

REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-06-0461

The public reporting burden for this collection of information is estimated to average 1 hour per response, including gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments information, including suggestions for reducing the burden, to the Department of Defense, Executive Services and Con that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a control number.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE (DD-MM-YYYY) 3 NOV 06		2. REPORT TYPE FINAL REPORT		3. DATES COVERED (From - To) 15 MAY 03 TO 14 MAY 06	
4. TITLE AND SUBTITLE COMBINATORIAL ANALYSIS OF FUNCTIONAL INTERFACES AND SURFACES GENERATED VIA DIP-PEN NANOLITHOGRAPHY				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER F49620-03-1-0329	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) PROF THOMAS B. HIGGINS				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) HAROLD WASHINGTON COLLEGE PHYSICAL SCIENCE DEPARTMENT 30 EAST LAKE ST., CHICAGO, IL 60601				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 875 NORTH RANDOLPH STREET SUITE 325, ROOM 3112 ARLINGTON, VA 22203-1768 <i>Dr Hugh Belong</i>				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT APPROVE FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The effect of a n organic solvent atmosphere on ink deposition and deposition transport rate was also studies and quantified. Various chemical compounds spanning a range of hydrophobicities and meniscus solubilities were used as inks in DPN and deposited in a variety of solvent atmospheres such as ethanol, methanol, hexanes and methylene chloride. The data obtained in these experiments will improve our understanding of the factors that govern the rate of ink delivery from tip to substrate, especially for air or water sensitive adsorbates. Another interesting outcome of these studies was the observation that introduction of an organic solvent into an inert atmosphere will increase the diffusion rate of certain alkanethiols by orders of magnitude and hence increase the deposition rate of these materials onto solid surfaces. These studies are in the process of being written up for publication and submission to Langmuir is planned.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (Include area code)

Air Force Office of Scientific Research

Final Report (5/15/03 – 5/14/06)

for Grant: F49620-03-1-0329

**Combinatorial Analysis of Functional Interfaces and Surfaces Generated Via Dip-Pen
Nanolithography**

Principal Investigator

Thomas B. Higgins

tbhiggins@ccc.edu
Physical Science Department
Harold Washington College
30 East Lake Street
Chicago, IL 60601

Co-Principal Investigator

Chad A. Mirkin

chadnano@northwestern.edu
Department of Chemistry
Northwestern University
2145 Sheridan Road
Evanston, IL 60208-3113

May 15, 2006

20061130019

1. Objectives

This project involved a collaborative effort between Harold Washington College, a Minority Serving two-year college, and Northwestern University, a research-intensive university. The objectives of this collaborative research project were to:

1. Study surface-interfacial processes through utilization of a combination of Dip-Pen Nanolithography (DPN) and various inks.
2. Identify important kinetic and thermodynamic parameters that determine thin film robustness as a function of surface composition and morphology.
3. Develop a comprehensive reactivity scale for self-assembled monolayer structures on noble metal substrates.
4. Facilitate the transfer of important discoveries and advances in patterning technology and surface design to military laboratories.
5. Provide a cutting edge training environment for graduate students working in research areas of critical importance to the DOD.

2. Status of the Research Effort

Over the lifetime of this project, five Harold Washington College (HWC) undergraduate students were funded and pursued research jointly with Northwestern University (NU) graduate students, post-doctoral associates, and faculty. All of these students have matriculated from HWC, and at least four are pursuing STEM careers. Anu Amarnath is currently enrolled in the School of Pharmacy at the University of Illinois, Chicago. Lubna Swiess has graduated from Loyola University, Chicago with a B.S. in Chemistry. She is currently in the workforce. Karen Esteras is currently in the workforce. Angel Butron has been accepted to the Midwestern School of Nursing and begins courses in Fall 2006. Salome Ngatia has transferred to Smith College and plans to course a degree in biochemistry. Ms. Ngatia was recently awarded an ACS Scholars Award, partially as a result of her research activities related to this project.

These students studied the synthesis, surface properties, and phase separation of perfluorinated alkanethiols and n-alkanethiol ink mixtures on Au(111) surfaces. The micro- and nanoscale transport of mixed ink systems composed of hydrophobic and hydrophilic components were studied using microcontact printing (μ CP) and dip-pen nanolithography (DPN), respectively. These systems exhibit spontaneous phase separation at the nanoscale length scale and, when exposed to hydrophobic materials like buckminsterfullene or polystyrene nanospheres, template nanoparticle deposition onto the hydrophobic ink areas. This work provides a fundamental understanding of the nanoscale behavior of molecular ink transport, in the context of advanced patterning technologies, and highlights how this behavior contrasts to bulk behavior. Over the lifetime of this project, we have advanced both the quantitative and qualitative understanding of these systems. These results have been published in the *Journal of the American Chemical Society*.

The effect of an organic solvent atmosphere on ink deposition and deposition transport rate was also studied and quantified. Various chemical compounds spanning a range of hydrophobicities and meniscus solubilities were used as inks in DPN and deposited in a variety of solvent atmospheres such as ethanol, methanol, hexanes and methylene chloride. The data obtained in these experiments will improve our understanding of the factors that govern the rate of ink delivery from tip to substrate, especially for air or water sensitive adsorbates. Another interesting outcome of these studies was the observation that introduction of an organic solvent

into an inert atmosphere will increase the diffusion rate of certain alkanethiols by orders of magnitude and hence increase the deposition rate of these materials onto solid surfaces. These studies are in the process of being written up for publication and submission to *Langmuir* is planned.

The synthesis and DPN properties of bidentate alkane thiols derived from the trans-1, 2-dithiane-4, 5-diol moiety was undertaken. This synthesis pathway will serve as a model for bidentate DPN inks and allow us to synthesize a library of similarly structured compounds. The usage of these compounds in applications such as DPN will accelerate our ability to generate a multitude of nanostructures with a variety of physical and chemical properties. Inks of this sort are desired because their bi-dentate nature improves their surface stability.

In addition, studies have been undertaken to quantify and compare the relative stability of bulk self-assembled monolayers (SAMs) and patterned SAMs deposited by μ CP. Using DPN as a probe, the exchange rates of hydrophilic inks with hydrophobic monolayers under a variety of conditions has been probed. Analogous experiments involving hydrophobic inks and hydrophilic monolayers under a variety of conditions have also begun.

3. Research Accomplishments and New Findings

A. Undergraduate Interns

A formal undergraduate training and research program was initiated and sustained as a joint endeavor between two institutions, Harold Washington College, a two-year, primarily minority institution, and Northwestern University, a research-intensive university. This program allows talented and motivated undergraduates from HWC to pursue an individual research project using state-of-the-art facilities at NU.

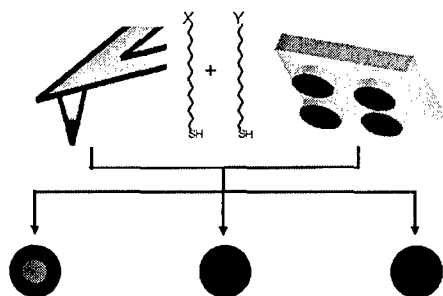
The HWC undergraduates who participated in this project learned how to read and interpret scientific literature, such as papers and communications from the *Journal of the American Chemical Society*; plan and carry out a chemical synthesis using air-free Schlenk techniques; independently operate analytical instrumentation, such as nuclear magnetic resonance, gas-chromatograph/mass spectrometry, and atomic force microscopy; and set-up and maintain a research laboratory. Without access to the facilities of NU, HWC would not be able to provide a comparable experience for its students.

B. Spontaneous "Phase Separation" of Patterned Binary Alkanethiol Mixtures

Over the lifetime of this project, significant progress was made using binary alkanethiol mixtures with hydrophobic and hydrophilic ω -functionalized tail groups as inks for patterning.

An unusual and near-complete phase separation process that produces nanostructures with hydrophilic interiors and hydrophobic peripheries was observed and studied. This phenomenon extends beyond dip-pen nanolithography (DPN) to micro-contact printing (μ CP), and can be used to increase the resolution of both techniques under certain conditions.

A fundamental issue of multi-component deposition processes pertains to the transport properties of a binary mixture of ink molecules onto surfaces (Scheme 1). In particular, does the transport of such mixtures result in a



Scheme 1. Possible outcomes of patterning a binary mixture of two alkanethiols using μ CP and DPN.

nano- or microstructure with a homogenous distribution of adsorbate molecules (Scheme 1, right), a structure with island-like phase separation (Scheme 1, middle), or a near-complete phase separation of the two adsorbates (Scheme 1, left)? Such studies of nanometer-scale mixing are important for two reasons. First, they advance our understanding of the fundamental properties and origins of phase separation of two-component mixtures. Second, they may allow one to deliberately tailor surface properties at the sub-50 nm length scale.

Surprisingly few examples of nanometer scale phase separation have been reported for binary SAM mixtures. Spontaneous random phase separation has been observed in scanning tunneling microscope (STM) images of co-adsorbed alkanethiol mixtures on atomically flat gold surfaces. These studies have established that phase separation of mixed SAMs is driven by polar head group interactions and cohesive interactions between the adsorbate molecules. In such systems, the adsorbates randomly form nanoscale domains with no particular order, (similar to Scheme 1, right).

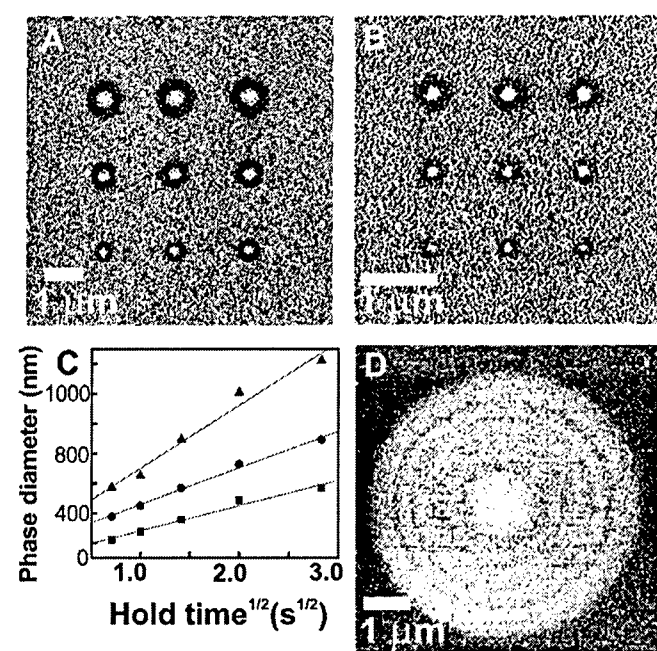


Figure 1. LFM images of phase separated structures patterned on Au surface with a binary ink coated tip. (A) MHA interior and ODT exterior dots and (B) MHA interior and PFT exterior dots formed by holding tip 8, 4, and 2 seconds. (C) Plot of phase diameter v holding time showing $t^{1/2}$ dependence for MHA/ODT dots (triangles, circles, and square represent entire dot, ODT phase, and MHA phase, respectively). (D) MHA/ODT ring structure made by repeatedly approaching surface (5 times).

the mixture is delivered to a surface via DPN, the resulting nanostructures are phase separated patterns composed of a roughly 1:1 ratio of MHA to PFT (Figure 1).

In a typical DPN experiment, AFM cantilevers were coated with binary ink mixtures and subsequently used for patterning. Different ink mixtures produce different types of

In order to increase our understanding of materials that can potentially be used as DPN inks, we studied mixed systems consisting of one hydrophilic and one hydrophobic thiol ink and different means of delivery of these systems to a gold surface. The printing methods we studied were DPN and μ CP using a micron-sized stamp as a printing device. To date our studies have concentrated on three inks: 1-mercapto-1H,1H,2H,2H-perfluorododecane (PFT), mercaptohexadecanoic acid (MHA), octadecane thiol (ODT). MHA and ODT are almost identical in molecular weight and structure with the exception of the ω -terminal group, where the acid groups of MHA can participate in hydrogen bonding. On the other hand, PFT is a shorter hydrophobic molecule with significantly weaker adhesive interactions than MHA or ODT.

Exposure of an ethanol solution consisting of a 1:1 mixture of MHA and PFT to an Au surface creates a bulk SAM comprised almost entirely of MHA. However, when an AFM tip is coated with a 1:1 mixture of MHA and PFT and

nanostructures. For example, an AFM tip coated with a binary mixture of MHA and ODT was held in contact with a gold surface for 2, 4, and 8 seconds. Each hold was replicated three times. The contact area was subsequently imaged by lateral force microscopy (LFM) using the same tip (Figure 1A). A central white (high contrast, high lateral force) domain can be seen that represents an area predominantly coated with MHA, while an outer dark ring (low contrast, low lateral force) of predominantly ODT is seen at the perimeter of each of the dots. When a binary mixture composed of MHA and PFT was deposited in a similar manner, similar structures with slightly higher LFM contrast form (Figure 1B). Although the dots are composed of two molecules, the diameter of each phase still shows $t^{1/2}$ dependence in accordance with ink transport models that are used to describe the DPN process (Figure 1C). Interestingly, when an MHA/ODT tip was brought repeatedly into contact with the surface, ring type structures are formed (Figure 1D), where each time the tip is in contact with the surface two additional rings are formed (one predominantly MHA, and the other predominantly ODT). In contrast, AFM tips coated with mixtures of equal parts of MHA and PFT produce nanostructures with a continuous core of MHA and a continuous outer coat of PFT when the “multiple tip approach” is used. This suggests that PFT is quickly and easily displaced by MHA, while ODT is not.

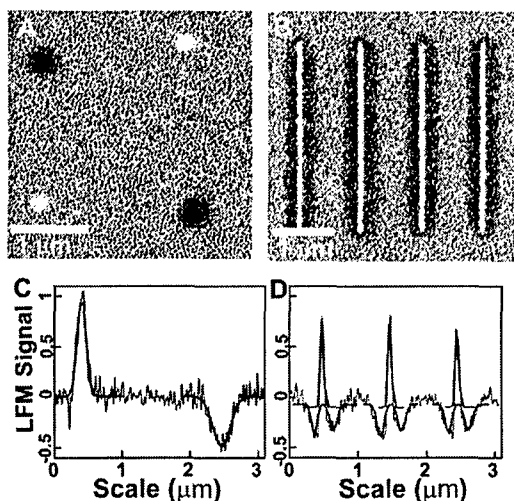


Figure 2. Comparison of the LFM properties of pure and phase separated DPN deposited alkanethiols on Au. (A) LFM image of pure MHA (white) and pure ODT (black) dots formed by DPN. (B) Four phase separated MHA/PFT lines deposited by moving coated cantilever at a rate of 0.4 $\mu\text{m/s}$. Corresponding plots show analyses of highlighted regions in each LFM image, where black line represents a Gaussian fit of averaged line scans (red).

Phase separation behavior is independent of the path of the tip and separated line structures assemble when an MHA/PFT tip is scanned in a line at a rate of 0.2 $\mu\text{m/s}$ (Figure 2B) where the interior of the structure is composed primarily of MHA and the exterior primarily of PFT. To obtain a better understanding of the degree of phase separation, structures comprised of pure MHA and ODT were patterned well (Figure 2A). The averaged frictional force profiles generated in these experiments show bands associated with patterns of MHA and ODT (Figure 2C). The frictional force profiles were modeled as Gaussian distributions, and the peaks of these plots used to evaluate the distribution of the two components in patterned binary structures. The friction force profile of segregated structures (Figure 2D), displays less intense peaks (~80%) than those of pure adsorbates (Figure 2C), which indicates a near-complete separation in the experiment described in Figure 2B. The interior of these structures is always comprised of the more hydrophilic MHA, which remains unchanged even when patterning is performed in an inert atmosphere saturated with methanol. Comparing LFM images collected from pure and mixed-ink

nanostructures suggests that mixtures of alkanethiols do indeed phase separate into domains, but factors such as molecular packing and orientation can contribute to the observed frictional force signal.

Many surface spectroscopic techniques, such as XPS or grazing angle FT-IR, are capable of discriminating between different alkanethiols, but this is not feasible for sub-100 nm features.

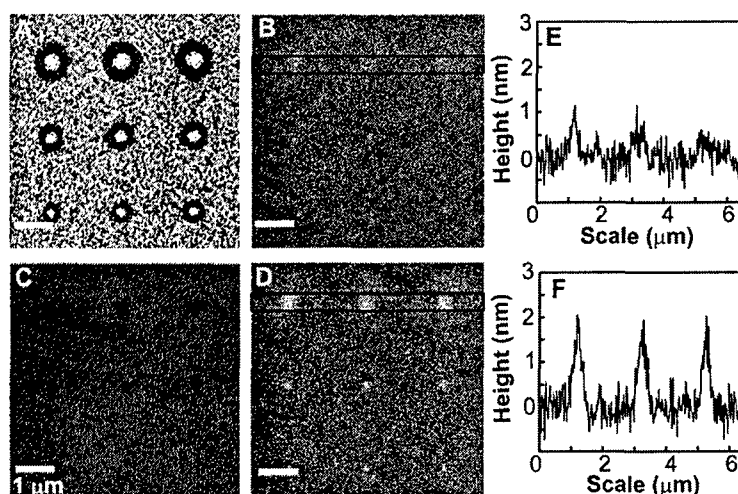


Figure 3. Probing the chemical composition of segregated binary ink patterns through selective metal-organic coordination to the terminal carboxy group of MHA. (A) LFM image of 3×3 MHA/ODT phase separated dot array. (B) Tapping mode height and (C) corresponding phase image of an ODT passivated dot array. Note that dots are of similar height to the background. (D) Tapping mode height image of dot array after coordinating a layer of MHA onto a Cu^{2+} incubated substrate. Averaged line scans of mixed-ink dots (E) before and (F) after growth of the MHA layer, which show a height increase of $1.6 \text{ nm} \pm 0.1 \text{ nm}$ only in the interior region of each dot.

Cu^{2+} . Excess material was washed away under a stream of ethanol and water, and the substrate is subsequently imaged in tapping mode. Patterned dots are undetectable in height mode (Figure 3B) since the heights of MHA and ODT are very similar. However, the interior of these dots is detectable in phase mode (Figure 3C), which indicates that the interior of these dots is different from the ODT passivated exterior regions. A metal-organic coordinating layer is then selectively adsorbed onto the MHA areas by incubating the sample for 15 minutes in a 1 mM CuClO_4 solution in ethanol, followed by rinsing and immersion of the Au film in a 1 mM MHA solution. After removal of physisorbed material with ethanol rinses, the sample is again imaged by using tapping mode to minimize sample damage. Height mode images (Figure 3D) show that only the interior regions of each of the dots have increased in height. Averaged line scan analyses of dots before (Figure 3E), and after (Figure 3F) coordination layer growth show that the interior region of each dot has increased in height by $1.6 \text{ nm} \pm 0.1 \text{ nm}$, a value that concurs with previously published results for the thickness of an MHA layer grown on a monolayer of Cu^{2+} . The chemical reactivity data agree with the frictional force data, thus showing that when the two alkanethiols are deposited simultaneously by DPN the more hydrophilic MHA will generate a central phase, while the more hydrophobic ODT will form an outer perimeter phase. The phase separation observed in the patterned nanostructures is presumably the result of enthalpic contributions, since entropy would favor mixing of the constituents within the generated patterns.

In addition, the heights of the alkanethiols used in this study are very similar. Therefore, height mode images are not useful for discriminating between the two different molecules, especially on polycrystalline Au films with an RMS roughness of 1 nm. To get around these limitations, we took advantage of the ability of the terminal acid groups of MHA to coordinate to metals such as Cu^{2+} and build metal-organic multilayers to provide additional evidence as to the chemical identity of the mixed-ink nanostructures. As shown in Figure 3A, an MHA/ODT mixed ink-coated tip was used to pattern an array (3×3) of dots, and the sample subsequently exposed for 10 minutes to a 1 mM ODT solution in ethanol, which renders unpatterned bare Au areas unreactive toward coordination to

Spontaneous phase separation driven by hydrogen bonding or van der Waals interactions is consistent with previous reports in bulk SAMs. Leggett et al. have determined the contribution from hydrogen bonding within an acid terminated monolayer to be equivalent to the van der Waals stabilization of nine methylene groups. MHA is only two methylene groups shorter than ODT, and therefore hydrogen bonding interactions would be expected to provide a major driving force for phase separation of a mixture of MHA and ODT. In the case of MHA/PFT mixtures, the driving force for phase separation is a combination of both hydrogen bonding as well as van der Waals interactions, since there are only two methylene units in PFT. This may explain why LFM contrast in the MHA/ODT system is lower than in the MHA/PFT system. Separation may also be enhanced by the water/air interface at the surface of the water meniscus formed during patterning. Furthermore, the kinetics of ink transport from tip to surface are certainly a factor in determining the ultimate nanopattern composition, especially with regard to adsorbate solubility and diffusion in water. For example, the solubility of MHA is at least three orders of magnitude larger than that of ODT. As a result, MHA molecules will certainly reach the Au surface at a more rapid rate than ODT. The difference of ink solubility in the meniscus explains why the predominantly MHA phase is always observed at the center of these binary structures. It also explains why introducing a methanol atmosphere influences the rate of transport and the magnitude of phase separation.

This phenomenon can, in principle, provide two advantages for a variety of chemical-based lithographies, such as μ CP and DPN. First, it can potentially increase the ultimate resolution of a variety of these techniques, and second, it can simultaneously generate multi-component structures. To test this, a binary mixture of 1:1 MHA:PFT ink (1 mM total concentration)

was coated onto a poly(dimethylsiloxane) (PDMS) stamp, and the stamp immediately applied to a gold surface. The resulting patterns show phase separated lines of alkanethiol (Figure 4A). The central region of the patterned lines is comprised of predominantly MHA, while the perimeter of these lines is made of predominantly PFT. Interestingly, the width of the PFT lines is 100 nm, which is 20 times smaller than the width of the stamp features (2 μ m). These features are also five times smaller than those obtained using conventional μ CP. Furthermore, only a few techniques are capable of patterning multi-component structures at sub-micrometer resolution, and each one suffers from certain drawbacks. Multi-component patterning has been demonstrated using conventional μ CP, but only at the micrometer length scale. Utilizing phase separation is advantageous because the pattern resolution and component registry are defined by the choice of ink pairs and by the stamp feature size. In addition, monolayer structures generated using the phase separation of binary ink mixtures can be further used to direct the assembly of a

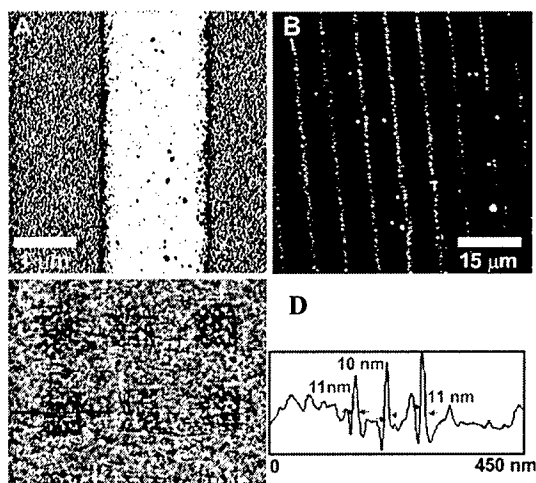


Figure 4. Phase separation of MHA/PFT to improve the resolution of DPN and μ CP. (A) LFM image of 2 μ m stamp applied to a gold substrate. (B) Dark field micrograph of templated C_{60} aggregates onto (A) after passivation with MHA and incubation in 0.2 mg/ml C_{60} solution in toluene. (C) DPN of binary mixed ink dots on Au(111) surface and (D) is line scan profile through highlighted region.

wide variety of materials. For example, when a 1:1 MHA:PFT stamped gold film (Figure 4A) is rendered hydrophilic by incubation in a MHA solution (2 min), and subsequently exposed to a toluene solution of C_{60} (0.2 mg/ml), aggregates will selectively assemble onto the hydrophobic PFT lines (Figure 4B). C_{60} aggregates assemble more readily on the PFT regions because of hydrophobic interactions. This provides additional evidence for the chemical identity of the phase separated regions. In addition to C_{60} , this procedure was also used to selectively deposit hydrophobic polystyrene spheres. Interestingly, if a binary ink mixture is deposited onto a Au(111) substrate using DPN, sub-15 nm MHA structures form in the interior of dots that have diameters as large as 50 nm (Figure 4C and D).

In conclusion, binary ink mixtures of alkanethiols exhibit near-complete phase separation behavior when deposited using micro- or nano-deposition tools such as μ CP and DPN, a consequence of the choice of ink pairs and the different transport properties of the chosen adsorbate molecules. Interestingly, the more hydrophilic alkanethiol always forms the interior phase, while hydrophobic alkanethiols will form the outer phase, when these mixtures are patterned using DPN or μ CP. This is in contrast to the bulk behavior of such adsorbates, in the context of SAMs formed from solution on gold substrates. By tailoring ink mixture composition, this phase-separation behavior can be exploited to print sub-100 nm lines in the case of μ CP, and sub-15 nm lines in the case of DPN.

C. The Effect of Organic Solvent on DPN Ink Deposition Rate

One objective of this study was to quantify how the presence of an organic solvent in the

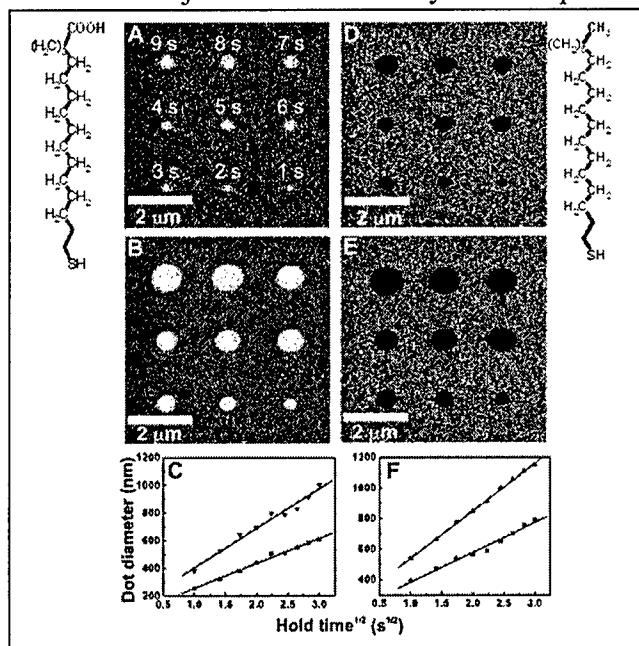


Figure 1. DPN of alkanethiol ink in the presence of organic solvent vapor. LFM images of MHA dots deposited at different hold times (1-9 sec) in (A) N_2 and (B) ethanol atmosphere. (C) Dot diameters are plotted as a function of (hold time) $^{1/2}$ before (square) and after (triangle) introduction of ethanol vapor into the chamber. LFM images of ODT dots deposited (1-9 s hold times) in (D) N_2 and (E) hexane atmosphere. (F) Plot of dot diameter vs (hold times) $^{1/2}$ for ODT deposition before (square) and after (triangle) introduction of hexane into the chamber.

atmosphere affects the deposition rate of alkanethiol inks onto a surface using Dip-Pen nanolithography (DPN). The importance of the water meniscus in DPN ink deposition as well as the relationship between relative humidity, ink deposition rate and nanostructure feature size has already been well established. We have extended these studies to organic meniscus systems. The results of a typical experiment are summarized in the plot of dot diameter vs. hold time (Figure 5). To date, inks studied include MHA and ODT, and the solvents studied include hexane, dichloromethane, methanol and ethanol.

The deposition rate of alkanethiol inks was recorded before and after one liter of organic solvent was introduced into an inert atmosphere glove box housing an AFM. The amount of organic solvent introduced into the chamber was held below saturation in order to prevent solvent condensation. Since the solubility of alkanethiols is significantly greater in organic solvent than that in water, the diffusion rate of ink from to surface is

also expected to be greater. The effect of patterning in a solvent-free versus a solvent-rich atmosphere is presented in Figure 5. An MHA coated tip was used to pattern nine dots with hold times ranging from 1-9 s under dry nitrogen conditions, and subsequent LFM images showed hold-time dependent dot diameters, Figure 1A. After introduction of ethanol into the chamber, the transport rate of MHA from the same tip onto the same substrate increased uniformly, Figure 1B. The presence of organic solvent adlayers most likely affects the resulting LFM image contrast due to changes in measured friction; however, this does not hinder dot diameter measurements. The diameter of all dots patterned with N_2 atmospheres and organic solvent atmospheres show a $t^{1/2}$ dependence, in accordance with our transport model,² and the model put forth by Jang et al.²³ Indeed, there is a marked increase in the transport rate of MHA under an ethanol atmosphere, Figure 1C. Furthermore, this observation is also general to other inks and solvent vapors, and ODT ink transport is enhanced under a hexane solvent atmosphere, Figure 1D-F.

A paper detailing the organic solvent studies is currently being prepared for submission to *Langmuir*.

D. Study of Relative Stabilities of Self-Assembled Monolayers

As part of our effort to develop a comprehensive reactivity scale for self-assembled monolayer structures, studies have been undertaken to probe the relative stabilities of SAMs deposited passively from solution versus SAMs patterned via μ CP. DPN is an ideal technique to probe this question, because it can be used both as a lithographic tool as well as an *in-situ* probe to measure adsorbate exchange kinetics.

In a typical experiment, a bulk monolayer of ODT adsorbed onto Au or a μ CP stamped

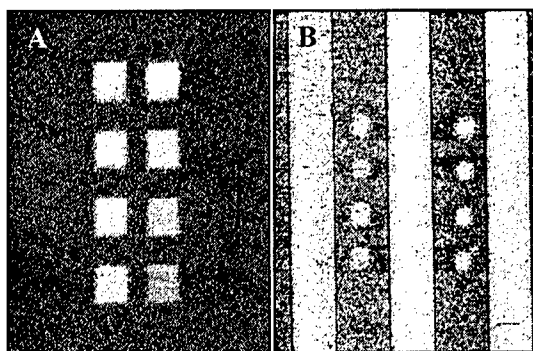


Figure 7: LFM image of MHA/ODT exchange studies. (A) Exchange on an ODT SAM substrate. Each box is $1\ \mu\text{m}$ square. The left column shows exchange at a constant scan rate (2 Hz) and varying set point (From the top: -0.1 nN, 0.1 nN, 1 nN and 2 nN.) The right column shows exchange at a constant set point (2 nN) and varying scan rate (From the top: 1 Hz, 2 Hz, 4 Hz, and 6 Hz.). (B) Exchange on an ODT stamped pattern. Each box is $0.5\ \mu\text{m}$ square. The left column shows exchange at a constant scan rate (2 Hz) and varying set point (From the top: -0.1 nN, 0.1 nN, 1 nN and 2 nN.) The right column shows exchange at a constant set point (2 nN) and varying scan rate (From the top: 1 Hz, 2 Hz, 4 Hz, and 6 Hz.).

ODT line pattern was used as the substrate and an MHA coated AFM tip used as the exchange agent. The tip was raster scanned one time over a $1\ \mu\text{m}^2$ area (ODT SAM substrate) or a $0.5\ \mu\text{m}^2$ area (PDMS stamped ODT substrate). Upon completion of the experiment, the substrate was washed copiously with ethanol to remove all physisorbed material and re-imaged with a clean tip, (Figure 7). White areas (high contrast, high lateral force) represent MHA and dark areas (low contrast, low lateral force) represent ODT.

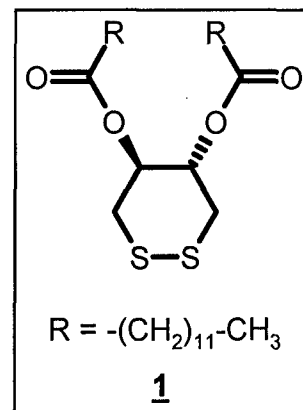
During the exchange studies, both scan rate (in Hz) and set point (in nN) were independently varied. The scan rates studied were: 1 Hz, 2 Hz, 4 Hz, and 6 Hz (set point held constant at 2 nN in all cases). The set points studied were: -0.1 nN, 0.1 nN, 1 nN and 2 nN (Scan rate held constant at 2 Hz in all cases.). With an ODT SAM substrate, Figure 7A, qualitatively less MHA was deposited at faster scan rates, but with an ODT stamped substrate, no qualitative differences were observed with respect to thiol exchange, Figure 7B.

An identical set of experiments has been preformed using an MHA monolayer and an ODT

coated tip. Preliminary results are in all respects similar to the ones obtained for the ODT monolayer/MHA ink system. Currently the applicability of tip mediated exchange with Au and Ag nanoparticles in addition to bulk noble metal surfaces is being explored.

E. Synthesis and Characterization of Bidentate Disulfide Inks

One of the objectives of this research project is to identify important kinetic and thermodynamic parameters that determine thin film robustness as a function of surface composition and morphology. Toward this goal, we have synthesized and characterized a new bidentate alkyl disulfide compound (**1**) that is based on a trans-1, 2-dithiane-4, 5-diol moiety. When this compound reacts with an Au surface, the disulfide bond breaks and the molecule is anchored to the surface via two sulfur atoms. Due to the chelate effect, this bidentate mode of binding will increase the robustness of SAM films and nanostructures especially when compared with monodentate thiols such as octadecane thiol (ODT) and mercaptohexanoic acid (MHA). Bulk self-assembled monolayers (SAMs) of (**1**) on Au were characterized using contact angle measurements. The average contact angle is 105°, which is slightly lower than the 112° contact angle reported for SAMs of octadecanethiol (ODT). Our preliminary electrochemical measurement shows a reductive desorption peak at ~950 mV vs Ag/AgCl. This new molecule (**1**) can be delivered to a surface via DPN (DATA)?.



4. Personnel Associated with the Project

Personnel at both institutions are actively involved in this project. All of the CCC undergraduates involved receive college credit for their work.

FY1

Project Participant	Status	Salary
Thomas Higgins	HWC Faculty	67 % Summer
Anand Amarnath	CCC Undergraduate Student	100 % Summer
Lubna Sweiss	CCC Undergraduate Student	100 % Summer
Kim McCumber	NU Graduate Student	Unfunded

FY2

Project Participant	Status	Salary
Thomas Higgins	HWC Faculty	67 % Summer
Michael Davis	HWC Faculty	25 % Summer
Anand Amarnath	CCC Undergraduate Student	100 % Summer
Karen Esteras	CCC Undergraduate Student	100 % Summer
Kim McCumber	NU Graduate Student	Unfunded
Khalid Salaita	NU Graduate Student	Unfunded

FY3

Project Participant	Status	Salary
Thomas Higgins	HWC Faculty	50 % Sabbatical
Thomas Higgins	HWC Faculty	67 % Summer

Chad Mirkin	NU Faculty	5 % Summer effort
Anand Amarnath	CCC Undergraduate Student	100 % Summer
Angel Butron	CCC Undergraduate Student	100 % Summer
Angel Butron	CCC Undergraduate Student	100 % Academic Year
Salome Ngatia	CCC Undergraduate Student	50 % Academic Year
Max Ovchinnikov	NU Postdoctoral Fellow	50 % Calendar Year
Aaron Brown	NU Graduate Student	17 % Calendar Year
Meisa Khoshbin	NU Graduate Student	21 % Calendar Year
Khalid Salaita	NU Graduate Student	Unfunded

5. Related Published/Submitted Papers

1. Zhang, Yi; Salaita, Khalid; Lim, Jung-Hyurk; Mirkin, Chad A. "Electrochemical Whittling of Organic Nanostructures," *Nano Lett.*, **2002**, 2(12), 1389-1392.
2. Salaita, K.; Amarnath, A.; Higgins, T.; Mirkin, C. "The Effect of an Organic Solvent Atmosphere On Ink Deposition In Dip Pen Nanolithography" – *manuscript in preparation*.
3. Salaita, K.; Amarnath, A.; Maspoch, D.; Higgins, T.B.; Mirkin, C.A. "Spontaneous Phase Separation of Patterned Binary Alkanethiol Mixtures" *J. Am. Chem. Soc.* **2005**, 127, 11283-11287.

6. Interactions/Transitions

This work directly impacts the commercialization of Dip Pen Nanolithography. We have been collaborating with Dr. Ray Eby at NanoInk to incorporate our findings into the commercial NSCRIPTOR platform. The diffusion coefficients and environmental influence on diffusion rate are factors essential to the DPN process.

7. Patents

None