## Journal of Experimental Nanoscience

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t716100757

# Feature size dependence on hysteresis due to relative humidity ramping and patterning order in dip-pen nanolithography

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**To cite this Article** Nafday, O. A. and Weeks, B. L.(2007) 'Feature size dependence on hysteresis due to relative humidity ramping and patterning order in dip-pen nanolithography', Journal of Experimental Nanoscience, 2: 3, 229 — 237, First published on: 15 June 2007 (iFirst)

**To link to this Article: DOI:** 10.1080/17458080701268909

**URL:** http://dx.doi.org/10.1080/17458080701268909

*Journal of Experimental Nanoscience*,
Vol. 2, No. 3, September 2007, 229–237

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# Feature size dependence on hysteresis due to relative humidity ramping and patterning order in dip-pen nanolithography

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(*Received December 2006; in final form February 2007*)

The water meniscus that forms between an atomic force microscope (AFM) tip and the substrate has been shown to have variable height and width due to relative humidity (RH) hysteresis. The current study investigates the effect of this variability in meniscus shape due to RH on the feature size of patterns written with mercaptohexadecanoic acid on a gold substrate, using dip-pen nanolithography (DPN). The patterns were written under conditions of increasing and decreasing RH cycles with different tip dwell times. The variation in resulting dot sizes during the RH ramping (up and down) cycles was then measured. DPN patterning was also performed with increasing and decreasing order of dwell times at constant RH, in order to quantify whether the order of patterning has an effect on feature size. Significant differences were observed in dot areas patterned over many RH ramping cycles; whereas the order of patterning was observed to have an effect only for dwell times $\leq 5$ s.

*Keywords*: Atomic force microscope; Dip-pen nanolithography; Mercaptohexadecanoic acid; Water meniscus; Relative humidity

## 1. Introduction

Today, Dip-pen nanolithography (DPN) has emerged as a widely used scanning probe lithography technique for manipulating materials at the nanoscale [1]. DPN is an application of the atomic force atomic force microscope (AFM) [2], which in itself is a primary tool for nanoscale investigations due to its ability to image surfaces at high resolution. A sharp AFM tip (silicon nitride ($Si_3N_4$), silicon or diamond, radius ~10–20 nm) is coated with inks [3–6] in the DPN method. Alkanethiols, specifically 16-mercaptohexadecanoic acid (MHA, HS $(CH_2)_{15}CO_2H$) is a general ink used to demonstrate DPN, and is often patterned on gold substrates because of the stable patterns formed by the strong gold-thiol bonds.

Thorough reviews related to DPN [7] and in general scanning probe lithography to explore supramolecular interactions [8] and nanochemistry aspects [9] among other

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*Journal of Experimental Nanoscience*
ISSN 1745–8080 print/ISSN 1745–8099 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/17458080701268909

applications, can be found in the literature. In DPN, the user has the freedom of choosing a variety of inks, and this has highlighted the need to study the ink transport process from the tip to the substrate to control the patterned feature architectures. The ink transport is suggested to occur through the bulk water meniscus [1] that forms between the tip and substrate as a result of capillary condensation. Studies investigating the role of the meniscus in DPN, specifically its effect on ink transport rates [10–13], direct imaging of its dynamic behavior [14, 15], and alternate ink transport mechanisms [16, 17] have identified meniscus shape dependence on relative humidity (RH).

While the role of the meniscus in DPN has been the subject of many studies, the effect of observed hysteresis in meniscus shape with RH on the patterned feature size has not been studied. The motivation behind this study was not only to investigate the effect of changing RH on feature size, but also to determine whether increasing and deceasing order of dwell times during patterning, results in differences in the patterned feature size. In previous work, the meniscus has been shown to exhibit hysteresis; the observed meniscus height at a certain RH during a RH ramp up cycle, is not the same as that observed during the RH ramp down cycle. In addition, the meniscus height during RH ramp up (15–100%) exhibits exponential growth after RH 70%, however on ramp down (100–15%) it shows a linear dependence on RH over relatively short equilibration times [14]. Logically, this hysteresis should have an effect on the size of patterned features as the ink molecules have been shown to be transported either through the bulk meniscus or at the meniscus interface. Since the meniscus size is not the same during ramp up and ramp down, we should observe a corresponding hysteresis in the patterned areas also if the ink is being transported through the meniscus.

This study investigates the effect of RH ramping on patterned feature size together with measuring the effect of the order of patterning (increasing/decreasing dwell times). The investigation of both these effects is important to the overall development of DPN as a feasible lithography tool as demonstrated by Salaita *et al.* in preparing DPN generated lithographic masters [18]. The study of the order in which the features are patterned is important because the meniscus formation is time dependent among other factors like substrate condition, contact angle, etc. Moreover in all the current DPN studies, it is implied that either a new meniscus is instantaneously formed when moving from patterning one feature to the next, or that the meniscus moves with the inked tip during the intermediate time frame. In either case, following an increasing or decreasing dwell time dot patterning scheme, at a fixed RH, should have little effect on the patterned dot size. The implicit assumption here, is that the meniscus formation at the new patterning site is quicker than the least dot dwell time in the patterning scheme. However, if the dwell time is very short, the tip moves to a new position before the ink has a chance to transport through the meniscus. In this scenario, one would expect significant differences in patterning rates and thus feature sizes.

## 2. Experiment section

DPN experiments were performed with MHA (90%) obtained from Sigma-Aldrich (St. Louis, MO). A 1 mM MHA solution in ethanol (95%) was prepared and sonicated to ensure uniform mixing. DPN patterning was performed using a Pacific Nanotechnology (Santa Clara, CA) Nano-R$^{TM}$ AFM with a RH control chamber built in-house. For increasing the RH, an ultrasonic humidifier was used. The RH was measured with a hygro-thermometer with an accuracy of ±3% RH and ±1°C. MHA DPN experiments were performed from 20% to 86% RH, sufficient time was allowed for each RH value to equilibrate before DPN patterning was started. The AFM was operated in contact mode at room temperature (24 ± 3°C). MHA dots were patterned on freshly sputtered gold deposited on cleaved 1 $cm^2$ mica sheets. Standard "A" type silicon nitride ($Si_3N_4$) AFM cantilevers provided by NanoInk Inc. (Skokie, IL), were used for DPN. The cantilever was inked with the 1 mM MHA solution and DPN generated dots were patterned by allowing the inked cantilever tip to be in contact with the gold. The patterns were imaged in lateral force microscopy (LFM) mode to reveal friction force contrast information.

The present paper is organized into two sections. The first section investigates the effect of multiple RH ramping (up and down) cycles on the hysteresis in dot feature size. In these experiments, dots were patterned in a range of dwell times (10–60 s), each patterning cycle consisting of a RH ramp up and ramp down. Thus in any particular cycle, the dots were patterned at each RH, ranging from 20% to 86% in ramps (up and down) of ~20%; at least five such cycles were performed during the course of a single experiment.

The second part of this paper investigates if the order of patterning affects dot feature size. Experiments were performed at 20% and 60% RH, while the dots were patterned by two schemes of dwell times in each run. In scheme 1 (S1), dots were patterned in the order 1 s to 30 s to 1 s and in scheme 2 (S2), dots were patterned in the order 30 s to 1 s to 30 s dwell times. In S1, the exact times were 1, 2, 5, 10, 15, 20, 25, 30, 25, 20, 15, 10, 5, 3, 2, 1 s in that order (4 by 4 array). Similarly for S2, the dwell times were 30, 25, 20, 15, 10, 5, 3, 2, 1, 2, 5, 10, 15, 20, 25, 30 s in that order, also a 4 by 4 array. The RH was kept constant; any particular run consisting of S1 and S2 scheme of dots being patterned one after the other, in that order. At 20% RH, 12 such runs were conducted while the experiments at RH 60% consisted of two separate experiments consisting of a total of 22 runs. At RH 60%, the first experiment consisted of 12 runs and the second consisted of 10 runs. The tip was freshly inked only at the start of an experiment at a particular RH. The experiments were repeated at a higher RH (60%) because a larger meniscus compared to that observed at RH 20%, would be expected to form. If the order of patterning affected feature size, then the ratios of dot areas patterned during an increasing order to those patterned in a decreasing order, would be expected to vary significantly and have values greater or lesser than unity.

It should be noted that the tip is always in contact with the gold substrate during patterning throughout the course of these experiments. Thus the tip creates a dot feature after dwelling for a certain time, and is rapidly moved to dwell at a different location without breaking contact with the substrate. Presently, we did not attempt to investigate the effect of breaking the water meniscus by withdrawing the tip nor did we observe the effect of tip speed between intermediate patterning on the water meniscus. The scope of this paper was to study the effect of RH hysteresis and patterning order on feature size, and although the effects of tip lifting on meniscus formation are possible, it may not matter whether the tip is lifted or continuously in contact with the substrate.

## 3. Results and discussion

The meniscus height is an important factor during the hysteresis process; at RH > 70% it has been shown to vary between 100 nm to 1200 nm [14]. The effect of the hysteresis in the meniscus on patterned feature size has not been quantified, since meniscus size is observed to be orders of magnitude larger than that predicted theoretically by the Kelvin equation [19]. The dot size dependence on RH (increase in dot area with increasing RH) of a hydrophilic ink like MHA is well known; however no direct measurement of feature size change due to RH hysteresis has been carried out. This information is useful for predicting feature size of other hydrophilic inks which show an increased transport rate with an increase in RH, similar to MHA.

Figure 1 shows the experimental manifestation of meniscus shape hysteresis on MHA dot size patterned at similar RH, during ramp up and ramp down. Figure 1a shows MHA dots at RH 70%, patterned on gold during a typical RH ramp up cycle. Figure 1b shows MHA dots at RH 70% during the same RH ramp down cycle. The measured dot sizes after 10 s to 60 s dwell times in figure 1a and b are clearly different, suggestive of meniscus hysteresis due to RH ramping. This difference in dot sizes was reproducibly obtained over multiple ramping cycles; although only the MHA dots of one cycle were shown for clarity. Figure 1c shows the measured dots sizes of figure 1a, b in the logarithmic scale, after 10 and 60 s dwell times, each cycle consisted of a RH ramp up and ramp down. Clear differences in dot areas are evident, as seen by the hysteresis between the filled (RH ramp up) and hollow symbols (subsequent RH ramp down). This hysteresis in dot areas was observed for all cycles over all (10 s to 60 s) dwell times, however only the 10 s and 60 s dwell times are presented for clarity.

Significantly, the difference in dot areas shown in figure 1c is similar to that observed by Peterson *et al.* [10], where the MHA dot areas (ink transport rates) during RH ramp up were observed to be lower than those observed during RH ramp down. The shape of the curves in figure 1c also seem to follow an exponential trend on RH ramp up, while a relatively linear behavior is observed on ramp down. This is similar to the meniscus height observations of Weeks *et al.* [14]. This qualitative curve comparison, although not observed in every experiment, is a direct effect of meniscus hysteresis due to RH, on patterned dot areas. In some experiments, opposite behavior was also observed, i.e. the dot areas during ramp *down* were *lower* than those observed during RH ramp up. This behavior may be explained by the different ink coating protocols and substrate (gold) preparation methods. Peterson *et al.* [10] followed a wick deposited MHA tip inking procedure, while our tip was coated from a MHA solution. The gold used by Peterson *et al.* [10] was template stripped gold while our experiments were conducted with sputtered gold. It should also be noted that the time scale of our experiments was at least an order of magnitude lower than the experiments of Peterson *et al.* [10]. A typical RH ramp up and ramp down cycle in our experiments took about two hours, whereas the hysteresis in ink transport rates reported by Peterson *et al.* [10] are observed over 20 hours. Moreover, the opposite hysteresis behavior observed in some experiments cannot be compared directly to the environmental scanning electron microscope (ESEM) observations of Weeks *et al.* [14]. The ESEM meniscus height observations were conducted with an *uninked* tip on gold and at a pressure of ~8 mbar, while our results were obtained with an inked tip at 1 bar. The local water meniscus formation

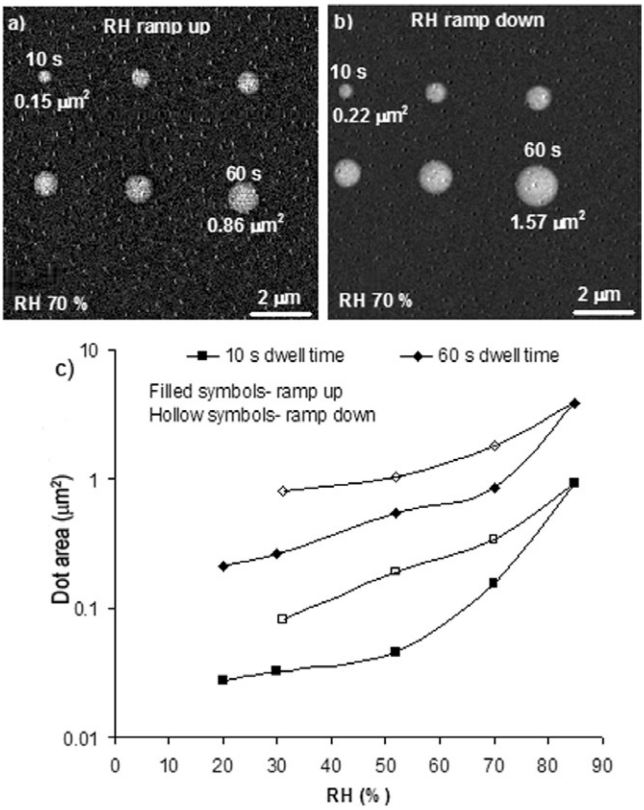

Figure 1. (a) Representative LFM images of MHA dots patterned in cycle 1 during ramp up at RH 70% after 10–60 s dwell times. (b) LFM images of dots patterned in cycle 1 during ramp down at RH 70% after 10–60 s dwell times. Although the RH is the same, there is significant difference in dot areas after the same dwell times, due to meniscus hysteresis. (c) Experimental evidence of hysteresis in meniscus shape on dot areas measured in figure 1a and b in the logarithmic scale, patterned after 10 s and 60 s dwell times, the cycle consisting of RH ramp up and ramp down. The dot areas shown were patterned during the same cycle. This hysteresis in dot areas was observed for all cycles of RH ramp up and ramp down.

conditions around an inked tip in contact with the substrate, are expected to be significantly different from those around an uninked tip, especially if the ink is a hydrophilic ink like MHA. Thus slight differences in tip condition, ink coating protocols, substrate preparation and pressure leading to different contact angles between the tip and the substrate may lead to lower ink transport rates during RH ramp down in some cases. However, regardless of whether the behavior is similar or opposite, there is significant hysteresis in dot areas during the RH ramp up and down cycles, which is the focus of this study.

The second part of this study was to investigate the effect of order of patterning on feature size. The order of patterning becomes important when DPN is employed as a lithography tool [18]. DPN generated features could potentially affect the quality of subsequent processes, highlighting the importance of investigating patterning order on feature size. The 1 s, 2 s and 4 s dwell time dots patterned by DPN, in the study by

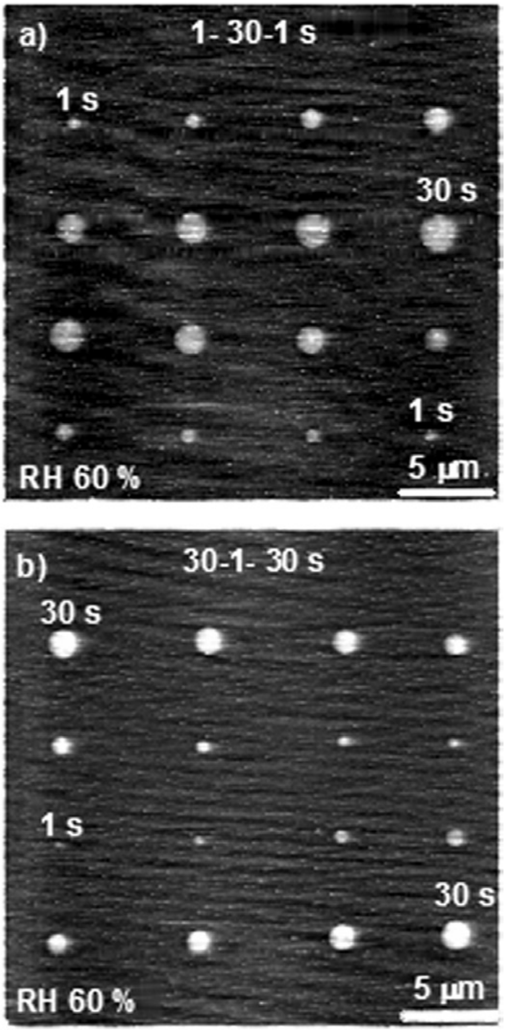

Figure 2. (a) LFM image of dots patterned by S1 (1–30–1 s) and (b) by S2 (30–1–30 s) at RH 60%. The dots in the 4 by 4 array in both 2a and b are patterned from left to right in each row, in that order.

Salaita *et al.* [18] are not only within the range of our patterning times (1 s to 30 s), but we also investigate the order in which they should be written, conceivably in other complex DPN patterning schemes. Potentially, the impact of the patterning order could affect feature size in processes similar to DPN, conducted at controlled RH like semiconductor chip lithography and circuit design. Figure 2 shows the representative MHA dots patterned with two different schemes (S1 and S2) at RH 60%, each scheme representing a different order of patterning dots. Figure 2a shows the dots patterned by S1 (1–30–1 s), representing an increasing order of dwell time dots being patterned first. Figure 2b represents the dots patterned by S2 (30–1–30 s),

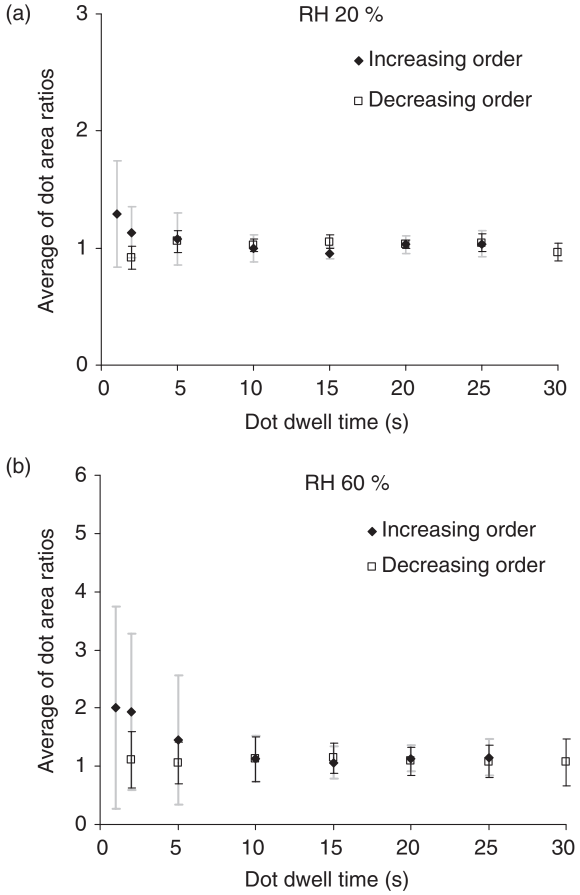

Figure 3. (a) Average values of the ratio of dot areas patterned at RH 20% over all 12 runs, by both increasing and decreasing order of dwell times are compared to each other. (b) A similar result is shown for both the dwell time patterning orders at RH 60%, over two separate experiments consisting of a total of 22 runs. In both 3a and b, for dwell times $\leq 5$ s, a significant difference during increasing and decreasing patterning orders is observed, suggesting that patterning order does have an effect on feature size. For dwell times greater than 5 s, the dot area ratios are within the error bars and around unity, suggesting no effect of patterning order.

representing a decreasing order of dwell time dots being patterned first. The dots obtained by both S1 and S2 contained two subsets of 1–30 s and 30–1 s each. In S1, there were two 1 s dwell time dots, while in S2, there were two 30 s dots patterned.

Figure 3 represents the average of ratio of the dot areas measured during the low to high dwell time (1–30 s, increasing order) and high to low dwell time (30–1s, decreasing order) patterning schemes over all runs. The dot area obtained after each common (2, 5, 10, 15, 20, 25 s) dwell time during the 1–30 s (increasing) dwell time patterning, was divided by the corresponding dot area obtained during 30–1 s (decreasing), in each run, by both S1 and S2. The average of dot area ratios thus obtained, is shown in figure 3a at RH 20%, over 12 runs. Figure 3b represents a similar comparison at RH 60%, where 22 runs were conducted. In any particular run, S1 and S2 patterning schemes were patterned alternately as mentioned earlier. The 1 s dwell time data could not be plotted because in the decreasing order of patterning (figure 3, hollow symbols), as there was only one 1 s data point in each run (see figure 2b); thus a ratio of the 1 s data point could not be obtained. Similarly, there was no 30 s ratio average data point in figure 3 for the increasing order of patterning (figure 2a).

The uncertainty while calculating the patterned dot diameters (areas) in each run, over all dwell times by both S1 and S2, was ~8%. Thus, when the ratios of areas (e.g., the ratio of the 2 s dot area during 1–30 s patterning, to the 2 s dot area during the 30–1 s patterning in each run) was calculated by propagation of errors, the resultant error in the ratios in each run was ~3%. Thus the estimated average uncertainty over all runs was found to be ~40%. This was similar to the standard deviation obtained over all runs. The average and standard deviations (denoted by error bars in figure 3) of the ratios were reported over all runs at each RH (20% and 60%). Moreover, in order to determine that the average ratios for all dwell times were statistically significant, a *t*-test analysis [20] was performed with 90% confidence, at both RH 20% and 60%. For the 2 s dwell time, the average ratio was found to be significantly different, while for the 5 s dwell time it was marginal. The ratios were found to be around unity (constant) for dwell times greater than 5 s (figure 3), signifying that the order of patterning dots does not affect feature size. This suggests that for short (1, 2, 5 s) dwell times, the patterned dot areas during an increasing patterning order are significantly different than those obtained during a decreasing patterning order.

A significant difference in the ratios implies that the order of patterning *does* matter for short contact times. Thus in order to reproducibly pattern features at a constant RH, we recommend using patterning schemes of dwell times greater than 5 s, thus eliminating any effect of patterning order. The $\leq$5 s dwell time schemes should be patterned separately from patterning schemes containing dwell times greater than 5 s. These observations should be seen as an additional control tool for obtaining reproducible feature sizes in DPN. It should be noted that the order of patterning features is RH independent. Thus rather than patterning order, it is the dynamic evolution (hysteresis) of the meniscus during RH ramping, that has a greater effect on feature size in DPN.

## 4. Conclusions

This study presents the first direct evidence of the effect of observed hysteresis in meniscus shape on patterned feature size. Differences in dots areas were reproducibly obtained during multiple RH ramping (up and down) cycles, although no particular trend in dot area behavior was observed. We also demonstrate that the order of patterning features, which becomes important during patterning in the transient meniscus regime, does not affect the feature size significantly after long dwell times. A significant difference in dot areas was observed for dwell times $\leq$5 s; the dot areas patterned during increasing and decreasing orders of patterning were significantly different at constant RH. Thus when patterning from long to short (and *vice versa*) dwell times, the features patterned may not be of similar area, especially at the short ($\leq$5 s) dwell times. We believe that the meniscus does travel with the tip to every new patterning position, although a more detailed study of the tip speed during the transition between patterns would elucidate the matter further. This knowledge of hysteresis in dot areas during RH ramping and the observed differences in dot areas (for short dwell times) when following increasing/decreasing dwell time patterning orders, may be applied to control feature size of hydrophilic inks similar to MHA.

## Acknowledgements

This work was supported by the Petroleum Research Fund and the Office of Naval Research (# N00014-06-1-0922).

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