount of ink on the tip is limited by the

Table 2 DPN parameters during line writing experiments

Ambient conditions	Material properties	Empirical estimation	Model fitting
$T = 298 \text{ K}$ $R_h = 33\%$	$E_d = 45 \text{ kJ/mole}$	$N\alpha = 1.57 \times 10^5 \text{ molecules/s}$ $R = 12.5 \text{ nm}$ $\alpha \sim 10^{-3} \text{ s}^{-1}$	$L = 5 \text{ nm}$ $a = 0.66$ $b = 2.34$

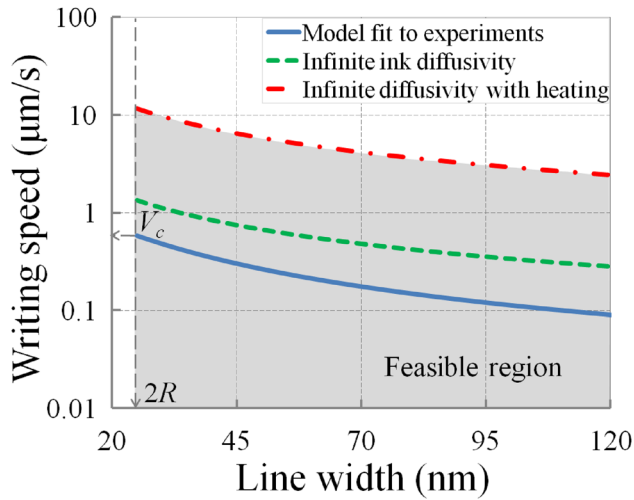


Fig. 3 Theoretical and practical rate limits for DPN line writing. The shaded region represents the feasible writing speeds for target line widths. Line of a particular width can be written at different writing speeds within this feasible region by varying other process parameters such as ink diffusivities or ambient conditions.

surface of the tip in contact with the meniscus and cannot be substantially increased. The ink detachment rate is an ink property and depends on the ambient temperature as shown in Table 1. On considering the melting point of the ink (65 °C) as a practical upper limit for temperature control, we find that α increases by a factor of about 9. This limit is also shown in Fig. 3. The shaded region represents the feasible operating line width and writing speed combinations across all writing conditions for a particular N . From Fig. 3, it is evident that due to the theoretical and practical limits, the increase in throughput is restricted to about 20 times of the typical rate.

3.2 Tool Life. In a manufacturing environment, tool life is an important parameter that determines the overall rate and cost of part production. For a laboratory scale DPN writing operation, tool life is often considered to be “infinite” with respect to the time scale of the operation. However, as DPN writing is driven by the amount of ink on the tip, it is obvious that the tool life is lim-

ited. An estimate of the tool life is important for operations such as large area patterning or high throughput manufacturing. Once the tool “runs out” of ink, one needs to re-ink the tip or replace it with a freshly inked tip, thereby leading to a loss in throughput. Thus, it is desirable to increase the tool life for high throughput operations. Even for low throughput operations, the surface area that can be processed at once is limited by the tool life. Tool life during DPN line writing can be quantified in two different ways: (i) based on the feasibility of continuous writing and (ii) based on the accuracy of the written pattern. In this section, we estimate the tool life for DPN writing based on these two criteria.

3.2.1 Continuous Writing Based Tool Life. As the amount of ink on the tip is limited, only a finite area can be written by the tip. This area sets an upper limit to the amount of writing that can be obtained from the tip and is given by N/ρ . However, this maximum area coverage can be achieved only via the limiting case of dot writing (i.e., $V=0$) performed for an infinite writing time. Due to ink transport rate limitations, continuous line writing is limited by the cut-off speed; i.e., discontinuous lines are obtained beyond the cut-off writing speed. As the cut-off speed depends on the amount of ink on the tip (Eq. (3)), it decreases with writing. Thus, discontinuous lines are obtained when this “instantaneous” cut-off speed falls below the operating speed. Therefore, this sets a practical limit to the area coverage if continuous line writing is desired while operating at a constant writing speed. If further continuous line writing is desired from the tip, one must reduce the writing speed. The fraction of total ink on the tip that can be transferred at a constant writing speed (V) is given by

$$F = 1 - \frac{V}{V_c} \quad (5)$$

To estimate the tool life corresponding to the continuous writing limit, we simulated the effect of loss of ink during writing at a constant speed. We considered line writing as a series of step sized lines and evaluated the loss of ink after writing each step. After each step, we used Eq. (1) to recalculate the width corresponding to the updated amount of ink on the tip. Using this technique, we determined the time taken for the amount of ink at the tip to drop below the threshold corresponding to the continuous writing limit. This limit is approached when the “instantaneous” cut-off speed reduces to the writing speed. For this simulation, we used the experimental conditions from our previous study [10] and a line step size of $2R$. The tool life at different writing speeds is shown in Fig. 4(a).

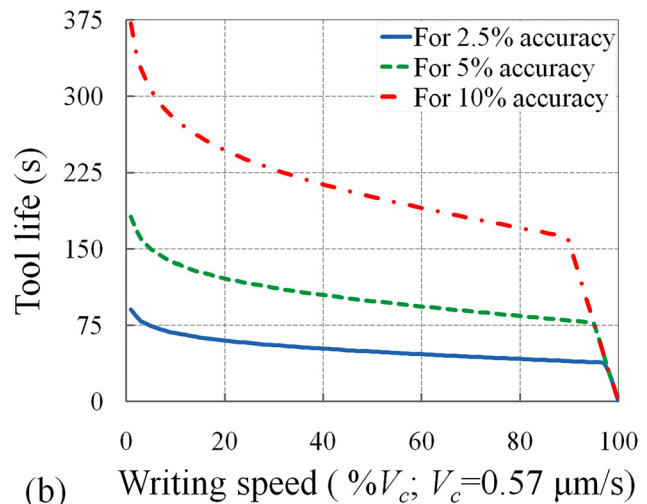
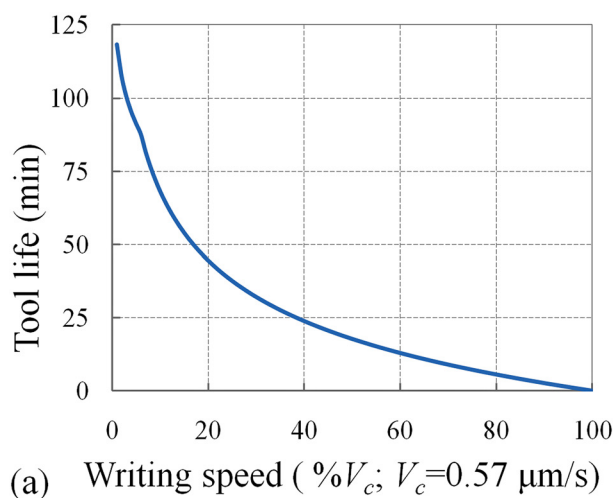


Fig. 4 Tool life for DPN line writing based on two different criteria. V_c represents the cut-off writing speed at the start of writing. The instantaneous cut-off speed decreases with writing due to loss of ink from the tip. (a) Tool life for continuous line writing and (b) tool life for accurate line writing. Abrupt drop in tool life at high writing speeds indicates the onset of discontinuous lines.

As the horizontal axis has been normalized using the initial cut-off speed, this tool life curve does not change on changing the initial amount of ink on the tip. For example, if the initial amount of ink is increased by a factor of 2, then the initial cut-off speed would also increase by a factor of 2; however, the tool life at (say) 50% the initial cut-off speed would remain the same. Tool life for continuous writing varies from about an hour at low writing speeds to about several minutes at high writing speeds. This measure of tool life is relevant to applications in which continuous lines are required; for example, during fabrication of conductive traces or interconnects for electronics applications.

3.2.2 Accuracy Based Tool Life. The tool life during DPN is further limited by the need for writing accurate lines. Although continuous lines can be obtained up to a limit, the width of the line keeps decreasing with continual writing. This is so because the width of the line is proportional to the amount of ink on the tip (Eq. (1)). Thus, if one needs to maintain line width within a given tolerance while writing at a constant speed, then the amount of ink on the tip should not be allowed to drop below a threshold. This threshold value then sets a limit to the tool life as writing beyond this limit would lead to inaccurate lines. We used the same technique as detailed in Sec. 3.2.1 to account for the loss of ink during writing. In our simulations, we continued writing as long as the error in the width was less than the allowable tolerance in width. The tool life for different line width tolerances is shown in Fig. 4(b). As expected, the tool life for accurate writing is much less than the tool life for continuous writing and varies from about 5 min for 10% accuracy to about a minute for 2.5% accuracy. The corresponding line lengths can be obtained from the writing speed and the tool life and lie between tens of micrometer for high speed writing to about a micrometer for low speed writing. If accurate lines longer than these are required, then one must reduce the writing speed. Accuracy based tool life is relevant to applications in which accurate lines are required; for example, during fabrication of photomasks.

3.3 Quality. Feature size accuracy and process variation are important measures of process quality. Several process control techniques are used to produce accurate parts and reduce process variation. These include (i) operating the process under low sensitivity conditions, (ii) reducing the variation in the process parameters or material properties, and (iii) changing the controllable parameters based on the state of the process. As the control effort can be significantly reduced by operating at low sensitivity conditions, it is important to identify such conditions. At present, low sensitivity conditions for the DPN process are not known. Therefore, here we have quantified the sensitivity of line width to the input parameters: (i) writing speed and (ii) the nondimensional model parameters a and b . This sensitivity information may then be used to determine the necessary input parameter tolerances that one must maintain in order to produce lines within the desired width tolerances.

3.3.1 Parameter Sensitivity. We evaluated the sensitivity of line width to the process parameters by performing partial derivatives $\partial/\partial V$, $\partial/\partial a$, and $\partial/\partial b$ on both sides of Eq. (1). The sensitivity of width to the writing speed and the parameters a and b are given by

$$\frac{\partial w}{\partial V} = -c \frac{w}{V} \quad (6)$$

$$\frac{\partial w}{\partial a} = -c \frac{w}{a} \left(1 - \frac{b\rho V w}{N\alpha} \right) \quad (7)$$

$$\frac{\partial w}{\partial b} = -c \frac{w}{b} \left(\frac{b\rho V w}{N\alpha} \right) \quad (8)$$

In Eqs. (6)–(8) the nondimensional parameter “ c ” represents

$$c = \frac{1}{1 + \frac{2R\rho V}{N\alpha} \left(\frac{w - 2R}{2R} + \ln \frac{w}{2R} \right)} \quad (9)$$

The parameters V , a , and b can be independently varied to control DPN writing. Equations (6)–(9) provide a means to compare the effect of changes in these parameters on line width under various writing conditions. As parameters a and b incorporate the effect of ambient conditions and the ink-surface properties, they may also be used for environment control or material selection. The sensitivity of line width to these parameters at different writing speeds is shown in Figs. 5(a) and 5(b). We observe that the sensitivity to writing speed decreases with an increase in the writing speed, i.e., while writing narrower lines. Similarly, sensitivity of width to the parameters a and b decreases with an increase in the writing speed. This behavior is consistent with the material addition based writing mechanism. When the writing speed is low, a higher amount of ink is transported to the substrate per unit length of the line. Therefore, similar changes in the process parameters manifest as a larger change in the width at lower writing speeds than at higher speeds. The sensitivity of line width to other parameters may also be obtained from Eq. (1). For example, line width sensitivity to changes in meniscus radius (R) and meniscus height (L) are given by

$$\frac{\partial w}{\partial R} = -c \frac{w}{R} \left(3 - \frac{1}{c} - \frac{2b\rho V w}{N\alpha} \right) \quad (10)$$

$$\frac{\partial w}{\partial L} = -c \frac{w}{L} \left(\frac{(b-1)\rho V w}{N\alpha} \right) \quad (11)$$

Sensitivity of line width to R and L at different writing speeds is shown in Figs. 5(c) and 5(d). The drop in sensitivity at high writing speeds is consistent with the material addition based writing mechanism.

Herein, we have used Eqs. (6)–(11) to identify that the sensitivity of line width to process parameters decreases with an increase in the writing speed. These equations can also be used to identify the low sensitivity regimes for other process parameters. For example, as shown in Fig. 6, the sensitivity of line width to nondimensional parameters a and b decreases with an increase in parameters a and b . This decrease in sensitivity can also be explained via the material addition based writing mechanism. As a and b increase, the ink flow rate during writing decreases. Thus, similar changes in the parameters manifest as a smaller change in the width at high a and b values. Although operating at higher a and b values would reduce the sensitivity, one may still decide to operate at low a and b values so as to increase the rate. For general writing, the optimum operating conditions based on rate and sensitivity may be obtained using Eq. (1) and Eqs. (6)–(11).

3.3.2 Parameter Tolerances. In order to maintain the line width within a tolerance band, one must maintain the process parameters within the corresponding tolerance bands. The sensitivity equations, i.e., Eqs. (6)–(11) can be used to estimate the allowable variation in the process parameters or material properties for the desired line width tolerances. For example, the change in width (Δw) corresponding to a small change in writing speed (ΔV) can be obtained as

$$\Delta w \sim \Delta V \frac{\partial w}{\partial V} \quad (12)$$

The allowable variation in the writing speed corresponding to a $\pm 2.5\%$ width tolerance is shown in Table 3. This information about the allowable speed variation is crucial for designing an appropriate tip positioning system for DPN. Similarly, information on allowable variations in other process parameters may be obtained from the sensitivity of width to model parameters a and b . For example, allowable variations in the surface diffusivity can be estimated from the allowable variations in the parameter a . The allowable variation in surface diffusivity for $\pm 2.5\%$ width tolerance is shown in Table 3. This information has direct relevance to the sample preparation method as it determines the level of control necessary during sample preparation. For example, the surface

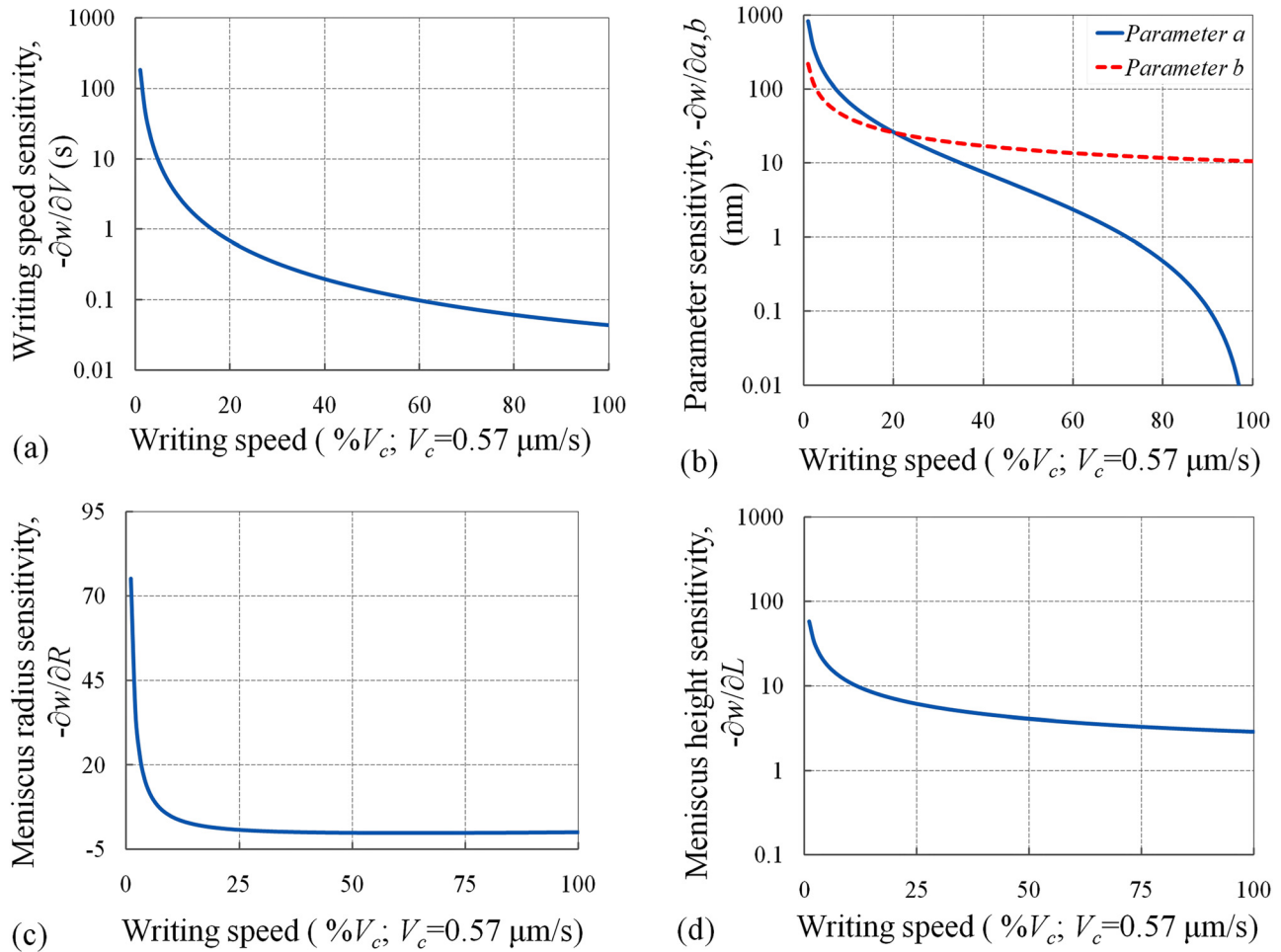


Fig. 5 Sensitivity of line width to changes in process parameters at different writing speeds. (a) Sensitivity to writing speed and (b) sensitivity to nondimensional process parameters a and b ; at V_c , $\partial w/\partial a = 0$. (c) Sensitivity to meniscus radius; $\partial w/\partial R$ is positive beyond $0.39V_c$ and zero at V_c . (d) Sensitivity to meniscus height.

diffusivity should be controlled within $\pm 16.9\%$ for low speed writing but may vary by as much as -81.3% to $+\infty$ for high speed writing. To determine the allowable tolerance on the ambient con-

ditions, one would require models that relate the meniscus geometry to the ambient conditions. Unfortunately, such models are not available at present; hence, it is not possible to obtain quantitative

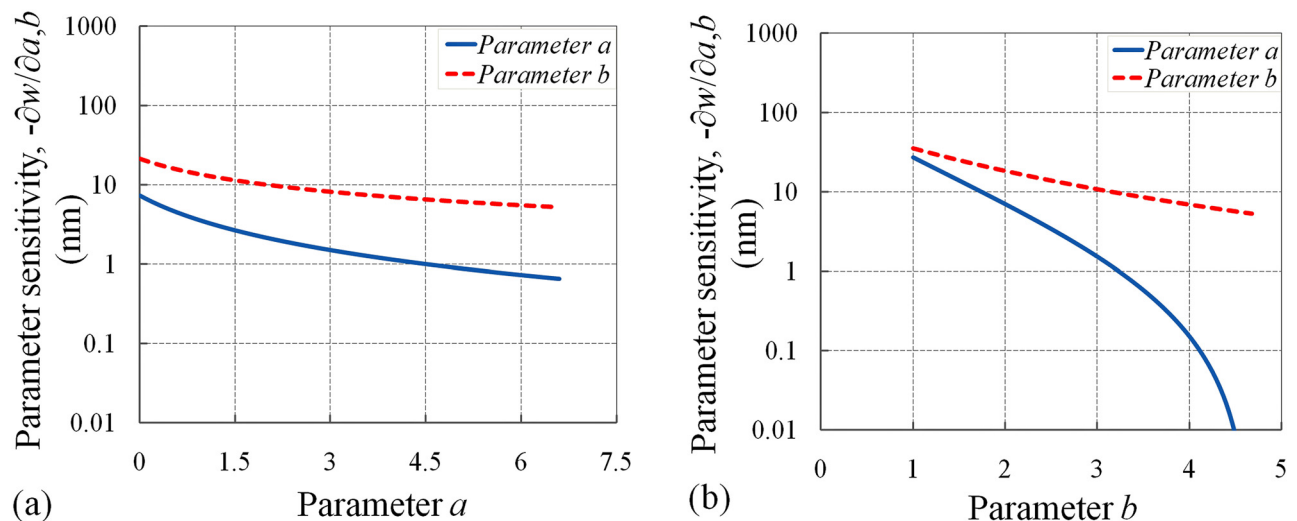


Fig. 6 Sensitivity of line width to changes in nondimensional parameters a and b at different values of parameters a and b . The writing speed is fixed at $0.5V_c$; $V_c = 0.57 \mu\text{m/s}$. (a) Sensitivity at different values of parameter a and (b) sensitivity at different values of parameter b .

Table 3 Manufacturing metrics of the DPN process at different writing conditions

Manufacturing metric	Writing condition	Value
Area processing rate	Typical	$\sim 1 \mu\text{m}^2/\text{min}$
	Upper limit	$\sim 20 \times$ typical values
Tool life	For continuous lines	$\sim 5 \text{ min}-1 \text{ h}$
	For accurate lines	$\sim 1-5 \text{ min}$
Process control (within $\pm 2.5\%$ of target width)	Tolerable writing speed variation	$\mp 13.0 \text{ nm/s}$
	Tolerable surface diffusivity variation	$\mp 4.6 \text{ nm/s}$
	High speed ($w = 30 \text{ nm}$)	∞ for $2.5\% \Delta w$; -81.3% for $-2.5\% \Delta w$
	Low speed ($w = 80 \text{ nm}$)	$\pm 16.9\%$

information on environment control. Nevertheless, from the sensitivity of width to the meniscus geometry (R and L), it is qualitatively known that the environmental control requirements at low writing speeds are more stringent than at high writing speeds.

4 Manufacturing With DPN

Process characterization is relevant to manufacturing as the process characteristics may be used to (i) predict whether a part can be produced within the constraints of rate and quality, (ii) identify the process niches for manufacturing, (iii) verify whether the current equipment/system is appropriate, and (iv) design a manufacturing system that is appropriate for the process and the part. We have characterized the DPN process in Sec. 3 and summarized the manufacturing metrics in Table 3. Herein, we discuss DPN limits and niches and demonstrate how this information can be used to design a system that is appropriate for high throughput and high quality manufacturing.

4.1 DPN Process Limits. For high throughput writing, it is desirable to operate at high writing speeds. Lines of the desired width can be written at a higher speed by changing the appropriate process parameters. Rate of the DPN process is determined by (i) the diffusion based ink transport mechanism, (ii) the ink detachment rate at the tip, and (iii) the amount of ink on the tip. Thus, high throughput writing can be obtained by (i) increasing the ambient temperature and humidity for faster ink diffusion or by selecting a faster diffusing ink-surface system, (ii) increasing the ambient temperature to speed up ink detachment at the tip, or (iii) by loading a higher amount of ink on the tip. Although all of these techniques may be used to increase the rate, they suffer from theoretical and practical limits as discussed in Sec. 3.1. Consequently, the DPN process is rate limited to about 20 times of the typical writing speed. This limit is about 10^4 times less than the typical writing speeds during the electron beam lithography process [18], which is conventionally used for low volume fabrication operations such as for making photomasks.

For high quality DPN writing, one needs to produce accurate parts with low process variations. This can be achieved via process control. Although one may theoretically achieve an arbitrary precision via process control of multiple variables, it is currently not feasible for DPN. Due to lack of in situ process monitoring capabilities, it is not possible to use closed loop feedback control based on real time line width measurement. Instead, process control is achieved via control of the individual process parameters within tolerable limits. Thus, the quality of the feature is limited by the precision of the equipment being used for controlling the process parameters. The achievable feature quality can be calculated from the parameter sensitivities (Eqs. (6)–(11)) and the precision of the process control equipment.

4.2 DPN Niche. Although DPN is feasible for writing a range of line widths, it is evident from Table 3 that the process characteristics vary with the writing conditions. Depending on the manufacturing requirements, one set of writing conditions may be preferable over the others. For high throughput writing, it is evident

that high speed writing is favorable. Interestingly, high speed writing is also favorable for high quality part production. DPN process is more “forgiving” at higher writing speeds. This is because sensitivity of line width to the process parameters decreases with an increase in the writing speed. This is consistent with the material addition based bottom-up writing mechanism. Thus, the niche for DPN lies in high speed writing of narrow lines. This is in contrast with the top-down approaches, such as nano-imprint lithography [19], in which process control complexity scales inversely with line widths. Here, the terms “high speed” and “narrow” are relative and scale with the cut-off velocity and the tip radius, respectively.

4.3 System Design for DPN Manufacturing. DPN has traditionally been implemented via atomic force microscopy (AFM) based legacy instruments that closely resemble a job-shop manufacturing environment. Use of AFM based systems has persisted primarily due to their familiarity and flexibility of use in a laboratory environment. Although such systems seem to be appropriate for low volume production, it is currently not known whether they are optimal for high throughput and high quality manufacturing. Herein, we identify the equipment design needs for high throughput and high quality manufacturing based on the DPN characteristics discussed in Secs. 3 and 4.1. These design needs may then be used as guiding principles for modifying the existing systems or for developing new systems.

4.3.1 Throughput. Due to transport rate limitations, only a limited improvement in throughput can be achieved via an increase in the processing rate. Thus, for large improvements in throughput one must (i) modify the process mechanism or (ii) introduce parallelization. Parallelization may be introduced either (i) by using multiple tips for processing on the same part or (ii) by using multiple workstations. Both of these approaches, i.e., process modification and parallelization, have been demonstrated in the past. Several DPN variants, such as nanofountain lithography [20] and electrochemical DPN [21], have been developed that improve throughput via forced ink flow mechanisms. This increases the transport rate beyond the concentration driven diffusion limits. Similarly, 2D probe arrays with 55,000 tips have been used for improving DPN throughput via parallelization [22]. Although both of these are effective techniques, they have their drawbacks. For example, forced ink flow mechanisms increase the complexity of the process. Also, as the probes in the 2D array cannot be individually actuated, such arrays severely restrict the part geometries. These drawbacks may partly be overcome by using multiple workstations, each operating with a single tip. However, this approach has not been attempted in the past due to the high cost of an AFM system. This approach may become feasible with the development of low cost nanopositioners that have a small footprint.

4.3.2 Tool Life. Tool life determines the area that can be patterned at once. It also has a significant effect on the overall throughput if the tool setup time is comparable to the tool life. Tool setup time during DPN writing is highly dependent on the skill of the AFM operator. Even for a skilled operator, typical setup times are comparable to the tool life for accurate line writing, i.e., about 1–5 min. Thus, tool setup would lead to a considerable loss of

throughput if high quality writing is required. Throughput may be increased either by (i) increasing the tool life or (ii) by reducing the tool setup time. The tool life can be increased by introducing in situ tip re-inking procedures for fast re-inking. For example, in situ re-inking via ink wells has been demonstrated in the past that allows for tip re-inking without removing it out of the AFM system [23]. Although this technique eliminates the need for tool replacement, it is not much faster than a complete tool change. Instead, the tool setup time can be significantly reduced by introducing high accuracy tool-surface fixtures for rapid tool change. By using these fixtures, one may rapidly align the tip with respect to the surface for both single and multiple probe tips. This would not only allow for rapid tool change but also reduce the level of operator skill required for performing DPN.

4.3.3 Exploiting the DPN Niche. DPN is usually performed in a tightly controlled environmental chamber with a closed loop AFM positioning system. These stringent process control requirements, coupled with the large size of the workstation, limit the scale-up potential of DPN for high throughput processing. However, from DPN characterizations in Secs. 3 and 4, it is evident that process control at high writing speeds is less stringent than at low writing speeds. Thus, for such writing conditions the existing equipment may be replaced by simpler and smaller equipment, without any loss of performance. For example, the AFM based positioner may be replaced by low cost open loop flexure based nanopositioners [24] or the environment control chamber may be replaced by stage surface heaters. Such simpler equipment would not only reduce the cost of the equipment but would also enable scaling-up the DPN process.

5 Conclusions

We have characterized the DPN process in order to identify the system modifications that would enable high throughput and high quality DPN nanomanufacturing. We found that (i) theoretical and practical constraints limit the DPN processing rate to about 20 times the typical rate of $\sim 1 \mu\text{m}^2/\text{min}$, (ii) tool life for high quality line writing is limited to about 1–5 min, and (iii) the sensitivity of line width to the process parameters decreases with the writing speed. These DPN characteristics are relevant to nanomanufacturing as the following conclusions can be drawn from them. First, for obtaining a high throughput, process mechanism modification via forced ink flow or parallelization would have a higher impact on the rate than modifications in the writing conditions or the ink/surface properties. Second, there is a need for accurate fix-

tures that would enable rapid tool change during high quality line writing. Third, the niche for DPN line writing lies in high speed writing of narrow lines. Thus, low cost and simple equipment may be used for performing high speed writing. Results of the DPN characterization are summarized in Fig. 7.

We have also demonstrated the central role of process characterization in selecting/designing appropriate nanomanufacturing systems. Although microscopy instruments have been traditionally used for performing DPN, we found that such systems are not ideal for all writing conditions. For example, when high quality line writing is desired, the absence of rapid tool changing mechanism severely restricts the throughput. Similarly, for high speed writing it may be possible to obtain similar level of process control via a set of simpler and lower cost equipment, thereby significantly improving the scale-up potential. Thus, process characterization is useful for either modifying the existing systems or for developing alternate systems that are appropriate for manufacturing. This process driven system design technique may also be used for designing manufacturing systems for other nanoproducts. Thus, this work provides a framework for process driven design of systems that are appropriate for the desired manufacturing goals.

6 Limitations and Future Work

Herein, we have characterized the DPN process based on a three step ink-transport mechanism that is limited by mass diffusion and the amount of ink on the tip. For ink-surface systems that are not limited by these factors, this characterization would not be directly applicable. For example, during DPN writing with electrically charged species there may be additional factors that enhance or limit ink transport. For such ink-surface systems, one would need to incorporate these additional factors into the process model.

Process control in DPN is usually performed via control of the ambient temperature and relative humidity. Ambient conditions have an influence on the process outcome via (i) the temperature dependent material properties and (ii) temperature and humidity dependent meniscus geometry. Thus, the effect of these parameters is implicitly accounted via the model parameters “*a*” and “*b*”. Although our model quantifies the allowable variations in *a* and *b* corresponding to desired line width tolerances, it does not do so for the ambient conditions. This is because of the absence of appropriate models that relate the ambient conditions to the meniscus geometry. Thus, there is a need to develop appropriate models for temperature/humidity dependent meniscus geometry.

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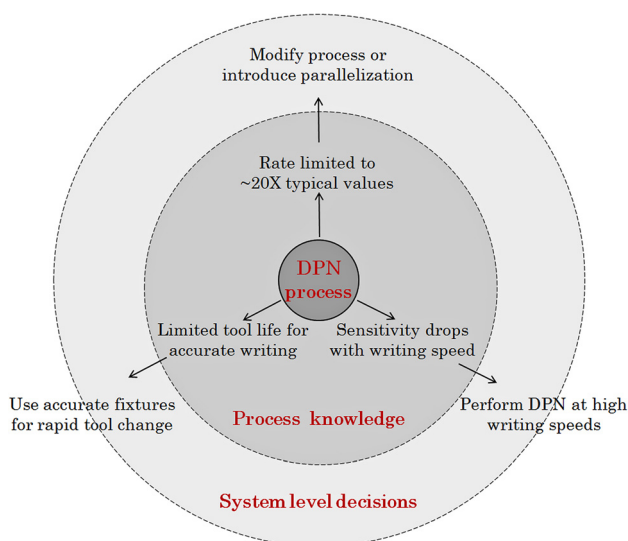


Fig. 7 Process driven system design for DPN nanomanufacturing

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