Optimized Surface Patterning Tools for Sub-Attoliter Volume Fluid Deposition

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ABSTRACT

The Bioforce Nanosciences Nano eNabler^{TM} is a benchtop molecular printer which allows users to deposit fluids with extreme accuracy and repeatability. Unfortunately, until recently the minimum spot size that could be repeatedly achieved was a few microns in diameter. For most cellular applications this is sufficient [1]; however, our goal was to achieve sub-micron diameter writing for all applications. The Nano eNabler^{TM} uses a micromachined cantilever surface patterning tool as depicted in Figure 1 to deposit the fluid of interest. The deposition relies solely on surface tension driven flow and is therefore not limited by molecular diffusion like dip-pen based printers.

In order to reduce the spot size during deposition, a detailed model of the flow dynamics was created and used to determine the most important variables during deposition. Several areas for improvement were discovered. Ultimately, this led to the development of an oxide coated channel configuration in which the top and sides of the SPT were still nitride. This design leverages the difference in contact angle between the dissimilar materials to provide additional fluid confinement and thus should yield smaller spots.

Keywords: microfluidics, deposition, surface patterning.

1 INTRODUCTION

Over the last decade a number of techniques have been developed for depositing very small volumes of fluids on various surfaces. These techniques include modified ink-jet printing, polydimethyl siloxane stamping, and dip pen lithography to name a few. BioForce Nanosciences developed a technique based on an open flow channel embedded on a micromachined cantilever (Figure 1a). The cantilever called a surface patterning tool or SPT relies solely on capillary action to drive fluid from an on-board reservoir to the cantilever tip. The SPT is held in place on an optical column while a piezoelectric XYZ stage moves the sample into contact with the tip. Similar to other scanning probe microscopy systems, a laser focused on the SPT provides feedback that sample surface and tip are in contact. Both optical and laser intensity feedback are provided to the user so that they may monitor the deposition process. The Nano eNabler^{TM} also provides regulation of the relative humidity inside the sample chamber through the use of water vapor and dry nitrogen. An image of the BioForce Nanosciences Nano eNabler^{TM} bench-top molecular printer is provided in Figure 2.

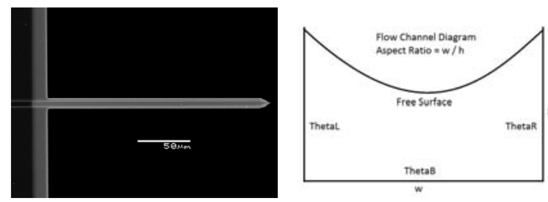

Figure 1 (a) 10 µm surface patterning tool with 1 µm channel at the tip. (b) Geometry of the flow channel.

The Nano eNabler^{TM} has a myriad of applications including surface patterning for cell cultures, biosensor functionalization, small volume biomolecular assays, and drug discovery. The Nano eNabler^{TM} can be equipped with different size SPTs in order to achieve different spot sizes during writing. Most users find that the standard tools meet their needs providing spot sizes between 1 µm and 60 µm. However, a number of emerging applications require consistent sub-micron spot sizes on various surfaces.

In order to fully understand the writing dynamics a detailed model of the fluid flow and contact mechanism was developed. This model takes into account the primary variables of interest for writing applications including temperature, relative humidity (RH), fluid viscosity, channel material and dimensions. Since the SPT uses and open reservoir and channel, evaporation is a major concern. In order to facilitate ease of deposition, a low vapor pressure solvent such as glycerol is typically added to the aqueous solution of interest. Glycerol which is hydroscopic by nature retains an 80/20 balance with water under RHs between 40% and 70% which is the recommend range of RH for most applications.

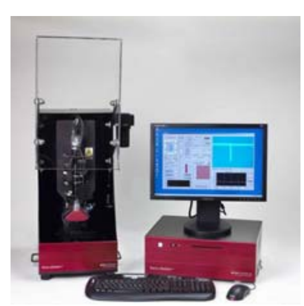

Figure 2. BioForce Nanosciences Nano eNabler^{TM}

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Capillary flows in microchannels have been studied by numerous groups [2-4]. Specific solutions for flow in closed microchannels of various geometries have been reported. In general, these solutions rely on an aspect ratio simplification. As can be seen from Figure 1b, the aspect ratio is typically defined as

$$\lambda = \frac{w}{h} \tag{1}$$

where w is the channel width and h is the channel height. In most cases the aspect ratio is either much greater or much smaller than 1. In the case of the 10 µm SPT from Bioforce Nanosicences, the aspect ratio is approximately equal to 1.

Recently, more attention has shifted to the description of flows in open channels which behave differently due to the air liquid interface at the top of the channel [3,5]. The capillary pressure in a rectangular microchannel with nonuniform surface properties has been given as

$$\Delta P = \gamma \left(\frac{\cos\theta_b + \cos\theta_t}{h} + \frac{\cos\theta_l + \cos\theta_r}{w} \right) \tag{2}$$

where γ is the surface tension [6]. This expression contains the assumption that the liquid meniscus in filling the microchannel spans the entire cross section of the channel [7]. In order to deposit fluid onto a surface, the substrate is brought into contact with the SPT which is held at an acute angle. The SPT angle is typically 12 degrees but can be changed to 24, 36, or 48 degrees depending on the application. The SPT mounting angle also impacts the spot size as will be discussed below.

In this paper, a comprehensive writing dynamics model is developed and tested. The results of the model are presented. Conclusions drawn from the model were then applied to the fabrication of new SPTs. The experimental data is shown for comparison with the model predictions. The overall results show that sub-micron diameter spots can be deposited on most surfaces using the existing SPTs with minor modifications.

2 THEORETICAL FORMULATION

The steady flow of an incompressible Newtonian liquid is considered for the rectangular channel geometry shown in Figure 1b. The free surface between the liquid and the air has a constant radius of curvature when the channel width *w* is much less than the characteristic capillary length [8]. This condition is typically true for sub millimeter channel widths. Therefore the gravitational terms can be ignored which greatly simplifies the governing equation.

For fully developed laminar flow at low Reynolds number the governing Navier-Stokes equations reduce to a balance between the axial pressure gradient and the viscous shear stresses in the cross-sectional plane. Thus, the governing equation can be represented as

$$\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = \frac{1}{\mu}\frac{\partial p}{\partial x} \tag{3}$$

where *u* is the velocity component in the axial direction, µ is the viscosity of the fluid and *p* is the pressure. The no-slip boundary condition is imposed on the channel walls such that *u* = 0. For the liquid-air interface, the boundary-condition imposed is

$$\mu \nabla u \cdot \hat{n} = \tau \tag{4}$$

where $\hat{n}$ is the unit outward normal to the interface and τ is the shear stress [9]. Since gas viscosities are generally orders of magnitude smaller than liquid viscosities, interfacial shear forces will often be very small compared to the forces exerted by the channel walls. Due to this fact, uniformity of the shear stress over the interface is assumed for simplicity.

The velocity profile within the channel can be solved analytically for the case of one dimensional flow which is representative of the case of interest where the channel is fully filled and has an aspect ratio of one. In this case, the velocity profile is given as

$$V(z) = \frac{1}{\mu}\frac{\partial y}{\partial x}\left(z^2 - zh\right) \tag{5}$$

where *h* is the height of the channel. The flow rate is then given as

$$Q = \frac{1}{3}\frac{w}{\mu}\frac{\Delta p}{L}h^3 \tag{6}$$

where *L* is the length of the flow channel. The total volume of fluid deposited can then be directly related to the amount of time that the tip is in contact with the surface.

However, the morphology of the deposited spot is dependent upon a number of additional factors primarily the contact angle of the surface, the rate of evaporation and the mount angle of the SPT. The height of the spot and its roundness are controlled by the surface contact angle θ_s. The total volume of the spot is also affected by the rate of evaporation which can be approximated as

$$R = \left(P_v N - P_p\right)\sqrt{\frac{MW}{2\pi RT}} \tag{7}$$

where P_v is the vapor pressure, N is the mole fraction of water, P_p is the partial pressure, MW is the molecular weight of water, R is the gas constant and T is the temperature. The amount of water that has evaporated can then be calculated by multiplying the evaporation rate by the surface area of the droplet. Without the addition of a low-vapor pressure solvent such as glycerol, the evaporative process is dominant and fluid deposition becomes virtually impossible except at very high relative humidity.

For the deposition process, one additional factor is of critical importance. Due to the acute mount angle for the SPT, the end of the tip interacts with the fluid as the deposition occurs. The shape and material characteristics of the tip then play a role in the formation of the spot on the surface. Since the SPT is typically 2 microns thick, when the surface comes in contact, the tool bends slightly. This bend increases the interaction between the flow channel and the substrate surface. There is a minimum withdraw distance required to separate the tip from the surface. The SPT must be strong enough not to break due to surface tension effects from the deposited droplet when the stage is pulled away from the tip. This minimum withdraw distance is then used with the stage velocity and mount angle to estimate the increase in interaction time between the tip and the surface.

3 MODEL RESULTS

A computational model was developed in MATLAB to investigate the SPT deposition process in order to further optimize the SPT and the control software present on the Nano eNabler™. A number of parameters were included in the model including all of those described in Section 2. An abbreviated list of the parameters of interest is listed as follows: temperature (°C), RH (%), pressure (Pa), concentration of glycerol (%), contact speed (m/s), channel height, width, length (m), SPT thickness, width, length (m), contact angles for channel sides, bottom, SPT top, and writing surface, and SPT mount angle.

As can be seen from the list above, there a numerous parameters which can be changed to investigate the behavior of the SPT. However, the physical parameters of the channel and SPT are limited by the types of tools available for testing. For this reason, the model was limited to the 10µm SPT which produces the smallest spots. At the tip, the channel is only 1 µm by 1 µm. The contact angle is also set by the SPT material. The temperature was set to 23°C, the pressure to 101325 Pa and the relative humidity to 45%.

For the initial model runs, values were chosen intuitively based on the behavior of past experimental results. This was done to test some of the fundamental assumptions of the model. For example, the spot size should grow as a function of dwell time. This can be seen in Figure 3.

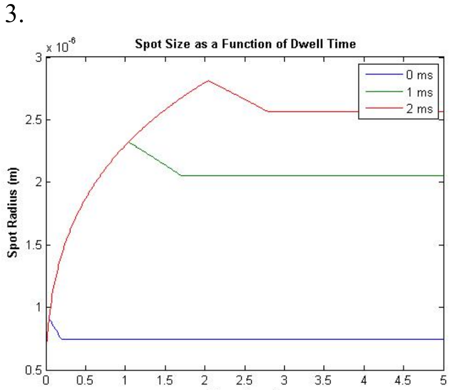

Figure 3. Spot size as a function of additional dwell time with evaporation.

For this particular case, the surface was chosen to have a contact angle of 59° which approximates polystyrene. A one ms additional dwell time produces roughly a 2 µm radius spot. In addition to dwell time, the contact angle of the surface should also greatly impact the final spot diameter. Once again the model predicts the anticipated behavior as shown in Figure 4.

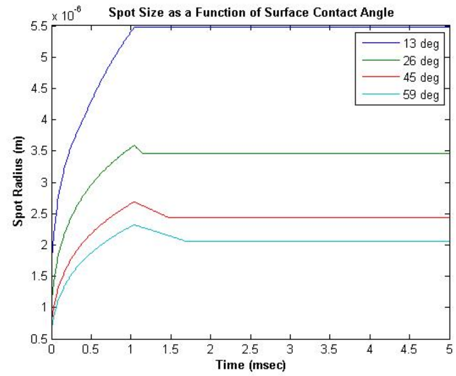

Figure 4. Spot size as a function of surface contact angle with evaporation.

Finally, the result of different mount angles is shown in Figure 5. Here a surface contact angle of 26° was chosen with an additional write time of 0 ms and an initial glycerol concentration of 10%. The plot illustrates the spot volume in m^3.

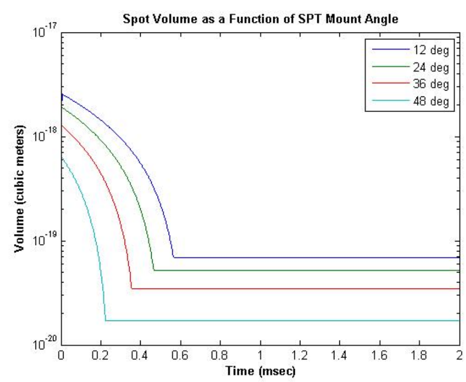

Figure 5. Spot volume as a function of SPT mount angle.

4 EXPERIMENTAL RESULTS

The goal for the experiments described here was to leverage the model predictions to deposit sub-micron diameter spots with the final goal of achieving 100 nm diameter depositions. Based on model recommendations, SPTs were fabricated and tested with the Nano eNabler™. The test results are presented below.

4.1 Apparatus

Initial test were performed with stock 10 µm NiOx SPTs from Bioforce Nanosciences. The bulk of the SPT is silicon nitride but the channel and top surface are silicon dioxide. A Nano eNabler™ equipped with a 20X optical objective was used for data acquisition. The SPTs were filled with an aqueous solution of 10% glycerol. This allowed for adequate writing under the environmental conditions of interest. The writing occurred at 23°C at atmospheric pressure with a relative humidity of 45%. All the tests were conducted on clean glass microscope slides with a measured contact angle of 13°.

4.2 Data and Results

Figure 6a shows a 5 by 5 pattern of 1 μm spots deposited on glass. The pattern is difficult to see due to the lack of contrast between the fluid and the glass substrate. In order to enhance the image and measure the spot sizes an image analysis routine was constructed in MATLAB. The results of that routine are shown in Figure 6b. A 10 by 10 array of 700 nm spots is shown in Figure 6c along with its processed image in 6d. It should be very evident how difficult it becomes to visualize transparent spots on a transparent substrate. The image processing algorithms developed aid substantially in determining spot size and morphology.

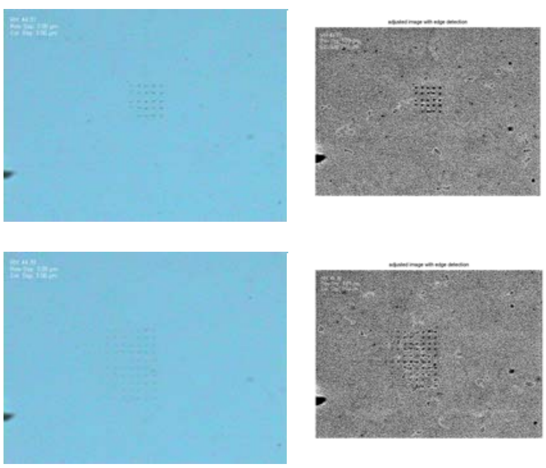

Figure 6. (a) 5 by 5 array of 1 μm spots on 3 μm centers. (b) Processed image of (a). (c) 10 by 10 μm array of 700 nm spots on 3 μm centers. (d) Processed image of (c).

As can be seen from the figures above, the standard NiOx SPT is capable of generating micron to sub-micron spots on glass. Tests on other surfaces have not been conducted at this time but, we expect that the spot diameters will be even smaller on higher contact angle surfaces such as polystyrene.

4.3 Future Work

In order to further improve writing consistency and minimize spot size, new SPTs will be fabricated with different materials inside versus outside the channel. The hope is that the channel confinement provided by differing contact angles will help isolate the deposition fluid and help prevent spreading of the fluid across the SPT surface. SPTs using a combination of silicon nitride and silicon oxide are currently being designed and fabricated. Additional surfaces will also be tested for spot size and morphology.

5 CONCLUSIONS

During the course of the work presented here, a number of revelations occurred which have dramatically changed the capabilities of the Nano eNabler™. Before the comprehensive model of the SPT deposition process was created, most users thought that sub-micron radius spots were impossible to generate using current tools. However, it was found that limiting factor was not the tool itself but the controller software. With minor changes to the software to minimize the dwell time, sub-micron spots were successfully deposited. Unfortunately, our goal of 100nm spots has not yet been realized, but the model has indicated that additional reduction in spot size diameter could be obtained through a channel confinement SPT. This is currently the direction of SPT research.

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