ELECTRIC CHARGING AND NANOSTRUCTURE FORMATION IN POLYMERIC FILMS USING COMBINED AMPLITUDE-MODULATED ATOMIC FORCE MICROSCOPY ASSISTED ELECTROSTATIC NANOLITHOGRAPHY AND ELECTRIC FORCE MICROSCOPY

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ABSTRACT

Chemically induced rearrangements of amphifunctional molecules have been demonstrated using strong nonuniform electric fields ($10^8$-$10^{10}$ V/m) induced in the vicinity of nanoscale asperities. Electrostatic interactions utilizing these rearrangements of alkylthiolates assembled on Au(111) result in the nanopatterning of raised nanostructure (1.5 - 9 nm high, 15 - 100 nm wide) arrays on a second time scale by manipulating an atomic force microscope (AFM) tip above the monolayer. It is suspected that, as a result of the oxidative cleavage initiated by a weak bias of the tip, the S end of the alkylthiolate chain carrying a sulfenium cation is attracted to the (lifting) tip, forming bi- and higher-layer structures in the vicinity of the tip apex. Stabilization of the multiple-layered structures is accomplished via mutual attraction and entanglement of hydrocarbon chains. The rearrangements suggest a novel and general approach for nanoscale architecture in self-assembled systems.

Water condensation is shown to have a major influence on electric charge transport and nanostructure formation in polymer-, and semiconductor-thin-film surfaces in the proximity of a biased Atomic Force Microscope (AFM) tip. The water forms a meniscus bridge between the AFM tip and the surface to form a three-component system comprised of the AFM tip, water meniscus, and the surface. The associated electric field in the meniscus is spatially non-uniform and has a magnitude of the order of $10^8$-$10^{10}$
V/m. An intensive experimental analysis of the input and output electric currents in the AFM tip/water meniscus/surface system, performed at various relative humidity levels between 10 and 60%, indicates that the magnitude of the output current, drained from surface, reaches values as large as several $\mu$A which exceeds the input current, injected via the AFM tip (0.01-10 nA), by at least an order of magnitude. This effect is particularly evident when the relative humidity is greater than 20-25%, suggesting that the water meniscus is ionized by the strong electric field to produce electrons. Since the method described here for nanopatterning is applicable for materials with significantly different physical, electronic, and optical properties, and is dependent largely on the ambient humidity level and the strength of the electric field, it is suggested that the method may be extended to a variety of other materials.

We utilized a hybrid technique, based on lithography exploiting atomic force microscope tip manipulation combined with modified Electric Force Microscopy to study surface electric charging (deposition and evolution) of poly-methyl methacrylate (PMMA) and polystyrene (PS) films. Two distinct regimes were observed: 1) Mass transport regime related to electric breakdown due to the negative surface charging followed by stable nanostructure formation (negative tip bias); 2) Occasional - to - no feature formation regime attributed to elastic deformation of polymer surface followed by the surface relaxation in the case of positive surface charging (positive tip bias).
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CHAPTER I
INTRODUCTION

1.1 General Overview

The Atomic Force Microscope has enabled us to resolve nanometer size features on a material’s surface. In some cases we can even resolve the atomic structure, showing the location of single atoms in a lattice. It has also proved useful for manipulation of matter at the nanoscale through mass transport of material facilitated by the application of strong non-uniform electric fields. In the first stage of this work we shall show how these strong electric fields can also be used to manipulate matter by inducing chemical modifications utilizing a tip lift up technique we call Z-lift AFMEN. In the second stage of this work we shall show how the humidity of the ambient air affects electric charge transport and nanostructure formation. The third stage focuses on how we can utilize the atomic force microscope to not only manipulate matter at the nanoscale but also the magnitude and location of charges on the surface of polymeric films.

1.2 Stage I: Rearrangements in an Alkylthiolate Self-Assembled Monolayer Using Electrostatic Interactions between Nanoscale Asperity and Organomercaptan Molecules

Nanoscale patterning based on scanning probe microscopy (SPM)\(^1\) has already enabled single-atom placement,\(^2\) atomic manipulations,\(^3\) local surface modification (e.g., scanning probe oxidation of semiconductors\(^4\) and dip-pen lithography\(^5\)), and controllable
dielectric surface reshaping.\textsuperscript{6} Self-assembled monolayers (SAMs) have been studied intensively as a potential platform for SPM patterning during the past decade.\textsuperscript{7-11} Mechanical nanoshaving,\textsuperscript{10} selective monolayer removal,\textsuperscript{8,9,11} local oligomeric substitution,\textsuperscript{9} and insertion\textsuperscript{7} using SPM have all been demonstrated. Aggregates of amphifunctional\textsuperscript{12} molecules with asymmetrical chemical affinity to the surface are useful for molecular engineering and nanotechnology.

The objective of the first stage of this work is to study the behavior of polar amphifunctional molecules for the purposes of nanoscale architecture in a strong nonuniform electric field. An approach for the spatially selective rearrangement of a SAM, based on the electrostatic interactions between a biased atomic force microscope (AFM) tip and the SAM, will be considered. Although this approach is conceptually similar to the AFM-assisted electrostatic nanolithography (AFMEN) previously demonstrated for polymers,\textsuperscript{6,13-15} the specific structural characteristics of the amphifunctional molecules play a major role, in contrast to the ponderomotive manipulation of the dielectric continuum essential in AFMEN.\textsuperscript{6,15} The local molecular rearrangements and intermolecular attraction of hydrocarbon chains of alkylthiolates assembled on a Au(111) surface will be studied to form multilayered nanostructures with spatially localized layers of molecules assembled atop the original SAM. We focus on the study of alkylthiolate SAMs because functionalized long-chain hydrocarbons are typically used for supramolecular architectures.\textsuperscript{16} Although only one type of organomercaptan (CH\textsubscript{3}- (CH\textsubscript{2})\textsubscript{18}-SH) self-assembled on the Au(111) surface will be studied, it is suspected that the technique may be extended to SAMs containing different chain lengths and additional substitutions.
A weak electric bias of -10 to -40 V applied to an AFM tip produces an electrostatic field with a magnitude of $10^8 - 10^{10}$ V/m at the 1-10 nm scale. The field triggers substantial chemical and physical phenomena at the tip-surface junction. A field induced physical phenomenon is water condensation from an ambient environment, resulting in the formation of a water bridge (meniscus) between the AFM tip and the surface.\textsuperscript{17,18} The field induced chemical phenomena include water dissociation and ionization, ion-radical and free-radical production, and interfacial electrochemical processes. These are important instruments for molecular manipulation and modification at the nanoscale.

In this stage, the focus is on the chemical modifications associated with the strong electric field. A traditional way of SAM modification is based on electrochemically induced desorption. Oxidative cleavage of a sulfur metal bond followed by the induced removal of the molecules from organic films on the positively biased metal substrates leads to the formation of depressions in SAMs.\textsuperscript{8-9,11} Schoer et al.\textsuperscript{8} reported a scanning tunneling microscope tip-induced desorption of $n$-octadecylmercaptan from gold surfaces and concluded that the process is electrochemical in nature. An important feature of this process is the presence of significant overpotentials required, due to the possible kinetic limitations of the counterelectrode processes at the tip interface and the conductivity of the tip-substrate junction. A threshold voltage is required to modify the monolayer.\textsuperscript{9} It was found that the magnitude of the threshold voltage decreases as the duration of the voltage pulse increases.\textsuperscript{9}
1.3 Stage II: Influence of Water Condensation on Charge Transport and Electric Breakdown between an Atomic Force Microscope Tip and Polymeric Surfaces

Electrostatic manipulation of macromolecules\textsuperscript{19-22} and biological objects\textsuperscript{23} at the nanoscale is a useful and innovative approach for various aspects of nanotechnology such as ultra-dense data storage, molecular electronics, and bio-nano-electromechanical systems. In most cases, the key tool for the manipulations of molecules on surfaces is an electrically biased atomic force microscope (AFM) tip operated under ambient humidity. Humidity plays an important role in water-meniscus-generated friction at the nanoscale\textsuperscript{24} and is also a critical factor that affects electric current density in the tip-surface junction with regards to nanoscopic feature patterning and their lateral resolution. It has also been shown that nanometer-size menisci of organic liquids may sustain chemical reactions\textsuperscript{25}, and that the properties of menisci depend on the field-induced polarization of the water layer adsorbed on the surface, the surface energy, and ambient water condensation from humid air\textsuperscript{26}. A modeling of induced water condensation\textsuperscript{27}, and free energy analysis of the system comprising of the tip, a water bridge, and a polymeric surface suggests water polarization due to the external electric field plays an essential role and affects tip dynamics\textsuperscript{28}. Furthermore, it has been shown that the formation of a water meniscus in the proximity of an AFM tip is a major factor in electric charge transport\textsuperscript{29} and generation of charge carriers\textsuperscript{30} at the tip-surface junction. Experimental Analysis\textsuperscript{19-22, 29, 30} of electric currents generated by a weakly biased AFM tip through various polymeric films (including polystyrene, polymethylmethacrylate, and fluorinated polybenzoxazole) of different molecular structure and molecular weights in the range 2,000 – 2x10\textsuperscript{6}, and also through the surface of Si(111) suggests the following scenario: a negatively biased AFM
tip (-1 to - 40 V), either dwelling or slowly moving 0.5 – 5.0 nm above the surface, mediates an electric breakdown in the water meniscus due to field-induced water ionization as demonstrated on Si(110) surface\textsuperscript{30}. The ionization of water produces electrons (e-), protons (H+) and hydroxyl radicals (OH•) according to the following reaction\textsuperscript{31}.

\[
\text{H}_2\text{O} \rightarrow \text{e}^- + \text{H}^+ + \text{OH}^-
\]

The field required to induce the latter process is of the order of \(10^9\) V/m, which is the typical magnitude of the electric field in the proximity of a weakly biased AFM tip apex\textsuperscript{31}. The result of this chemical reaction is an abundance of electrons, which carry the current through the water meniscus. Other radical species generated through field induced ionization may be consumed by recombination and related processes.

The behavior of the water meniscus between a surface and a nanoasperity under conditions of extreme electrostatic field is complicated. The objective of Stage II is to experimentally study and describe the influence of ambient humidity, from which the water meniscus is formed by condensation, on nanostructure formation of the surfaces of thin films of polymers. The choice of these materials with completely different physical, electronic, and optical properties in this study is not accidental: an understanding of how amorphous surfaces and macromolecules respond to maskless functionalization is important for photovoltaic cell design and fabrication.

In 1995 electric scanning force microscopy (EFM) emerged as a technique for analyzing electrically polar substances$^{32}$. Since then EFM has proved to be an effective tool for mapping of organic monolayers$^{33}$, imaging of electrostatic surface potential in semiconductors$^{34}$, charge density mapping in biological systems$^{35}$, probing of dipole-dipole interactions in single silicon nanoparticles$^{36}$, analysis of dielectric heterogeneous polymer blends$^{37}$, and for investigation of emission effects in multi-walled carbon nanotubes$^{38}$. The puzzle remains as to how contact electrification occurs between sharp asperities and amorphous dielectric materials such as polymers with narrow energy bands. Previous studies of contact electrification of polymer surfaces demonstrated local charging of PMMA$^{39}$, electrostatic nanoscale patterning of electrets$^{40}$, and recently, electrostatic patterning in low molecular weight PMMA for proposed directed nanoassembly$^{41}$.

The motivation of Stage III was to elucidate the physical reasons of electric charge formation, stability and dissipation on the surfaces of PMMA and PS at the nanoscale. The prime objective was developing the technique to inject the charge, investigate surface charge build-up and evolution under biased atomic force microscope (AFM) tip. The questions to be investigated were: 1) How the formation of electric charge is related to electric current flowing through the polymers and 2) What physical processes occur in the polymers during charge retention. To accomplish this goal, we
have combined an Amplitude Modulated AFM Electrostatic Nanolithography (AM-AFMEN)\(^4\) with in-house modified EFM for electric charge injection and visualization.
CHAPTER II

BACKGROUND

2.1 Atomic Force Microscope Basics

The invention of the Scanning Tunneling Microscope (STM) led to a new class of instruments called Scanning Probe Microscopes (SPM). Scanning Probe Microscopy includes AFM (atomic force microscopy), STM (scanning tunnel Microscopy), and NSOM (near-field scanning optical microscopy). The conceptual setup for in SPM tool is shown in Figure 2.1. A tip is mounted on the head, which scans the sample. Fine horizontal and vertical translations are performed with high precision piezoelectronics. During imaging of the surface some parameter (e.g. Height / Force for AFM, current for STM) is kept constant by means of a feedback loop.

Figure 2.1. Schematic setup for scanning probe microscope.
In Atomic Force Microscopy a sharp tip is attached to a sensitive force sensor (cantilever) shown in Figure 2.2. During imaging the tip is deflected due to interactions with the surface profile of the material being studied and a laser beam is reflected from the top of the cantilever and is projected onto a highly sensitive photodetector Figure 2.3. The deflection of the laser beam is proportional to the deflection of the cantilever with some gain factor $g$. The value of this gain factor is normally 300 – 1000. This means that a cantilever deflection of 0.01 nm is amplified to 3 – 10 nm of beam deflection. This deflection is large enough to generate a measurable voltage. As the sample is manipulated below the tip via the piezoelectric stage a topography image is obtained.

Figure 2.2. SEM image of an AFM tip attached to cantilever.
Figure 2.3. A laser beam is deflected from reflective cantilever to a position sensitive photodetector.

The AFM used in our experiments is a Digital Instrument Dimensions 3100 shown in Figure 2.4. This unit is mounted on a Micro-g Vibration Isolation System. This system is used to dampen any vibrations that would inhibit the quality of measurements. The unit is also equipped with a hood that, when closed, eliminates vibrations in the air. Due to the sensitivity associated with measurements taken at the nanoscale these two systems are vital in acquiring good quality images. The unit is also
Figure 2.4. Digital Instruments Dimensions 3100 Atomic Force Microscope equipped with hood and humidity control system mounted on a Micro-g Vibration Isolation System.
equipped with an in-house designed humidity control system which can be used to
decrease the relative humidity of the air inside the chamber to the desired level. It will be
shown later that the relative humidity becomes a crucial parameter in our research.

Figure 2.5 shows the AFM control station. The Dimensions 3100 AFM is controlled by a
Nanoscope IV controller connected to a PC equipped with two monitors. Also included
in the control station is a function generator and lock-in amplifier used for performing
electric force microscopy. Also shown are two oscilloscopes and a pico-ampermeter
used for performing surface charge measurements.

Figure 2.5. The AFM control station. Two monitors and equipment (sweep function
generator, lock in amplifier, oscilloscope and picoampermeter) to perform surface charge
measurements.
2.2 AFMEN (AFM-assisted Electrostatic Nanolithography) Technique and Applications

Atomic Force Microscopy Electrostatic Nanolithography (AFMEN) is a technique that can be used for patterning and functionalization at the nanoscale (20 – 100 nm). It is a technique that has shown to be applicable to a wide variety of materials including PMMA, PS, CdS, Si, and SBR. We will demonstrate that the process is also effective for electric charging at the nanoscale in PMMA, PS, and CdS. The general AFMEN technique is depicted in Figures 2.6 – 2.8. In Figure 2.6 we see the AFM tip approximated by a sphere of radius R located at a distance h (1-5 nm) above a thin polymer film covering a conductive plane.

![Figure 2.6. Schematic setup of standard AFMEN protocol. AFM tip is approximated by a sphere of radius R located at a distance h above a thin polymer film covering a conductive plane.](image.png)
polymer film (20 – 100 nm) covering a grounded Au-Pd substrate. A bias voltage is applied between the tip and conductive plane. The close proximity of the tip to the plane allows a small voltage (-10 to -30 V) to produce an enormous electric field ($10^8$ – $10^{10}$ V/m) in the area below the AFM tip. This electric field triggers dielectric breakdown through the thin polymer film causing current to flow between the tip and conductive plane. This results in localized joule heating in the polymer directly below the tip. Isotherms are the red curved lines in Figure 2.7 determined from time dependant heat transfer calculations$^{19}$. The black arrows indicate direction of the electric field gradient.

Figure 2.7. Joule heating from current flow increases temperature in polymer above the glass transition shown here as light grey area under the tip. Red lines indicate isotherms while the black arrows indicate the direction of the electric field gradient$^{19}$. 

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When the polymer temperature goes above the glass transition, the softened polarizable polymer melt is then attracted towards the tip through electrostatic pressure based on the Clausius-Mossotti relation shown in equation (1)\textsuperscript{19}.

\[
p = \frac{\varepsilon_0 E^2 (\varepsilon - 1)(\varepsilon + 2)}{2 \varepsilon} \frac{1}{3}
\]

(2.2.1)

The black arrows inside the light grey portion of Figure 2.8 indicate the direction and magnitude of the electrostatic pressure. A raised structure is created through mass transport of the material surrounding the area beneath the AFM tip.

![Diagram of polymer and AFM tip](image)

Figure 2.8. Raised structure formed through mass transport of material due to electrostatic pressure generated by the large non-uniform electric field\textsuperscript{19}.

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Figure 2.9 shows an image created using AFMEN technique of a very robust raised formation in polybenzoxazole that is 60 nm high.

![Image](image.png)

**Figure 2.9.** This image is of a raised formation 60 nm high created in polybenzoxazole.

2.2.1 AM-AFMEN

The previous description of the AFMEN technique is a very general form of a very versatile tool that can be used for patterning or functionalization of a wide variety of materials. Since it creation in 2003 there have been many variations that allow for added parameters giving more control over formation of nanostructures. Figure 2.10 shows that there are many different modifications of the original AFMEN protocol, the first of which is called Amplitude Modulated AFMEN (AM-AFMEN)\(^{20}\). It was first created in 2003 and allows for more control over height of nanostructures.
The original AFMEN technique was done using contact mode. AM-AFMEN utilizes tapping mode shown in Figure 2.11. During tapping mode the cantilever vibrates at a mechanical frequency $\omega_0$ (200 – 400 kHz). This allows for a greater range of height over which the surface influences the oscillation amplitude. In contact mode the height above the polymer film is 1 to 5 nm. We can see from Figure 2.12 that the range over which the tip interacts with the surface during tapping mode (solid line) increases to 30 nm. The dashed line corresponds to tapping mode with an applied bias of -9V. The dotted line corresponds to -18V. The tip maintains surface contact until a critical distance is reached. At that point the amplitude increases with increasing distance.
Figure 2.11. Schematic setup of AM-AFMEN protocol. The tip oscillates 0 to 300 nm above the surface at a frequency of 200 – 400 kHz. A bias applied between the tip and conductive film allows for feature formation.

This allows for a means to control tip to surface distance. Figure 2.13 shows the dependency of oscillation amplitude on bias voltage for constant tip to film distances 30nm (curve 1) and 50 nm (curve 2)\textsuperscript{20}. Figure 2.14 shows how the aspect ratio depends on bias voltage. The aspect ratio (height to width ratio) can be as large as 0.2. This is significantly higher than that available in contact mode. The oscillating tip to surface distance is thought to cause a catastrophic dielectric breakdown though the film\textsuperscript{20}. 
Figure 2.12. Dependency of tip oscillation amplitude with respect to distance between tip and polymer for bias and non-bias situations. The solid line corresponds to 0V bias, the dashed line -9V, and the dotted line -18V. From this one can see that the distance over which the tip interacts with the surface increases with increasing voltage to over 300 nm.
Figure 2.13. Dependency of oscillation amplitude on bias voltage for constant tip to film distances 30nm (curve 1) and 50 nm (curve 2).

Figure 2.14. Aspect ratio dependency on bias voltage for 30 nm polystyrene film on Au-Pd substrate.
2.2.2 Z-lift AFMEN

A further improvement in controlling the process of forming structures on the surface of the polymers is Z-lift AFMEN\textsuperscript{22}. In this protocol the height (Z-lift) is varied by using the piezoelectric stage while applying bias voltage. The voltage and height profiles are shown in Figure 2.15.

Figure 2.15. Voltage and tip retraction profiles during Z-lift AFMEN protocol.

Initially, the tip is brought close to the surface and a zero reference point is found. The voltage is ramped from zero to the required value (form -40V to 40V) in a short time (typically 0.001-0.02s). After the voltage is established the tip is retracted from the surface (typically 0-300 nm) or pushed to the surface (-20 – 0 nm) at various rates. Figure 2.16 shows an array of the dots that were created using Z-lift AFMEN.
Figure 2.16. AFM image of a partial array of dots (viewed at 180°) patterned on a 25 nm thick 110 k $M_w$ PS film. The initial voltage ramp is held constant at 0.025 s and every row denotes a voltage increase ($-25$ to $-30$ V) and every column denotes an increase in the $z$-lift value ($-30$, $-20$, $0$, $+20$, $+40$, $+60$, $+80$, $+100$, $+200$, and $+300$ nm). The right line scan shows the section of dots created during the application of $-29$ V for the varying $z$-lift values. The bottom line scan shows the section of dots created by varying the voltage ($-25$ to $-30$ V) while keeping the $z$-lift value constant at $+200$ nm.\textsuperscript{22}
Along the X axis the value of the z-lift parameter is changed. Along the Y direction, voltage is changed. Z-lift AFMEN allows for more control over the tip to surface distance through certain variable parameters. These parameters are Z-lift rate (0.5 – 2.0 µm/s), initial voltage ramp (0.1 – 0.2 seconds), and bias voltage (0 – 40V). The advantage to this protocol is repeatability and ability to produce variable height nanostructures with a high degree of precision. The disadvantage is that structure formation is limited by the rate at which the cantilever can be retracted\textsuperscript{22}.

2.2.3 Z-AM-AFMEN

The next step in the evolution of AFMEN was a combination of z-lift AFMEN and AM-FMEN called Z-AM-AFMEN\textsuperscript{47} shown in Figure 2.17. This technique combines the two protocols to produce a method that allows even more control over feature formation. It has been utilized to induce cross linking at the nanoscale in SBR\textsuperscript{46} and it shall be demonstrated in this research that it is an effective way to deposit charge at the nanoscale\textsuperscript{47}. The tip is brought towards the surface to a distance where the vibration amplitude is suppressed by at least three orders of magnitude monitored through the tip’s vertical deflection signal on an oscilloscope. This tip’s position is selected as a reference point (Z = 0). The tip is retracted from the reference point (Z-lift) at a distance varied between 10 and 500 nm and a positive/negative electric pulse (1…40 V) is applied to the tip.
2.3 Existing Techniques for Electric Charge Visualization

A Kelvin probe is a simple device used to measure contact potential between a probe and a sample. When two materials with dissimilar work functions come into contact with each other there is a contact potential that arises between the two. A Kelvin probe simply measures the voltage difference between the materials. The Kelvin Probe Microscope is derived from the Kelvin Probe. It can be used to image samples that present a distribution of electrical properties on inhomogeneous materials. It can be used to detect phase separation, chemical recognition, molecular orientation, or photo induced...
charge separation\textsuperscript{32-39}. The advantage to using KPM is that it can be used to make quantitative measurements of surface potential of nanometer size objects with a resolution of about 10mV. It also does not perturb the system to be measured so it can be used to analyze in situ study of operating electronic devices. KPM can be used on a wide variety of surfaces both conductors and semiconductors over a large range of distances from nm to \( \mu \text{m} \). The disadvantage to this technique is that it uses slow interleave mode. In order for KPM to work, one must maintain a constant probe to sample height, and therefore a topography image must be taken first. The Kelvin probe must then retrace the sample surface.

2.3.1 Electric Force microscopy (EFM)

Electric force microscopy can be used to analyze charges or DC voltages on or near the surface of a semiconductor material. EFM is derived from AFM tapping mode using conductive tips. The purpose of EFM is to map the electric field gradient associated with changing charge densities on the surface on a material. As the tip oscillates mechanically above the sample, the cantilever’s resonant frequency (phase) changes with changes in the electric field gradient. Detection of these changes at the photodetector output leads to electric field gradient image. The main disadvantage to this technique is also that it utilizes a slow interleave (2 pass) mode.
2.3.2 Surface Potential EFM (SP-EFM)

Surface potential EFM is used in conjunction with amplitude (or frequency) modulated AFM mode. It uses conductive probes with an applied AC and DC bias between the tip and sample. The applied AC frequency must differ from the cantilever resonant frequency by at least two orders of magnitude. An external lock in amplifier is required to allow for simultaneous topography and electric characteristics (surface potential, trapped charges, capacitance) to be extracted from the photodetector output at different frequencies. If a voltage occurs between the tip and the sample, the resulting force can be written as equation (2.3.1)

\[ F = \frac{1}{2} \frac{dC}{dz} V^2 \]  

(2.3.1)

where \( C \) is the tip to sample capacitance. The voltage \( V \) may be comprised of DC and AC components and can be written as equation (2.3.2)

\[ V = (V_{cp} + V_{dc}) + V_{ac} \sin \Omega t \]  

(2.3.2)

where \( V_{cp} \) is the voltage that arises from the contact potential between the tip and sample, \( V_{dc} \) is an applied DC voltage, and \( V_{ac} \) is an applied AC voltage with a frequency \( \Omega \). Substitution of equation (2.3.2) into (2.3.1) yields a force comprised of three terms. The first term is designated as the DC force \( (F_{dc})\):

\[ F_{dc} = \frac{1}{2} \frac{dC}{dz} \left( (V_{dc} + V_{cp})^2 + \frac{1}{2} V_{ac}^2 \right) \]  

(2.3.3)

This force bends the cantilever continuously but is difficult to detect. The second term is given in equation (2.3.4). It has a simple linear dependence on the contact potential.
and the capacitative coupling \( \frac{dC}{dz} \). The third term, designated \( F_{2\Omega} \), is given in equation (2.3.5). It depends on the local capacitative coupling. By maintaining a constant

\[
F_{2\Omega} = -\frac{1}{4} \frac{dC}{dz} V_{ac}^2 \cos 2\Omega t
\]

(2.3.5)
tip to sample height we can use signal processing to analyze force signal \( F_{\Omega} \) to observe changes in contact potential or capacitance. Interleave mode may be used to maintain a constant height, or in the case of a weak interaction between the tip and sample, we may use the AFM feedback loop. Figure 2.18 shows a weak interaction. The cantilever mechanical frequency is labeled as \( \omega_0 \). The \( F_{\Omega} \) and \( F_{2\Omega} \) force signals do not contribute very strongly to resulting signal measured at the photodetector. The AFM feedback loop can then utilize the resulting signal to maintain the proper tip to sample separation. This enables simultaneous topographical and electrical images to be taken. If there is a strong interaction as depicted in Figure 2.19 we see that the resulting signal can no longer be used to obtain topography images without serious degradation in sharpness and accuracy. Without this accuracy it is impossible to maintain the constant height needed for accurate electrical force images. To overcome this, we use what is called Nano-Kelvin mode shown in Figure 2.20. This mode uses a Kelvin loop that continuously monitors the force signal \( F_{\Omega} \) and injects a DC voltage that nullifies the contact potential voltage resulting in \( F_{\Omega} = 0 \). Doing this not only provides a clean signal for the AFM feedback loop, but also enables direct measurement of the contact potential between the tip and sample.
Figure 2.18. Weak electrostatic interaction.

Figure 2.19. Strong electrostatic interaction.
Nano Kelvin Mode

\[ F_{\Omega} = \frac{dC}{dz} (V_{dc} + V_{cp}) V_{ac} \sin \Omega t \]

Inject DC Voltage that exactly cancels Contact Potential Voltage Using Kelvin Feedback Loop

Figure 2.20. Nano-Kelvin mode. Kelvin Loop is use to nullify the \( F_{\Omega} \) signal by injecting a DC voltage to the tip enabling a means to measure directly the contact potential and provide a means to obtain simultaneous topography and electric force images.

The situation is shown schematically in Figure 2.21. The standard AFM is shown inside the dotted box. A laser reflects to the photodetector from the cantilever which vibrates at a mechanical frequency \( \omega_0 \). A topographical image is obtained from the photodetector output signal and the AFM feedback loop controls the piezoelectric stage to maintain constant height. During SP-EFM an AC voltage is applied between the tip and the sample and also to the reference input of a lock in amplifier.
Photodetector output is connected to the input of the lock in amplifier. The lock in amplifier multiplies the photodetector output by the reference AC signal and integrates it over time. All frequencies not equal to and in phase with the reference signal are nullified due to the orthogonality of sinusoidal functions. The force signals $F_{\Omega}$ and $F_{2\Omega}$ give rise to the electric force images. A Kelvin loop works by analyzing the electric force signal and injecting a DC voltage to the tip which nullifies the force signal.
If there are charges present at or near the surface of the material then a Coulombic force arises between the static charges on the material and the charges that are induced on the tip due to the AC signal. This force adds another term to the $F_\Omega$ signal shown in equation (2.3.6).

$$F_\Omega = \left( \frac{dC}{dz} \left( V_{dc} + V_{cp} \right) - \frac{Q_\delta C}{4\pi\epsilon_0 z^2} \right) V_{ac} \sin \Omega t$$  \hspace{1cm} (2.3.6)$$

From this relation the signs and positions of the charges may be obtained. Quantitative measurements of charge are problematic, but relative magnitudes show up very clearly on the electric force images\textsuperscript{48}.
CHAPTER III
EXPERIMENTAL PROCEDURES

3.1 Stage I

To prepare a SAM sample, cleaved mica was placed in a vacuum chamber and baked at 300 °C at a pressure of 10^{-7} Torr for 24 hours to remove surface contamination. Four Au rods of diameter 1 by 30 mm^2 were then vacuum evaporated from a resistively heated tungsten basket onto the mica surface at a base pressure of 10^{-8} Torr. Prior to the evaporation, the tungsten basket and the chamber were preheated to 120 °C to avoid contamination. After the evaporation, the Au-mica surface was annealed at 330 °C for 2 hours. Then the heating was stopped, and the samples were allowed to gradually cool overnight to room temperature. The substrate was annealed again at 460 °C for 4 hours. A SAM was deposited from the solution of 100 mL of n-nonadecylmercaptan (10^{-3} mol/L in ethanol) and maintained at room temperature for 30 min. The samples were again rinsed in ethanol and dried under nitrogen.

A Veeco Dimension 3100 AFM, utilizing conductive cantilevers from MicroMasch (CSC11/W2C, force constant varied from 0.1 to 0.9 N/m), was used for z-lift electrostatic nanolithography (ZEN). The height of the nanostructures produced can be determined by controlling the cantilever height (z-lift) during the application of voltage. The AFM tip was brought, in contact mode, into close proximity (0.5-1 nm) to the SAM, and the feedback loop was disabled. The tip was manipulated above the sample
surface, patterning an array of dots typically over a square area of 0.5 x 0.5, 1 x 1, or 4 x 4 μm. The bias voltage was varied from -10 to -40 V and applied at each marked point of the array (not between the points) for a time period of 1-100 ms to ensure control over the voltage profile. After the voltage was established, the AFM lever was displaced in the vertical direction by an amount determined by the z-lift parameter and typically varied between -50 and 400 nm at a velocity varied between 1.0 and 2.0 μm/s through displacement of the cantilever’s piezo-drive (z-lift). Then the voltage was removed, and the cantilever was returned to the reference point and stabilized. Finally, the feedback loop was re-engaged, and the tip was translated to the next point of the array. The whole procedure normally required 1-40 s to pattern the array. The relative humidity (H_r) 35-60% was monitored using a hydrometer with an extended probe inserted under the AFM hood.

3.2 Stage II

Polymer films were deposited onto conductive Au-Pd surfaces evaporated on Si (111) as follows. (1) From a 1% wt. solution of poly-(methylmethacrylate) (PMMA), molecular weight 850k diluted in toluene spin cast at 2000 rpm for 20 sec, followed by 6000 rpm for another 20 sec, and (2) from a 0.5% wt. solution of polystyrene, 110k molecular weight spin cast at 3000 rpm for 20 sec, also followed by 6000 rpm for another 20 sec. Each sample was cured for 20 minutes on a hot plate at a temperature 125 C which is above the glass transition points of PMMA and PS. Part of the film on each sample was removed to allow a conductive electrode to be attached. The thickness of the films was estimated to be between 20 and 40 nm and therefore suitable for Atomic Force
Microscopy assisted Electrostatic Nanolithography (AFMEN) protocol which is typically employed for films thinner than 1 μm. AFMEN protocol\textsuperscript{19-23} utilizes a controlled electric bias (0-50 V) through a thin dielectric film (20-300 nm) between an AFM tip and a planar counter electrode beneath the film. An electric breakdown at the nanoscale deforms the dielectric film (softens polymer) directly under an AFM tip via localized Joule heating. A dielectric is polarized and electrostatically attracted to an AFM tip in very strong electric field ($10^8 - 10^{10}$ V/m) generating features. AFMEN allows rapid creation of nanostructures as small as 5-50 nm wide, and 0.5 – 100 nm high without external heating of the dielectric of AFM tip-surface junction\textsuperscript{19-23}.

3.2.1 AFM Electrostatic Nanolithography

A Veeco Metrology 3100 Dimensions scanning probe microscope (SPM) with a Nanoscope IV controller was used to execute standard AFMEN protocol\textsuperscript{1}. Typically, the tip is manipulated at a height of 0.5 – 1 nm above the surface and over 1-4 μm square area, exposing the surface to 1-2 s electric pulses at randomly selected points. The specifics of the protocol can be found elsewhere\textsuperscript{19-22}. It is essential that the AFMEN protocol sustains water meniscus formation when operating in contact mode. A positive or negative tip bias voltage was applied which varied between 0 and 50 V DC magnitude. The input ($i_{in}$) and output ($i_{out}$) electric currents were monitored with a 5400 Keithly pico-ammeter. The input current was measured by connecting the pico-ammeter in series between the Analog 2 output of Nanoscope IV controller and the tip directly; this current was observed to vary linearly with respect to the bias voltage, although some non-linear deviations were observed when large nanostructures were formed in the surface. The
output current was measured using the same pico-ammeter connected in series between a conductive substrate and the ground. The currents were digitized and recorded on a PC.

3.2.2 Humidity Control System

The humidity during the experiment was controlled by isolating the entire AFM system in a closed hood which was supplied by a filtered gas intake line. A desiccant filter and compressed air or N$_2$ was used to provide the gas supply. An exhaust line was incorporated to allow moist air to escape and to avoid pressure build up under the hood. The exhaust and intake ports are located inside the hood at opposite ends. An internal fan ensures that the air inside is mixed thoroughly and the humidity was monitored continuously using wet/dry thermometers and a web cam under the hood. Three different hydrometers (two digital and one based on wet/dry bulbs) were used to monitor the humidity level. The experimental arrangement yields a minimum level of humidity (10%) under the AFM hood. Once the desired humidity is reached, the intake and exhaust ports are closed using valves located outside of the unit. The internal fan is then shut off leaving a stable condition to perform experiments with AFM.

3.3 Stage III

Two high molecular weight polymers: 850,000 mw PMMA and 110,000 mw PS were studied. Both obtained from Air Force Research Laboratories at Wright Patterson Air Force Base in Dayton Ohio. The films were spin-cast onto conductive Au layer evaporated on silicon using the following procedures: (1) A 1% wt. solution of PMMA diluted in toluene was spin cast at 2500 rpm for 30 s, followed by 6000 rpm for 20 s, and (2) A 0.5% wt. solution of PS was spin cast at 3000 rpm for 30 sec, also followed by
6000 rpm for 20 sec. The samples were cured for 60 minutes on a hot plate at a temperature 125 °C above the glass transition points of both polymers. Part of the film on each sample was removed and copper-based conductive electrode was attached. The thickness of the films was measured by scratching part of the film followed by AFM profiling and was estimated to be between 20 and 60 nm for all the samples.

3.3.1 Amplitude Modulated AFM Electrostatic Nanolithography (AM-AFMEN)

The experimental study was conducted on Veeco Metrology Digital Instruments (DI) 3100 Dimensions AFM employing a Nanoscope IV controller. Non-contact, conductive Micromash tips (cantilever was 90 μm long and 35 μm wide; resonant frequency between 200 and 350 kHz; force constant 5 N m⁻¹) were mounted on a tip holder isolated from the rest of the electric circuits. C++ code, combined with a DI nanolithography package, was used to manipulate the AFM tip in the following way: The tip was brought towards the surface to a distance where the vibration amplitude was suppressed by at least three orders of magnitude monitored through the tip’s vertical deflection signal on Tektronix TDS 220 oscilloscope. This tip’s position was selected as a reference point. The tip was retracted from the reference point at the distance varied between 1 and 10 nm and a positive/negative electric pulse (1…40 V) was applied to the tip for 1 sec. The input current through an AFM tip and the output current through the polymer films were recorded using a 5400 Keithly pico-Ammeter. To measure the output current, the Ammeter was connected in series between Au substrate and the ground, while for the input current measurement, it was connected in series between the Analog 2 of the controller and the tip (Figure 3.1).
3.3.2 Modified Electric Force Microscopy

A modified fast EFM\textsuperscript{48} without lift-up option similar to Kelvin Probe EFM (KPFM)\textsuperscript{49} was used to monitor the electric charge distribution and its sign at the sample surfaces. A function generator was used to apply a 25 - 30 kHz sinusoidal modulation reference signal to the AFM tip and a digital lock-in amplifier to resolve the tip’s vertical deflection (Figure 3.1). EFM images (with corresponding topographical images) of PS and PMMA surfaces have been recorded 20-30 s after AM-AFMEN protocol was completed.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.1.pdf}
\caption{Schematic presentation of AM-AFMEN protocol combined with EFM. A biased AFM tip is brought towards the surface of polymer film (thickness was in the range 20 to 60 nm). The oscillating tip is retracted from the surface on 1-20 nm and a bias voltage of 10 volts was applied. In case of negatively charged tip, the nanostructures, 1-10 nm high and 50-150 nm wide were patterned in the surface. In case of positively charged tip the nanostructures were not patterned most of the time. After AM-AFMEN protocol was completed, EFM was performed to monitor electric charge. The image was collected 20-30 sec after lithography protocol was completed.}
\end{figure}
CHAPTER IV
RESULTS AND DISCUSSION

4.1 Stage I

Typical nanostructures patterned in SAMs are shown in Figure 4.1. The structures, in the form of dots and depressions (holes), were patterned depending on the AFM tip bias (ranging from -9 to -15 V), the voltage pulse duration (0.1 - 2 sec), the relative humidity (35 - 60%), and the z-lift (50 - 400 nm). The optimization of these parameters permits thousands of controllable structures to be patterned routinely in the SAM. A trend in the raised structure formation presented in Figure 4.1 (c-e) indicates that z-lift (varied between 90 and 120 nm) is a main factor affecting their dimensions (the height varied from 1 to 9 nm; the width varied between 15 and 60 nm). The height becomes smaller as z-lift decreases. The formation of the holes is affected mainly by $H_r$: even a small increase in ambient humidity ($H_r = 46-53\%$) results in the formation of larger holes, as presented in Figure 4.1 g-k. It is suggested that the spatial chemical modification of the SAM occurs in the following way: The AFM tip, in contact mode, approaches a group of SAM molecules and dwells above them at 0.5-2 nm height. As the negative voltage (-9 to -15 V) is applied to the tip, a strong nonuniform localized electric field polarizes the tip-surface junction and enhances water condensation. The surface of Au(111) serves as an anode in the nanoscale electrochemical cell formed by the tip, the surface and water minisucs.
Figure 4.1. Images of raised formations in self-assembled alkylthiolate monolayers (a) A 6 by 6 array of raised dots patterned in a self-assembled alkylthiolate monolayer on Au(111) using ZEN of an AFM tip manipulated over an area of 1 by 1 μm. The bias voltage was varied between -10 and -15 V (voltage ramp was 10 ms); the z-lift parameter was 300 nm; the height of the dots was determined to be between 2 and 4 nm; the temperature was $T = 24$ °C, and $H_r = 40\%$. (b) A fragment of an array: six nanodots of 2 - 4 nm height patterned at -12 V at a z-lift of +100 nm; a three-dimensional presentation is shown in the inset. (c-e) Formation of dots at a constant humidity, $H_r = 35\%$, and a voltage varied between -9 and -12 V. The height of the dots grows as the z-lift magnitude increases. Insets: (c) z-lift: 90 nm, average height: 1.85 nm; (d) z-lift: 100 nm, average height: 4.01 nm; (e) z-lift: 120 nm, average height: 7.92 nm. The average width varies between 20 and 100 nm. (f) The formation of a 4 by 4 array of the holes (protrusions) over an area of 600 by 600 nm by increasing the voltage to -25 to -30 V and $H_r = 40\%$. The formation of holes at a voltage varied between -9 and -15 V at (g) $H_r = 46\%$ and z-lift = 24 nm, (h) $H_r = 49\%$ and z-lift = 25 nm, and (k) $H_r = 53\%$ and z-lift = 30 nm.
It has been verified experimentally that a bare Au(111) surface with no SAM does not undergo tip induced modification under the conditions used for SAM patterning. This suggests that the alkylthiolate moiety is the basic structural unit involved in nanostructure formation on the SAM. The anodic process occurring in the nanoscale cell is the oxidative cleavage of the sulfur-gold bond resulting in the formation of a sulfenium cation (RS+). This species is known to be stable for days in bulk nonaqueous solution at the preparative electrosynthesis scale (20-50 mL volumes).\textsuperscript{50} The chemical reaction for the oxidative process is as follows:

\[
R - S - A u \bullet A u_n - e^- \rightarrow R - S^+ + A u \bullet A u_n
\]  
(1.1)

It is known from macroscopic electrochemistry that the oxidative desorption of the organomercaptans from the gold surface normally occurs for potentials greater than +0.8 V (vs Ag/AgCl) in aqueous KOH solution.\textsuperscript{51} This corresponds to 3.9 V on the absolute potential scale, so even a weak positive bias of the metal substrate should result in dissociative electron transfer from the adsorbed mercaptan to the Au substrate in the vicinity of the AFM tip. An average magnitude for the Faradaic current flowing through the tip-sample junction required to desorb an SAM in the vicinity of a 30-nm sharp AFM tip is on the order of 10-15 A through a 21.4 Å\(^2\) surface area per adsorbed site,\textsuperscript{16} and it takes approximately 0.1 s to complete this process. This current is substantially lower than the typical current between a biased AFM tip and a conductive substrate, indicating that the conductivity at the tip-substrate junction does not limit the electrochemical process.

Sulfenium cations build up a positive charge at the gold surface electrostatically attracted to the negatively biased AFM tip. It becomes thermodynamically favorable for
the monolayer structure to rearrange itself so that the end of the molecule carrying the sulfenium cation is attracted to the AFM tip, as shown in Figure 4.2. An estimate of the maximum energy required for such a rearrangement corresponds to the binding energy of one hydrocarbon chain to its neighbors in the original monolayer structure, which is about 1.2 eV (26.6 kcal/mol), as calculated from molecular mechanics based on an ab initio force field. Thus, the energy gained by moving a sulfenium cation, carrying full electronic charge magnitude, through a potential difference of several volts (typical tip bias) significantly exceeds the energy necessary to rearrange the hydrocarbon chain. The alkyl chains further assemble with each other to maximize the free energy due to the intermolecular interaction.
Figure 4.2. Schematic presentation of the nanoscale architecture stages. (a) An unbiased AFM tip is positioned above the SAM at 0.5-2 nm. (b) A negative bias of -9 to -15V is applied to an AFM tip, inducing an oxidative cleavage of the S-Au bonds and the formation of sulfenium cations. (c) An additional molecular layer atop the original monolayer is formed as the AFM tip is retracted from the surface (z-lift). (d) Sulfenium cations are reduced to sulfenyl radicals; the structure stabilizes via S-S radical cross-linking (the hydrocarbon chains assemble, stabilizing the nanostructure). The AFM tip is lifted from the monolayer and the sequence of the operations is repeated.
As soon as the monolayer is rearranged, the sulfenium cations undergo reduction to sulfenyl radicals in the proximity of the negatively biased AFM tip:

\[
\text{Alk} - S^+ + e^- \rightarrow \text{Alk} - S^\bullet
\]  \hspace{1cm} (1.2)

This electrochemical step does not involve any covalent bond breaking, thus it requires lower activation energy than the S-Au oxidative cleavage. The sulfenium cations produced at the gold substrate and displaced to the AFM tip by a strong electric field are likely to be reduced at the tip. The high magnitude of the field near the tip apex corresponds to the high concentration of sulfenyl radicals, leading to radical dimerization:

\[
\text{Alk} - S^\bullet + \text{Alk} - S^\bullet \rightarrow \text{Alk} - S - S - \text{Alk}
\]  \hspace{1cm} (1.3)

AS-S cross-linking produces a stable disulfide accompanied by the AFM tip retraction (z-lift). This combination may lead to double- and higher-layered nanostructures patterned in the SAM. The basic steps of this process are depicted in Figure 4.2.

The dimensions of the patterned nanostructures were analyzed statistically. Figures 4.3a and 4.5 present the probability distributions for the height and the width of the nanodots, sampled over 200 randomly selected nanostructures. The maximum height of the nanostructures was measured relative to the average (not modified) surface level, and the width was measured at the half-height. The probability distribution for the dimension \( \hat{\xi} \) (height or width) is defined as

\[
p(\hat{\xi}_\kappa) = \frac{1}{\Delta \hat{\xi}} \frac{\Delta N_\kappa}{\sum_\kappa N_\kappa}
\]  \hspace{1cm} (1.4)

where \( \Delta N_\kappa \) denotes the number of dots in the sample having a value of \( \hat{\xi} \) between \( \hat{\xi}_\kappa \) and \( \hat{\xi}_\kappa + \Delta \hat{\xi} \). The probability distribution for the nanostructure height (Figure 4.1.3)
Figure 4.3. Height of nanostructures formed in SAM. (a) Probability distribution for the height of the structures patterned in a monolayer self-assembled on Au(111). The height discretization step $\varepsilon$ was 0.4 nm. (b-e) Schematics of different types of multilayer structures in the SAM with corresponding heights above the original monolayer. The height range for each proposed structure is based on the length of the linear CH$_3$-(CH$_2$)$_{18}$-S- fragment, which was near 25 Å. (b) Multilayer structure $h_1$ (c) Multilayer structure $h_{2a}$ (d) Multilayer structure $h_{2b}$ (e) Multilayer structure $h_3$. 
presents a decaying progression of the local maxima, with the statistical weight decreasing as the nanostructures become higher. It is suspected that the distribution presents a superposition of multilayered structures, patterned in the SAM according to the mechanism described above. The schematics of several proposed multilayer structures with corresponding heights above the original monolayer are presented in Figure 4.3(b-e). The height range for each proposed structure is based on the length (near 25 Å) of the linear $\text{CH}_3 \times (\text{CH}_2)_{18} \times \text{S}$- fragment in its fully extended conformation. It was found that the variation of the height of the proposed structures follows the maxima on the height probability distribution, as can be seen in Figure 4.3a, especially for the structures depicted in Figure 4.3(b-d). The exact position and the shape of a given maximum in the probability distribution is a result of the balance between enthalpic and entropic factors, depending on the conformational details of the hydrocarbon chain entanglements in the modified regions of the SAM as well as on the density and/or distribution of the desorbed sites on the gold substrate.

The structures with a higher number of layers are less thermodynamically stable compared to those with a low number of layers because the multiple layers of the nanostructures patterned in the SAM are held together by Van der Waals and entropic (entanglement) interactions of the hydrocarbon chains. This results in a reduction in the statistical weight of consecutive maxima in the height probability distribution, as presented in Figure 4.3a. Additionally, we observe that the higher and less stable nanostructures tend to reorganize into more thermodynamically stable layers. This transformation normally requires several hours.
Representative examples of the temporal evolution of the height, and the width of four nanodots patterned in the SAM are shown in Figure 4.4a,b. Analyzing curves 1 and 2 presented in Figure 4.4a, it can be seen that the height of the structures decreases from 5 to 2-3 nm after 2 hours and remains almost constant after that. This suggests that \( h_{2b} \)-type structures evolve into \( h_{2a} \) and \( h_{1} \) structures. The evolution of the width of the same structures presented in Figure 4.4b suggests that organomercaptan molecules either remain undisturbed or slightly change their lateral distribution after being raised by the tip vertically. This trend is in agreement with width probability distribution presented in Figure 4.5. The maximum of the structure width matches well with the radius of the tip measured between 30 and 40 nm. The evolution of 7-8 nm \( h_{3} \)-type structures presented by curves 3 and 4 in Figure 4.4 indicates their evolution into \( h_{1} \) thermodynamically stable structures. This trend suggests that the stability of a multilayered nanostructure can be tuned using appropriate functionalization of the hydrocarbon chains.

The width of the nanostructures, in contrast to their height, is primarily determined by the surface area under the tip where the oxidative desorption and the field-induced rearrangement of the SAM occurs. This is determined by the spatial distribution of the electric field at the tip-monolayer junction. The field can be calculated by solving the Laplace equation for electrostatic potential, with boundary conditions corresponding to the electrically biased tip of a given shape dwelling above the dielectric (SAM) deposited on a conductive (Au) bilayer.\(^\text{15}\) The electric field distribution was calculated numerically using a finite difference discretization of Laplace’s equation.
Figure 4.4. Temporal evolution of the height and the width of four arbitrary selected nanostructures (dots). (a) Height vs. Time. (b) Width vs. Time. Curves 1 and 2 represent the evolution of the structures shown in Figure 4.1d and patterned at a z-lift of 100 nm and a bias voltage of -10 V. Curves 3 and 4 represent the evolution of the structures shown in Figure 4.1e at a z-lift of 120 nm and a bias voltage of -12 V. The humidity was maintained at 35%.
Figure 4.5. Probability distribution for the width of the nanodots patterned in an alkylthiolate monolayer self-assembled on Au(111). The width discretization step parameter was selected as 2 nm.

The variation of the electric field magnitude at the Au surface with respect to radial coordinates (parallel to the surface, going outward from the tip apex) is presented in Figure 4.6. The calculation was performed for a tip bias of -10 V and a tip of curvature 35 nm, as determined from the scanning electron micrograph of the tip presented in Figure 4.7. The height and the average dielectric permittivity of the SAM were set at 2.7 nm and 2.5, respectively (the dielectric permittivity of paraffin varies between 2 and 3). The tip-sample separation (measured from the top of the SAM) was selected as 1.5 nm.
Figure 4.6. Variation of the electric field magnitude $E$ at the surface with respect to the radial coordinate $r$. The tip bias was selected as -10 V, the tip radius was chosen as 30 nm, the height of the SAM was estimated as 2.7 nm, and the average dielectric permittivity was selected as 2.5. The tip-sample separation was 1.5 nm. The region of the strongest electric field was found to be near 40 nm in diameter (confined to $r < 20$ nm), corresponding to the typical width of the nanostructures.
Figure 4.7. Scanning electron microscope image of a conductive MicroMasch tip with a radius of tip apex of around 35 nm.

As can be seen in Figure 4.6, the region of the strongest electric field is nearly 40 nm in diameter (confined to $r < 20$ nm), which is in quantitative agreement with the width probability distribution of the nanodots presented in Figure 4.5. This suggests that bundles of alkylthiolate moieties are attracted to the tip, pulled out of the monolayer row, and positioned as multiple layers atop the original monolayer.
The relative humidity ($H_r$) during these nanopatterning experiments was varied between 35 and 60%. The experiments were conducted at room temperature (between 20 and 25°C). The humidity was an important factor affecting the process. The aspect (height-to-width) ratio of the nanostructures typically decreases with $H_r$. No raised nanostructures could be patterned at humidities exceeding 55%. It is known that organomercaptan oxidation depends on the amount of water available in the reaction. At ambient humidities higher than 50%, the water meniscus at the tip-sample junction suppresses the formation of raised structures. It is suspected that alkylthiolate’s anodic oxidation under such conditions occurs according to the following scheme:

$$ R\text{-S-Au} \cdot \text{Au}_n - 5e^- + 3\text{H}_2\text{O} \rightarrow R\text{-SO}_3^- + \text{Au} \cdot \text{Au}_n + 6\text{H}^+ \quad (1.5) $$

In this reaction, an alkylsulfonate anion leaves the reaction space, and no sulfenium cation production occurs, so the rearrangement of the SAM molecules should not occur. The pronounced strong effect of the ambient humidity on the nanopatterning suggests an additional means of control over the nanostructure formation process.

4.2 Stage II

The system in the present study is effectively an electrochemical cell comprised of the tip, a water bridge, unsaturated water vapor formed in vicinity of the tip due to electrostatic attraction of water molecules to the biased tip, and a surface film. The system is shown schematically in Figure 4.8. The humidity in the system is maintained and controlled by a dynamic filtered air flow method.
Figure 4.8. Experimental configuration of the tip/water meniscus/surface system. The system is effectively a nanoscale electrochemical cell. The water monolayer on the dielectric and other surfaces has been omitted for clarity.

Figure 4.9 presents topographical images of the surfaces illustrating the effect of humidity on surface functionalization of two different materials: poly-methacrylate (PMMA), and polystyrene (PS). For all the samples, AFMEN protocol 1 was applied under variable humidity conditions ($H_r$ varied from 10 to 60%). For PMMA samples nanostructures (raised dots) are formed on the surface and their width decreases with humidity from 50-70 nm ($H_r = 43\%$, Fig. 4.9a), to 15-25 nm ($H_r = 14\%$, Fig. 4.9c). The tip moves above the dielectric surface over a square 2 by 2 μm area patterning an array of 8 dots. Nanostructures are formed for negative voltages between -10 to - 15 V at each marked point (but not between the points) for an exposure time between 0.1 and 2 sec. The height of the features, however, remains essentially independent of the humidity and was determined to be between 2 and 4 nm. We have observed that in AFMEN the
tip-sample separation typically varies between 0.5 and 5 nm, and this separation determines the height of water meniscus, and thus the feature height. A similar trend was observed in PS samples. The width of the structures patterned using the very same conditions decreases with humidity from 90 nm ($H_r$ above 50%, Fig. 4.9d) to 14 nm ($H_r$ < 15%, Fig. 4.9f). Once again, the height of the nanostructures is not affected substantially by the humidity, and was found to be in the range of 1-4 nm. Although both positive (0+30 V) and negative (0-32 V) tip bias is used, the raised structures are patterned for negative bias only. Ablation of the surface is observed for the positive tip bias above + 20 V.

Figure 4.9 Examples of patterning and functionalization of PMMA and PS films. (a) PMMA at $H_r$ = 43%. (b) PMMA at $H_r$=30%. (c) PMMA at $H_r$=20%. (d) PS at $H_r$ above 50%. (e) $H_r$=23%. (f) $H_r$ was less than 15%.
To analyze conductivity processes and charge transport, substantial amounts of $i$-$V$ data were collected. Figure 4.10 (a & b) presents a comparison of $i$-$V$ dependencies, recorded at different humidity levels, for PMMA and PS, films deposited on Au conductive substrates. The plots show the input ($i_{in}$) and output ($i_{out}$) currents. The results for PMMA are presented in Figure 4.10 (a) $H_r=43\%$, (b) $H_r=20\%$, and (c) $H_r=14\%$ for negative and positive tip bias. We define forward bias when the AFM tip is negative and reverse bias when it is positive. For the 10-nm PMMA film at $H_r = 40\%$, Figure 4.10(a), under negative bias the input current varies between 2.6 and 96 nA and the output current exhibits sharp increase from the pA range up to $10^3$ nA exceeding input current by at least one order of magnitude. The raised circular structures are formed in the film for an output current above $10^3$ nA as shown in Figure 4.10(a). For positive bias the input current varies between 7 pA and 0.5 nA and the output current never exceeds 0.012 nA for the entire range of bias voltages from +1 to +30 V. For the 30-nm PMMA film at $H_r = 20\%$, Figure 4.10(b) under negative bias the input current varies between 0.12 and 7.2 nA and the output current again changes two orders of magnitude from 200-250 pA to 70-315 nA. Raised structures are formed in the polymer surface when the output current jumps by an order of magnitude. For positive bias the input current varies between 20 pA and 0.7 nA, while the output current varies between 4 pA and 0.6 nA. In case of negative tip bias, a nearly linear $i$-$V$ dependence was observed for the experimental points above the electric breakdown threshold was observed. For the 30-nm PMMA film at $H_r = 14\%$, Figure 4.10(c), under negative bias the input current varies between 3 and 365 nA, while the output current changes in steps between 0.06 and 0.12 nA, 1.22 and 1.36 nA, 14.6 and 17 nA. No abrupt change of the output current is observed and no evidence of
nanostructures formed can be provided at this level of humidity. In summary, the pattern is different for the positive and negative bias voltages. For negative bias, an abrupt change of the output current with respect to the input current was observed, while $i_{in}$ varied between 0.1 and 365 nA, the output current abruptly jumped from 10-100 pA to $10^3$ nA at humidity levels exceeding 20% as shown in Figure 4.10 and 4.11. The magnitude of the bias voltage, at which the output current abruptly changed several orders of magnitude, varied from -5 V to - 20 V. It was found that $i-V$ dependencies do not show the same trend for $H_t$ lower than 20%. Although $i_{out}$ shows step-like behavior, its magnitude in this case never exceeds $i_{in}$ as shown in Figure 4.12. In all our observations, the output current has never exceeded the input current for positive bias.
Figure 4.10. Input (open triangles), and output (closed triangles) currents versus tip bias voltage for a 10-nm PMMA film at $H_r = 40\%$. 
Figure 4.11. Input (open triangles), and output (closed triangles) currents versus tip bias voltage for a 30-nm PMMA film at $H_r = 20\%$. 

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Figure 4.12. Input (open triangles), and output (closed triangles) currents versus tip bias voltage for a 30-nm PMMA film at $H_r = 14\%$. 
For the 30 nm PS film, the results are presented in Fig. 4.13 $H_r = 50\%$ (e) $H_r = 26$-30\% (f) $H_r = 10$-12\% for negative and positive tip bias. At $H_r = 50\%$, Figure 4.13 and under negative bias the input current varies between 20 pA and 1 nA, and the output current between 4 pA and 12 nA showing dramatic increase above the bias voltage -15 -18 V exceeding the input current for an order of magnitude. For positive bias, the input current varies between 30 pA and 0.7 nA and output current between 10 pA and 45 pA never exceeding the input current. Raised nanostructures formed in case of negative bias, and depressed structures formed in case of positive bias, as indicated on the inset of Fig. 4.9. At $H_r = 26$-30\% under negative bias, Figure 4.14, the input current varies between 10 pA and 0.3 nA, the output current changes between 1 pA and 11 nA exceeding input current for the bias larger than -20 V. For positive bias, the input current varies between 15 pA and 1.1 nA and output current between 1 and 8 pA. Nanostructures repeatedly formed for negative bias only. At $H_r = 10$-12\% under negative bias, Figure 4.15, the input current varies between 12 pA and 250 pA and the output current between 5 pA and 60 pA. For positive bias, the input current varies between 15 pA and 1.1 nA and the output current was very low, varying between 5 and 110 pA. No nanostructures were patterned for the positive tip bias. Once again, the patterns for negative and positive tip bias differ. The output current for the negative bias at humidity level above 25\% jumped several orders of magnitude up to 1-2 nA ($H_r = 50\%$) and to 1 nA ($H_r = 26$-30\%). This trend was neither observed at low humidity nor for reverse tip bias; the nanostructures only formed under negative tip bias.
Figure 4.13. Input (open triangles), and output (closed triangles) currents versus tip bias voltage for a 30-nm PS film at $H_r = 50\%$. 
Figure 4.14. Input (open triangles), and output (closed triangles) currents versus tip bias voltage for a 30-nm PS film at $H_t = 26$-30%. 

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Figure 4.15. Input (open triangles), and output (closed triangles) currents versus tip bias voltage for a 30-nm PS film at $H_r = 10-12\%$. 
The overall similarity of the current-voltage trends for both PMMA and PS substrates suggests that the water meniscus plays a major role in supplying charge for the process. Generation of electrons in the meniscus is triggered at voltages exceeding a substrate-specific threshold, provided that the relative humidity stays above 20%. As a consequence, the measured output current increases while the input current stays limited. For polymeric films, the current inside the film is carried by electrons under the breakdown regime\textsuperscript{19,21}.

Water vapor tends to condense in tiny pores and cavities due to the combined influence of geometrical confinement and intermolecular attraction between the water molecules through hydrogen bonding. The thresholds for the pressure and the humidity required for water condensation are especially low when the confinement length scale is comparable to the size of the molecules\textsuperscript{52}. Nanoscale confinement of water vapor at an AFM tip – surface junction results in a distinct water meniscus in the liquid phase under ambient conditions. The size of the meniscus, as experimentally observed by Rozhok et al\textsuperscript{53} and Weeks \textit{et al.}\textsuperscript{54} and theoretically shown by Jang et al\textsuperscript{55} and Paramonov \textit{et al.}\textsuperscript{56}, grows with ambient humidity. The electric field in the tip-surface junction further enhances water condensation\textsuperscript{57}, which strongly affects the surface functionalization with biased AFM tip.

Electrons in the region between a conductive AFM tip and a conductive backplane may originate from the three following sources: 1) electrons tunneling from the conductive tip, 2) water ionization\textsuperscript{19,30}, and 3) electrons generated on defects and impurities inside of the polymer film\textsuperscript{57}. The fact that $i_{\text{out}}$ was found to be greater than $i_{\text{in}}$ for most cases at $H_r$ above 20-25\% suggests that factor (A) is not the major one. The
electric breakdown was observed in various polymer films of different chemical structure\textsuperscript{19-22}, but was independent of the defect density and impurities concentration. This experimental fact suggests that the major factor for unusually high electric current drained through the polymeric films (1-1000 nA), and also through the surface of semiconductor (10-1000 nA) should \textit{not} be charge generation on the defects and impurities. Although factors 1) and 2) may play a dominant role in other experimental situations, this study allows separation of the factor 2) by simultaneously monitoring the input and output currents.

4.3 Stage III

Figures 4.16 and 4.17 present $i$-$V$ dependencies for input ($i_{\text{in}}$) and output currents ($i_{\text{out}}$) for negative and positive tip bias in PMMA and PS respectively, recorded at constant humidity level of 25\%. For the negative tip bias the trend was observed that the output current may exceed the input current by an order of magnitude. The nanostructures were formed in polymer films and they remained intact for at least 7 days of samples monitoring. For the positive tip bias the structures either relaxed in minutes, or no structures were formed in the same films and the output current never exceeded the input current. The abrupt output current increase level may be associated with field-induced water ionization resulting in electrons supply through the following reaction: $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^- + e^-$ inside the meniscus formed in AFM tip-surface junction\textsuperscript{59}. 
Figure 4.16. Input (open circles) and output (closed circles) currents as a function of tip bias voltage for 40-nm PMMA film (a): negative bias; (b): positive bias at $H_r = 25\%$. 
Figure 4.17. Input (open circles) and output (closed circles) currents as a function of tip bias voltage for 50-nm PS film (a): negative bias; (b): positive bias at $H_r = 25\%$. 

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The charge and topography images are presented in Figure 4.18. Figure 4.18(a) (on the left) shows the EFM image of negative charge formed on the surface of PMMA corresponding to the nanostructure shown on the right image. The tip bias was -17 V and $H_r = 25\%$. Figure 4.18(b) (top) shows the EFM image of the PMMA surface under a positive tip bias at +15 V and the bottom a topography image. For this specific voltage (+15 V) no structures were formed at or above at $H_r = 25\%$. Figure 4.18(c) (on the left image) shows the EFM image of negative electric charge on the surface of PS associated with two raised structures as shown on the right image. The tip bias was -25 V and $H_r = 26\text{-}30\%$. Figure 4.18(d) (top) shows positive charge formation on the surface of PS under positive tip bias, while the bottom image shows that no structures were formed on the surface of PS at tip bias of +18 V at $H_r = 26\text{-}30\%$. For the higher positive tip bias (above +30V) we have systematically observed the trend when accumulation and dissipation of positive electric charge was accompanied by temporary nanostructure formation typically relaxing after 10-15 minutes.

Figure 4.19 shows a sequence of combined topography/EFM images in the surface of 50-nm PS film. The EFM observations for the PMMA and PS films can be summarized as follows: Two distinctly different regimes were observed for all samples. The first regime takes place under negative bias, resulting in stable nanostructure formation related to the electronic breakdown as illustrated in Figure 4.18(a), 4.18(c), and 4.20. In this case, EFM reveals an excess of negative electric charge on the polymer surface as seen from the dark areas on the EFM images (Figure 4.18(a), and (c)). The charge dissipates very slowly as can be seen from Figure 4.20.
Figure 4.18. EFM and topography images of PMMA and PS. (a) Left: EFM image of negative charge formed on the surface of PMMA under tip bias of -17 V and at $H_r = 25\%$. Right: corresponding nanostructure formed in the surface. (b) Top: EFM image of the PMMA surface under a positive tip bias at +15 V. Bottom: corresponding topography image indicating that no structures were formed (c) Left: EFM image of two regions of negative electric charge on the surface of PS formed under a tip bias of -25 V and at $H_r = 26-30\%$. Right: corresponding raised structures (d) Top: Positive charge formation on the PS surface under positive tip bias, + 28 V, and at $H_r = 26-30\%$. Bottom: no structures were formed. The exposure time was 1 sec.
The second regime occurred under positive bias below 30 V as presented in Figures 4.18(b) for PMMA and 4.18(d) for PS. No distinct surface features were formed during this regime, as can be seen from the topographical images. The white areas on the surface are associated with positive electric charge of ionic character. An ionic electric current under the positive tip bias expected to be less than electronic current. This trend was supported by $i$-$V$ dependencies: The output current for positive tip bias was several orders of magnitude less than for negative bias. It was determined that charge accumulated on the surface dissipates after 1-5 hours. The dynamical charge dissipation for the tip bias above +30V recorded in PS films was accompanied by temporary nanostructure formation shown in Figure 4.21. These features were not stable. A plausible explanation could be based on the relaxation of macromolecules elastically displaced by electrostatic forces and finally brought to original position due to the surface tension.$^{60}$.
Figure 4.19. Temporary formation of nanostructures (left column) and positive electric charge dissipation (right column) in a 50-nm PS film. The tip was retracted from the surface on 5 nm and +30 V have been applied for 1 sec. The nanostructures relaxed and the charge dissipated after about 20 minutes. (a) 30 sec; (b) 300 sec; (c) 900 sec after exposure.
Regime 1: Surface charging in PMMA, PS with negative bias: Stable (fixed) nanostructures formed; negative charge drains slowly

Figure 4.20. Regime I: Surface charging with a negative bias tip in PS and PMMA. Negative charge drains slowly; takes hours to dissipate. Images on the far left are electric force images paired with topography images. Set of images on the far right show the decay of charge over 10 hour period.
Regime 1: Reversible deformation in PS using positive bias (+20V)

Figure 4.21. Electric force and topography images for PS using a positive bias tip voltage (+20V). The topography image shows a rapid decay due to relaxation of macromolecules due to surface tension. Positive charge is shown here to dissipate much faster than for the negative bias case.
CHAPTER V

CONCLUSIONS

5.1 Stage I

A novel concept for nanopatterning in SAMs based on electrostatic interactions between an AFM tip and the monolayer has been suggested. Formation of the multilayered nanostructures (1-9 nm height) occurs through the conformational rearrangement of organomercaptan moieties. A weakly (-9 to -15 V) biased tip induces spatially controlled desorption of the molecules, localized to the nanoscale region on the surface, followed by the reorganization of the desorbed species and the stabilization of the nanostructure by intermolecular interactions. Bonding between the desorbed sulfur ends of alkylthiolates enhances the nanostructure stability. Nanostructure height primarily depends on the z-lift parameter, while the width is determined by the combination of the AFM tip’s apex radius and associated electric field distribution. The demonstrated concept provides an additional spatial dimension for nanoscale architecture in SAMs. Selection of the patterning conditions (primarily, the humidity of the ambient air) and of the functionalization of alkyl chains would provide enhanced control over the multilayer structure formation and tuning of the nanostructure stability.
5.2 Stage II

Experimental analysis of the electric current-voltage behavior and the surface functionalization of polymer and semiconductor surfaces, using AFMEN protocol, have been performed for various relative humidity levels. Our results, combined with the previous studies\textsuperscript{19,21,40} suggest that electrons supplied by water ionization are responsible for the sustainable electric current in the tip-sample junction. Furthermore, the current through the films exceeds the input current through the tip by an order of magnitude for relative humidity levels $H_r > 20\text{-}25\%$. The magnitudes of the electric currents, which were estimated based on the calculated electric field distribution in the tip-sample junction and the water self-diffusion rate, agree with the measured current levels indicating that water ionization in the meniscus is a likely factor contributing to the large output current. For the polymer films, the nanostructure formation process is associated with mass transport (displacement) of the macromolecules in a strong electric field gradient. The observed characteristics of nanostructure formation are primarily determined by the water meniscus. The lateral size of the nanostructures fabricated at different levels of humidity decrease with humidity. Interestingly, the structures patterned at relative humidity below 20\% were 15-25 nm in diameter – which is smaller than the curvature of the AFM tip apex, and provides an additional means of control over patterning at the nanoscale.
5.3 Stage III

We have developed a technique, which combines nanolithography with Electric Force Microscopy to study electric charging of the polymer films at the nanoscale. Experimental analysis suggests that the electric charging of the polymer films can result in the two regimes with each regime separated on two scenarios. In the case of negative charging regime: 1) Negative charge is accumulated on the surface without electric breakdown. No structures formed in the samples for electric field strength \( E < 0.4 \text{ V nm}^{-1} \). 2) Electric breakdown accompanied by mass transport occurs for \( E > 0.4 \text{ V nm}^{-1} \) (PMMA films), and 0.425 \text{ V nm}^{-1} (PS films). In the case of the positive charging regime: 1) Positive charge buildups and dissipates without nanostructure formation for \( E < 0.6 \text{ V nm}^{-1} \). 2) Temporary nanostructures form in PS and positive electric charge dissipates in 1-2 hours for \( E > 0.6 \text{ V nm}^{-1} \). It is suspected that surface deformation occurs, which could be related to the combination of elastic response of polystyrene molecules, electrostatic and surface tension forces. Clearly, further study is required to explain the exact nature of the mechanism leading to feature formation and relaxation for the high positive bias.
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