Dip-Pen Nanolithography: What Controls Ink Transport?

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The influence of temperature and humidity on the growth rates of 1-octadecanethiol (ODT) and 16-mercaptohexadecanoic acid (MHA) monolayers deposited onto a gold substrate has been systematically studied in the context of dip-pen nanolithography (DPN) experiments. By analyzing a statistically meaningful data set, we conclude that for both inks the deposition rate increases with increasing temperature, and that this temperature dependence is strongly affected by relative humidity, chemical nature of the ink and substrate, and writing speed. We attribute these observations to the different solubilities of the ink molecules in water (both the water in the meniscus and on the cantilever walls). In addition, we report a set of experiments that demonstrate meniscus formation even at 0% relative humidity due to residual water that moves to the point of contact between tip and sample.

Introduction

Dip-pen nanolithography, a method for directly depositing molecules from an "ink"-coated atomic force microscope (AFM) tip onto a substrate of interest, is a powerful tool for creating microscale and nanoscale patterns of small molecules,[1,2] biological macromolecules,[3−5] conducting polymers,[3] and inorganic materials.[6,7] The technique also has been used to study monolayer growth and exchange processes in-situ with kinetic control over such processes.[8,9] Although DPN has emerged as a useful tool for fabricating nanostructures, the mechanism of ink transport is far from understood, and a data-consistent, quantitative analysis of the factors that influence it has not been carried out. Some researchers have proposed that the meniscus is central to the transport process,[1,10,11] while others have concluded that in some cases water plays no role in the transport process.[12,13]

The patterning process in a DPN experiment can be broken into two elementary processes, Scheme 1. The first step is molecular transport from the tip to substrate, which in many cases involves dissolution of ink into the meniscus that naturally forms between the tip and sample. The second step is ink adsorption onto the surface and monolayer formation. Both the transport and adsorption of ink molecules often depend on several variables, including temperature, humidity, the physicochemical properties of the ink and surface, writing speed and tip−substrate contact force. To develop and fully control DPN, it is essential to increase our understanding of the relative importance of these variables for a set of representative inks and substrates.

In this paper, we report a systematic study of how temperature and humidity affect DPN patterning of two of the most widely studied inks, 1-octadecanethiol (ODT) and 16-mercaptohexadecanoic acid (MHA), when deposited onto polycrystalline gold. ODT and MHA form hydrophobic and hydrophilic self-assembled monolayers (SAMs), respectively, on Au, and both adsorbates lead to well-packed monolayers with a molecular density of 4.6×10^{14} mol/cm^2.[14] This holds true for both solution and DPN deposited monolayers.[8]

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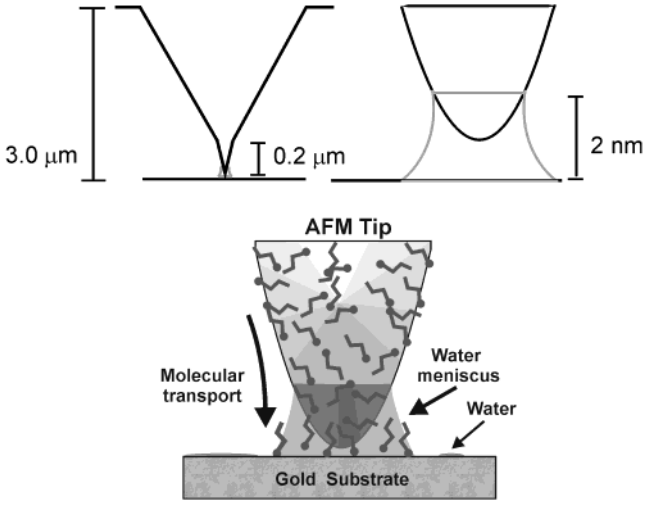
SCHEME 1: Schematic Diagram of the DPN Process



Experimental Section

All DPN experiments were performed using a Park Scientific CP AFM[15] encased in a plastic glovebox.[16] The temperature was controlled with two fan heaters (a total power of 800 W), which were used to raise the temperature to the desired setting but turned off during DPN data acquisition. For all experiments, the chamber containing the AFM was flushed with dry nitrogen,[17] prior to adjusting the relative humidity with water vapor monitored with a Fisher Scientific digital hygrometer.[18] With this system, the temperature could be controlled between 22 and 33 °C, and the relative humidity could be adjusted from 0 to 100%. Corresponding fluctuations of temperature and relative humidity during deposition of inks did not exceed ±0.2 °C and ±2%, respectively. UHV experiments were carried out with a Omicron VT UHV SPM in tapping mode. Line patterns and dot patterns were generated on gold-coated silicon oxide substrates.[19] AFM cantilevers (model no. MSCT-AUHW, purchased from ThermoMicroscopes) with a spring constant of 0.05 N/m were used for all DPN experiments.

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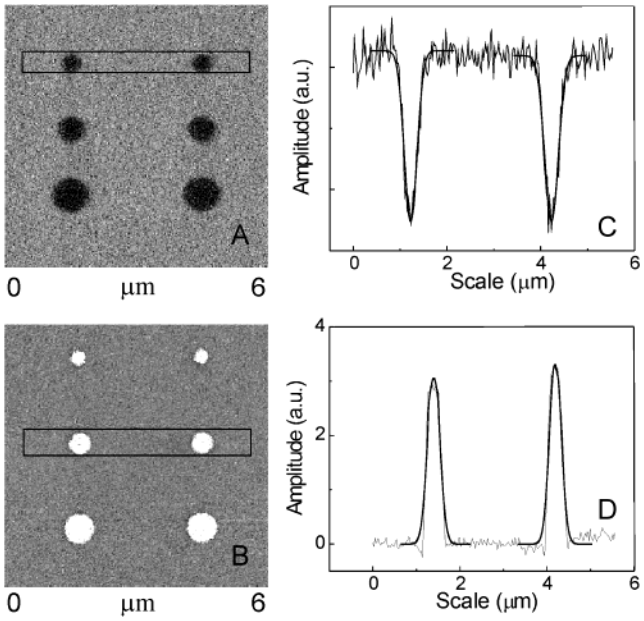


Figure 1. LFM images of (A) ODT and (B) MHA dots patterned onto a gold substrate under tip−substrate contact force of 0.5 nN and holding times of 2, 4, and 8 s; the frictional force profiles of (C) ODT and (D) MHA dot patterns. Thick lines represent Gaussian fits.

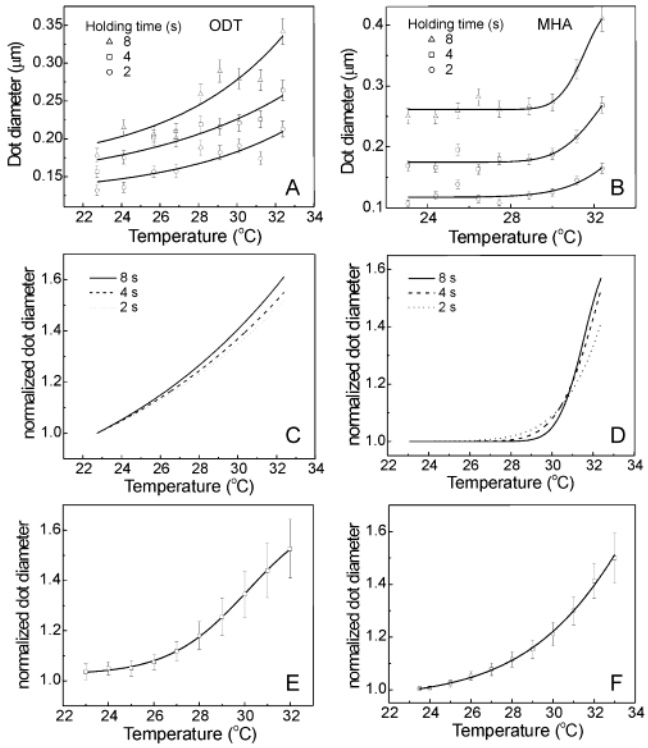


Figure 2. The temperature dependencies of the growth rate of (A) ODT and (B) MHA SAMs constructed from LFM images of dots (analogous to depicted in Figure 1), which were generated at nine different temperatures in the 22−33 °C temperature range (holding times: 2, 4, and 8 s); (C) and (D) normalized dependencies of the data presented in plots A and B; (E) and (F) normalized temperature dependencies of the growth rate of ODT and MHA dot patterns (respectively) constructed on the basis of 10 experiments performed under the same experimental conditions. The error bars are standard deviations.

Prior to ink-loading, all tips were cleaned in piranha solution (3:1; v:v; concentrated H_2SO_4:H_2O_2) for 30 min at room temperature. (Caution: piranha is an aggressive and explosive chemical. Never mix piranha waste with solvents. Check the safety precautions before using it.) ODT-coated tips were prepared by thermal evaporation of ODT onto the tips at 65 °C for 30 min. MHA-coated tips were prepared by immersing the entire cantilever into an acetonitrile solution saturated with MHA according to literature procedures.[1,2]

Results

Growth Rate as a Function of Temperature. To test the dependence of ink transport and nanostructure growth rate on temperature, we held an ink-coated tip (MHA or ODT) in contact (0.5 nN) with a gold surface for 2, 4, and 8 s at a designated temperature, Figure 1A,B. This patterning experiment was repeated nine times at nine different temperatures in the 22−33 °C temperature range. The time interval between patterning was 10 min,[20] which corresponds to a temperature ramping rate of 0.1 °C/min. If one analyzes the features generated in these experiments with respect to frictional force, one can see that there is a concentration gradient of the ink with coverage decreasing from the center to the edge of the dot, Figure 1C,D. In a plot of the average frictional force over the area defined by the DPN generated features and surrounding unmodified gold (rectangular boxes in Figure 1A,B), one can see bands associated with the patterned areas,[21] Figure 1C,D. In the case of ODT, the negative bands appear in the plot because the frictional force of the patterned areas is lower than that of bare gold, Figure 1C. In contrast, in the case of MHA, which forms a monolayer with a higher frictional force than the bare gold, positive bands appear in the plot, Figure 1D. The full width at half-maximum (fwhm) values for these bands can be used as an estimate of feature size and as benchmarks for studying the growth process as a function of temperature or humidity. The frictional force profiles were modeled as Gaussian distributions (thick lines, Figure 1C,D), and the data from these experiments were used to construct plots of dot diameter as a function of temperature, Figure 2. One can see that the growth rates for these two molecules (as measured by the change in dot diameter) increase with increasing temperature, which is consistent with previous reports.[13,22] These relationships can be modeled well as exponential dependencies without saturation but are complicated by other variables including tip coating and contamination of ink and gold substrate (vide infra). As a result, when one plots the statistical data for many experiments (10) the error bars for each data point are quite large, Figure 2E,F. In addition, a study of influence of temperature on the growth rate at different but fixed relative humidities shows that the growth rate increases faster with increasing humidity, Figure 3. It should be noted that the increase of the growth rate with increasing humidity is always observed for MHA, but the results are less consistent for ODT. In the discussion section, we will consider some of the reasons for variations in the growth rate of ODT SAMs.

Growth Rate as a Function of Humidity. To explore the role of humidity on ODT or MHA transport in a DPN experiment, dot patterns were deposited onto a gold substrate at holding times of 2, 4, and 8 s at a fixed temperature and intentionally varied humidities. In a typical experiment, the chamber with the AFM was flushed with dry nitrogen for an hour prior to commencing any experiments. The humidity was then adjusted by introducing water vapor into the chamber. The lowest relative humidity explored in these particular experiments was 5%. Others have suggested that MHA cannot be patterned below 15% relative humidity,[11] but in our hands and with our experimental apparatus, both ODT and MHA can be easily patterned onto a gold substrate at all humidities studied, Figure

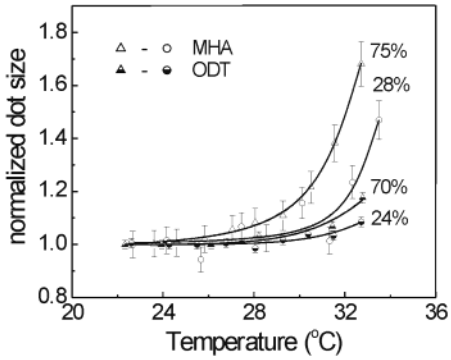


Figure 3. The temperature dependencies of the growth rates (as measured by change in normalized dot size) of ODT and MHA SAMs at different humidities. Each point is an average of three or more experiments. The fitted curves represent the temperature dependence for ODT and MHA dots generated with a tip−substrate contact force of 0.5 nN and a holding time of 4 s.

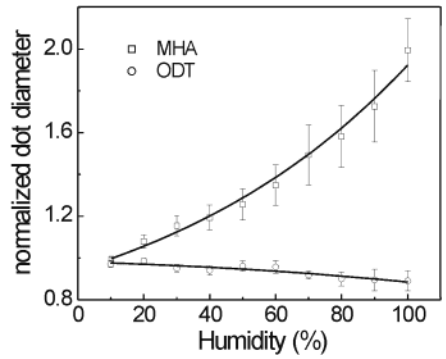


Figure 4. The humidity dependencies of the growth rate of ODT and MHA dot patterns based on 10 experiments performed under the same experimental conditions (tip−substrate contact force of 0.5 nN and holding times of 2, 4, and 8 s). The error bars are standard deviations.

4. Moreover, separate studies carried out by us according to the method of Sheehan and Whitman for doing DPN at 0% relative humidity[12] show that both molecules can be deposited onto gold even after the ink-coated tip and gold substrate were kept at 0% humidity for 24 h. The plots in Figure 4 show normalized dot diameter of ODT and MHA dot patterns as a function of humidity at fixed contact times (a measure of growth rates). These plots were constructed on the basis of averaging 10 experiments performed under the same conditions. In each experiment the relative humidity of the chamber was gradually increased from 5 to 100%. Nine dot patterns of MHA or ODT were deposited, as described above, at nine fixed humidities. The equilibration time between each set of experiments was 10 min. The analyses of the LFM images were performed according to the procedure described above. The effect of humidity on the growth of ODT and MHA patterns was found to be different, Figure 4. The growth rate of ODT SAMs at fixed temperature slightly decreases with increasing humidity, while the growth rate of MHA SAMs dramatically increases. The study of the relationship between growth rate and humidity at different temperatures reveals that for MHA the effect is more pronounced at higher temperatures, Figure 5A. For ODT, Figure 5B, growth rate at fixed temperatures shows little dependence on relative humidity, an observation consistent with that made by Sheehan and Whitman.[12] Note that the error bars associated with these measurements are as large as any numerical dependence on humidity that we would assign.

Additional Factors Affecting DPN Ink Transport. As described above, the growth rates of DPN patterns are affected

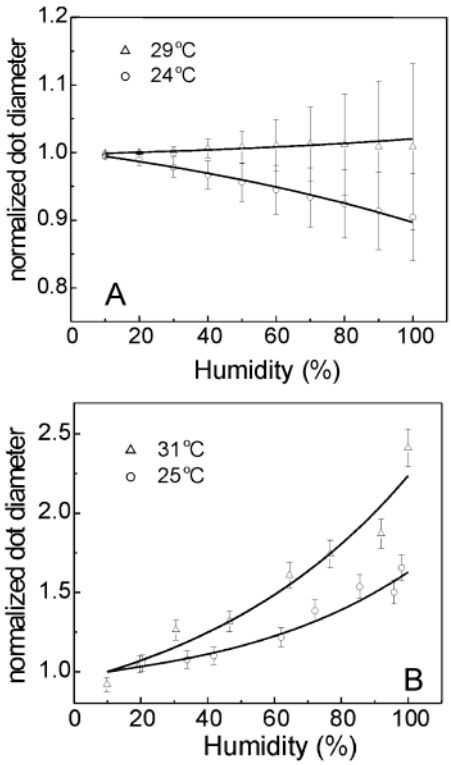


Figure 5. The humidity dependencies of the growth rate of (A) ODT and (B) MHA at two different temperatures. Plot A is based on four and six trials done at 29 °C and 24 °C, respectively. Plot B is based on three experiments performed at 25 °C and 2 experiments at 31 °C.

by temperature and humidity, but temperature and humidity are not the only factors that influence the deposition and growth rates. Indeed, moving the tip to form a line as opposed to holding it in place to form a dot affects growth rate and its dependence on both temperature and humidity, Figure 6. Growth rates for lines and dots were studied at a fixed writing speed and contact time, respectively, at a fixed humidity as a function of temperature (Figure 6A,B), or at a fixed temperature as a function of humidity (Figure 6C,D). In all cases, line width increases faster than dot diameter at all temperatures and humidities studied for both ODT and MHA. The difference in the growth rate is likely due to the large concentration gradient created in the line writing experiments as compared with the dot generation experiments. In the case of lines, as the ink-coated tip traverses the surface, it is exposed to clean gold creating a large driving force for ink deposition whereas in the case of the dots the system is closer to equilibrium; after the early stages of deposition much of the area of the gold substrate under the tip has been modified with the chemisorbing ink. Another potential reason for the difference in growth rates for lines and dots pertains to the water meniscus formation. The establishment of the meniscus and transport of water between the tip and surface are time dependent. For example, it has been shown that the meniscus does not fully form at high scan speeds.[23]

The Role of Humidity on Meniscus Formation. To test the role of humidity on meniscus formation, a NaCl crystal was used as a substrate. NaCl, like Au, is hydrophilic, but is very sensitive to water formation between tip and sample. Indeed, one can visualize the NaCl solvating effects of the water at the point of contact between tip and sample. For example, if one holds a bare tip[24] in contact with a NaCl crystal[25] for 1 min and then images the contact area as well as the surrounding area, one can see nanometer deep wells formed where the tip

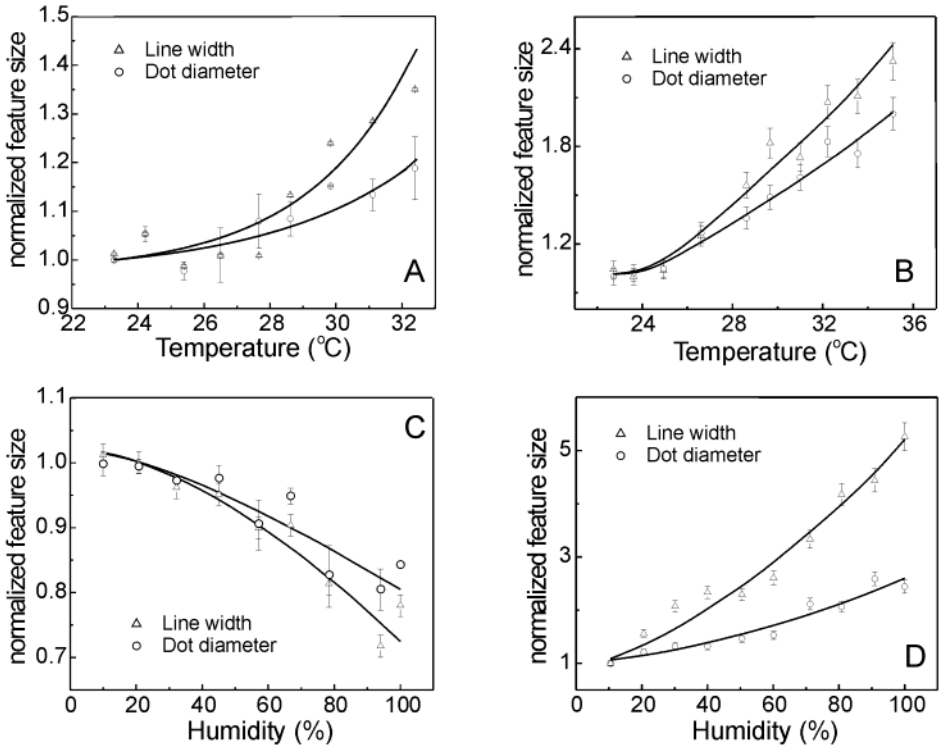


Figure 6. The temperature dependencies of the growth rate of dots and lines for (A) ODT and (B) MHA inks; the humidity dependencies of growth of (C) ODT and (D) MHA lines and dots. The holding time for ODT dots is 8 s, that for MHA dots is 3 s; the writing speed for ODT lines is 0.4 μm/s, that for MHA lines is 0.3 μm/s

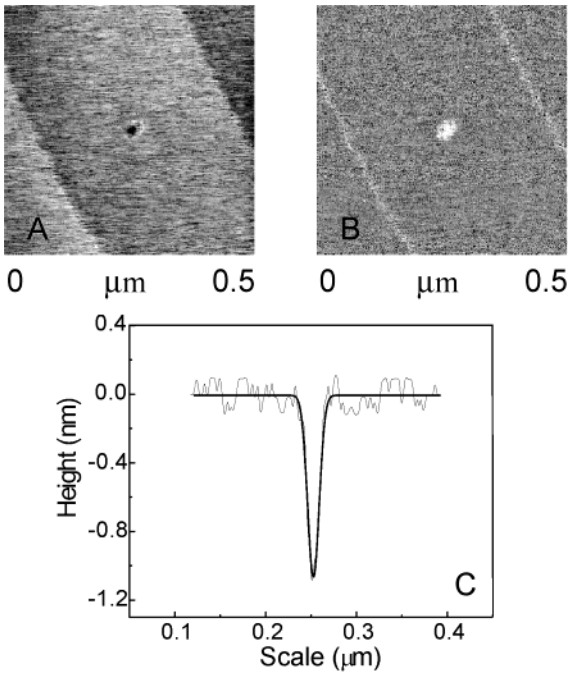


Figure 7. (A) AFM and (B) LFM images of a sodium chloride surface after a bare tip was held in contact with the surface for 1 min at 30% relative humidity; (C) the topography profile of an etch pit created on a NaCl substrate.

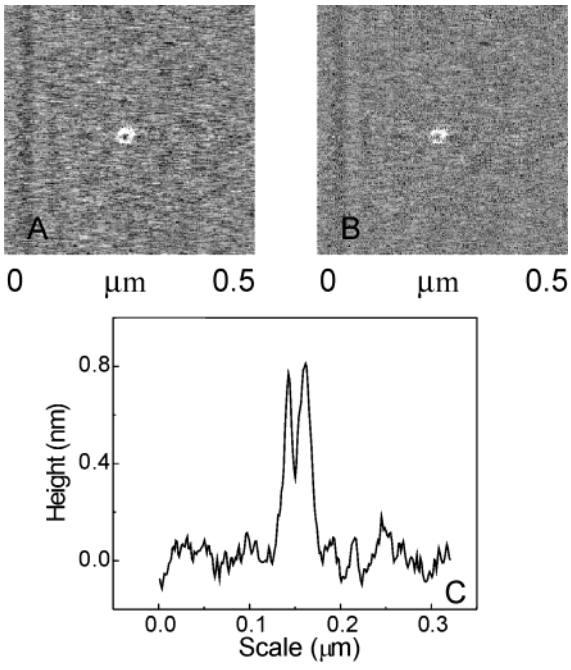
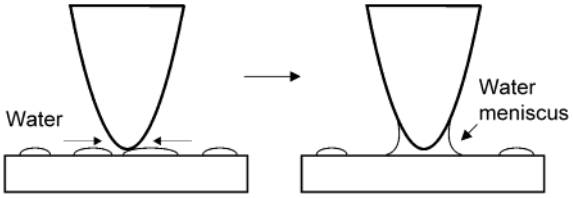


Figure 8. (A) AFM and (B) LFM images of a sodium chloride surface after a bare tip was held in contact with the surface for 1 min at 0% relative humidity, (C) the topography profile of an etch pit created on a NaCl substrate.

was in contact with the substrate, Figure 7. Significantly, if one studies this effect as a function of humidity, one can see that the meniscus forms even at low humidities, including the zero percent relative humidity conditions studied by Sheehan and Whitman,[12] Figure 8. The positive height profile of the feature in the AFM image appears as a result of recrystallization of a small amount of NaCl dissolved in the water meniscus near the periphery of the wells. To make sure that the observed features are due to water dissolution of the NaCl rather than mechanically induced tip damage, we measured the pit formation as a function of humidity. Indeed, the size of the pits (both diameter and depth) increase with increasing atmospheric water content over the 0−70% range. These data will be presented in a detailed manuscript elsewhere,[26] but the idea that water does not collect between tip and sample at low relative humidities[12] is incorrect. The meniscus must form from the residual water

SCHEME 2: Formation of the Water Meniscus from Residual Water on Sample and Tip Surfaces



that is on the substrate and tip, and it is well-known that when the tip is in contact with a substrate, the thermodynamically preferred location of that water is at the interface between tip and sample (a capillary force drives residual water to the point of contact between tip and surface),[27,28] Scheme 2. Finally, the only way to eliminate water from the system is to do the analogous experiments under UHV conditions. Indeed, under such conditions where the water meniscus does not form, we did not observe any changes in the surface topology of the NaCl even after scanning an 80 nm × 80 nm area for 1h.[26]

Discussion

The mechanism for ink transport in a DPN experiment is complicated, dependent on several variables, and could be different for different ink and substrate combinations. Regardless, without treating the substrate and tip to ultrahigh-vacuum conditions prior to doing a DPN experiment, water will always exist between an ink-coated tip and substrate as demonstrated with the NaCl substrates. Therefore, in discussing the DPN ink-transport process, we will assume that molecular transport from tip to surface occurs in the presence of water. Below we consider the role of some of the more important variables.

The Temperature Effect. As the temperature increases in a DPN experiment, the number of molecules solvated, diffusion rate of the molecules across the meniscus, and the adsorbate diffusion rate on the surface will be increased. Indeed, the total number of solvated molecules taking part in the transport process increases with increasing temperature because the ink dissolution/desorption process, which involves breaking and making of van der Waals interactions, is facilitated. Ink solubility is a thermally activated process and, therefore, increases with increasing temperature. The rate of ink dissolution into the meniscus depends on the strength of the intermolecular forces of the ink, temperature, the chemical composition of the ink including contaminants and cosolvents, and tip-coating uniformity. On the basis of 40 temperature experiments (duplicates of those depicted in Figure 2), we suggest that the primary factor in determining the temperature dependence of the growth rate, especially in the case of MHA, is the water solubility (desorption) of the ink molecules, a conclusion consistent with that of De Yoreo and co-workers.[11] The solubilities of both MHA and ODT, which are very low in water,[29] increase with increasing temperature. The thermoactivated dissolution process can be described by the van't Hoff equation:

$$S(T) = S(T_m)\exp\left[\frac{-\Delta H_f}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \qquad (1)$$

where $S(T)$ and $S(T_m)$ are equilibrium solubilities of the ink at melting and arbitrary temperatures, and ΔH_f is the ink enthalpy of fusion. The value ΔH_f represents the activation barrier to ink dissolution E. R is the gas constant, T_m is the melting point, and T is the temperature of the experiment in question. It is important to note that the magnitudes $S(T_m)$, ΔH_f, and T_m can be significantly affected by ink composition, including contaminants and cosolvents. The $\Delta H_f/RT$ ratio determines the shape of the growth rate dependence on temperature curves. In addition, it is important to note that the physical and, sometimes even, chemical composition of the ink is changing during an experiment and from experiment to experiment, which makes accurate modeling of the actual data from a DPN experiment difficult. Therefore, to compare data obtained with different tips on different days, we normalize each set of data so that the first value on each curve is unity. By normalizing, we minimize the contributions of extraneous factors, such as differences in probe sharpness, ink coating, hold time, and contact force, which can be highly variable from experiment to experiment, Figure 2C,D.

Figure 3 describes the dot size dependence of ODT and MHA on temperature at two different humidities. From these plots, one can see that the dot size (a measure of growth rate) at fixed contact time increases with increasing temperature, an effect which becomes more pronounced at high humidity, especially for the more hydrophilic MHA, Figure 3. These data are consistent with the humidity dependence of MHA deposition, Figure 4. The observed results for ODT look unusual at first glance; ODT is hydrophobic and might be expected to be independent of atmospheric water content, but we also observe slightly faster growth at higher humidity, Figure 3. As we show below this observation does not contradict the results of the humidity studies, Figure 4, where we observe, if anything, a small decrease in growth rate with increasing humidity.

The diffusion rate of molecules, υ, in the meniscus should follow a square root temperature dependence, $\upsilon \sim \sqrt{kT}$.[30] The increase in feature growth rate due to temperature, therefore, results from changes in both ink deposition and surface/reorganization diffusion rates. The latter depends on temperature according to the Stokes−Einstein equation: $D = kT/6\pi\eta a$. Here, k is Boltzman's constant, T is the temperature, η is the dynamic viscosity, and a is the average diameter of the molecules. The deposition and organization of molecules on the surface is consistent with the diffusion model of J. Jang et al.[10] Depending upon the relative magnitudes of the ink deposition and surface diffusion rates, a monolayer or multilayer structure can be formed as the initial surface structures. In the case of the multilayer, the molecules that are not chemisorbed can diffuse to the perimeter of the chemisorbed structure to continue feature growth. From the experiments described herein, we suggest that the transport of molecules from tip to surface, which is driven by ink-surface chemisorption forces, is dramatically affected by the molecular density gradient between the AFM tip and the gold substrate. This is clearly observed in the experiments, which compare growth rates and average feature heights for dots and lines, Figures 6 and 9. Note that the average feature height for a line is very dependent upon writing speed since an unmodified gold surface is constantly generated in the line writing experiment. By moving the tip as opposed to keeping it stationary, the maximum concentration gradient is kept constant. One can use the average heights b and areas A of the line and dot features, Figure 9, to calculate feature volume bA and compare the relative growth rates for the two processes. Such an analysis shows that the dynamic deposition growth rate (moving the tip) is approximately twice the static growth rate (holding the tip).[31] In addition, from the analysis of average feature height as a function of tip writing speed, Figure 9, one can determine the relationship between the writing speed and density of layer deposited. In the case presented in Figure 9, a relatively high-density monolayer is formed if the writing speed

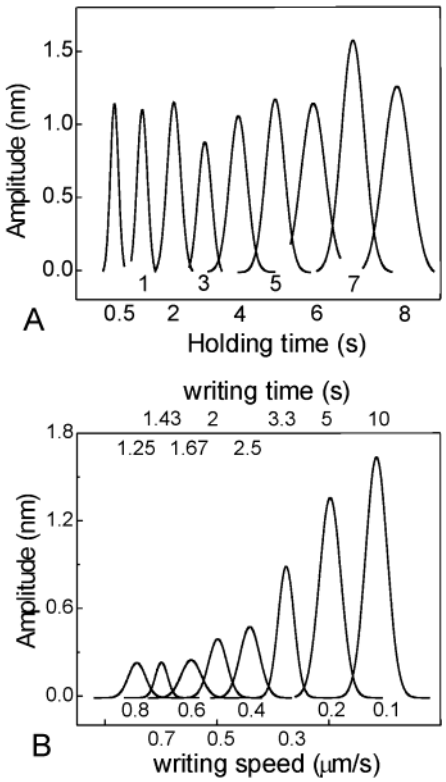


Figure 9. The topography profiles of ODT (A) dots and (B) lines generated at different holding times and writing speeds. The curves represent the Gaussian fits, which model original data as described in the Experimental Section for LFM images (see Figure 1).

is 0.1 μm/s. These data show that at slow scan speeds, there is a large enough flux to form relatively full monolayers, whereas incomplete monolayer formation occurs at fast scan speeds. Note that in the case of the low-density monolyers, the actual structure consists of bare gold and islands that are fully formed SAMs.[8]

The Humidity Effect. We have shown that ink solubility, in large part, determines the deposition rate dependence on temperature. To understand the dependencies of the feature growth rates of ODT and MHA on humidity (Figure 4), one must consider the mechanism of adsorbate adsorption and self-organization of molecules on gold. Because there is clearly water on the gold surface at all humidities, water must affect the adsorbate adsorption and self-assembly (SA) processes. In all cases studied thus far, including ODT and MHA, increasing humidity should impede the ink adsorption process. Indeed, the water acts like a resist layer that inhibits ink molecules from accessing and adsorbing to the bare gold substrate. Therefore, in the case of DPN ink transport there are two competing humidity dependent factors that affect the rate of ink transport. In the one case by increasing humidity, one increases the size of the meniscus and amount of ink that can be transported. In the other case, one is increasing the water "blocking layer" on the gold, which impedes ink transport. If one considers the ODT and MHA humidity dependencies, one can understand the observed results, Figure 4. In the case of ODT, the ability of the water blocking layer to impede chemisorption overrides (albeit by a small amount, Figure 3) the benefits one gets from increasing meniscus size. In the case of MHA, which has a higher solubility in water, increasing humidity and the absolute amount of MHA in the meniscus are the overriding factors.

The Effects of Meniscus Shape and Size. It is important to note that meniscus size and shape, which can change as a function of temperature, humidity and deposition conditions (rate, surface hydrophobicity, and tip hydrophobicity) due to the changing composition of the meniscus and surface, also can affect the observed deposition rates. For example, an increase in the number of molecules being transported will result from an increase in the cross section of the water meniscus at higher humidity. In addition, changes in the surface tension of the meniscus at higher humidities and as the monolayer forms will affect transport rates. These effects will be highly molecule dependent and also influenced by the type of monolayer formed (hydrophobic or hydrophillic). As humidity is increased there will be a reduction of capillary forces that distribute molecules from the tip to the substrate due to the relative sizes of the menisci at low and high humidities.[23] Finally, tip contamination, which can significantly affect ink solubility, and depletion of inks during transport experiments can dramatically influence experiments aimed at studying transport. These could be factors contributing to the different results and, therefore, conclusions drawn by the different laboratories studying these processes. Ink contamination with residual cosolvents or other materials will decrease the melting point of the ink and affect its solubility.

In conclusion, we have investigated the effects of temperature and humidity on DPN patterning of ODT and MHA molecules. Ink solubility is a key factor in determining temperature and humidity dependence of the growth rate. For both inks, there is an increase in the deposition rate with increasing temperature, but different solubilities of the molecules as well as the adsorbed water layers on the Au substrates influence SAM growth rates. In the absence of UHV, water is always present in a DPN experiment and will affect ink transport. The magnitude of the effect will depend markedly on the ink solubility in water. This has been clearly demonstrated with oligunucleotides and shown to be a powerful method for controlling the deposition of such molecules on both noble metal and oxide substrates.[5] Finally, one should not conclude from these studies that it is impossible to do DPN without a meniscus. To the contrary, we have recently shown that in the case of ODT, one can still make crude patterns in UHV.[26] Therefore, the important point of this manuscript is that as long as one works under ambient conditions, water will play a role in the DPN ink-transport process.

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(16) Plas Labs, 917 E. Chilson Str., Lansing, MI 48906. Phone: (517) 372 7177, (800) 866 7527.
(17) Air Products and Chemicals. Nitrogen: Nitrogen, 99.998%. Oxygen less than 0.0010%. Hydrogen less than 0.0002%. Methane less than 0.0001%. Carbonaceous gases less than 0.0001%. Dew point −90 °F.
(18) Fisher Scientific, Fisherbrand Certified Traceable Digital Hygrometer/Thermometer, Instant model.
(19) Gold-coated substrates (60 nm Au, 10 nm Ti on Si) were prepared according to procedure described in Weinberger, D. A.; Hong, S.; Mirkin, C. A.; Wessels, B. W.; Higgins, T. B. *Adv. Mater.* **2000**, *12*, 1600.
(20) To determine the appropriate equilibration time between experiments, 10, 30, and 60 min time intervals were studied. We found that the use of larger intervals (30 and 60 min) made no appreciable difference in the observed temperature dependence.
(21) The bands assigned to the patterned area include a small tip-convolution contribution. This artifact has an insignificant effect on the force gradient analysis (<10%). Assuming a standard silicon tip with a 10 nm radius of curvature and a tightly formed dot that is 1.6 nm high, tip convolution creates a lateral force contribution 5.4 nm from the edge of the dot. Since the smallest dots generated in these experiments were 100 nm, the contribution to the gradient distribution is relatively insignificant.
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(24) Piranha-cleaned tips were utilized to exclude deposition of contaminants accumulated on the tip. However, treating tips in piranha makes silicon probes hydrophilic which results in a decrease in the resolution of the LFM images. Formation of the meniscus was also confirmed with tips modified with ODT and dodecylamine. Notably, the use of tips coated with 1-dodecylamine provides significantly better LFM images compared to those taken with bare tips (Piner, R. D.; Hong, S.; Mirkin, C. A. *Langmuir* **1999**, *15*, 5457).
(25) NaCl samples were prepared from commercially available NaCl plates (International Crystal Labs, 11 Erie St., Garfield, NJ 07026, Phone: (973) 478-8944) and cleaved with a scalpel under ambient conditions prior to use. The size of each sample was approximately $5 \times 7 \times 1.5$ mm^3.
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(29) According to Meylan W. M.; Howard P. H. *Environ. Toxicol. Chem.* **1996**, *15*, 100, ODT's solubility in water is 2.37×10^{-4} mg/L at 25 °C, while 8-hexadecanoic acid, $C_{16}H_{30}O_2$, which is closely related to MHA in chemical structure, has a solubility of 1.33×10^{-1} mg/L.
(30) This relationship follows from the kinetic theory of matter, which relates a particle's kinetic energy with temperature by $mv^2/2 = 3/2kT$.
(31) This relationship will depend on the particular contact time and writing speed chosen. For example, for the MHA dot and line patterns generated with a holding time of 4 s, and writing speed of 0.5 μm/s (respectively), or for ODT dots and lines patterned at a contact time of 3 s and a writing speed of 0.2 μm/s, the growth rate of lines is twice that of dots.