ABSTRACT

GUY, LAURA. Systematic Study of Film Growth in Short Chain Alkylsilanes Including Issues of Phase Segregation and Islanding. (Under the direction of Laura Clarke).

The role of islanding and phase segregation in long and short chain alkylsilanes formed by self assembly is described. Structural factors controlling orientation and structure of surface bound molecules are obtained through a series of systematic studies. Long chain molecules such as Octadecyltrichlorosilane (OTS) showed greater island formation and polymerization during film growth than short chain molecules such as Propyltrichlorosilane. The monochlorosilane 11-Bromodecyldimethylchlorosilane showed no islanding.
Systematic Study of Film Growth in Short Chain Alkylsilanes including issues of Phase Segregation and Islanding

by
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A thesis submitted to the graduate faculty of North Carolina State University in partial fulfillment of the requirements for the Degree of Master of Science

Physics
Raleigh, North Carolina
2008

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BIOGRAPHY

Born in Aurora Illinois, Laura received her elementary and high school education in Aurora. Laura excelled in science and mathematics early in her education.

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Chapter 1: General Introduction

1.1 Self Assembled monolayers (SAMs) Introduction

1.1.1 Terminology

An alkane is a straight chain of carbon atoms, which are fully saturated, that is, having only single bonds between the carbons and thus a maximum number of hydrogen atoms. Alkanes are generally non-reactive and hydrophobic (water-hating). When alkanes are a part of a larger molecule, they are called an alkyl group. Thus, alkyl groups consist solely of singly bonded carbon and hydrogen atoms arranged in a chain, for example a methyl or ethyl group. Silanes consist of a silicon atom attached to four other atoms or groups. Chlorosilanes are reactive, chlorine-containing chemical compounds, used in many chemical processes. Each such chemical has at least one silicon-chlorine bond. All chlorosilanes react with water to produce hydrogen chloride and one or more of the silicon-chloride bonds becomes a silicon-OH bond. So-called hydroxylated silanes are highly reactive and will eventually bond to another OH on a solid oxide surface or react with another hydroxylated chlorosilane. Water is a bi-product of this reaction.
1.1.2 Self-assembled monolayers

Self-assembled monolayers (SAMs) are single molecule thick layers which form and then terminate at a single monolayer spontaneously, resulting in a sheet of individual molecules closely packed together. The self-assembly of monolayers was first reported in 1980[^1]. Self-assembled monolayers (SAMs) have proven to be important in several
fields of study such as physics, chemistry and material science [see for instance, \(^2,^3\)]. SAMs are utilized in biosensor technology to observe pathogenic bacteria \(^4\). SAMs allow microcontact printing and the subsequent ability to control cell attachment, to become reality \(^5\). Fabrication of molecular biomaterials is dependent on self-assembled monolayers, which serve as patterned substrates \(^6\).

In this thesis, we will study monolayer self-assembly of mono and trichlorosilanes terminated with the substituted alkyl groups. In short, any self assembly process that results in a monolayer requires the bottom of the molecule to be reactive, the top of the molecule to be non-reactive, and the molecules to tend to stand up-right. The bottom of the molecule reacts with the surface, molecules all stand each other up, and additional molecules cannot reach the surface to react. This results in a thin film of molecules, one molecule thick. Figure 1.2 illustrates a self assembled monolayer.

![Figure 1.2 Sketch of the molecular structure and forces of self-assembled monolayers.](image)

Alkanesilane and substituted-alkanesilanes will be used in this work. The typical structure of these substituted alkylsilane compounds is shown in figure 1.3.
Figure 1.3 a.) general structure of monochlorosilane (single-footed chlorosilane) b.)
general structure of a trichlorosilane (three-footed chlorosilane) X is the terminal
group which is a methyl for an alkylsilane and can be a variety of other groups
(such as amine, chloromethyl, or bromomethyl groups) for substituted alkylsilanes.

The terminal group, indicated with X in figure 1.3, can be a methyl group but it can also
be a functional group such as an amine, thiol, chloromethyl or bromomethyl. It is evident
terminal groups which are reactive towards the chloro group on the silicon atom cannot
be used as this would result in intermolecular and possibly intramolecular reactions.

The possibility to introduce a wide range of terminal functional groups provides a
variety of surface properties. Formation of a SAM can transform a substrate from
hydrophilic (water loving) to hydrophobic (water hating) and allow the ability to tune
hydrophilicity by changing the molecule used to form the monolayer. In addition,
substituted alkyl silanes allow us to use molecules at a variety of heights (different
number of carbons) and with a variety of terminal groups (charged, polar, and non-polar).
Thus we can investigate how the chain length of the molecules alters both the molecule-
molecule interaction and the molecule-substrate reaction during film growth, in addition to exploring how the terminal group modifies these quantities.

### 1.1.3 Other non-monolayer reactions with alkyltrichlorosilanes

Alkylchlorosilanes are reactive and will hydrolyze rapidly with any trace of water present to form silanol (Si-OH) groups. These silanol groups can then react with surface hydroxyl groups by a condensation reaction eliminating water (Figure 1.1b). A direct condensation reaction of the chlorosilanes with surface hydroxyl groups is also possible with HCl as a byproduct. If the alkylchlorosilane reacts with a surface OH group, then the molecule is covalently anchored to the surface. Additional bonds are made from neighboring molecules reacting with each other to form a highly cross-linked network (figure 1.1c). The main problem with chlorosilanes is that molecules in the hydrolyzed silanol state can react with both the surface and with each other. Especially during deposition from solution, the molecules have a high probability of encountering each other rather than the surface. This will result in the formation of polymerized clusters of molecules which grow in solution and subsequently bind or adsorb to the surface. Extended silane condensation (forming large polymers) prior to adsorption to the surface has to be prevented so that a homogeneous coating can form.

Polymerization does not occur for monofunctional silanes (See Figure 1.3 a) where an intermolecular reaction results in a dimer which cannot bond to other molecules or the surface. However, monofunctional silanes typically have, in lieu of chloro groups, two bulky methyl groups on the silicon atom which may sterically hinder a close packing
and lead to low-density monolayers. In addition, because the monochlorosilane cannot react with each other, they will only react at locations on the surface where an -OH group is present. Thus, for surfaces with a low -OH content, full monolayers may not be possible.

Studies have been conducted to better understand the mechanisms that cause islanding and polymerization. Research conducted by Wasserman [7] shows evidence indicating that on average only one silanol group attaches to the substrate while the other two bind to nearby molecules forming a cross-link of trichlorosilanes. Allara suggests that molecules are mobile on the water layer above the substrate, enabling them to form a two-dimensional cross-linked networks that ‘floats’ on the water layer and only then reacts to bind to the surface. [8] Wang found polymerization (and possibly islanding) occurs in the formation of OTS monolayers. [9] From their studies, they concluded that both the presence of water and use of older solutions increased the likeliness of islands or polymerization. When water was present, a rough, non-uniform, layer formed on the surface. This was the result of large aggregates. When water was not present, a smooth monolayer formed on the surface and aggregates were not found.

1.2 The purpose of the study:

In this thesis we will examine causes of island formation and polymerization of various molecules. Three reasons for island growth that are hypothesized are as follows. We will be using multiple molecules (both polar and non-polar), substrates and temperatures to base our conclusion.
The first two possible processes involve interactions between the upper portion of the molecules (not the reactive silane portion).

(1) Van der Waals interactions between the chains can cause chains to associate. In particular, long chain alkanes form densely packed monolayers due to van der Waals forces between the carbon chains. These forces provide a driving force to the self-assembly. Van der Waals forces are caused by attractive forces between electrically neutral molecules. These forces develop because of the rapid shifting of electrons within molecules causes some parts of the molecule to become momentarily dipolar. For this reason, weak, transient forces of attraction can develop between particles that are actually neutral[10].

The longer the chain length of the molecule, the more van der Waals interactions influence the film growth kinetics and morphology. We have hypothesized Octadecyltrichlorosilane (OTS), Pentyltrichlorosilane (Pentyl), and 11-Bromundecyltrichlosilane may exhibit islanding that is influenced by van der Waals forces due to their long chains. It has previously been established that an increase in chain length leads to an increase in Van der Waal forces between chains [11].

(2) Van der Waals processes will dominate for pure alkyl molecules (where the chain does not have a permanent dipole) with a sufficiently long alkyl chain. If the molecule does have a permanent dipole, dipole-dipole interactions could be another mechanism for islanding. Dipole-dipole interactions are the forces that occur between two molecules with permanent dipoles (as shown in Figure 1.4). The potential energy between two dipoles, $U = \frac{1}{4\pi\varepsilon_0} \frac{p^2}{r^3}$, where $p$ is the dipole moment (generally
measured in Debye, where 1 D = 3.3 x 10^{-30} \text{ C-m}) and \( r \) is the distance between dipole centers. Dipole-dipole interactions could force islanding for molecules too short to be significantly influenced by van der Waals interactions, for instance, the 3-aminopropyltrichlorosilane, or could enhance intermolecular interactions for longer molecules, such as 11-bromoundecyltrichlorosilane.

Figure 1.4 Dipole-dipole interaction, forces that occur between two molecules with permanent dipoles.

(3) A third process that could lead to islanding involves interactions of the lower portion of the molecules. Imagine a scenario where an individual molecule binds directly to a hydroxyl group on the substrate (perhaps the case for a short, non-polar silane). Assuming the molecule is already fully hydroxylated (a reasonable assumption when a thin film of water is present on the strongly hydrophilic surface), the single silanol (Si-OH) on the surface has been replaced by two hydroxyls (the two unreacted feet of the molecule). If hydroxyl density is a limiting factor in film formation, another molecule will be more likely to react near the first (simply because of the increased hydroxyl density) even if there is no molecule-molecule interaction. Generally the hydroxyl density on silica is quoted as \( \sim 5 \times 10^{14}/\text{cm} \). This provides one -OH on average every 20Å, which is similar in size to the footprint of a silane, leading to the well-known fact
that all three hydroxyl groups are unlikely to bind with the surface for tricholorosilane film formation and crosslinking (binding to other molecules) is likely. Hydrogen bonding of Si-OH "feet" of neighboring molecules could also contribute to islanding.

The ability to tailor the functionality of the molecules making up the SAM, allows SAMs to be ideal systems for the investigation of fundamental principles governing intermolecular forces (Van der Waals interactions, and hydrogen bonding), molecular substrate interactions, and molecule-solvent interactions that affect interfacial properties such as wetting, ordering, growth, and corrosion.

In our case, we want to tune the polarity of the molecule, the height of the molecule and the substrate the film is grown on. Controlling islands and polymerization in film growth will enable us to make mixed SAMs, two evenly distributed molecules on the same substrate.

Controlling the distribution of two molecules on one substrate will allow us to study the rotational dynamics of the molecules, via observations of rotating polar entities. From individual methyl groups to long chain alkanes, rotation is important in hydrocarbon systems. Studying rotator phases in SAMs is of particular interest in the future [12].

The next few sections summarize techniques we will utilize in this thesis to characterize island growth in self-assembled monolayers.
1.3 Characterization of SAMs using contact angle, ellipsometry, and Atomic Force Microscopy:

The characterization of self-assembled monolayers is non-trivial: because of its molecular dimensions, a SAM is ‘invisible’ for any form of conventional microscopy. Therefore other techniques are required which typically probe only one property of the SAM. To get a more complete picture of the structure, order and properties of the SAM, applications of several techniques is necessary. In the following paragraphs we will briefly elucidate the techniques that have been used in this thesis.

1.3.1 Contact angle measurements:

A simple method for evaluating surface properties of a (SAM-modified) surface is the measurement of the contact angle of a droplet, typically water, with the surface, (Figure 1.5). Such wettability measurements give a direct indication of the surface hydrophobicity or hydrophilicity. Here we report static contact angles.

![Schematic representation of water droplet with contact angle θ from the surface.](image)

**Figure 1.5 a.)** Schematic representation of water droplet with contact angle θ from the surface.
1.3.2 Optical ellipsometry measurements:

One of the most widely used methods for determining SAM or thin film thickness is optical ellipsometry. Reflection of linearly polarized light from a surface produces elliptically polarized light. The perpendicular and parallel components of the linearly polarized light reflect differently from the surface, causing a relative phase shift in either component which leads to elliptically polarized light following reflection. The phase shift of both components of linearly polarized light can be measured and used to characterize the reflecting surface [13]. A diagram of an ellipsometer is shown in figure 1.6

![Diagram of an ellipsometer](image)

Figure 1.6 Diagram of the components of an ellipsometer.

In this work, measurements are made at a single wavelength and a single incident angle with a null ellipsometer. A null ellipsometer has two linear polarizers and a wave retarder. A PCSA setup is a polarizer, compensator, sample and analyzer arranged in a sequence, see figure 1.6. The compensator is a wave retarder and the analyzer is a
second polarizer. With the combination polarizer and compensator, any polarization state can be generated. If this polarization state is set in such a way that the light is linearly polarized after reflection from the sample, it can be extinguished by rotation of the analyzer so that its transmission axis is perpendicular to the polarization of the reflected light \(^{14}\).

Ellipsometry is widely used to study film growth on various surfaces. For the study of SAM surfaces, ellipsometry can be used to establish that a single monolayer is formed and help to assess the extent of the reaction following the addition of other layers to a modified substrate.

1.3.3 Atomic force microscopy (AFM) measurements:

![Figure 1.7 Schematic operating principle of AFM.](image)

In atomic force microscopy (AFM), repulsive and attractive forces between tip and sample are measured by detecting the deflection of a laser beam focused on the backside of a tip as shown in figure 1.7. AFM can be operated in different modes (e.g. contact, tapping and non-contact), each having its own characteristics. In this thesis we
use tapping mode AFM where the tip is oscillated perpendicular to the sample and the tip-sample forces are detected via changes in oscillation amplitude and frequency. This method combines relatively high resolution and low applied force measurements of soft materials. For lithium niobate, contact mode is necessary. Contact mode is in the repulsive regime of the inter-molecular force curve. As the name suggests, contact mode allows the tip and sample to remain in close contact as the scanning proceeds. In contrast to STM, AFM does not require conductive tips and samples but the different nature of the interaction and the ‘large’ curvature radius of AFM tips (~10nm) limits the AFMs resolution. Nevertheless, AFM microscopes are excellent for imaging where conventional, optical microscopes fail.

1.4 Concluding remarks:

Although many challenges and problems have been encountered and addressed in SAM chemistry, many aspects of structure-property relationships remain to be explored. In particular, a limited number of reports in the literature discuss effects directed toward understanding short chain molecules. It is hoped that through a series of systematic studies, involving multiple molecules, an understanding of structural factors controlling orientation and structure of surface bound species can be obtained. In particular, the goal of this research is to understand the role of islanding and phase segregation in short chain alkylsilanes through ellipsometry, contact angle and atomic force spectroscopy (AFM). By exploring film formation for shorter chains we can address how the molecule attaches to the substrate. The significance of Van der Waals interactions should be negligible with
short chain molecules, thus for non-polar molecules, if islanding is reported, an alternative explanation for this effect will need to be developed.

**Chapter 2: Design of our experiments**

In this chapter we discuss the design of our experiments including details of the substrate, our experimental protocol designed to prevent polymerization, the molecules and substrates used, and the roughness of bare fused silica. Finally, we will define what we consider an island and polymerization.

**2.1 Silica Surfaces:**

Silicon dioxide occurs in many forms - as sand or crystalline quartz or as an artificial product produced in the laboratory. Silicon dioxide also grows spontaneously on silicon surfaces when exposed to ambient conditions, forming a layer about 2 nm in thickness. In this thesis, unless otherwise noted, SiO\(_2\) refers to this intrinsic layer of silicon dioxide on silicon.

**2.2 Polymerization prevention:**

In polymerization, monomers are bound together to form a more extended (usually linear) structure. A two-dimensional polymerization is one way to think of the formation of a self-assembled monolayer (figure 2.1) where water adsorbed to the surface (as opposed to water in solution) reacts with the molecules to form hydroxylated silanes which can then condense into a two dimensional sheet.
Polymerization occurs when water is present during film growth. Good polymerization occurs when a monolayer of crosslinked molecules has occurred (Figure 2.2). Bad polymerization occurs when molecules become hydroxylated in solution and attach to other molecules rather than the substrate (Figure 2.1).
surface, such as silica. After the monolayer is formed, the sample is then submerged in dry toluene while still in the dry box to further avoid excess water. The sample is then taken out of the dry box and immediately dried with a stream of nitrogen. Ellipsometry and contact angle measurements are then performed. We then use AFM to determine if the sample has formed islands or has polymerized. Using the AFM scans, we can then begin to understand if islanding does occur, what causes it.

2.3 Forces which drive islanding

As discussed in Chapter 1, this thesis explores three possible mechanisms for island formation: van der Waals interactions (occurring for sufficiently long molecules), dipole-dipole interactions (occurring for molecules with permanent dipole moments) and other factors which might cause islanding even for shorter, non-polar molecules. Here we discuss why all trichlorosilane may island, given a particular set of conditions.

For trichlorosilanes in particular, the presence of multiple, reactive groups can lead to islanding. Molecules with three chloro may only have one chlorosilane attaching to the substrate. This allows the other two chloro atoms to create two new hydroxyls. In a condition where few native hydroxyl sites are available on the substrate, molecules that have two hydroxyls that did not attach to the surface will increase the number of local hydroxyls increasing the chances of another molecule attaching right next to the molecule that originally settles at that particular spot. As more molecules attach to these local hydroxyls, an abundance of molecules form in a small area and an island begins to form.
The fewer the number of OH groups on the surface the greater the chances the molecule will bind to another molecule rather than binding to the surface.

2.4 Approach to understand islanding

In this thesis, the temperature, substrate and molecules will be varied to determine the cause of islanding for various molecules.

The molecules used in this thesis are as follows: Octadecyltrichlorosilane (OTS) a non-polar 18 carbon (n=18) molecule, Pentyltrichlorosilane (Pentyl) a n=5 non-polar molecule, Propyltrichlorosilane (PTS) a non-polar 3 carbon molecule, 11-Bromoudecyltrichlorosilane (11-Bromo, 3) a n = 11 polar molecule with a dipolar terminal group (a bromomethyl), 3-Aminopropyltrimethoxysilane (3-APS) a dipole or polar molecule with n = 3 and a amine terminated group. The dipole moment of NH₂ is 1.73D [15]. We expect the dipole moment of the bromomethyl to be similar as most small molecules have dipole moments in the 1.5 - 2.0 D range. All of these molecules are trichlorosilanes. In addition we studied, 11-Bromoudecyldimethylchlororsilane (11-Bromo, 1), which is identical to 11-Bromo,3 molecule but with one reactive chlorinated "foot".

Using a variety of substrates will allow for better understanding of the role van der Waals interactions play. In long chain systems, van der Waals interactions are assumed to cause islanding. However for short chain molecules if islanding is still observed, alternative hypotheses need to be generated, which in turn will help to clarify the mechanism of islanding in long-chain systems. As one of our hypotheses deals with substrate characteristics (such as OH- density) utilizing different substrates will allow us
to further examine the reasons for islanding. The substrate used will determine the number of hydroxyls. Changing the substrate will alter the number of OH groups that the molecule can attach to. If fewer OH groups are on the surface of the substrate, fewer molecules can attach to the substrate. This may cause molecules to be more likely to attach to each other rather than the surface, this may lead to islanding. It is also possible that the number of OH groups does not play a significant role in film formation.

We have chosen to use silica because it is well studied and its high number of hydroxyls on its surface. Lithium niobate is not as well explored however, the smooth surface of a single crystalline, annealed wafer may help us further analyze film growth. I have not been unable to get a literature value for an accurate number of hydroxyls of lithium niobate. If the number is less than that of fused silica I would suspect the islanding to increase, if greater than fused silica I would expect a decrease in islands.
2.3 SiO$_2$ AFM images and example of islands and polymerization:

Figure 2.3 Blank samples of SiO$_2$ varies ± 4Å.

Figure 2.3 shows AFM images (tapping mode) of native silicon-dioxide coated silicon wafers from our laboratory without a self-assembled monolayer. Literature values indicated that the native oxide found on wafers in the thickness range (1-3nm) has a RMS roughness less than 1Å [16]. The thickness of our intrinsic SiO$_2$ layer (after UV-ozone cleaning) is about 16Å by ellipsometry. Our native oxide layer of SiO$_2$ on silicon has a surface height (the relative variation in height by AFM) of 2-6Å, and an rms value that varies from 1.101Å to 1.372Å, according to AFM (figure 2.3). RMS roughness was used to describe the fluctuation in surface height around an average surface height. The rms roughness was recorded over the entire area of each 1×1µm AFM scan.
Our substrate was cleaned with an UV ozone cleaner for 20 minutes while
letting oxygen flow over the substrate for the first five minutes. After cleaning, the
substrate was rinsed in deionized water and dried with a stream of nitrogen. UV ozone
cleaning will result in a hydrophilic surface cleaned of organic contaminants. Some
silicon dioxide may be removed in this process. As discussed above, a layer of oxide
results when silicon is exposed to atmospheric air. This oxide layer is called native oxide
and has a thickness between 0.6 and 1.5nm \([17]\). De Palma et. al. found that UV ozone
cleaning procedures form a slightly thicker, denser and smooth oxide film than the
original native oxide, which may be helpful in forming high quality monolayers\([18]\).

Figure 2.4 OTS forming islands. Peak of molecule is approximately the height of the
molecule. The top of the islands are flat.

As an example of island growth on SiO\(_2\), a sample of OTS shows evidence of
islanding in film growth after 1 hour. The large peak represents the height of an island,
20Å that is comparable to the height of the molecule, 26Å, figure 2.4. Although only one
island is observed here, the film is more than fifty percent coverage (by ellipsometry) so most of the islands in this case have already coalesced into a full film.

**Figure 2.5** In an 11-bromoudecyltrichlorosilane experiment the peaks are much greater than the height of the molecule and the peaks are no longer flat.

The peak in the height profile in figure 2.5 represents polymerization. The height of the peak, 100Å is much greater than the height of the 11-bromoudecyltrichlorosilane (11-BDTS), 13.3Å. This full coverage sample has a contact angle of 105° and a thickness of 13.6Å determined by ellipsometry.
Chapter 3: Results of film growth at room temperature:

3.1 Octadecltrichlorosilane (OTS) Growth:

3.1.1 Background:

![Figure 3.1 Schematic drawing of trichlorosilane. R indicates the head group and n indicates the number of carbons. R and n can be varied.](image)

![Figure 3.2 Schematic representation of OTS on SiO2.](image)

Octadecyltrichlorosilane (OTS) monolayers have been the most studied silane monolayer. Here we cite two classic papers as examples. Wasserman found uniform film
growth of OTS monolayers based on results from ellipsometry, contact angle, and X ray reflectivity measurements. [19] Cohen found partial monolayers had island formation dispersed in a non-uniform manner. OTS is the most studied trichlorosilane and thus a serves as a model molecule.

3.1.2 Results:

Figure 3.3 Octadecyltrichlorosilane (OTS) a.) height of OTS versus time b.) contact angle OTS versus deposition time.

OTS films were prepared under cleanroom conditions with minimal water exposure (as described above). For our films, 6.3µl of OTS combined with 50µl of dry toluene. Ellipsometry indicates no clear saturation point, although growth does slow dramatically at about 10 hours, when the observed height is about 24 Å. After 20 hours, the observed height has increased to 26Å thick. Wasserman reported the theoretical length of reacted OTS as 26.2Å.

These results lead us to hypothesize two different possibilities: either most of the film grows quickly and it takes a long time to fill in the remaining "holes" or there is
already a monolayer at ~24Å (10 hours) and then polymerization slightly increases the height.

Static contact angles with water were measured before and after OTS deposition. The contact angle of the original surface (5°) reflected the expected hydrophilicity. The contact angles (109°) for the OTS-covered substrate are, as expected, strongly hydrophobic. This angle falls in the range from 102 to 114° expected for hydrocarbon-terminated surfaces \[^{20}\]. De Palma found the contact angle of \((n\text{-decyl})\text{trichlorosilane}\) to be 109.2° which concurs with our results for long carbon chains. The OTS contact angle, (figure 3.3), shows a flat area from 5-20 hours. This area could indicate a monolayer. At 20 hours there is another increase which could be the result of polymerization. The contact angle expected for polymerized material is not clear, and could vary from <40° if Si-O-Si bonds were the primary component of the aggregate surface to 110° if methyl groups terminate the surface. Thus it is difficult to predict how polymerization should affect the contact angle. If polymerization is the cause of the increase in contact angle at 20 hours that would indicate that the polymerized aggregates are primarily hydrophobic.

After two hours in solution, the first evidence of polymerization is observed in our AFM images, figure 3.4c. The height profile of the 2 hour sample shows a peak of 120Å which cannot be the result of individual 26 Å molecules. The number of very tall features increases with increasing deposition time, which is consistent with vertical polymerization where molecules interact in solution and then such aggregates deposit (by physiosorption or chemisorption) onto the surface. Based on AFM studies detailed below, after 15 hours, larger aggregates cause the molecule height to slightly increase.
In order to test the hypothesis that the differences in contact angle and ellipsometry are due to polymerization, a quantitative analysis of the AFM images can be completed. After 22 hours, according to AFM, 6% of the surface is covered with polymerization. If the height of a polymerized aggregate is in the range of 50 to 100 Å, and assuming that ellipsometry on a surface with different heights follows the arithmetic average height, this would increase the height by 3 to 6 Å. Thus if the film were saturated at 10 hours (24 Å), we would expect a maximum of 3-6 Å of further growth in the next twelve hours, which is consistent with our observations that the film grows about 2-3 Å during this time.

This calculation would seem to indicate that for our procedure, a full coverage monolayer is formed at about 10-11 hours, with a height of 24 Å and a contact angle of ~90 - 95°. At this point some polymerization is already present, recalling that polymerization is first observed by AFM at 2 hours. These values are slightly lower than those reported in the literature (26 Å and >100°). It may be that longer deposition times would yield higher values but the presence of trace amounts of water in our solution makes this process similar in time scale to the formation of polymerized aggregates, which prevents our ability to observe a perfect monolayer.
Figure 3.4 1 µm x 1 µm AFM images of an OTS sample set: (a) after 30 min.; (b) 1 hour; (c) 2 hours; (d) 12 hours; (e) 15 hours; and (f) 22 hours. SiO2 substrates were immersed into 1mM OTS solutions immediately after cleaning procedures while in a cleanroom environment. The dark background is the SiO2 substrate, while the lighter regions represent higher OTS film areas.
Figure 3.5 Cross section analysis of AFM images indicating film growth at (a) after 30 min.; (b) 1 hour of OTS.
Figure 3.6 Cross section analysis of AFM images indicating film growth at (a) after 2 hours; (b) 12 hours of OTS.
Figure 3.7 Cross section analysis of AFM images indicating film growth at (a) after 15 hours; (b) 22 hours of OTS.
Parts a-f of Figure 3.4 shows flattened AFM topographic (1µm x 1µm) scans of six SiO₂ samples immersed in OTS solution for 30 minutes, 1 hour, 2 hours, 12 hours, 15 hours, and 22 hours respectively. These samples were prepared immediately after the substrate cleaning procedure.

After a few minutes of immersion time, OTS islands are observed on the surface. The extent of this island growth for a 30 minute sample is shown in figure 3.5a. Cross sections of this image indicate a mean island height of 20Å ± 4.0Å and a surface root-mean-square (rms) roughness of 2.978Å. Four line sweeps were measured to determine the height profile across each sample. Line sweeps were recorded over areas that appeared to have no islanding and areas that appeared to have islanding. Recording height profiles over areas with large aggregates helps determine if the aggregate is an island or polymerization. Line sweeps across areas that show no large features indicates the roughness of the film without aggregates. Since the theoretical length of a covalently bound OTS molecule is 26Å, these islands represent one monolayer of OTS molecules.

The 1 hour sample (Figure 3.5b) also shows islanding. The height of the islands remains about 20Å with the average island size remaining about 0.10 - 0.15µm. Two height profile show clear steps, which could be features in the surface or different types of film growth (see below). In the 1 hour sample, the areas with no large aggregates show a slightly increased roughness. Overall, the rms roughness of the 1 hour sample is 7.341Å. This could be the result of an increase in islands, non-island growth across the sample, or both.
Figure 3.6a was immersed for 2 hours and has an rms roughness of 19.14 Å. The height profile shows features 160 Å tall indicating the start of polymerization. Many more islands and some polymerization are now observed. Islands still maintain the same height of about 20 Å, whereas polymerization aggregates vary in height from 50 - 120 Å.

The 12 hour sample (Figure 3.6b) shows a secondary nucleation of smaller more faint islands (0.02 µm in diameter) which occur between the initial primary islands. It should be noted that the size of the primary islands for the 12 hour sample is reduced to 0.05 µm with respect to the 30 min sample, indicating the area in between islands is filling in. On a bare surface, an island appears as a large flat topped peak, approximately 20 Å in height. If molecules join the exterior of existing islands, then islands grow in size and coalesce into a full film. Alternatively, if patches of associated molecules are present in solution (perhaps hydrogen bonded) and only such patches attach to the surface, rather individual molecules, instead of larger islands, more islands of the same size should appear. Finally, if island growth can take place simultaneously with single molecule growth, the background of single molecules will continuously increase, slowly filling in like water rising between islands. In this case, only a fraction of the island is now showing as it sticks out of the monolayer. This makes the island appear smaller and the surface smoother.

The 15 hour sample has, figure 3.7a, a decrease in large features, indicating the monolayer below is filling in (by any of the three processes listed above). Here a single island-like feature (trace C) is observed, along with polymerization aggregates. The rms
roughness drops to 7.517Å, (despite the presence of some polymerization) which is also consistent with filling in of the monolayer.

As the immersion time increases, at 22 hours, all line-scanned features appear to be aggregates (Figure 3.7b), and the surface rms roughness has increased to 12Å.

In conclusion, we have investigated the growth behavior of OTS films on SiO₂ substrate. AFM images indicate that self-assembled monolayers of OTS on SiO₂ form by an island growth mechanism, in agreement with most studies.

3.2 Pentyltrichlorosilane (Pentyl):

![Graphs showing growth curves](image)

**Figure 3.8 Growth curve of Pentyltrichlorosilane.**

The growth curves of pentyltrichlorosilane shown in figure 3.8, are consistent with a simple saturating growth at about 500 minutes (8.3 hours), with no further increase in thickness out to 1000 minutes (16.7 hours). The contact angle saturates at about 100°, which is consistent with a methyl-terminated surface, and the observed thickness is about 9 Å.
Figure 3.9 Pentyltrichlorosilane growth after a.) 1 min. b.) 10 min, c.) 20 min, d.) 1 hour, e.) 4 hours, f.) 10 hours.
Figure 3.10 Pentyltrichlorosilane cross section analysis of AFM images indicating film growth after a.) 1 min. b.) 10 min.
Figure 3.11 Pentyltrichlorosilane cross section analysis of AFM images indicating film growth after a.) 20 min. b.) 1 hour.
Figure 3.12 Pentyltrichlorosilane cross section analysis of AFM images indicating film growth after a.) 4 hours, b.) 10 hours.
5.4μl of Pentyltrichlorosilane is combined with 50μl of dry toluene. Figures 3.9a and 3.10a, indicates island growth 1 minute into the deposition, which is less clear but still present at 10 minutes. At 20 minutes, figures 3.9c and 3.11a, in addition to islanding, polymerization occurs. This trend of observing both islands and polymerization continues in figures 3.9d and 3.11b, taken at 1 hour. After 4 hours (figures 3.9e and 3.12a), polymerized aggregates are the dominant features on the surface. At 10 hours, ellipsometry indicates full coverage. AFM images show polymerization on the surface, which is likely sufficient to alter the ellipsometric values, as shown in the OTS case. However, away from the aggregates, the surface is smooth with a roughness similar to that of bare silica, but with very different topographical features. Compare for instance, height profiles in figures 3.5 and figure 3.6. This leads us to believe that a smooth film has formed.

Islanding increases at the start of the deposition and decreases and plateaus 5-8 hours into the deposition. The rms value increases from 1.279Å to 4.957Å within the first 5 hours then levels off. We measured a rms of 4.802Å after 22 hours of deposition time, figure 3.32. Again, as in the OTS case, this elevated value at the end of a long deposition sequence seems to be attributable to polymerization.

3.3 Propyltrichlorosilane (PTS):

Since island growth is observed in long chain silanes such as OTS, a natural question to ask is whether short chain molecules such as propyltrichlorosilane (PTS) also form by this mechanism. As seen above, pentyltrichlorosilane (Pentyl), containing five
carbon atoms does appear to exhibit islanding, which is consistent with some literature predictions. A previous report concluded that PTS does not form islands during film growth \(^{21}\). Our results indicate islanding does occur, but at a smaller scale than OTS.

![Figure 3.13 Growth curve of propyltrichlorosilane (PTS).]

PTS has a height of approximately 4.5 Å and a contact of angle of 82°. From contact angle and thickness measurements, it appears saturation occurs at 40-50 minutes.
Figure 3.14 1 µm x 1 µm AFM images of a PTS sample set: (a) after 5 min.; (b) 10 min; (c) 15 min; and (d) 20 min.

Figure 3.15 Height profiles of PTS after 5 minutes.
Figure 3.16 Height profiles of PTS after a.) 10 minutes b.) 15 minutes.
3.0μl of PTS added to 50μl of dry toluene. Throughout the PTS film growth the large features never exceed the height of the molecule indicating islands have formed but no polymerization has occurred. This result differs from the OTS and Pentyl molecules. As a reminder, polymerization was first observed at 2 hours for OTS with a monolayer growth time of about 10 hours, or 20% into the growth process. For Pentyl, which saturates at monolayer growth at ~8 hours, polymerization is first observed at 20 minutes or <5% into the deposition. For PTS, with deposition times up to 20 minutes (or 50% of full coverage), no polymerized aggregates are observed, that is, the maximum height on any line sweeps is 8Å, which is the maximum also observed on a blank silicon wafer (see Chapter 1) and only about two times the height of the molecules. Thus features of 8Å

Figure 3.17 Height profiles of PTS after 20 minutes.
height could be roughness due to the fused silica substrate, or monolayer features super-imposed on such a background, but are not consistent with polymerized aggregates, which should be much larger.

After 5 minutes, islanding starts to appear with a diameter of approximately 0.3µm, as shown in height profile 3.14, in particular. After 10 minutes, figure 3.16a, the island size may increase slightly in diameter, and secondary islands start to appear at only 0.06µm in diameter. The film height remains at approximately 8Å. An island-like feature is particularly clear in height profile 3.16b. 15 minutes into the deposition, island-like features are still present (see sweeps A and B) and a possible increase in the number of ∼0.3µm diameter islands is observed. After 20 minutes, few possible islands remain on the surface indicating the film has begun to fill in between the islands.

Van der Waal forces are unlikely to be responsible for islanding in PTS at room temperature. Since the top portion of the molecule is non-polar, a dipole-dipole interaction is not responsible for the island formation. Thus if these results can be confirmed, they would indicate a possible alternative cause for islanding. The absence of polymerization in the PTS case (or more likely, the elimination of polymerization for other molecules), must also be understood to ensure that polymerization is not mistaken for islanding here, due to the very small height of the molecule.

3.4 3-Aminopropyltrimethoxysilane (3-APS):

3-APS is one of the most commonly used organosilanes for formation of self-assembled monolayers, particularly for biological purposes. [22, 23].
Figure 3.18 Growth curve of 3-Aminopropyltrimethoxysilane (3-APS).

Figure 3.19 1 µm x 1 µm AFM images of a 3-APS sample set: (a) after 5 min.; (b) 10 min.; (c) 15 min.; and (d) 20 min.
Figure 3.20 a.) A clean silicon wafer b.) A sample treated with 3-APS for 6 minutes, indicating \( \frac{3}{4} \) coverage of a monolayer.
Figure 3.21 a.) A sample treated with 3-APS for 10 minutes, representing a homogenous monolayer with small islands. b.) A sample treated with 3-APS for 20 minutes, representing a homogenous monolayer.
From ellipsometry results, after only 1 minute, the fast reacting 3-APS has already grown to 4.6Å with a contact angle of 40°. According to our growth curves 3-APS grows to 7.5Å in 15 minutes then levels off. 3-APS reaches its maximum contact angle of 53° after only ten minutes.

15μl of 3-APS added to 50μl of acetone. 3-aminopropyltrimethoxysilane surfaces observed by atomic force microscopy in tapping mode appeared very smooth with a root mean square roughness of 0.137 nm in a one micron square area. The film displays initial growth dominated by islands, which then fill in to complete the monolayer. As in the PTS case, polymerization is not observed in the 3-APS reaction. This is in contrast to the Pentyl and OTS depositions. Setting the time to 3-APS monolayer-coverage at 10 -15 minutes, 3-APS shows many islands at ~50% coverage (6 min/ 12.5 min.), whereas PTS at 50% growth (20min./40 min.) is already smooth. Islands in the PTS case appear to be slightly larger than the 3-APS features. If reproduced, these results might indicate a different mechanism for PTS and 3-APS. In 3-APS dipole-dipole interactions should affect film growth, whereas in PTS, both van der Waals and permanent dipole interactions should be absent.

3.5 11-Bromoundecyltrichlorosilane (11-Bromo, 3):

It is evident that long chain non-polar silanes form islands, but little research has been conducted on film growth of long chain polar silanes such as 11-bromoundecyltrichlorosilane. 6.0μl of 11-Bromo,3 was added to 50μl of dry toluene.
Figure 3.22 Growth curve of 11-Bromodecyltrichlorosilane.
Figure 3.23  1 µm x 1 µm AFM images of a 11-Bromodecyltrichlorosilane (11-Bromo,3) sample set:  a.) 5 min, b.) 2 hours c.)6 hours, d.) 11 hours, e.) 16 hours, f.) 22 hours.
Figure 3.24   Height profile of samples treated with 11-Bromo,3 
   a.) 5 min, b.) 2 hours.
Figure 3.25  Height profile of samples treated with 11-Bromo,3
a.) 6 hours, b.) 11 hours.
Figure 3.26 Height profile of samples treated with 11-Bromo,3
  a.) 16 hours, b.) 22 hours.
11-Bromo,3 shows polymerization 5 minutes into the deposition (figure 3.24a). The size of these large polymerized aggregates increases with time, growing from 40Å to 200Å over the course of the deposition, and essentially preventing a clear study of islanding effects. The polymerized aggregates found in 11-Bromo, 3 are larger and more frequent than those found in the longer chain OTS molecule. This may be due to the dipole-dipole interaction since OTS is not polar and 11-Bromo,3 is a polar molecule. Although 3-APS is also a polar molecule, the polymerization and islands are dramatically less than 11-Bromo,3. The amount of islanding and polymerization in 11-Bromo,3 may be attributed to the combination of its long chain and polarity.

Two contrasting arguments can be made concerning polymerization with respect to chain length: In the first, one might argue that polymerization will increase for decreasing chain length as reactivity (as measured by time to monolayer growth) tends to increase with decreasing size. In this argument, more reactive molecules will react with the trace amounts of water in solution and then condense into aggregates more quickly. For instance, comparing the times to monolayer coverage for the four molecules thus far studied (comparing only toluene depositions, which sets aside the 3-APS data) as a function of carbon number: C3 (PTS, 40 min.), C5 (Pentyl, 8 hours), BrC11 (11-Bromo,3, 12 hours), C18 (OTS, 10 hours), confirms that smaller molecules form monolayers more quickly. This could be due either to increases in the innate reactivity (with the longer chain stabilizing the silane) or alternatively, reactivity might be very similar for the various molecules, but film growth could be limited by steric effects (for instance, the time needed for a long molecules to penetrate into a partially complete film
and react). However, the hypothesis that shorter molecules will result in increased polymerization is contradicted by the data: shorter molecules do not exhibit more polymerization, either comparing absolute times or relative time in comparison with monolayer formation.

A second alternative argument is as follows. One could argue that molecule-molecule interactions rather than reactivity rates dominate the polymerization process. In other words, as intermolecular interactions increase (say with increasing chain length or dipole-dipole interactions), polymerization increases simply because molecules in solution tend to be associated and thus in close proximity to react with each other, rather than the surface, should water be encountered. Such a process would also lead to islanding, where a surface-bound and solution molecules could tend to associate, leading to reaction of the molecule in solution with the surface immediately adjacent to the original surface-bound silane. Strong intermolecular interactions could also be associated with decreases in reactivity. For instance, the presence of dipole-dipole interactions in 11-Bromo,3 could decrease the speed of film growth. The data presented in this thesis is most consistent with this picture - that intermolecular interactions (of the alkyl portion of the alkylsilane) lead to increased polymerization, which is clearly undesirable when attempting to fabricate monolayer films.

Islanding however, seems to be present in all cases, indicating perhaps a different mechanism, or a least the presence of different energy scales and forces, than for the formation of polymerized aggregates. Again, we note that because polymerization appears to be absent only for shorter molecules, additional studies are needed to confirm
that features are absent and not simply undistinguishable from background fluctuations in the fused silica.

3.6 11-Bromodecyldimethylchlorosilane (11-Bromo,1):

A vapor deposition of 11-Bromo,1, a molecule with only one reactive Si-Cl bond that can attach to the surface (single footed), was also conducted. In this case, both vertical polymerization in solution and crosslinking of molecules on the surface should be prevented. The cleaning procedure was the same as the solution depositions (see above). However here, a vapor deposition was utilized. 7μl of 11-Bromo,1 was deposited in individual beakers placed on a hot plate at 100°C for various times. After film growth the sample was dried under a stream of nitrogen.

![Figure 3.27 Growth curve of 11-Bromodecyldimethylchlorosilane.](image)

Figure 3.27 Growth curve of 11-Bromodecyldimethylchlorosilane.
Figure 3.28 11-Bromodecyldimethylchlorosilane (11-Bromo,1) AFM images with deposition time a.) 1 min. b.) 3 min, c.) 6 min, d.) 10 min.

Figure 3.29 Cross sectional height profile of 11-Bromo,1 after 1 minute.
Figure 3.30 Height profile of 11-Bromo,1 after a.) 3 min. b.) 6 min.
From ellipsometry and contact angle measurements, saturation at a maximum coverage occurs at about 15 minutes. Interestingly ellipsometry measurements do not change after about eight minutes, whereas contact angle does not saturate until about 15 minutes. The values for thickness and contact angle are also lower than expected. The observed height of 11-Bromo,1 (13 Å) film is slightly lower than that of the three-foot equivalent molecule 11-Bromo,2 (14-15 Å), indicating that perhaps the molecules are not fully upright, which could be a consequence of the lack of crosslinking. An alternative hypothesis could be that polymerization in the 11-Bromo,3 film could artificially raise the ellipsometric value. Contact angle measurements are much lower for the single-footed molecule film as opposed to 11-Bromo,3, decreasing from 105 -110° to about 80°.
Again, this could indicate poor packing in the single-foot film or the effect of polymerization. As seen in the OTS case, polymerization for long-chain molecules tended to increase the contact angle of the film.

AFM studies on 11-Bromo,1 show possible islanding and no signs of polymerization. The height profiles of figures 3.28a-3.28c (1-6 minutes) do not show any peaks or any growth greater than 6Å. This seems to indicate that film growth in this time frame involves molecules mostly parallel to the surface, which should be possible with only a single attachment point and low molecular density. The island-like features observed, for instance, in height profile C of figure 3.28a and profile C of figure 3.28b) are of unknown origin, perhaps groups of unattached interacting molecules laying parallel to the surface. Further studies are probably merited to explore these features. After 10 minutes, figure 3.31d, small islands start to form with a height of 12Å. These relatively sharp features seem to represent island-like growth. Further studies beyond 10 minutes should shed light on the saturation of contact angle at closer to 15 minutes.

With only single reactive foot on these molecules, when attached to the substrate, there are no reactive groups available to attach to other molecules (i.e., crosslinking). If the reactive group of a particular molecule does not attach to the substrate it does not become part of the permanently attached (covalent) film. However, interactions between bound and unbound molecules could lead to an absorbed monolayer component. When 11-Bromo,1 is rinsed in methanol after film growth, the height of the substrate decreases according to ellipsometry. This may indicate the molecule is no longer perpendicular to the surface but rather tilted at an angle or that material has been removed from the
surface. When a trichlorosilane-derived film is rinsed in methanol after film growth, the film height remains the same indicating no change in the film's structure. Further studies of this effect are underway.

3.7 Overall trends

![Graph showing RMS values of 3-APS, PTS and 11-Bromo,1.](image)

Figure 3.32 Rms values of 3-APS, PTS and 11-Bromo,1.
Figure 3.33 Rms values of OTS, Pentyl, 11-Bromo,3.

The surface roughness of our samples has a characteristic pattern during film growth regardless of which molecule is used, as shown in Figures 3.32 and 3.33. Taking PTS as an example (Figure 3.32) roughness increases until about 15 minutes (roughly 50% coverage) and then decreases. The same trend is followed for OTS, Pentyl, and 11-Bromo,3 with maximum roughness occurring at 10-12 hours in each of these cases (or close to 100% coverage). 3-APS roughness peaks at about 5 minutes (50% of coverage), but then increases for unknown reasons. 11-Bromo,1 has very low roughness for its entire measurement range. Because roughness, and in fact feature height, reported by AFM is a measure of the distance between the lowest feature on the surface and the highest (rather than an actual measure of thickness), this trend can be explained as follows. When island-based film growth begins, roughness (summed over the entire sample) will increase (proportional to molecule height) as the AFM has to traverse over
the difference between islands and bare fused silica. As more islands form (time increases), roughness should increase. However, as the spaces between islands become filled, this trend should reverse as more of the substrate is now converted into a smooth monolayer and transitions from monolayer height to the original fused silica surface become rarer. In this regime (taking place after ~50% coverage), roughness will decrease and in the absence of polymerization, after film growth is complete, the original rms roughness of the fused silica could be recovered. In this model, the maximum roughness should occur somewhere after 50% coverage (which is true for PTS, 3-APS, Pentyl, 11-Bromo,3, and OTS), and with a maximum magnitude proportional to the molecule height. This trend is well-illustrated in Figure 3.33 for Pentyl, 11-Bromo,3 and OTS. Figure 3.33 shows OTS, the tallest of the three molecules, has the greatest surface roughness and Pentyl, the shortest of the three molecules, has the smallest rms. Similarly, the maximum roughness for 3-APS and PTS is much smaller, as can be seen in Figure 3.32. Polymerization may affect this trend, because as time increases, additional polymerization could increase roughness substantially, as large polymerized material deposits on the surface; however this trend was not observed for any of the molecules that displayed polymerization.

11-Bromo,1 was the only film growth study that did not display this pattern. Significantly, very little or no islanding was seen in this case; in addition, significant evidence showed that molecules could lay close to parallel with the surface. Considering a film growth process without islanding, molecules first attach sparsely to random positions throughout the sample and have ample opportunity to lay close to parallel with
the surface (constrained only by the single bond to the surface and the methyl groups).

As density increases, molecules continuously increase in angle to the substrate (standing up) until a full monolayer is formed. This gradually, continuous increase in height should maintain (or slightly) increase the surface roughness at the innate fused silica level, in contrast with the island model of growth which dramatically increases roughness. Thus, we conclude that unlike all tricholorosilanes measured, 11-Bromo,1 appears to have at least some component of continuous (non-islanding) growth.
Chapter 4: Film growth at a variety of temperatures on SiO2

4.1 OTS 80°C:

Figure 4.1 1 µm x 1 µm AFM images of an OTS at 80°C sample set a.) after 1 hour, b.) 4 hours, c.) 10 hours, d.) 14 hours, e.) 18 hours, f.) 22 hours. SiO2 substrates were immersed into 1mM OTS solutions immediately after cleaning procedures while in a cleanroom environment.
Figure 4.2 Height profiles of OTS at 80° a.) after 1 hour, b.) 4 hours.
Figure 4.3 Height profiles of OTS at 80° a.) after 10 hour, b.) 14 hours.
Figure 4.4 AFM images of OTS at deposition temperature 80°C, a.) 18 hours, b.) 22 hours.
Figure 4.1a shows no islands of OTS after one hour of deposition at 80°C, unlike OTS immersed for 1 hour at room temperature, figure 3.4b, which showed islands of 20Å. In fact, fewer large features occur at all temperatures, and during the entire experimental range, no definitive island structures can be identified (although candidate features are present). Polymerization is present from four hours forward. We have not completed a full growth curve (ellipsometry and contact angle versus time) for OTS at 80°C, however, some quantitative comparisons of polymerization at different absolute times seem to show lower levels of polymerization aggregates throughout the deposition. At 10 hours, the polymerization (any height over 30Å for OTS) for this sample covers 3% of the surface. In comparison, figure 3.4d is a sample that was immersed for 12 hours at room temperature and has 7% of its surface covered in molecules that have polymerized. 22 hours into the deposition, the 80°C sample, figure 4.1f, has a few places where polymerization has occurred covering 4% its surface. After 22 hours at room temperature, figure 3.4f, 7% of the sample contains polymerization. We conclude that heating OTS on SiO₂ seems to decrease the likelihood of islanding and polymerization.
4.2 OTS 0ºC:

Figure 4.5 AFM images of OTS at 0ºC for; a.) 1 hour, b.) 5 hours, c.) 8 hours, d.) 12 hours, e.) 16 hours, f.) 22 hours.
Figure 4.6 Height profile of OTS at 0°C for; a.) 1 hour, b.) 5 hours.
Figure 4.7 Height profile of OTS at 0°C for; a.) 8 hours, b.) 12 hours.
Figure 4.8 Height profiles of OTS at 0°C for a.) 16 hours, b.) 22 hours.
A visual inspection of the figure 4 shows an increase in features at all time points in comparison to data from OTS growth at higher temperature. Island-like structures are observed in figure 4.1d and 4.1f. Again, we have not completed a full growth curve for OTS at 0°C examining ellipsometry and contact angle to determine the time to monolayer growth. Comparison of polymerization coverage areas at absolute times (not relative growth times) show increases in formation of large aggregates despite the likelihood that the reaction rates are lower at lower temperatures. As is the case throughout this work, it is not clear whether these aggregates are bound to the surface, simply adsorbed, or in fact, if the molecules within an aggregate are bound to each other or simply interacting via van der Waals and other non-covalent forces. Here, one suspects that some aggregation may be due to non-covalent interactions between these long chain molecules, perhaps without bonding of the silane group. After 12 hours, figure 4.1d, polymerization has occurred on 12% of the surface, 5% more than at room temperature. At 22 hours (figure 4.1f) polymerization has occurred over 14% of the surface, twice as much as found at room temperature. Cooling the samples during film growth appears to increase polymerization and islanding in OTS.
Finally, we examine the roughness versus deposition time for the three OTS growth temperatures. The rms is greatest when OTS is grown at 0ºC and lowest when grown at 80ºC. This may be attributed to the increase in islanding and polymerization at the lower temperatures. Whereas, at room temperature the maximum roughness observed is 7 Å, 0 ºC depositions have a roughness that peaks near 20 Å, and maximum roughness is somewhat decreased for the 80 ºC deposition to about 5 Å. These results follow the overall pattern in our data and other published reports that islanding and polymerization in OTS generally decreases with increasing deposition temperature. Given that van der Waals interactions between the long C18 chains are the most likely dominant intermolecular interaction, we hypothesize that increasing temperature disrupts these interactions and thus minimizes aggregate and island formation.
4.3 PTS 60°C:

Figure 4.10 PTS deposited at 60°C a.) 5 min b.) 10 min c.) 15 min d.) 20 min.
Figure 4.11 Height profiles of PTS deposited at 60°C a.) 5 min b.) 10 min.
Figure 4.12 Height profiles of PTS deposited at 60ºC a.) 15 min b.) 20 min.
For PTS, polymerization will be considered any height greater than 10Å. After 5 minutes, figure 4.10a, 2% of the surface has polymerized aggregates. At 10 minutes 9% of the surface has polymerized, at 15 minutes, 10%, and at 20 minutes, 10% of the surface is covered with molecules that have polymerized, figures 4.10b, 4.11a, 4.11b. In other words, about 10% of the surface is covered with polymerize aggregates from 10 minutes on. After 20 minutes of being immersed at room temperature, less than 0.1% of the surface shows polymerization. PTS grows with less polymerization at room temperature than it does at 60ºC.

With respect to island growth, which was noticeable at room temperature, island-like features may be present but are not definitively identified in the AFM data. Thus it is possible that islanding is minimized at 60ºC, despite the increase in polymerization. This could be consistent with an increase in molecule reactivity at the elevated temperature, in other words, molecules react quickly with each other (forming polymerization) and the surface, minimizing islanding. An alternative hypothesis is that the features identified as islands in the room temperature growth are in fact small polymerization, and the size of the polymerization simply increases with increasing temperature at the same time points.
4.4 C3 0°C:

Figure 4.13 PTS at 0°C a.) 5 min, b.) 10 min, C.) 15 min, d.) 20 min.

Figure 4.14 Height profile of PTS at 0°C after 5 min showing island formation.
Figure 4.15 Height profiles of PTS at 0°C after a.) 10 minutes b.) 15 minutes.
Polymerization is also present at 0°C, although at a much lower level than 60 °C. PTS grows with less polymerization at room temperature than it does at 0°C. This may indicate that the absence of polymerization at room temperature is coincidental, and that further reproduction of that data is needed. Interestingly, island formations are again present at 0°C, perhaps indicating that island formation for PTS decreases with increasing temperature. This result parallels that of OTS, with temperature increase allowing interactions between molecules to be overcome, which in turn minimizes islanding. The source of the intermolecular interactions for PTS is unclear as both van der Waals interactions and dipole-dipole interactions should be minimized. Perhaps the "feet" of
the molecules interact, for instance via hydrogen bonding. This effect would be unimportant for molecules with larger interactions (i.e., van der Waals forces between two long chains or dipole-dipole interactions), but could dominate in the PTS case.

Figure 4.17 Roughness values of PTS film growth at 60ºC, room temperature, and 0ºC.

The rms roughness of PTS never reaches above 2.0Å when grown at room temperature, and peaks at about 15 minutes. For the elevated temperature deposition, the roughness is higher and peaks at a lower time, indicating that film growth may be faster. At 0ºC, the curve looks to be just peaking (which would be consistent with a much slower growth process) or may simply not follow the form of the other curves. Recall that in previous roughness curves, polymerization did not appear to play a large role in surface roughening, with even molecules displaying significant polymerization (11-Bromo, three foot, and OTS) showing the same patterns in roughness as depositions with no
polymerization (i.e., APS and PTS). Thus the PTS temperature data is quite complex, with the roughness curve indicating that island formation increases at higher temperatures (in contrast with our observations of the AFM images) and may increase even further at lower temperatures. Thus, much more study is needed to understand the PTS growth mechanisms.

Chapter 5: Self assembled monolayers on Lithium Niobate

5.1 Project Goals and Motivation:

In this chapter, self-assembly of polar and non-polar molecules will be used as a model for nano-scale construction on lithium niobate, a ferroelectric material. Islanding and polymerization of polar and non-polar molecules will be compared on both annealed and non-annealed lithium niobate. We choose to grow SAMs on lithium niobate for two reasons: (1) it is a single crystal which gives it a smooth surface, (2) its ferroelectric properties.

Image devices, piezoelectric sensors and capacitors all require polar materials such as ferroelectrics. Lithium Niobate (LiNBO₃) is one example of a metal-oxide ferroelectric, and is widely used in industrial applications. We are using single crystal lithium niobate where the z-axis (generally aligned with the ferroelectric dipole) is perpendicular to the surface. Thus, we can access to different polarization directions on the two different sides of any particular wafer. All of the experiments reported here were conducted on the so-called, "positive" side of the wafer.
5.2 Single Faced Poled Lithium Niobate:

The lithium niobate substrates were purchased from Crystal Technologies and were z-cut. They were annealed at a slow rate of 1.5°C per minute until reaching 200°C, then at a faster rate of 35°C per minute until reaching 1000°C. The lithium niobate then dwelled at 1000°C for 2 hours and cooled until 150°C before removing.

5.3 Blank Annealed Lithium Niobate:

Figure 5.1 AFM images of blank annealed Lithium Niobate.
Figure 5.2 Height profiles of blank annealed Lithium Niobate.
Clean blank annealed lithium niobate (figure 5.1) showed many features of various sizes on its surface. Some of these features are likely steps between crystalline layers and could have very low surface roughness (essentially atomic) within the step. However, due the size of AFM sweeps as limited to $1 \, \mu m \times 1 \, \mu m$, and the size of characteristic silane islands we wish to observe (about the size of the step features), this surface is not well suited to studying film growth. The surface roughness of figure 5.1a is 5.041nm, 5.1b is 5.419nm, 5.1c is 5.498nm. The high surface roughness is three times larger than the largest molecule (OTS) used. This makes it nearly impossible to analyze film growth.
5.4 Blank LiNb not annealed:

Figure 5.4 AFM images of non-annealed blank Lithium niobate indicating a surface roughness of 63.07Å.

Figure 5.5 Non-annealed blank Lithium niobate surface roughness of 40Å.
Figure 5.6 Non-annealed blank Lithium niobate surface roughness of greater than 40Å.
Non-annealed lithium niobate did not show particular features but still exhibited a high surface roughness and sloping backgrounds with changes $\sim 40 \, \text{Å} / 1 \, \mu\text{m}$. The next step was to bind polar and non-polar molecules to the lithium niobate sample. The same solution phase deposition technique (as for preparation of the silica samples) was used to attach the molecules to the surface. Solution phase deposition was conducted by immersing the lithium niobate into OTS (non-polar) or 11-Bromodecyltrichlorosilane (polar) solutions in toluene. Binding of the molecules took place on both sides of the lithium niobate. In this thesis, I only discuss film growth on the positive face (side) of the lithium niobate.

5.5 Film growth on LiNb

We demonstrated binding of OTS to an annealed single faced poled lithium niobate substrate using AFM (figure 5.7). It is difficult to determine the height of the OTS on the substrate considering the roughness of lithium niobate is greater than the height of the molecule (26Å). The surface roughness of a blank non-annealed clean lithium niobate is 63.07Å, while the surface roughness of a clean blank annealed lithium niobate was 54.19Å.
Figure 5.7 Annealed Lithium Niobate with full coverage of OTS with a surface roughness of 64Å.

OTS was grown on annealed lithium niobate and a change in surface morphology was observed. However, much more investigation is needed to reach conclusions regarding this experiment.

We were unsuccessful in definitively determining the binding of 11-bromodecyltrichlorosilane to a non-annealed lithium niobate substrate. Small features can be seen in the AFM images (Figure 5.7), but it can not be determined if these features are 11-Bromodecyltrichlorosilane islands or the surface of the lithium niobate.
Figure 5.8 Non-annealed lithium niobate with 11-bromodecyltrichlorosilane with a surface roughness of 68.31Å.

Figure 5.9 Non-annealed lithium niobate with 11-bromodecyltrichlorosilane with aggregates reaching heights of 30Å.
Figure 5.10 Non-annealed lithium niobate with 11-bromodecyltrichlorosilane with aggregates reaching heights of a.) 20Å b.) 60Å.
Future work could include Auger Electron Spectroscopy and XPS in addition to AFM. Auger Electron Spectroscopy (AES) probes the elemental composition of a surface by measuring emitted electron energy from an Auger process when the surface is exposed to electrons in the range 2–50 keV. When used in conjunction with AFM, AES provides mapping of the surface elemental distribution. This spectroscopy instrumentation should be able to detect Auger-active elements, such as bromine, within the μm scale, which would be beneficial in collecting additional information on lithium niobate; however substrate charging may limit such experiments. XPS, which has fewer charging effects, but lower spatial resolution, may be a suitable complement or alternative.

Chapter 6: Summary and Outlook

6.1 Islanding and Polymerization

At room temperature, long chained polar and non-polar molecules show islanding and polymerization in film growth. Polar and non-polar short chain molecules also exhibit islanding, but polymerization seems to be minimal at room temperature. Single footed molecules show no signs of islanding or polymerization resulting in a uniform film growth. Temperature studies were conducted on OTS (non-polar long chain) and PTS (non-polar short chain) and the results were complex. OTS seems to have decreases in islanding and polymerization as a function of increasing temperatures. However, PTS
showed the highest quality film growth, with minimal polymerization, at room
temperature. In attempting to study film morphology for trichlorosilanes on lithium
niobate, we were unable to distinguish binding of the polar 11-Bromodecyltrichlorosilane
due to the roughness of the lithium niobate surface being greater than the height of the
molecule. It may be possible to grow OTS, and other long chained molecules, on
annealed lithium niobate.
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