Ink Diffusion in Dip-Pen Nanolithography: A Study in the Development of Nano Fountain Probes

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Abstract

The intention of this research was to investigate the ink diffusion that takes place in dip-pen nanolithography in order to better understand how to enhance the possibilities of nano fountain probes. Varying concentrations of 16-mercaptohexadecanoic acid in ethanol were used as ink in dip-pen nanolithography, and the relationships between contact time, concentration, and ink diffusion were studied. It was found that for all concentrations, ink diffusion showed a dependence on contact time, but some concentrations showed a stronger dependence than others. After comparing results across different concentrations, it was also shown that there is a specific, nonlinear relationship between ink diffusion and concentration. In addition, it was shown that dip-pen nanolithography has limitations in multiple-trial studies. Further investigation could indicate which inks are most appropriate for nano fountain probes.

Introduction

In 1959, when Richard Feynman delivered his historic "There's Plenty of Room at the Bottom" speech declaring that "it is a staggeringly small world that is below," few in the audience probably imagined that in 40 years' time, an entire paragraph of that speech would be written in an area one thousand times smaller than the period ending this sentence.[1] Indeed, it is a small world that is below, and we are quickly learning that manipulating this small world is not nearly as difficult as we once imagined.

In recent years nanolithography, or the area of nanotechnology devoted to "writing" with molecular inks, has emerged at the forefront of bottom-up nanotechnology. The invention of dip-pen nanolithography (DPN) making it possible to manipulate structures with unprecedented precision.[2] While DPN allows routine patterning with a lateral resolution as small as 15 nm, its most notable limitations involve molecular ink flow. DPN involves dipping an atomic force microscope (AFM) tip into an ink, and then depositing this ink onto the substrate. Over time, all the ink can be used up, meaning that the tip must be redipped into the ink for extended use.

In order to improve upon this technology, a natural step would be to develop some way of providing continuous ink flow. In fact, a new method called fountain-pen nanolithography (FPN) has been developed that incorporates a microfluidic system into traditional DPN techniques to enable continuous ink feed.[3] One type of FPN device being developed is known as the nano fountain probe, which can be mounted to a commercial AFM instrument. This chip has an on-chip ink reservoir connected by microchannels to a volcano-shaped dispensing tip. The ink flows from the reservoir, through the channels, and is deposited at the tip. Since the cross-sectional dimensions of these channels are 5 µm in width and 0.5 µm in height, capillary action provides the force needed to drive the ink through the channels to the tip, where it is deposited with an atomic force microscope in the same manner as DPN

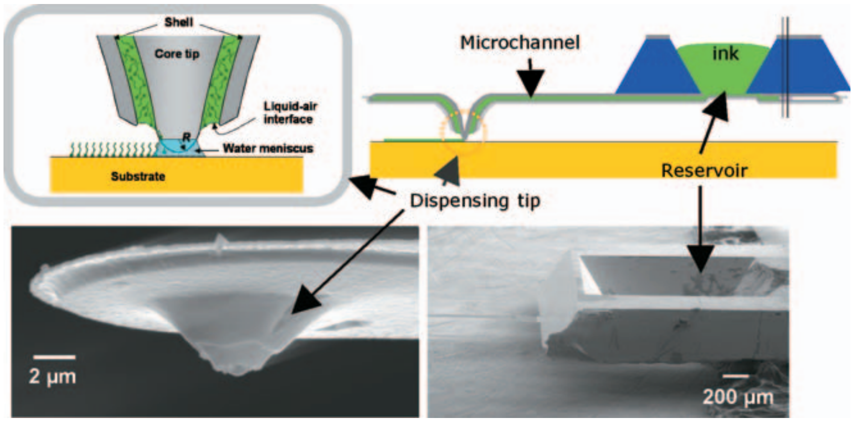

Figure 1: Diagram and SEM images of nano fountain probe. The image in the upper left corner shows deposition of ink (represented in green), while the image at the upper right illustrates the spatial relationship between the ink reservoir and the dispensing tip.

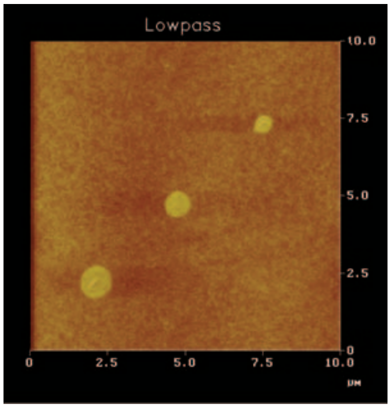

Figure 2: Lateral force image of patterned dots after dip-pen nanolithography has been performed with MHA molecules on an Au substrate (10μm x 10μm).

(Figure 1). With an ink reservoir, ink can be deposited over a much longer period than with DPN, but without sacrificing spatial precision.

Now the challenge is to improve the nano fountain probe so that it is a viable replacement for traditional DPN techniques. One of the first steps in this direction involves determining which inks can be used in the device, and in what concentrations. In this project the goal was to investigate the effects of varying the concentration and contact time on the behavior of the molecular inks used in DPN and FPN. This information could then be used to further develop nano fountain probes, making them a vast improvement over traditional DPN techniques.

Background

The exact mechanisms by which DPN works are still not fully understood.[4–7] Still, several pieces of this process seem to follow certain rules. A model, known as the "two-dimensional random walk model," has been proposed to explain the diffusion of the ink molecules.[4] In this model ink deposited from a tip fixed in position can be thought to move on a two-dimensional lattice with trapping sites. In other words, molecules of ink are considered immobile once they reach a bare metal site on the substrate (a "trapping site"), and molecules that have not yet reached a site naturally find the unoccupied trapping sites closest to the tip. In this way the molecules can be thought to move outward from the tip, flowing on top of previously trapped molecules to find available sites, until enough molecules have been immobilized to create a status of equilibrium (when the dot reaches its maximum size). The transport of the molecules is driven, in a way, by a simple concentration gradient; molecules move from areas of high density (around the tip) to those of low density (farther away).

There are two substances that are most commonly used in dip-pen nanolithography: octadecanethiol (ODT) and mercaptohexadecanoic acid (MHA). Both of these substances have been studied to create diffusion models and find relationships between diffusion rates and other factors. It has been found that temperature is one of the key factors in determining diffusion rates of ink substances. For both ODT and MHA, the molecular transport rate increases exponentially with increasing temperature. Humidity is another important factor, and it appears that the temperature dependence observed is strongly affected by relative humidity.[5,6,7] In addition, factors such as the concentration of the ink substance are believed to affect diffusion rates, but the exact nature of this relationship is unclear. Our intent was to explore the effects of changing ink concentrations and contact times on dot size.

Approach

Sample Preparation

Solutions of 16-mercaptohexadecanoic acid (MHA) in ethanol were prepared in the following concentrations: 2.0, 1.0, 0.5, 0.4, 0.3, 0.2, and 0.1 mM. These solutions were all prepared by dissolving MHA powder into ethanol solution and then heating (if necessary) to allow the MHA to fully dissolve. Silicon nitride cantilever probes were then immersed in the solutions for approximately 30 seconds and then dried using tetrafluoroethane. The tip was then loaded onto a commercial AFM instrument (Dimension 3100, Digital Instruments).

Concentration and Contact-Time Experiments

In order to investigate the relationships among ink-diffusion rates, concentration, and contact time, traditional DPN techniques were used. The AFM was programmed so that the silicon nitride tip made contact with the gold substrate at three points, each with a different contact time. The first test had contact times of 50, 100, and 150 seconds, and the second test had contact times of 20, 40, and 60 seconds. Environmental conditions were kept relatively constant: each experiment had a temperature range of 1° C and a humidity range of 5 percent. However, over the course of these experiments, the overall temperature range was from 20° to 27° C, and the humidity range was from

57 to 68 percent. (Since changes in humidity and temperature are known to affect diffusion rates,[7] each data set would not be directly correlated to another; rather, trends would be analyzed.) After performing DPN, the resulting substrate was then analyzed using lateral force microscopy (or an analysis of changes in surface friction), and an image was produced depicting a frictional map of the substrate. This image could then be analyzed to determine the diameter of the ink "dots" deposited on the substrate (Figure 2). For each ink concentration, the deposition was repeated three times (in other words, nine ink dots were deposited), and the data were averaged from the tree trials. Each experiment was run several times, with different cantilevers, in order to prevent the effects of specific tip shapes determining ink deposition.

Multiple-Trial Studies

In order to test the effects of multiple trials on traditional dip-pen nanolithography, the same test was repeated several times to determine whether there were changes over time. A 1 mM solution was used, and only one dot was deposited, with a contact time of 150 seconds. The tip contacted the substrate for 150 seconds, then the surface was scanned to determine the ink diffusion, then the tip was reengaged and contacted the substrate for another 150 seconds in a different location. This was repeated 10 times, and the results were analyzed in the same manner as before.

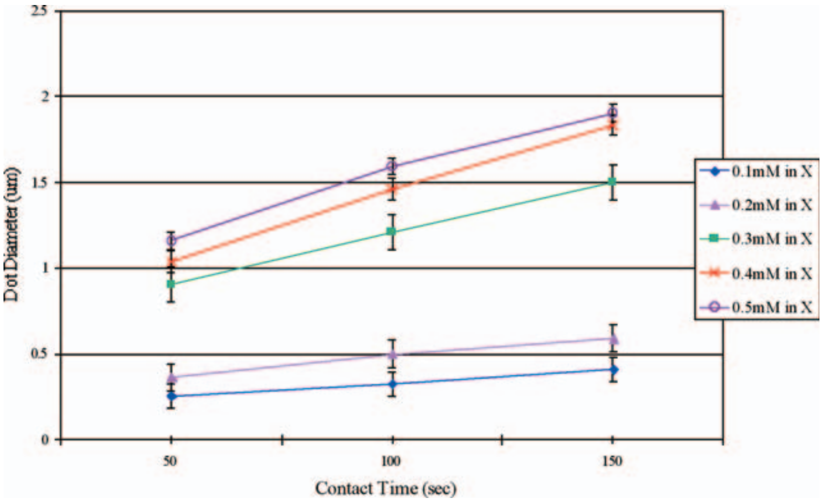

Figure 3: Graph of dot diameter vs. contact time for 50, 100, and 150 seconds (23.0° to 23.6° C, 59 to 62 percent humidity).

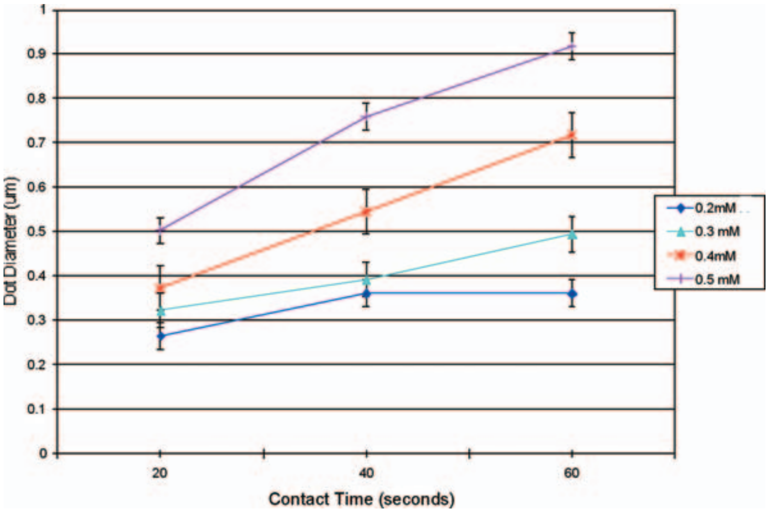

Figure 4: Dot diameter vs. contact time for 20, 40, and 60 seconds (22.0° to 22.9° C, 57 to 62 percent humidity).

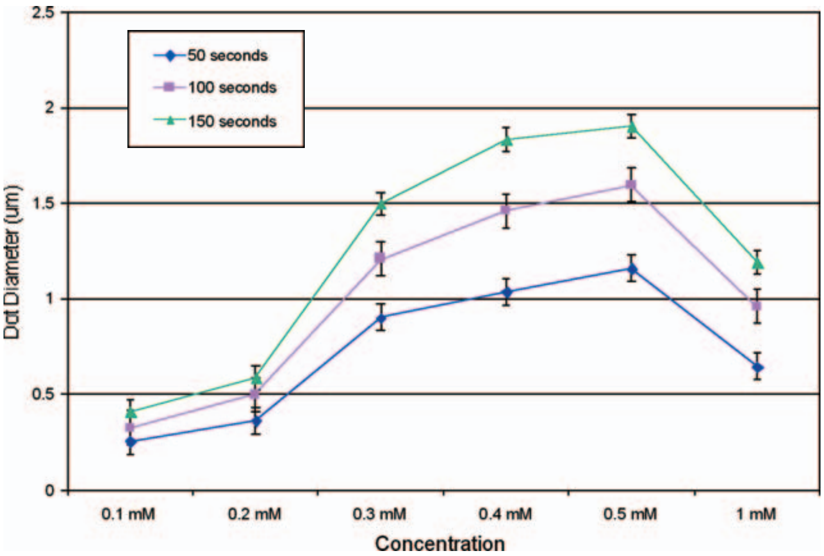

Figure 5: Dot diameter vs. concentration for three contact times (23.0° to 23.6° C, 59 to 62 percent humidity).

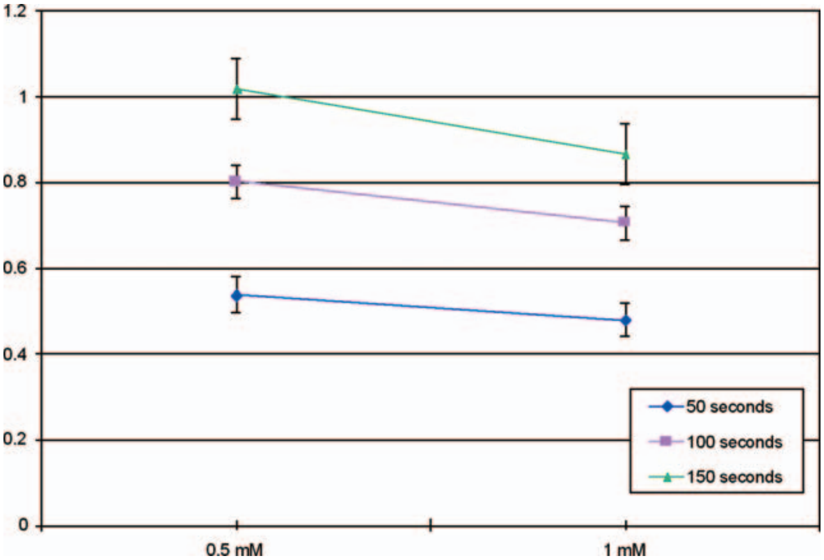

Figure 6: Dot diameter vs. concentration for three contact times (20.5° to 20.9° C, 64 to 67 percent humidity).

Results

Concentration and Contact-Time Experiments

After performing dip-pen nanolithography with various concentrations of MHA in ethanol, it is clear that there is a relationship between contact time and dot diameter. For each of the concentrations tested, the dot diameter increased with increasing contact time. As shown in Figures 3 and 4, however, higher concentrations showed more of a dependence on contact time than lower ones. In both figures we see that the slope of the line in the graph increases with every increasing concentration. In other words, the higher the concentration, the more the dot diameter seems to be affected by contact time. The implications of this information are pertinent when it comes to nanolithography precision. We see that for larger concentrations. The inks are much more sensitive to changes in contact time than are lower concentrations. This means that if lower concentrations are used (around 0.1 or 0.2 mM), contact time does not need to be precisely controlled to produce similar results. For a fountain-pen device, this would mean that a lower concentration would allow for more flexibility in contact time, without sacrificing much precision.

We can also see from the data that there is a relationship between concentration and dot diameter. Generally speaking, the larger the concentration, the larger the dots were, as shown in Figures 5. In this figure, however, we also see that the 1 mM solution does not follow the trend of the others. This test was run twice, both with similar results, and then an additional study was conducted comparing just 0.5 mM to 1 mM (Figure 6). In all of these tests, the 1 mM solution did not produce the largest dot diameters, and, in fact, in the first test three other solutions produced larger dots (Figure 5).

When a larger concentration of 2.0 mM was tested, we can see that the trend continues, as shown in Figure 7. The dot diameter increases steadily with increasing concentration until the concentration reaches 0.5 mM, after which the dot diameter begins to decrease. This decrease could be attributed to an increase in viscosity. In other words, higher concentrations have higher viscosities and this could cause an eventual decrease in the diffusion rate of the ink from the tip, though this is a theory that would have to be tested. Nonetheless, it is apparent that 1.0 and 2.0 mM solutions produce smaller dots than a 0.5 mM solution and that this information could be important in the enhancement of nano fountain probes. For example, higher concentrations approaching saturation are less than ideal for microchannels. In a saturated solution particles can leave solution and clog the channels preventing good flow. However, if high diffusion rates can be achieved by lower concentrations, far from saturation point, these solutions may be better suited for FPN devices.

Multiple-Trial Studies
After performing multiple trials of the same experiments, it is clear that trial number has a dramatic effect on dot diameter. In Figure 8, we see the results of 12 separate experiments. With the exception of only one experiment (number 7), the dot diameter decreased by a significant amount after each trial. By the third trial, there was a significant discrepancy in dot diameter from the first trial. In order to further test this behavior, a test was repeated with only one concentration for 10 trials instead of just 3. In Figure 9, we see that the dot diameter in both the x and y directions decreases steadily across the 10 trials. We can also see, though, that this relationship is nonlinear; the amount by which the diameter decreases is larger in earlier trials than in later ones. Nonetheless, the change in dot diameter between the first trial and the last is significant: in the x direction there is a decrease from 1.016 µm to 0.195 µm, and in the y there is a decrease from 1.014 µm to 0.197 µm, decreases of 80.8 percent and 80.6 percent, respectively. These changes are significant and demonstrate the limitations of dip-pen nanolithography. If over a course of only 10 trials the dot diameter decreases by more than 80 percent, it is fair to assume that over long periods of time, DPN is not sufficiently precise. The need for a fountain-pen device that can provide continuous ink flow is apparent; such a device would theoretically produce 0 percent depletion in dot diameter over an extended period of time and would therefore be much more useful.

Conclusions

It seems that there are definite relationships among concentration, contact time, and DPN dot size. In general, longer contact times create larger dots, though this dependence is stronger for higher concentrations than for smaller ones. We see that a 0.1 mM solution is the least affected by changes in concentration. It is also clear that there is a relationship between concentration and dot diameter. Higher concentrations cause larger dot diameters until this reaches a maximum at 0.5 mM, after which the sizes start to decrease. This may be due to an increase in viscosity or an unknown factor. We have also shown in this study that multiple trials of

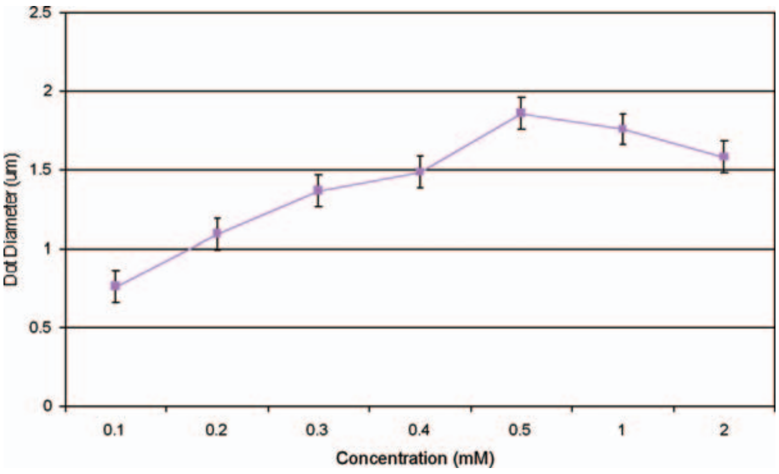

Figure 7: Dot diameter vs. concentration for contact time of 150 seconds.

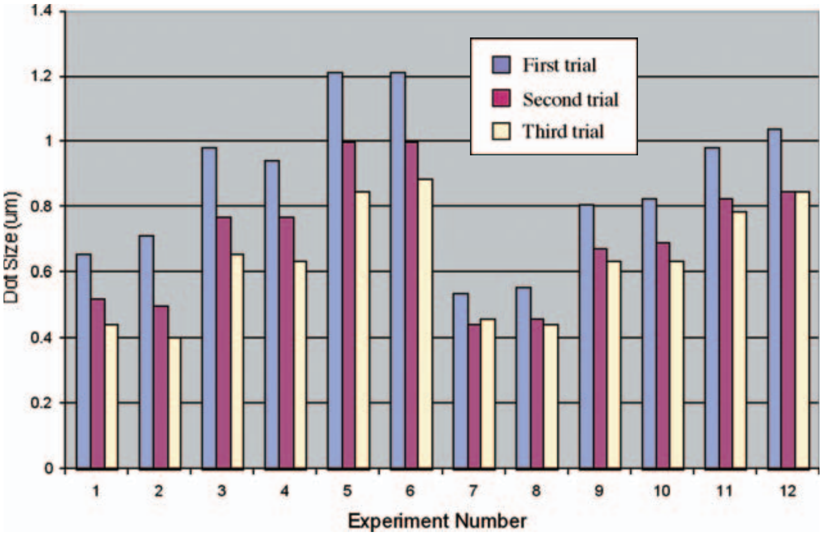

Figure 8: Dot diameter across three trials for 12 different experiments (0.5 mM, 20.9° to 21.7° C, 61 to 65 percent humidity).

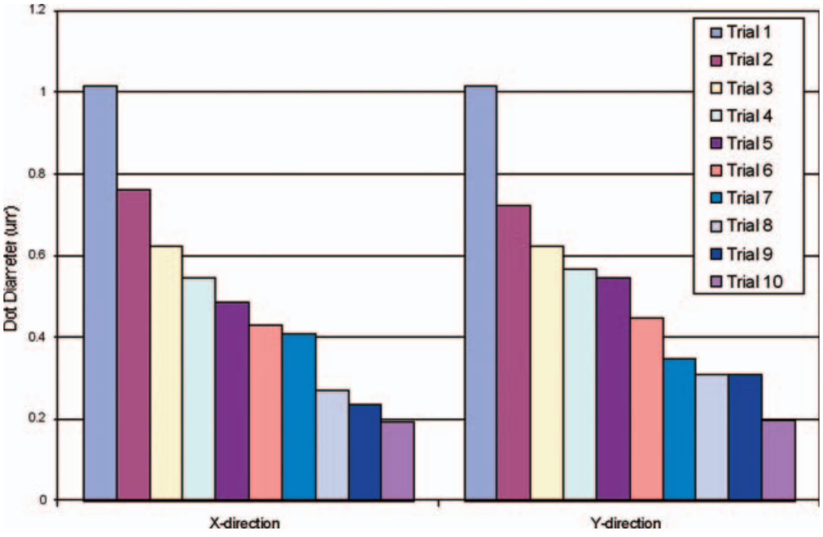

Figure 9: Change in dot diameter across 10 trials (1 mM, 22.7° to 23.1° C, 45 to 50 percent humidity).

DPN using the same tip result in dramatic decreases in dot diameter when other conditions are more or less constant.

Further studies are required to determine the exact nature of these relationships for other inks and other concentrations. In order to fully understand the behavior of these inks and to determine which ones are best suited to nano fountain probes, more studies must be done to determine exactly which concentrations produce the desired diffusion rates, as well as those that work most effectively in the microchannels. Through these studies nano fountain probes could one day become a viable replacement for traditional dip-pen nanolithography tips.

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