INVESTIGATION OF GROWTH KINETICS OF SELF-ASSEMBLING MONOLAYERS
BY MEANS OF CONTACT ANGLE, OPTICAL ELLIPSOMETRY,
ANGLE-RESOLVED XPS AND IR SPECTROSCOPY

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Absorption of octadecanethiol and p-nitrobenzenethiol onto gold surfaces from ethanol solutions has been studied by means of contact angle, optical ellipsometry, angle-resolved XPS (ARXPS), and with grazing angle total reflection FTIR. Growth of the monolayers from dilute solutions has been monitored and Langmuir isotherm adsorption curves were fitted to experimental data. A saturated film is formed within approximately 5h after immersion in solutions of concentrations ranging from 0.0005mM to 0.01mM. We found, that the final density of monolayer depends on the concentration of the solution.
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CHAPTER 1

INTRODUCTION

Self-assembled monolayers (SAMs) have been known since 1946 when Zisman published work on the preparation of a monomolecular layer by adsorption of a surfactant onto a clean metal surface [1]. The potential of these structures was not recognized until the 1983 publication by Nuzzo and Allara, who showed that SAMs of alkanethiolates on gold can be prepared by adsorption of disulfides from dilute solutions [2]. Since then, SAMs have been widely investigated because of their promising application in many important areas of research and development [3-24] like molecular electronics, lithographic patterning, chemical force microscopy, corrosion resistance, lubrication, wetting, etc. Most studies have been conducted using organothiols and disulfides on metal surfaces, especially alkanethiols on gold [14-24], due to their ease of preparation and stability. However, SAMs of aromatic thiols have recently received much attention [25-32]. Their interesting properties, like high conductivity and nonlinear optical characteristics [25-37], make them attractive candidates for future applications. There have been studies on several aromatic thiols like 4-mercaptopyridine [28-30] and 4-nitrobenzenethiol (NBT) [31-33]. NBT and 3-mercapto-5-nitrobenzimidazole (MNB) have been used for the treatment of gold electrodes in organic thin film transistors (OTFTs) [34-35]. These aromatic thiols can form electron donor-acceptor pairs at the interface between the organic semiconductor and the electrode. As a result, the doping density at the interface is higher
than the bulk, so the contact resistance is reduced. However, little information about the film forming process of these nitroaromatic thiol monolayers on gold can be found in the literature [36-37].

In this work I grew and characterized two kinds of monolayers on gold: octadecanethiol (ODT) and p-nitrobenzenethiol (NBT). The first molecule, well described in literature [14-24], was used as a calibration standard for the kinetics studies. NBT monolayers formed by self-assembly, to my knowledge, have never been thoroughly characterized. I used contact angle measurements, ellipsometry, angle-resolved x-ray photoelectron spectroscopy (ARXPS) and grazing angle total reflection Fourier transform infrared spectroscopy (GATR-FTIR) to characterize the ODT and NBT monolayers on gold.
CHAPTER 2

SELF ASSEMBLED MONOLAYERS

Theory of Self-Assembly

Self-assembled monolayers (SAMs) are molecular assemblies that are formed spontaneously by the immersion of an appropriate substrate into a solution of an active surfactant in an organic solvent [1, 39].

Even though the definition is relatively broad, it has been demonstrated, that only some molecular species form – under specified conditions – true monolayers. These include organosilicon molecules on hydroxylated surfaces (SiO₂ on Si, Al₂O₃ on Al, glass, etc.) [40-52]; alkanethiols on gold [15,18,19,53-28]; alkanethiols on silver [59]; and alkanethiols on copper [60-62]; dialkyl sulfides on gold [63]; dialkyl disulfides on gold [64]; alcohols and amines on platinium [63]; and carboxylic acids on aluminum oxide [11,12,65] and silver [66]. Generally one can divide SAMs into two types, differing by the kind of substrate used. In the first type the surface is amorphous, and packing and ordering are defined by intermolecular interactions. In the second type, where the surface is crystalline, similar to that of Au, the overlayer structure is determined by the substrate crystallinity.

From an energetic point of view, a self-assembling surfactant molecule can be divided into three parts (Fig. 1). The first part is the head group that provides the most exothermic process, i.e. chemisorption on the substrate surface. The very strong molecule-substrate interaction results in an apparent pinning of the head group to a specific site on the surface.
through a chemical bond. The energies associated with chemisorption are of the order of 40-45 kcal/mol for Au-S bond formation [67,68].

Fig. 1. A schematic view of the forces in a self-assembled monolayer.

As a result of the exothermic headgroup-substrate interactions, molecules try to occupy every available binding site on the surface, and in this process they push together molecules that have already adsorbed. This implies that one assumes some surface mobility prior to final pinning, otherwise one cannot explain the formation of crystalline molecular assemblies [67,68]. It is this spontaneous molecular adsorption that brings molecules close enough together and allows for the short-range, dispersive van der Waals forces to become important.

The second molecular part is the core of the molecule – for example the alkyl chain in the case of alkanethiols. The energies associated with interchain van der Waals interactions are of the order of a few (<10) kcal/mol (exothermic). This range of energies is not sufficient to
account for adsorption, and it should be stressed, that the first and most important process is chemisorption. Only after molecules are put in place on the surface can formation of an ordered and closely packed assembly start.

The third molecular part is the terminal group, which in the case of a simple alkyl chain is a methyl group (CH$_3$). These surface groups are thermally disordered at room temperature, as is apparent from helium diffraction [60] and FTIR studies [69]. This part of the molecule, however, is very important to the physical properties of the monolayer. This group also limits the assembling process to a single monolayer.

Structure of Alkanethiol Monolayers on Gold

The chemisorption reaction for the alkanethiols assembling process on Au is believed to be [70]

\[
\text{Au}(s) + \text{RS-H(solv)} \leftrightarrow \text{RS-Au(s)} + \frac{1}{2}\text{H}_2\text{(solv)}
\]

This reaction proceeds at a gold surface where the thiols react with the metal to form a gold thiolate monolayer (Au-SR) and hydrogen. The double-sided arrow in reaction (i) indicates the system is in dynamic equilibrium. Interesting evidence that SAMs are dynamic systems was provided by scanning probe microscopy investigations [71]. The island structures formed by the alkanethiolate monolayer on an evaporated gold substrate exhibited macroscopic shape changes over times as short as minutes. Similar evidence is provided by kinetics studies, which are discussed later in this work.

Electron diffraction studies on the arrangement of alkanethiol molecules on a gold surface conducted by Strong and Whiteside [58] show that the symmetry of sulfur atoms in a
monolayer of docosanethiol on (111) gold is hexagonal with an S-S spacing of 4.97 Å, and a calculated area per molecule of 21.4 Å². Thus, while the chain spacing is equivalent to the second nearest-neighbor gold spacing, the monolayer lattice vector is in the same direction as the principal gold lattice direction (110), and therefore they concluded that the monolayer is not epitaxial to the gold lattice.

The bonding between the Au(111) surface and the sulfur atom in the hollow site has both σ- and π- character. The σ-bonding involves primarily the S p-orbitals and Au 6s-orbitals with significant contribution from the Au p- and d-orbitals [3]. The Au p-orbitals contribute significantly to the π-bonding orbitals as well. It appears that the π-interaction is responsible for the linear structure in the hollow site. The equilibrium surface-S distance is 1.978 Å which gives 2.586 Å for the Au-S distance. The S-H distance is 1.353 Å. In the CH₃S on Au(111) case, the equilibrium geometry was also linear (Au(111)-S-CH₃ angle =180°). The Au(111)-S distance is 1.950 Å, which gives an Au-S distance of 2.530 Å. The chemisorption arrangement suggested from these calculations is consistent with the picture suggested by Chidsey and Loiacono [55], which is based on the Strong and Whitesides data [58]. The calculations confirm that the hollow site on the Au(111) surface is the more stable binding site, and that the chemisorption is not epitaxial. Fig. 2 shows the arrangement of metal atoms on the (111) surface (white dots) and hollow sites (denoted by black dots) that are arranged in an hexagonal relationship with respect to each other, as is indicated by lines connecting six molecules. With the gold atoms at their bulk value (2.884 Å) these hollow sites are 4.99 Å apart, which is in excellent agreement with the electron diffraction [58], helium diffraction [56], and STM data [72].
A useful tool for estimating alkyl chain orientations in self assembled monolayers is FTIR spectroscopy. In an oriented monolayer, transition dipoles show varying tilt angles, and the orientation of various molecular features can be estimated from the relative intensities of the bands observed in the FTIR spectrum. The C-H stretch region is quite characteristic for long-chain alkyl monolayers, with relative methylene and methyl C-H stretch intensities markedly different from those found in isotropic states. Nuzzo et al. [2,64] and Porter et al. [18] used this technique to estimate the orientation of the chains in long alkyl-chain thiols and disulfides on gold. The tilt angle of the chain axis from the normal in thiol monolayers on gold was estimated to be on the order of 20-35° [18]. Further discussion on the use of FTIR in SAM characterization will be presented in later chapters.
Although many characterization methods can be used for determination of self assembled monolayers (SAMs) quality and properties [3,75], there are few that have proven to be useful and relatively easy to perform in the study of molecular monolayers on a regular basis.

It is important to perform the characterization techniques in the proper sequence, because some of the measurement techniques can alter the properties of the film. Usually the first technique used, due to its nondestructive character, is optical ellipsometry [3,75,80-85]. The measured thickness is an important indication of film quality. Contact angle measurements provide information about the properties of the surface of the monolayer as well as the packing density [3,73-79]. SAMs are also studied using x-ray photoelectron spectroscopy [3,14,15,75,89-101] and, probably most insightful, infrared spectroscopy [3,12-14,18,75]. All four methods have been applied in this work to study monolayer growth and properties. Combined results of these techniques should provide a clear picture of the monolayer structure and the formation process.

3.1. Contact Angle

Technique Principle

The contact angle is defined as the angle between the tangent to the droplet of a liquid placed on a flat, homogenous surface, and the surface. The contact angle of a small, sessile (free-
standing) drop, is a function of the surface free energy, and is defined by the Young-Dupré equation [73]

\[ \gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \]  

(3.1.1)

where \( \theta \) is the contact angle, \( \gamma \) is the interfacial free energy per unit area, and \( LV \), \( SV \), and \( SL \) refer to liquid-vapor, solid-vapor, and solid-liquid interfaces, respectively.

Fig. 3. A sessile drop on a solid surface in equilibrium with the vapor phase.

Fig. 3 presents an illustration of the parameters used in the Young-Dupré equation. The angle of a drop on a solid surface is the result of the balance between the cohesive forces in the liquid and the adhesive forces between the solid and the liquid. If there is no interaction between the solid and the liquid, the contact angle will be 180°. As the interaction between the solid and the liquid increases, the liquid spreads until \( \theta = 0^\circ \), and equation 1 becomes:

\[ \gamma_{LV} = \gamma_{SV} - \gamma_{SL} \]  

(3.1.2)

When water is used to measure the contact angle, one determines the hydrophilic or hydrophobic character of the surface. A smooth solid surface exposing closely packed methyl
groups (-CH\textsubscript{3}) has been found to exhibit highly hydrophobic properties. Water contact angles for such a surface range from 105º-110º [3,74]. On the other hand, a solid surface exposing closely packed methylene groups (-CH\textsubscript{2}-), as on a smooth polyethylene surface, gives a water contact angle of 100º-103º.

When investigating monolayers composed solely of alkane chains, one can expect a simple relationship between the value of the contact angle and quality of the investigated monolayer. In disordered, or liquid-like monolayers, methylene groups are more exposed to the surface, and therefore the contact angles decrease [3,16,75,76]. The gold substrate is highly hydrophilic\textsuperscript{1}, so any exposed substrate decreases the contact angle. If molecules do not completely cover the substrate, so that the substrate is exposed to the drop of water, one should observe contact angles of <102º, depending on the degree of surface coverage.

The contact angle will mostly be affected by the terminal group of the molecule under investigation. In the case of -NO\textsubscript{2} or –OH terminal groups, when the tail group of the molecule is polar, the wetting properties should be more hydrophilic, resulting in smaller contact angles than for methyl group-terminated monolayers.

Contact angle measurements, while simple, can provide significant information. Whitesides and co-workers [79] used contact angle measurements to show the effect of burying the polar group in the monolayer by changing the length of the R group in a HS-(CH\textsubscript{2})\textsubscript{16}-OR monolayer. They concluded that a group buried under more than two methylene groups does not influence the wettability of the monolayer. Studies on mixed monolayers with hydrophilic and hydrophobic terminal groups were conducted by Ulman [16,76]. Such heterogeneous SAMs

\textsuperscript{1} There has been long-term argument whether water wets gold is or not, with many publications on either side. This history has been reviewed by Smith [77,78]. The present consensus seems to be that absolutely pure gold is hydrophilic with water contact angle =0º. The reports of nonwetting of Au are an indication of the ease with which a gold surface becomes contaminated. This has also been confirmed by my experience (see chapter on contact angle results).
show direct correlation between percentage of hydrophilic (hydrophobic) molecules in the monolayer and wettability.

Apparatus

Static contact angles were measured with a Rame-Hart GONIOMETER 100-00. Fig. 4 is a photo of the instrument.

Fig. 4. Photo of the Rame-Hart GONIOMETER 100-00

Procedure of Measurement

Prior to each measurement, the alignment of the goniometer was checked and the syringe was filled with fresh DI water. Drops were placed on the surface of the samples in the ambient environment. Readings of drops, such as that shown in Fig. 3, were taken in several places for each sample. Angles were read to ~ ±1° and were reproducible from spot to spot and from sample to sample to ±3°. The reported value is an arithmetic mean of the recorded values.
3.2. Ellipsometry

Technique Principle

Ellipsometry is an optical technique for determining properties of surfaces and thin films [3,8,12-15,80-85]. Some of the advantages of ellipsometry are that it is nondestructive, has high sensitivity and a large measurement range (from fraction of monolayers to several micrometers). One must distinguish between single wavelength ellipsometry, which can measure only two parameters, and spectroscopic ellipsometry, which can analyze complex structures such as multilayers, interface roughness, inhomogeneous layers, anisotropic layers, and much more. In present case, single wavelength ellipsometry has been used.

When plane polarized light interacts with a surface at some angle, it is resolved into its parallel and perpendicular components (s- and p-polarized components, respectively). These components are reflected from the surface in a different way; i.e. the amplitude and phase of both components are changed. When the s- and p-polarized reflected light beams are combined, the result is elliptically polarized light. The shape and orientation of the ellipse depends on the angle of incidence, the direction of the polarization of the incident light, and the reflection properties of the surface [80].

Knowing the polarization of the incident beam and measuring the polarization of the reflected beam, the relative phase change, Δ, and the relative amplitude change, Ψ, can be calculated. Ψ and Δ are used to determine the ratio between the s-polarized and p-polarized light reflected off the surface;

\[ e^{i\Delta} \tan \Psi = \frac{E_{\text{reflected (p)}}}{E_{\text{incident (p)}}} \frac{E_{\text{reflected (s)}}}{E_{\text{incident (s)}}} \]  (3.2.1)
or:

\[ e^{i\Delta} \tan \Psi = \frac{r_p}{r_s} \]  

(3.2.2)

\( \Psi \) and \( \Delta \) relate directly to Fresnel’s equations [80-82].

\[ r_p = \frac{n_1 \cos \Theta_0 - n_0 \cos \Theta_1}{n_1 \cos \Theta_0 + n_0 \cos \Theta_1} \]  

(3.2.3.a)

\[ r_s = \frac{n_0 \cos \Theta_0 - n_1 \cos \Theta_1}{n_0 \cos \Theta_0 + n_1 \cos \Theta_1} \]  

(3.2.3.b)

where:

\( \Theta_0 \) - angle of incidence

\( \Theta_1 \) - angle of refraction

\( n \equiv N - iK \) - complex index of refraction, 0 and 1 of medium and film respectively

For the simplest three layer model (ambient medium, film, substrate) one defines the Fresnel reflection coefficients between medium and film as \( r_{01}^p \) and \( r_{01}^s \) and similarly between film and substrate as \( r_{12}^p \) and \( r_{12}^s \), then:

\[ e^{i\Delta} \tan \Psi = \frac{(r_{01}^p + r_{12}^p e^{-2i\beta})(r_{01}^s + r_{12}^s e^{-2i\beta})}{(1 + r_{01}^p r_{12}^p e^{-2i\beta})(1 + r_{01}^s r_{12}^s e^{-2i\beta})} \]  

(3.2.4)

where

\[ \beta = 2\pi(d/\lambda)(n_1^2 - n_0^2 \sin^2 \Theta)^{1/2} \]  

(3.2.5)

and \( d \) is the film thickness.

This is known as the Drude Extension to the Fresnel model.
Data analysis is conducted by creating a model of a given sample and theoretical values of $\Psi_c$ and $\Delta_c$ are calculated. Next the unknown parameters of the model, such as thickness and refractive index are varied until a best fit between the measured $\Psi_m$ and $\Delta_m$ and calculated $\Psi_c$ and $\Delta_c$ is obtained. The mean squared error is used to measure the goodness of the fit. The solution for the thickness and refractive index is not unique, therefore a reasonable estimate for the film structure is required to obtain useful information.

**Apparatus**

The ellipsometer used in all thickness measurements in this work was an EL X-01R from Micro Photonics Inc. It is a single wavelength, variable angle ellipsometer. A schematic description of the instrument is shown in Fig. 6a. and a photograph is shown in Fig. 6b.
The light source, L, is a HeNe laser ($\lambda=632.8\text{nm}$) followed by a polarizer. The beam is reflected from the sample at an angle $\theta$. The ellipsometer has the capacity to vary the angle from 30 to 90 deg in 5 deg intervals by changing the position of both arms of the ellipsometer. After being reflected, the beam passes through the analyzer prism and into the detector.

The EL X-01R ellipsometer is able to measure thin films between 0.1 and 600nm, with a typical accuracy of 0.1nm. Because of high sensitivity, the thickness of an atomic layer can be measured. Also, in contrast to other methods (e.g. electron microscopy), ellipsometry is a non-destructive method that requires no vacuum and no special sample preparation.
Procedure of Measurement

In order to create the most realistic model of a sample, after each evaporation of gold on silicon substrate, a piece of the Au-coated substrate was handled the same way as the rest of the samples in order to use it as a background sample. The Au coated sample was UV/O₃ treated and rinsed with ethyl alcohol. After drying, this substrate was used to measure the refractive index of the substrate. Values of refractive index and loss index for evaporated gold substrates were found to vary between n= (0.244-0.718), and k= (3.517-3.753) respectively. This difference is probably due to different evaporation rates of Au and hence different surface roughness of the Au coated substrate. The Au films were thick enough that the measurement did not sample the silicon substrate.

Next, the three layer (air-SAM-gold substrate) optical model of the sample was created, assuming a refractive index of the organic monolayer of 1.50 for ODT [3] and 1.62 for NBT. The value of refractive index for NBT monolayer was determined by modeling ellipsometric data of fully grown NBT films, assuming thickness of the layer of 0.9nm. The refractive index of the substrate was taken from the measurement of a clean sample from the same substrate.

Ellipsometry measurements were made on freshly prepared SAM samples that were washed in ethanol and dried with N₂, as described above. The thickness of each sample was measured in a minimum of three different spots. All measurements were taken at an angle of incidence of 45 deg. The thickness of the monolayer for each measurement was obtained by fitting the data to a three-layer model.
3.3. X-ray Photoelectron Spectroscopy

**Technique Principle**

Surface analysis by x-ray photoelectron spectroscopy (XPS) is accomplished by irradiating a sample with monoenergetic soft x-rays, and analyzing the energy of the emitted photoelectrons [86-88]. MgKα or AlKα x-rays (1253.6eV and 1486.6eV respectively) have limited penetrating power in a solid, of the order of 1-10 micrometers. The x-rays interact with atoms in the surface region by the photoelectric effect, causing electrons to be emitted. The sampling depth is limited by the escape depth of the emitted photoelectrons and is typically limited to <10nm [87,88]. The emitted electrons have kinetic energies given by:

\[
E_{\text{kin}} = h\nu - E_B - \phi_s \tag{3.3.1}
\]

where \( h\nu \) is the energy of the incoming photon, \( E_B \) is the binding energy of the atomic orbital from which the electron originates, and \( \phi_s \) is the spectrometer work function. Because the binding energy of an electron to a given atom is not a fixed value but is affected by the chemical environment the atom is located in, the peak of the kinetic energy of the emitted electrons is within a certain range. The change in value of kinetic energy due to interaction between atoms is called a chemical shift.

XPS is the surface analytical tool of choice when surface composition and the composition as a function of depth are under study. XPS has proven to be a very useful technique in the characterization of SAMs [3,75,11,14,15,19,20,89-101]. Allara and Nuzzo used XPS to study the displacement of trifluoroacetic acid by stearic acid [11]. In another study Allara and Nuzzo compare qualities of alkanethiol monolayers grown on different metal substrates by
comparing intensities of photoelectrons emitted from samples of different substrates [14]. XPS has also been used to determine the atomic composition and chemical shifts for monolayers [15,19,20,89]. Fisher et al. applied photoelectron spectroscopy to investigate the interaction of vapor-deposited Al atoms with CO₂H groups at the surface of self-assembled monolayers of alkanethiols [90-92]. Different XPS studies involving organic monolayers concentrate on measuring attenuation lengths of photoelectrons in hydrocarbon films [93,94], to show the ability of XPS to quantitatively measure film thickness.

Angle-resolved XPS (ARXPS) has also been employed for the determination of thickness and orientation of SAMs and multilayer films [95-101]. Parallel Angle Resolved XPS is a non-destructive means to obtain elemental and chemical state information as a function of depth [101].

**Apparatus**

ARXPS analyses were performed with the VG Theta Probe at Thermo Electron Corporation. In contrast to conventional ARXPS this system has several important advancements. One of the advantages of the Theta Probe is that the analysis area is independent of emission angle (Fig. 7) and all angle spectra are taken simultaneously. Also, the analysis position, charge compensation conditions and energy resolution remain constant throughout the measurement.
**Fig. 7.** Analysis area in conventional ARXPS and Theta Probe ARXPS

*Advantage,* the data system developed for the VG Theta Probe, gives the unique capability of constructing non-destructive depth profiles using the Maximum Entropy method [102]. Fig. 8 shows Theta Probe system.

**Fig. 8.** ARXPS VG Theta Probe system. Used with permission from Thermo Electron Corp., www.thermo.com.
Procedure of Measurement

Samples were mounted on a standard Theta Probe sample holder and analyzed using the standard microfocused, monochromatic Al Kα X-ray source. The size of the X-ray spot was 400 µm in diameter. Angle resolved spectra were obtained by acquiring 16 angle channels simultaneously in each scan. A non-destructive depth profile was constructed from the data using Maximum Entropy methods. The thickness of the layers was calculated using the multi-layer thickness calculator part of the Advantage data system.

3.4 Infrared Spectroscopy

Technique Principle

Over the last two decades infrared (IR) spectroscopy has emerged as an important tool for probing molecular structures and modes of bonding at chemically modified surfaces. Improvement in IR instrumentation has led to a widespread use of this technique for thin film analysis.

IR Spectroscopy takes advantage of asymmetrical molecular vibrations [105]. Such vibrations cause a net change in dipole moment between two atoms vibrating in the molecule. If the natural vibrational frequency of the molecule matches the frequency of the incident radiation, a transfer of energy takes place resulting in an absorption of the incident radiation. The frequency of oscillation of two atoms can be expressed in a simple form:

\[
\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}
\]  

(3.4.1)

Where \( \mu \) is the reduced mass of an atomic system:
\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]  

(3.4.2)

where \( m_1 \) and \( m_2 \) are the masses of the atoms at the end of the bond, and \( k \) is the force constant – a measure of the stiffness of the bond (referred as to a spring in Hook’s law).

Based on classic electromagnetic wave theory Allara et al. developed computational methods for IR spectra simulation [12,103]. The simulated spectrum is compared with the experimental spectrum, and molecular orientation is determined by comparing the quality of the fit of the calculation to experiment. Their work has brought great advancement in the understanding of the monolayer structure. They were able to estimate molecular tilt and twist inside a molecular monolayer by comparing the calculations to experimental data. This method has been successfully applied by other research groups [13,14,18,60,69,106-110].

IR Spectra simulations have not been performed as part of this project. In this work I compare features of the acquired spectra with previous publications [12-14,18,60,69] and use the general trends in peak positions and intensities to determine crystallinity of the film.

**Apparatus**

Absorption spectra were obtained using a NEXUS 470 FT-IR spectrometer (Nicolet) with a grazing angle ATR (GATR™ (Harrick Scientific Corporation, Ossining, NY, www.harricksci.com)) attachment. The GATR is a single reflection horizontal ATR accessory especially suited for analyzing coatings and thin films, including monolayers on silicon wafers and flat metal substrates [111,112]. It employs a 65° angle of incidence and a Ge ATR crystal. It is specifically designed to take advantage of the sensitivity enhancement that occurs for an extremely thin film sandwiched between a silicon or a metal substrate and a Ge ATR crystal under the condition of supercritical internal reflection. This enhancement quickly decreases as
the distance between the substrate and Ge crystal increases beyond 1/100 of a wavelength. Therefore a rubber padded pressure applicator is applied to optimize the spectral sensitivity. The sensitivity achieved far exceeds the sensitivity obtained by more commonly used grazing angle single reflection spectroscopy [111,112]. The GATR attachment is simple to use yet has excellent sensitivity for organic monolayers compared with other FTIR techniques.

Fig. 9. GATR attachment. Used with permission from Harrick Scientific Corporation, www.harric.com.

**Procedure of measurement**

An MCT detector cooled with liquid nitrogen was used for spectra aquisition. The spectral resolution was 4 cm⁻¹, the velocity of the moving mirror was 1.8 cm/s, and the number of scans used to obtain the interferogram was 200. Reference spectra were obtained from the same substrate as used for samples preparation. The pressure applied on the sample that was in contact with the Ge ATR crystal was 30oz/in. It is important to apply constant pressure to all the samples in order to be able to compare intensities of the features of the spectra. Higher pressure will result in more intense absorption, but too much force can damage Ge crystal.
CHAPTER 4

RESULTS

4.1 Materials and Sample Preparation

The chemicals used in this work were purchased from Aldrich Chemical Co. and were used without further purification. Octadecanethiol (ODT) and p-nitrobenzenethiol (NBT) have a nominal purity of 98% and 80% respectively. Absolute ethanol was acquired from AAPER Alcohol. Gold used for the substrate preparation was 99.999% purity.

Gold substrates were prepared by thermal evaporation of gold from tungsten boats onto Si wafers. Silicon wafers with native oxide were used and a thin Cr adhesion layer was deposited before gold evaporation. Depositions were carried out in the base vacuum of $10^{-6}$ Torr. Thickness of the layers and rate of depositions were monitored by a quartz crystal thickness monitor placed near the wafers. Typical deposition rates were 0.2-0.5 Å/s and the thicknesses were about 20 Å for Cr and 400Å for the Au layer. Prepared wafers were cut into 1 in$^2$ pieces. Particles were removed using compressed nitrogen and an ultrasonic ethanol bath. Pieces are blown dry with nitrogen and cleaned in a UV/O$_3$ cleaner for 5 minutes to remove organic impurities. Immediately after cleaning, pieces were immersed into freshly prepared solutions in covered Petri dishes. All glassware was cleaned with NOCHROMIX® (GODAX Laboratories, Inc., Takoma Park, MD, www.godax.com) solution and rinsed with ethanol prior to use. All handling was carried out in a class 1000 clean room at ambient temperature. Ethanolic solutions
of both ODT and NBT were prepared in volumetric flasks. Concentrations used were 1x10^{-5} M, 5x10^{-6} M, 1x10^{-6} M and 5x10^{-7} M. Immersion times ranged from 1 min to 26h. After removal from the growth solution each sample was immediately rinsed for approximately 30 sec and sonicated for 1 min in ethanol to ensure removal of physisorbed molecules. The samples were again dried with nitrogen and characterized.

4.2 Contact Angle

Sessile drop contact angles of water were measured on the series of samples prepared by immersion into solutions of different concentrations for time periods ranging from 1 min to 26h. Concentrations used for ODT molecule solutions were: 0.01mM, 0.005mM and 0.001mM. Fig. 10 and Table 1 summarize contact angle values of the ODT films. Each value is an arithmetic mean of a minimum 5 readings taken from at least two different samples. Values of contact angles for all three series vary with time of immersion, showing rapid growth of the monolayer within first the few minutes after immersion. For a fully developed monolayer, the contact angle was between 105-110°, which is in good agreement with the literature [3,11-16]. These values were reached in about 5h of immersion and suggest that the monolayer is well oriented and tightly packed, exposing the low-energy methyl surface. I was not able to demonstrate a similar growth of the NBT monolayer, for which the contact angle was about the same for all samples, and measured approximately 65-70 degree. I speculate that the wettability of the monolayer exposing the NO2 group is similar to the bare Au substrate. Even though the contact angle for a clean gold substrate had been reported to be 0°, it is a theoretical value obtained only for absolutely clean gold surfaces [74]. The ease with which a gold surface becomes contaminated has been an ongoing dispute in the literature [77,78]. My experience also
confirms that this theoretical value is very difficult to obtain and contact angles of freshly cleaned Au substrates changes very rapidly from 0° to 30° within several minutes, reaching a value of 70° within several hours, even if handled under clean room conditions. Similar behavior was observed for Au substrates immersed in ethanol. Attempts to measure contact angles with different liquids (hexadecane, decane, THF, iodomethane) yielded similar results.

Table 1. Contact angle of sessile water drop of ODT film

<table>
<thead>
<tr>
<th>Time in solution</th>
<th>0.01mM</th>
<th>0.005mM</th>
<th>0.001mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 min</td>
<td>92</td>
<td>87.7</td>
<td>79.7</td>
</tr>
<tr>
<td>5 min</td>
<td>100</td>
<td>95.8</td>
<td>84.8</td>
</tr>
<tr>
<td>10 min</td>
<td>105</td>
<td>101.3</td>
<td>89.2</td>
</tr>
<tr>
<td>20 min</td>
<td>103.2</td>
<td>102.5</td>
<td>90.2</td>
</tr>
<tr>
<td>40 min</td>
<td>105.5</td>
<td>106</td>
<td>91.3</td>
</tr>
<tr>
<td>1.5 h</td>
<td>106</td>
<td>106.7</td>
<td>103.7</td>
</tr>
<tr>
<td>3 h</td>
<td>106.2</td>
<td>106.6</td>
<td>103</td>
</tr>
<tr>
<td>5 h</td>
<td>106</td>
<td>107.2</td>
<td>106.7</td>
</tr>
<tr>
<td>8 h</td>
<td>106</td>
<td>-</td>
<td>107</td>
</tr>
<tr>
<td>17.5 h</td>
<td>106.2</td>
<td>107.3</td>
<td>106.3</td>
</tr>
<tr>
<td>22 h</td>
<td>107.5</td>
<td>106.6</td>
<td>105.7</td>
</tr>
<tr>
<td>24 h</td>
<td>105.7</td>
<td>107</td>
<td>106.7</td>
</tr>
</tbody>
</table>

The results of the measurement are very consistent. For most data points the standard deviation is approximately 1° (Fig. 11).
Fig. 10. Contact angle values for ODT monolayer grown in ethanol solutions as a function of immersion time. a) data points over the entire range of immersion times, b) data points for up to one hour of immersion.
Fig. 11. Contact angle values for ODT. Error bar represents standard deviation of readings. Each point is an average of a minimum of five readings from ad least two different samples. a) 0.001mM series, b) 0.005mM series, c) 0.01mM series
4.3 Ellipsometry

Ellipsometry was used to determine the average thickness of the monolayer and to monitor progress of film growth. The ODT monolayer thickness measured by ellipsometry changes from 0 nm to approximately 2.0 nm in approximately 5h of immersion time. The thickness remains constant for longer immersion times. Table 2 and Fig. 12 presents the ODT film thickness as measured by ellipsometry. Each value is an average over a minimum of 7 measured points from a minimum of two different samples. The standard deviation of the measurement is plotted in Fig. 13. The large error in these measurements (up to 0.8nm) is due to the nature of the samples. At very low film thicknesses, as occurs in sub-monolayer stages of SAM formation, the changes in the ellipsometric angle $\Psi$ is well below the experimental uncertainty in the angle measurement[84]. Nevertheless, the final value determined for saturated ODT monolayer is in reasonable agreement with the literature values: 24Å [3,75,83], 20Å [15], and 19Å+2 [113] for octadecanethiol on gold substrates.

Table 2. Ellipsometric thickness (nm) of ODT film

<table>
<thead>
<tr>
<th>Time in solution</th>
<th>0.01mM</th>
<th>0.005mM</th>
<th>0.001mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 min</td>
<td>0.394</td>
<td>0.197</td>
<td>0.234</td>
</tr>
<tr>
<td>5 min</td>
<td>1.163</td>
<td>0.482</td>
<td>0.328</td>
</tr>
<tr>
<td>10 min</td>
<td>1.384</td>
<td>0.879</td>
<td>0.388</td>
</tr>
<tr>
<td>20 min</td>
<td>1.814</td>
<td>1.408</td>
<td>0.473</td>
</tr>
<tr>
<td>40 min</td>
<td>1.887</td>
<td>1.738</td>
<td>0.455</td>
</tr>
<tr>
<td>1.5 h</td>
<td>1.829</td>
<td>2.022</td>
<td>0.862</td>
</tr>
<tr>
<td>3 h</td>
<td>1.816</td>
<td>1.942</td>
<td>1.483</td>
</tr>
<tr>
<td>5 h</td>
<td>1.644</td>
<td>2.059</td>
<td>1.827</td>
</tr>
<tr>
<td>8 h</td>
<td>1.973</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>17.5 h</td>
<td>2.012</td>
<td>1.927</td>
<td>2.118</td>
</tr>
<tr>
<td>22 h</td>
<td>2.180</td>
<td>2.105</td>
<td>2.118</td>
</tr>
</tbody>
</table>
Similar regions of rapid film growth and saturated monolayer formation were also observed in the case of the NBT molecule (Fig. 14 and Table 3). For this monolayer, the final thickness is determined to be about 0.9 nm. This is the expected value, taking into account the length of the molecule (about 10 Å). However, the large errors in the measurement (Fig. 15) suggest the film thickness should be analyzed by other techniques.

Table 3. Ellipsometric thickness of NBT film

<table>
<thead>
<tr>
<th>Time in solution</th>
<th>0.01mM</th>
<th>0.005mM</th>
<th>0.001mM</th>
<th>0.0005mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 min</td>
<td>0.450</td>
<td>0.243</td>
<td>0.109</td>
<td>0.000</td>
</tr>
<tr>
<td>5 min</td>
<td>0.458</td>
<td>0.433</td>
<td>0.144</td>
<td>0.016</td>
</tr>
<tr>
<td>10 min</td>
<td>0.568</td>
<td>0.546</td>
<td>0.196</td>
<td>0.316</td>
</tr>
<tr>
<td>20 min</td>
<td>0.397</td>
<td>0.739</td>
<td>0.371</td>
<td>0.183</td>
</tr>
<tr>
<td>40 min</td>
<td>0.748</td>
<td>0.685</td>
<td>0.519</td>
<td>0.195</td>
</tr>
<tr>
<td>1.5 h</td>
<td>0.698</td>
<td>0.705</td>
<td>0.659</td>
<td>0.515</td>
</tr>
<tr>
<td>3 h</td>
<td>0.814</td>
<td>0.742</td>
<td>0.850</td>
<td>0.630</td>
</tr>
<tr>
<td>5 h</td>
<td>0.955</td>
<td>0.856</td>
<td>1.103</td>
<td>0.651</td>
</tr>
<tr>
<td>8 h</td>
<td>-</td>
<td>-</td>
<td>0.821</td>
<td>-</td>
</tr>
<tr>
<td>17.5 h</td>
<td>1.057</td>
<td>0.958</td>
<td>1.029</td>
<td>0.895</td>
</tr>
<tr>
<td>22 h</td>
<td>1.107</td>
<td>0.933</td>
<td>0.997</td>
<td>0.886</td>
</tr>
</tbody>
</table>
Fig. 12. Ellipsometric thickness of the ODT monolayer as a function of immersion time. a) data points over the entire range of immersion times, b) values of the ellipsometric thickness for up to one hour of immersion.
Fig. 13. ODT ellipsometric thickness data points. Each point is an average of a seven readings. a) 0.001 mM series, b) 0.005 mM series, c) 0.01 mM series
Fig. 14. Ellipsometric thickness of NBT film as a function of immersion time. a) data points over the entire range of immersion time, b) values of ellipsometric thickness for first hour of immersion
Fig. 15. Ellipsometric thickness of NBT film. Points are an average of a minimum seven measurements on minimum of two different samples. a) 0.0005mM series, b) 0.001mM series, c) 0.005mM series, d) 0.01mM series
4.4 X-ray Photoelectron Spectroscopy

In order to verify the ellipsometric data, angle resolved x-ray photoelectron spectroscopy (ARXPS) measurements were performed on representative samples of fully grown ODT and NBT monolayers. The thickness determined by XPS was 19±2Å for ODT and 6±2Å for NBT monolayers, which is consistent with the ellipsometric measurements.

Fig. 16. ARXPS depth profile ODT film

Fig. 17. ARXPS depth profile of NBT film
Additionally, depth profiles were constructed from the angle resolved data (Fig. 16 and 17) using maximum entropy methods. The ARXPS profiles for both samples indicate that the sulfur is localized at the self-assembled monolayer/gold interface. The XPS data did not show any impurities for the ODT film. For the NBT monolayer, the oxygen profile sharply increases towards the surface, while the nitrogen appears throughout the film. This may suggest, that not all molecules are “standing”, and some of them might be “laying” on the surface. Also, adsorption of species other than p-substituted nitrobenzenethiol is possible. No impurity elements were found in NBT film.

High energy resolution XPS spectra on ODT and two NBT samples were performed as well. Fig. 18 presents the C1s region of the XPS spectrum with spectra of the ODT monolayer and two NBT monolayers. The C1s spectrum from the ODT sample consists of a very strong component at a binding energy of 285.0 eV and a much weaker component at higher binding energy. The stronger component was assigned to CH2 groups. The C1s spectra for both NBT samples consist of several components, the strongest of which appears at 284.2 eV. This component was assigned to aromatic carbon. There are components of significant intensity at binding energies between 286-289 eV, attributable to the carbon-nitrogen and carbon-sulfur groups.
Quantitative results of XPS measurement for the ODT sample and two NBT samples are included in Table 4, together with theoretical values of elemental composition for both monolayers. In all cases, measured composition is very similar to the theoretical values.

Table 4. Theoretical and measured values of elemental composition for the ODT and NBT monolayers

<table>
<thead>
<tr>
<th>Element</th>
<th>ODT (exp.)</th>
<th>ODT (th.)</th>
<th>NBT (exp. 1)</th>
<th>NBT (exp. 2)</th>
<th>NBT (th.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>3.4</td>
<td>5.2</td>
<td>6.2</td>
<td>6.7</td>
<td>10</td>
</tr>
<tr>
<td>C</td>
<td>96.9</td>
<td>94.7</td>
<td>67.2</td>
<td>60.7</td>
<td>60</td>
</tr>
<tr>
<td>N</td>
<td>---</td>
<td>---</td>
<td>5.1</td>
<td>7.2</td>
<td>10</td>
</tr>
<tr>
<td>O</td>
<td>---</td>
<td>---</td>
<td>21.5</td>
<td>25.4</td>
<td>20</td>
</tr>
</tbody>
</table>
4.5 Infrared Spectroscopy

Fourier transformed infrared (FTIR) spectroscopic measurements were performed. Fig. 19 shows an example of the IR spectrum of an ODT SAM with assigned vibrational modes [105].

![FTIR spectra of ODT monolayer](image)

There are three frequency modes below 1500 wavenumbers which are characteristic of alkanes; symmetric C-H deformations of the CH$_3$ group at 1380 cm$^{-1}$, asymmetric C-H deformations of the CH$_3$ group at 1450 cm$^{-1}$, and C-H vibrations of the CH$_2$ group at 1465 cm$^{-1}$. These vibrations are of low to medium intensity. More intense features used in the literature to characterize an ODT monolayer [12-14,18] are found in the C-H stretching region between
The band at 2965 cm\(^{-1}\) is assigned to the CH\(_3\) asymmetric in-plane CH stretching mode, \(\nu_a(CH_3, ip)\). The bands at 2879 and 2937 cm\(^{-1}\) are assigned to the CH\(_3\) symmetric CH stretching mode, \(\nu_s(CH_3, FR)\); this band is split due to Fermi resonance interactions with the lower frequency asymmetric CH\(_3\) deformation mode. The peak at 2937 cm\(^{-1}\) overlaps with the CH\(_2\) asymmetric stretching mode \(\nu_a(CH_2)\) at 2917 cm\(^{-1}\) and appears as broadening of the later. The band at 2850 cm\(^{-1}\) was assigned to the symmetric CH\(_2\) stretching mode, \(\nu_s(CH_2)\). Porter et al. showed that these exact positions of the CH stretching peaks for ODT films are indicative of a well arranged, crystalline monolayer [18]. In the same work they showed that the position of the peak frequencies for the \(\nu_a(CH_2)\) modes provide insight into the intermolecular environment of the alkyl chain in the assemblies. A shift to lower wavenumber for this peak is characteristic of well ordered molecules and implies that the alkyl chains are fully extended with all-trans conformations, whereas a shift to higher wavenumber positions suggest a disordered, liquid-like layer. They report 2917 cm\(^{-1}\) as the value for the \(\nu_a(CH_2)\) peak for a well-ordered monolayer. The growth time when this value was reached in this work depended on the solution concentration the samples were grown in. Peak positions for the \(\nu_a(CH_2)\) mode are summarized in Table 5.

Table 5. Peak position summary for \(\nu_a(CH_2)\) mode stretching in ODT samples.

<table>
<thead>
<tr>
<th>Time in solution</th>
<th>1 min</th>
<th>5 min</th>
<th>10 min</th>
<th>20 min</th>
<th>40 min</th>
<th>1.5 h</th>
<th>3 h</th>
<th>5 h</th>
<th>17 h</th>
<th>23 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 mM</td>
<td>2921</td>
<td>2919</td>
<td>2917</td>
<td>2917</td>
<td>2917</td>
<td>2917</td>
<td>2917</td>
<td>2917</td>
<td>2917</td>
<td>2917</td>
</tr>
<tr>
<td>0.01 mM</td>
<td>2920</td>
<td>2919</td>
<td>2919</td>
<td>2917</td>
<td>2917</td>
<td>2917</td>
<td>2917</td>
<td>2917</td>
<td>2917</td>
<td>2917</td>
</tr>
<tr>
<td>0.005 mM</td>
<td>2925</td>
<td>2923</td>
<td>2921</td>
<td>2921</td>
<td>2919</td>
<td>2919</td>
<td>2917</td>
<td>2917</td>
<td>2917</td>
<td>2917</td>
</tr>
<tr>
<td>0.005 mM</td>
<td>~2923</td>
<td>2921</td>
<td>2919</td>
<td>2919</td>
<td>2919</td>
<td>2919</td>
<td>2917</td>
<td>2917</td>
<td>2917</td>
<td>2917</td>
</tr>
<tr>
<td>0.001 mM</td>
<td>~2925</td>
<td>~2925</td>
<td>~2925</td>
<td>~2925</td>
<td>~2925</td>
<td>~2925</td>
<td>2919</td>
<td>2919</td>
<td>2917</td>
<td>2917</td>
</tr>
<tr>
<td>0.001 mM</td>
<td>-</td>
<td>~2925</td>
<td>2923</td>
<td>2923</td>
<td>2921</td>
<td>2921</td>
<td>2919</td>
<td>2919</td>
<td>2917</td>
<td>2917</td>
</tr>
</tbody>
</table>

Reported by Porter et al. for crystalline-like ODT monolayer [18] 2917
In two separate runs for each concentration series, it is clearly visible that a dense monolayer is grown much faster in less dilute solutions. In the case of the 0.01mM solution, the value of 2917 cm\(^{-1}\) is reached within 10 to 20 minutes; for the 0.005mM solution 1.5-3h, and for the 0.001mM solution in 5h. In all cases the position of the 2917 cm\(^{-1}\) peak is constant after it is once reached.

Development of the peaks in the C-H stretching region between 2800 cm\(^{-1}\) and 3000 cm\(^{-1}\) is shown in Fig. 20 through 22. Initially only the \(\nu_a(CH_2)\) mode can be seen. With increasing immersion times \(\nu_s(CH_2)\), \(\nu_a(CH_3,ip)\), and \(\nu_s(CH_3,FR)\) bands are observed. The positions and relative intensities of the peaks change as the molecules adjust position in the monolayer. Knowing that only the component of incident light that is parallel to the plane of incidence gives measurable absorption [114], we can determine the molecular orientation as a function of film growth. Absorption of the CH\(_3\) group does not change significantly once the complete monolayer is formed. This is expected since in the monolayer surface groups are thermally disordered at room temp [60,69]. Decreasing intensity of the \(\nu_a(CH_2)\) mode was associated with tilting of the molecules and interactions between them [12]. The final intensity ratio between the \(\nu_s(CH_2)\) and \(\nu_a(CH_3,ip)\) stretching modes was approximately 1:1, which is consistent with the value reported by Porter et al. [18]. This ratio was observed only in the 0.01mM solution and was never achieved in more dilute solutions. This fact can be explained by existence of the equilibrium between adsorption and desorption of the molecules on the surface. Monolayer formed in less concentrated solutions will never achieve maximum packing density. This is discussed more in chapter 5.
Fig. 20. FTIR spectra of 0.001mM ODT series. Spectra were obtained using an MCT nitrogen-cooled detector at the spectral resolution of 4 cm\(^{-1}\), the velocity of the moving mirror was 1.8 cm/s, and the number of scans was 200.
Fig. 21. FTIR spectra of 0.005mM ODT series. Spectra were obtained using an MCT nitrogen-cooled detector at the spectral resolution of 4 cm$^{-1}$, the velocity of the moving mirror was 1.8 cm/s, and the number of scans was 200.
Fig. 22. FTIR spectra of 0.01mM ODT series. Spectra were obtained using an MCT nitrogen-cooled detector at the spectral resolution of 4 cm\(^{-1}\), the velocity of the moving mirror was 1.8 cm/s, and the number of scans was 200.
The IR spectrum of NBT shows several vibrational modes characteristic for p-substituted benzenes and an –NO$_2$ group [105] (Fig. 23). Aromatic nitro- compounds have strong absorption due to the asymmetric and symmetric stretching vibrations of the NO$_2$ group at 1570-1483 cm$^{-1}$ and 1370-1320 cm$^{-1}$, respectively [105]. This latter mode for para-substituted nitro-compounds occurs at 1355-1335 cm$^{-1}$. In the case of NBT, these vibrational modes have been found at 1342 cm$^{-1}$ (symmetric NO$_2$ stretch) and 1517 cm$^{-1}$ (asymmetric NO$_2$ stretch). Also, a band attributed to C-N stretching vibrations was found at 854 cm$^{-1}$ (for aromatic nitro-compounds this band is usually observed at 865-835 cm$^{-1}$ [105]).

Fig. 23. General IR spectra of NBT monolayer. The film was grown in 0.01mM solution for 24h. Spectra were obtained using an MCT nitrogen-cooled detector at the spectral resolution of 4 cm$^{-1}$, the velocity of the moving mirror was 1.8 cm/s, and the number of scans was 200
Other bands found in the NBT spectrum have been attributed to various ring vibrations. A number of C-H in-plane deformation bands occur in the region 1290-1000 cm\(^{-1}\). The bands are sharp, but weak in intensity. They are normally not important for interpretation purposes \[105\]. Three peaks were attributed to the ring carbon-carbon stretching vibrations at 1594 cm\(^{-1}\), 1571 cm\(^{-1}\) and 1469 cm\(^{-1}\). These modes are usually observed in the region 1625-1430 cm\(^{-1}\). The band in the region from 1625-1590 cm\(^{-1}\) is only observed when the substituents in the para positions are different, resulting in a lack of symmetry. When NO\(_2\) is directly conjugated to the ring, a doublet is observed at 1625-1575 cm\(^{-1}\) (peaks at 1594 and 1571 cm\(^{-1}\) in NBT spectrum).

The region of the IR spectra from 800 cm\(^{-1}\) to 1600 cm\(^{-1}\) has been chosen to monitor formation of the monolayer (Fig.s 24-27). Clearly an intense NO\(_2\) symmetric stretching peak at \(\sim1344\) cm\(^{-1}\) is most characteristic and intense for the NBT spectra, hence, was chosen to monitor the monolayer growth. This stretching mode has the additional advantage that similarly to the CH\(_3\) group in the alkanethiol, NO\(_2\) surface groups have more freedom of movement, so that the intensity of absorption of this band will be directly proportional to the degree of the surface covered (number of molecules).

Table 6. Peak intensity of NO\(_2\) stretching mode measured as a height from the base to the top of the peak.

<table>
<thead>
<tr>
<th>Time in solution</th>
<th>1 min</th>
<th>5 min</th>
<th>10 min</th>
<th>20 min</th>
<th>40 min</th>
<th>1.5 h</th>
<th>3 h</th>
<th>5 h</th>
<th>17.5 h</th>
<th>22 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 mM</td>
<td>.0108</td>
<td>.0328</td>
<td>.0340</td>
<td>.0406</td>
<td>.0410</td>
<td>.0408</td>
<td>.0449</td>
<td>.0422</td>
<td>.0467</td>
<td>.0482</td>
</tr>
<tr>
<td>0.005 mM</td>
<td>.0064</td>
<td>.0198</td>
<td>.0366</td>
<td>.0396</td>
<td>.0394</td>
<td>.0401</td>
<td>.0338</td>
<td>.0397</td>
<td>-</td>
<td>.0432</td>
</tr>
<tr>
<td>0.005 mM</td>
<td>.0053</td>
<td>.0069</td>
<td>.0208</td>
<td>.0431</td>
<td>.0483</td>
<td>.0494</td>
<td>.0444</td>
<td>.0434</td>
<td>.0456</td>
<td>.0473</td>
</tr>
<tr>
<td>0.001 mM</td>
<td>.0000</td>
<td>.0020</td>
<td>.0042</td>
<td>.0067</td>
<td>.0114</td>
<td>.0218</td>
<td>.0349</td>
<td>.0446</td>
<td>.0427</td>
<td>.0486</td>
</tr>
<tr>
<td>0.001 mM</td>
<td>.0000</td>
<td>.0000</td>
<td>.0060</td>
<td>.0079</td>
<td>.0101</td>
<td>.0265</td>
<td>.0391</td>
<td>.0455</td>
<td>.0411</td>
<td>.0459</td>
</tr>
<tr>
<td>0.0005 mM</td>
<td>.0000</td>
<td>.0000</td>
<td>.0000</td>
<td>.0026</td>
<td>.0037</td>
<td>.0042</td>
<td>.0081</td>
<td>.0118</td>
<td>.0307</td>
<td>.0275</td>
</tr>
</tbody>
</table>
Table 6 summarizes the intensity of the NO\textsubscript{2} stretching peak at \(~1340\text{ cm}^{-1}\) for four different solution concentrations for several experiments. The intensity of this mode averaged for each concentration was plotted against immersion time (Fig. 28). Similar to the ellipsometry and contact angle results for ODT, the average uptake is much faster for samples grown in higher concentration solutions, but for all series the FTIR peak intensity stabilizes after about 5 h of immersion. The peak position of the NO\textsubscript{2} stretching frequency is presented in Table 7. As in the ODT case, the NO\textsubscript{2} peak position shifts about 8 cm\textsuperscript{-1} from the initial position of 1334 cm\textsuperscript{-1} for low-concentration, short-immersion time samples, to final position of 1346 cm\textsuperscript{-1}. This is 10 cm\textsuperscript{-1} lower than the position in the bulk spectra of NBT which was measured to be 1332 cm\textsuperscript{-1}.

The value of 1346 cm\textsuperscript{-1} is obtained only in more concentrated solutions. This result can be explained when one consider that there exists an equilibrium between adsorption and desorption processes [106-110]. Packing density and order of monolayer grown in higher concentrated solutions will never be achieved for SAMs grown in more dilute solutions.

Table 7. Peak position of NO\textsubscript{2} stretching mode.

<table>
<thead>
<tr>
<th>Time in solution</th>
<th>1 min</th>
<th>5 min</th>
<th>10 min</th>
<th>20 min</th>
<th>40 min</th>
<th>1.5 h</th>
<th>3 h</th>
<th>5 h</th>
<th>17.5 h</th>
<th>22 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01mM</td>
<td>1338</td>
<td>1344</td>
<td>1344</td>
<td>1346</td>
<td>1346</td>
<td>1346</td>
<td>1346</td>
<td>1346</td>
<td>1346</td>
<td>1346</td>
</tr>
<tr>
<td>0.005mM</td>
<td>1336</td>
<td>1340</td>
<td>1340</td>
<td>1344</td>
<td>1344</td>
<td>1344</td>
<td>1344</td>
<td>1344</td>
<td>-</td>
<td>1346</td>
</tr>
<tr>
<td>0.005mM</td>
<td>1334</td>
<td>1338</td>
<td>1340</td>
<td>1342</td>
<td>1344</td>
<td>1344</td>
<td>1344</td>
<td>1344</td>
<td>1346</td>
<td>1346</td>
</tr>
<tr>
<td>0.001mM</td>
<td>----</td>
<td>----</td>
<td>1334</td>
<td>1336</td>
<td>1336</td>
<td>1340</td>
<td>1342</td>
<td>1344</td>
<td>1344</td>
<td>1344</td>
</tr>
<tr>
<td>0.001mM</td>
<td>----</td>
<td>1334</td>
<td>1334</td>
<td>1336</td>
<td>1340</td>
<td>1342</td>
<td>1342</td>
<td>1344</td>
<td>1344</td>
<td>1344</td>
</tr>
<tr>
<td>0.0005mM</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>1330</td>
<td>1334</td>
<td>1336</td>
<td>1336</td>
<td>1338</td>
<td>1342</td>
<td>1342</td>
</tr>
<tr>
<td>Bulk NBT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1332</td>
</tr>
</tbody>
</table>
Fig. 24. FTIR spectra of 0.0005mM NBT series. Spectra were obtained using MCT nitrogen-cooled detector at the spectral resolution of 4 cm\(^{-1}\), the velocity of the moving mirror was 1.8 cm/s, and the number of scans was 200.
Fig. 25. FTIR spectra of 0.001mM NBT series. Spectra were obtained using MCT nitrogen-cooled detector at the spectral resolution of 4 cm\(^{-1}\), the velocity of the moving mirror was 1.8 cm/s, and the number of scans was 200
Fig. 26. FTIR spectra of 0.005mM NBT series. Spectra were obtained using MCT nitrogen-cooled detector at the spectral resolution of 4 cm\(^{-1}\), the velocity of the moving mirror was 1.8 cm/s, and the number of scans was 200
Fig. 27. FTIR spectra of 0.01mM NBT series. Spectra were obtained using MCT nitrogen-cooled detector at the spectral resolution of 4 cm⁻¹, the velocity of the moving mirror was 1.8 cm/s, and the number of scans was 200
Fig. 28. NO$_2$ mode intensity as a function of immersion time. Upper and lower graphs the same set of values on a different timescale.
4.6 Kinetics Studies

The surface coverage data for both ODT and NBT show a characteristic increase over time. The film growth can be described as an isothermal adsorption. Among many theories of adsorption, the Langmuir isotherm [115-117] was one developed to describe single layer adsorption.

The Langmuir isotherm model is based on several assumptions:

- The surface of the solid has a finite number of active centers
- One active center can accommodate only one adsorbate molecule
- A molecule can be bound to the surface either chemically or physically
- Adsorption is limited to one monolayer
- Adsorption to one site is independent of the occupancy condition of the adjacent site (molecules do not interact)
- Molecules are immobile on the surface of the solid
- The energy of adsorption is constant and does not depend on the degree of coverage \( \theta \)

(eq. 1)
- There exists an equilibrium between the species adsorbed on the surface and ones remaining in the solution

The ratio of the number of molecules adsorbed, \( n_a \), to the number of active centers, \( n_{a, \text{max}} \), is called the degree of coverage \( \theta \).

\[
\theta = \frac{n_a}{n_{a, \text{max}}} \quad (4.6.1)
\]
Although the Langmuir theory is clearly based on an ideal model, many researchers working on the kinetics of self-assembly [8,84,106-110,118,119] found it suitable for the description of the adsorption process.

A Langmuir isotherm dictates that the rate of surface reaction is given by [115-117]

\[
\frac{d\theta}{dt} = k_a (1 - \theta)C - k_d \theta
\]  

(4.6.2)

where \(\theta\) is fraction of the monolayer, \((1 - \theta)\) is the fraction of the surface not covered with molecules, \(C\) is the concentration of the solution and \(k_a\) and \(k_d\) are association and dissociation rate constants respectively. Integrating eq. 2 one obtains

\[
\theta(t) = \frac{C}{C + (k_a / k_d)}[1 - \exp(-(k_a C + k_d)t)]
\]  

(4.6.3)

This equation can be simplified by the substituting \(k_{\text{obs}} = k_a C + k_d\) and \(K' = C/(C + (k_a / k_d))\), giving

\[
\theta(t) = K'[1 - \exp(-k_{\text{obs}}t)]
\]  

(4.6.4)

\(\theta\) can only have values between 0 and 1. \(K'\) and \(k_{\text{obs}}\) were fit independently and the results are presented in Table 7. The comparison of the calculated coverage to the experimental data is shown in Figs. 29 and 30 for ODT and NBT monolayers, respectively.

Plotting \(k_{\text{obs}}\) vs \(C\) you can determine \(k_a\) and \(k_d\) from the slope and the intercept of the line, respectively (Fig. 31). After determining the equilibrium constant for the monolayer system

\[
K_{eq} = k_a / k_d
\]  

(4.6.4)

the steady-state fractional coverage of the gold surface \(\theta(\infty)\) can be calculated as
\[ \theta(\infty) = \frac{C}{C + (1/K_{eq})} \]  
\( (4.6.5) \)

Values of fractional coverage are included in Table 8.

Table 8. Values of \( k_{obs} \) and \( \theta(\infty) \)

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>solution concentration</th>
<th>( k_{obs} (s^{-2}) )</th>
<th>( \theta(\infty) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODT</td>
<td>0.01mM</td>
<td>0.0017</td>
<td>0.988</td>
</tr>
<tr>
<td></td>
<td>0.005mM</td>
<td>0.0009</td>
<td>0.977</td>
</tr>
<tr>
<td></td>
<td>0.001mM</td>
<td>0.00017</td>
<td>0.895</td>
</tr>
<tr>
<td>NBT</td>
<td>0.01mM</td>
<td>0.0025</td>
<td>0.961</td>
</tr>
<tr>
<td></td>
<td>0.005mM</td>
<td>0.0014</td>
<td>0.924</td>
</tr>
<tr>
<td></td>
<td>0.001mM</td>
<td>0.00033</td>
<td>0.709</td>
</tr>
<tr>
<td></td>
<td>0.0005mM</td>
<td>0.0002</td>
<td>0.549</td>
</tr>
</tbody>
</table>

The fractional coverage decreases as the solution gets more dilute for both molecules. In higher concentration solutions (0.01mM and 0.005mM) \( \theta(\infty) \) is close to 1, but drops below 0.9 in less concentrated solutions. For an NBT monolayer grown in 0.0005mM solution, fractional coverage reaches only 0.5. By comparing \( \theta(\infty) \) values for ODT and NBT film growth it is seen that the adsorption/desorption reaction is shifted more towards adsorption for ODT as compared to NBT. That means that for the same concentration ODT, the monolayer will always be more densely packed than for NBT from a similar concentration solution.

The Gibbs energy of adsorption can also be found directly from the equilibrium constant data

\[ \Delta G_{ads} = -RT \ln K_{eq} \]  
\( (4.6.6) \)

Calculated in this manner, the Gibbs energy of adsorption is -9.35 kcal/mol and -8.62 kcal/mol for ODT and NBT, respectively. This value is comparable to the value obtained by Karpovich and Blanchard [110]. For SAMs of ODT grown in hexane and cyclohexane solutions they
determined the value of the Gibbs energy of adsorption to be -5.6 kcal/mol and -5.5 kcal/mol respectively. The difference can be attributed to the impact of the solvent and different measurement technique (in the above work authors used quartz crystal microbalance, QCM, to monitor monolayer growth).

Table 9. Values of $k_a$, $k_d$ and $\Delta G_{ads}$

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>$k_a$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_d$ (s$^{-1}$)</th>
<th>$\Delta G_{ads}$ (kcal.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODT</td>
<td>169.6</td>
<td>0.00002</td>
<td>-9.35</td>
</tr>
<tr>
<td>NBT</td>
<td>243.3</td>
<td>0.0001</td>
<td>-8.62</td>
</tr>
</tbody>
</table>

The Langmuir isotherm fit together with normalized experimental data is shown in Fig. 29 for ODT and in Fig. 30 for NBT. Equation 4 was fit to the normalized ellipsometric data, but normalized contact angle (for ODT) and normalized IR intensity data (for NBT) were also included in the graphs for comparison. A good fit of the Langmuir isotherm to the experimental data is a considered proof that self-assembled systems are in dynamic equilibrium.
Fig. 29. Langmuir isotherm fit to normalized ellipsometric data for ODT film. Contact angle data are included for comparison.
Fig. 30. Langmuir isotherm fit to normalized ellipsometric data for NBT film. Normalized IR intensity data are included for comparison.

\[ y = 169.59x + 2 \times 10^{-5} \]

Fig. 31. \( k_{\text{obs}} \) versus solution concentration as determined from Langmuir isotherm fit. Association and dissociation constants (\( k_a \) and \( k_d \)) are the slope and intercept of the line.

\[ y = 243.29x + 0.0001 \]
CHAPTER 5

CONCLUSIONS

The combination of experimental methods used in this work shows that the adsorption process of self-assembled monolayers can be monitored while growing in highly dilute solutions. Contact angle data, ellipsometry measurements and infrared spectroscopy all show an initial region of monolayer growth followed by a saturation region. This growth trend has been modeled using a Langmuir isotherm of adsorption.

Two different molecules were used, octadecanethiol (ODT) and p-nitrobenzenethiol (NBT). ODT, well characterized in the literature, served as a comparison for kinetics studies of NBT monolayer growth. The NBT self-assembled monolayer growth kinetics was characterized for the first time in this work by four different methods.

For fully formed ODT monolayers, the contact angle was measured to be ~107. The thickness determined by ellipsometry was 2.0 and 0.9 nm for ODT and NBT monolayers respectively. Ellipsometric data were verified by angle resolved x-ray photoelectron spectroscopy (ARXPS) measurement on representative samples. Thickness determined with ARXPS was 1.9 and 0.6 nm. As a final confirmation of monolayer quality Fourier transformed infrared (FTIR) spectra were obtained using grazing angle total reflectance (GATR) attachment.

Angle resolved XPS and grazing angle total reflection FTIR used in this work, are recent improvements to well established techniques. ARXPS data give the unique capability of
constructing non-destructive depth profiles of the samples. Grazing angle total reflection FTIR is especially suited for organic monolayers.

Langmuir adsorption isotherm agreement with experimental data is a direct proof for SAMs being equilibrium systems. Calculation of the Gibbs energy for absorption yielded values of -9.35 kcal/mol and -8.62 kcal/mol for ODT and NBT films respectively. The steady-state fractional coverage values shows that in highly dilute solutions, ODT forms denser monolayers than the NBT.

The two monolayers have been for the first time characterized simultaneously by the four methods used in this work. Future investigation should be focused on performing FTIR spectra simulation that would give more deep explanation on exact arrangement of the molecules inside the monolayer.
REFERENCES


[38] Q. Zhang, H. Huang, H. He, H. Chen, H. Shao, and Z. Liu, Surface Science 440 (1999) 142-150


[77] T. Smith, J. Colloid Interface Sci. 75 (1980) 51


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