

Effect of Environmental Conditions on Dip Pen Nanolithography of Mercaptohexadecanoic Acid

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To better understand the process of Probe Mediated Deposition (PMD), or Dip-Pen Nanolithography (DPN), we have studied the transport of an amphiphilic molecule, mercaptohexadecanoic acid (MHA), from the tip of an atomic force microscope (AFM) onto a gold substrate. The process was studied as a function of relative humidity (RH), total elapsed patterning time, and procedure for coating the AFM tip with MHA. Molecular transport is strongly dependent on the conditions of the AFM tip, such as prior cleaning techniques, and whether MHA was deposited dry onto the AFM tip, or from a solution. The transport rate of MHA decreases in a roughly exponential manner over about one hour to a rate that is less than a fourth that of the original transport rate. While the molecular transport rate was independent of RH for 52% RH or less, increasing the RH to 70% about doubled the transport rate, and at 98% RH an increase of about 500% was observed. Our data suggest that the MHA is mobile in the absence of a water meniscus, supporting a dual transport mechanism, whereby at low RH, thermal diffusion drives the “dry deposition” of MHA. As RH increases above ~52%, there is sufficient water present at the tip–substrate interface for aqueous transport of solvated MHA to augment the transport rate.

Introduction

Molecular transport from an AFM tip was first reported by Jaschke and Butt¹ in 1995 with a publication describing the Probe Mediated Deposition (PMD) of octadecanethiol (ODT) and other thiol molecules onto a mica substrate. PMD has since been developed as a nanoscale patterning tool^{2,3} under the name Dip-Pen Nanolithography (DPN). Molecular inks, including alkanethiols,^{1–7} and biological^{8–11} and inorganic materials,^{12,13} have been patterned through the use of PMD, primarily onto a gold substrate. It was suggested early on in the development of PMD that water present on surfaces at nonzero relative humidity (RH)^{14–16} would lead to meniscus formation around the AFM tip,^{17,18} and that this meniscus was responsible for the transport of molecular inks.

Although the exact nature of the molecular transport remains unclear, further investigations indicate that the transport mechanism depends on the chemical properties of the ink itself. For example, ionic substances, such as DNA and salt complexes^{4,11,12,18} with high solubility and low vapor pressure, have been seen to fit well with meniscus-based transport models, as salts are immobile at near-zero RH and demonstrate a humidity-dependent molecular transport rate (MTR). However, it has been shown that the transport rate of ODT, with a low water solubility, a melting point near room temperature,¹⁹ and an appreciable vapor pressure, is independent of humidity.^{4,5} Previous studies have also shown that transport rates of ODT and mercaptohexadecanoic acid (MHA) strongly increase with

increased temperature^{4,20} under a dry atmosphere. Although solubility also increases with increased temperature, the increase in transport rate with temperature far exceeds the increased expected solubility. Furthermore, the surface population of water molecules at constant absolute humidity will decrease with increased temperature. Under a nitrogen atmosphere, the presence of a potential meniscus, and thus meniscus-driven transport, is ever more unlikely with increased temperature. A second transport model is therefore required whereby dry deposition, driven by the concentration gradient, occurs by means of thermally activated diffusion.^{4,5}

MHA consists of a fifteen-carbon aliphatic chain, terminated with a thiol at one end and a carboxylic acid group at the other. The largely nonpolar thiol and hydrocarbon part of the chain resembles ODT, while the carboxylic acid group makes MHA a hydrogen-bonded complex in the solid state. Water competes for this hydrogen bonding. As a result, MHA is more soluble in water than is ODT, and the carboxylic group can ionize to form a weak acid in solution. Thus, the molecular characteristics of amphiphilic MHA with respect to polarity fall between those of nonpolar ODT and salts. Because ionic and nonpolar molecules may have different transport mechanisms, the behavior of amphiphilic molecules such as MHA may provide additional information about the interactions involved in PMD. Additionally, monolayers of MHA are especially useful because the exposed carboxyl group²¹ can react with amino-terminated molecules, which is useful in the selective functionalization of surfaces.²² We propose that the position of MHA on a polarity scale between nonpolar ODT and salts results in the observed patterning behavior of MHA resembling that of both ODT (at low RH) and salts (at high RH).

In this paper, we report how the MTR of MHA depends on RH, total elapsed patterning time, and the method used to coat

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the AFM tip. Contrary to previously published results,⁶ we show herein that with the right cleaning and inking techniques, substantial molecular transport occurs in the absence of water (0% RH) and is minimally impacted below 60% RH. However, the MTR is noticeably enhanced above 70% RH and greatly enhanced at a RH of 98–100%. Also contrary to previously published results,⁴ we have been able to pattern with an AFM tip coated with MHA without the use of any solvent, indicating that a coadsorbed solvent is not necessary for PMD of MHA. Lastly, we report that the MTR of MHA drops off considerably over time, possibly due to molecular depletion at the tip. This behavior contrasts with that of ODT for which long steady-state molecular transport rates have been reported.⁵

Experimental Section

All AFM work was performed on a Digital Instruments Multimode-Nanoscope IIIa, (Santa Barbara, CA) in the Lateral Force Microscopy (LFM) imaging mode, using Thermo Microscope's Coated Sharpened Microlevers, model MSCT-AUHW with tip "A". Humidity was controlled ($\pm 2\%$) by placing the entire AFM assembly into a sealed Plexiglas chamber. The chamber was connected to an Electrical-Tech Systems (ETS) environmental control system (ECS), model 517, which controlled the water content via a dry N_2 gas flow and an ETS Ultrasonic Humidifier containing millipure H_2O . Uniform humidity was achieved in less than 10 min, as measured by a digital hygrometer.

All PMD was performed on freshly exposed 4–8 mm² template stripped gold surfaces, prepared as described in the literature.²³ Gold-coated mica used for sample preparation was purchased from Molecular Imaging (cat# 61-200).

All AFM tips, immediately prior to the MHA coating procedure, were cleaned in fresh Piranha solution (3:1 vol/vol, concentrated H_2SO_4 and 30% H_2O_2 ; *use caution in handling and disposal; reacts violently with organics*) for 30–45 min, rinsed thoroughly with millipure H_2O , and dried under a gentle N_2 flow.

Solution Deposition of MHA. The cleaned tips were placed in freshly prepared 1 mM MHA/acetonitrile solution for 20 s, then blown dry with a light flow of dry N_2 . This was repeated a minimum of three times, after which the tip was tested for MHA transport to the gold substrate at ambient humidity (about 50%). The cycle was repeated, if necessary, until writing was observed, or until the top surface of the cantilever was covered with enough MHA to prevent adequate laser reflection. Although the majority of tips would provide nice patterning behavior after the first three dips, some would fail to write despite having an MHA covering that was visible under optical microscopy after four dipping cycles.

Wick Deposition. Several cleaned tips were placed on the edge of a piranha-cleaned piece of Si (110) wafer or glass slide, and placed in a piranha-cleaned glass Petri dish. Milligram quantities of MHA (s) were then placed in the vicinity of the tip, but not in direct contact with the tip. Next, the dish was covered in aluminum foil, sealed, and placed in an oven at 100 °C for 1–2 h. The MHA melted and flowed onto the AFM cantilever via capillary effects, providing an adequate coating. When the cantilever was beyond the area reached by the liquid MHA, some MHA was still deposited via sublimation. However, the very low molecular transport rate from these tips indicates that coating from sublimation alone under our experimental conditions results in inadequate MHA coverage.

Powder Deposition.²⁴ Finely powdered MHA was placed on the cleaned tips, pointing upward, which were then heated to 100 °C for 30–45 min.

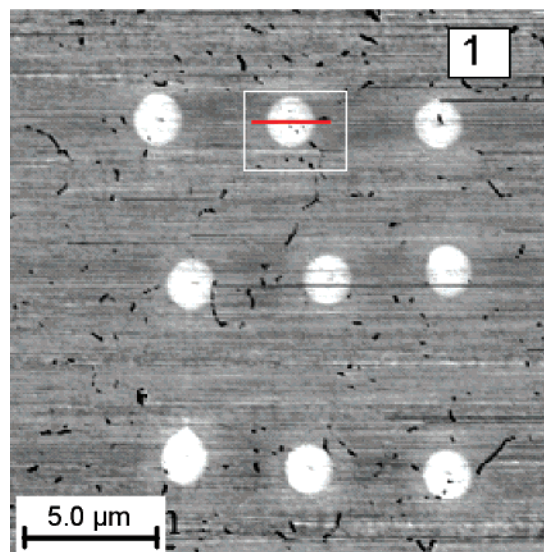


Figure 1. An example of a 9-dot array of powder-deposited MHA, with each dot corresponding to a 60-s dwell time.

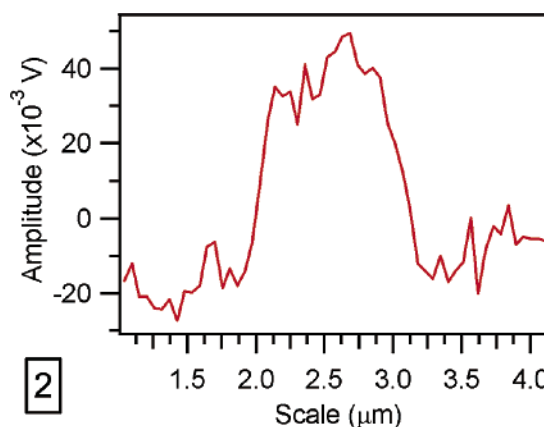


Figure 2. Frictional force profile of the line indicated in Figure 1.

Unless noted, MHA was deposited on the AFM tip either by powder or wick deposition to eliminate the possibility of coadsorbed solvent affecting the patterning process. Placing pure MHA on the tip surface requires care in order to deposit a sufficient amount for patterning, but not an excess that will cause substantial interference with cantilever reflectivity.

SEM observations (not shown) indicate that acetonitrile solution deposition of MHA results in an MHA coating that is thinner, but more uniform, than that resulting from solutionless deposition methods.

Generation and Imaging of Patterns. An array of nine dots was created by bringing the AFM tip into contact with the gold surface for a predetermined dwell time with the aid of DI nanolithography software (Figures 1 and 2). After patterning, each array was immediately imaged with the same tip in LFM imaging mode. Monolayer coverage of MHA has a higher friction signal than bare gold and appears white in LFM images. The total molecular dose to the surface was determined by measuring the area of the dots. MHA bonds to the gold surface through a sulfur–gold interaction, forming ordered monolayers with a molecular surface density of 4.64 molecules/nm².^{21,25} The molecular dose to the surface is the product of the surface area of the patterned dot and this molecular density. Because some dots deviated from a perfect circle, both the length and width of the dots were measured and the values were averaged to calculate coverage.

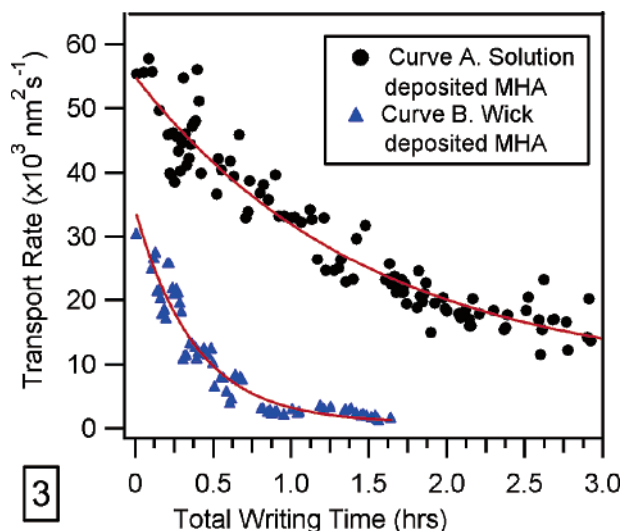


Figure 3. Equilibration data are shown for two different AFM-tip-coating protocols. Data were then fit to an exponential curve yielding relaxation times. *Curve A:* Solution-deposited MHA, patterned at 23 °C and 32% RH, had a relaxation time of 1.5 ± 0.1 h. *Curve B:* Wick-deposited MHA, patterned at 22 °C and 41% RH, had a relaxation time of 0.38 ± 0.04 h.

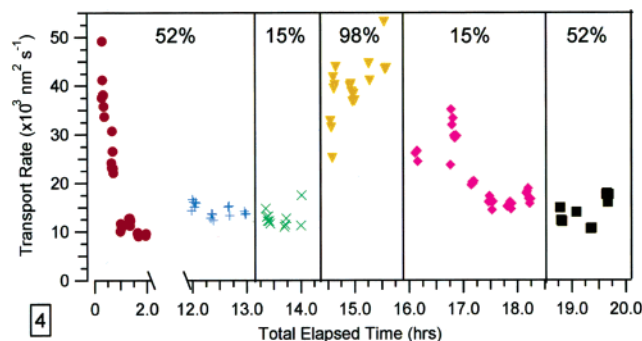


Figure 4. MTR of a single wick-deposited MHA tip as a function of time with changes in RH. Data were taken continuously, as allowed by imaging times (1–5 min), using a 60-s dwell time. Following equilibration, the tip was lifted from the surface and left for 10 h at ambient conditions, 42–50% RH and 23 °C, as denoted by the break in the x-axis.

Results

Initial Decrease in MTR to Equilibrium. Following the coating procedure, each tip was placed in a sealed Plexiglas chamber for a period ranging from 20 min to 2 h at ambient laboratory conditions before beginning any deposition to ensure consistency in environmental conditions. At the beginning of patterning experiments with MHA, the MTR decreased over time in a roughly exponential manner to a relatively steady value (see Figure 3). This decrease to equilibrium was reproducibly observed for acetonitrile solution deposition as well as for solutionless deposition schemes.

To show that the time-dependent equilibrium effect was a direct result of extended writing and not a result of sublimation, a freshly coated tip, whose MTR was established through a series of patterned arrays, was left in ambient conditions (37–47% RH and 21–23 °C) for up to 10 h without contact with the substrate before subsequent transport rate measurements were made. No decrease in transport rate was observed. However, increases in MTR of 0–40% were observed, implying that molecular redistribution occurred on the AFM tip, bringing MHA molecules from regions of higher molecular density to

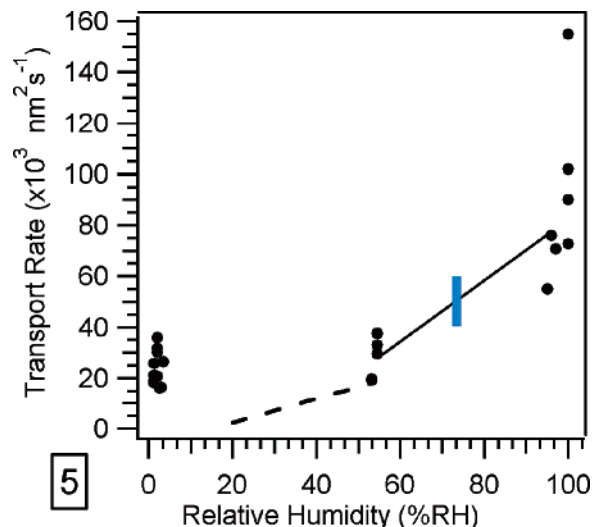


Figure 5. MTR of a single wick-deposited MHA tip as a function of relative humidity (RH) at ~1%, ~50%, and ~100%. (denoted by black dots) The dotted line (refers to previously published data⁶), the solid line, and the blue bar are addressed in the Discussion.

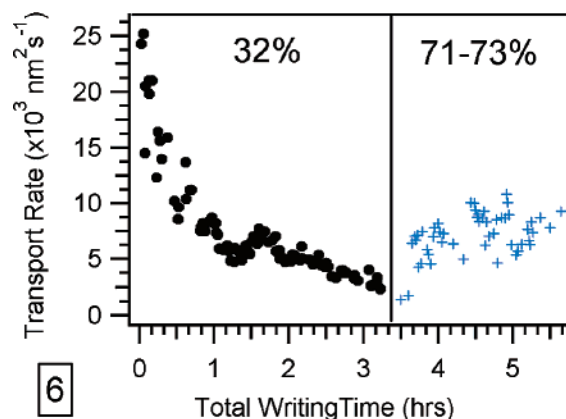


Figure 6. MTR of a powder-coated AFM tip showing both the exponential equilibration and increase with changes in RH.

depleted regions closer to the end of the tip. Although this equilibrium behavior was reproducibly observed, the initial transport rate and equilibration time did have a considerable variation from tip to tip.

Relative Humidity Dependence. After the MTR reached near steady state, data were continuously taken at different RH except during an ~15-min pause after each change in RH, which allowed for equilibration to the new RH. The 15-min pause itself resulted in no observable change in the MTR, as indicated in Figure 4. However, the initial long (10 h) pause did result in a 40% increase in the MTR. Although there was little or no observable humidity dependence of the MTR for changes in RH between 0% and 50% RH, the MTR increased sharply for RH greater than 90% (Figures 4 and 5 represent two different experiments), and was also observed to increase about twofold for RH as low as 71% (Figure 6).

Discussion

Our data imply that MHA is unique among studied molecules, owing its transport to both thermal diffusion (dry deposition) and meniscus mechanisms.⁴ We observe considerable transport at near-zero relative humidity, and our studies find no significant correspondence between humidity and MTR at relative humidities less than 52%. Combined with the previously reported

exponential temperature dependence of MHA,^{4,20} low relative-humidity transport fits well with the thermal diffusion model of dry deposition.^{4,5} However, above 70% RH, we observe an increase in MTR, particularly at RH > 98% where the MTR sharply increases with RH, implying a transport process that can be strongly dependent on the presence of a water meniscus.

Studies using sum-frequency generation (SFG) and scanning polarization force microscopy (SPFM) have shown that below 20% RH, less than a single layer of water molecules exist on surfaces of mica, gold, and graphite.¹⁵ However, investigation of water-film thickness performed on gold surfaces using scanning tunneling microscopy¹⁶ concluded that the film consisted of 30–50 nm islands that increased in thickness from about 2 nm at RH = 20% to 10 nm at RH = 45%. It has been suggested that water would remain on a hydrophilic surface even at 0% relative humidity (unless that surface was placed in ultrahigh vacuum conditions) and that this water accounted for transport at 0% RH.²⁰ Our data show no observable increase in MTR for all humidities less than 52%, implying that even if surface water is present, it is not responsible for molecular transport. The sharp increase in MTR at very high RH implies that a significant amount of water must be present around the tip before dissolution allows a large enough molecular flux from tip to surface to impact the MTR.

The achievement of PMD transport of MHA resulting from solutionless AFM tip-coating protocols (powder and wick deposition) is in contrast to a previous report by Schwartz.⁴ However, our observations imply that solution application of MHA onto the AFM tip assists subsequent molecular transport. Despite SEM observations (not shown) that solution deposition resulted in lower (but more uniform) molecular coverage on the AFM cantilever, solution-deposited tips consistently had a longer relaxation time and a higher molecular transport rate after relaxation (Figure 3) than did tips coated by solutionless means. It is possible that residual acetonitrile enhances molecular transport, or that solution deposition delivers a molecular distribution or crystal structure of MHA with a greater population of mobile surface molecules.

The data in Figure 5 appear to be in sharp contrast to those of Weeks et al.,⁶ who observed a steep increase in dot size with increasing humidity above 20% RH. Below 20% RH they found that MHA deposition was inconsistent from tip to tip, and at times nonexistent. However, Weeks et al.⁶ presented their data in terms of dot diameter. Replotting the data as transport rate (proportional to the *square* of the dot diameter) vs %RH, yields the linear dependence shown by the dashed line in Figure 5 between 20% RH and 60% RH. If we plot the ~100% increase observed in Figure 6 from 52% RH to 72% RH into Figure 5 (blue band), we see that our present study also gives a roughly linear dependence of MTR on humidity from 52% RH to 98% RH (indicated with solid line), but with significantly higher transport rates at low humidity and a shift toward higher humidity at the onset of humidity dependence. One major difference between the experimental procedure of Weeks et al.⁶ and that of our current work is the method of tip and substrate preparation. While in the current study we were thorough in cleaning the tips with piranha solution, using no coadsorbed solvent on the AFM tip, and in using fresh template-stripped gold substrates; in Weeks et al.,⁶ tips were used as-provided by the manufacturer direct from storage on silicone backing in plastic boxes. The implication is that contamination on tip and/or substrate and differences in the surface structure of the gold films in the study of Weeks et al.⁶ may have both inhibited dry

deposition of MHA and promoted the onset of meniscus formation. Given the importance of surface chemistry in controlling surface diffusion and of interfacial energies in controlling meniscus formation, adsorbed contaminant and/or coadsorbed species can have profound effects on PMD transport.

We also observed a previously unreported temporal decrease in MTR over a 1–4 h span, leading to a near-constant MTR. To explain this new phenomenon, we propose that the MHA on the AFM tip near the tip–surface interface initially present after the coating procedure becomes depleted over time so that molecules must migrate from further up the tip, lowering the concentration gradient and decreasing the MTR. A possible explanation for the contrasting observed behavior of ODT⁵ could be an increased molecular mobility of ODT on the AFM tip.

After returning from the substantially enhanced MTR observed at 98% RH to 15% RH (Figure 4), an exponential-like decrease in transport rate was observed. Because the adjustment of humidity within the chamber occurs much more rapidly, we propose that this decrease is likely to be the result of the same depletion process proposed above. This implies that not only can the water meniscus accelerate transport from tip to substrate; it can also reestablish a uniform coating on the AFM tip. Not surprisingly, this redistribution takes place much more slowly at lower RH, as indicated by the 10-h waiting period necessary at lower RH to observe a 40% increase in MTR (Figure 4).

Conclusion

Our observations indicate that the transport of MHA is consistent with a two-mechanism process: thermally activated surface diffusion and dissolution. Surface diffusion is responsible for dry deposition at low-to-moderate RH as demonstrated by humidity invariance of the MTR up to approximately 50% RH, and is consistent with reported increases in MTR with increased temperature.^{4,20} However, at high RH the transport rate of MHA is greatly enhanced due to dissolution followed by bulk transport. The cleanliness and structural state of the substrate appear to have a strong impact on the magnitude of the surface diffusion flux as well as on the humidity at which the meniscus becomes important.

Unlike the reported behavior of ODT,⁵ the MTR of MHA decreases exponentially with the total writing time over a period of 1–4 h relaxing to a much lower rate. This relaxation effect suggests that molecular transport is affected by the mobility of molecules further up the AFM tip as well as at the tip–substrate interface. Moreover, the *abrupt* increase in MTR followed by a longer relaxation to the initial lower MTR, which results from momentarily bringing the system to higher humidity, shows that the creation of the meniscus acts to replenish MHA molecules near the contact point by transporting them from higher, undepleted regions of the tip.

Increased understanding of molecular transport, specifically how it depends on the combination of molecular characteristics and environmental factors, provides a means to improve the control of PMD for patterning of presently used molecular inks as well as for new ones. This understanding also provides additional qualitative insight as to a particular molecule's chemical properties, specifically aqueous solubility and surface mobility.

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