

# **Interfacial Engineering of MicroStructured Materials**

by

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## Abstract

The tribological behavior of octadecyltrichlorosilane self assembled monolayers (OTS-SAMs) has been successfully exploited to reduce energy losses and to produce adequate adhesion barrier properties on many MEMS surfaces. Unfortunately, performance discrepancies are reported in the literature between films produced on smooth surfaces as compared to typical MEMS surfaces maintaining topographical roughness. Rational explanations in terms of reproducibility issues, production considerations, and the scale of measurement technique have been introduced to account for some of the variation. The tribological phenomena at the micro-scale are complicated by the fact that rather than inertial effects, the forces associated with the surface become dominant factors influencing the mechanical behavior of contacting components. In MEMS, real mechanical contacts typically consist of a few nanometer scale asperities. Furthermore, various surface topographies exist for MEMS device fabrication and their corresponding asperity profiles can vary drastically based on the production process.

This dissertation presents research focusing on the influence of topographical asperities on OTS film properties of relevance for efficient tribological improvement. A fundamental approach has been taken to carefully examine the factors that contribute to high quality film formation, specifically formation temperature and the role of interfacial water layer associated with the sample surface. As evidenced on smooth surfaces, the characteristics for successful tribological performance of OTS films are strongly dependent on the lateral packing density and molecular orientation of the monolayer. Limited information is available on how monolayers associate on topographical asperities and whether these topographical asperities influence the interfacial reactivity of MEMS surfaces. A silica film produced from a low temperature, vapor-phase hydrolysis of tetrachlorosilane with a tunable topography is

introduced and leveraged as a novel investigative platform for advanced analytical investigations often restricted to use on smooth surfaces. This tunable surface allows intellectual insight into the nature of surface properties associated with silica surfaces, the uptake of interfacial water and the subsequent influence of surface morphology on OTS film formation. FTIR analysis was utilized for an examination of interfacial properties on both smooth Si(100) surfaces and on the tunable MVD topography in combination with an investigation of OTS film formation mechanism. A dilute etchant technique is developed to provide topographic contrast for AFM imaging to allow direct examination of film packing characteristics in relation to surface asperities. A relationship between monolayer adsorption characteristics and topographical asperities with observed variations in monolayer order resultant from surface roughness has been elucidated. Results show that the packing structure of OTS monolayers is dependent on the local asperity curvature which is qualitatively different from that observed on flat surfaces.

In addition, a difference in surface reactivity is observed as a result of different surface topographies with thicker silica layers maintaining a thicker interfacial water layer resulting in a higher coverage of OTS monolayers at similar reaction times and conditions. This work shows changes in surface reactivity as a consequence of different morphological surface characteristics and preparation procedures. Additional research is presented on a new class of SAM, namely octadecylphosphonic acid and its monolayer formation mechanism and properties are compared to conventional OTS monolayers. This monolayer is translated to investigative probes based on Aluminum oxide specifically tailored for a tribological comparison across multi-scale friction regimes.

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Part I

# Interfacial Engineering of Microelectromechanical Systems

## Chapter 1

### Introduction to MEMS Research

Knowledge of the fundamental mechanisms of friction has remained elusive despite over 300 years of careful thought and experimentation [3]. Tribological properties in nano- and micro scales between two sliding solid surfaces have drawn much attention, as they significantly affect the performance of microelectromechanical systems and provide crucial information for understanding the fundamental mechanisms and origin of friction and wear [4]. As mechanical devices are made ever smaller in size they are limited by these very phenomena. The expansion of interest in friction, wear, and lubrication at small length scales has been fueled by both scientific curiosity and technological need. New high resolution force probes have provided unprecedented access to fundamental processes at interfaces, which nevertheless remain poorly understood due to their inherent complexity.

Tribological performance is highly dependent on surface interactions. When two surfaces are pressed against each other initial solid-solid contact occurs at the surfaces' high points. This area where the asperities touch is usually an extremely small fraction of the total area covered by the surfaces, but the forces generated between the contacting atoms are responsible for most tribological phenomenon. In order to alleviate these adhesion-related problems, both the topography and the chemical composition of the contacting surfaces must be studied and controlled. One commonly used method of tailoring the surface properties is based on deposition of self-assembled monolayers (SAMs).

Polycrystalline silicon, silicon oxide and aluminum oxide are major components of many MEMS devices found to consist of a multitude of topographical asperities. As SAMs have been applied to surfaces of varying topographical complexity, many discrepancies associated with tribological performance have been identified. SAM growth kinetics and interfacial

properties as deposited on MEMS devices are often inferred from information learned on smooth surfaces, due to the inherent difficulties with analyzing surfaces of topographical complexity. Research indicates that monolayers need to maintain a specific packing density and molecular orientation as deposited on surfaces of low roughness in order to provide a high tribological response. In translating these monolayers to surfaces with inherent roughness and varying topographical asperities, it becomes essential to determine how monolayers associate on these ‘points of contact’ as this will be a determining factor for the effectiveness of tribological improvement provided by the monolayer. This research investigates SAM adsorption on various surface topographies and various surface types that are similar to those that exist in MEMS devices. Valuable comparisons are made between surfaces of higher complexity and surfaces traditionally utilized for SAM observation in an attempt to determine the influence of topographical asperities on OTS monolayer performance.

## **1.1 Background Research**

### **1.1.1 Interfacial Phenomenon in MEMS Devices**

Micro electro-mechanical systems (MEMS) are miniature size devices that contain sensing and actuating components in very small packages. Several applications, such as accelerometers, digital mirror devices (DMD<sup>(TM)</sup>), pressure sensors, gyroscopes, resonators, and many others have been realized using MEMS technologies, and many new ones are under development [5]. The use of small micromechanical devices has proven difficult as indicated by the inability to overcome the failure modes and reliability issues of the current test structures. Commercially successful MEMS devices, to date, have either non moving parts or contacts whose lateral motion is very restricted. Many more exciting applications can be attained with MEMS devices consisting of moving, touching, and rubbing structures. These include gears and motors that can enable much more complicated mechanical functions at the micro- and nanoscale. However, the effects of adhesion, friction, and wear of MEMS

devices are challenging the development and commercialization of more sophisticated micro machines.

The tribological behavior of contacts in MEMS technologies differs from those in macroscopic engineering structures. At the macroscopic scale, millions of asperities give rise to the parametric relationships described by Amontons law, which states that the friction coefficient is independent of apparent contact area and applied load. In MEMS, real mechanical contacts typically consist of a few nanometer-scale asperities that touch. At these small scales, Amontons law breaks down and individual asperity contact behavior must be considered [1]. Additionally, forces that are negligible at the macro scale become significant at the microscopic scale. At the macro scale, gravity dominates over adhesion. However, at the micro- and nanoscale, the gravitational body forces are negligible and adhesion becomes significant. Adhesion is generally caused by capillary, electrostatic and van der Waals forces, and in some cases by chemical forces such as hydrogen bonding in solid bridging [6]. At separations on the order of a micrometer, there has been reported occurrence of unwanted sticking phenomenon. This phenomenon aptly named ‘stiction’ is present during the release process when the surface tension of the draining rinse liquid draws the micro structure into contact with the underlying substrate (release stiction). In-use-stiction occurs, when intentionally or accidentally, parts come into contact. Strong interfacial adhesion between micro- and nanoscale structures (asperities) induces high friction and wear, leading to failure of MEMS devices.

The topography of MEMS devices and their corresponding asperity profiles are influenced by the fabrication process. Three main MEMS fabrication processes are surface micro machining (SMM), silicon-on-insulator (SOI) technology, and electro forming. A more in-depth review of the different micro fabrication methods can be found elsewhere [7]. Each method employed for material deposition, patterning, and etching to create MEMS structures, leaves behind unique surface morphologies on both sidewall and in-plane surfaces. An example of sidewall surfaces from each of the micro fabrication methods indicated above are

shown in Figure 1.1 [1]. Because of this surface roughness ranging from a few to a hundred nanometers, only a few asperities make actual physical contact when opposing surfaces with similar surface morphologies are brought together under a given load. As these surfaces slide past one another, some contacts are broken, while new ones are formed. However, the total number of contacting asperities is relatively constant during sliding, assuming the total load and adhesive forces do not vary.

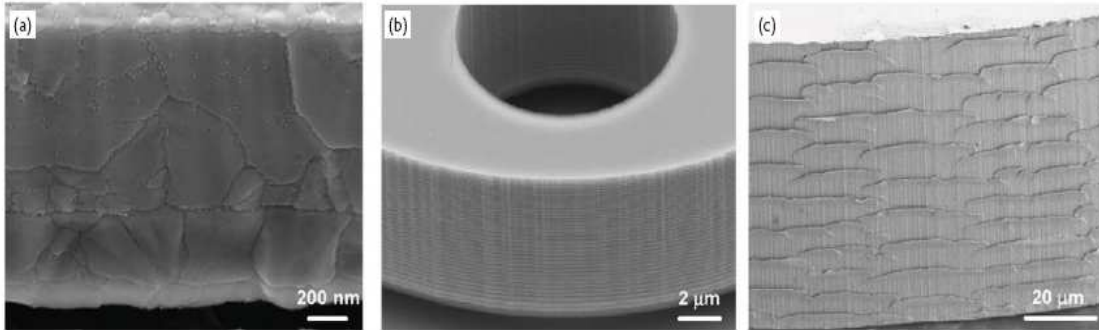


Figure 1.1: SEM images of surface morphology of MEMS fabricated by (a) Si micro machining, (b) SOI, and (c) electro forming processes adapted from reference [1].

Various surface engineering techniques have been introduced to reduce adhesion in MEMS. One general approach is to avoid the formation of water layers on the surfaces of MEMS/NEMS by surface treatments that provide a stable hydrophobic surface, thereby eliminating capillary forces [8]. Another approach is to change the surface interaction forces by using surface roughening or texturing techniques to reduce the real area of contact [9,10]. Many attempts have been made to create MEMS devices with a specific surface topography in order to control the tribological processes, unfortunately many of these processes have proven unreproducible and expensive for mass production. As a consequence, much research has been dedicated to the chemical modification of MEMS devices with coatings designed to tailor the interfacial properties. The chemical modification of MEMS devices must render the surfaces hydrophobic in order to eliminate capillary forces, be stable both under ambient

and elevated temperatures, be hard and wear resistant, and electrically conductive to minimize charge trapping [6]. In addition, these coatings must be conformal to insure uniform deposition to MEMS devices.

### **1.1.2 Overcoming Interfacial Interactions with Self-Assembled Coatings**

One commonly used method of tailoring the surface properties is based on deposition of self-assembled monolayers (SAMs). SAM coatings have been demonstrated to provide anti-stiction and low friction characteristics [11]. SAMs are composed of molecules that spontaneously chemisorb and organize into a close-packed assembly on a substrate [12]. They are ideal for studying the fundamental chemical and physical phenomena, since they can be attached to a variety of different substrates, form well-defined and uniform interfaces, and can be tailored structurally to study the resulting effects on friction and other properties [13].

Figure 1.2 illustrates a self-assembling molecule, which includes an anchoring group with a strong preferential adsorption to the substrate, an alkyl chain and a terminal functionality (head group). The organization of the self-assembling molecules in SAMs is governed by the interplay between the packing of the molecules on the substrate, the interaction of the molecular head groups with the substrate and any interactions between the molecular terminal groups both with each other and with any liquids or vapors in contact with the SAM-modified surface.

### **1.1.3 Self-Assembled Octadecyltrichlorosilane Monolayers as a Candidate for Overcoming Interfacial Interactions**

Octadecyltrichlorosilane SAMs have been demonstrated as one of the most promising candidates for the tribological improvements applicable to MEMS devices. The formation and structure of octadecyltrichlorosilane (OTS) monolayers, as deposited by the solution methods have been studied extensively on various substrates and under different deposition

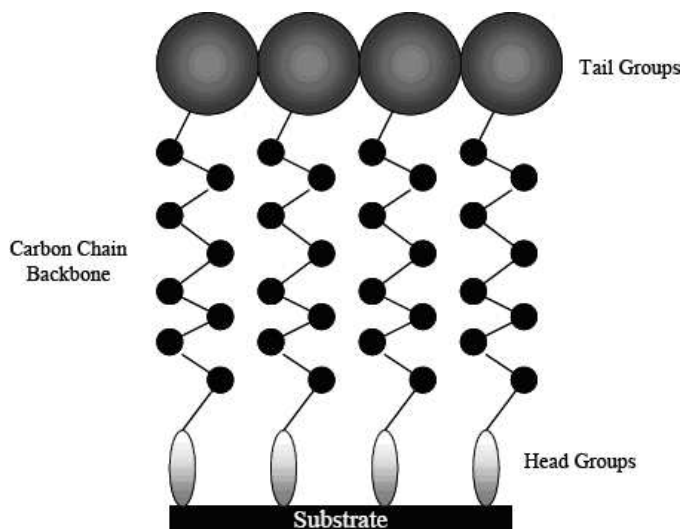


Figure 1.2: Representation of the three parts of self-assembled monolayer illustrating the head groups, tail groups, and carbon chain backbones.

conditions [2, 14–22]. When physisorbed on an appropriate surface, the OTS molecules organize themselves into crystalline or near crystalline order depending on temperature, with a terminal end that is hydrophobic. This tendency has proven helpful in for many applications including biosensors [23, 24] microelectronics [25], thin film optics [26], water-resistant coatings [27], and anti-corrosive coatings [28]. These films have been successfully deposited on a variety of substrates including silica, alumina, mica, glass [29–32] and are frequently employed on surfaces that are rough, such as polycrystalline silicon and silicon nitride [33].

Atomically smooth surfaces have served as model systems allowing the characterization of the growth kinetics and interfacial chemistry for both full monolayer films and partial OTS SAMs. The formation of OTS monolayers is postulated to occur through a condensation reaction between a hydroxylated substrate surfaces and the hydrolyzed chlorine atoms of OTS. The hydrolyzed OTS molecules physisorb onto the substrate surface via hydrogen bonding and finally form  $\text{Si}(\text{Silane})\text{-O-Si}(\text{Substrate})$  bonds and  $\text{Si}(\text{Silane})\text{-O-Si}(\text{Silane})$  cross linking covalent bonds [34]. This is illustrated in Figure 1.3.

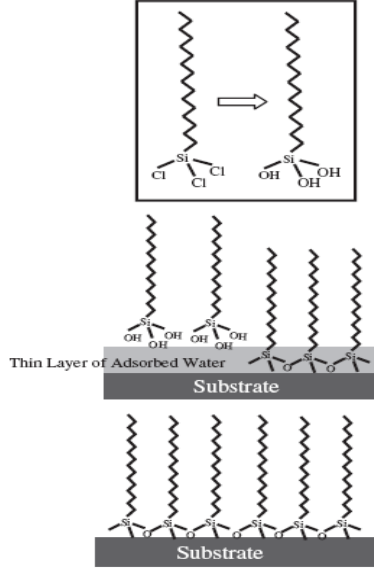


Figure 1.3: Proposed reaction mechanism of OTS monolayer adsorption onto a hydrated surface.

The self assembly process is highly sensitive to experimental conditions such as reaction time, reaction temperature, solvent type, concentration, and the post deposition immobilization procedure [19,35–41]. Two mechanisms of growth are described in the literature. In the mechanism known as the “uniform” model, silane molecules initially are distributed homogeneously over the substrate in a disordered, liquid like manner [15–17,42]. The average tilt angle of the adsorbed chains is greater than  $15^\circ$  because of lower packing densities and gauche conformations for the chains. With increasing coverage, the disordered film is transformed into a more ordered, quasi-crystalline structure. In the mechanism known as the “island” model, domains of densely packed well-ordered, fully extended OTS molecules are heterogeneously grown on the substrate, and these domains are separated by uncovered regions of the substrate [2,19]. These islands typically have dimensions on the order of hundreds of nanometers. With increasing deposition time, more domains are adsorbed until complete coverage of the substrate is achieved. In the “island model” OTS film is considered to be close-corresponding to fully extended chains, with the chemisorbed chains in an all trans conformation with an average tilt angle  $<15^\circ$  away from the surface normal [12]. The

two mechanisms of growth are distinguished in the literature based on formation temperature and will be described in the sections below.

The importance of the water content on the substrate surface in determining the reactivity, surface coverage, and chain packing of OTS monolayers has been emphasized, and conflicting results have been presented as to the role of substrate surface properties such as the availability of free OH groups and the level of hydration required for an ordered OTS film [17, 38, 42]. Although the presence of an interfacial water layer has been concluded as essential, debate still remains as to the degree of hydration necessary for uniform coverage and to the role this water layer plays in surface attachment of OTS molecules. Angst *et al.* found that the degree of hydration on the surface of SiO<sub>2</sub> was essential for film order, showing that a films produced on non hydrated SiO<sub>2</sub> were less ordered than films of OTS deposited on well-hydrated SiO<sub>2</sub>, providing evidence that the contact angles of water and thicknesses of the monolayers were lower on the non hydrated surfaces [17]. Wang *et al.* used FTIR to studied the adsorption of OTS monolayers on a fully dehydrated and dehydroxylated silica surface of fumed silica in comparison to an as received silica surface and a superhydrated silica. The dehydrated and dehydroxylated surface, which maintains only isolated or geminal OH groups adopted a disordered structure. In the case of OTS attached to a hydrated surface known to exist at 3.1 OH/nm<sup>2</sup> they found a slight increase in the trans conformation, but noted that when excess surface water is present on a superhydrated fumed silica, the trans bands of OTS become even more pronounced suggesting a higher ordered monolayer [43]. On the other hand, LeGrange *et al.* deposited OTS on hydrated and dehydrated substrates of fused silica [38] observing ordered, complete SAMs of OTS on hydrated substrates and decreased coverages on dehydrated substrates. Tripp and Hair used infrared spectroscopy to determine that there is no direct reaction of OTS with the surface hydroxyl groups and the OTS binds only to a small extent with the first water layer on the surface of fumed silica. It was proposed that a nominal amount of water was needed for monolayer formation with that too little water resulting an incomplete monolayer, whereas

with thick water layers the OTS polymerized [44]. Several groups have shown that the density of siloxane bonds between the adsorbed silane film and substrate is small [38, 41, 42]. It has been speculated that OH groups on the surface affects the mobility of the adsorbed OTS molecules [18] acting as nucleation and bonding sites for the formation and stabilization of the monolayers, but without an intervening water layer successful OTS monolayer formation is restricted. Parikh and Brzoska suggested that a mobile water layer on the surface was necessary to decouple the OTS monolayer from the underlying substrate allowing improved lateral packing of the hydrocarbon tails. However, they concluded that on flat surfaces, it was not possible to directly measure the amount of adsorbed water or to determine the hydration state of the substrate [19, 41].

Partial OTS monolayers deposited on smooth surfaces have revealed that the self-assembly process results in the formation of films with distinct characteristics as a function of deposition temperature. These regimes are illustrated in Figure 1.4. Each regime is characterized by changes in molecular arrangement including packing density, chain conformation, and orientation with respect to the substrate [45]. The occurrence of three distinct temperature regimes have been equated to the notion of a transient Langmuir film during SAM formation [2, 41]. The (hydrolyzed) precursor molecules retain their mobility for sufficiently long times allowing for the observation of transformations between different condensed two dimensional phases of the film [40]. The existence of two characteristic temperatures have been determined,  $T_0$  and  $T_c$ . For  $T < T_0$ , self-assembly proceeds initially by island growth only, the substrate between islands remaining essentially unfilled; such a growth pattern is expected if a Langmuir film nucleates liquid-condensed (LC) domains coexisting with the gas phase below the triple point. Thus,  $T_0$  can be identified with  $T_t$ . For  $T > T_0$ , island growth is observed to occur more slowly, while the substrate between islands is gradually filled in with OTS molecules. This growth regime, which has been observed by various authors, is attributed to nucleation of LC domains coexisting with a liquid-expanded (LE) phase [46, 47]. This mechanism operates only up to a characteristic temperature  $T_c$ , above

which there is no island nucleation but homogeneous growth instead. More specifically, for low temperatures of  $T < 16\text{ }^{\circ}\text{C}$ , the OTS-based monolayer forms by island growth, the islands consist of fully extended chains, and essentially no OTS molecules are found on the substrate between islands. For  $T > 40\text{ }^{\circ}\text{C}$ , growth is homogeneous and disordered with no island growth observed. For  $16\text{ }^{\circ}\text{C} < T < 40\text{ }^{\circ}\text{C}$ , islands of extended chains are observed (islands) surrounded by a uniform background of chains that are disordered (e.g., contain gauche defects). Figure 1.4 is adapted from the works of Carraro *et al.* and illustrates the three growth regimes.

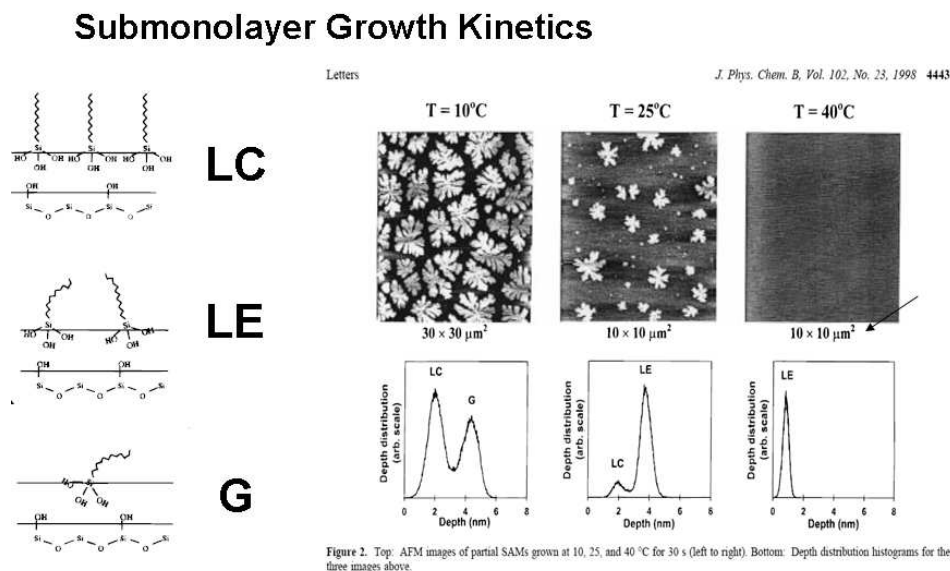


Figure 1.4: Submonolayer growth regimes for OTS film formation as influenced by temperature adapted from reference [2].

## Thermal stability

Investigations of the thermal degradation mechanisms of OTS monolayers, evidence that, the thermal stability of OTS monolayers is dependent on the environmental conditions under study. Kluth *et al.* studied the thermal decomposition mechanism on Si(100) surfaces by annealing under vacuum, finding that decomposition occurs through cleavage of C-C and Si-C bonds followed by the removal of the headgroup Si-O. Results indicate that the silicon

head groups remain on the surface even after the monolayer has decomposed until about 827 °C [48]. In contrast, Kim *et al.* investigated OTS thermal decomposition in air finding that the monolayers are stable up to about 220 °C and above 220 °C the monolayers primarily decompose through C-C bond cleavage, with a gradual reduction in chain length. They also show the siloxane headgroups remaining on the surface following the decomposition of hydrocarbon fragments until about 480 °C, offering, that an air environment accelerates the decomposition process [49]. Other studies have shown that water contact angles on octadecyltrichlorosilane (OTS)-coated surfaces remain the same upon annealing for 5 min to temperatures as high as 400 °C, in a nitrogen environment, and that above this temperature the contact angle was observed to decrease, indicating degradation of the films [50]. Whereas, Calistri-Yeh *et al.* have studied the thermal stability of OTS SAMs on Si(100) by annealing their specimens for 2 h at temperatures over 125 °C in air with observed permanent structural changes of octadecyltrichlorosilane (OTS) monolayers in air above 127 °C [51]. Mirji *et al.* examined OTS monolayers on planer Si(100)/SiO<sub>2</sub> and mesoporous SBA-15 substrates finding that the OTS layers are thermally stable up to a temperature of 260 °C in air [29]. No direct comparison between different annealing conditions and the thermal decomposition temperatures has been examined or determined in the literature.

## Chemical and Immersion Stability

Immersion stability studies of organosilane monolayers deposited on silicon oxide surfaces, indicate that, while these films are stable in dry environments for long periods of time [52], the stability is severely compromised in aqueous conditions. Maccarini investigated the immersion stability of OTS films on silicon, showing that, the films did not exhibit any appreciable changes after 24 h of exposure to water [53]. Extending the water exposure time to the OTS film has yielded different results. For example, Parker monitored the contact angle of various monolayers on silicon oxide surfaces in a five week immersion experiment, concluding that, OTS monolayers immersed in water were relatively stable [54].

While the work of Anderson *et al.* obtained similar contact angle data over a 5 week period, but included additional ellipsometric and AFM data that suggested the OTS monolayers stability was compromised [55].

The chemical stability of OTS SAMs has not been reported extensively in terms of solvent interactions. Iimura *et al.* studied the chemical stability in organic solvents (e.g. benzene, ethanol, chloroform), in acidic (pH 1) conditions and in alkaline solutions (pH 13) observing no dramatic changes in the intensity of the observed CH<sub>2</sub> stretching bands in all three conditions [56]. In contrast, Geerken *et al.* investigated the chemical stability of OTS in different aqueous solutions with varying pH-values for several days, finding that the coatings are stable from pH 2 to pH 10. But, found that when treated with sodium hydroxide (pH-13), the contact angle decreased dramatically suggesting that the Si-O bond is susceptible toward hydrolysis at alkaline conditions [57].

#### 1.1.4 Disparity in Tribological Improvements

For any given pair of interfaces, there are many possible frictional mechanisms at work including phononic, electronic, and viscoelastic dissipation [58]. The recent development of experimental tools, like the surface force apparatus (SFA) [59] and scanning probe microscopy (SPM) has allowed a molecular level study on the friction and wear [60]. Researchers have used model systems such as mica, graphite, atomically smooth flat metals, and self-assembled monolayers to reveal the details of these underlying phenomena. It is well understood that frictional behavior and appropriate models to describe this behavior are intimately linked to length scales, with measurements taken on the nanoscale often not translating into reliable information on the micro scale and even still different than macro scale measurements. Research shows that values measured for microscopic friction are much lower than the values obtained at the macro scale. As explained by Bhushan, contact stresses at low loadings do not exceed the sample hardness, which minimizes plastic deformation. And when measured for small contact areas and very low loads used in microscopic studies, indentation hardness

and modulus of elasticity, are higher than the macro scale. Lack of plastic degradation and improved mechanical properties reduce the degree of wear. In addition, the small apparent areas of contact reduce the number of particles trapped at the interface, thus minimizing the ‘ploughing’ contribution to frictional force [61].

In addition, there are several challenges in associating the frictional properties observed with AFM to tribological behaviors of MEMS. The sliding velocity of the contact in AFM is typically 24 orders of magnitude slower than that of real contacts in MEMS. Because of the sharpness of the AFM contact, the contact pressure is typically on the order of a few gigapascals, which is several orders of magnitude higher than the contact pressures expected in real systems. The frictional response at the nanoscale contains an adhesive component. The adhesive friction components decrease as the size of contact increases from the nanoscale to the micro scale, and eventually become negligible in the macro scale. Finally, relating the behavior of one single asperity to larger contact phenomena requires understanding how to model multiple contacts that are continually being broken, reformed, and sheared at different contact pressures at which elastic and plastic deformation may constantly occur. The integration of single asperity behaviors to capture the behavior of a real rough interface has not yet been achieved. Most MEMS applications lie in micro structural level resulting in the development of in-situ direct measurement platforms using micro machined structures which measure stiction [62] and friction and wear [63,64] at the micro scale.

Investigations of SAM coated smooth surfaces, despite the measurement scale, have shown that the frictional properties are influenced by molecular tilting, inter atomic interactions, interface stability, adhesion to substrate, and gauche defect formation [65]. Dissipation of frictional energy in SAMs through the formation of gauche defects has been thoroughly investigated by Salmeron and coworkers, concluding that increased disorder correlates with higher gauche defects and an easier dissipation of frictional energy [66]. The tribological behaviors of several self-assembled monolayers have been reported [25, 33, 67–69], and one

characteristic of these films is that friction has been shown to be closely associated with film structure [70–73].

SAMs considerably reduce friction and adhesion proving useful in various MEMS devices [64]. Unfortunately, as these films have been applied to the surfaces of MEMS devices, the tribological improvement afforded by these films is consistently less than reported on smooth surfaces regardless of the measurement technique and length scale examined. In addition, a variation in the improvement afforded exists across the same length scale. Because most MEMS devices consist of a multitude of topographical features dependent on the fabrication process, it is suggested by this author that the variation in friction measurements appears to not only be linked to the measurement range, but dependent on a combination of the topography of the surface and interfacial coating quality. This is a fundamental issue and requires a more in depth analysis of OTS film formation on MEMS devices.

#### **1.1.5 Self-Assembled Octadecylphosphonic Acid Monolayers as a Candidate for Overcoming Interfacial Interactions**

Phosphonate monolayers are a new class of SAMs that show significant potential to define new directions in MEMS technology. Phosphonate SAMs provide a model system for exploring the relationship between friction and molecular structure, as well as for determining how attaching SAMs to a variety of substrates influences friction. Moreover, phosphonate SAMs are technologically important because they can be deposited on mica and many different metal oxide surfaces, unlike the more commonly studied alkane thiol SAMs [74–76]. These materials have also been deposited on conventional silicon surfaces although some controversy exists as to whether or not these material maintain the same stability as there self assembled counterparts on metal oxide surfaces [77]. These material have the potential to overcome the limitations of silane-based SAMs with respect to immersion and thermal stability [78].

The necessity for an ultra thin, lubricant film to minimize adhesion, friction, and wear between surfaces in contact for MEMS/NEMS is clear. The tribological mechanisms for surfaces coated with phosphonate SAMs have not yet been studied extensively, although these monolayers have recently begun to attract the attention of tribology research groups [25,79]. Friction force measurements with the phosphonate monolayer coated smooth alumina demonstrated a remarkable improvement in performance when compared to untreated alumina surfaces the coated surfaces exhibited remarkable robustness and resistance to wear over each experiment. In addition to offering a physical protective barrier, the monolayers, by virtue of their inert hydrophobic nature, also provide a degree of chemical protection. The hydrophobic coatings have been shown to repel humidity and protect alumina substrates from embrittlement caused by water, and the nature of the phosphonate alumina bond also appears to prevent chemical attack of the alumina by any water that does penetrate the monolayer [80].

A study of alkylphosphonic acids on flat Al sheets showed that SAM formation of alkyl phosphonates on Al surfaces relies on the hydroxylation of the oxide (alumina) layer. Generally, chemisorption of alkylphosphonic acid occurs by proton dissociation to form an alkylphosphonate species. The phosphonic acids undergo a condensation reaction with surface bound aluminohydroxyl ( $-Al-OH$ ) species to form aluminophosphonate compounds with  $H_2O$  as a byproduct [81]. An inelastic electron tunneling spectroscopy study of the adsorption and structure of alkyl phosphonic and alkyl phosphoric acids suggested that tridentate species were formed with the aluminum oxide surface [82]. It has been shown that ODP adsorbs preferentially to Aluminum surfaces that are hydroxylated in air and that an increase in the surface hydroxyl density can accelerate adsorption kinetics [83]. Such an acceleration can be explained by the adsorption of the phosphonic acid via surface hydrogen bonds prior to the condensation reaction, leading to the finally adsorbed phosphonate [84]. Due to the nature of the surface reaction between alkylphosphonic acids and OH surface species this self

assembled monolayer offers a unique opportunity for tribological improvement and should be compared with the existing knowledge of OTS monolayers.

## Chapter 2

### Investigative Summary for Part I

Part I (Chapters 4-8), investigates the interfacial structure of self-assembled coatings as influenced by surface topography and surface reactivity to unravel some of the discrepancies associated with tribological performance. Initial work focuses on OTS monolayers, identified as one of the most promising candidates for the tribological improvements, restricted in use due to inconsistent results when translated to MEMS surfaces. Literature reveals many factors relevant for the production of consistent monolayers. This work attempts to expand on that knowledge by including a “missing link”- Is it possible for monolayers to maintain their molecular order and conformational strength on topographical asperities?

To create surfaces of comparable topography, as encountered on MEMS devices, a Molecular Vapor Deposited (MVD) silica layer is introduced. This surface is a novel platform, with a tunable topography amenable to advanced surface analysis, often restricted to use on smooth surfaces. The reactivity of the MVD silica surface toward OTS film formation is compared to traditional silicon oxide surfaces with an examination of film formation kinetics and interfacial water structure. The MVD silica layer allows for the visual examination of the self assembly process on individual topographical asperities, in conjunction with, a spectroscopic examination of the reactive surface and the final conformational order of the films. Interfacial water structure is identified as a key element in preparing ideal OTS monolayers and a correlation between water structure and surface topography is identified and explored.

In addition, this silica layer is not a line of sight deposition and has been translated onto surfaces of varying geometrical complexity, enabling the production of a high surface area material. This material is utilized for studies of monolayer loading and the influence of curing mechanisms on the stability of OTS films.

This work is followed in Chapter 9, by an examination of the self assembly of octadecylphosphonic acids on aluminum oxide surfaces. This work is aimed at producing high quality films on surfaces with varying degrees of curvature (spherical balls) and on surfaces that exhibit interfacial surface roughness. The expanded goal is comparing tribological characteristics across nanoscale and micro scale regimes. For consistency these surfaces are produced under identical conditions and at the same time. An investigation of the deposition mechanism of ODP films is performed on an aluminum oxide surface and compared with a spherical aluminum oxide powder. After determining the appropriate deposition characteristics, these films are translated onto QCM crystals, and SPM probes / AFM cantilevers, with spherical aluminum oxide balls of 100  $\mu\text{m}$  diameter attached for tribological analysis by an outside collaborating team.

## Chapter 3

### Methodology

#### 3.1 Analytical Tools and Techniques

In the study of monolayers and thin films on surfaces, both their surface and bulk properties are important. In this chapter, several analytical methods are introduced for characterization of the monolayers and thin films produced throughout this document. Contact angles with water as liquid are measured to evaluate wetting properties and to get information on surface order. Ellipsometry is used to measure the thickness and uniformity of freshly prepared films. FTIR spectroscopy is used to learn about molecular orientation, packing behavior and coverage. TGA analysis is used to obtain material loading information in conjunction with surface imaging techniques (SEM and AFM) to learn about the surface topography and particle size distributions.

##### 3.1.1 Contact Angle

To study the hydrophobicity and the uniformity of the modified substrates, the static contact angle of a water drop lying on the substrate (sessile drop) was measured. The quality of a stable monolayer and thin film can be estimated from wetting measurements. The contact angle is not a property of the liquid or the substrate but the interaction between them. 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 or wetting the solid and the liquid, the contact angle will be  $180^\circ$ . As the interaction between the solid and liquid increases, the liquid spreads until  $\theta = 0^\circ$ . Water contact angle measurements are obtained by the sessile drop method on a Ramé-Hart

model 200 automated goniometer (Ramé-Hart, Inc. Mountain Lakes, NJ) using DROPimage Standard software. Measurement error for this technique is  $\pm 2.0^\circ$ .

### 3.1.2 Ellipsometry

An ellipsometer measures the changes in the polarization state of light when it is reflected from a sample. If a thin film on a surface changes in thickness, then its reflective properties will also change. Measuring these changes in the reflective properties can allow for a determination of the actual change in film thickness. The most important application of ellipsometry is to study thin films. In the context of ellipsometry a thin film is one that ranges from essentially zero thickness to several thousand angstroms. The sensitivity of an ellipsometer is such that a change in film thickness of a few angstroms is usually easy to detect. For a clean surface,  $\Delta$  and  $\Psi$  are the output of an ellipsometry measurement and can be interpreted into layer thickness provided the right model for the surface is utilized. These two parameters are directly related to the complex index of refraction ( $\hat{n}$ ) of the surface. In order to interpret the ellipsometry data into layer thickness it is necessary to know or assume values for the refractive index for each separate layer on the surface.

$$\hat{n} = n(1 - ik) \quad (3.1)$$

The complex refraction index is a representation of the optical constants of a material, it is represented by Equation 3.1 where  $n$  is the ordinary refraction index and  $k$  is the extinction coefficient. The real part or index of refraction,  $n$ , defines the phase velocity of light in material:

$$\nu = c/n \quad (3.2)$$

where  $\nu$  is the speed of light in the material and  $c$  is the speed of light in vacuum. The imaginary part or extinction coefficient,  $k$ , determines how fast the amplitude of the wave decreases. The extinction coefficient is directly related to the absorption of a material and

is related to the absorption coefficient by

$$\alpha = 4\pi k/\lambda \quad (3.3)$$

where  $\alpha$  is the absorption coefficient and  $\lambda$  is the wavelength of light. Once a film having a different index of refraction  $n_f$  is coated on the surface,  $\Delta$  and  $\Psi$  are related to the complex indices of both the film and the substrate, and to the film thickness. Typically, the compensator is set at an angle of  $70^\circ$  and the experimental data are expressed as

$$\delta\Delta = \Delta_0 - \Delta \quad (3.4)$$

$$\Delta\Psi = \Psi_0 - \Psi \quad (3.5)$$

Where  $\Delta_0$  and  $\Psi_0$  are the ellipsometric angles characteristic of the clean substrate surface, and  $\Delta$  and  $\Psi$  are those measured for the substrate with the film. From  $n$  and  $k$ , we can calculate the thickness of the film.

In the experiments that follow, ellipsometric measurements are conducted on a nulling type ellipsometer (Rudolph AutoEL III, Rudolph Research, Fairfield NJ) equipped with a He-Ne laser ( $\lambda = 632.8$  nm) at a  $70^\circ$  angle of incidence relative to the surface normal. Herein, reported values for film thicknesses are the averages from four different positions measured on each sample.

For films near the cycle thickness for the particular substrate-film combination under investigation (extremely thin films fall into this category), simultaneous determination of both the film thickness and refractive index is difficult, given that the measured parameters, the angles  $\Delta$  and  $\Psi$ , are very insensitive to changes in refractive index in these regimes. For this reason, an accepted value for the refractive index of silicon oxide,  $n = 1.46$ , is used in this investigation for measurements of silicon dioxide produced from oxygen plasma and MVD silica layer treatment. The refractive index of the silicon surface is set at  $n = 3.858 + 0.018i$ .

For ellipsometric measurement of the organic films on silicon oxide, a single film model has been proposed [85] and is used in this work. Briefly, the thickness of the initial oxide layer is measured using a refractive index of  $n = 1.46$ . After the organic film is deposited, the sample is remeasured using the same refractive index and the total thickness of the organic layer is the difference between these two measurements.

For ellipsometric measurement of the organic films on aluminum oxide, a double film model is used. A single model is used to determine the initial thickness of the aluminum oxide layer with set values of  $k_s = 6.384$  and  $n_s = 1.428$  and  $n_l = 1.615$ . After determination of the initial oxide layer thickness  $t_l$  the values are used to determine the thickness of the organic film on top of the aluminum oxide layer. The sample is re-measured using a refractive index of 1.45 and the total thickness of the organic layer is reported.

### **3.1.3 Atomic Force Microscopy**

Atomic force microscope (AFM) images are collected in air (21 °C, ~45% relative humidity) on a commercial AFM (Pacific Nanotechnology Nano-R AFM, Pacific Nanotechnology, Santa Clara, CA) in non-contact mode using silicon AFM tips with resonant frequencies in the range of 150-210 kHz and force constants in the range of 4.5-14 N/m (MikroMasch, Wilsonville, OR). Images are collected at a scan rate of 0.8 to 1 Hz. Optimal tip geometry is represented by a pyramid shape with an ideal tip radius of 10 nm.

### **3.1.4 Fourier transform infrared (FTIR) spectroscopy**

#### **Specular reflectance FTIR spectroscopy**

Infrared reflection absorption spectroscopy (IR-RAS), also known by the synonym RAIRS and specular reflectance FTIR has been used for nearly 40 years to study thin films deposited or adsorbed on metal surfaces. The high reflectivity of the metal surface, combined with a grazing angle of incidence, give a relatively long path length in the thin film with the result that nanometer-thick films can readily be studied. For s-polarized light, the reflected beam is

out-of-phase with the incident beam, giving a node in the electric field at the surface. For p-polarized light the two fields are in phase, resulting in a strong preference for vibrations with transition dipoles normal to the surface: the so-called surface selection rule. Since s-polarized light carries no interfacial information, s-polarized light is commonly used as a background scan. As a result, a ration of the s-polarized light scan with the p-polarization scan, is often used used to eliminate artifacts arising from bulk-phase absorptions. This technique is very useful giving information about the direction of the transition dipoles of an adsorbed organic thin film. Theoretical consideration of the IR spectroscopy of the monolayers adsorbed on a metal surface showed that the reflection-adsorption spectrum is measured most efficiently at high angles of incidence, typically at  $80\text{--}85^\circ$ , and that only the component of incident light, which is parallel to the plane of incidence, gives measurable absorption [86]. Figure 3.1 presents a schematic description of a mono molecular film on a mirror, with an incident light and direction of the polarization. In order to study orientation, polarized light is directed on the film. The polarized light electrical vector coinciding with the dipole of the infrared active moiety increases in absorption intensity, thereby revealing the band assignment and the orientation of the molecular group.

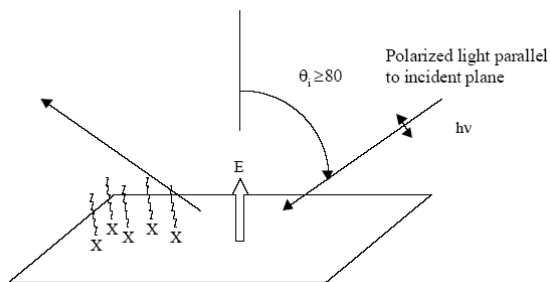


Figure 3.1: Illustration of the polarized light electrical vector as influence by p-polarization at an angle of incidence greater than  $80^\circ$ .

In the results that follow, phosphonate monolayers, were characterized using FTIR spectroscopy (PerkinElmer Spectrum 2000 spectrometer) equipped with a liquid nitrogen cooled in MCT detector. The samples were analyzed using a specular reflectance accessory with an angle of incidence of  $83^\circ$ . The intensity of the methylene vibrations in the spectra

is a direct function of the tilt angle of the alkyl chain. This unique property of the grazing-incident experiment allows the calculation of the molecular orientation from FTIR spectra. For example, as illustrated in Figure 3.2, the molecule on the right illustrates an optimal rectangular adsorbed molecule of an alkyl phosphonic acid molecule on a metal surface with both the symmetric and asymmetric methylene ( $\text{CH}_2$ ) vibrations ( $\nu_s$  and  $\nu_a$ ), parallel to the metal plane. Therefore, the methylene groups in a perpendicular, all-trans optimal configurations would not have any transition dipole moments in the direction normal to the investigated surface which is necessary for signal. As a consequence the alkyl chain will not be picked up by the p-polarized light. Once the alkyl chain tilts from the normal to the plane as shown Figure 3.2 on the left, the symmetric and asymmetric vibrations of the methylene groups are no longer are parallel to the surface and thus will appear in the grazing incident spectra. A measure of the degree of order for films investigated with specular reflectance spectroscopy can be obtained by the ratio of the intensity of the symmetric and asymmetric methylene groups.

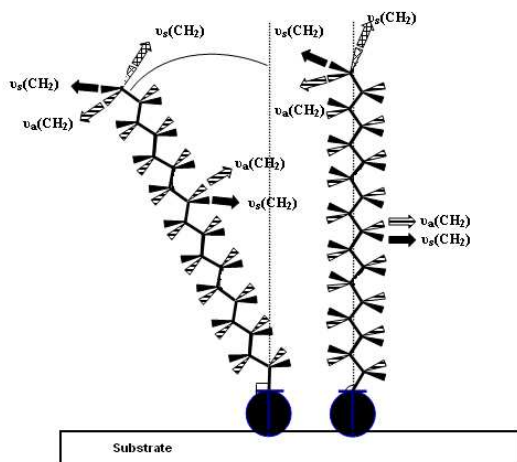


Figure 3.2: Influence of molecular tilt on the orientation of methylene stretches for phosphonate molecules on metal surfaces. Methylene stretches from an all trans (perpendicular orientation) are not identified with specular reflectance spectroscopy (p-polarized IR) due to an electric field oriented normal to the substrate at an angle of incident of  $> 80^\circ$ .

## Attenuated Total Reflection Spectroscopy

Attenuated total reflectance (ATR), is a infrared spectroscopy technique, which enables samples to be examined directly in the solid or liquid state without further preparation. ATR uses a property of total internal reflection called the evanescent wave. A beam of infrared light is passed through the ATR crystal in such a way that it reflects at least once off the internal surface in contact with the sample. This reflection forms the evanescent wave which extends into the sample, typically by a few micrometers. The beam is then collected by a detector as it exits the crystal. In order to utilize the evanescent effect crystals are utilized that are made from an optical material with a higher refractive index than the sample being studied. In the case of a liquid sample, pouring a shallow amount over the surface of the crystal is sufficient. In the case of a solid sample, it is pressed into direct contact with the crystal to ensure a more intimate contact avoiding any trapped air as that would distort the results.

To obtain internal reflectance, the angle of incidence must exceed the so-called critical angle. This angle is a function of the real parts of the refractive indices of both the sample and the ATR crystal:

$$\Theta_c = \sin^{-1}(n_2/n_1) \quad (3.6)$$

Where  $n_2$  is the refractive index of the sample and  $n_1$  is the refractive index of the crystal. The evanescent wave decays into the sample exponentially with distance from the surface of the crystal over a distance on the order of microns. The depth of penetration of the evanescent wave  $d_p$  is defined as the distance from the crystal-sample interface where the intensity of the evanescent decays to  $1/e$  (37%) of its original value. It can be given by:

$$d_p = \lambda/2\pi n_1 [\sin^2\theta - (n_2/n_1)^2]^{-\frac{1}{2}} \quad (3.7)$$

Where  $\lambda$  is the wavelength of the IR radiation. For instance, if the ZnSe crystal ( $n_1=2.4$ ) is used, the penetration depth for a sample with the refractive index of 1.5 at  $1000\text{ cm}^{-1}$  is estimated to be  $2.0\text{ }\mu\text{m}$  when the angle of incidence is  $45^\circ$ . If the Ge crystal ( $n_1=4.0$ ) is used under the same condition, the penetration depth is about  $0.664\text{ }\mu\text{m}$ . The depth of penetration and the total number of reflections along the crystal can be controlled either by varying the angle of incidence or by selection of crystals. Different crystals have different refractive index of the crystal material.

In the results that follow, OTS monolayers and interfacial water layers, were characterized using FTIR spectroscopy (PerkinElmer Spectrum 2000 spectrometer) equipped with a liquid nitrogen cooled in MCT detector. The samples were analyzed using horizontal attenuated total reflection (HATR) accessory, which consists of a steel plate with an attenuated total reflection (ATR) element sealed to it that rests on top of an optical alignment box. The optical alignment box contains two planar mirrors and focal mirrors which can be adjusted to focus the infrared beam on the incident face of the ATR crystal. All spectra are recorded at room temperature at  $4.0\text{ cm}^{-1}$  resolution with 500 co-added scans.

Throughout this document both trapezoidal silica ATR elements and ZnSe ATR elements are used ( $50 \times 20 \times 2\text{ mm}^3$ ,  $45^\circ$  face angle) enabling acquisition of spectral data from  $4000$  to  $1500\text{ cm}^{-1}$  for the silicon and  $4000$  to  $550\text{ cm}^{-1}$  for the ZnSe. The refractive index of silicon is nearly constant over the spectral range under study, and a value of 3.42 is used herein. The refractive index is about 2.67 at  $550\text{ nm}$ , and about 2.40 at  $10.6\text{ }\mu\text{m}$ . For water, the refractive index at  $1635\text{ cm}^{-1}$  is taken as 1.32 [87]. Consequently, the critical angles for total internal reflection for the systems under study are as follows: for silicon/water,  $22.7^\circ$ . Since the HATR accessory operates at a fixed angle of incidence of  $45^\circ$ , and the calculated critical angles are far less than  $45^\circ$ , dispersion effects can be neglected [86].

### 3.1.5 TGA Analysis

This system consists of an isolated thermo balance, an IR furnace, quartz sample chamber, purge inlets and outlets, and a capillary connection to a mass spectrometer. Sample weight loss is measured as a function of temperature under various environments. The thermo balance is maintained at 40 °C in a well insulated, gas purged chamber isolated from the furnace by a water cooled plate. Evolved gas products are analyzed by a quadrupole mass spectrometer (Pfeiffer ThermoStar) via a heated transfer line. The technical specifications for this unit can be found in more detail on the manufacturers' website, but include a weighing accuracy of  $\pm 0.1\%$  and a weighing precision of  $\pm 0.01\%$ . The furnace consists of four symmetrically placed IR lamps with a quartz lined sample compartment that is a chemically inert and resistant to adsorption of off-gas products.

## 3.2 Experimental Techniques

### 3.2.1 Sample Preparation and Cleaning

#### Plasma Cleaning

Silicon samples are prepared by dicing the silicon wafers into 8mm  $\times$  8mm squares. Both silicon samples and silicon ATR crystals are cleaned using the same procedure as described below. The silicon samples are sonicated in acetone for ten minutes and then again in isopropanol for ten minutes and then dried under a stream of nitrogen. Samples are etched for ten minutes in concentrated HF to remove the native oxide layer, rinsed in copious amounts of deionized water, and then dried under a stream of nitrogen. Samples are then loaded into a custom-built vacuum deposition system, the design of which is based on a previously described system [88], for oxygen plasma treatment. Briefly, the vacuum deposition system consists of a rotary vane pump (base pressure 0.4 Pa) which is coupled to a glass reaction chamber that contains perforated electrodes which can be biased to create an *in situ*, capacitively-coupled radio frequency (RF) plasma (13.56 MHz). The glass reaction

chamber is also coupled to a vapor delivery system which allows for the introduction of the vapors of various volatile precursors into the glass reaction chamber. MKS Baratron capacitance manometers are used to monitor the system pressure up to  $1.3 \times 10^4$  Pa. A simplified schematic and photograph of the vacuum deposition system can be seen in Figure 3.3.

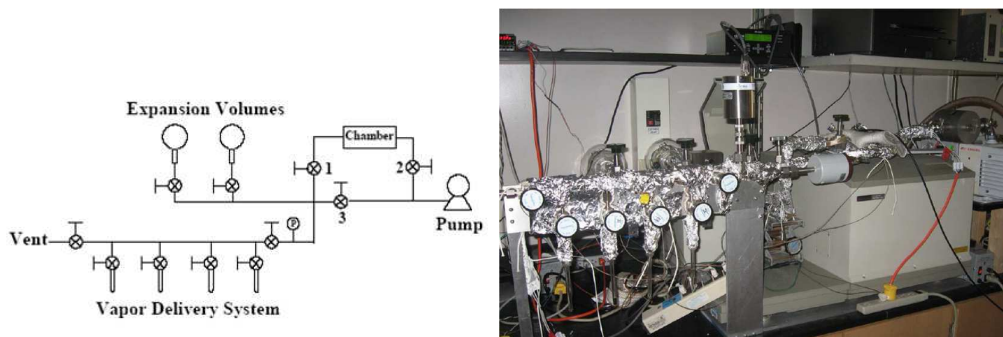


Figure 3.3: Schematic (left) and photograph (right) of the custom vacuum deposition system and FTIR employed in this work.

After introducing the samples into the vacuum system, the system is evacuated to a pressure of less than 2.6 Pa. Oxygen gas is then allowed to flow through the system, and an oxygen background is established by multiple pump-purge cycles with oxygen gas. Then, the oxygen pressure is allowed to stabilize around 33.3 Pa, at which point the chamber is isolated from the pump. An RF plasma is struck at 25 W forward power, and the samples are exposed to the plasma for five minutes. This treatment grows an oxide layer about 2.0 nm thick on the silicon surface. The samples are removed from the vacuum deposition system and etched again for ten minutes in concentrated HF, rinsed in copious amounts of deionized water, and dried under a stream of nitrogen. An additional oxygen plasma treatment is employed to re-grow an oxide layer. This iterative cleaning method is repeated until inspection by contact angle and AFM indicate that a clean (contact angle  $< 5^\circ$ ), flat (RMS roughness  $\sim 0.2$  nm) surface has been obtained, but usually two iterations suffice.

## UV Ozone Cleaning

### Etched Silicon Samples

Silicon samples and silicon ATR crystals are cleaned using the same procedure as described below. The silicon samples are sonicated in acetone for ten minutes and then again in isopropanol for ten minutes and then dried under a stream of nitrogen. Samples are etched for ten minutes in concentrated HF to remove the native oxide layer, rinsed in copious amounts of deionized water, and then dried under a stream of nitrogen. The samples are then placed into a UV Ozone cleaning chamber and treated with UV ozone in air. Samples are placed approximately 1.0 cm below the UV ozone bulbs. The treatment duration is 10 minutes with a measured oxide thickness of about 2.0 nm thick on the silicon surface. Inspection by contact angle indicate that a clean reactive oxide surface with a contact angle  $< 5^\circ$ .

### Native Silicon Samples

Treated with the same procedure as described above except etching step is neglected and the treatment duration is extended to 30 minutes. The measured oxide thickness about 2.0 nm thick on the silicon surface. Inspection by contact angle indicate clean reactive oxide surface with a contact angle of  $< 5^\circ$ .

## Piranha Cleaning

Silicon samples and silicon ATR crystals are cleaned using the same procedure as described below. The silicon samples are sonicated in acetone for ten minutes and then again in isopropanol for ten minutes and then dried under a stream of nitrogen. Samples are etched for ten minutes in concentrated HF to remove the native oxide layer, rinsed in copious amounts of deionized water, and then dried under a stream of nitrogen. Samples are exposed to a Piranha solution consisting of (3:1 v/v)  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  for a 30 minute duration. The measured oxide thickness was  $\sim 1.0$  nm thick on the silicon surface. Inspection by contact angle indicate that a clean reactive oxide surface with a contact angle  $< 5^\circ$ .

## **MVD Silica Layer Deposition**

Deionized water and tetrachlorosilane are loaded into clean glass vials, and then connected to the vapor delivery system. The precursors are degassed by employing multiple freeze-pump-thaw cycles with liquid nitrogen. For vapor coating, freshly cleaned silicon samples are loaded into the vacuum deposition system. The system is evacuated until the pressure is less than 2.6 Pa, and then the samples are treated with an oxygen plasma by the method described in Section 3.2.1 for substrate surface conditioning. After the plasma pre-treatment, the chamber is again evacuated to a pressure less than 2.6 Pa, and then water vapor and tetrachlorosilane vapor is admitted into the chamber and allowed to react while being isolated from the pump. Detailed precursor dosing requirements associated with the various silica layer thicknesses have been previously reported and will not be discussed further. Using the taxonomy of Anderson, [55] the silica layers produced in this work range from type I to type IV surfaces when referring to the reference article previously indicated.

## **OTS Deposition**

Prior to coating, freshly cleaned silicon samples and silicon ATR crystals are treated with an oxygen plasma by the method described in Section 3.2.1. Samples coated with MVD silica layer are used immediately after their preparation. The samples are coated with octadecyltrichlorosilane by the method described below. Clean silicon samples and MVD silica layer samples are coated simultaneously from a single coating solution. It is also important to note that all glassware used were cleaned via the same method as the silicon wafers and is pre-coated with the appropriate precursor to eliminate competitive adsorption with the walls of the glassware. OTS growth is carried out under atmospheric conditions with about  $\sim 45\%$  relative humidity. Freshly cleaned silicon samples and freshly prepared silica layer samples are placed into a 50 ml beaker of Optima grade hexanes either chilled to 10 °C or at room temperature and allowed to equilibrate for 2 minutes prior to OTS deposition. Solutions of OTS (0.5 mM) are prepared in 50 ml of Optima grade hexanes in a

secondary beaker. To grow liquid condensed islands, the OTS adsorption reaction is allowed to proceed for the specified times at 10 °C, significantly lower than the critical temperature for the LC phase in this system. Then the samples are removed, rinsed in two stages of neat hexanes that are also chilled to 10 °C. The samples are then dried under a stream of nitrogen. The samples are allowed to set for 1 hour at room temperature prior to analysis. A similar procedure is utilized for deposition of the room temperature (mixed regime) samples at a deposition temperature of 22 °C.

## **Cleaning of Aluminum and Aluminum Oxide Samples**

### **Cleaning of Aluminum Samples**

E-Beam Sputtered aluminum samples with 4500 Å of aluminum metal on 1000 Å of thermally grown silicon oxide are diced into 8mm × 8mm squares and 2.54cm × 5.08cm rectangles. Prior to use the aluminum samples are sonicated in acetone for ten minutes and then again in isopropanol for ten minutes and then dried under a stream of nitrogen. Prior to coating, freshly cleaned sputtered aluminum samples are treated with an oxygen plasma by the method described in Section 3.2.1 for 2.0 minutes to activate the surface. Inspection by contact angle and AFM indicate that a hydrophilic clean surface with contact angle < 5° and surface roughness of ~4.3 nm RMS. The measured aluminum oxide thickness was ~2.5 nm.

### **Cleaning of Aluminum Spheres**

Aluminum oxide spheres were obtained from Denka Corp. (China) and sieved to collect particles ranging in size from 75 to 100 μm. The BET surface area for the spheres gives a surface area of 0.2 m<sup>2</sup>/g. The sieved aluminum oxide spheres are sonicated in acetone for 10 minutes and filter dried and then sonicated again in isopropanol for 10 minutes and filter dried. The spheres are then placed into an oven at 120 °C for 1 hour for final drying. Prior to coating, the spheres are treated with an oxygen plasma by the method described in Section

3.2.1 for 2.0 minutes to activate the surface and to remove hydrocarbon contamination. The uncoated samples are placed into an oven set at 60 °C for 10 minutes prior to analysis.

### **Phosphonate Deposition**

A 5.0 mM phosphonate solution is prepared by sonicating 200 mg of Octadecylphosphonic Acid (97% Strem Chemical [4724-47] in 100 ml of 2-Propanol. After activation of the aluminum surface with plasma treatment, as described above, the samples are submerged into the 5.0 mM solution for different time durations. These samples are removed from solution and rinsed 3 times in neat 2-Propanol and dried under a stream of nitrogen. For a 4 hour deposition representative of full monolayer coverage on the surface of sputtered aluminum the thickness was measured at 25.1 Å, with a measured contact angle 110° and a RMS roughness of ~3.7 nm.

Aluminum oxide spheres are coated following a similar procedure, but under continual stirring, and subsequent rinse with 2-Propanol performed using vacuum filtration and vacuum collection. These samples are subsequently dried in an oven set at 60 °C for 10 minutes for solvent removal prior to analysis.

## Chapter 4

### Formation of Octadecyltrichlorosilane Monolayers on a Molecular Vapor Deposited (MVD) Silica Layer

#### 4.1 Introduction to the MVD silica layer

Previous studies have shown that the vapor phase hydrolysis of tetrachlorosilane results in the deposition of a thin, uniform silica film with chemical properties similar to those of conventionally prepared silica materials. This MVD silica layer is a highly hydroxylated surface, but unlike conventional silica surfaces, it possesses no observable free surface silanol groups, a fact believed to be due to the unusually high concentration of hydroxyl groups present. Despite the lack of free silanol groups, the silica layer has been shown to support the attachment of organosilicon compounds [55]. A novel property of the MVD silica surface is the ability to create a reactive surface with a variable degree of surface roughness as well as different topographical asperities (*i.e.* peak sizes, peak shapes). This tunable surface is used to investigate the influence of surface topography on the interfacial characteristics of subsequently deposited layers as illustrated in the following sections.

This silica layer can be deposited at low temperatures to a wide variety of substrates, including glasses, metals, fibers, polymers, and plastics and can overcome the limitations associated with traditional methods for depositing silicon oxide layers that requires temperatures in excess of 300 °C [89]. Prior work by Anderson *et al.* has demonstrated that the vapor deposited thin silica film can be utilized as a novel substrate for in situ surface studies on silica using infrared spectroscopy. Infrared spectra of silica films prepared by this method compare favorably with spectra collected by the conventional thin film technique. Furthermore, the uniformity of the thin vapor deposited silica film on the supporting infrared window reduces the likelihood of portions of the film falling off during an experiment, an

improvement over the traditional thin film method. This method is the only experimental technique put forth so far that can be used to study the vapor deposited silica films as they exist on surfaces, and it can also be used to investigate reactions on the newly formed, pristine silica layers. In fact, this material has been deposited on the surface of FTIR crystals allowing for an investigation of the interfacial properties associated with the self assembly of OTS monolayers, as evidenced, in the following sections. In addition, this silica layer is not a line of sight deposition and has been deposited onto surfaces of varying geometrical complexity, enabling the production of an advanced high surface area material utilized for advanced analysis with TGA commonly limited to high surface area particles.

## **4.2 Utilization of MVD silica layer as a Novel Platform to Study OTS Monolayers**

The role of free surface hydroxyl groups, hydration requirements, and the nature of the surface attachment of OTS molecules on silicon oxide surfaces remains controversial despite extensive investigation. Given the MVD silica layers reactivity toward organosilane deposition, in spite of, the lack of free surface silanol groups, in conjunction with the ability to examine the self assembly process and interfacial reactivity with FTIR, we were motivated to study the growth characteristics of OTS monolayers as compared to those observed on traditional silica surfaces.

In this chapter, we report the results of a comparative study of the adsorption of OTS films on oxidized Si(100) surfaces representative of a traditional silica surface and a MVD silica layer. These surfaces are analyzed to determine the amount of physisorbed water present under adsorption conditions in order to ascertain the influence of the water structural layer on the OTS monolayer adsorption mechanism and overall film quality. This investigation includes the effects of reaction temperature and immersion times on the organization of an OTS monolayer, and includes investigation of both the submonolayer and full monolayer

growth regimes. The film properties and formation kinetics are examined using infrared properties, ellipsometry, AFM, and contact angle measurements.

## **Experimental Details**

### **Materials**

Silicon wafers, p-type, with (100) orientation were obtained from University Wafer (Boston, MA). Octadecyltrichlorosilane and tetrachlorosilane were obtained from Gelest, Inc. (Morrisville, PA) and used as received. Concentrated hydrofluoric acid (HF, 49%), acetone, isopropanol, and Optima grade hexanes (0.01% water) were obtained from Fisher Scientific (Fair Lawn, NJ). Deionized water (18 M $\Omega$ -cm) was obtained from a Millipore filtration system.

### **Methods**

Cleaning methods, MVD silica layer formation, and OTS monolayer formation techniques for the various samples have been previously described in Chapter 3.

#### **4.2.1 Investigation of Water Layers on the MVD Silica Surface.**

Initial efforts focused on investigating the interfacial region of the surface of silicon substrates under adsorption conditions. The amount and structure of adsorbed water layers associated with the MVD silica layer is compared to those found on traditional silicon oxide surfaces. Asay and Kim have reported on the data analysis methods for studying the evolution of the adsorbed water layer thickness on silicon through ATR-FTIR spectroscopy [90], and the same technique is employed in the present study. Briefly, the thickness of the adsorbed water layer is determined by comparing the intensity of the water O-H bending mode absorption located at 1635 cm<sup>-1</sup> to the intensity of the same peak for a bulk liquid water sample on the same surface under study, which is limited by the depth of penetration of the evanescent wave. The thickness determined in this manner can be converted to the

number of monolayers by dividing by the mean van der Waals diameter of water, which is 2.82Å [90–92]. The position of the O-H bending mode located at 1635 cm<sup>-1</sup> has been shown as constant and is not influenced by the degree of hydrogen bonding or structure of water present on the ATR surface [93].

The adsorption of water onto the MVD silica surface and the oxidized silica surface was conducted by varying the relative flow rates of two nitrogen steams- one is dry and the other is saturated with water vapor. This set-up was adapted by works done by Barnette *et al.* [94] and allowed for investigation of water adsorption under varying relative humidities ranging from 0% to 80%. All experiments were run at 27 ±0.5 °C. A clean oxidized silicon ATR crystal was placed into a teflon ATR holder, designed for this work as shown in Figure 4.1, and purged with nitrogen until no difference was noted in the spectra. This spectra was utilized as the background spectra for examining the water adsorption on the oxidized Si(100) surface. An atomic force micrograph for the oxidized Si(100) surface is illustrated in Figure 4.2 with a corresponding ellipsometric oxide thickness of 2.0 nm and RMS roughness value of 0.18 nm.

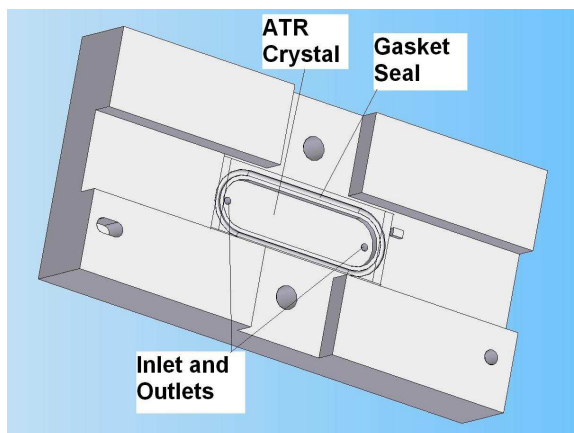


Figure 4.1: Custom built teflon ATR assembly sealed from ambient conditions with inlet and outlet purge assemblies for controlling relative humidity.

An atomic force micrograph for the MVD silica layer is illustrated in Figure 4.2 B with a corresponding average ellipsometric thickness of 18.0 nm and RMS roughness value of 1.3 nm. FTIR analysis of the MVD silica layer after extensive nitrogen purging is represented in the

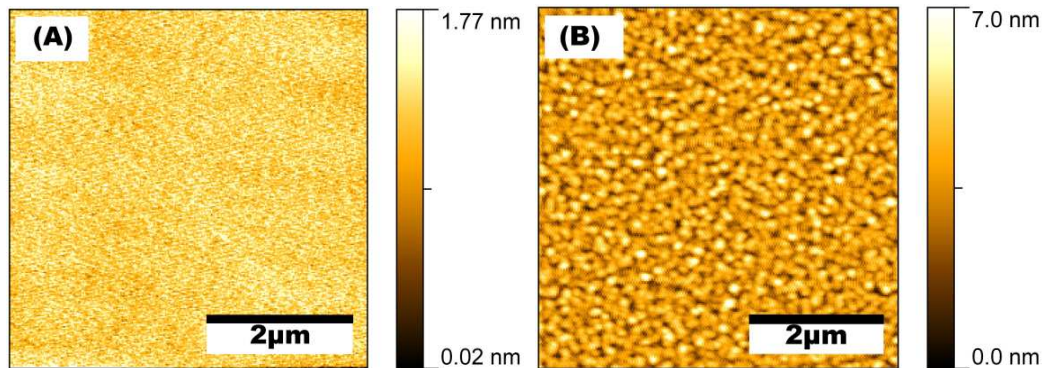


Figure 4.2: Two dimensional AFM scans of (A) a clean oxidized Si(100) surface, RMS roughness is 0.14 nm, and (B) Silica layer deposited on clean silicon surface, RMS roughness is 1.3 nm, thickness is 18.0 nm.

inset view on Figure 4.3. Major peaks present in the spectra include a broad feature centered at  $3400\text{ cm}^{-1}$  indicative of the OH stretching frequencies of associated silanols present in a distribution of geometrical arrangements and chemical environments, while isolated silanols known vibrate at  $3747\text{--}3750\text{ cm}^{-1}$  are absent in the MVD silica films. This MVD silica surface lacks the peak associated with physisorbed water normally located at  $1635\text{ cm}^{-1}$  indicating a MVD silica layer void of physisorbed water. The ATR spectra for the MVD silica film is utilized as the background spectra for experiments involving water absorption on the MVD silica layer. Contact angle measurements indicated a  $\text{CA} = <5.0^\circ$  indicative of a highly hydroxylated surface on both the oxidized Si(100) surface and the MVD silica surface.

After the background spectra were collected for the oxidized silicon ATR and the MVD silica layer coated ATR, the films were exposed to increasing levels of relative humidity, which resulted in the adsorption of physisorbed water as indicated by the broad feature at  $3100$  and the peak at  $1635\text{ cm}^{-1}$ . The pure water spectra collected for calculating maximum adsorption intensity was scaled in magnitude to the 80 % RH spectra to visually compare peak positioning for bulk liquid water applied to each crystal. Water structure is determined by examination of the water O-H stretching region of the spectrum from  $3700$  to  $2800\text{ cm}^{-1}$ . The peak position of the OH vibrational peak is very sensitive to the degree of hydrogen

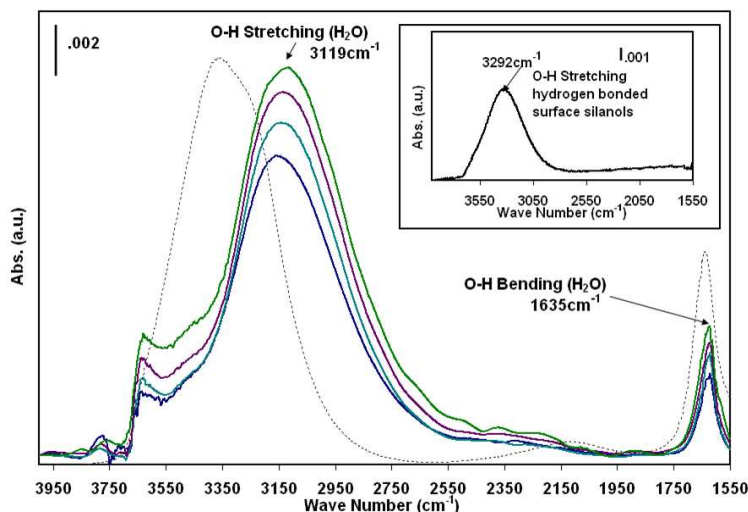


Figure 4.3: ATR-FTIR spectra of adsorbed water on the surface of a MVD silica layer on an oxidized silicon ATR crystal at increasing relative humidities. The peak positions of ice-like  $3119\text{ cm}^{-1}$  and the position of the O-H bending mode is marked at  $1635\text{ cm}^{-1}$ . The direction of increasing relative humidity is from bottom to top. Spectra correspond to relative humidities of 20%, 40%, 60% and 80% with an accuracy of  $\pm 2.0\%$ . [Inset View]-Background spectra for water adsorption study illustrating O-H stretching region associated with hydrogen bonded surface silanols. Note peak absence at  $1635\text{ cm}^{-1}$  indicative of physisorbed water.

bonding and is often used to study the structure of water [95–97]. While liquid water exhibits a broad vibrational peak at  $3400\text{ cm}^{-1}$  condensed water at ambient conditions has been shown to exhibit both liquid-like peak characteristics and ice-like peak characteristics as indicated by two peaks centered near  $3200\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$  corresponding to ice-like and liquid water, respectively [98].

In the case of silicon oxide covered with silanol groups, the structure of adsorbed water at room temperature as a function of relative humidity (RH) was discussed previously [93]. For comparison purposes this data is presented in Figure 4.4. Each line represents a different partial pressure relative to saturation pressure of water ( $P/P_{sat}$ ) or relative humidity at  $27^\circ$ . This study, indicated that the ice-like and liquid water isotherms grow together, and at nearly an equal rate, across all relative humidities studied.

The results of water adsorption onto the surface of a MVD silica-modified silicon ATR crystal are presented in Figure 4.3. In order to determine the thickness of bulk water that

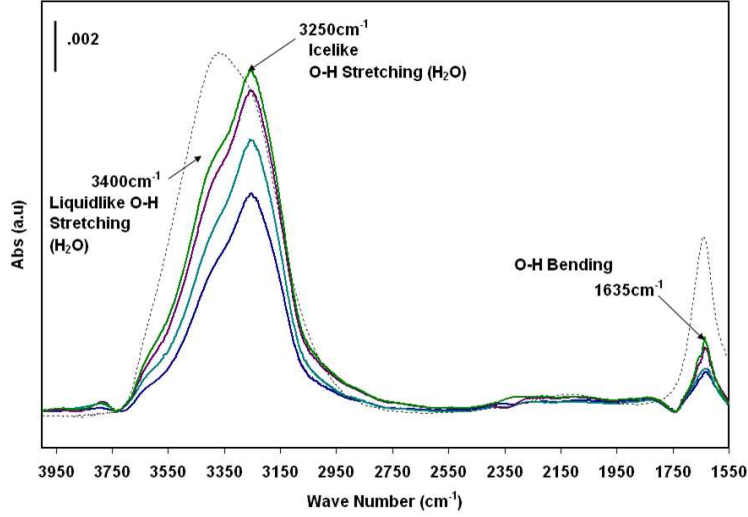


Figure 4.4: ATR-FTIR spectra of adsorbed water on the surface of an oxidized silicon ATR crystal at increasing relative humidities. Ice-like and liquid water are indicated with arrows at  $3250\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$ , respectively, and the position of the O-H bending mode is marked at  $1635\text{ cm}^{-1}$ . The direction of increasing relative humidity is from bottom to top. Spectra correspond to relative humidities of 20%, 40%, 60% and 80% with an accuracy of  $\pm 2.0\%$

the evanescent wave interacts with, the thickness of the silica layer is subtracted from the depth of penetration of the evanescent wave. For example, for the silicon/silica system, the depth of penetration is approximately 505 nm at a  $45^\circ$  angle of incidence. In this experiment, the silica layer is 18.0 nm thick. This means that the adsorption measured for a bulk water sample on a silica film corresponds to 487.0 nm of water (505-18.0 nm). For the MVD silica surface the depth of penetration is determined by considering the silica layer as impervious to liquid water. Prior research performed by Anderson *et al.* has shown this to be a valid means to determine the depth of penetration and more details can be found in that work [93]. At 80% RH, the amount of adsorbed water is equivalent to nearly 20 monolayers, and is approximately 4.5 times greater than on the clean silicon surface, at similar relative humidities. The structure of the adsorbed water on the MVD silica layer is dominated almost entirely by ice-like water. Furthermore, the ice-like water structure has an adsorption peak centered near  $3119\text{ cm}^{-1}$ , which is  $127\text{ cm}^{-1}$  lower than on clean silicon oxide. It was concluded that more adsorbed water was on the surface of the MVD silica,

which was more tightly bound compared to that existing on traditional silica surfaces. This was evidenced by a water absorbance spectrum dominated by an ice-like structure shifted to lower energy. This shift to lower energy indicates that water has a stronger degree of hydrogen bonding with the MVD silica-coated surface relative to the clean silicon oxide [99].

It is postulated that the MVD silica layer maintains a more ordered water structure due to a higher degree of hydrogen bonding caused by the high concentration of hydroxyl groups present. It is also suspected that the high degree of hydrogen bonding induces preferential water orientation in subsequent layers contributing to the stability of the increased water monolayers. Du *et al.* found that interfacial orientation and bonding structure of water are strongly influenced by the electrostatic interaction and hydrogen bonding of molecules with the surface at fused quartz/water interfaces [97]. Work by Yang *et al.* on water/silica interfaces suggests that a more ordered water structure (ice-like) is associated with vicinal silanol groups, due to a higher local surface electrical field on the silica [100]. As previously described, the MVD silica layer is highly hydroxylated and maintains no free OH groups and the surface consists of mainly vicinal groups. GunKo *et al.* provides further evidence toward electrostatic influences showing that the hydrophobidization of silica surfaces (limiting the availability of OH groups) modifies the state of water by lowering the electrostatic field [101]. The extent of the electrostatic influence on subsequent layers is still a subject of debate. Ewing [102] argued that only the first interfacial layer of water is affected by the electric field while the work by Shen [103] indicates that electric fields can induce polar ordering of interfacial water molecules up to a few monolayers. Argyris *et al.* performed modeling studies on the water structure on crystalline silica substrates indicating a correlation between the local density of hydroxy groups and preferential orientation of the interfacial structure of water, illustrating that water molecules in the first layer of a fully hydroxylated surface have hydrogen down orientations, where as nonhydroxylated surfaces have water molecules with OH bonds parallel to the surface [104]. Work done by Ostroverkhov utilizing Phase-Sensitive Surface Spectroscopy on a quartz/water interface assigns ice like stretching regions existing

between 3050 and 3200  $\text{cm}^{-1}$  with the peaks indicated at the low-frequency component, usually labeled as the ice like peak, first appearing as a negative peak centered at 3050  $\text{cm}^{-1}$  at low pH, but reverting to a dominant positive peak centered at 3200  $\text{cm}^{-1}$  at high pH. Suggesting that as pH increases, the quartz surface becomes more deprotonated (and negatively charged with a resulting surface field), and thus indicating that water molecules exist with their H bound to the surface [105]. All of these works are supportive of our postulated interfacial orientation induced by an electrostatic interaction from the highly hydroxylated silica surface.

A second explanation for the observed increase in hydrogen bonding and ice like orientation of water molecules on the MVD silica surface could be attributed to the inherent topography associated with the MVD silica layer. Recent studies suggest that water confined in nanoscopic regions exhibit different thermodynamic characteristics in comparison to bulk measurements [106]. Both Goertz and Li found that the viscosity of water for nanometer scaled separations were approximately  $10^6$  times greater than that of bulk water for highly hydrophilic surfaces indicating a more structured water present in nanoscopic regions [107, 108]. Unfortunately, for the present analysis, it is difficult to elucidate answers in terms of nanoscale confinement as it has been shown that ATR infrared spectroscopy have large penetration lengths ( $>100$  nm) that hinder the study of the buried interface [98]. As discussed by Castrillon *et al.* when examining water in nanoscale confinement, a distinction must be made between: (i) interfacial water, and (ii) confined water, as interfacial water is commonly understood as being found between fluid phases (bulk vapor or liquids) and a solid substrate, while confined water exists between two solid surfaces [109]. The confinement length scales for the water existing between the solid surfaces as experienced in this system is greatly over examined and the influence of nanoscopic regions is indistinguishable from the interfacial water.

Results show that the MVD silica layer supports a higher amount of water on the surface at increasing levels of relative humidity (approximately 4.5 times greater) than on traditional

silicon oxide surfaces. This increased amount of water is found to be more highly hydrogen bound to the surface in comparison to the monolayers investigated on traditional silicon oxide surface, suggesting that the MVD coated surface maintains a more ordered water structure due to a stronger degree of hydrogen bonding compared to water layers formed on traditional silicon oxide surfaces.

#### **4.2.2 Influence of Formation Time and Temperature on OTS Monolayer Formation on a Highly Hydrated MVD Silica Surface**

As evidenced in the previous section, the MVD silica layer supports a higher amount of water on the surface at increasing levels of RH as compared to traditional silica surfaces. For the results presented in this section, the relative humidity was held constant at  $\sim 45\%$ , consistent with prior research notations found to produce high quality OTS films as applicable to traditional silicon oxide surfaces.

In order to examine the OTS monolayer formation mechanism on the MVD silica surface as compared to traditional oxidized silica surfaces, two regimes of OTS film growth are examined. The first is a room temperature case representative of the mixed regime (LC and LE phase) followed by a case at  $T = 10\text{ }^{\circ}\text{C}$  representative of the lower temperature regime  $T < T_0$  (only LC phase) with film formation times ranging from 5.0 seconds to 1.0 hour. A 20 second OTS submonolayer deposition on the smooth Si(100) surface at room temperature is shown in Figure 4.5B and the  $10\text{ }^{\circ}\text{C}$  case is shown in Figure 4.5A. These figures clearly show a distinction between the different deposition phases as influenced by the temperature. For the reduced temperature case presented in Figure 4.5A only island growth is present with no deposition in the surrounding areas consistent with previously reported results [2]. The islands formed at reduced temperatures maintain average height values of roughly 2.0 nm as shown in the height profile in Figure 4.5A. The room temperature case, as shown in Figure 4.5B, shows island growth surrounded by a secondary disordered phase. The height profile of the room temperature case is illustrated in Figure 4.5B and is significantly lower than the

reduced temperature deposition with island average height values at roughly 1.4 nm. This decreased height value is attributed to the presence of two phases on the surface made up of a LC phase (ordered islands-light features) surrounded by a LE phase (disordered-dark features) randomly distributed. Hence, the measured height values represent the difference in thickness between the disordered and ordered island phases. Due to the roughness associated with the MVD silica layer surface, AFM could not be utilized to examine the submonolayer growth regime on the MVD silica surface. Generally, not enough contrast was visible between the OTS film and the underlying substrate and the features remained hidden and undiscernable from the underlying surface topography.

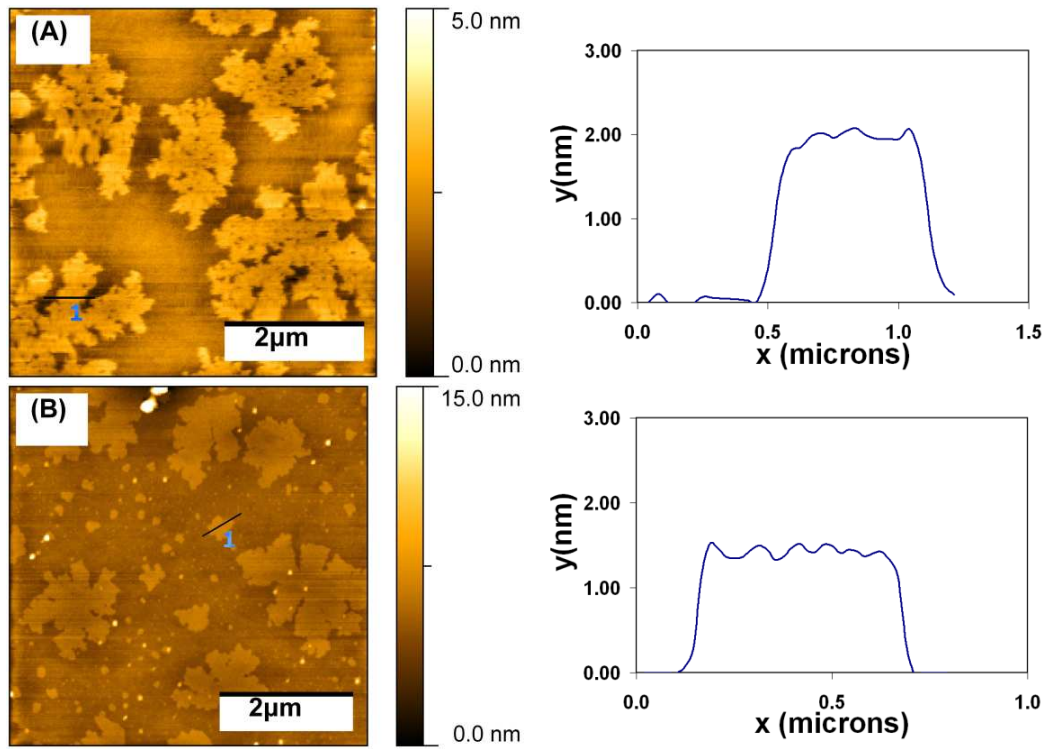


Figure 4.5: AFM micrographs of OTS monolayer formation (A) A 20 second OTS submonolayer deposition on native silicon oxide at 10 °C. (B) A 20 second OTS submonolayer deposition on native silicon oxide at room temperature.

The values measured for the thickness of the OTS film as a function of immersion time ranged from 6.0 to 28.3 Å for both the room temperature case and the 10 °C case on the oxidized Si(100) surface. The values measured on the MVD silica layer ranged from 3.7 to

31.5 Å. All data sets showed an increase in thickness as a function of immersion time. The maximum thickness obtained on the oxidized Si(100) surface is 28.3 Å, consistent with values found in the literature [42] and close to the theoretical value of 26.2 Å [65]. A refractive index of 1.45 is used in calculating the OTS thickness, yet this value may not be reliable for low coverage samples as partial OTS monolayer can have differences in the refractive index that are dependent on the phase present [15]. Also, the standard deviation of a data set of multiple ellipsometric measurements of the MVD silica layer thicknesses is on the order of  $\pm 1.0$  nm. Such a large standard deviation for the MVD silica layer thickness makes it impossible to determine the true thicknesses for the films deposited onto the MVD silica layer surface, since the precursor used in this study form films with thicknesses of roughly three nanometers or less. Average values are presented in Figure 4.6 and should not be considered conclusive values.

The contact angle measurements for all experimental data sets showed an increase with respect to immersion time. At increased immersion times the values obtained for the 10 °C case on the oxidized Si(100) surface and the MVD silica layer were similar to those obtained at room temperature regardless of the deposition conditions. At decreased immersion times the contact angle for the room temperature cases was significantly lower on both with values of 39.0° and 41.0°, in comparison to 63.8° and 69.8° at reduced temperatures. This data was consistent with the differences in overall coverages as measured by ellipsometry and indicated that the OTS films assembled more rapidly at the reduced temperature compared to the room temperature conditions. All of the contact angle data regardless of the temperature regime plateaus at higher deposition times at values greater than 100° and are indicative of a complete monolayer.

Although AFM provides information on the microscopic structure of OTS film growth, it does not reveal molecular structure and conformation changes within the film and can not provide visual contrast on the MVD silica surface. To obtain structural information FTIR analysis was performed on the films as a function of immersion time and temperature on the

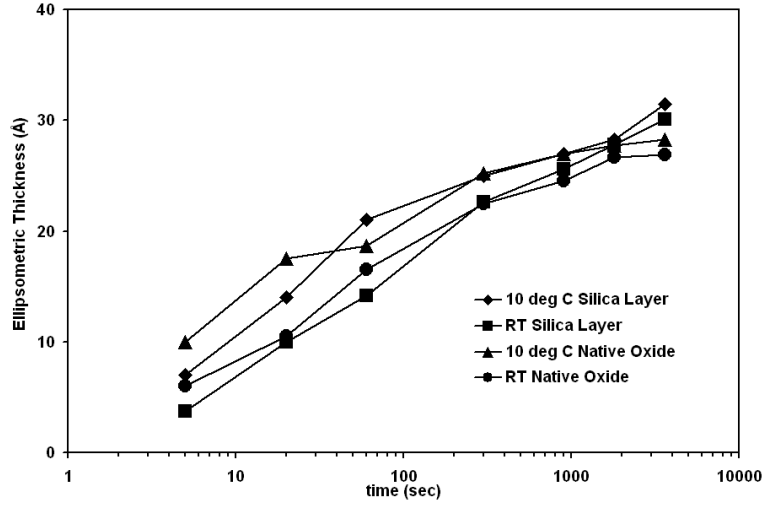


Figure 4.6: Ellipsometric film thickness vs immersion time for octadecyltrichlorosilane films on oxidized Si(100) and MVD silica layer at 10 °C and room temperature. See text for film formation conditions and details of extraction of thickness from ellipsometric parameters. Experimental uncertainty of the thickness is estimated at  $\pm 2.0$  Å.

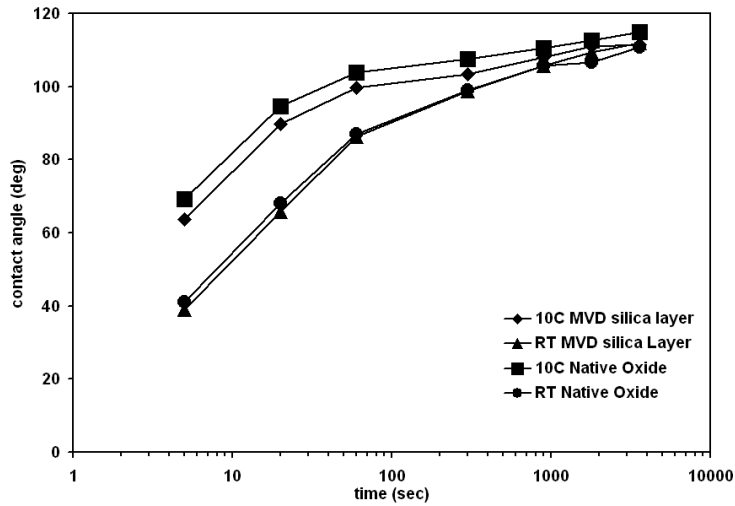


Figure 4.7: Water contact angle vs immersion time for octadecyltrichlorosilane films on oxidized Si(100) and MVD silica layer at 10 °C and room temperature.

oxidized Si(100) and the MVD silica surfaces. For FTIR analysis, the background spectra for films deposited on the oxidized Si(100) surface, was a clean uncoated silicon ATR crystal plasma treated to grow an oxide layer thickness 2.0 nm. For the films deposited on MVD silica layer the background spectra was the as deposited MVD silica layer. To characterize the conformational order of the octadecylsiloxane monolayers, we use the methylene stretching modes as a benchmark. On a native silicon oxide surface the frequencies of the methylene antisymmetric and symmetric stretches are in the range of 2915-2920 and 2846-2850  $\text{cm}^{-1}$ , respectively, for alkyl chains in an all-trans conformation with extended chains, and shift toward 2928 and 2856  $\text{cm}^{-1}$  when the chains are in a liquid like disordered phase [110].

Our data as demonstrated on an oxidized Si(100) surface and illustrated in Figure 4.8 is in agreement with work previously done by Lee *et al.* showing that at the lower reaction temperature 10 °C the intensity of the FTIR peaks in the  $\nu_s(\text{CH}_2)$  and  $\nu_a(\text{CH}_2)$  bands increase in proportion to immersion time [36]. At the reaction temperature of 10 °C the peak positions for the  $\nu_s(\text{CH}_2)$  and  $\nu_a(\text{CH}_2)$  bands remain constant at 2850 and 2918  $\text{cm}^{-1}$  regardless of immersion time. The OTS SAMs prepared at the higher reaction temperature are notably different. In Figure 4.8 the intensity of the peaks also increases in proportion to increasing the immersion time. But, there is a notable decrease in the wave number of the methylene antisymmetric and symmetric stretches ranging from 2919 and 2852  $\text{cm}^{-1}$  at the lower immersion times to values at higher immersion times of 2918 and 2850  $\text{cm}^{-1}$ . The resulting increase in intensity in both cases indicate that the density of the OTS monolayer increases in proportion to immersion time. Additional information can be obtained by examining the peak widths as a function of immersion time. For the room temperature case the peak widths at lower immersion times are very broad becoming more narrow at increased film formation times. Research provided by Parikh *et al.* explained that this peak broadening at room temperature was indicative that the monolayers formed consist of a mixture of conformationally ordered and disordered chains representative of both a LE phase and a LC phase. Thus, indicating that for the room temperature case, as the

deposition times increase, the film becomes more dense and the chains become more ordered as evidenced by the decreasing peak widths and shift in the antisymmetric and symmetric bands to lower energy. For the reduced temperature case, the peak widths remain constant regardless of immersion time indicating only an ordered LC phase present that increases in density in proportion to immersion time.

The results presented in Figure 4.9 are the FTIR spectra for films formed on the MVD silica layer as a function of immersion times and temperatures under study. These spectra follow the same trends as identified on the native silicon oxide. The peak positioning and increasing intensities are consistent with what was observed on the oxidized Si(100) surface indicating that the growth mechanism as influenced by time and temperature are equivalent mechanistically as measured with FTIR on the MVD silica layer.

### 4.2.3 Conclusions

A MVD silica layer has been demonstrated, amenable to FTIR analysis allowing for an examination of interfacial properties in combination with an investigation of OTS film formation mechanism. This MVD silica layer consists of a highly hydroxylated surface that lacks free OH groups possessing a high affinity to physisorbed water resulting in an approximately 4X increase in amount absorbed as a function of relative humidity as compared to traditional silicon oxide surfaces. Results indicate that the MVD silica layer supports an ordered water structure that is more tightly bound due to a higher degree of hydrogen bonding associated with the hydroxylated surface. An examination of the growth process of OTS films from submonolayer coverage to full monolayer deposition as influenced by temperature is in agreement with films produced on native silicon oxide surfaces. In contrast to previously reported results, the quality of the films obtained are comparable to those formed on traditional silicon oxide surfaces, despite a higher amount of water present and a lack of free OH groups. These results suggest that the role of free OH groups on the formation mechanisms for OTS film formation are inconsequential, further highlighting the importance of interfacial water on the OTS film formation process. We show that high quality OTS films can be formed on a highly hydrated surface suggesting that the OTS deposition mechanism is not only influenced by the amount of water present on the surface, but may dependent how tightly bound the water is to the surface, indicating a link between the interfacial waters' availability and reactivity. This work supports the use of an MVD silica layer as a novel platform to study OTS monolayer formation, further enabling the ability to probe the influence of surface topography and the interfacial water layer on the self-assembly process.

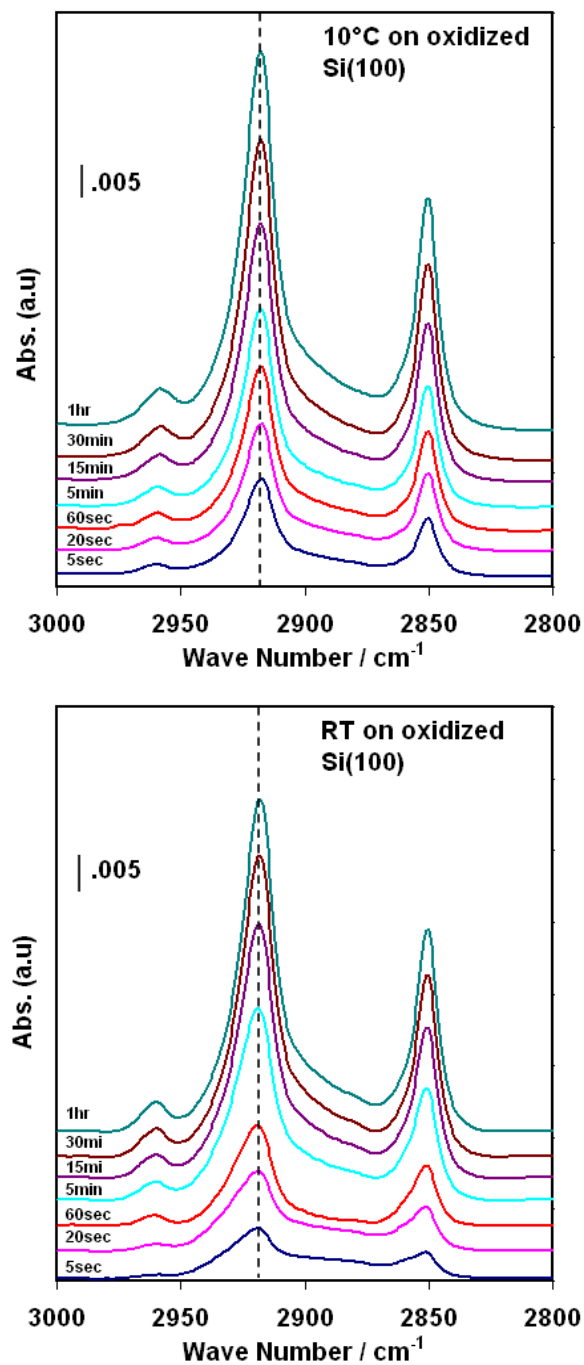


Figure 4.8: Representative FTIR spectra of OTS monolayer formation as a function of immersion time: (Top) OTS monolayer formation on oxidized Si(100) at 10 °C and (Bottom) OTS monolayer formation on a oxidized Si(100) at room temperature.

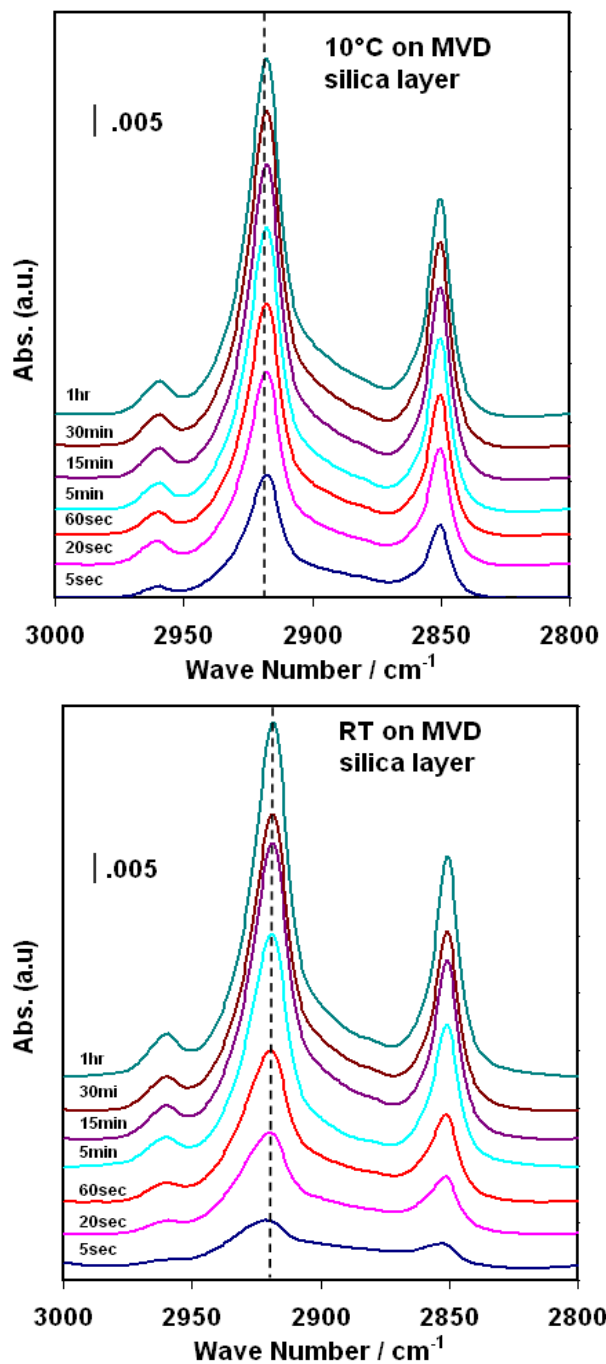


Figure 4.9: Representative FTIR spectra of OTS monolayer formation as a function of immersion time: (Top) OTS monolayer formation on MVD silica layer at 10 °C and (Bottom) OTS monolayer formation on a MVD silica layer at room temperature.

### 4.3 High Surface area MVD Silica Support for TGA Analysis of OTS Monolayers

#### Introduction

While the OTS formation processes and bonding structure have been the subject of extensive investigation, comparatively less is known about monolayer stability as influenced by post processing steps. Monolayer stability has great technological importance because the reliability of a device often depends critically on the integrity of its surface functionality imparted by the coating. In addition, an understanding of the films thermal stability is necessary for successful integration with MEMS devices in terms of processing and use conditions. Prior understanding of the degradation mechanisms of OTS films has relied heavily on techniques such as FTIR, contact angle analysis, X-ray reflectivity, and ellipsometry which give an indication of the state of order of the alkane chains and structural changes as influenced by temperature.

TGA analysis is another technique that can provide information about the monolayer formation and degradation mechanisms, namely, the lateral surface uniformity as indicated by overall surface coverage. TGA analysis has found limited use due to the inability to resolve small changes in mass relative to the low film loading associated with planer substrates (*i.e.* Si(100)). As a consequence, high surface area support materials are often used to provide high loadings necessary for experimental resolution when examining thin films. High surface area materials such as silica particles and mesoporous materials such as SBA-15 have proven effective at enabling a limited investigation of monolayer loading and degradation mechanisms. Unfortunately, in the case of fumed silica, the available free volume for monolayer attachment is affected by two factors, namely, the state of aggregation/agglomeration and the curvature of the primary particles. Since fumed silica consists of aggregated/agglomerated particles, only a limited portion of the surface area is actually accessible to OTS molecules [111]. The curved surfaces of the silica particle offer additional constraints to monolayer formation with

the degree of curvature influencing the efficiency of space occupied by all-trans octadecyl chains at full surface coverage [112]. In the case of mesoporous SBA-15, a high surface area support has been demonstrated, that consists of both a curved surface in combination with a large amount of pores. The size of the pores in the SBA-15 has been shown to influence OTS molecule adsorption.

In this section, a high surface area support is demonstrated that has a lower degree of curvature in comparison to the previously reported silica support materials that is nonporous in nature. This high surface area material created through the deposition of MVD silica layers onto cellulose templates is capable of sustaining OTS loading values measurable with TGA analysis. In addition the properties of this support material enable the deposition of monolayers with film characteristics more similar to those found on a planar silicon oxide surfaces. It is suggested that this material provides a more valid substrate for comparing thermal events as related to monolayer films with TGA analysis.

## **Materials**

Silicon wafers, p-type, with (100) orientation were obtained from University Wafer (Boston, MA). Cabosil M-5 (200 m<sup>2</sup>/g) fumed silica was obtained from Cabot Corporation. Octadecyltrichlorosilane and tetrachlorosilane were obtained from Gelest, Inc. (Morrisville, PA) and used as received. Acetone, isopropanol, and Optima grade hexanes (0.01% water) were obtained from Fisher Scientific (Fair Lawn, NJ). Deionized water (18 M $\Omega$ -cm) was obtained from a Millipore filtration system. Cellulose cotton supports were obtained from Fisher Scientific.

### **4.3.1 Production of Fibrous MVD Silica Support**

A templating technique was utilized to produce the fibrous silica support. The MVD silica layer was deposited onto cellulose cotton balls. Briefly, the cotton balls were cleaned with a 30 sec O<sub>2</sub> RF plasma treatment explained in section 3.2.1 and followed with 10 cycles

of MVD silica layer deposition as described in section 3.2.1 (20 torr H<sub>2</sub>O and 20 torr of SiCl<sub>4</sub> per cycle). The thickness of the silica layer was approximated at 1  $\mu\text{m}$  as measured by ellipsometry on a Si(100) reference wafer cleaned and oxidized as indicated in Chapter 3. After removal from the vacuum system, the templated MVD silica was placed into a furnace and heat treated to 700 °C for 4 hours to remove the cellulose material, revealing the MVD silica support. Prior analytical evaluations were performed with TGA purged under air that determined this heat treatment procedure resulted in complete removal of the cellulose leaving a thin white fibrous material. Thermal treatment in this manner as illustrated by Anderson *et al.* on MVD silica surfaces, has shown that when the MVD silica surface is treated at temperature  $> 400$  °C that that surface silanols in closest proximity to each other, bridge bond into new Si-O-Si bonds lowering the reactivity of the silica surface toward organosilane deposition. To counteract this effect the MVD silica support was reinserted into the MVD deposition chamber and coated with an additional cycle of the MVD silica in essence reactivating or reconditioning the surface with available surface silanols. The available surface area of the silica support was measured at 60 m<sup>2</sup>/g with BET. A SEM image of the MVD silica surface after reconditioning is shown in Figure 4.10 revealing a fibrous material with a low degree of curvature with an average width of 10.0  $\mu\text{m}$  approximately 4 times greater than the length of an extended OTS molecule. This material is considered to be nonporous based on BET surface area results, in conjunction to, the calculations based on uniform MVD silica coverage to the exposed surface area of the cotton fiber. These calculations resulted in approximately  $\frac{1}{2}$  the measured value, as expected, the surface area of the reactive material is dual sided in nature reflecting reactivity of the outer MVD silica layer and the MVD silica layer that was originally attached to the cellulose fiber.

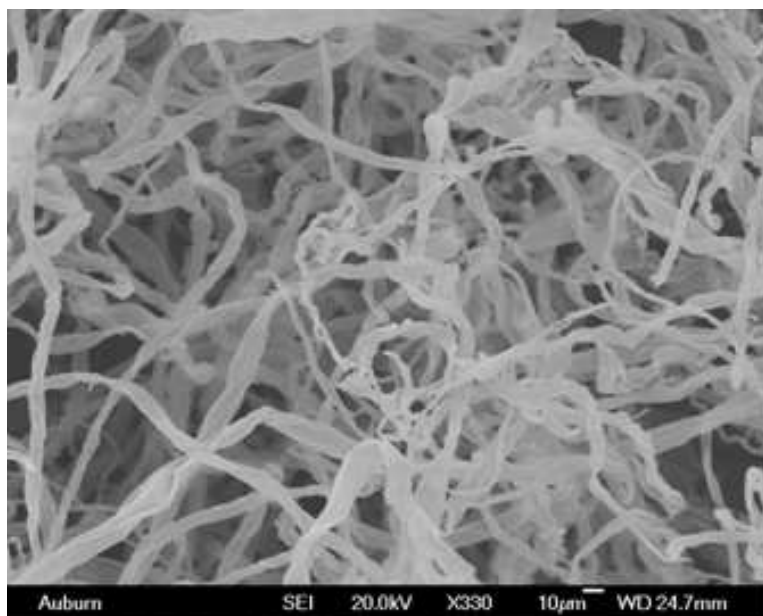


Figure 4.10: SEM image of reconditioned fibrous MVD silica support with average fiber width of  $10.0\ \mu\text{m}$  and surface area of  $60\ \text{m}^2/\text{g}$ .

## OTS deposition

A 1-hour room temperature deposition of OTS monolayers was performed on both fumed silica powder and MVD silica fibers (pre and post reactivation) following the procedure illustrated in Section 3.2.1. Samples were analyzed immediately without the 1 hour set up time previously described in section 3.2.1.

### 4.3.2 Analysis of OTS Monolayers on Fumed Silica and Fibrous MVD Silica Supports without Post Treatment

#### Fumed Silica

Thermogravimetric analysis of fumed silica powder before and after OTS adsorption is shown in Figure 4.11. The thermal analysis was carried out in the temperature range from 30 to  $650\ ^\circ\text{C}$ , in nitrogen, at a heating rate of  $10\ ^\circ\text{C}/\text{min}$ . The TGA pattern of fumed silica powder shows a total weight loss of  $\approx 1.0\%$  over the temperature range from ambient to  $650\ ^\circ\text{C}$ . The initial weight loss up to a temperature of  $120\ ^\circ\text{C}$  can be associated with the breakup

of the hydrogen bonded network, excess solvent removal and removal of adsorbed water from silica. The second stage of weight loss from 120 to 650 °C can be associated with desorption of the adsorbed water, as well as, water generated by the condensation of free silanols.

A multi-step weight loss is observed in case of OTS monolayers on fumed silica. The weight loss occurred in three distinct regions, from ambient to 120 °C and 120 to 350 °C and 350 to 650 °C. The total weight loss observed is 2.5% in the entire temperature range from ambient to 650 °C. The weight loss in the first step is approximately the same as the weight loss in case of bare fumed silica and is attributed to physisorbed water. In the temperature range, 120 - 350 °C, the weight loss of the OTS coated support was higher than that of fumed silica, and was attributed to Si-O-Si cross linking events and the release of associated water, although, it is difficult to determine if this loss might also represent the start of decomposition. We attribute the decomposition of the OTS layer to the weight loss in the temperature range 350 to 650 °C as has been reported for a monolayer thermally treated in nitrogen. To obtain an estimate of the extent of coverage of OTS on the surface, 100 % coverage was calculated assuming a maximum possible value of 5 molecules/nm<sup>2</sup>, and using 200 m<sup>2</sup>/g as the surface area of fumed silica. Therefore, the percent coverage for fumed silica was 8.4%, and much lower than the amount calculated, suggesting an incomplete monolayer and non uniform coverage. For the temperature range under investigation the silica molecules are assumed to still remain on the surface. Low loadings are typical of silica materials, as illustrated in Figure 4.12, due to the aggregated/agglomerated particles, which allow only a limited portion of the surface area to be accessible to OTS molecules. An additional consideration for the observed loadings stem from the assumption of an ideal monolayer consistent with an all trans packing density (5.0 molecules/nm<sup>2</sup>). These films were produced at room temperature and previous investigations have demonstrated disorder will exist in the films. In assuming no diffusion limitations due to aggregated particles and completely accessible surface area, the density of an ideal all trans OTS monolayer is estimated at 1.1 molecules/nm<sup>2</sup> and suggests more tilt with the OTS molecules indicative of disorder.

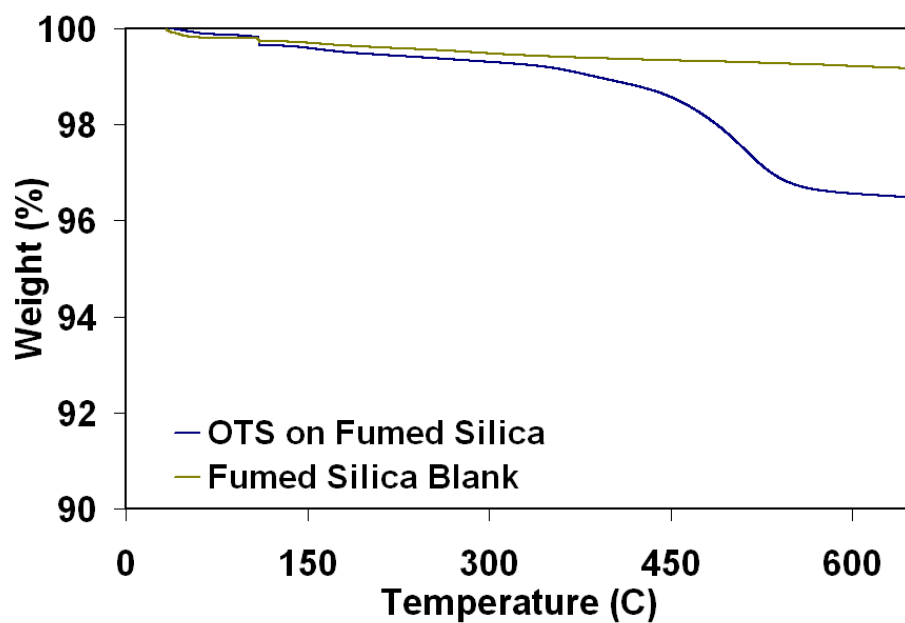


Figure 4.11: TGA plots of fumed silica (top) before and (bottom) after adsorption of OTS.

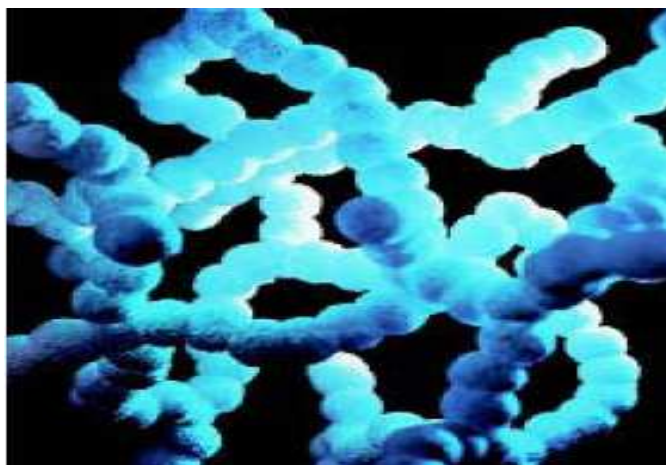


Figure 4.12: Illustration of fumed silica (Cabosil M5) from manufacturer's website with a BET surface area of 200m<sup>2</sup>/g.

## Fibrous MVD Silica Support

The weight loss events observed on the fibrous MVD silica and the OTS coated fibrous MVD silica (conditioned) were similar to those noted on the fumed silica. As a reference, the unconditioned MVD silica was included in the analysis showing that as expected no deposition of OTS occurred given the decreased functionality associated with the formation process. In general, the MVD silica blank followed the same trends as observed for the fumed silica and the observed weight loss temperatures were comparable. One exception found on the OTS coated MVD silica fiber is a larger weight loss event occurring between ambient temperatures and 120 °C. We attribute this to the fact that no post treatment was performed on the OTS modified MVD silica surface and residual solvent from the coating process likely remained. Generally, these supports were gelatinous after rinsing in solution and it seemed to take longer for the solvent to completely evaporate compared to the fumed silica. Weight loss in the second step ranging from 120 to 350 °C was larger than that of the blank MVD silica and was attributed to Si-O-Si cross linking events and the release of water associated and/or the beginning of thermal decomposition. The weight loss in the range of 350 to 650 °C was attributed to the decomposition of OTS. The same procedure, as previously described, was used to estimate the surface coverage associated with the OTS film. For the temperature range under investigation the silica molecules are assumed to still remain on the surface. The film coverage on the MVD silica fiber was calculated at 51.0% from the loss associated in the range of 350 to 650 °C. This value was significantly higher than what was obtained on the fumed silica surface under identical deposition conditions suggesting a 6X increase in material present. This increase in material is significant considering that the available surface area for the fibrous silica was only 60 m<sup>2</sup>/g as compared to 200 m<sup>2</sup>/g for the fumed silica. Performing a similar calculation to that performed on the fumed silica the density of an ideal all trans OTS monolayer on the surface of the MVD fibrous silica is estimated at 2.1 molecules/nm<sup>2</sup>.

A higher calculated weight loss in the second step ranging from 120 to 350 °C, in combination with the higher overall loadings, were suggestive that the weight loss events in this range can be attributed to the release of water from Si-O-Si cross linking events and not the beginning of thermal decomposition. From this observation a need for post processing of the OTS layers is indicated, such that, thermal decomposition can be observed without interference from possible cross linking events. The section that follows supports this conclusion and includes an analysis of the thermal decomposition mechanism as influenced by different post processing environments.

It is more feasible that the accessible surface area for the fibrous silica is greater as compared to the fumed silica verses more molecules per unit area as the depositions were performed under similar deposition conditions. The MVD silica when deposited on a planer substrate, as shown in the previous section, exhibits a similar reactivity toward OTS film formation as compared to traditional silica materials. In conclusion, results suggest that due to the lack of porosity, a low degree of surface curvature, and the increased loadings obtained, that the fibrous silica, provides a more representative support material for the determination of loading information for comparison to the films produced on planer substrates.

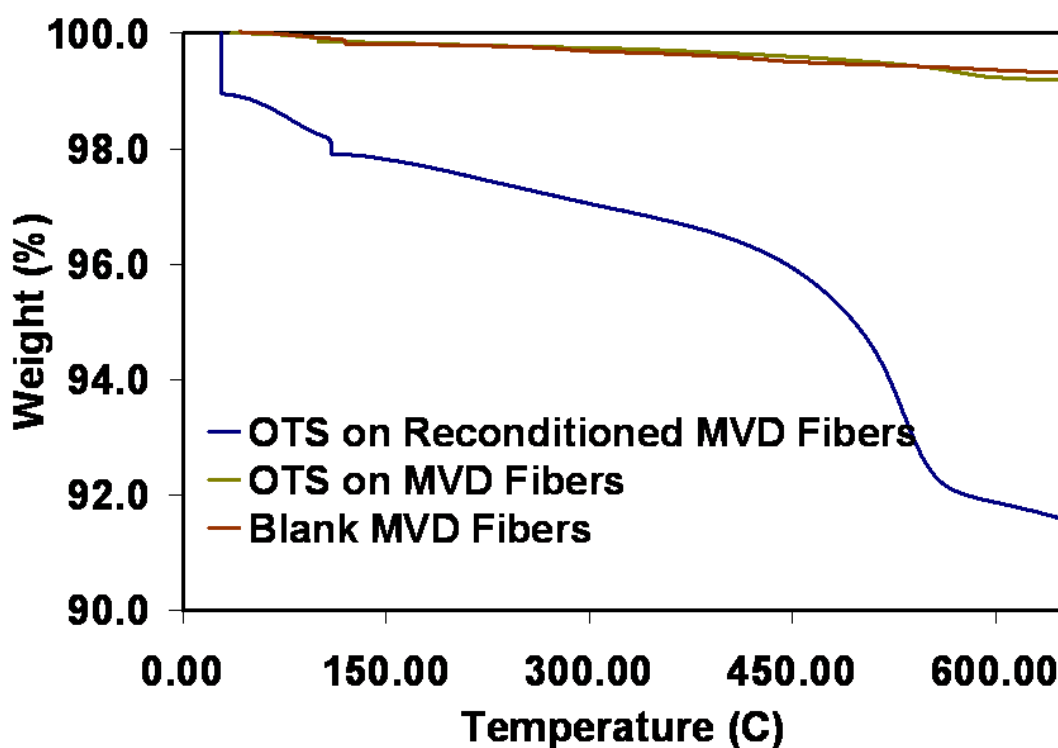


Figure 4.13: TGA analysis of blank fibrous MVD silica and OTS monolayer films on fibrous MVD silica fibers (with and without reconditioning) without post treatment.

#### 4.3.3 Analysis of OTS films on Fumed Silica and Fibrous MVD Silica after Thermally Annealing with Different Gases

It has been suggested that heating OTS films to temperatures between 120 and 150 °C, results in the stabilization of the monolayer, through the formation of cross-linking between adsorbed OTS molecules. [44,113]. Sung *et al.* has indicated a timescale for cross linking or grafting to the substrate showing that in solution the (hydrolyzed) precursor molecules deposited at 10 °C retain their mobility for sufficiently long times indicating that the lifetime of the mobile state is 10 minutes [40]. The results presented by Wang *et al.* suggest that thermal annealing creates an adsorbed monolayer that is no longer mobile, either because of attachment to the underlying substrate, to other OTS molecules, or due to removal of adsorbed water [112]. Conditions necessary for appropriate post processing and the influence of curing conditions on the stability of an OTS monolayer remain as undefined parameters. It

is the intent of this work to utilize TGA-MS to examine the influence of different annealing gases on the stability and degradation scheme of OTS Monolayers produced on an MVD silica surface.

## Experimental

OTS Monolayers are deposited onto the MVD silica support following the same methodology as described in the previous section. After deposition the monolayer/support system is placed into the TGA under different environments (Air, Nitrogen, and Helium) and ramped to 120 °C and thermally annealed at this temperature for a 1 hour duration. Typical loading amounts are 10 mg of the OTS / MVD fiber support. After annealing, the gas is changed to nitrogen and the system is purged of the initial curing gas. The temperature is subsequently ramped at 10 °C to 600 °C and the thermal weight loss events are monitored.

## Results

A distinction between the different annealing gases and decomposition features is apparent from the TGA analysis. Two distinct weight loss events are evident from the thermally annealed OTS film, most evident, in the differential plots shown in Figure 4.15. The first event is in the range of 150 °C to 400 °C and second from 400 °C to 600 °C. The weight loss data for the helium and nitrogen treatment are comparable, in the range from 150 °C to 400 °C, but the profile obtained for air annealing is different. The decomposition of OTS monolayers, on the MVD silica thermally annealed under air starts at a lower temperature (250 °C) compared to those treated under helium and nitrogen (370 °C). It has been shown that thermal decomposition occurs at lower temperatures in an air environment, as such air may be trapped in the film from the annealing process contributing to the increased thermal degradation at lower temperatures. The data indicate that the rate of decomposition is slightly faster for the helium annealed samples in the 400-600 °C regime. Based on the overall weight loss of the OTS monolayer an estimated OTS coverage ranging from 51 to 38% for

the three cases is determined. It is not suspected that the annealing procedure influences the overall coverage attained on the MVD silica (*i.e.* lower on He and N<sub>2</sub>). It is suspected that thermally annealing the OTS monolayer under a nitrogen and helium environment produces an OTS film with a higher thermal stability in the range of 150 to 600 °C, but that treatment to a higher temperature would eventually result in the same overall weight loss and loading. It appears that the OTS films cured under air undergo thermal decomposition at a faster rate at lower temperatures and result in the most significant weight loss. But, in the case of the nitrogen cured sample more fragments will remain up to 600 °C.

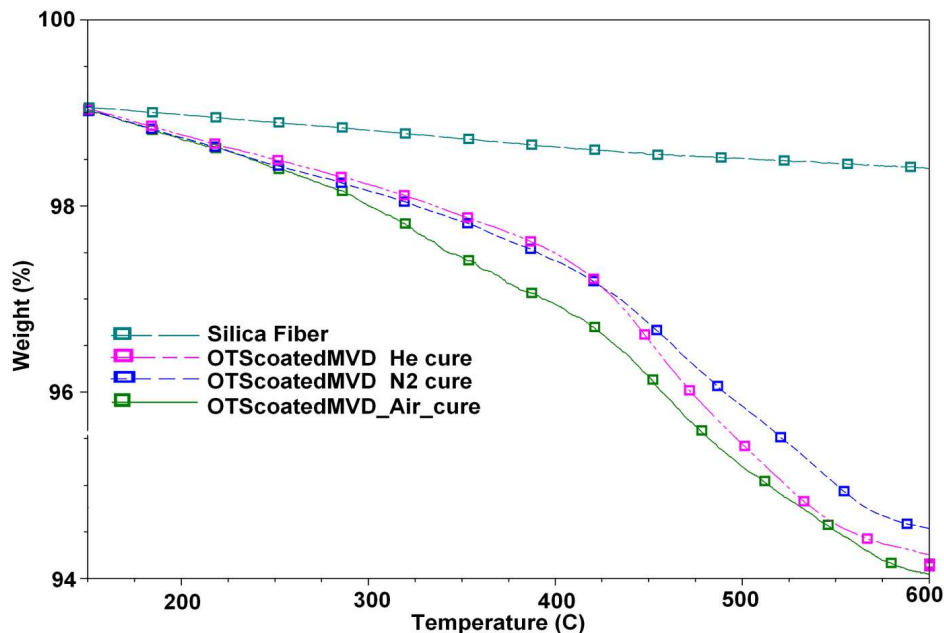


Figure 4.14: Weight change as a function of thermal treatment under nitrogen from 150 °C to 600 °C at a ramp rate 10 °C/min for three OTS monolayers on fibrous MVD silica previously annealed for 1 hour at 120 °C three different environments (He, N<sub>2</sub> and Air)

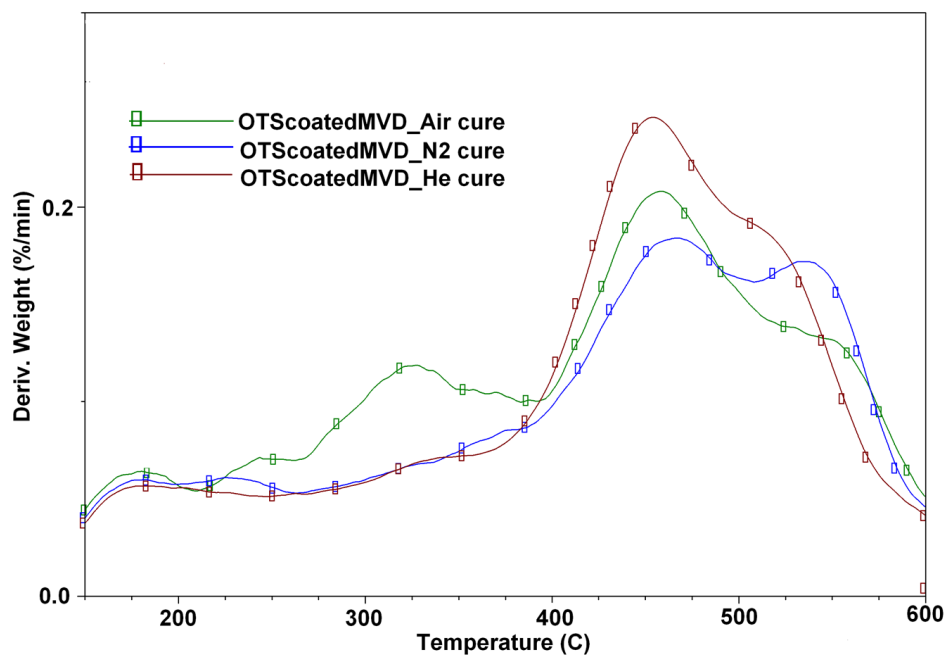


Figure 4.15: Derivative weight loss in (%/min) as a function of thermal treatment under nitrogen from 150 °C to 600 °C with a ramp rate 10 °C/min for three OTS monolayers annealed for 1 hour at 120 °C under three different environments (He, N<sub>2</sub> and Air).

#### 4.3.4 Conclusions

A novel high surface area silica support capable of sustaining loadings measurable with TGA analysis is introduced. This support exhibits a similar reactivity toward OTS film decomposition, as compared to, other high surface area silica materials and sustains higher loadings. In addition, results suggest that due to the lack of porosity, low degree of surface curvature, and the increased loadings obtained, that the fibrous silica, provides a more representative support material for the determination of loading information for comparison to the films produced on planer substrates. This support has been utilized to determine the influence of annealing environments on the thermal stability of OTS films. It was shown that films annealed under an air environment decomposed at lower starting temperatures and to a greater extent than those annealed under inert atmospheres. This support will enable future examinations of the influence of different annealing procedures and annealing environments.

## Chapter 5

### OTS Island Formation on Topographical Asperities: Implications Toward Tribological Response

#### 5.1 Motivation

To date, the interfacial phenomenon responsible for causing stiction, friction, and wear hinder the commercialization of MicroElectroMechanical Systems (MEMS) [50, 114–117]. Consequently, substantial research has focused on ways to overcome the interfacial phenomenon by controlling the topography and the chemical composition of the contacting surfaces [6, 118]. The most common method for overcoming the interfacial interactions focuses on tailoring the surface properties with self-assembled monolayers (SAMs) [11]. Octadecyltrichlorosilane (OTS) monolayers have received considerable research and attention [2, 19–22] with demonstrated success for tribological improvement [6, 33, 68]. Unfortunately, variation in the amount of tribological improvement afforded by these films has been identified as the films have been translated from smooth surfaces to MEMS surfaces [68, 119, 120]. Some of the observed variation has been explained in terms of differences in topographical contact points, associated tribological mechanisms and the length scale of the measurement technique [121–123]. But, reported variation exists between films produced on similar surfaces regardless of topographical characteristics as analyzed with the same measurement technique [124–127].

OTS monolayer growth kinetics and interfacial properties as deposited on MEMS surfaces are generally accepted from investigations of film formation on smooth surfaces. These investigations have revealed distinct regimes of growth dependant on formation temperature that are differentiated by changes in packing density, chain conformation, and orientation with respect to the substrate [45]. Despite the revelation of three distinct growth regimes,

most published literature investigating OTS monolayers for friction and adhesion improvement have relied heavily on OTS SAMs produced at room temperature (mixed regime). Yet, recent works indicate differences in friction improvements attainable based on the phase of OTS present. Work done by Flater *et al.* illustrated a disparity in friction measurements on monolayers deposited from the mixed regime on smooth silicon surfaces. The monolayers, which were deposited at room temperature, consisted of a mixture of the liquid condensed (LC) phase represented by densely packed islands and a surrounding disordered liquid expanded phase (LE) [72]. These results showed that OTS islands resulting from a LC phase produced a lower friction value when compared to the surrounding disordered LE phase. It was postulated that gauche defects in the chains or vacancies in the LE phase result in an increase in friction. A congruent study by Masuko *et al.* showed that the friction reducing performance for an OTS monolayer on a smooth silicon wafer corresponded to the SAMs molecular density and the degree of molecular orientation [128]. The importance of the deposition temperature on OTS film formation is evident with different friction characteristics obtainable based on the phase present. It is suspected that some of the reported variability in friction measurements as observed on similar surfaces can be explained with this observation.

When OTS monolayers are deposited onto MEMS surfaces, it becomes equally important to determine the interfacial properties, namely, molecular arrangement and packing density on the topographical points of contact (asperities). Research indicates that the packing density of monolayers not only depend on deposition temperatures, but that the adhesion between SAMs and silicon oxide surfaces can vary significantly when assembly takes place on surfaces with curvature as compared with flat surfaces [129, 130]. Molecular dynamics simulations of SAMs under compression have shown, during the initial stages of compression by an asperity, that without strong lateral chain-chain interactions that gauche defects within a monolayer appear and begin to propagate, reducing overall order within the film [131]. The loosely packed nature of a disordered film increases the frictional forces. Thus, understanding

the relationship between monolayer order on the contacting asperities may help predict their ability to act as lubricant films for MEMS.

An example AFM image for polysilicon is shown in Figure 5.1 and illustrates the topographical complexity associated with MEMS devices. A line scan shows the inherent roughness of these surfaces and gives a better representation for the surface features in contact during friction measurements.

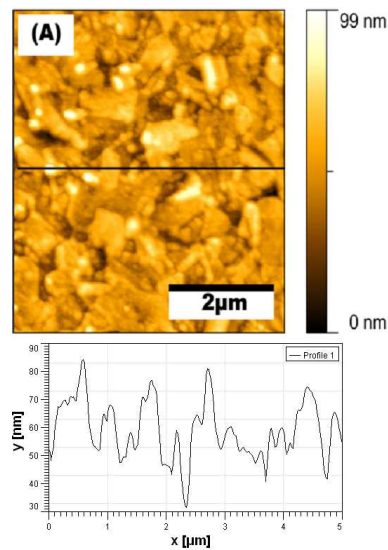


Figure 5.1: Example polysilicon surface and line profile of surface roughness

Unfortunately, limitations exist in the ability to identify what phases are present on the topographical features, due to an inability to inspect the exact location of the monolayer coating. Atomic Force Microscopy (AFM) is a valued technique for topographical investigation and has been successful in monitoring the growth mechanisms and coating quality on smooth surfaces [2, 21, 30, 132, 133]. But with added topographical roughness, AFM, can not be readily utilized to examine the submonolayer to full monolayer growth process on technologically relevant substrates, such as polycrystalline silicon. Generally, the monolayer characteristics remain hidden and undiscernable from the underlying surface roughness. Consequently, alternative techniques are employed to obtain information about the OTS film quality on surfaces with inherent roughness and/or curved surfaces. Techniques such as FTIR [44, 134], micro-gravimetric analysis [135] and TGA [29, 112] have provided structural information such as lateral packing density (loading) and orientation. However, the data obtained is only indicative of the average or bulk values, and rely on certain assumptions about packing density for calculations. They can not reveal details about how the films exist on individual asperities. Recently, Bush *et al.* showed that Kelvin Probe Microscopy could be utilized to study OTS film formation on polysilicon surfaces. Their work focused on obtaining contrast between the LC and LE phase on polysilicon surfaces. Results suggested that partial OTS films formed at low temperatures preferentially deposited along the grain boundaries of polysilicon, leaving the topographical features uncoated [45]. The reason for this preferential absorption was not completely investigated and warrants further research.

In this investigation, OTS films deposited from the liquid condensed phase, are applied onto surfaces of varying topographical complexity to examine molecular assembly as influenced by surface asperities. A MVD silica surface, amenable to FTIR analysis, known to support the same growth mechanisms of OTS monolayers [136] as compared to traditional silicon surfaces is utilized. This surface enables a tunable degree of surface roughness with additional control over different topographical asperities (*i.e.* peak sizes, peak shapes). In order to provide topographic contrast for AFM imaging, an etchant technique is developed,

which as described, removes only the MVD deposited silica that is not ‘protected’ by densely packed OTS islands. The film characteristics on the MVD silica surfaces are compared to films produced on an oxidized Si(100) surfaces as examined via ellipsometry, contact angle analysis, atomic force microscopy (AFM), and FTIR.

## **Experimental Details**

### **Materials**

Silicon wafers, p-type, with (100) orientation were obtained from University Wafer (Boston, MA). Octadecyltrichlorosilane and tetrachlorosilane were obtained from Gelest, Inc. (Morrisville, PA) and used undistilled. Concentrated hydrofluoric acid (HF, 49%), acetone, isopropanol, and Optima grade hexanes (0.01% water) were obtained from Fisher Scientific (Fair Lawn, NJ). Deionized water (18 M $\Omega$ -cm) was obtained from a Millipore filtration system.

### **Methods**

Cleaning methods, MVD silica layer formation, and OTS monolayer formation techniques for the various samples have been previously described in Chapter 3.

### **Etching Process**

A dilute solution of HF is utilized for the removal of exposed silica. This solution is made from a 1:700 v/v HF:Deionized water. Each sample was allowed to etch for 1 minute and removed from the solution and then rinsed with copious amounts of Deionized water. The samples are then dried under a stream of nitrogen. More details are provided in the sections that follow.

## 5.2 Introduction of an Etchant Procedure for Obtaining Topographical Contrast with AFM Imaging

In order to provide topographic contrast for AFM imaging, a unique etchant technique was developed and utilized, which removes only the MVD deposited silica that is not ‘protected’ by densely packed OTS islands. This work was prompted by studies done by Komeda *et al.* [137] using a similar methodology to reveal properties of the  $\text{SiO}_2$  near the  $\text{SiO}_2/\text{Si}$  interface.

Our study utilized, ATR-FTIR and AFM analysis to examine OTS film characteristics as influenced by exposure to a dilute HF etchant. This investigation included examination of both submonolayer films and full monolayers deposited at room temperature deposition (mixed regime LC and LE phases) conditions and those deposited at reduced temperatures  $T=10^\circ\text{C}$  (LC phase). A comparison was made to films deposited on MVD silica surfaces and traditional oxidized (Si(100) surfaces). Etch rate was determined for the various MVD silica morphologies, indicating that an etch time of 1 minute was sufficient to remove exposed MVD silica providing contrast for OTS film investigation with AFM. It was determined that the dilute HF etching technique had no influence on a full monolayer film regardless of formation temperature, but distinct differences were observable in the submonolayer growth regime.

Two cases are presented to illustrate the use of the etching procedure. The first case consists of two experiments examining a 20 second submonolayer OTS deposition at room temperature (mixed regime) on a bare oxidized silicon ATR and on a MVD silica layer coated oxidized silicon ATR. The bare oxidized silicon surface had a 0.2 nm RMS roughness and oxide thickness of 1.9 nm and the an AFM images of this surface is illustrated in Figure 5.3A. A MVD silica layer was deposited onto a second oxidized silicon ATR and is referred to as MVD silica 0 with an oxide thickness of 30.0 nm and a 1.0 nm RMS roughness. An AFM image of the MVD silica layer is shown in Figure 5.4A. The second case consists of two experiments examining a 20 second submonolayer OTS film deposition at  $10^\circ\text{C}$ (LC regime)

on a similar oxidized silicon ATR surface and a second ATR that was coated with same MVD silica layer previously detailed.

For the FTIR analysis, the background spectra for the OTS Island coated MVD silica layer was the “as deposited” MVD silica layer and the background spectra for the silicon oxide layer was a clean plasma oxidized silicon ATR crystal with 2.0 nm of oxide. To characterize the conformational order of the octadecylsiloxane monolayers, we use the methylene stretching modes as a benchmark. On a native silicon oxide surface the frequencies of the methylene antisymmetric and symmetric stretches are in the range of 2915-2920 and 2846-2850  $\text{cm}^{-1}$ , respectively, for alkyl chains in all-trans conformation with extended chains and shift toward 2928 and 2856  $\text{cm}^{-1}$ , respectively when the chains are in a liquid like disordered phase [110].

We have previously demonstrated that the growth process of octadecyltrichlorosilane (OTS) films on MVD silica layers from submonolayer coverage to full monolayer deposition are consistent with the growth mechanisms found on oxidized silicon surfaces [136]. Briefly, this work showed that when OTS films are deposited at reduced temperatures, the molecules densely assemble at the early stage of formation and grow two dimensionally with the same packing density representative of an all trans conformation and as the immersion time increased there was a monotonous increase in coverage with a continued all trans conformation [36]. The OTS films prepared at room temperature are notably different. The intensity of the peaks also increases in proportion to increasing the immersion time indicating a density increase. But, there is a decrease in the wave number of the methylene antisymmetric and symmetric stretches ranging from 2919 and 2852  $\text{cm}^{-1}$  at the lower immersion times to values at higher immersion times of 2918 and 2850  $\text{cm}^{-1}$  indicating the formation of a more ordered film as film growth progresses. Additional information was obtained by examining the peak widths as a function of immersion time. For the reduced temperature case, the peak widths remain relatively constant regardless of immersion time. But, for the

room temperature case the peak widths at lower immersion times are very broad and become more defined as the deposition time increases. This increase in peak width for the room temperature case compared to that of the 10 °C case was indicative that the monolayers produced at room temperature exhibit both a LE phase and LC phase simultaneously evidenced by conformationally ordered and disordered chains. The same trends were observed for the cases presented here.

The FTIR spectra shown in Figure 5.5 illustrates the influence of the etchant on OTS submonolayer films by examining the methylene antisymmetric and symmetric peaks before and after the contrast enhancing etchant procedure. For the 20 second room temperature case on the oxidized silicon ATR crystal the methylene antisymmetric and symmetric peaks are very broad and shifted to a higher wavenumber indicative of a more disordered film exhibiting characteristics of both a LE phase and LC phase. The same trend is evident for films grown on the MVD silica layer, but the broadening effect is greater suggesting that a higher degree of disorder exists on this film. It is suspected that this higher degree in disorder is associated with the increased roughness associated with the MVD silica layer in this study. After the etchant treatment, the methylene antisymmetric and symmetric peaks shift to  $2918\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$  and the broadening effect is diminished, which is more in agreement with alkyl chains in all-trans conformation. These results further suggest that the LE phase was removed with only the LC phase remaining as indicated by peak location. An AFM image of the OTS film after the etchant treatment is presented in Figure 5.4B, consisting of nothing but the remaining LC phase. Prior to the etchant treatment the AFM image was uninformative and did not allow for visualization of the OTS deposition.

Figure 5.6 shows the results of a 20 second 10 °C OTS film deposition on both the oxidized silicon and the MVD silica layer before and after the etchant treatment. In this instance the methylene antisymmetric and symmetric peaks remain constant regardless of the etchant treatment on both surfaces. This result indicates that the etchant procedure does not remove densely packed OTS Islands. An AFM image of the 10 °C deposition case

on the MVD silica layer is presented in Figure 5.4C. After the etchant treatment, the OTS coated MVD silica layer consists of densely packed islands similar to those found on a smooth silicon surface under the same deposition conditions.

Our work has therefore confirmed that after dilute HF etching, the OTS films deposited at reduced temperatures on both the native oxide surfaces and MVD silica layers remain unchanged. But, the films produced in the mixed regime were found to be susceptible to selective removal of the disordered phase. It was concluded that the packing density for OTS films contributed to the differences. It is also noted that the MVD silica layer has a higher degree of surface roughness in comparison to Si(100) surfaces and the degree of disorder is increased on this surface under room temperature conditions, but for the reduced temperature case no change in monolayer order is observed after etching. Utilizing the dilute etchant procedure allows for an increase in obtainable contrast for AFM imaging by removing MVD silica layers not protected by a densely packed OTS phase. This technique was utilized for the remainder of this work focusing on submonolayer films produced at reduced temperatures providing topographic contrast for AFM imaging.

### **5.3 Reduced Temperature Deposition of OTS Films as Influenced by Surface Topography**

In this work, densely packed octadecyltrichlorosilane islands resulting from low temperature deposition conditions, are deposited onto native silicon oxide surfaces and onto silicon oxide surfaces created via molecular vapor deposition (MVD). A two-dimensional AFM scan of a clean silicon sample after the pre-deposition oxygen plasma treatment can be seen in Figure 5.3A. The cleaning procedure detailed in Section 3.2.1 produces a clean, flat silicon oxide surfaces, as evidenced in the figure. Various MVD silica layers exhibiting different topographies were produced for this study. The procedure described in Section 3.2.1 produces a thin, rough, silica-like surface which is very rich in reactive sites for further surface modification by organosilane chemistries [138]. After silica layer deposition, samples are

characterized with ellipsometry, contact angle analysis, and AFM. For simplicity, the vapor grown silica layers examined in this section of work are labeled as MVD Silica 1 - MVD Silica 5 and the native oxide surface is identified as Si(100) oxide.

Relevant data for films deposited on the clean silicon oxide surface and for films deposited on the MVD silica layer surface are given in Table 5.1. In this work the MVD silica layer surfaces range from 10-35 nm thick with RMS roughness values ranging from 1.0-6.0 nm. Due to the non-uniform nature of the silica layer surface, the standard deviation of a data set of multiple ellipsometric measurements of silica layer thicknesses is on the order of  $\pm 1.0$  nm. Such a large standard deviation for the MVD silica layer thickness makes it impossible to determine the true thicknesses for the films deposited onto the MVD silica layer surface, since the precursor used in this study form films with thicknesses of roughly three nanometers or less. As is evidenced in the Table 5.1, all silica layers exhibit a contact angle of  $< 5^\circ$  indicative of a hydrophilic surface capable of sustaining OTS monolayer growth.

It is interesting to note that AFM measurements performed on different morphological silica layers often yielded the same RMS roughness values. This is demonstrated in some of the examples shown in this work. In order to illustrate the topographical differences in a more pronounced manner the AFM images were transformed into three dimensional representations on a slightly magnified scale. This is illustrated in Figures 5.7A-E. The scaling of these images were arbitrarily set in order to give an easier comparison of the data. Rendering the images in this fashion allows for an easier recognition of the distinct differences in topographical asperities, that would remain unnoticed, if only RMS roughness values were compared.

After initial characterization the silica layers were modified with a submonolayer OTS films deposited from the liquid-condensed phase (10 °C for 20 seconds) as presented in Section 3.2.1. The atomic force micrograph shown in Figure 5.3B, shows the OTS islands obtained on a native oxide Si(100) surface. Island growth was allowed to proceed until islands formed at an intermediate size of 1 to 2  $\mu\text{m}$ . It has been shown that additional ordering of

SAM molecules occurs in islands in this size range due to a more complete cross-linking or covalent bonding to the substrate, which eliminates rotational defects or other confirmation or changes [45].

As shown in Figures 5.8A-E, partial OTS monolayers grown from the liquid condensed phase on the MVD silica layers, are readily observed after the etching process with AFM imaging. It is evidenced from the AFM images that the OTS deposition is different on all the surfaces illustrated. At low roughness values, illustrated in Figure 5.8A, the islands appear to form unrestricted and similar to those observed on the native oxide surface as shown in Figure 5.3B. As the MVD silica roughness values increase, in Figure 5.8B-E, islands preferentially deposit in the lower portions of the topography (valleys) with the highest points (asperity peaks) being selectively removed during the etching process. This removal, as previously described, is attributed to the presence of a low density disordered film present on the highest points.

In addition, the MVD silica layers illustrated in Figures 5.8A-E maintain observable differences in the shape of the topographical asperities. For example, the MVD silica layers identified in Figure 5.7C and 5.7D have similar RMS roughness values as measured with AFM. The topographical asperities associated with the silica layer as represented in Figure 5.7C have a sharper topographical peaks in comparison to those in Figure 5.7D that appear more rounded. Increased OTS film coverage is observed on the rounded topographical peaks as shown in Figure 5.8D than on the sharper peaks shown in Figure 5.8C. The same trend is observed when comparing the sharp peaks associated with Figure 5.7E in comparison to those on Figure 5.7D with island adsorption location shown in Figure 5.8D-E. This indicates that OTS film deposition is influenced by the asperity curvature. As a result more of the densely packed film is able to form on the topographical asperities that maintained a more gradual rise in the slope of valley to peak. Thus, the higher the peak curvature the less likely densely packed islands form suggesting a correlation between the shape and size of the asperity.

As illustrated in Figure 5.9, it is hypothesized that the asperity curvature inhibit effective chain-chain hydrophobic interactions, which ultimately stabilize the islands. As a result, a decrease in the packing density allows the etchant to penetrate between the OTS chains and attack the exposed silica layer, suggesting that little to no deposition of the high density OTS phase occurred on the highest points of the topographical asperities of high curvature. A 2-dimensional representation of this hypothesized effect is illustrated in Figure 5.9. It is concluded, that the OTS chains will have a higher crosslinking probability with asperities of lower curvature.

A similar conclusion was observed by the work of Wang *et al.* in analyzing OTS monolayer adsorption on the surface of spherical particles. This work derived a means to estimate the efficiency of space occupied by “ideal” all-trans octadecyl chains at full surface coverage as influenced by surface curvature [112] for spherical powder analysis.

The packing efficiency, with which the molecules occupy the available volume is defined as  $V/V_S$ . If it is assumed that the octadecyl chain is in an all-trans rigid rod (comparable to OTS molecules) then the length can be assumed at 2.0 nm and cross section of  $0.2\text{nm}^2$ , then the number of OTS molecules,  $N$ , which can be accommodated on a  $d$ -nm spherical particle, is  $\pi d^2/0.20$  and the total volume  $V$ , occupied by the  $N$  molecules, is  $2\pi d^2$ . The volume available for occupation by the OTS molecules,  $V_S$ , is  $\pi[(d+4)^3 - d^3]/6$  so  $V/V_S$  is calculated according to the following equation (taken from ref. [112]):

$$\frac{V}{V_s} = \frac{12d^2}{[(d+4)^3 - d^3]} \quad (5.1)$$

This model was used to explain how, the curvature of the silica particles creates free volume between the chains, and how the resultant differences in free volume can thus affect the packing of the OTS alkyl chains, finding that in the case of the 7nm particles, only 60% of the available volume is in fact occupied by the OTS molecules, whereas 90% and 96% is occupied for the 40nm, and 106nm beads, respectively.

If the topography of the surface is considered to be made up of spherical particles of varying radius of curvature (hemispherical in this case) then a limiting value of 400 nm is necessary for 99% coverage with much higher values necessary for 100% coverage. Obviously, this is a simplistic explanation and can not be quantitatively determined from measured AFM values and would prove even more difficult to approximate on a polysilicon surface with a multitude of asperity dimensions. The MVD surfaces represented here show differences in the sagittal curvature and transverse curvature of the surface asperities and limit the validity of surface curvature models for determining optimal packing density.

In addition to the preferential adsorption described, the films evidenced increasing extents of OTS island coverage under the same adsorption conditions corresponding with increasing MVD silica layer thickness. This observation is suggestive of an increase in surface reactivity associated with thicker MVD silica coverages. This effect is presently under investigation and will be the subject of future reports focusing on the interfacial water layer found on the MVD silica layer under adsorption conditions and its possible contribution to this observation.

## 5.4 Conclusions

In this work Atomic Force Microscopy was utilized to investigate the formation of OTS films on surfaces exhibiting various topographical asperities. A dilute etchant technique is introduced, providing topographic contrast, for AFM imaging by removing only the MVD deposited silica that is not “protected” by densely packed OTS islands. Preferential film formation is observed in the lower regions of the MVD silica surfaces with the highest points (asperity peaks) being selectively removed during the etchant process. This removal is attributed to the presence of a low density disordered film present on the highest points. The extent of coverage to the surface asperities is suspected to depend on the curvature associated with the asperities. With increasing asperity curvature (sharpness) effective chain-chain hydrophobic interactions are reduced resulting in a decrease in packing density allowing the

etchant to penetrate between the OTS chains and removing the exposed MVD silica layer. From these results, it is determined that the LC phase do not deposit uniformly on the asperities. Based on this conclusion and due to published literature investigating OTS monolayers for tribological improvement on MEMS devices, it is suspected that the LC phase will deposit differently on every surface investigated and be dependant on the overall profile of the asperities. It is postulated that this is a contributing factor for why friction measurements vary from group to group and sample to sample on MEMS devices. The results warrant future consideration when trying to utilize OTS monolayers, regardless of temperature regime, on rough surfaces.

|                  | MVD Silicon Oxide |               |          | OTS Island Layer |                   |
|------------------|-------------------|---------------|----------|------------------|-------------------|
|                  | CA                | Thickness (Å) | RMS (nm) | CA               | OTS Thickness (Å) |
| Si(100)oxide     | <5°               | 18.6          | 0.17     | 85.4°            | 26.2              |
| MVD SilicaLayer1 | <5°               | 119           | 1.55     | 92.3°            | 26.4              |
| MVD SilicaLayer2 | <5°               | 175           | 1.89     | 92.2°            | 28.5              |
| MVD SilicaLayer3 | <5°               | 211           | 3.96     | 94.0°            | 25.4              |
| MVD SilicaLayer4 | <5°               | 255           | 3.97     | 88.3°            | 24.4              |
| MVD SilicaLayer5 | <5°               | 316           | 6.30     | 91.4°            | 27.3              |

Table 5.1: Water contact angle (CA), thickness, and RMS roughness (RMS) for deposited films.

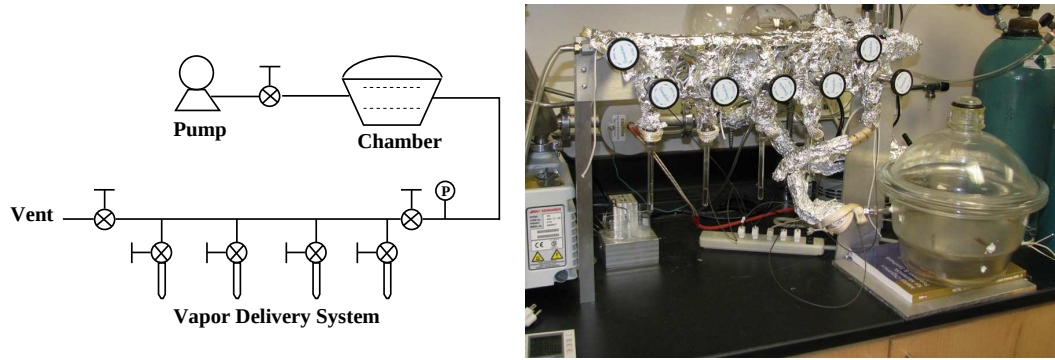


Figure 5.2: (Right) Simplified schematic of MVD system (Left) Photograph of MVD Silica system.

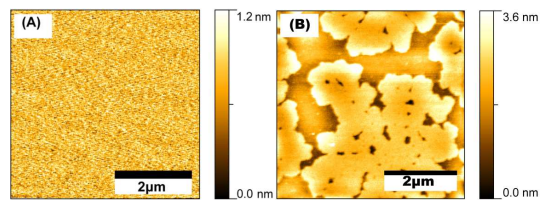


Figure 5.3: Two dimensional AFM scans of (A) a clean silicon surface, RMS roughness is 0.14 nm, and (B) 20 second OTS island film deposited on clean silicon surface "A".

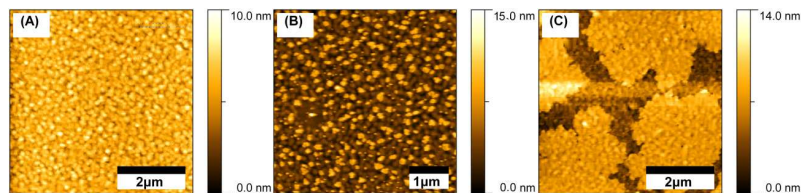


Figure 5.4: (A) AFM image of a MVD silica layer surface with thickness of 50.0 nm and a RMS roughness of 1.00 nm. (B) AFM image of a 20 second OTS deposition at room temperature on surface "A" after 60 seconds of etching. (C) AFM image of a 20 second OTS deposition at 10 °C on surface 'A' after 60 seconds of etching.

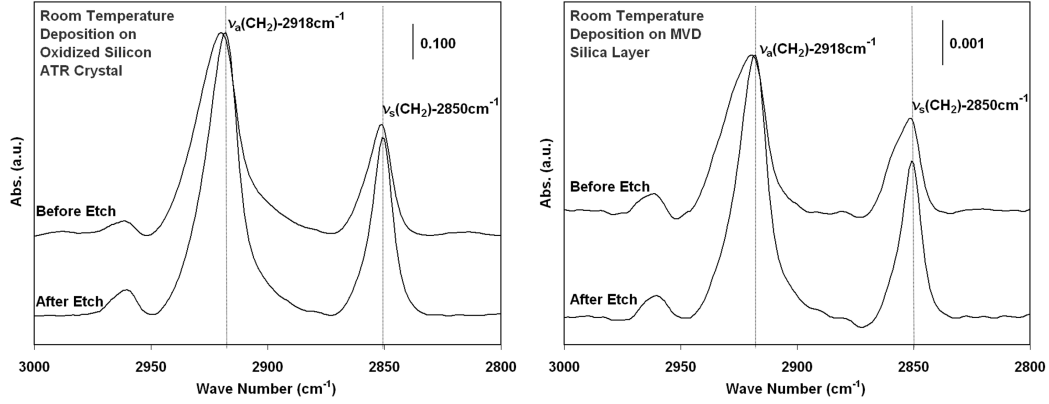


Figure 5.5: FTIR analysis of 20 second room temperature OTS island film deposition on an oxidized silicon ATR and on a MVD silica layer before and after etching.

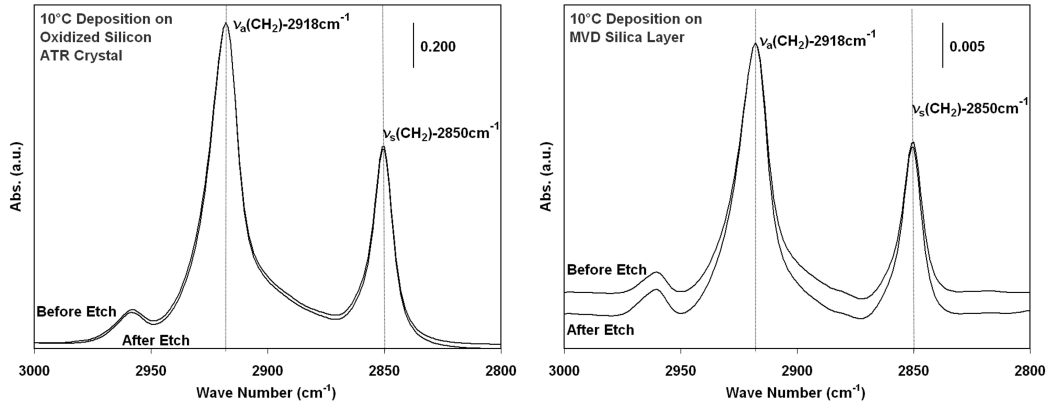


Figure 5.6: FTIR analysis of 20 second 10 °C OTS island film deposition on an oxidized silicon ATR and on a MVD silica layer before and after etching.

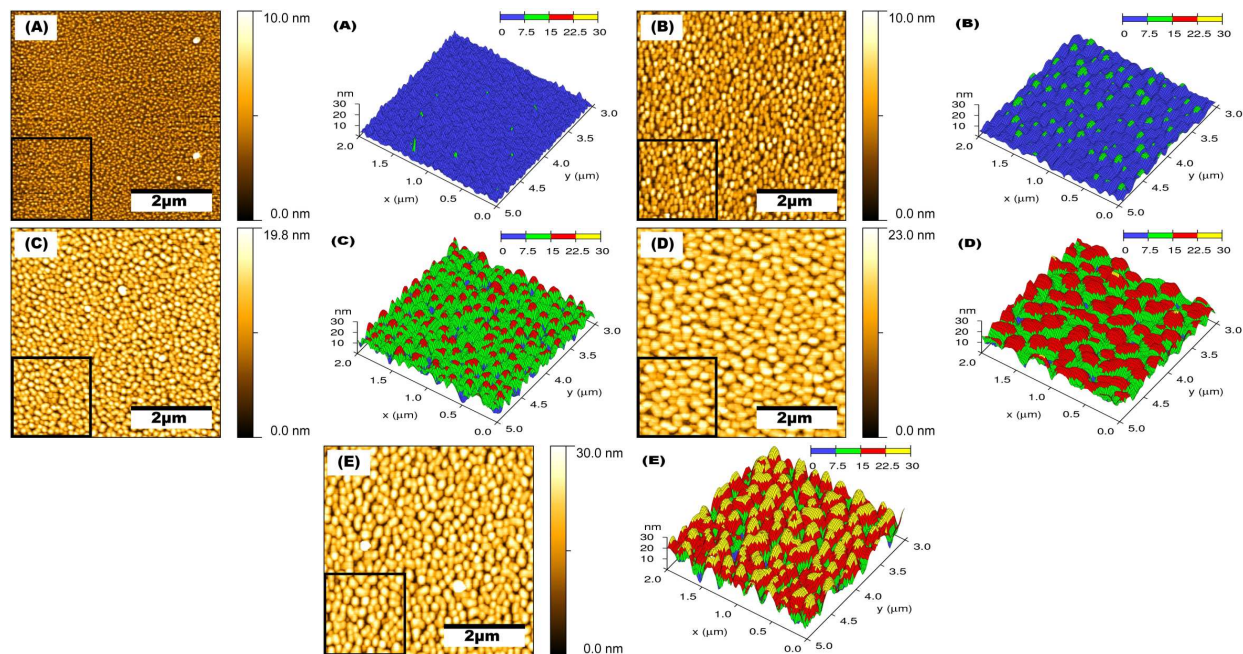


Figure 5.7: (Left) Two-dimensional representation of AFM data A-E of MVD deposited silica layers. (Right) Three dimensional representation of AFM data A-E on MVD deposited silica layers ( $2 \times 2 \mu\text{m}$ ) represented. Scaling arbitrarily set to highlight data.

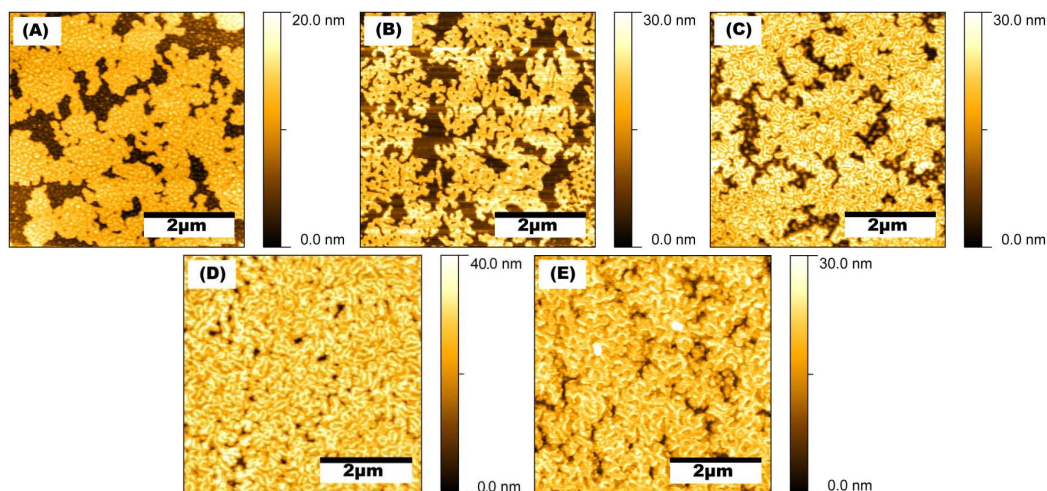


Figure 5.8: (A-E) 20 second OTS island film deposition on MVD silica surfaces of varying roughness and topography after exposure to etchant procedure.

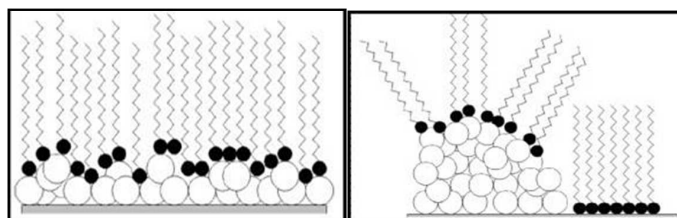


Figure 5.9: Illustration of proposed influence of topographical asperities on packing ability of OTS molecules.

## Chapter 6

### Influence of MVD Surface Topography on Interfacial Water Layers- Implications Toward OTS Monolayer Formation

#### 6.1 Motivation

The adsorption of water under ambient conditions has an important role in interfacial reactivity of surfaces. These surfaces adsorb water either, molecularly or dissociatively, with strongly bound surface hydroxyl groups acting as chemically reactive groups influencing surface properties like surface energy, chemical reactivity, catalytic activity, surface charging and adsorption and desorption of foreign molecules [139]. The thickness of the water film at sub-saturation conditions depends critically on the strength of the chemical bonds of water to the substrate, as well as hydrogen bonds between water molecules within the adsorbed water layer. The properties of these thin water films, in particular their thickness, structure and hydrogen-bonding to the substrate, as well as, within the water film are up to now not understood very well [140]. Investigations on smooth silicon oxide surfaces by Asay and Kim revealed changes in the molecular configuration and thickness of this adsorbed water layer as a consequence of increasing humidity [90], indicating the presence of an interfacial water layer with ice-like and liquid like bonding characteristics.

The behavior of water next to any surface is a result of the delicate balance between long-range interactions, the short-range water-surface atoms interactions, and the driving force for water molecules to keep their hydrogen bonds network intact. Although the short range interactions are not expected to depend significantly on the morphology of the surface, the hydrogen bonding network is quite sensitive to this aspect, as has been demonstrated, by recent molecular dynamics simulations where the issue of hydrogen bonding at interfaces is directly examined [141,142]. Studies by Trakhtenberg *et al.* of ice layers deposited on smooth

surfaces have revealed that the average interaction between the adsorbed water molecule and the surface is weaker than on a rough one. This is due to the fact that if the roughness is on the dimension of a few molecules, the adsorbate interact with several sites on the surface simultaneously. On the other hand, on the smooth surface the interaction is only with a single site indicating that on a smooth surface, the water molecules distribute more evenly. As a result, on a smooth surface, the adsorbed water molecules are more free to move and can arrange themselves in the most stable configuration. It has also been indicated that due to the relatively weak adsorbate surface interaction, in the case of smooth surfaces, the adsorbate desorbs from the surface at lower temperature [143]. In the case of a rough surface, water penetrates through structural irregularities on the surface allowing the water molecules to interact more with the surface and the surrounding chains, and therefore remain on the surface [144].

Researchers focusing on OTS monolayer formation have indicated, that the amount of water present on a silica surface, influences the formation mechanism and monolayer film properties. Most of these investigations have relied on high surface area materials to quantify water levels, but little analysis is performed to quantify the bonding structure of water associated with the interfacial surface on planar substrates. Through the use of a tunable MVD silica layer, we have produced thin silica surfaces of varying morphological characteristics that can be probed with FTIR to examine the interfacial regions. As described in section 4.2.1, the MVD silica layer has been shown to support a more extensive hydrogen bound water layer than traditional silicon substrates with a comparable reactivity toward OTS monolayer formation mechanisms, suggesting a link between water availability and surface reactivity. This investigation, however, examines only one surface type. The investigation in section 5.2 shows that, island adsorption amounts increased, as a result of an increase in MVD silica layer thickness regardless of RMS roughness values. At low roughness values, as illustrated by sample A in Figure 5.8, the islands appear to deposit unrestricted and similar to the native oxide depositions as shown in Figure 5.3B. At higher roughnesses, the islands

appeared to deposit more restricted to the lower portions of the topography (valleys). The influence of substrate roughness on the reactivity of the interfacial water layer remains an undefined parameter. The work described in this Chapter attempts to determine if substrate morphology influences the interfacial water layer that exists on the surface of MVD silica layers under adsorption conditions and thus its reactivity.

## **Experimental**

### **Materials**

Silicon wafers, p-type, with (100) orientation were obtained from University Wafer (Boston, MA). Tetrachlorosilane were obtained from Gelest, Inc. (Morrisville, PA) and used as received. Concentrated hydrofluoric acid (HF, 49%), acetone, and isopropanol were obtained from Fisher Scientific (Fair Lawn, NJ). Deionized water (18 M $\Omega$ -cm) was obtained from a Millipore filtration system.

### **Methods**

Cleaning methods and MVD silica layer formation schemes for the various samples have been previously described in Chapter 3.

## **6.2 Results**

Here, we present new evidence on the effect of surface topography on the structure and thickness of vapor deposited water layers. Various MVD silica layer surfaces are deposited onto plasma oxidized silicon FTIR crystals and exposed to  $\sim 45\%$  relative humidity. FTIR analysis of the interfacial water provides information with regards to the bonding structure and thickness of layers. It is known that water can form a varying degrees of a hydrogen bond networks depending on the physical and chemical conditions of the environment. When water is completely self-associated, each water molecule has four hydrogen bonds with its nearest neighbors forming a tetrahedral arrangement as evidenced on a smooth silicon oxide

surface. This is usually seen in crystalline ice structures exhibiting a broad vibrational peak at  $3250\text{ cm}^{-1}$  at or below the freezing point. Above the freezing temperature, the most thermodynamically stable structure of condensed water is the liquid form. In the liquid phase, the water molecule has on average two to three hydrogen bonds and exhibits a broad vibrational peak at  $3400\text{ cm}^{-1}$ .

In this work four MVD silica surfaces of varying topography and thickness are presented. The vapor deposition of MVD silica onto silicon oxides results in the formation of a robust silica layer ranging in thickness from 18.0 nm to 65.0 nm thick, as determined by ellipsometry on coated silicon substrates. AFM micrographs of the various silica films are shown in the inset views in Figure 6.2 through Figure 6.5. We obtained several images of area  $5.0\text{ }\mu\text{m} \times 5.0\text{ }\mu\text{m}$  for each substrate. The roughness values given represent the average over three images. The RMS roughness values range from 1.5 nm to 5.6 nm with a measurement deviation of  $\pm 0.1\text{ nm}$ .

The results of water adsorption onto the surface of the MVD silica-modified silicon ATR crystals are presented in Figure 6.2 to Figure 6.5. The MVD silica layers are utilized as the background spectra. The presence of the MVD silica layer on the surface determines the depth of penetration of the evanescent wave, but the silica layer itself is considered impervious to liquid water. In order to determine the thickness of bulk water that the evanescent wave interacts with, the thickness of the silica layer is subtracted from the depth of penetration of the evanescent wave. For example, for the silicon/silica system representing in Figure 6.2, the depth of penetration is approximately 505 nm at a  $45^\circ$  angle of incidence. In this experiment, the silica layer is 18.0 nm thick. This means that the adsorption measured for a bulk water sample on a silica film corresponds to 487 nm of water ( $505.0 - 18.0\text{ nm}$ ) at  $1632\text{ cm}^{-1}$  as measured with FTIR. All thickness calculations were based on bulk water adsorptions calculated in this manner.

The data set presented represent water adsorption at 45% relative humidity consistent with humidity conditions indicated for uniform OTS monolayer deposition on smooth silicon

oxide surfaces. The data in Figure 6.2 through Figure 6.5 show that the adsorbed water layer that exists on the MVD silica coated surfaces are dramatically different from sample to sample. In fact, water adsorption thicknesses range from 3.9 nm to 12.69 nm. The structure is dominated almost entirely by ice-like water in all four cases. But, the extent of hydrogen bonding, as represented by the shifting of the ice like adsorption peak at  $3200\text{ cm}^{-1}$ , indicates significantly different bonding strengths between the water and the MVD silica layer, as a consequence of, different sample morphologies.

Data from Figure 6.2 was previously presented in Section 4.2 and illustrates a MVD silica layer that is 18.0 nm thick with a RMS roughness of 1.5 nm that was compared with water adsorption on a traditional silicon oxide surface. The absorption spectra for bulk water on the MVD silica layer is presented, scaled down in size, to allow for a comparison of peak positioning. The arrows are representative of the  $3250$  and  $3400\text{ cm}^{-1}$  peaks associated with an ice like and liquid like structure, respectively and the water adsorption band located at  $1632\text{ cm}^{-1}$  represent water bending modes. The structure of the adsorbed water on the MVD silica layer was dominated by ice-like water. Furthermore, the ice-like water structure had an absorption peak centered near  $3119\text{ cm}^{-1}$ , which is  $127\text{ cm}^{-1}$  lower than the ice like peak associated with silicon oxide. It was concluded that more adsorbed water was on the surface of the MVD silica, which was more tightly bound compared to that existing on traditional silica surfaces. This was evidenced by a water absorbance spectrum dominated by an ice-like structure shifted to lower energy, greater signal intensity as compared to bulk water on the smooth silicon oxide, and a similar reactivity toward OTS monolayer formation.

The MVD silica layer in Figure 6.5 is 36 nm thick with an RMS roughness of 5.6 nm and showed the highest shift in the absorbance spectrum with peak positioning of  $3107\text{ cm}^{-1}$ , which is 143 wavenumber less than the peak associated with ice like water on smooth silicon oxide surfaces. The peak positioning for the interfacial water observed on MVD silica layer in Figure 6.4 and in Figure 6.3 were  $3183\text{ cm}^{-1}$  and  $3225\text{ cm}^{-1}$ . These MVD layers had

measured oxide thicknesses of 65 nm and 30 nm with a RMS roughnesses of 4.8 and 2.6 nm, respectively.

Trakhtenberg *et al.* performed FTIR analysis of pure ice and found two forms of ice distinguished by their FTIR spectra: an amorphous form, which is characterized by a peak at about  $3250\text{ cm}^{-1}$  with a shoulder at about  $3400\text{ cm}^{-1}$ , and a partially crystalline form, which exhibits an absorption peak at about  $3230\text{ cm}^{-1}$  with two shoulders at about  $3150$  and  $3350\text{ cm}^{-1}$  [143]. Additional structural investigations have found, ice like water molecules absorbing with a preferential structure have been shown to exhibit IR characteristics measured at  $3050\text{ cm}^{-1}$  as a consequence of surface field [105]. The results presented for this work are more in agreement with the absorbance values characterizing a partially crystalline form of ice vs. the amorphous form found to exist on smooth silicon oxide surfaces. In fact, all of the water spectra associated with the MVD silica layer suggest a partially crystalline form of ice present with varying degrees of hydrogen bonding on the surface at 45% humidity. This shift to lower energy indicates the interfacial water layer has a stronger degree of hydrogen bonding known to induce preferential orientation with the MVD silica-coated surface relative to the Si(100) surfaces.

In terms of interfacial water thickness, all four surfaces maintained more water on the surface, as compared to what has been measured on smooth silicon substrates. The MVD silica layer shown in Figure 6.2 was the thinnest MVD silica surface with a measured oxide thickness of 18.0 nm with a calculated interfacial water layer of 3.90 nm at 45% relative humidity. The thickness of water measured on the thickest MVD silica (65nm) layer was 12.7 nm thick at 45 % relative humidity, a value that is approximately 25% greater than the amount measured on a smooth silicon oxide surface at 98% relative humidity. The interfacial water layer thickness trended with increasing thickness of the MVD silica layers. The values obtained for the MVD silica layers shown in Figures 6.3 and in Figures 6.5 with silica thicknesses of 30 nm and 36 nm, respectively yields water amounts of 11.0 nm and 10.0

nm. The thickness values of the MVD silica layers are within the experimental variance for the ellipsometric technique and are considered to be very similar.

The roughness values associated with the MVD silica layer are between 7 and 25 times higher than those measured on a clean silicon oxide surface. It has been suggested by other researchers that in the case of a rough surface, structural irregularities on the surface allow water molecules to interact more with the surface forming a more tightly bound network [144]. Based on the data, it is postulated that the different silica morphologies exhibit varying degrees of hydrogen bonding which are dependent on topographical morphology. As explained in a Section 4.2 water found in nanoscopic regions are known to exhibit a more structured water character with thermodynamic properties differing from the bulk. Again, the confinement length scales for the water existing between the solid surfaces as experienced in this system is greatly over examined and the influence of nanoscopic regions is indistinguishable from the interfacial water.

No direct correlation between the degree of hydrogen bonding, the measured RMS roughness and interfacial water layer thickness values could be found. The only trend identified was between increasing water amounts and the MVD silica layer thickness. This is best illustrated in Figure 6.1 showing all four samples over layed at the same 45% relative humidity. This figure shows that as the thickness of the MVD silica layer increases the interfacial water layer thickness increases.

Evidence shows that more water is absorbed onto MVD silica layers as opposed to amounts found on traditionally smooth silicon surfaces as a function of relative humidity. Of additional complexity, it is believed that the shifting observed in the OH stretching region corresponding to different degrees of hydrogen bonding are interrelated to the morphology of the surface. Although, no direct trends between interfacial water structure and RMS roughness as influenced by specific topographical characteristics can be deduced, it is confirmed that the amount present vary as a function of the thickness of the silica layer.

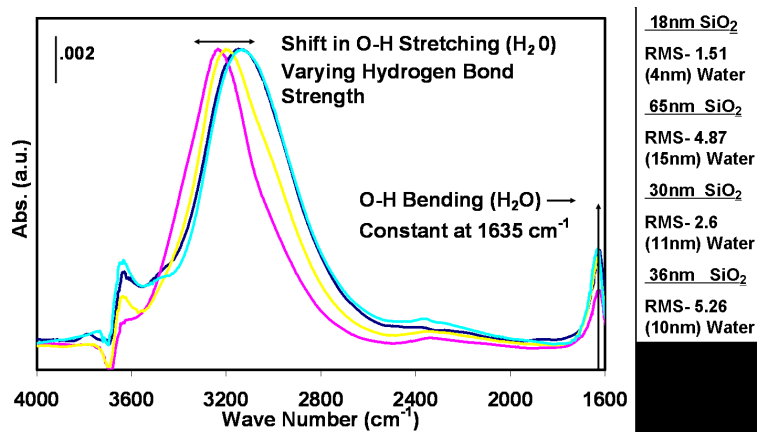


Figure 6.1: ATR-FTIR Spectra of adsorbed water at 45% relative humidity on various silica layers ranging in thickness from 18 to 65 nm. Bending mode at  $1635\text{ cm}^{-1}$  is constant but varying degrees of hydrogen bond strength presented.

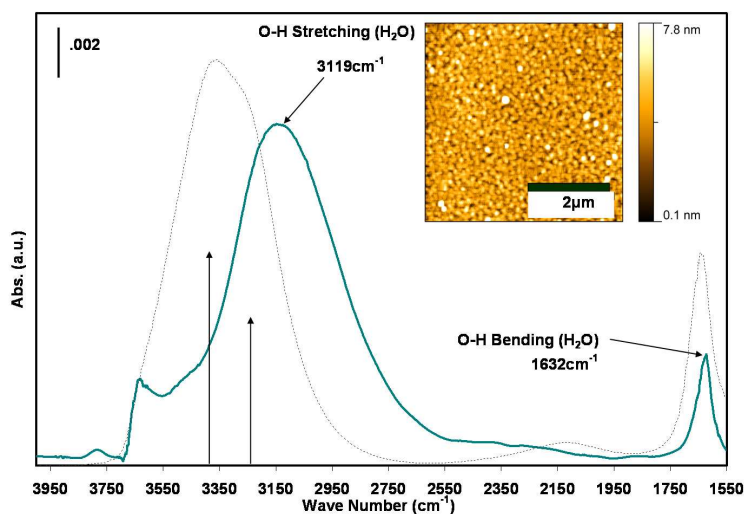


Figure 6.2: ATR-FTIR spectra of adsorbed water on the surface of a MVD silica layer on an oxidized silicon ATR crystal at  $\approx 45\%$  relative humidity. The peak positions of ice-like  $3119\text{ cm}^{-1}$  and the position of the O-H bending mode is marked at  $1632\text{ cm}^{-1}$ . [Inset View] Corresponding AFM Image  $5\mu\text{m} \times 5\mu\text{m}$ . Dotted line is a scan of pure liquid water on the MVD silica layer scaled down in size for peak position comparison.

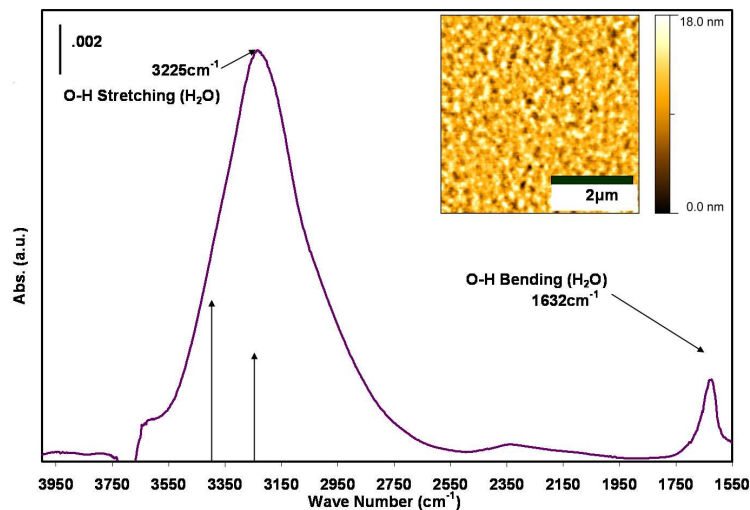


Figure 6.3: ATR-FTIR spectra of adsorbed water on the surface of a MVD silica layer on an oxidized silicon ATR crystal at  $\approx 45\%$  relative humidity. The peak positions of ice-like  $3225\text{ cm}^{-1}$  and the position of the O-H bending mode is marked at  $1632\text{ cm}^{-1}$ . [Inset View] Corresponding AFM Image  $5\mu\text{m} \times 5\mu\text{m}$ .

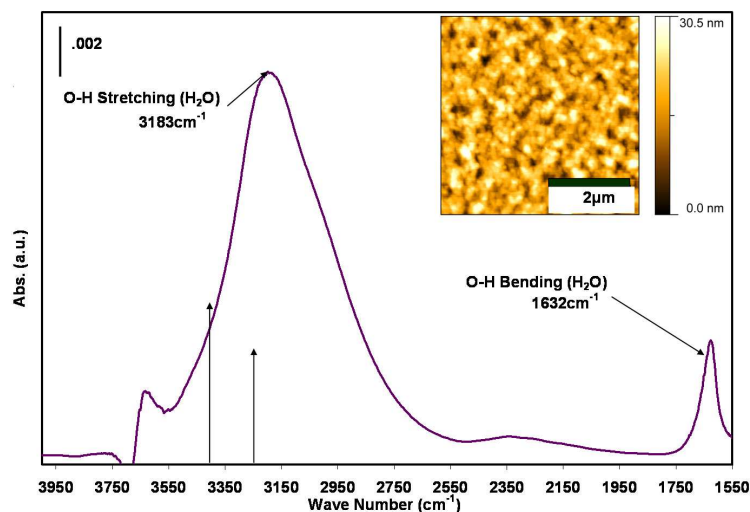


Figure 6.4: ATR-FTIR spectra of adsorbed water on the surface of a MVD silica layer on an oxidized silicon ATR crystal at  $\approx 45\%$  relative humidity. The peak positions of ice-like  $3183\text{ cm}^{-1}$  and the position of the O-H bending mode is marked at  $1632\text{ cm}^{-1}$ . [Inset View] Corresponding AFM Image  $5\mu\text{m} \times 5\mu\text{m}$ .

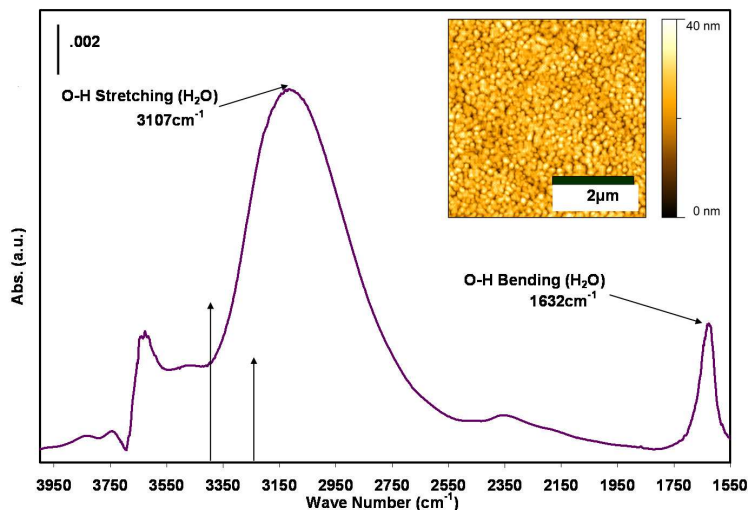


Figure 6.5: ATR-FTIR spectra of adsorbed water on the surface of a MVD silica layer on an oxidized silicon ATR crystal at  $\approx 45\%$  relative humidity. The peak positions of ice-like  $3107\text{ cm}^{-1}$  and the position of the O-H bending mode is marked at  $1632\text{ cm}^{-1}$ . [Inset View] Corresponding AFM Image  $5\mu\text{m} \times 5\mu\text{m}$ .

### 6.3 Conclusions

MVD silica surfaces varying in RMS roughness values and different thicknesses are presented. Water adsorption onto the MVD silica surfaces changes as a consequence of different morphological characteristics with increasing water thickness as a consequence of increasing MVD silica layer thickness. All of the MVD silica layers exhibit FTIR characteristics representative of an oriented highly hydrogen bound water layer. The amount of water absorbed onto the MVD silica layers was significantly higher than, what has been previously reported on smooth silicon oxide surfaces, with measurable variability from surface to surface. The extent of hydrogen bonding is shown to contrast, suggesting, water layers are more tightly bound to some samples versus others. It is suspected that the surface morphology is the contributing factor for the increased water adsorption and the varying degrees of hydrogen bonding observed. No correlation was confirmed between the degree of hydrogen bonding, the thickness of the MVD silica layer, and the RMS roughness values. The results suggest an interdependency between the characteristics under study. It is apparent from this investigation that additional considerations must be included in order to determine the surface

characteristics responsible and possible correlations. As a consequence of this investigation, it is postulated that the interfacial reactivity associated with the MVD silica surfaces will vary as a consequence of morphology adding an additional consideration for OTS monolayer formation on rough silicon oxide surfaces.

## Chapter 7

### Influence of Cleaning Procedures on Interfacial Water Layers on Silicon Oxide Surfaces- Implications Toward OTS Monolayer Formation

#### 7.1 Introduction

Octadecyltrichlorosilane film adsorption on silicon oxide surfaces is dependent on the interfacial water layer present under formation conditions. It is known that adsorbed water has an important role in interfacial reactivity and that the reaction of silicon oxide surfaces with water vapor leads to hydroxylation, influencing the reactivity and adsorptive properties. At sufficiently high relative humidities bulk water will condense on the surface forming thin water films that can alter the electrical and ionic conductivity of the surface, its adhesive and tribological properties, and the reactivity of the surface toward other gases in the atmosphere [140]. The properties of these thin water films under ambient conditions are noted as different from those of bulk water; for instance, the dielectric constant of water at interfaces is about 6, compared to 78 in the case of bulk water [145] and there is a proposed existence of an “ice like” and a “liquid like” structure that changes as a function of relative humidity [90]. The degree of hydration necessary for uniform coverage and the role this water layer plays in surface attachment of OTS molecules remains unclear. In general, attempts at controlling the surface reactivity on silicon surfaces during OTS film formation consist of maintaining a restricted environment to limit the amount of water present. This methodology has afforded mixed results with monolayer characteristics and quality still varying from study to study.

Adding additional complexity, the choice of preparation procedures for silica surfaces is known to influence surface characteristics. For example, water adsorption is dependent on the cleanliness of a surface- with contaminants (*i.e.* hydrocarbons) forming a hydrophobic barrier layers resulting in non-uniform water adsorption. Work done by Donose *et al.* examined

three commonly applied cleaning methods: the RCA ammonium and hydrogen peroxide wet cleaning method, a water plasma cleaning method, and a UV/ozone cleaning method and indicated that clean surfaces were produced with identical hydrophilicity, RMS roughness, and surface charge [146]. Yet, friction force measurements on the RCA cleaned surface were found to be several times greater than the other two cleaning methods. It was suggested that slight deviations in surface roughness generated the observed increase in friction due to increased water adsorption. Sirghi *et al.* found that small changes in surface roughness, drastically, affected the adhesive force measurements measured between a silicon AFM probe and a silicon oxide surface with surface roughness leading to a higher adhesive response for water [147]. In addition, studies on glass and quartz surfaces, have revealed changes in the thickness and structure of bound water dependent on initial surface treatments [148]. Various techniques have been used to evaluate the structure and thickness of water monolayers as a function of relative humidity on silicon oxide surfaces [90, 94, 140, 147, 149] and even these studies demonstrate a variety of different preparation procedures with conflicting results.

A multitude of preparation methodologies are identifiable in OTS monolayer literature and to date no preferred method has been established. Ultimately, researchers use various methods relying on surface measurements, such as: ellipsometry for measuring initial silicon oxide thickness, contact angle measurements and surface imaging techniques that examine surface energy and RMS roughness values to ensure consistency with what is expected of a uniform oxide film. There has been no examination of the interfacial water layer properties as influenced by preparation conditions, namely, the thickness, structure and degree of hydrogen bonding with the substrate. The importance of the interfacial water layer on OTS deposition has been established, but variation in monolayer properties exist at similar relative humidities, as does a difference in methodology used to prepare silicon oxide surfaces. This work is intended to examine any structural differences that may exist in the interfacial water layer as influenced by preparation methodology on traditional Si(100) in order to ascertain if changes in surface reactivity occur ultimately influencing OTS monolayer growth.

## Experimental Details

### Materials

Silicon wafers, p-type, with (100) orientation were obtained from University Wafer (Boston, MA). Tetrachlorosilane were obtained from Gelest, Inc. (Morrisville, PA) and used as received. Concentrated hydrofluoric acid (HF, 49%), acetone, isopropanol, Sulfuric Acid A298-212 Technical Grade, and Hydrogen Peroxide H325-500(30%) were obtained from Fisher Scientific (Fair Lawn, NJ). Deionized water (18 M $\Omega$ -cm) was obtained from a Millipore filtration system.

### Methods

Cleaning methods and preparation methodologies for the various samples have been previously described in Chapter 3.

## 7.2 Results

The influence of cleaning methodology on interfacial water layers in terms of structure and thickness at ambient temperatures under increasing levels of relative humidity is described. Four different cleaning methodologies are applied to silicon FTIR crystals and evaluated in terms of initial oxide thickness, RMS roughness and contact angle. All cleaning methodologies evidenced oxide surfaces with a  $CA < 5^\circ$  indicative of a clean and highly hydrophilic surface free of surface contamination with a layer of high density silanol groups on the surface. The oxide thicknesses ranged from  $\sim 1.0$  to  $2.0$  nm. The RMS roughness values were evaluated by using AFM images of the wafer surface and were comparable across all cleaning procedures (RMS  $\sim 0.2$  nm), but atomic resolution is not achievable with the AFM system utilized in this investigation.

Four cleaning procedures were selected for this investigation. Three of these consisted of a stepwise removal of native oxide followed with concurrent regrowth via different oxidation

techniques. This included oxidation with an RF Oxygen plasma treatment (HF-Plasma), UV-Ozone oxidation (HF-UVOzone), and chemical regeneration of oxide with a piranha solution (HF-Piranha). Detailed information is listed in Chapter 3 for conditions utilized for oxide regrowth. The fourth condition was a comparison to previously reported data and involved UV/Ozone oxidation cleaning of the pre-existing native oxide (Native Oxide-UV Ozone).

To investigate the evolution of adsorbed water, the clean oxidized silicon ATR surfaces were purged with dry nitrogen, until no differences were noted in the spectra. Each dried surface was utilized as the corresponding background spectra for investigation water adsorption under varying relative humidities ranging from 20% to 80%. All experiments were run at  $27 \pm 0.5$  °C. The adsorption of water onto the oxidized silica surfaces was conducted by varying the relative flow rates of two nitrogen streams- one is dry and the other is saturated with water vapor. As described in subsequent chapters, the data analysis method for studying the evolution of the adsorbed water layer thickness on silicon through ATR-FTIR spectroscopy, is as described by Asay *et al.* [90]. The thickness of the adsorbed water layer is determined by comparing the intensity of the water O-H bending mode absorption located at  $1635 \text{ cm}^{-1}$  to the intensity of the same peak for a bulk liquid water sample on the same surface under study, which is limited by the depth of penetration of the evanescent wave. The thickness determined in this manner can be converted to the number of monolayers by dividing by the mean van der Waals diameter of water, which is  $2.82 \text{ \AA}$  [90–92]. The position of the O-H bending mode located at  $1635 \text{ cm}^{-1}$  has been shown as constant and is not influenced by the degree of hydrogen bonding or structure of water present on the ATR surface [93].

The results of water adsorption on the oxidized silicon ATR crystals surfaces are presented in Figure 7.1 to Figure 7.2. The absorption spectra for bulk water on the oxidized silica layer is presented, scaled down in size, to allow for a comparison of peak positioning. The arrows are representative of the  $3250$  and  $3400 \text{ cm}^{-1}$  peaks associated with an ice like and liquid like structure, respectively and the water adsorption band located at  $1635 \text{ cm}^{-1}$

represent water bending modes. For comparative purposes, a silicon ATR crystal was cleaned following the method utilized in the work of Asay *et al.*, by cleaning a native oxide layer without initial oxide removal and regrowth. This was accomplished by UV/Ozone treatment in air for 30 minutes and resulted in an ellipsometric oxide thickness of 1.8 nm. The results presented are in good agreement with Asay and Kims previously reported data.

Asay and Kim describe three distinct growth regions, which occur approximately from 0-20% RH, from 20-60% RH, and from 60-100% RH. The first region is dominated by the formation of an ice-like water structure, which continues to grow to about 20% RH, after which point the formation of ice-like water slows, and the adsorption of liquid water begins. Above 60% RH, no further increase in the ice-like water structure is observed, but the growth is completely dominated by adsorption of liquid water. At nearly 100% RH, they report an adsorbed water layer that is approximately 10 monolayers thick (about 5 monolayers at 80% RH).

Our results in Figure 7.1 (top) are consistent with these observations. The position of the ice like peak is  $3258\text{ cm}^{-1}$  and the liquid like peak is found to evolve at  $3400\text{ cm}^{-1}$  and exhibit the same structural evolution as a consequence of increasing relative humidity. The range of thicknesses obtained from 20-80 % relative humidity are consistent with reported values revealing an average thickness at 20% RH of  $\sim 0.5\text{ nm}$  increasing to  $\sim 1.5\text{ nm}$  at 80% as illustrated in Figure 7.3. Studies show that a bare silicon wafer covered with a layer of native oxide ( $\text{SiO}_{2-x}$ ), maintains siloxane rings which are very stable against hydrolysis, therefore exhibiting properties more hydrophobic in nature. It is suspected that this hydrophobic characteristic contributes to the observed structural evolution of the interfacial water. Studies of hydrophobic surfaces have revealed that water adsorption is dependent on surface defects with water first nucleating on these spots in a well ordered manner becoming more disordered at increasing thicknesses. Native oxide surfaces are known to exist with defects in the  $\text{SiO}_x$  structure. It is suspected that water condenses at these defects first allowing for a more ice like bonding character (higher hydrogen bonding) [150] with

subsequent layers interacting less with the surface thus display more bulk like properties at increasing thicknesses.

Major differences are identified between the surfaces initially treated with HF in comparison to the UV/Ozone treatment of native oxide. HF etching is a common technique found in silicon processing literature. Etching the native oxide (and any impurities it contains) of Si(100) in aqueous HF is known to produce a hydrogen-terminated Si surface stable against native oxidation in air for a few hours [151]. In fact, studies indicate that HF processing creates a Si(100) surface that is detectably smoother than the native oxide techniques resulting in a more homogeneous post oxidation Si/SiO<sub>2</sub> interface [152,153]. Unfortunately, H-terminated silicon surface are active in air and if oxidation is not controlled, surfaces can degrade morphologically to form nonuniform oxides at room temperature and adsorb contaminations [154]. In addition, Grunthaner and Maserjian found that an HF stripped silicon surface oxidized at a faster rate than a surface where no HF strip was performed [155]

A variety of techniques have been introduced to control oxidation on H-terminated silicon surface resulting in an Si/SiO<sub>2</sub> interface. The sample illustrated in Figure 7.2 (top) was treated with HF and then RF Plasma exposed for oxide layer growth. This treatment resulted in an oxide layer 2.0 nm with more adsorbed water as compared to all other cases under study with an interfacial water thickness ranging from 1.1 nm at 20% RH to a final thickness of 2.4 nm at 80% RH. A significant advantage of plasma processing stems from lower oxidation temperatures which minimizes dopant diffusion and the generation of oxide defects. Unfortunately, the high electric fields present during the processes can cause damage to the resultant oxide, in particular, a high density of interface traps often result [156]. It is suspected that the cleaning of the surface by oxygen plasma induces charge on the surface [157], which can affect the adsorbed water layer structure [158].

The sample illustrated in Figure 7.2 (bottom) was treated with HF and then UV/Ozone exposed for oxide layer growth. This treatment resulted in an oxide layer measured at 2.0 nm. Hydrogen-terminated silicon surfaces, have been found to be readily oxidized by ozone

at low temperatures. Ciu *et al.* found that room temperature ozone treatment results in the formation of various stoichiometric ratios of oxide films as a consequence of exposure time with film thicknesses measured above 1.5 nm maintaining more bulk like properties as represented by Si-O-Si peak frequencies [159]. This HF/Ozone treatment resulted in the lowest measured thicknesses in the water structural layers as compared to all other cases with an interfacial water thickness ranging from 0.1 nm at 20% RH to a final thickness of 0.7 nm at 80% RH. This lower level of water adsorption is again contributed to the interfacial charge associated with the oxide surface as ozone-grown oxides are found to exhibit less charge trapping as compared to other oxidation methods [160]

Sulfuric-hydrogen peroxide acid mixtures ( $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  aka piranha treatment) are known to produce uniform SiOH on the surface of silicon surfaces by oxidizing the contaminants present on the surface along with surface oxidation, leading to the formation of a wet-chemical oxide ( $\text{SiO}_{2-x}$ ) rendering the surface hydrophilic after water rinsing, with the installation of SiOH groups. For the data presented in Figure 7.1 (bottom) this technique was used post HF etching. The resultant oxide was measured at 0.8 nm and was the thinnest oxide analyzed. The thickness range for the interfacial water layers was between that found on the HF/Ozone and HF/Plasma samples ranging from 1.0 nm to 1.3 nm thick at 20% and 80% RH.

As evidenced, surfaces initially treated with HF passivation display similar growth structures regardless of the oxidation treatment exhibiting ice-like and liquid water peaks growing together, and at nearly an equal rate, across all relative humidities studied. In contrast, the different oxidation schemes produce varying relative thicknesses (amounts) of interfacial water as a function of relative humidity. This suggests that the interfacial water layer exists in a similar hydrogen bound state on each HF treated surface and that the initial conditioning of the silicon surface determines the bonding structure. Previous studies indicate that HF processing creates a Si(100) surface that is detectably smoother resulting in a more homogeneous post oxidation Si/SiO<sub>2</sub> interface [152, 153]. It is suspected that the HF treatment

results in a more uniform oxide film regardless of the oxidation methodology. The reactivity of this surface as inferred from the “binding structure” should be equivalent. It is speculated that varying degrees of charging associated with the oxidation procedure are responsible for the observed thickness differences. Surface charging can lead to a more ordered water layer with water molecules dipoles being more oriented in the plane of the sample with the extent of charging affecting the overall thickness obtained. The native oxide surface exhibited a different structural evolution, and is postulated that, this is due to the hydrophobic nature of the oxide in addition to a rougher silicon oxide layer with inherent defects associated with ozone treatment without removal of the native oxide. From STM experiments ozone exposure on native oxide surfaces were found to etch the surface and thus to affect the surface structure resulting in a rougher surface [156]. The evolution of interfacial water appears more consistent with water adsorption on a hydrophobic surface this is speculated to be due to defects and the chemistry of native  $\text{SiO}_2$  surface.

### 7.3 Conclusions

Different surface treatments resulted in different water structural layer characteristics on oxidized silicon surfaces. Surfaces initially stripped of the native oxide showed similar structural evolution as influenced by the etchant and initial surface roughness. Different thicknesses were observed on all HF treated samples as a consequence of charging effects associated with the oxidation techniques. The native oxide sample showed a different structural evolution indicating a decrease in the degree of hydrogen bonding as compared to the other techniques. The thickness of the water structural layers found on the native oxide layers were consistent with previously reported results. Different interfacial water structures and thickness have been identified based on different surface treatments. This difference in absorption suggest varying interfacial reactivity in terms of the surface energy, chemical reactivity, surface charging and will ultimately influence adsorption of OTS molecules. These

findings highlight the importance of the pretreatment procedure and offer an explanation for why variation in reported results regarding OTS films still exist.

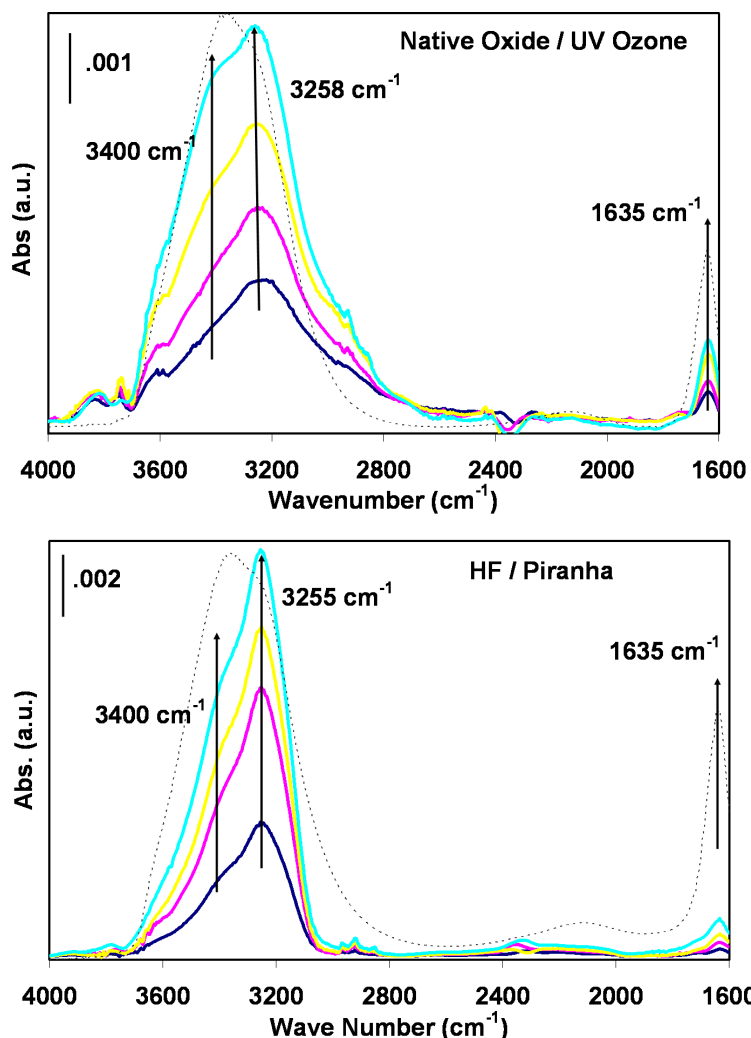


Figure 7.1: ATR-FTIR spectra of adsorbed water on the surface of an oxidized silicon ATR crystal at increasing relative humidities. (Top) Native oxide exposed to a 30 minute UV ozone treatment with a measured oxide thickness of 1.8 nm. Ice-like and liquid water are indicated with arrows at  $3258\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$ , respectively, and the position of the O-H bending mode is marked at  $1635\text{ cm}^{-1}$ . (Bottom) HF Removal of native oxide followed by Piranha oxidation with an oxide thickness of 0.9 nm. Ice-like and liquid water are indicated with arrows at  $3255\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$ , respectively, and the position of the O-H bending mode is marked at  $1635\text{ cm}^{-1}$ . The direction of increasing relative humidity is from bottom to top. Spectra correspond to relative humidities of 20%, 40%, 60% and 80% with an accuracy of  $\pm 2.0\%$

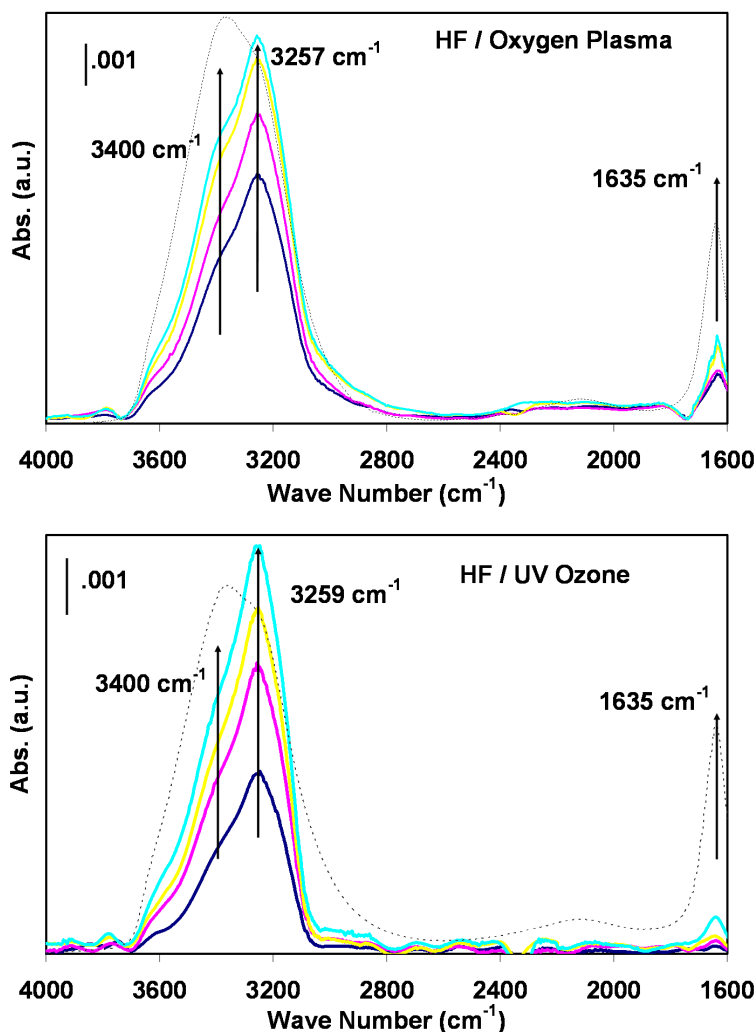


Figure 7.2: ATR-FTIR spectra of adsorbed water on the surface of an oxidized silicon ATR crystal at increasing relative humidities. (Top) HF removal of native oxide followed by RF oxygen plasma treatment with a measured oxide thickness of 2.0 nm. Ice-like and liquid water are indicated with arrows at 3257  $\text{cm}^{-1}$  and 3400  $\text{cm}^{-1}$ , respectively, and the position of the O-H bending mode is marked at 1635  $\text{cm}^{-1}$ . (Bottom) HF Removal of native oxide followed by UV Ozone oxidation with an oxide thickness of 2.0 nm. Ice-like and liquid water are indicated with arrows at 3259  $\text{cm}^{-1}$  and 3400  $\text{cm}^{-1}$ , respectively, and the position of the O-H bending mode is marked at 1635  $\text{cm}^{-1}$ . The direction of increasing relative humidity is from bottom to top. Spectra correspond to relative humidities of 20%, 40%, 60% and 80% with an accuracy of  $\pm 2.0\%$

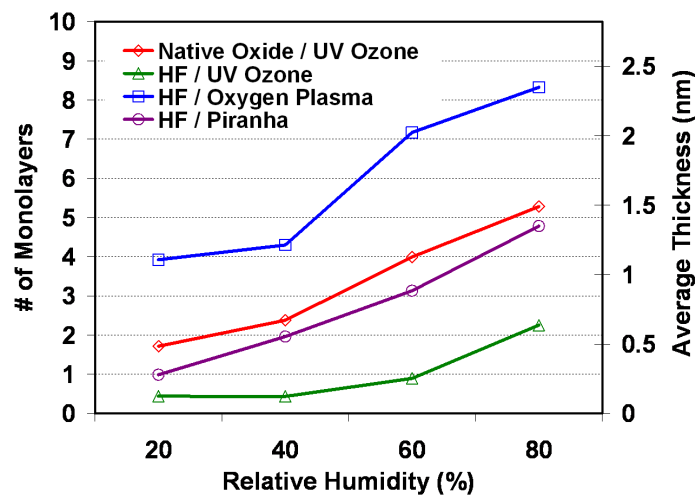


Figure 7.3: Comparison interfacial water layer thickness as influenced by cleaning methodologies on Si(100) with increasing levels of relative humidity.

## Chapter 8

### Overall Conclusions / Contribution to OTS Monolayer Formation

Controlling friction, adhesion and wear on MEMS surfaces is of critical importance for the proper functioning of MEMS devices. In recent years, many studies have been dedicated to understanding how OTS monolayers modulate friction, adhesion and wear in such devices. It has been deduced that assembly conditions and film composition play a critical role in the performance of the film as indicated by the films ability to create well ordered assemblies on smooth surfaces. Research shows that reaction conditions have dramatic affects on the formation properties of OTS films. There is an identified correlation between OTS monolayers ability to form densely packed monolayers and the level of friction and adhesion abatement attainable.

In most studies of friction and adhesion of MEMS interfaces, it is assumed that the structure of SAMs formed and their properties are comparable to those observed when assembled on flat surfaces. If an OTS monolayer exists in an ideal densely packed state on smooth surfaces, gauche defects within the structure, contribute to the weakening of lateral chain-chain interactions reducing film integrity. MEMS surfaces such as those of polycrystalline silica deviate from the traditional tribological observations on smooth surfaces. Typically, MEMS surfaces consist of nanoscopic asperities that interact during intentional or intermittent contact and it is the asperities and the monolayer film on the asperities that dominate the tribological properties of these surfaces.

Unfortunately, resultant tribological improvements have proven unpredictable as the monolayers have been translated to MEMS surfaces with topographical asperities. This has been demonstrated by friction and adhesion studies performed on MEMS test platforms created from machined polycrystalline silicon.

This dissertation evidences a relationship between monolayer adsorption characteristics and topographical asperities with observed variations in monolayer order resultant from surface roughness. Results show that the packing structure of OTS monolayers is dependant on local asperity curvature varying significantly from that observed on flat surfaces. A silica film produced from the low temperature, vapor-phase hydrolysis of tetrachlorosilane with a tunable topography was leveraged as a novel investigative platform to reveal the influence of surface topography on OTS film formation.

An examination of interfacial properties of the MVD silica layer revealed a highly hydroxylated surface lacking free OH groups with an ordered water structure that is more tightly bound due to a higher degree of hydrogen bonding associated with the hydroxylated surface. In contrast to previously reported results, the mechanism of OTS films growth is found to be comparable to those formed on traditional silicon oxide surfaces, despite a higher amount of water present and a lack of free OH groups. As a consequence, it was evidenced, that the role of free OH groups on the formation mechanisms for OTS film formation are inconsequential, highlighting the importance of interfacial water on the OTS film formation process. It is shown that high quality OTS films can be formed on a highly hydrated surface as evidenced with traditional analytical techniques optimized for smooth silica surfaces.

A dilute etchant technique was developed to provide topographic contrast for AFM imaging enabling an investigation true monolayer location relative to topographical asperities. The results evidence a preferential monolayer adsorption and variation in molecular packing density influenced by surface topography. It is shown that the adsorption of OTS monolayers occurs differently on various surface topographies with preferential adsorption occurring in the lower regions of the surface leaving exposed topographical asperities. The extent of coverage to the surface asperities is suspected to depend on the curvature associated with the asperities. Surfaces with higher curvature support monolayers less laterally interacted on the peaks. This will result in a lowered tribological characteristics based on

asperity-asperity interactions. From these results, it is determined that the LC phase do not deposit uniformly on the asperities.

In addition, a difference in surface reactivity is observed as a result of different surface topographies with thicker silica layers maintaining a higher coverage at similar reaction times and conditions. This observation lead to a detailed investigation of the interfacial water layer and changes in surface reactivity. Water adsorption onto the MVD silica surfaces is shown to change as a consequence of different morphological characteristics. All of the MVD silica layers exhibit FTIR characteristics representative of an oriented highly hydrogen bound water layer. The amount of water absorbed onto the MVD silica layers was significantly higher than what has been previously reported on smooth silicon oxide surfaces with measurable variability from surface to surface. The extent of hydrogen bonding is shown to contrast suggesting water layers are more tightly bound to some samples versus others. It is suspected that the surface morphology is the contributing factor for the increased water adsorption and the varying degrees of hydrogen bonding observed. No correlation was confirmed between the degree of hydrogen bonding and the RMS roughness values. But, the extent of water present on the surface correlates well with the thickness of the MVD silica layer. The higher content of interfacial water causes an increase in the rate of adsorption as observed under similar reaction conditions and increased coverage. As a consequence of this investigation, it is postulated that the interfacial reactivity varies as a consequence of morphology adding an additional consideration for OTS monolayer formation on rough silicon oxide surfaces.

Based on these observations it is suspected that OTS monolayers will deposit differently on every surface investigated and be dependent on the overall profile of the asperities. In addition, the interfacial reactivity associated with adsorbed water will vary based on the interfacial topography. It is postulated that this is a contributing factor for why friction measurements vary from group to group and sample to sample on MEMS devices and warrants future considerations when trying to utilize OTS monolayers deposited from the mixed regime on surfaces.

In addition, different surface treatments (etching and oxidation methods) resulted in different water structural layer characteristics on smooth oxidized silicon surfaces. Surfaces initially stripped of the native oxide showed similar structural evolution as influenced by the etchant and initial surface roughness. Different thicknesses were observed on all HF treated samples as a consequence of charging effects associated with the oxidation techniques. The native oxide sample showed a different structural evolution indicating a decrease in the degree of hydrogen bonding as compared to the other techniques. The thickness of the water structural layers found on the native oxide layers were consistent with previously reported results. Different interfacial water structures and thicknesses have been identified based on different surface treatments. This difference in absorption suggest varying interfacial reactivity in terms of the surface energy, chemical reactivity, surface charging and will ultimately influence adsorption of OTS molecules. These findings highlight the importance of the pretreatment procedure and offer an explanation for why variation in reported results regarding OTS films still exist on smooth surfaces.

A novel high surface area silica support is introduced capable of sustaining loadings measurable with TGA analysis. This support exhibits a similar reactivity toward OTS film decomposition as compared to other high surface area silica materials and sustains higher loadings. In addition, results suggest that due to the lack of porosity, low degree of surface curvature, and the increased loadings obtained, that the fibrous silica, provides a more representative support material for the determination of loading information for comparison to the films produced on planar substrates. This support has been utilized to determine the influence of annealing environments on the thermal stability of OTS films. It was shown that films annealed under an air environment decomposed at lower starting temperatures and to a greater extent than those annealed under inert atmospheres.

It is concluded that MEMS researchers focused on using OTS monolayers for friction and adhesion improvement must first understand the consequence of surface topography and interfacial reactivity on the deposition mechanics and overall film quality. Ultimately, this

work indicates that variation in topographical asperities will result in an unpredictable OTS monolayer deposition dependant on surface topography. This unpredictable film will result in device to device variation in tribological performance. Future work in the field should be aimed at controlling surface topography and understanding what characteristics are required to ensure an optimal film.

In conclusion this work shows that researchers must determine a nominal surface topography and interfacial water structure required for successful utilization of OTS monolayers for friction and adhesion improvement on rough surfaces.

## Chapter 9

### Self-Assembled Octadecylphosphonate Monolayers on Metal Oxide Substrates

#### 9.1 Motivation

This research is a portion of a collaborative research effort designed to bridge the scientific and technical areas of micro/nano tribology. The overall goal of this research is to improve understanding of the molecular origins of friction by investigating microscopic, multi-asperity interfaces in well-controlled experiments and by comparing results across velocity regimes. More specifically, in order for these comparative efforts to be successful it is necessary that the interfaces be structurally identical. The intent of this portion of the collaborative effort was to optimize the coating methodology necessary to produce an optimal densely packed monolayer translatable to various technologically relevant substrates in an effort to provide an uniform interface comparable across different micro/nano tribological techniques.

#### 9.2 Background

The principal research tools of nanotribology have been the AFM, the quartz crystal micro balance (QCM), the surface force apparatus (SFA), and MD simulations, along with myriad extensions and refinements of these [4, 61, 120]. Unfortunately, there have been relatively few attempts to compare measurements of friction between different tribological instruments. The information revealed about friction is decidedly instrument dependent, since the contact area, pressures and velocities accessible to a specific instrument affect the friction of the interface. Well controlled comparisons of friction results from different techniques are important in order to gain a better understanding of friction in different

physical regimes. To date there have been few comparative studies between the techniques of AFM and SFM. Many more comparative studies of this kind are needed before researchers in micro/nanotribology can be sure that different techniques reveal consistent information about frictional affects. To enable this type of comparison it is necessary to utilize the same interface and substrate materials. SAMs are to be utilized given their ability to form well defined and uniform interfaces. These interfaces can be tailored to study the resulting effects on friction and other properties.

### 9.2.1 Research Objectives

Various surface engineering techniques have been introduced to reduce friction and adhesion and one general approach is to avoid the formation of water layers on the surfaces by interfacial treatments that provide a stable hydrophobic surface, thereby eliminating capillary forces. To be effective, such chemical modification, must also be stable both under ambient and elevated temperatures, be hard and wear resistant, and prove conformal on surfaces with inherent roughness. Much research has been dedicated to the chemical modification of surfaces with coatings designed to tailor the interfacial properties indicating that despite the measurement scale, the frictional properties are influenced by molecular tilting, inter atomic interactions, interface stability, adhesion to substrate, and gauche defect formation. Dissipation of frictional energy in SAMs through the formation of gauche defects has been thoroughly investigated concluding that increased disorder correlates with higher gauche defects and an easier dissipation of frictional energy thus stressing the importance of uniform film structure and tribological improvement.

Phosphonate monolayers are the focus of this investigation as they show significant promise to define new directions in MEMS technology and have the potential to overcome the limitations of silane-based SAMs with respect to immersion and thermal stability. Prior investigation of alkylphosphonic acids on flat Al sheets showed that SAM formation of alkyl

phosphonates on Al surfaces relies on the hydroxylation of the oxide (alumina) layer. Generally, chemisorption of alkyl phosphonic acid occurs by proton dissociation to form an alkylphosphonate species. Due to the nature of the surface reaction between alkylphosphonic acids and OH surface species, this class of self-assembled monolayers, could overcome some of the plaguing reproducibility issues associated with silane chemistries such as hydration control, inherent processing difficulties, and polymerization concerns as related to metal substrates. In addition to offering a physical protective barrier, the monolayers, by virtue of their inert hydrophobic nature, also provide a degree of chemical protection [80]. The tribological mechanisms for surfaces coated with phosphonate SAMs have not yet been studied extensively, although these monolayers have recently begun to attract the attention of tribology research groups [25, 79]. Friction force measurements with the phosphonate monolayer coated smooth alumina demonstrated a remarkable improvement in performance when compared to untreated alumina surfaces the coated surfaces exhibited remarkable robustness and resistance to wear over each experiment.

For comparison purposes, octadecylphosphonic acid monolayers (ODP) were selected as the SAM of choice for this study enabling a tribological comparison to an already extensively studied silane counterpart octadecyltrichlorosilane (OTS) with proven efficacy. Although the bonding mechanism associated with ODP is significantly different than that proposed for OTS, the hydrophobic properties associated with its 18 carbon segments should provide a similar tribological improvement assuming a comparable packing efficiency. The phosphonic acids undergo a condensation reaction with surface bound alumino hydroxyl (-Al-OH) species to form aluminophosphonate compounds with  $H_2O$  as a byproduct [81]. An inelastic electron tunneling spectroscopy study of the adsorption and structure of alkyl phosphonic and alkyl phosphoric acids suggested that tridentate species were formed with the aluminum oxide surface [82] but other groups have suggested a bidentate species [161]. It has been shown that ODP adsorbs preferentially to aluminum surfaces that are hydroxylated in air and that an increase in the surface hydroxyl density can accelerate adsorption kinetics [83]. Such an

acceleration can be explained by the adsorption of the phosphonic acid via surface hydrogen bonds prior to the condensation reaction, leading to the finally adsorbed phosphonate [84].

After considering several metal oxides, we have chosen to focus on aluminum oxide as the structural material. Two aluminum oxide substrate materials reactive toward ODP deposition were identified and evaluated in this work. Based on its commercial availability as a quartz micro balance electrode and its promise as a component in device fabrication the first focused on an oxidized aluminum surface. The second support material was aluminum oxide spheres. These spheres are representative of those to be attached to AFM and SFM probes through collaborative efforts, but obtained in bulk with a larger distribution in size as compared to those mounted to the tribology probes. Acquisition and utilization of this representative material allowed for additional analytical insight before direct translation of the ODP films to those spheres attached to the tribology probes.

In order to prepare an ideal interface a detailed mechanistic study was performed to analyze the quality of these films. In the study of monolayers and thin films on surfaces, both their surface and bulk properties are important. Several analytical methods are introduced for characterization of the monolayers and thin films produced throughout this work. The deposition quality was assessed in terms of packing density and uniformity with FTIR, TGA, ellipsometer, contact angle analysis and TGA.

## **9.2.2 Results**

### **Sputtered Aluminum Surfaces**

The ODP monolayer formation mechanism was investigated on an oxidized sputtered aluminum surface. The surfaces were cleaned and plasma oxidized as described in Chapter 3. The clean oxidized surfaces were analyzed with AFM and ellipsometry and an initial oxide thickness was measured at 2.5 nm with a RMS roughness of 4.3 nm. This surface is illustrated in Figure 9.2 following the plasma oxidation. The sputtered aluminum surface was compared to the surface of an aluminum coated quartz crystal micro balance and the surface

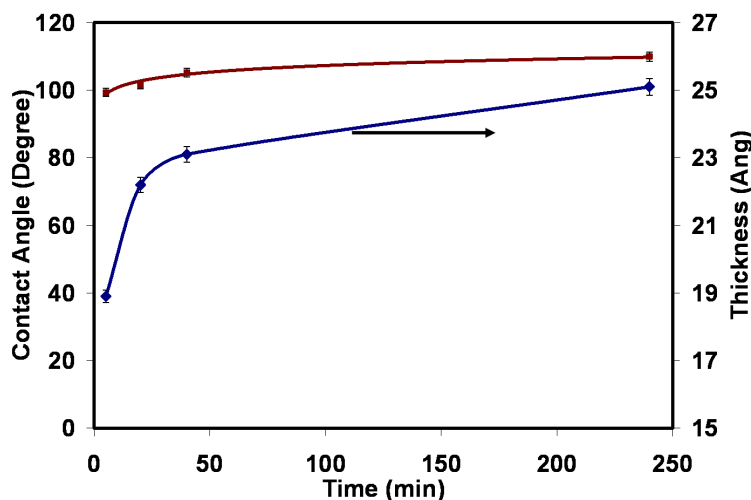


Figure 9.1: Water contact angle (squares) and ellipsometric film thickness (diamonds) vs. immersion time for ODP films on oxidized aluminum oxide surfaces at room temperature.

roughness and oxide values were found to be similar. Due to the limited availability and high cost associated with the quartz crystal micro balance substrates initial characterization experiments focused solely on the sputtered aluminum surface.

Deposition of the ODP monolayers as described in Chapter 3 were performed at room temperature under atmospheric conditions with film formation times ranging from 5 sec to 4 hours. Contact angle measurements ranged from 99 to 109.9° consistent with previously reported results obtained on similar aluminum oxide surfaces [83]. Contact angle measurements indicated that no significant changes in contact angle were observable after 1 hour of deposition. But, ellipsometric measurements indicated that coverage increased as a function of immersion time with thickness measurements ranging from 18.9 Å to 25.1 Å at higher immersion times. These results are illustrated in Figure 9.1.

AFM was performed on each substrate before and after deposition, generally, not enough contrast was visible between the phosphonate film and the underlying substrate with features indiscernable from the underlying surface topography. For illustration a monolayer formed after 4 hours of deposition on the sputtered aluminum substrate with a contact angle of 109.9° is illustrated in Figure 9.3 for comparative purposes with Figure 9.2.

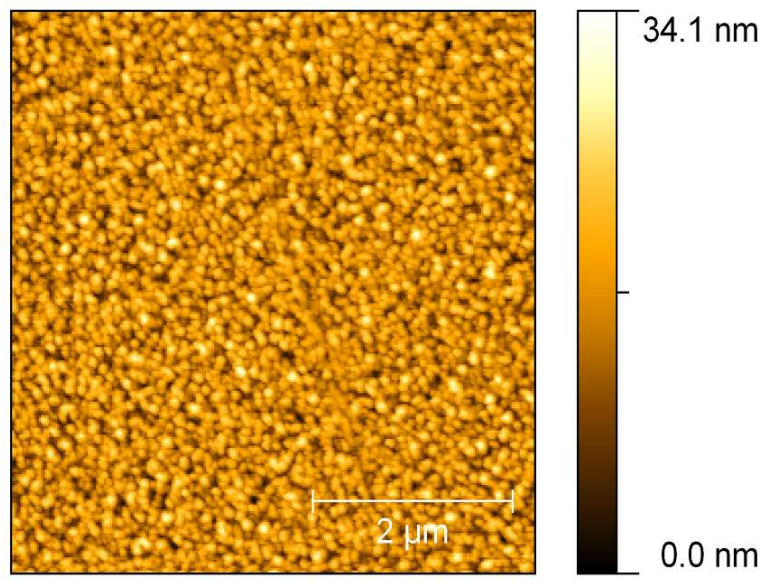


Figure 9.2: AFM image of a  $5\ \mu\text{m} \times 5\ \mu\text{m}$  plasma cleaned MVD aluminum wafer with RMS roughness of 4.3 nm and oxide thickness of 2.5 nm.

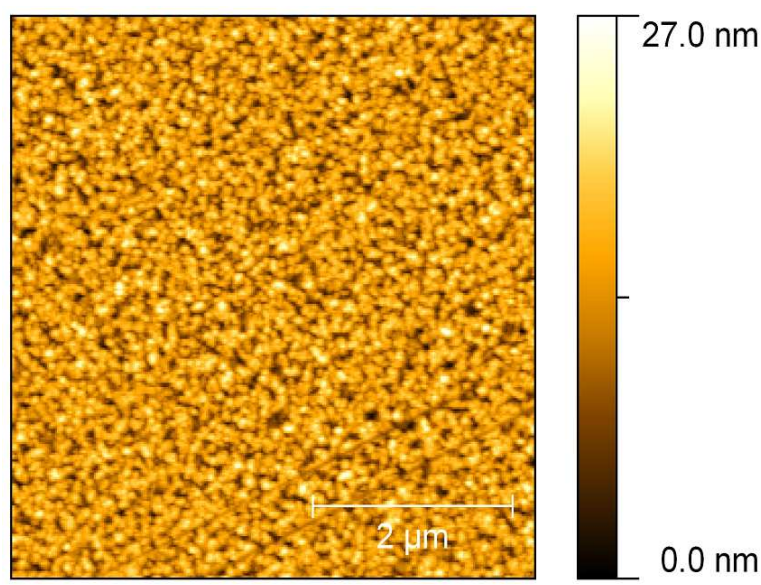


Figure 9.3: AFM image of a  $5\ \mu\text{m} \times 5\ \mu\text{m}$  240 minute deposition of ODP on plasma cleaned MVD aluminum wafer with RMS roughness of 4.67 nm, contact angle  $109.0^\circ$  and ODP thickness of thickness of 2.5 nm.

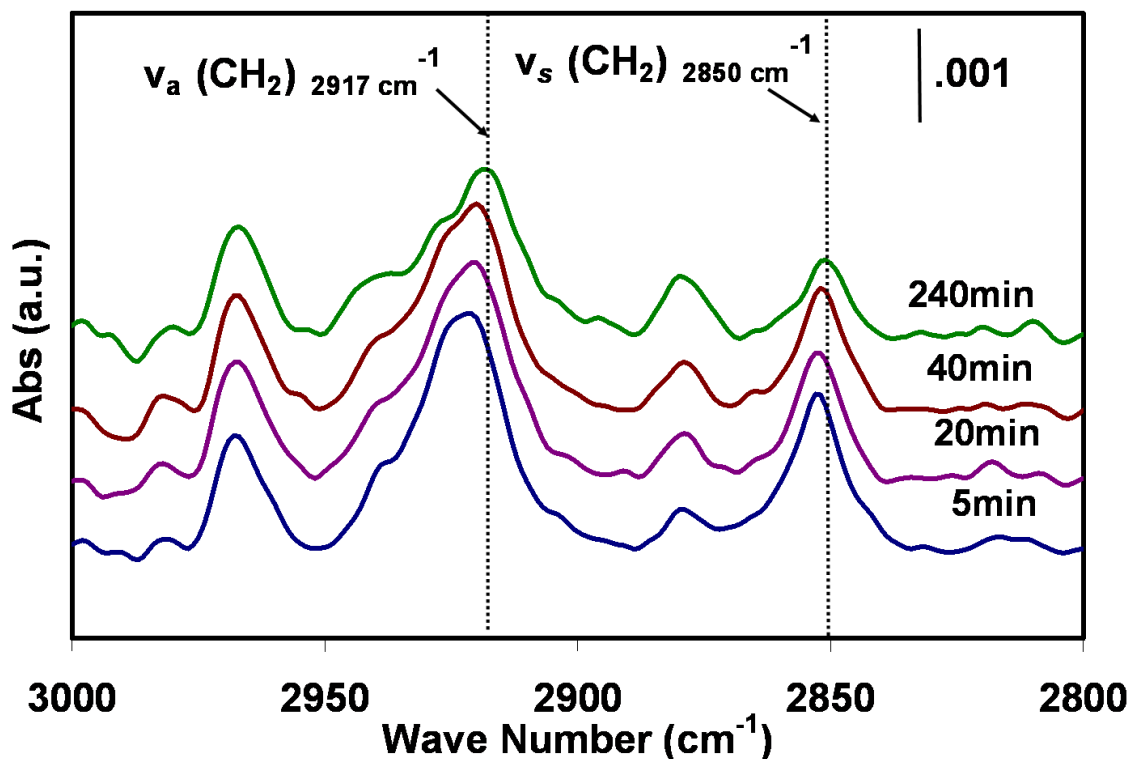


Figure 9.4: Representative FTIR spectra of ODP monolayer formation on “plasma activated” aluminum surface as a function of immersion time at room temperature.

Although AFM provides information on the microscopic structure of OTS film growth, it does not reveal molecular structure and conformation changes within the film and, as demonstrated, can not provide visual contrast on surfaces with topographical roughness. To obtain structural information infrared reflection absorption spectroscopy (IR-RAS) was performed using a Perkin Elmer Spectrum 5000 spectrometer equipped with a liquid nitrogen-cooled MCT detector. The reflection spectra were collected using a Perkin Elmer Specular reflectance accessory, mounted in the sample chamber, set to reflect light at an angle of 83°. A ZnSe wire grid polarizer was mounted on the accessory and was aligned to allow only p-polarized radiation to reflect from the surface. The background spectra for ODP films deposited on the oxidized aluminum surface was a clean aluminum surface with a measured oxide layer thickness of 2.5 nm. FTIR analysis was performed on the films adsorbed on the oxidized aluminum surface as a function of immersion time.

The results presented in Figure 9.4 are the FTIR spectra for films formed on the oxidized aluminum layer as a function of immersion times at room temperature. In general, mean orientation, packing density and interfacial bond formation of the self assembled monolayer can be analyzed in terms of polarized IR-RAS analysis given that films are produced on a reflective underlying metal substrate. The prominent feature of these spectrum is the presence of symmetric and asymmetric methyl  $\text{CH}_3$  and methylene  $\text{CH}_2$  -stretching vibrations. As shown in previous studies the methylene stretches are the most commonly monitored- as the frequency of the gives an indication of orientation and the packing density for long-chain SAMs.

Figure 9.4 shows two types of changes in the FTIR spectra as the film formation time was increased. The first observation is that the position of the  $\nu_s$   $\text{CH}_2$  mode is decreasing with increasing adsorption time to a final value of  $2917\text{ cm}^{-1}$  after 4 hours of ODP adsorption. A similar trend is seen with the  $\nu_a$   $\text{CH}_2$  mode with values decreasing from  $2853\text{ cm}^{-1}$  to  $2850\text{ cm}^{-1}$ . This shift in wavenumber for the two methylene stretching modes is indicative of a more ordered film. For completely disordered structures, the frequency of the asymmetric  $\text{CH}_2$  stretching is close to that of a liquid alkane ( $\sim 2924\text{ cm}^{-1}$ ). For well-ordered SAMs, the frequency is expected is close to that of a crystalline alkane ( $\sim 2915\text{-}2918\text{ cm}^{-1}$ ). This indicates that as the surface coverage increases, the order in the monolayer gradually increase (with the wavenumber for  $\nu_s$   $\text{CH}_2$  and  $\nu_a$   $\text{CH}_2$  modes decreasing) becoming progressively more ordered. An additional observation is a consistent broadness of the peaks associated with both the symmetric and asymmetric  $\text{CH}_2$  modes, which will be detailed later, in this document.

A second change appears in the intensities of the  $\text{CH}_2$ -stretching vibrations, which decrease as a function of immersion time. With increasing time of adsorption the  $\text{CH}_2$  band intensities decrease while the  $\text{CH}_3$  band intensities remain almost constant, in response to the selection rules associated with polarized IR-RAS, indicating that the alkyl chain orients itself with its long axis more normal to the aluminum surface. An optimal rectangular adsorbed

molecule with no tilt will have no intensity due to the fact that  $\text{CH}_2$  groups would not have a transition dipole moment in the direction normal to the investigated surface necessary for signal.

Ellipsometric data in combination with the infrared data suggest that the ODP monolayer adsorption mechanism initially consists of molecules randomly distributed on the substrate. As the surface coverage increases, the order of the monolayer gradually increases consistent with a decrease in tilt angles of the chains as indicated by a decreasing IR band intensity data (Figure 9.4) and are congruent with increasing ellipsometric film thickness values. Final film thickness values are measured at  $\sim 2.5$  nm, but the ellipsometric model utilized for thickness extraction assumes the the film refractive index remains constant during the self-assembly process and is equal to the fully formed monolayer. As indicated with ellipsometric measurements in previous reports on OTS monolayers, this is not a valid assumption and data only give representative trend information and not exact measurements [162]. The surface roughness associated with the sputtered aluminum substrates adds complexity to the exactness of the ellipsometric values. Investigations performed by Pellerite *et al.* on  $\text{H}_{16}\text{PA}$  and  $\text{H}_{22}\text{PA}$  show a range of thickness values between 1.7 nm and 2.7 nm, respectively, on an aluminum oxide surface with similar roughness values and the data from this study are in agreement with this range [163].

Tillman *et al.* derived a means to estimate the molecular orientation in terms of inclination angle from surface normal with IR-RAS. In accordance with the surface selection rule, IR-RAS spectra only contain vibrational absorptions with species oriented in the p-plane thus perpendicular to the surface. Non-oriented random hydrocarbon chains exhibit high  $\nu_a \text{CH}_2/\nu_a \text{CH}_3$  ratio because the C-H stretch of the methylene groups has a dipole moment in the p-plane [12, 164].

The mean inclination angle can be derived from the  $\nu_a$  CH<sub>2</sub>/ $\nu_a$  CH<sub>3</sub> peak ratio, and was calculated according to the following equation (taken from ref. [162]):

$$\frac{I_{CH_2}}{I_{CH_3}} = \frac{2}{3} \frac{n \cdot \cos^2(\Phi^\circ)}{\cos^2(\Phi^\circ - 55^\circ)} \quad (9.1)$$

Where n represents the methylene/methyl ratio,  $\frac{2}{3}$  is the ratio of hydrogen in a methylene group to a methyl group and the angle of inclination calculated by  $(90^\circ - \Phi^\circ)$ . The calculation for OTS films produced in that work gave a value of  $I_{CH_2}/I_{CH_3}$  equal to 0.9 with a calculated angle of inclination of  $(90^\circ - \Phi^\circ) = 15^\circ$ , this value was corroborated to orientational results observed with ATR spectroscopy and ellipsometric measurements, consistent with was approximated as vertical, extended alkyl chain axes. It is important to note that subsequent research on monolayers produced at reduced temperatures result in a more tightly packed monolayer with reduced tilt angles and actually represent optimal all trans orientations while the monolayers presented by Tillman are evidenced as a mixture of ordered and disordered phases.

The  $I_{CH_2}/I_{CH_3}$  ratios measured for the phosphonate monolayers formed as a function of immersion time are shown in Figure 9.5. The  $I_{CH_2}/I_{CH_3}$  ratio decrease as a function of immersion time, indicative of alkyl chain orientation, approaching the surface perpendicular, removing the  $\nu_a$  CH<sub>2</sub> from the p-plane. At formation times of 4 hours the angle of inclination was calculated at  $16^\circ \pm 0.8^\circ$ ) suggesting a similar packing arrangement as found in OTS monolayers formed at room temperature.

| Time (min) | I_(CH <sub>2</sub> )/I_(CH) <sub>3</sub> | Inclination angle (Degrees) |
|------------|------------------------------------------|-----------------------------|
| 5          | 3.94                                     | 36.1°                       |
| 20         | 1.70                                     | 22.2°                       |
| 40         | 1.39                                     | 19.8°                       |
| 240        | 1.05                                     | 16.8°                       |

Figure 9.5: Calculated inclination angles and  $I_{CH_2}/I_{CH_3}$  ratios as a function of immersion time

Literature discusses three forms of arrangement possible for phosphonic acid adsorption mono-, di, and tridentate for binding the phosphonate headgroup to metal oxide surfaces. However, our IR data alone do not allow a direct determination of the preferred binding mode in the system studied here. But, calculations suggest an evolution from tridentate (of about  $35^\circ$ ) at low immersion times to lower binding modes (of about  $16^\circ$ ) as film formation proceeds. This indicates a decrease in alkyl chain tilt angles and points to a more organized film. As evidenced by the broadening affect previously mentioned, the agreement in calculated angle of inclination to OTS monolayers produced at room temperature, it is suspected that a small amount of disorder is still present in our ODP films even after high immersion times. Deposition of OTS films at room temperature at increased immersion times show a diminution of the peak broadening affect on smooth surfaces. Given the influence of the interfacial water on OTS adsorption mechanisms, molecules are more free to rearrange to thermodynamically stable conformations. But, friction force microscopy has shown that ordered phase and a disordered phase are still present in OTS films. In conjunction with film order studies presented previously of OTS on surfaces with varying degrees of roughness, the surface roughness associated with the sputtered alumina will have a higher degree of disorder as a consequence of surface features. In addition in the low frequency regions of the spectra we note peaks associated with P=O groups with vibrations in the range from 1180-1220  $\text{cm}^{-1}$  indicative of incomplete cross linking.

It is speculated that the growth mechanism associated with the phosphonate film under study contribute to varying bonding structures that may limit complete cross linking. In addition, consideration must be given for the influence of the nanoscopic curvature associated with this surface, as curvature has been shown to influence the order of self assembled films. It is suspected that the orientation could improve if studies were performed on a planer atomically smooth substrate. The utilization of a smooth substrate has been proposed for phase II of this investigation but is not part of this body of work.

## Spherical surface

In the case of spherical surfaces, methods such as ellipsometry, contact angle analysis, and IR-RAS are not applicable. ATR-FTIR spectroscopy was used to investigate the state of order for the alkane chains. However, ATR-FTIR measurements are useful only for monitoring trans/gauche sequences in the alkyl chains (order), and can not be used to measure lateral interaction packing. TGA analysis is utilized to obtain this information by measuring weight loss as a function of temperature under a nitrogen atmosphere. A electron micrograph of the ODP spheres used for this research is shown in Figure 9.6 and consists of mainly spherical particles with an average diameter  $75\text{ }\mu\text{m}$ .

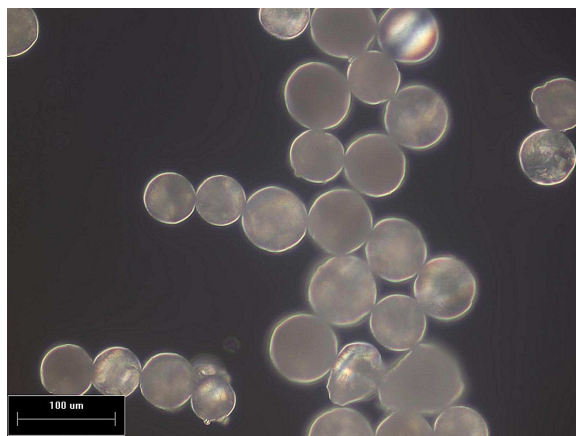


Figure 9.6: Electron micrograph of spherical alumina powder with a distribution in size ranging from  $75\mu\text{m}$  to  $100\mu\text{m}$  utilized for ODP deposition and subsequent FTIR analysis and TGA analysis.

Research has shown that the decomposition mechanism is similar to that identified for OTS monolayer, but the temperatures are elevated [165]. The thermal degradation of the monolayers occurs via destruction of the hydrocarbon chains with phosphorus remaining on the surface after the pyrolysis.

Spherical alumina powder was cleaned and coated with ODP monolayers following the methods indicated in Chapter 3. ODP depositions were performed as a function of different immersion times with data indicating an increase in weight loss observed at increasing immersion. The highest immersion time was 4 hours, consistent with results from planer

investigations. A typical TGA weight loss curve for the monolayers of ODP supported on the alumina spheres is shown in Figure 9.8. The most prominent feature was the dramatic weight loss in the temperature region from  $\sim 200$  to  $\sim 700$  °C, which was not present in the TGA of bare alumina and was assigned to the degradation of the surface adsorbed organic species. The onset of the weight loss was  $\sim 250$ - $300$  °C and the temperature of the maximal rate of the weight loss ( $T_{MAX}$ ) was  $\sim 400$ - $600$  °C. To obtain an estimate of the extent of coverage of OTS on the surface, 100 % coverage was calculated assuming a maximum possible value of 5 molecules/nm<sup>2</sup>, and using 0.2 m<sup>2</sup>/g as the surface area of alumina spheres. Therefore, the percent coverage for the spherical alumina was 0.042%, and lower than the amount calculated, suggesting an incomplete monolayer and non uniform coverage. We point out, however, that the weight loss (from 200 to 700 °C) was 15-20% lower than the weight of the monolayers as determined from calculations based on the an all trans film arrangement and surface area available. But, the proposed decomposition mechanism in this range indicates that only part of grafted molecules degraded into volatile products while a portion of the monolayers ( $\sim 15$ - $20\%$  by TGA curves in weight) remain on the surface (until 800 °C). Re-calculating the loading percentages assuming that the inorganic species remain on the surface resulted in 99.4% loading efficacy.

ATR-FTIR analysis was performed at increasing immersion times. Figure 9.7 shows two types of changes in the FTIR spectra as the film formation time was increased. The first observation is that the position of the  $\nu_s$  CH<sub>2</sub> mode is decreasing with increasing adsorption time to a final value of 2917 cm<sup>-1</sup> after 4 hours of ODP adsorption. A similar trend is seen with the  $\nu_a$ CH<sub>2</sub> mode with values decreasing from 2853 cm<sup>-1</sup> to 2850 cm<sup>-1</sup>. A second observation is the increase in intensity associated with these modes. These observations indicate that as the surface coverage increases, the order in the monolayer gradually increase (with the wavenumber for  $\nu_s$ CH<sub>2</sub> and  $\nu_a$ CH<sub>2</sub> modes decreasing) becoming progressively more ordered and are consistent with what was observed on the planer substrates. ATR-FTIR does not allow for a direct determination of the degree of order present.

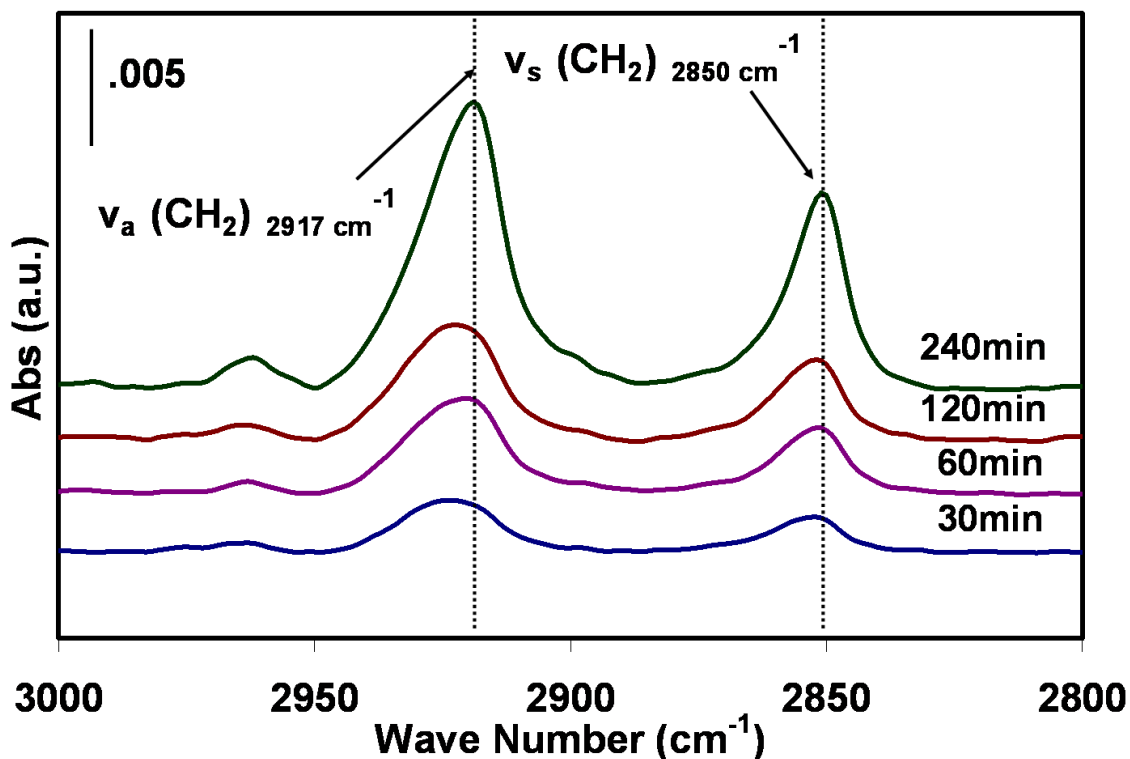


Figure 9.7: Representative FTIR spectra of ODP monolayer formation on “plasma activated” aluminum oxide spheres as a function of immersion time at room temperature.

Monolayer films were translated to quartz crystal micro balance crystals and ODP spheres attached to AFM and SPM probes based on the conclusions found in this research. A holder was designed for this effort as illustrated in Figure 9.9 to allow for deposition to be performed at the same time to various surfaces. Collaborative results are under way and will determine the efforts that follow.

### 9.2.3 Conclusions to Phosphonate Work

Octadecylphosphonic acid monolayers (ODP) were investigated for a tribological comparison across different measurement regimes. Two aluminum oxide substrate materials reactive toward ODP deposition were identified and evaluated. A detailed mechanistic study was performed to analyze the quality of these films. Results show that ODP evolves from a tridentate bonding structure to a lower bonding configuration at increased immersion times

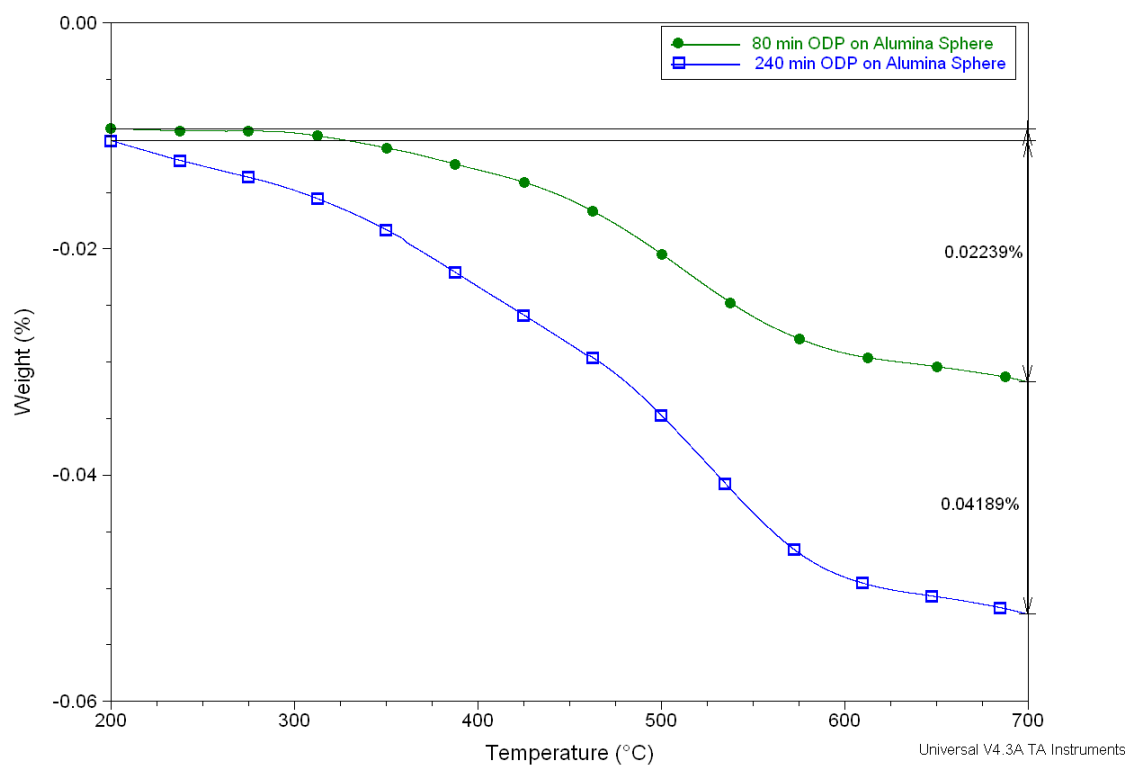


Figure 9.8: TGA weight loss as a function of temperature under nitrogen at a ramp rate of 10 °C/min comparison between two different immersion times. Scan of uncoated alumina spheres are removed from baseline.

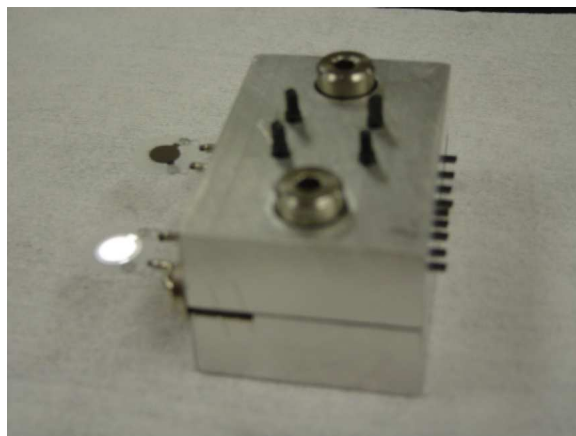


Figure 9.9: Photograph of holder designed for holding AFM Cantilevers, SPM Probes, and Quartz Crystal Micro balance Assemblies for simultaneous phosphonate monolayer deposition.

with increasing film order. As produced on rough oxidized aluminum surfaces, they maintain a small degree of disorder. Films adsorbed on the spherical particles show an increase in order as a function of immersion time and maintain a lower degree of disorder more indicative of an all trans orientation. Films were produced under identical conditions and sent for collaborative tribological measurement.

## Part II

# Interfacial Engineering of a Catalytic Fischer Tropsch MicroReactor

## Chapter 10

### Motivation

While the Fischer-Tropsch reaction system is rich in character, there is no fundamental kinetic model to describe the reaction, and therefore reactor design becomes an empirical exercise. It is generally understood that operating FT reactions at low pressure and high temperature will favor methane whereas high pressure and lower temperature will favor wax products. Conventional reaction engineering approaches (isothermal reactors, isobaric reactors, plug flow or tubular reactors) have been used extensively and successfully to characterize this reaction. However, due to lack of fundamental knowledge about the reaction details, it is not always clear how or why alteration of key process parameters will affect product distribution and selectivity. It is known that both process pressure and temperature influence selectivity and product distribution. We intend to explore the effects of time varying pressure and temperature as well as space varying temperature and pressure in order to learn if or how these factors can be tailored to provide a targeted product and selectivity. The fundamental goal of this project is to leverage microreactor technology combined with a micro fibrous catalyst support system (MCSS) to probe the effects of high gradient (both temporal and spatial) process conditions on reactive systems to advance fundamental knowledge in interfacial control over reactor operation. As a platform for this effort, Fischer-Tropsch synthesis is investigated over silica supported cobalt catalyst in a nickel wire micro fibrous matrix. The principal objectives of this work include (1) identifying a microreactor capable of performing the FT reaction, while being easily tunable for operating parameters such as pressure gradients, temperature profiles, and reactor geometries (2) developing an active catalyst material that can be incorporated into the micro reactor system easily and controllably (3) systematically probing of the operating parameters in the micro reactor

to leverage the reduction in size as compared to conventional systems utilizing the advantages in improved heat and mass transfer (4) Utilization of the micro reactor to investigate Fischer-Tropsch synthesis weighing conversion and activity verses information learned from the third objective. This is an extensive investigation that will not be fully envisioned by the end of this dissertation. As a first chapter for this research, this work will only focus on understanding the effect space varying pressure as influenced by the MCSS material and its subsequent influence on product distribution and selectivities as related to Fischer Tropsch synthesis. These experiments will be studied under isothermal conditions. The next phase of this investigation will include an analysis of the influence of microreactor geometry as a means to control the pressure gradient within the reactor.

## **10.1 Background Research**

### **10.1.1 Introduction to MicroReactors**

Microreactors are miniaturized chemical reaction systems, which contain reaction paths with at least on dimension in the range of tens of microns to approximately 1 mm in size. The small reactor dimensions lead to a relatively large surface area-to-volume ratio and increased driving forces for heat and mass transport. Therefore, microreactors are especially suited for fast reactions with a large heat effect, where they allow for nearly isothermal conditions at high reactant concentrations, or for operation in the explosive regime, which is not possible in large-scale equipment [166].

Short characteristic length scales intensify heat and mass transport because the conduction and diffusion lengths are short as compared to those of large scale systems. A high heat transfer rate enables a direct control of the process temperature, e.g. fast preheating to the process temperature or cooling and quenching of reaction products to prevent the formation of unwanted side products. The high heat transfer rate in combination with small overall equipment size enables fast start-up and shutdown of the entire process. Fast start-up is a benefit for on demand production and fast shutdown will increase safety in case

of failure. Down scaling a high temperature unit operation, can increase the temperature gradient between the inside and the outside of the unit proportionally. On the other hand, a large temperature gradient also gives a high driving force for heat transfer. Short diffusion lengths improve mass transport limited process rates and a large surface area to volume ratio enables a more efficient use of exchange surfaces for e.g. heterogeneous catalytic reactions and membrane processes.

The throughput of the process can be increased per unit volume, by making more efficient use of these exchange surfaces. Due to the small length scales, Reynolds numbers in micro systems are low, in the order of 1-1000 and therefore a laminar flow pattern will exist inside micro channels. Laminar flow can complicate mixing of different media. The small volume and precise geometry of micro structures can give a short and well-defined residence time. In this way, the residence time of the chemical process can be optimized, resulting in higher yield and higher reaction product selectivity compared to large scale systems.

Next to these process-yield and selectivity enhancing features, micro-chemical systems are inherently safe. The high heat removal capabilities prevent hot spot formation. Runaway chain reactions like flames and explosions are averted. The short diffusion length scales promote the adsorption of free gas phase radicals at the walls and accordingly terminate these homogeneous reactions. Moreover, in case of failure, the small hold-up of reactants will give less waste and low environmental impact. The influence of erosion and corrosion on construction materials will have a larger impact on a micro system compared to a macroscopic system. The surface area to volume ratio and inherently the hydrodynamic properties of a micro system will change more drastically for a certain diameter change by erosion and or corrosion. The construction materials will need to be highly erosion and corrosion resistant or will need a protective coating. Although these materials are often more expensive and/or harder to utilize in a high precision fabrication process, less material is needed to build a micro system. Micro systems can therefore enable the use of exotic and costly materials.

Another advantage of micro-chemical-systems is the scale-up by scale-out or numbering-up the system. The throughput of one single channel might be low, but by using more channels in parallel, production can easily be increased. Using micro structures with the same dimensions, no scale-up research is necessary, saving time and money on research. However, to ensure a good flow distribution between parallel micro-systems or inside a stack of channels, the relative difference between the channel diameters should be kept small and also a flow distributor will be necessary. Extensive reviews on micro-chemical-systems can be found in the books of Ehrfeld *et al.* [167], Hessel *et al.* [168], and Lowe *et al.* [169].

It is important to note that micro reactors do not affect the overall reaction mechanisms and kinetics. The main impact in micro reactor design is to focus on intensifying mass and heat transport as well as improving flow patterns. A decrease in the linear dimensions causes a difference in the temperature, concentration, density, or pressure gradients. Consequently, the driving forces for heat transfer, mass transport, or diffusional flux per unit volume increase when using micro reactors.

### 10.1.2 Catalyst Considerations

For an optimal heterogeneous catalytic reactor design, many variables must be analyzed to maximize reactor performance in terms of yield and selectivity. To this end, an integrated approach should begin at the micro-level by an optimal design of the catalyst itself by considering features such as catalyst size, shape and uniform distribution of the active material. The active materials used as catalysts are often expensive metals, and in order to be utilized effectively, they are dispersed on large surface or supports. The reactant diffuses from the bulk fluid within the porous network of the support, reacts at the active catalyst site, and the product diffuses out. The transport resistance of the porous support alters the concentration of chemical species at the catalyst site as compared to the bulk fluid. The consequence of concentration gradients is that reactions occur at different rates, depending on position of

the catalyst site within the porous support. As far as the size of the catalyst pellet is concerned, it should be realized that although the use smaller size of the catalyst pellet would be optimal, it is often the pressure-drop considerations that outweigh other consideration in view of the fact that the pressure drop considerably increases as the size of the catalyst in the heterogeneous reactor is decreased. Therefore, any optimal design should explicitly take into consideration of the issue of the pressure-drop since most of the reactor designs used so far are the traditional catalyst particulates packed into microreactors that normally suffer from poor intra particle mass / heat transfer, low contacting efficiency, high pressure drop, mechanical attrition, and catalyst clumping in a way [170]. Our research intends to overcome many of these limitations by focusing on the incorporation of an MCSS catalyst that has been identified as a unique catalytic system which will be further expanded on and investigated in this work.

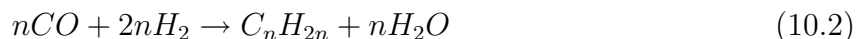
### 10.1.3 Introduction to Fischer Tropsch Synthesis

#### Chemistry

In Fischer-Tropsch synthesis, liquid hydrocarbon fuels are produced from lighter gases. This process was first put to large-scale industrial use by Germany during World War II. There continues to be intense academic and commercial interest in improving Fischer-Tropsch synthesis because it offers a source of liquid hydrocarbon fuels as opposed to the increasingly costly process of extracting oil from the ground. Furthermore, Fischer-Tropsch synthesis could make a significant beneficial environmental impact by capturing methane and other greenhouse gases that might otherwise be released from remote oil wells.

A problem with Fischer-Tropsch synthesis is that it is difficult to control the products resulting from the synthesis. FT synthesis is a surface polymerization reaction. The reactants, CO and  $H_2$ , adsorb and dissociate at the surface of the catalyst and react to form chain initiator  $CH_3$ , methylene  $CH_2$  monomer and water. The hydrocarbons are formed by  $CH_2$  insertion into metal-alkyl bonds and subsequent dehydrogenation or hydrogenation to

an -olefin or paraffin, respectively. The pioneering work by Fischer and Tropsch in the 1920.s led to the realization that hydrocarbon chain formation proceeds via the stepwise addition of one C-atom at the time. Detailed product analysis studies indicate that the reaction produces a vast array of hydrocarbons and oxygenates over a large boiling range. The major reaction products at high pressure operation are linear paraffins, linear 1-olefins, and linear 1-alcohols. At lower pressures, the selectivity for mono-methyl branched hydrocarbons and internal-olefins increases. The formation of aromatics is only observed at higher temperatures on Fe-based catalysts and is not observed on Co catalysts. The Fischer-Tropsch reaction is represented in the following equations,



Equation 10.1, relates to the production of paraffins and Equation 10.2 to that of olefins. Alcoholic products can also be formed either as by-products or as main product depending on the catalytically active metal and the pressure. A whole range of products with different lengths of the carbon chain can be obtained. Two important side reactions generally also proceed during the process they are the water gas shift conversion reaction and the Boudouard reaction. The water gas shift conversion involves reaction of carbon monoxide with water, which is formed during the reaction (Equation 10.1 and 10.2), to hydrogen and carbon dioxide.



The water gas shift conversion can be favorable for the Fischer-Tropsch synthesis starting with CO-rich synthesis gas as is obtained from gasification of coal or heavy oil fractions

through partial oxidation ( $H_2/CO$  molar ratio approximately 1). The water gas shift conversion raises the  $H_2/CO$  ratio. In contrast, synthesis gas produced from natural gas initially already possesses a high  $H_2/CO$  ratio. Hence, the hydrogen-to-carbon monoxide ratio can become undesirably elevated due to the water gas shift conversion. The second side reaction mentioned above is the Boudouard reaction. This reaction occurs preferably on the active metal surface and involves the conversion of carbon monoxide into carbon dioxide leaving carbon behind on the surface (Equation 10.4)



The carbon deposition can eventually lead to deactivation by, for example, blocking of active sites, disintegration of the catalyst bodies or plugging of the reactor by formation of very strong carbon fibrils.

Anderson shows that a polymerization-like process effectively describes the product distribution of the Fischer-Tropsch synthesis. This results in the so-called Anderson-Schulz-Flory (ASF) product distribution:

$$W_n = n(1 - \alpha)^2 \alpha^{n-1} \quad (10.5)$$

where  $W_n$  represents the weight fraction of all hydrocarbon products with carbon number  $n$ , and  $\alpha$  is chain growth probability, which is the rate of growth per the sum of growth and termination rates [171]. Similar molecular weight distributions were already observed during polycondensation by Schulz and free-radical polymerization by Flory [Hinderman *et al.*, 1993]. The entire product spectrum is characterized by a single parameter, *i.e.* the chain growth probability defined as:

$$\alpha = \frac{\sum_{i=n+1}^{\infty} \Phi_i}{\sum_{i=n}^{\infty} \Phi_i} = \frac{r_p}{r_p + r_t} \quad (10.6)$$

where  $r_p$  and  $r_t$  are the rates of chain propagation and termination, respectively, and  $\Phi_i$  is the mole fraction of the product spectrum containing  $i$  carbon atoms. Equation 10.5 implies that the Fischer-Tropsch reaction is not selective toward a single reaction product or a specific carbon range, with methane as only exception. Methane can be produced with 100 % selectivity. The Fischer-Tropsch synthesis, however, can selectively produce one type of reaction product, *i.e.* the selectivity towards 1-olefins or paraffins can be optimized. Wax formation is favored at low temperature, high pressure, low  $H_2/CO$  feed ratios, and large residence times. Mass transport issues have a strong influence on the degree to which readsorption modifies the product distribution. [172] An illustration of the distribution of products is provided in Figure 10.1. The most important aspects for FT reactor development are the high reaction heats and the large number of products (gas, liquid and waxy hydrocarbons). An optimal design of a commercial scale reactor requires detailed information of the hydrodynamics, reaction kinetics, catalytic system and FT chemistry. Kinetic information is crucial for reliable design and scale up of commercial Fischer-Tropsch processes [173].

#### 10.1.4 Catalysts for Fischer Tropsch synthesis

On investigating the Fischer Tropsch systems employed for catalytic synthesis of hydrocarbons, it is clear that cobalt and iron are the most commonly used due to their overall reactivity and cost [174] [175]. Iron catalysts for the Fischer-Tropsch synthesis generally consist of precipitated iron, which is promoted with potassium and copper to obtain a high activity and selectivity, and with  $Al_2O_3$  and  $SiO_2$  added as structural stabilizers. Typically for these relatively cheap Fe-based catalysts, Fe-carbide appears to be the active phase for Fischer-Tropsch synthesis. Fe-oxides are also formed and these are active toward the water-gas shift reaction. A high water-gas shift activity causes these catalysts to be flexible toward the  $H_2/CO$  feed ratio of the synthesis gas. This allows the utilization of a large variety of feed stocks. Iron catalysts can use synthesis gas with a  $H_2/CO$  ratio below 2, because excess

of CO is converted with water to carbon dioxide and hydrogen in the water gas shift (WGS) reaction. However, the water-gas-shift activity of the catalyst also results in a low carbon efficiency of the gas-to-liquid process.

Cobalt catalysts are usually supported on an inert support due to the higher cobalt price and better catalyst stability. The active phase is metallic cobalt; the water-gas shift activity of Co-based catalysts is low and water is the main oxygen containing reaction product. Cobalt catalysts are suited for producing high yields of long-chain alkanes in FT synthesis. Davis *et al.* stated that cobalt catalysts exhibit two distinct advantages for some applications [176]. The first being a lack of the WGS activity allowing one to reject the oxygen in CO as water rather than CO<sub>2</sub> such that carbon efficiency of the cobalt catalyst is double the efficiency of the iron catalyst at high conversion levels. The second advantage of the cobalt catalyst is it can be added to a support that can provide robustness that iron catalyst does not have in unsupported state. An inert support is a support that does not, by itself, react in a Fischer-Tropsch synthesis, although it may interact with the catalytically active layer, and the shape and configuration of the inert support may play an important role in controlling the reaction. Examples of inert support materials include alumina and silica.

Cobalt was selected as the material of interest for this study. Preparation of cobalt supported catalysts involves several essential steps. Catalysts are commonly synthesized using aqueous impregnation with cobalt nitrate and promoters, followed by oxidative and reductive pretreatments. The activity and selectivity of cobalt supported catalyst toward different hydrocarbons is strongly dependent on preparation procedures [177]. These preparation procedures are known to contribute to the final properties associated with the active sites of the catalyst. Literature shows that for cobalt particles larger than 7-8 nm, Fischer Tropsch activity is a function of the number of surface metal sites [178]. Girardon has shown that controlling catalyst calcination process can influence cobalt particle size, reducibility, and catalytic properties [179].

It has been generally accepted that on cobalt catalysts the active phase for FT synthesis is cobalt metal and that the activities of cobalt catalysts depend on the number of active sites on the surface, cobalt particle size, and cobalt species [180]. The Fischer-Tropsch process is critically dependent on the effectiveness of the cobalt catalyst and there has been a significant effort in the optimization in the design of catalysts which optimize metal crystallite size, control dispersion, improve reducibility and increase overall stability. The interaction of cobalt with the metal oxide support and its dispersion characteristics have been shown to affect the electronic density as well as the structure of the metal crystallites and are assumed to play a role in the hydrocarbon selectivity and the catalyst activity.

Most of the industrial cobalt-based catalytic systems used in the FTS reaction are supported on  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  or  $\text{SiO}_2$  [181] [182]. Silica is commonly used as the support material due to its high surface area, porosity, stability, weak metal-support interaction and its inertness [183]. Iglesia *et al.* showed that FT synthesis rates were proportional to metal dispersion and were independent of support [174]. Others have indicated that catalytic supports significantly influence the extent of metal reduction, morphology, adsorption and catalytic properties of the active phase especially in well dispersed catalytic systems [184]. The problem lies in the fact that synthesis of highly dispersed cobalt catalysts requires strong interaction between the support and the cobalt precursor, but in turn, such strong interactions generally lower reducibility of such precursors [185]. A weak cobalt support interaction in silica-supported catalyst promotes high cobalt reducibility but, can favor agglomeration of support particles [170].

The porous structure of catalytic supports can strongly influence the catalytic behavior of many catalysts in a large number of reactions. Khodakov *et al.* showed that an increase in the pore size of the supports lead to an increase in  $\text{Co}_3\text{O}_4$  particle size and offers an improved reducibility of the intermediary CoO particles to metallic cobalt [186]. Narrow pore cobalt impregnated catalysts were shown to exhibit a decreased reducibility due to small cobalt intermediates this affect was correlated to lower Fischer Tropsch reaction rates and higher

methane selectivities. Catalytic support structures can also contribute to catalytic poisoning due to the nature of some of the Fischer Tropsch reaction products such as wax and carbon deposits, which can block the catalyst pores making them unavailable for reaction molecules. Given the complexities of using a cobalt catalyst much experimentation was performed on the cobalt catalyst system and will be discussed further in 10.3.2

## 10.2 Tunable Fischer Tropsch Microreactor Realization

One of the fundamental goals for this project was the realization of a microreactor capable of performing the FT reaction, while being easily tunable for operating parameters such as pressure gradients, temperature profiles, and reactor geometries. Various materials have been explored for microreactors, e.g., stainless steel because of its robustness and good thermal conductivity, ceramic materials for high temperature application, polymers for biological compatibility and silicon due to its mature fabrication infrastructure, low cost and mass production capability. Our initial efforts focused on the fabrication of micro reactors utilizing silicon wafers. Both wet chemical etching and plasma etching of single crystalline silicon have proven suitable for mass fabrication of various micromechanical components. As such, much information was available on the details of silicon processing. A draw back is that the equipment required is relatively costly, and there is a need for processing within a clean room. But, an advantage exists for batch processing because several structures can be realized in parallel on one wafer. A variety of simple geometric structures like grooves, channels or membranes can be realized by lithographic and thin film processing on a silicon wafer. Silicon micro machining also benefits from existing bonding processes, either thermally or anodically, which can be used for assembly of multiple layers. We successfully fabricated multiple reactor geometries in silicon. Subsequent sealing of the reactor also proved successful via anodic bonding. The problems that we encountered dealt more with the attachment of the interconnections to and from the reactor. We were unsuccessful in creating a suitable connection that was gas tight. Various arrangements were tried and alternate connection

assemblies were manufactured. Other issues encountered included successful incorporation of the catalytic support within the reactor. It proved very difficult to incorporate the membrane uniformly within the reactor bed. Due to limited success we chose to investigate alternative fabrication schemes and materials.

## **Metal microreactor**

Realization of an all metal micro reactor presented an opportunity for a robust micro reactor with the potential for gas tight connections, sustainability of high temperatures and the ability of high pressure operation. This metal microreactor design also afforded a means of successfully manipulating the micro reactor geometry to create pressure gradients and temperature profiles. We manufactured the micro reactors utilizing metal sheets that could be compression sealed to eliminate gasket materials that inevitable caused leaks. These sheets could be manipulated by etching, cutting or stamping features into the metals.

The design and development of micro reactors have been driven in part by fabrication constraints and innovations to overcome leaks. For our application specific attention has to be applied to the interconnection techniques associated with gas phase reactions. It was determined that we were in need of a reactor capable of sustaining 450 °C for extended periods of time and that seals needed to be leak tight, withstand hydrocarbon products and maintain a max pressure of 80 psi. The other issues that needed to be addressed were the ease in fabrication, the ability to manipulate flow path designs to test for pressure gradients and temperature gradients, as well as create interconnections to the inlet gases and outlet product gases.

A preliminary micro reactor was successfully fabricated and utilized in the work that follows. A photograph of this microreactor is in Figure 10.22. This micro reactor is a simple channel geometry that consists of a single groove within which the catalyst membrane can be compression sealed. The pressure gradient across this reactor can be manipulated by changing the available volume within the membrane (compressing the membrane). Metal sheets

of differing thicknesses were utilized and examined in terms of pressure drop and residence time distribution determination, which will ultimately control how much compression is applied to the membrane. In addition, metal sheets were obtained with an alternative reactor geometry which will modify the pressure gradient across the reactor while maintaining the same reactor volume and catalyst loading. This is more of a cone type geometry and will be illustrated in sections that follow.

### **10.3 Development of catalyst material for incorporation into the micro reactor system**

#### **10.3.1 Micro fibrous Catalyst Support System (MCSS)**

Although the small dimensions of the microreactor reduce thermal and mass gradients, filling the microreactor with a catalyst of a reduced particle size can dramatically increase the pressure drop in the reactor. For a given bed length, a packed-bed with 60  $\mu\text{m}$  catalyst particles has a pressure drop  $\approx 275\times$  larger than a bed with 1 mm particles, and  $\approx 27500\times$  larger than a bed with 1 cm particles. In studies with the moderately fast phosgene reaction in the axial flow microreactor, gas flow rates of only 4.5 sccm with 53-71  $\mu\text{m}$  catalyst yielded a large pressure drop of 0.4 atm [187]. In general, a large quantity of catalyst is desirable for catalyst testing with microreactors to average out variances between catalyst particles. However, shortening the length of the catalyst bed is necessary to reduce pressure drop. In this work, we present a single channel microreactor for catalyst testing that uses a Micro fibrous Catalyst Support System which provides large void volume, an entirely open structure, large surface-to-volume ratio, high permeability, high thermal conductivity, and unique form factors instead of thin-films or coatings. This way, results are relevant to catalyst preparation techniques, catalyst-support interactions, and other issues in industrial catalysis. The Micro fibrous Catalyst Support System enables the use of practical flow rates and catalyst quantities while minimizing pressure drop. A comparison of the flow path of gases through a

microreactor with an MCSS catalyst vs a standard particle catalyst is illustrated in Figures 10.2 and 10.3. The microreactor design, fabrication, and characterization are presented.

## **Fabrication Methodology**

The fabrication of the Micro fibrous Catalyst Support System was performed by a wet-lay process. The base of the slurry is a cellulose pulp suspension. To this, an adjustable volume percent of nickel microfibers (typical diameter  $3.0\ \mu\text{m}$ ) are added and mixed followed by the desired volume percent of the silica support particles. This slurry is diluted and formed into hand-sheets using a typical paper forming technique where the majority of the slurry is poured over a fine screen allowing most of the free water to drain, leaving behind a dense mesh of cellulose and nickel fibers entangling the silica support particles. The hand-sheet is then air dried and oxidized in air at approximately  $400\ ^\circ\text{C}$  to remove the cellulose, leaving behind the nickel entrapped particles. A subsequent hydrogen reduction at  $900\ ^\circ\text{C}$  sinter the micro fibrous nickel network around the silica particles and produces a robust micro fibrous network. The micro fibrous network can be tailored in both void age and support loading, and can be mechanically formed post-fabrication by cutting, compressing or even welding. The finished micro fibrous media has tunable transport properties including effective thermal conductivity, mean distance between fibers and pressure drop. A SEM image of one example of this material is shown in Figure 10.8

### **10.3.2 Qualification of Micro fibrous Catalyst Support System (MCSS)**

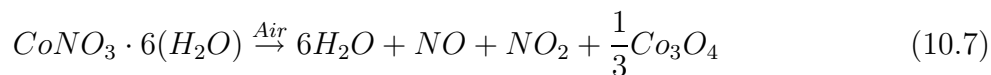
The Fischer-Tropsch process is critically dependent on the effectiveness of the cobalt catalyst and there has been a significant effort in the optimization in the design of catalysts which optimize metal crystallite size, control dispersion, improve reducibility and increase overall stability. The interaction of cobalt with the metal oxide support and its dispersion characteristics have been shown to affect the electronic density as well as the structure of the metal crystallites and are assumed to play a role in the hydrocarbon selectivity and

the catalyst activity. Due to the nature of our microreactor it was impossible to incorporate an existing catalyst into our system. Work was needed to identify an active material that was capable of being utilized in a microreactor. Significant preliminary investigations were required as it was necessary to start from scratch and examine all the steps in the preparation procedure. This effort prompted a significant investigation of the impregnation procedure, calcination procedure, and reduction procedures necessary to produce a viable catalyst material. Reduction of supported  $\text{Co}_3\text{O}_4$  species in hydrogen has been a subject of a large number of investigations. Reduction of  $\text{Co}_3\text{O}_4$  has been shown to produce  $\text{CoO}$  within the temperature range of 200-300 °C. The amount of metallic cobalt produced in the second reduction step and the temperature range associated with the reduction is controlled by the ease of  $\text{CoO}$  reduction to metallic Cobalt. A final qualification was performed by utilizing our optimized catalyst material in an existing macro scale FT reactor.

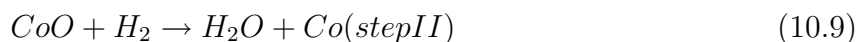
### Calcination and Reduction Mechanism for Cobalt Nitrate Hexahydrate

Preliminary analysis involved understanding the reaction mechanisms for the calcination and reduction of cobalt nitrate hexahydrate. The reaction mechanisms as indicated below were found in the literature review.

#### Calcination Mechanism



#### Reduction Mechanism



It was determined that due to the nature of both reactions that TGA-MS could be utilized to examine the calcination and reduction mechanisms. Runs were performed on cobalt nitrate hexahydrate to measure the extent of both calcination and reduction. TGA-MS allowed for a measurement of weight loss as a function of reaction temperature. From this analysis we were able to determine the extent of calcination and reduction and identify the temperature at which these events occurred. The calcination results are shown in Figure 10.4. The results were in good agreement with the values calculated based on stoichiometry. The reduction mechanism as shown in Figure 10.5 are also in agreement with the calculated values. Two distinct peaks were identifiable for the reduction mechanism which allowed for a correlation of reduction amount and reduction temperatures. It can be seen from Figure 10.5 that step 1 occurs at 283 °C and step 2 of the reduction occurs between 320-400 °C. The mass spectral data allowed identification of the evolved gases as the reactions proceeded. These gases were in agreement with the mechanisms proposed in the literature. Quantitatively, the mass losses at steps I and II are 6.9% and 20.7% respectively, while the mass loss at step II is approximately three times that at step I. This is in agreement with the reduction mechanism shown above. The water evolved from the reduction steps trends with the weight loss events and validates that the weight loss is due to the reduction mechanism proposed.

### **Investigation of the Reduction Properties for Silica Supported Cobalt as Influenced by Pore Size**

Initial investigations focused on the utilization of different silica support particles. As the interaction with the metal oxide support and its dispersion characteristics are of great importance it was necessary to understand the interactions that occurred between the silica support and the cobalt precursor. Co/SiO<sub>2</sub> catalysts were prepared by aqueous cobalt nitrate impregnations of silica with different pore sizes to study the effect of the pore size on the reduction profile. Cobalt nitrate hexahydrate impregnated silica catalysts were calcinated in air at 350 °C for 2 hours. Investigations revealed this calcination procedure regardless of pore

size consistently provided a high degree of conversion to  $\text{Co}_3\text{O}_4$ . An example is illustrated in Figure 10.6. Four different sized silica powders were utilized for impregnation of a cobalt loading of 20 wt%. The sample information and identifications are given as follows:

1. Silica Gel 60A Pore Size, 43-63 micron overall size
2. Silica Gel 150A Pore Size, 150-250 micron overall size
3. Silica Gel 250A Pore Size, 60-250 microns overall size
4. Silica Gel 150A Pore Size 75-150 micron overall size

Figure 10.7 represents the weight loss associated with the four catalysts of different silica pore size. Again, two distinct weight loss events associated with  $\text{Co}_3\text{O}_4$  reduction are illustrated. The results showed that the reduction proceeded in a two step process with the first reduction step occurring between 200 °C and 320 °C. All of the catalysts showed similar reduction percentages for the first step of reduction. This was as expected as the first reduction event is expected to occur easily. The second reduction step occurred between 320 °C and 700 °C depending on the pore size. Quantitatively, the mass loss at step II is expected to be approximately three times that at step I to be in agreement with the reduction mechanism shown above. It became evident during the investigation, that the catalysts with the larger pore sizes were more easily reducible to metallic cobalt. Based on the calculations full reduction weight loss is calculated to be 6.8%. The catalyst with the smallest pore size 6 nm showed the least amount of reduction at 5.0%. Sample 4 was chosen as our starting material given the extent of reduction and the particle size range. Future analysis will include a more in depth investigation of particle size as influenced by our reduction procedure.

### **Impregnation Procedure for MCSS**

The procedure consisted of creating the nickel micro fibrous silica support via a standard wet paper-lay process. A micro fibrous carrier consisting of a 2.0-3.0 vol. % of 3  $\mu\text{m}$  (dia)

Ni fibers was utilized to entrap 20-30 vol. % of 75-150  $\mu\text{m}$  diameter silica particulates with a pore size of 6nm. This process was followed by an oxidative treatment at a temperature of 400 °C to remove binders associated with the paper lay process and was followed by a hydrogen reduction at 900 °C that allowed the micro fibrous nickel network to be sintered together around the silica powder to form a more rigorous support. The sintered support was solution impregnated with a 15 wt.% cobalt nitrate hexahydrate and water solution. After completely immersing the sintered support in the 15 wt% cobalt nitrate hexahydrate solution, excess solution was removed via blotting relying on capillary forces to remove the excess material that was not incorporated within the silica pores. The material was again subjected to an oxidative treatment as previously described that removed the nitrate portion of the cobalt precursor and produced a cobalt oxide that could be subsequently reduced to the active metal prior to its utilization as a FT catalyst.

### **Catalyst Characterization**

SEM analysis was performed to characterize the surface features of the impregnated MCSS. Figure 10.8 on the right is a SEM image of the fabricated micro fibrous support just prior to impregnation. It can be seen that the silica particulates are of various shapes and are anchored within the nickel matrix. Figure 10.8 on the left is a SEM image of an individual silica particle used for comparison purposes. Figure 10.9 right is an SEM image of the micro fibrous entrapped silica supported cobalt catalyst with 75-150  $\mu\text{m}$  silica pore size prior to reduction. It is interesting to note, that the cobalt catalyst which was expected to be only associated with the silica support was actually distributed uniformly throughout the micro fibrous matrix. An individual particle was investigated in Figure 10.9 and shows that the cobalt catalyst also coated the surface of the particles.

The fact that the cobalt catalyst was distributed non uniformly throughout the micro fibrous matrix was an intriguing result. But, due to this fact there were questions on the actual loading percentages associated with the cobalt. The loading that was assumed was

not accurate. It has been stated in the literature that when doing solution impregnation the active catalyst will diffuse into the pores of the silica support and remain. Subsequent reduction would reduce the cobalt oxide to active metal cobalt within the pores. Given the interaction of the impregnating solution and the support an alternative impregnation method was necessary.

Additional catalyst samples were produced that utilized a more rigorous attempt to remove the excess catalytic solution. These attempt included a vacuum impregnation step. The catalyst was exposed to excess solution of the cobalt nitrate solution previously described. The catalyst membrane was placed securely onto a vacuum plate and excess solvent was removed via vacuum. This procedure was repeated 3 times and the weight gain achieved was in agreement with what was calculated after an overnight drying procedure at 90 °C. This procedure was adopted as the standard procedure for all subsequent MCSS fabrication. Additional analysis utilizing optical microscopy confirmed that the impregnation solution was no longer present in the network and only accumulated on the silica particle surface and on in its' pores.

### **10.3.3 Catalyst Support Manufacturing Procedure**

The procedure consisted of creating the nickel micro fibrous silica support via a standard wet paper-lay process. A micro fibrous carrier consisting of a 2.0-3.0 vol. percent of 3  $\mu\text{m}$  (dia) Ni fibers was utilized to entrap 20-30 vol. percent of 75-150  $\mu\text{m}$  diameter silica particulates with a pore size of 6nm. This process was followed by an oxidative treatment at a temperature of 400 °C to remove binders associated with the paper lay process and was followed by a hydrogen reduction at 900 °C that allowed the micro fibrous nickel network to be sintered together around the silica powder to form a more rigorous support. The sintered support was solution impregnated with a 15 wt% percent cobalt nitrate hexahydrate and water solution. After completely immersing the sintered support in the 15 wt% percent cobalt nitrate hexahydrate solution, excess solution was removed via vacuum filtration to

remove the excess material that was not incorporated within the silica pores. This procedure was repeated 3 times and the support was dried in an oven at 90 °C overnight. The material was again subjected to an oxidative treatment that removed the nitrate portion of the cobalt precursor and produced a cobalt oxide that could be subsequently reduced to the active metal prior to its utilization as a FT catalyst.

#### **10.3.4 Utilization of Catalyst Support in Standard FT Reactor**

Initial experiments were performed to determine the applicability of the MCSS catalyst for Fischer Tropsch synthesis. A preliminary catalyst was prepared following the procedure detailed in Section 10.3.3 and was incorporated into an existing macro scale gas phase reactor. A standard sample was also manufactured that consisted of a nickel micro fibrous silica support that was void of the reactive catalyst, which was analyzed in order to determine the reactivity of the support material. The procedure used to produce this standard was the same as listed in Section 10.3.3, but without the subsequent cobalt nitrate loading. It should be noted that this catalyst is being testing in a high temperature reactor that has proven to be repeatable successful in prior runs. The macro scale experiment utilized the catalyst powder 4 (15nm Pore size, 100nm Avg particle size). This material showed promise as a potential Fischer Tropsch catalyst. It is important to note that the information learned from these experiments will not be directly transferable to our microreactor due to the different reaction pressures utilized for our system.

Two runs were made on the Wilmore 202 gas phase reactor utilizing the micro-fibrous material for FTS. The first was a blank run without the reactive catalyst. The second used a 15 % Cobalt loading on a silica supported nickel mesh. The Fischer-Tropsch Synthesis reaction was performed in a stainless-steel reactor (di-.5 inch, l = 2in). The reactor was loaded with 1 g of catalyst (1.7 g of overall micro-fibrous material). Prior to the catalytic experiments, the catalysts were reduced with hydrogen in situ at 300 °C. The reduction time was 4 hours. After the reduction step, the temperature was lowered to 250 °C under H<sub>2</sub>

and the reactant gas mixture ( $\text{H}_2\text{:CO:N}_2$ , v/v 63:33:1,  $\text{N}_2$  was the internal standard) was introduced at a total flow rate of 50 SCCM). The pressure was slowly increased to 250psi. Once the reaction temperature was achieved the reaction was led to proceed during a 24 hour period. Periodic sampling and temperature adjustments were made during this period to monitor there effects on catalytic activity. During reaction, the reactor effluent passed through a cold trap at 10 °C to collect both lighter products (water, alcohol, and hydrocarbons) and wax products. The effluent gases were depressurized and analyzed periodically by on-line gas chromatography.

A Varian 3800 gas chromatographic system equipped with a TCD detector was developed for the rapid on-line analysis of light Fischer-Tropsch products. A Haycep DB100/120 (part number 2836PC) packed column separates the most common  $\text{C}_1\text{-C}_5$  hydrocarbons. The packed column is used for the separation of methane, carbon monoxide, carbon dioxide, water and methanol. Retention characteristics for the analysis on the packed column are well characterized. The total analysis cycle is approximately 40 minutes. The heavier Fischer-Tropsch products are collected in a cold trap and are analyzed off-line. These products are injected into a liquid chromatograph Varian 3300 with a capillary tube (DB-5/ Part number 125-5032) that can resolve hydrocarbons from  $\text{C}_6\text{-C}_{30}$  utilizing a FID detector.

For the first experiment no liquid product was present in the cold trap. Analysis showed that minimal activity was associated with the nickel-based micro fibrous material void of catalyst indicating that any activity associated with the catalyst enhanced micro fibrous material would be due to the cobalt catalyst. The second experiment was performed with the 15 % Cobalt loading on a silica supported nickel mesh. The data in table 10.1 show a combination of results for the combination of the gas (analyzed via the TCD) and the liquid products collected (analyzed via the FID). The  $\text{CH}_4$  and  $\text{CO}_2$  selectivities are high, but that is to be expected with gas phase operation. Some interesting observations are that the olefin content of the liquid product was negligible and that the alpha value was quite high (79%),

although it should be noted that this owes most to the low temperature period. As such, this material shows considerable promise for gas-phase Fischer Tropsch synthesis.

| Date      | Reaction Temp (°C) | CO Conv | H <sub>2</sub> Conv | CH <sub>4</sub> Sel. | CO <sub>2</sub> Sel. |
|-----------|--------------------|---------|---------------------|----------------------|----------------------|
| 2/08/2008 | 214°C              | 100     | 94                  | 58                   | 24                   |
| 2/08/2008 | 214°C              | 100     | 93                  | 58                   | 25                   |
| 2/08/2008 | 204°C              | 100     | 90                  | 56                   | 26                   |
| 2/08/2008 | 195°C              | 99      | 93                  | 39                   | 20                   |
| 2/08/2008 | 194°C              | 40      | 49                  | 13                   | 1                    |
| 2/08/2008 | 204°C              | 100     | 90                  | 42                   | 37                   |

Table 10.1: Macro scale conversion data for cobalt impregnated silica supported nickel catalyst.

## 10.4 Systematic Probing of the Operating Parameters

The initial goals of this project include a complete analysis of the operating parameters associated with our designed microreactor. This included an analysis of the pressure drop through the reactor as influenced by the MCSS compression. Calculations were performed to characterize the flow characteristics within the reactor. Extended analysis included an analysis of the residence time distribution as influenced by compression.

### 10.4.1 Phase 1. Investigation of the Effect of Pressure Drop

- Investigate Pressure Drop as a function of (MCSS) compression
- Characterize the Residence Time Distribution as a function of compression

One of the main problems in using Micro reactors for heterogeneously catalyzed gas-phase reactions is the introduction of the catalyst in the reaction zone. The straightforward way is to fill the micro channels with catalyst powder. The size of the particles introduced generally ranges between 35 and 75  $\mu\text{m}$  in diameter, leading to a high pressure drop during the passage of fluid. In addition, each channel must be packed identically to avoid mis distribution, which is known to broaden residence time distribution while diminishing reactor performance. Another approach is create micro reactors with catalytically-active walls. The specific surface area is increased by chemical treatment of the channel walls or by their coating with a porous layer. The porous layer can serve as a catalyst or a support for a catalytic

phase. The main limitation of catalytic-wall micro reactors is the thickness of the porous layer. Since the majority of micro reactors are used for fast, highly exothermic reactions, the layer should be  $< 1\text{-}2\ \mu\text{m}$  in order to avoid mass/heat transfer limitations. Therefore, the total mass of the catalyst is too small for achieving high performance preferred for a unit of the reactor volume. In our micro reactor a micro fibrous catalyst support system (MCSS) with a structured catalytic bed consisting of entrapped particles in a sintered metal network whose void volume can be varied. Each (MCSS) possesses a 3-dimensional regular micro structure, resulting in a low pressure drop during the passage of reacting gases at higher void age. Our initial system investigations have included pressure drop investigation as a function of MCSS compression.

Pressure Drop Investigation Each of these experiments utilized the standard MCSS catalyst that incorporated the 15nm pore size (75-150 $\mu\text{m}$ ) particle size silica. These experiments were performed without the addition of the catalyst and represent the effects of solely the support system. The calculated ratio by weight for the silica to nickel fibers is 37.5 wt% Nickel / 62.5 wt% Si. Three different arrangements of the MCSS micro reactor were tested. (1) With compression to 1016  $\mu\text{m}$  and (2) with compression to 508  $\mu\text{m}$  and (3) with compression to 127  $\mu\text{m}$ . It should be noted that compression to the 127 micron completely blocked flow and was not included in the analysis. The pressure drop across the microreactor was measured with a differential pressure gauge placed at the reactor inlet and outlet. Calculations utilizing a modified reynolds number as suggested by the Taterchuk group revealed that the flow is in the laminar flow regime regardless of compression or void age these results are shown in Figure 10.12. This calculation is elaborated on in the powerpoint presentation and will be subsequently included.

A linear dependence on flow rate and pressure drop for both compressions has been found. The results were in good agreement with Darcy's Law and are presented in Figure 10.11. Darcy's law (Equation 10.10) for the pressure drop in a laminar flow was fitted to the

experimental data by a least-squares method,

$$\frac{\Delta P}{L} = \frac{\mu Q}{kA} \left[ \frac{Pa}{m} \right] \quad (10.10)$$

With the surface,  $A = f(\text{compression})$ ,  $L = .0381\text{m}$ ,  $\mu = 1.98\text{E-}05 \text{ Pa/sec}$ ,  $P = Pa$

The MCSS membranes consisted of identical loadings of silica at a 62.5 wt% loading. The difference in pressure drop caused by compression was very significant and is shown to be at least three orders of magnitude greater with a doubling of compression. This indicated that compression could significantly influence the residence distribution time by forcing a higher velocity to overcome the pressure differences.

#### 10.4.2 Residence Time of Distribution

The RTD was obtained from measured response curves to the step change in the reactor inlet from flow of He to O<sub>2</sub>. The responses were first obtained for the installation only (without reactor). The measurements were then done with the empty reactor without MCSS. Finally, reactor + MCSS were characterized. The  $F[t]$  function was obtained after a normalization of the concentration response. These three functions,  $F[t]$ , are shown in Figure 10.13 and Figure 10.14.

The axial dispersion in the micro reactor is however more visible when the function,  $F[t]$ , is transformed into a function,  $E(t)$ , as presented in Figures 10.15 and 10.16. The  $E(t)$  curve was calculated from the following equation:

$$E(t) = \frac{dF}{dt} \quad (10.11)$$

For the case indicated in Figures 10.13 and 10.14 at a flow rate of 5.0 ml/min the MCSS with the lower compression (1016  $\mu\text{m}$ ) increased its residence time only slightly over the empty reactor. But, upon compression to the 508  $\mu\text{m}$  range the residence time for the gas in the MCSS was much greater than the residence time of the empty reactor.

Further studies were performed with a variable flow rates as illustrated in Figures 10.17 and 10.19. Figure 10.18 represents the data obtained from the 1016  $\mu\text{m}$  compression at varying flow rates from 5.0 ml/min to 25.0 ml/min. There is a transition between 5.0 ml/min and 25.0 ml/min where the residence time is less affected by the MCSS and it appears that the effect of frictional drag becomes less inhibitive of flow or the compressibility of the gas starts to become more of an issue. Based on the information shown in Figure 10.18 as the flow rate is increased the dispersion becomes decreased at this compression.

Figure 10.19 represents the data obtained from the 508  $\mu\text{m}$  compression at varying flow rates from 5.0 ml/min to 25.0 ml/min. For this compression between 5.0 ml/min and 25.0 ml/min the residence time is greatly influenced by the MCSS and it appears that the effect of frictional drag becomes more of an issue. Based on the information shown in Figure 10.20 as the flow rate is increased the dispersion becomes decreased at this compression but to a much lesser extent than that at the lower compression.

Data has been collected for the 1016 compression as a function of temperature and appears to trend as expected. The RTD shown at 5.0 ml/min show that the distribution becomes more narrow as a function of increased temperature and is shown in Figure 10.21. Work has not completed on the lower compression material as a function of temperature.

There was a drastic differences in residence time based on compressibility coupled with the pressure drop.

## 10.5 Microreactor Utilization for Fischer Tropsch Synthesis

As directed by committee during the preliminary exam, the focus of this work became limited. Suggestions were to discontinue the pressure drop measurements, RTD studies, and catalyst investigations shifting focus to simple experimental observations. Namely,

- Goal 1. Determine if the System Works.
  - Experiments suggested:
  - Utilization of only one catalyst loading (same calcination procedure as with the macro reactor testing)
  - Limit catalyst compression to one setting (1014  $\mu\text{m}$ )
  - Measure product distribution as a F(reactor temperature) and F(flow rates) to determine system limitations and outcomes.
- Goal 2. Repeat experiments with a different bed geometry and compare selectivities.

## 10.6 Results and Conclusions

Experiments were carried out in the microreactor system as illustrated in Figure 10.22 under isothermal conditions. The micro fibrous catalyst support system (MCSS) is “sandwiched” by two separated heat transfer channels, which are designed to maintain a high heat transfer coefficient. The MCSS described above is snugly inserted in the microreactor providing the total length of the catalyst bed of 2.5 inches. The reactants can be preheated to a desired temperature in the upstream portion of the channel before entering the catalyst bed. The individual channel of the microreactor has the dimension of: 2.5” (x-direction) X variable (y-dir) X .25” (z-dir). The channel is filled with the MCSS and there is no gap between the catalyst pieces and the reactor walls. A thermocouple is placed on the outlet side just above the MCSS.

To begin the catalyst was activated in a 3% hydrogen / helium blend at 350 °C in situ overnight, followed by the introduction of the syngas feed with H<sub>2</sub>/CO ratio of 2. Before measurements were performed the system was equilibrated for 24-hours at a given flow rate. Initial settings ranged from 5.0 ml/min to 0.1 ml/min beginning with the highest settings and gradually stepped down to the lower values. From this initial test- a set flow rate of 0.1 ml/min was required to obtain measurable conversion. Noncondensed gases are analyzed using an on-line gas chromatography to determine CO conversion and light product selectivity. All process parameters such as temperature, pressure, flowrates were recorded.

At this point in time selectivity was only for CO<sub>2</sub> and methane with limited conversion. While maintaining the 0.1 ml/min flow rate experiments were performed with 24 hour equilibration with a reduction in temperature at 10 °C intervals. Once the temperature was reduced to 280 °C measurable conversion was not observed. From this information it was determined that the catalyst was not active and the conversion noted was due to thermal effects.

A new catalyst material was reduced ex-situ in the 3% hydrogen / helium blend at 350 °C at a higher flow rate of 100 ml/min (consistent with TGA analysis) and introduced into the microreactor system in an attempt to make the catalyst more reactive. Again, the catalyst was treated in a 3% hydrogen / helium blend at 350 °C overnight at 5.0 ml/min and followed by the introduction of the syngas feed with H<sub>2</sub>/CO ratio of 2. Before measurements were performed the system was equilibrated for 24 hours at a given flow rate. Initial settings ranged from 5.0 ml/min to 0.1 ml/min as the experiment before beginning with the highest settings and gradually stepped down to the lower values. From this initial test- a set flow rate of 0.1 to 2.0 ml/min was required to obtain measurable conversion. The lower flow rates gave higher conversions and better selectivities toward C<sub>4</sub> products as measured with GC. The best conversion values were obtained at 280 °C a temperature which was much higher than what was expected. This high temperature could be indicative of reduced thermal contact with the MCSS membrane. This microreactor system is a low pressure system relying on only

the pressure drop accross the reactor to aid in conversion. Results obtained for conversion were very poor and no products above C<sub>5</sub> were observed.

To close the loop on the experiments a different reactor geometry was analyzed (cone type) with a higher built in pressure drop. As no RTD distribution or pressure drop measurements were performed on this reactor it is difficult to determine the true influence of this geometry. The experiments were repeated with the *ex-situ* reduction of the catalyst. The catalyst amount was the same by mass even though a different geometry was placed into the reactor. The same experimental scheme as mentioned previously was performed stepping down flow rates and temperatures for comparative purposes. The results of the experiments were similar to what was observed previously and not direct trend data was obtained.

Work was discontinued on this project.

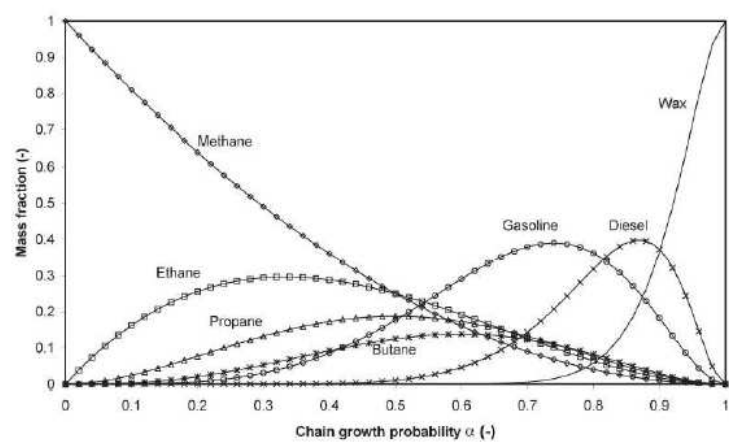


Figure 10.1: Typical Fischer Tropsch product distribution based on chain growth probability.

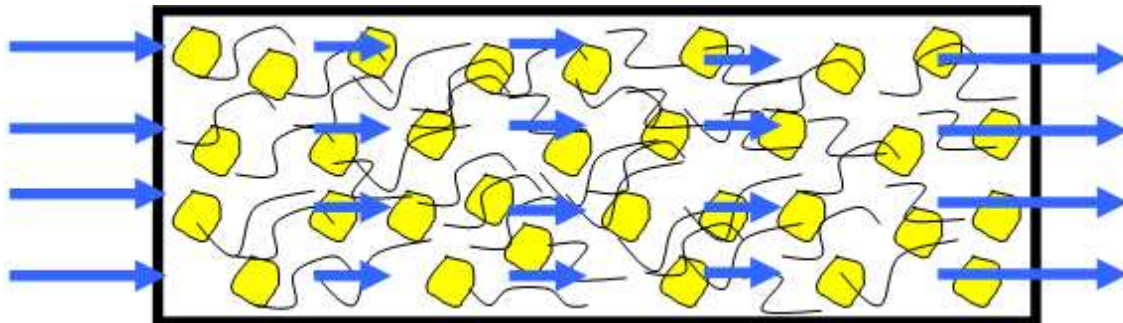


Figure 10.2: Representation of gas flow through a micro fibrous catalytic support system.

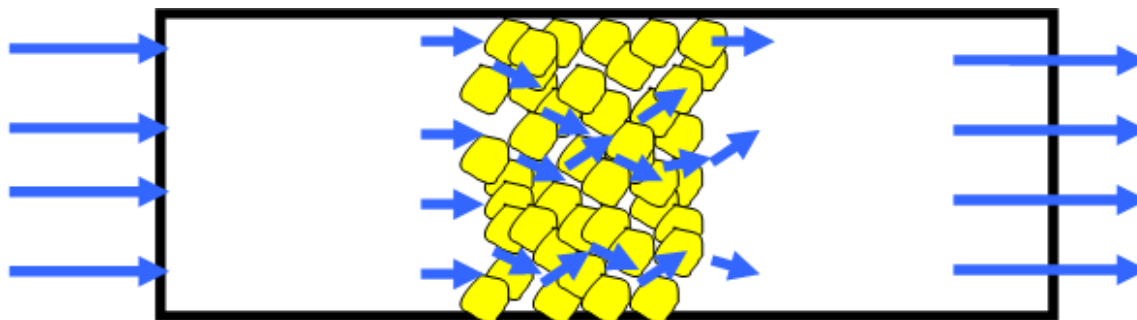


Figure 10.3: Representation of gas flow through a standard packed bed reactor.

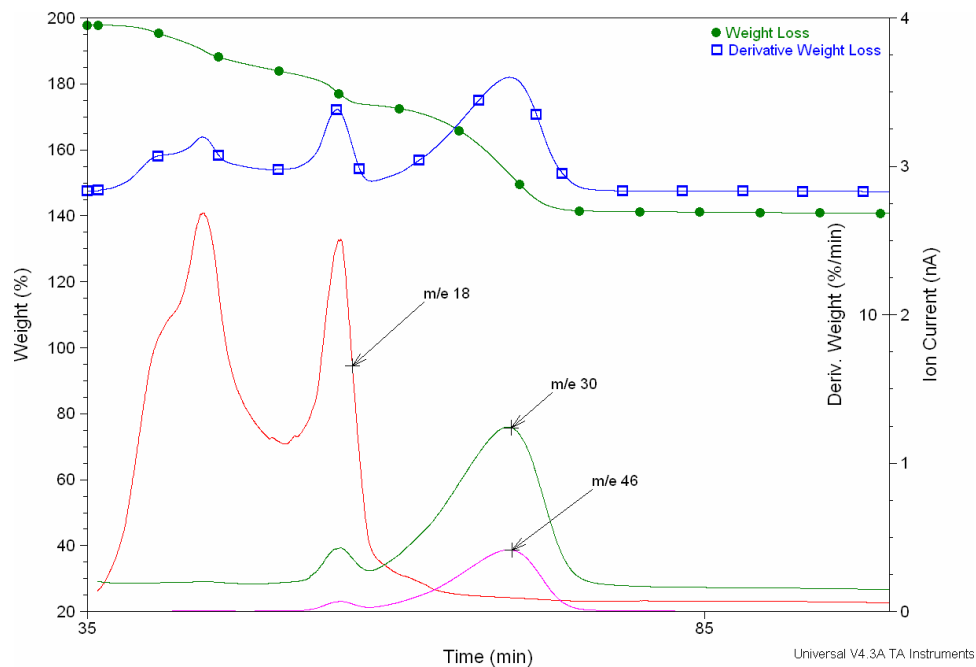


Figure 10.4: Calcination of unsupported cobalt nitrate powder in 100 ml/min air and a ramp rate of 10 °C/min.

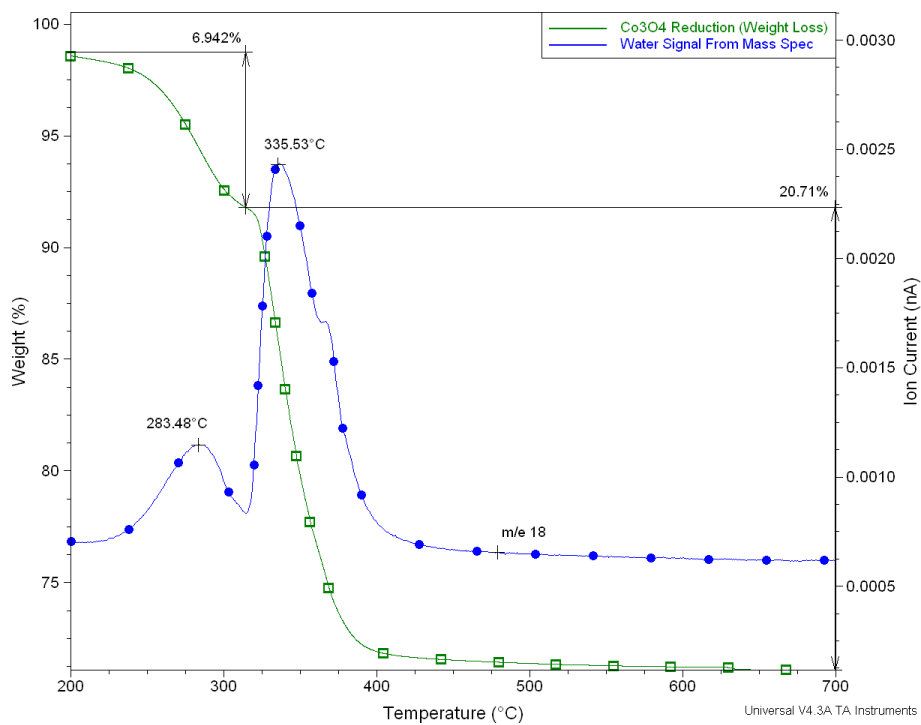


Figure 10.5: Reduction of unsupported  $Co_3O_4$  with a 100 ml/min 3%  $H_2$ / Helium flow and ramp rate of 10 °C/min.

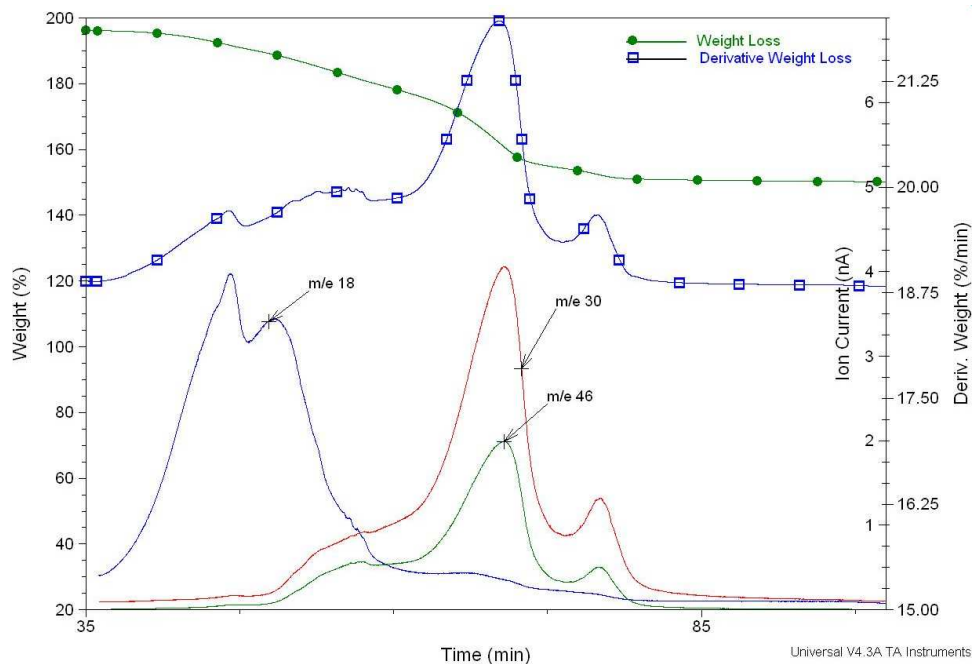


Figure 10.6: Calcination of silica-supported cobalt nitrate powder in 100 ml/min Air and a ramp rate of 10 °C/min.

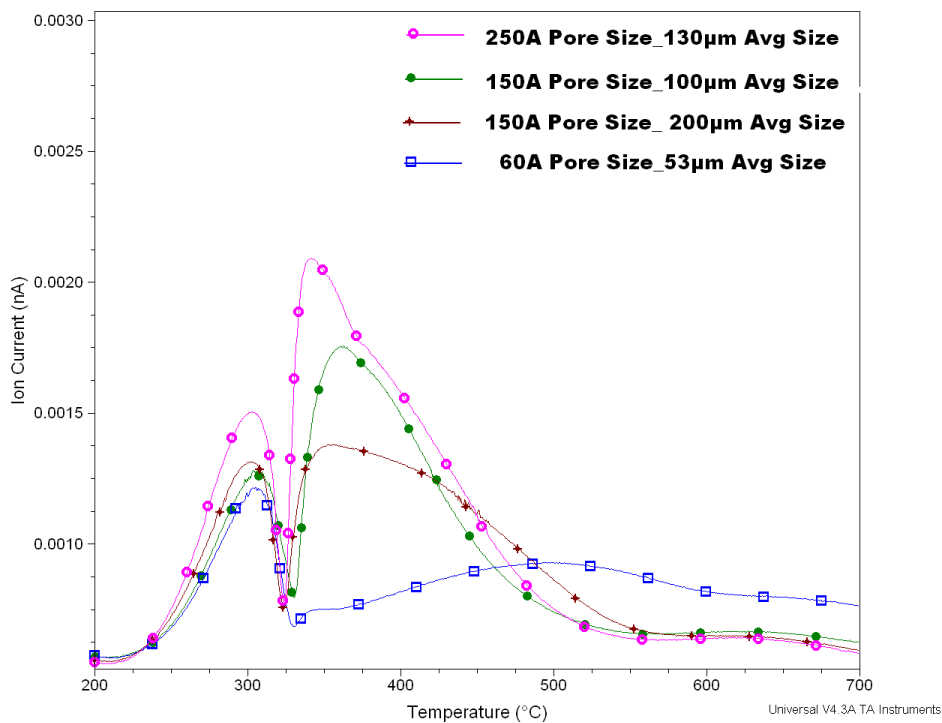


Figure 10.7: Water evolution during the reduction of  $Co_3O_4$  with a 100 ml/min 3%  $H_2$ /Helium flow and ramp rate of 10 °C/min as a function of pore size.

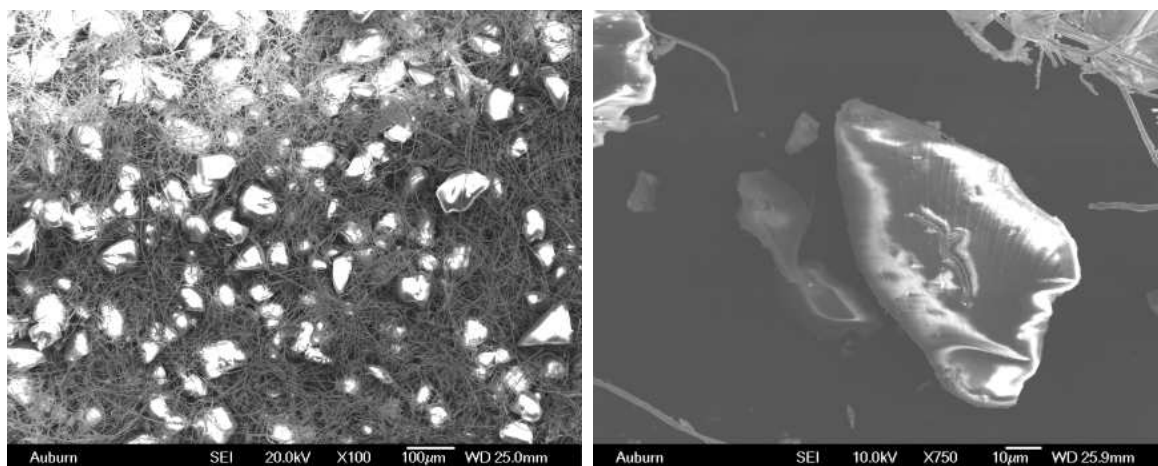


Figure 10.8: [Left] MCSS Sheet prior to solution impregnation. [Right] Individual particle from MCSS Sheet.

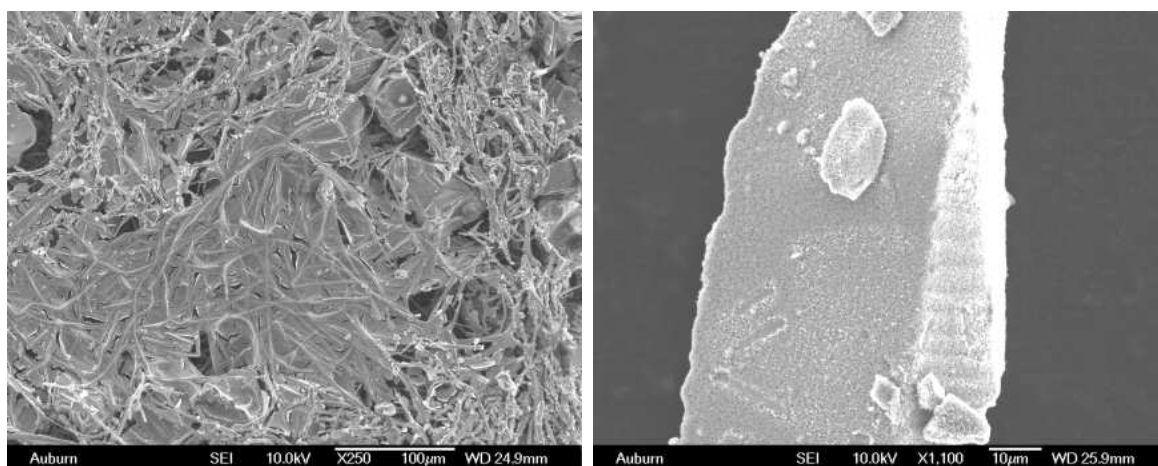


Figure 10.9: [Left] MCSS Sheet that has been impregnated and dried by blotting method and subsequently calcinated [Right] Individual particle after calcination.



Figure 10.10: Illustration of the microreactor system fabricated for this work.

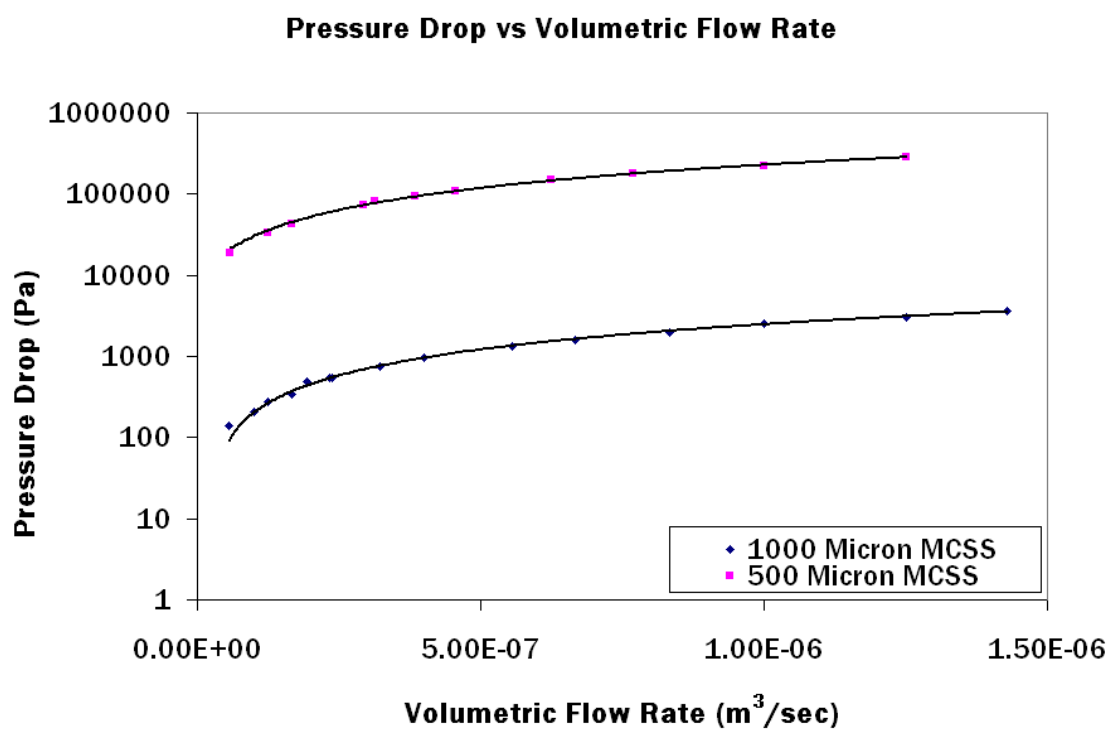


Figure 10.11: Measured pressure drop across the microreactor as a function of compression as fitted by Darcy's law.

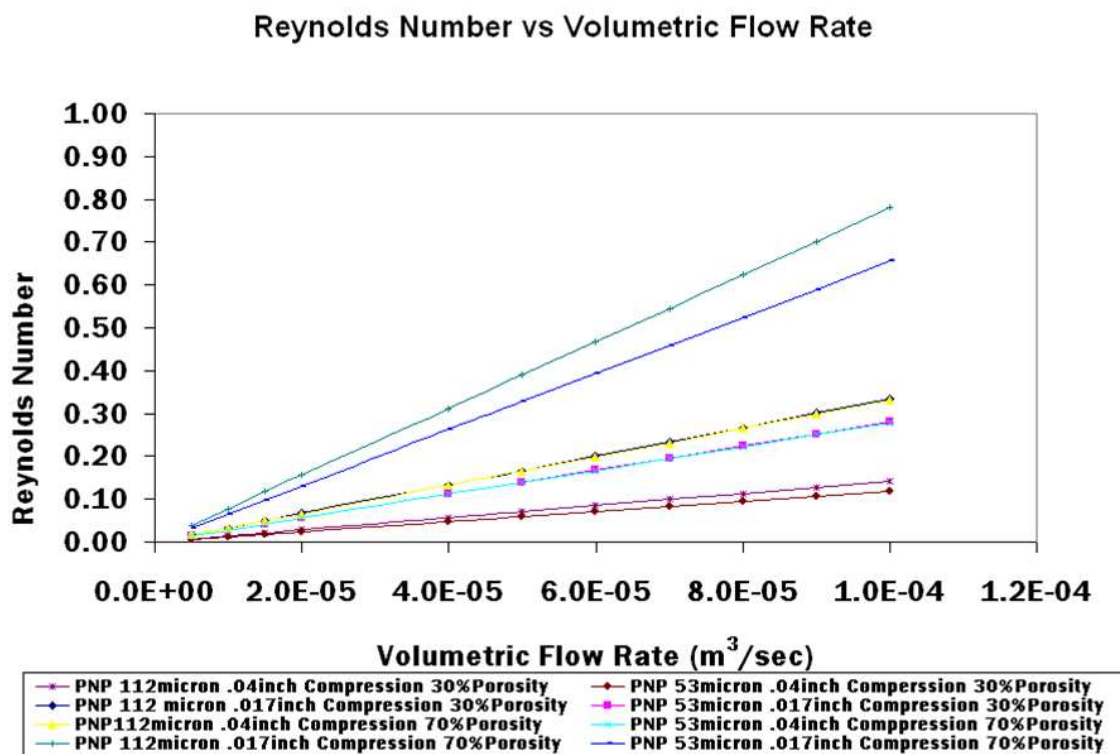


Figure 10.12: Reynolds number calculations in a MCSS as a function of variable compression, void volume, and volumetric flow rate.

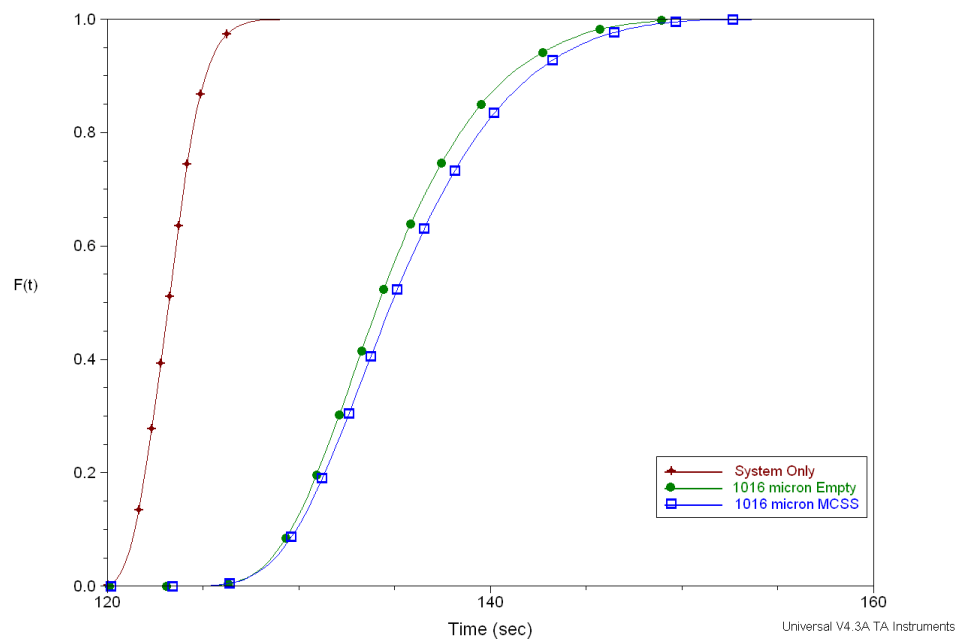


Figure 10.13:  $F(t)$  Break-through curve  $\text{He} \rightarrow \text{O}_2$  at 5.0 ml/min,  $T= 298 \text{ K}$  at 1016  $\mu\text{m}$  compression.

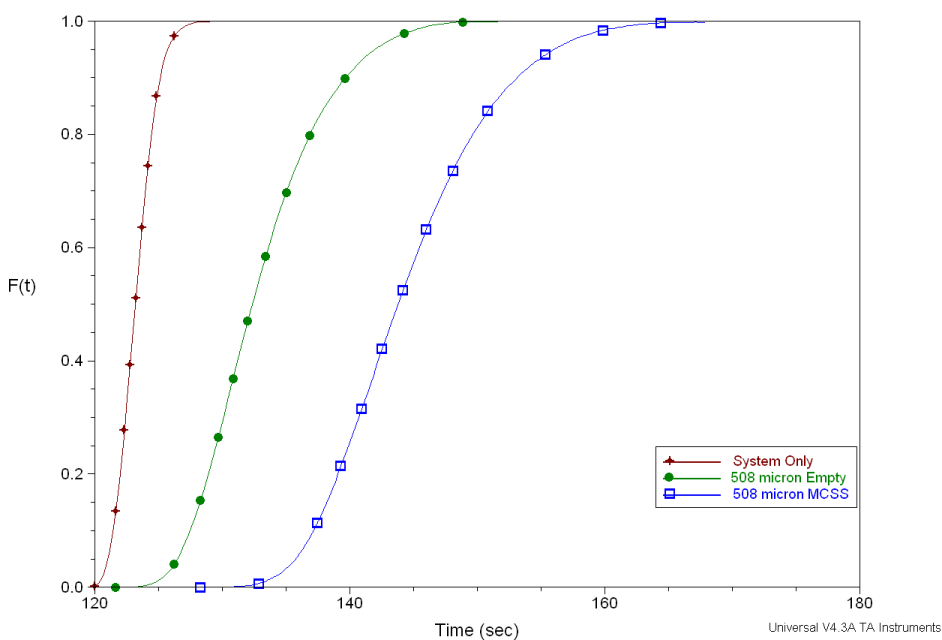


Figure 10.14:  $F(t)$  Break-through curve  $\text{He} \rightarrow \text{O}_2$  at 5.0 ml/min,  $T= 298 \text{ K}$  at  $508 \mu\text{m}$  compression.

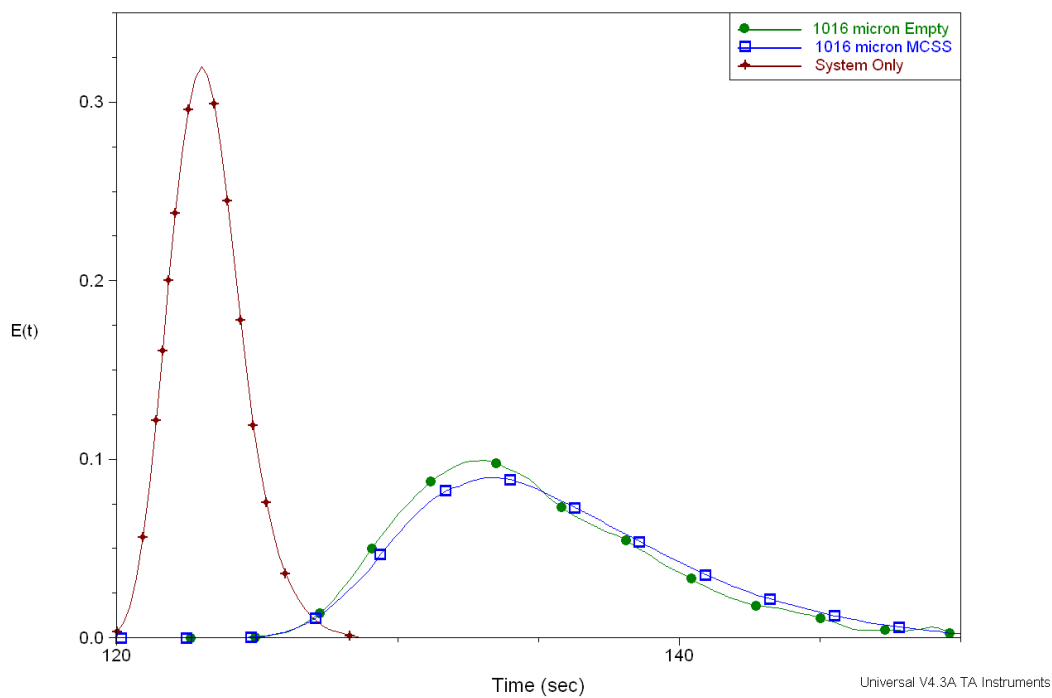


Figure 10.15:  $E(t)$  Break-through curve  $\text{He} \rightarrow \text{O}_2$  at 5.0 ml/min,  $T= 298 \text{ K}$  at  $1016 \mu\text{m}$  compression.

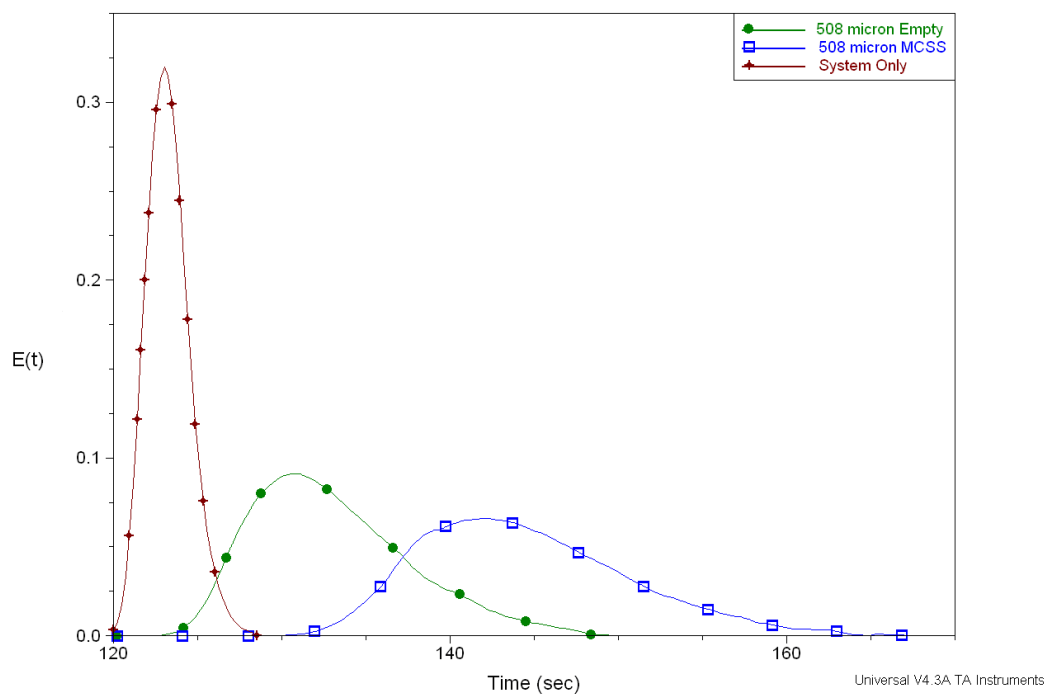


Figure 10.16:  $E(t)$  Break-through curve  $\text{He} \rightarrow \text{O}_2$  at 5.0 ml/min,  $T= 298 \text{ K}$  at  $1016 \mu\text{m}$  compression.

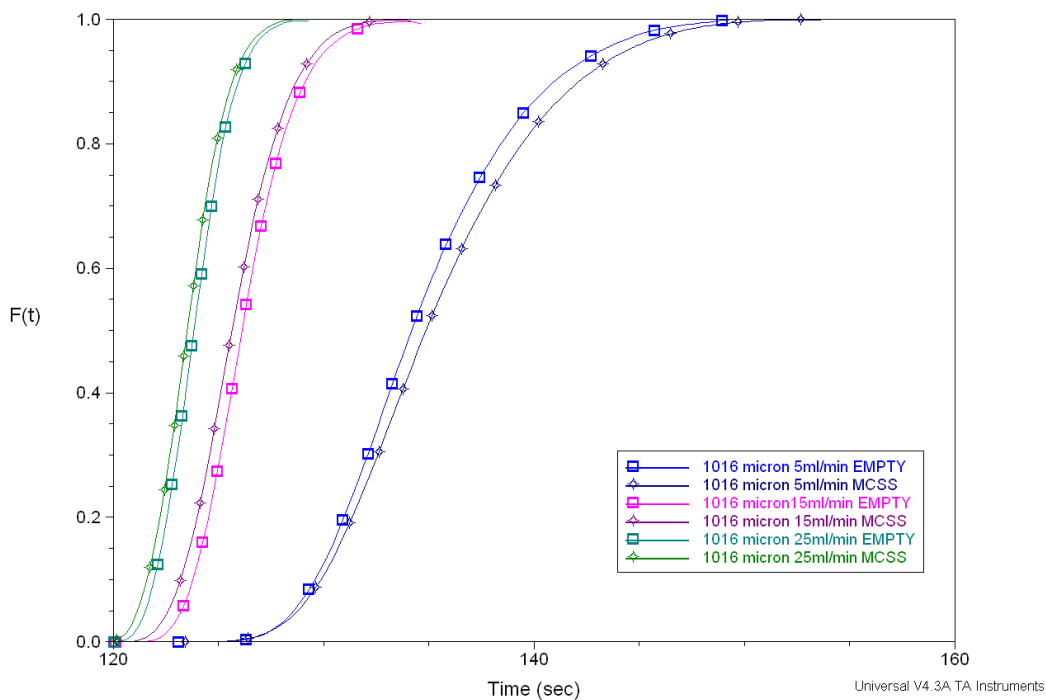


Figure 10.17:  $F(t)$  Break-through curve  $\text{He} \rightarrow \text{O}_2$  at variable flow rates,  $T= 298 \text{ K}$  at  $1016 \mu\text{m}$  compression.

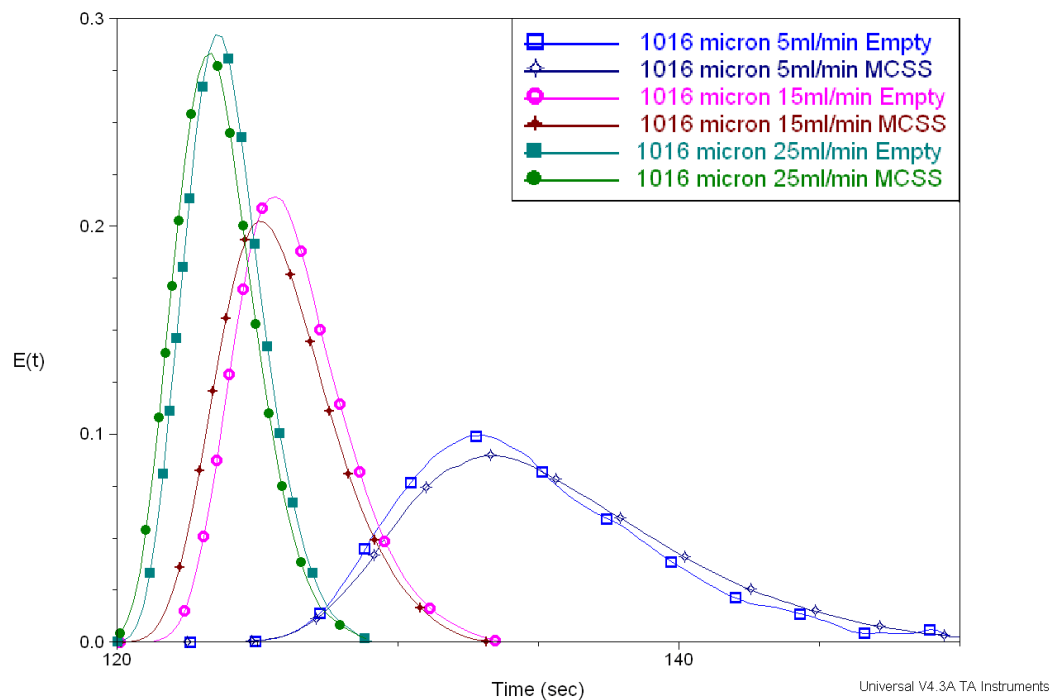


Figure 10.18:  $E(t)$  Break-through curve  $\text{He} \rightarrow \text{O}_2$  at variable flow rates,  $T= 298\text{K}$  at  $1016 \mu\text{m}$  compression.

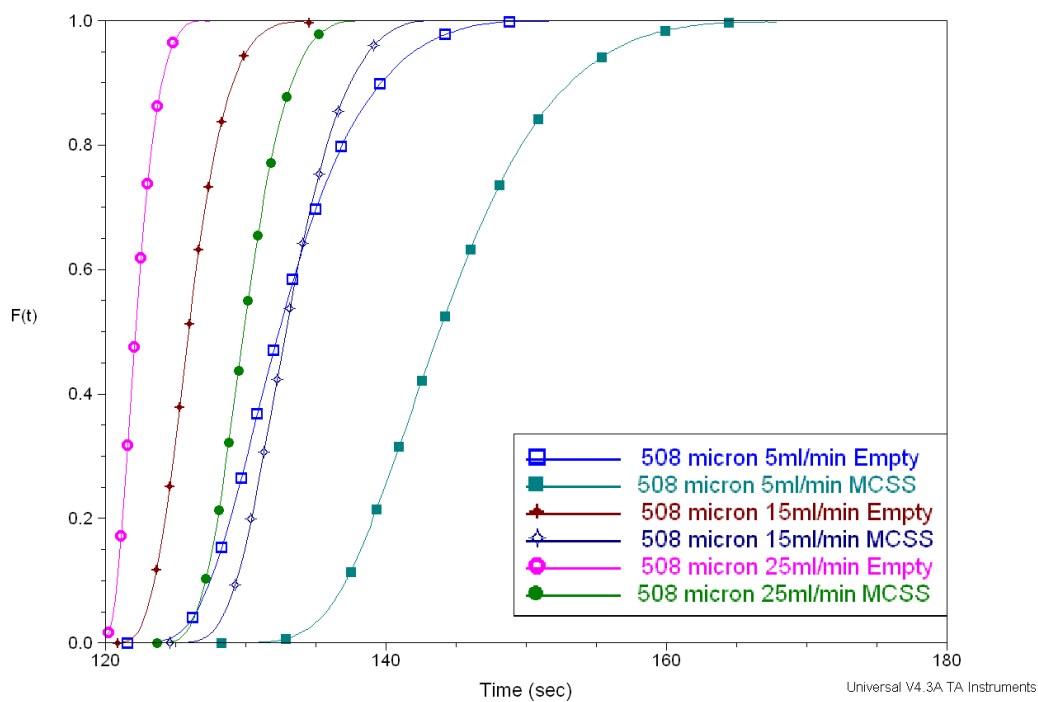


Figure 10.19:  $F(t)$  Break-through curve  $\text{He} \rightarrow \text{O}_2$  at variable flow rates,  $T= 298\text{K}$  at  $508 \mu\text{m}$  compression.

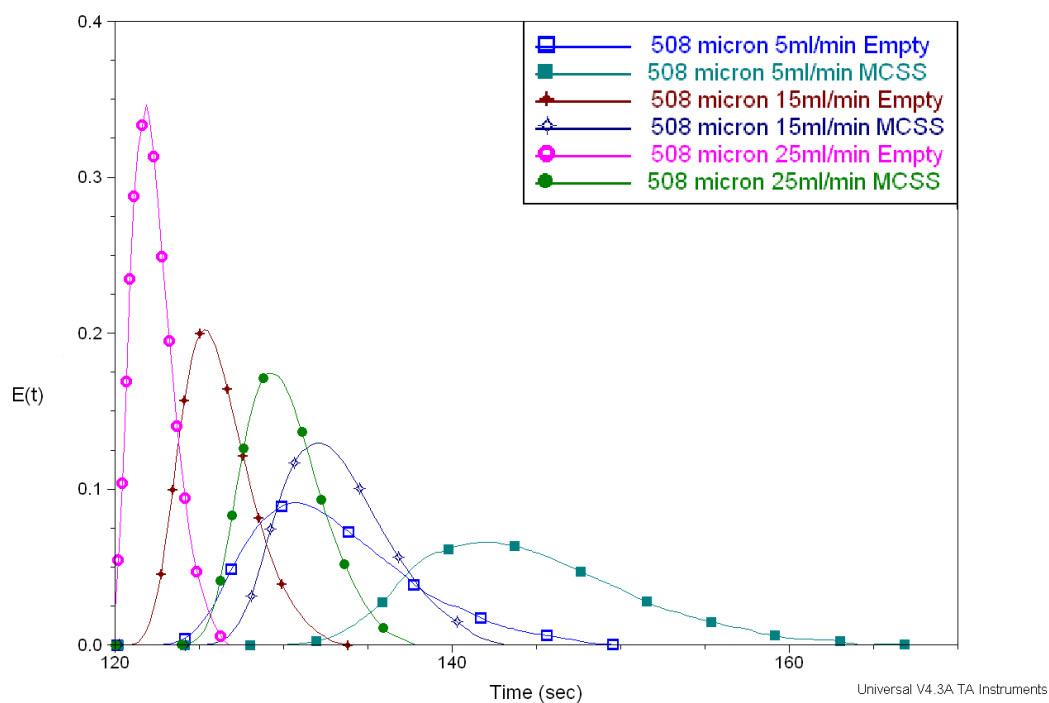


Figure 10.20:  $E(t)$  Break-through curve  $\text{He} \rightarrow \text{O}_2$  at variable flow rates,  $T = 298\text{K}$  at  $508\ \mu\text{m}$  compression.

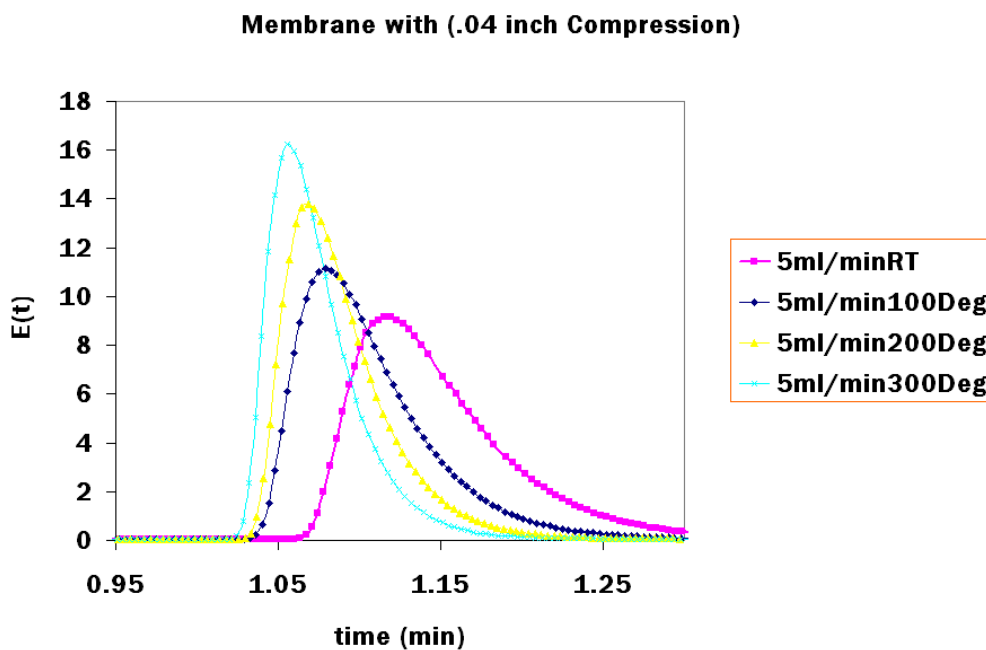


Figure 10.21: Residence time distribution as a function of temperature at a set flow rate of  $5.0\ \text{ml/min}$ .

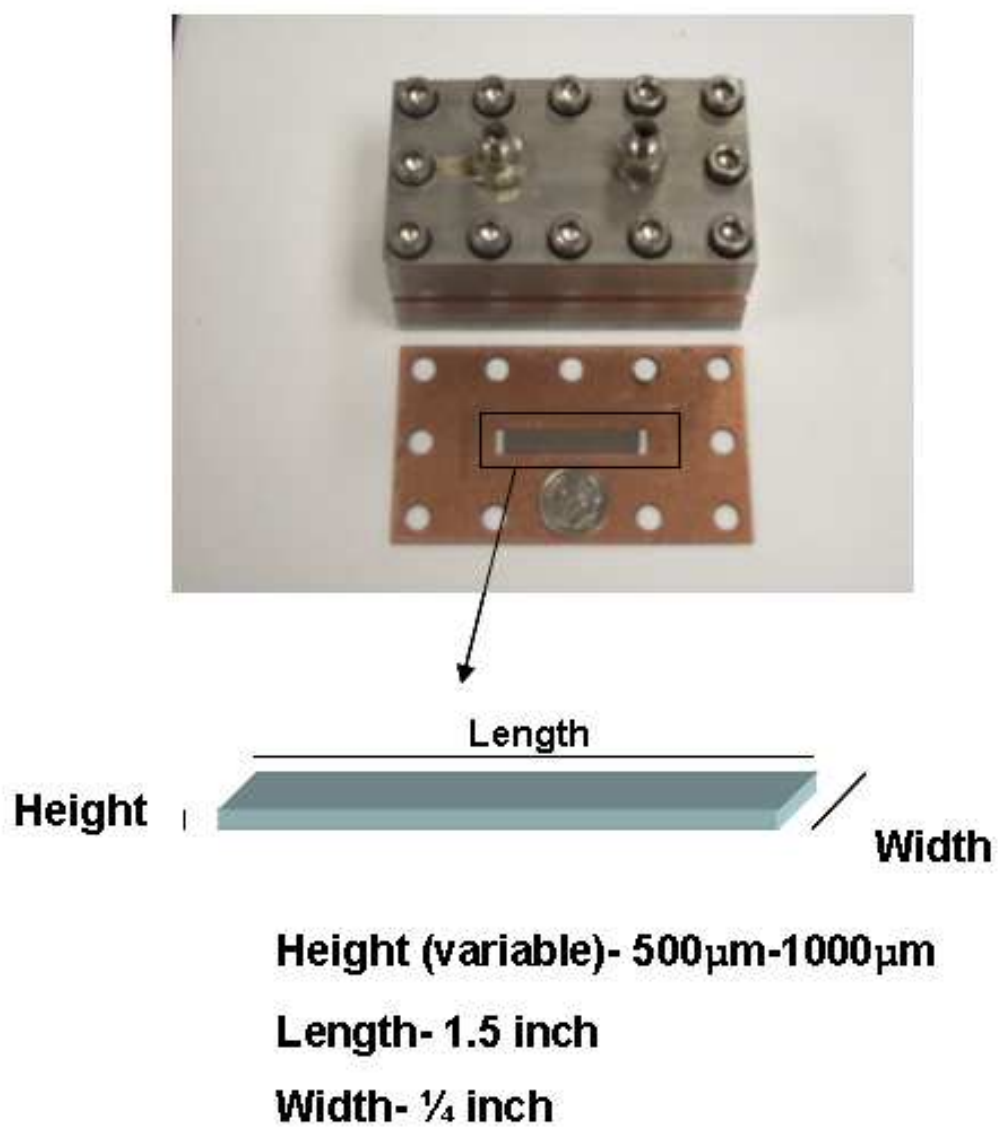


Figure 10.22: Photograph of microreactor fabricated for this work.

## Part III

# Interfacial Engineering of Microfluidic Devices

## Chapter 11

### Surface Engineering of Poly(dimethylsiloxane) Microfluidic Devices

#### 11.1 Motivation

Polydimethylsiloxane (PDMS) has become a material of choice for the fabrication of microfluidic devices. It is inert, bio-compatible and maintains a transparency that has proven convenient for visualization and detection. The flexibility of PDMS is suitable for the integration of flow control devices such as, micro valves and micro pumps, that can be easily incorporated due to PDMS ability to be manipulated via soft lithography [188]. Despite its advantages, the use of PDMS is limited because of poor control of its surface properties. Surface chemistry is of great importance in microfluidic devices due to the high surface area-to-volume ratio. There has been much research dedicated to modification of the surface properties of PDMS to overcome the limitations associated with microfluidic devices, such as; protein absorption, solvent incompatibility, and surface wet ability. Water vapor diffusion in PDMS also limit many applications that require increased temperatures and is particularly important as related to PCR Applications [189]. It is the limitation associated with temperature cycling as related to PCR investigations that prompted this work.

A Molecular Vapor Deposition (MVD) silica layer has been shown to deposit onto PDMS surfaces resulting in a stable reactive surface capable of sustaining much of the same chemistries associated with glass surfaces [190]. Due to its low-temperature deposition condition, controlled coverage and process tunability it is expected that this silica layer could also be capable of improving the water barrier properties associated with PDMS microfluidic devices. Investigations are performed to characterize the water diffusion as influenced by an added silica layer. Prior to this investigation, PDMS devices are custom fabricated and a

baseline testing method was established for water diffusion measurements. In addition, a detailed investigation of water vapor diffusion as influenced by curing conditions is illustrated as this information proved vital and unattainable current literature.

## 11.2 Background Research

There has been significant research aimed at miniaturized and fully integrated lab-on-chip systems for applications, such as drug screening, cellular assays, protein analysis, and point-of-care diagnostics. PDMS an inexpensive elastomeric polymer has emerged as a promising material for lab-on-chip applications [191]. The ease in fabrication with both rapid prototyping and mass production techniques as well as lower cost relative to silicon and glass makes it particularly attractive for the development of microfluidic applications [192]. These systems offer a drastically reduced liquid sample and reagent volume, and an increase the speed of analysis [192,193]. In addition, these miniaturized lab-on-chip systems, also known as micro-fluidic devices, offer the potential for parallel analysis of multiple samples on a single chip. Within these devices there must be precise micro-fluidic control via the integration of pumps, valves, mixers, separation units, reactors and detectors. Recent developments in miniaturization technology have already had a great impact on the biomedical research field. The MEMS-based polymerase chain reaction (PCR) chamber is one of the great progresses. PCR is a well-characterized method for the selectively identical replication of DNA molecules. By an enzymatic amplification process, the concentration of a DNA species is nearly doubled through a cycling between three different temperatures. In this way, the DNA concentration can be multiplied more than a million times by about 30 cycles of temperature.

PDMS is a silicon-based organic polymer consisting of repeated  $[\text{SiO}(\text{CH}_3)_2]$  units. The PDMS used for our micro structure application is a RTV-615 silicone rubber, (*i.e.* Room Temperature Vulcanizing) silicone composed of two components: a base and a curing agent. Upon curing, the siloxane base oligomers containing vinyl groups are linked to the hydrogen

containing curing agent oligomers through a hydrosilylation reaction, forming Si-CH<sub>2</sub>-CH<sub>2</sub>-Si linkages. The curing agent contains a platinum-based catalyst that is needed to catalyze the hydrosilylation reaction. As seen from the reaction diagram in Figure 11.1, the multiple reaction sites on both the base and curing agent oligomers allows for 3-D cross linking.

The ability of PDMS to serve as a useful substrate for microfluidic fabrication extends from advantages such as high gas permeability, good optical transparency, mold ability, non toxicity or bio compatibility, low curing temperature, and ease of sealing with other materials [194]. It can be bonded to a variety of materials including glass, quartz, silicon, polystyrene, and polyethylene after oxygen plasma oxidation [195]. Although PDMS has many advantages, there are some physical properties that limit its broad application. PDMS is hydrophobic, and small hydrophobic molecules, biopolymers, and cells can all irreversibly adsorb to the surface [196]. Water vapor diffusion in PDMS has also been shown to limit many applications that require increased temperatures.

There have been numerous investigations of water vapor diffusion in PDMS as related to membrane applications. The techniques involved have ranged from simple gravimetric techniques, quartz crystal micro balance measurements, spectroscopic systems based on vapor phase absorption of IR, and various iterations and improvements on vapor permeation cells [197,198]. Recognition of the problem of water vapor diffusion as applied to microfluidic devices has prompted some studies on ways to eliminate or reduce the diffusion of water. Lounaci *et al.* placed a PDMS microdevice in a controlled humidity chamber to control dehydration by manipulating the partial pressure of water around the microdevice thus controlling the driving force [199]. Other researchers have investigated techniques to deposit either internal barrier layers or external barrier layers. These investigations have incorporated solution coating methods, sol-gel techniques and CVD deposition of various materials ranging from oxide layers to different polymeric materials to produce barrier layers [189, 194, 200–202]. Although these investigations have provided some improvement, microfluidic devices are still

limited to applications that require reduced temperatures or are designed in such a way that water vapor diffusion is controlled.

### **11.3 Investigation of Water Vapor Diffusivity in PDMS Devices as Influenced by Curing Conditions**

One production step often overlooked and under-examined is the choice of the curing scheme as related to vapor diffusion properties within a microfluidic device. Despite the manufacturers' recommended curing time for PDMS, many unique protocols exist for the production of microfluidic devices. Many of the protocols have focused on ways of optimizing valving processes, modifying overall microfluidic device reactivity, or on improving inherent bonding difficulties in PDMS [203]. In fact, there are not many research groups who perform the same manufacturing protocol for microfluidic devices. While many curing techniques have been optimized and widely studied, it is hard to ascertain if one method has an advantage over another in terms of vapor diffusion properties. For example, the recommended cure time for RTV 615 is 24 hours at room temperature. But research indicates that PDMS curing can be accelerated by applications of heat for short periods and that too much heat will create a stiff PDMS structure which can prove detrimental to pumping processes [204]. It has also been shown that PDMS can be made more stable by thermally aging microfluidic devices [205]. Because chemical cross linking can alter the composition of a polymer, and can consequently increase or decrease molecular permeability, the choice of a curing regimen could drastically influence the cross linking in PDMS and have strong implications toward water vapor diffusivity [206].

This research focuses on a simple gravimetric approach that utilizes TGA-MS to investigate the steady state diffusion of water vapor from within a PDMS device as a function of temperature. PDMS test devices are created by utilizing two different curing mechanisms. The first being a 24-hr room temperature cure as recommended by the manufacturer and a second that relies on a brief exposure (1hr to 100 °C) followed by a 24 hour exposure to

room temperature. The intent of this work is to measure and identify any differences in the steady state diffusivity measurements of water vapor as a influence by curing conditions. The choice of temperature cycling ranges from ambient to 75 °C(lowest maximum) to 95 °C(highest maximum) both to expedite the measurement process and to mimic the conditions encountered in PCR measurements. This work was necessary to establish a baseline for diffusivity measurements as influenced by curing conditions and provides a means to decouple any changes in vapor diffusion as influenced by barrier layers and the various techniques utilized to incorporate the barrier layers. This work was necessary to provide a baseline for diffusivity measurements and provides a means to monitor our subsequent investigations on surface modification which will be explained in more detail in a later section.

## **11.4 Experimental Details**

### **11.4.1 Materials**

Silicon wafers, p-type, with (100) orientation were obtained from University Wafer (Boston, MA). GE Silicon RTV 615a and RTV 615b were purchased from Allied Electronics and used as received. Deuterated Water was purchased from Acros Organics packaged in 0.75 ml ampules with a molecular weight of 20.02 g/mol. Each ampule was opened just prior to use and the D<sub>2</sub>O was utilized within 10 minutes of opening.

### **11.4.2 Wafer preparation and cleaning**

Both silicon wafers and diced silicon samples are used in this work. Silicon samples are prepared by cutting the silicon wafers into 8mm × 8mm squares with a dicing saw. Silicon wafers and diced silicon are sonicated in acetone for ten minutes and then again in isopropanol for ten minutes and then dried under a stream of nitrogen. Samples are etched for ten minutes in concentrated HF to remove the native oxide layer, rinsed in copious amounts of deionized water, and then dried under a stream of nitrogen. Samples are then loaded into a custom-built vacuum deposition system, the design of which is based on a previously described

system [88], for oxygen plasma treatment. Briefly, the vacuum deposition system consists of a rotary vane pump (base pressure 0.4 Pa) which is coupled to a glass reaction chamber that contains perforated electrodes which can be biased to create an *in situ*, capacitively-coupled radio frequency (RF) plasma (13.56 MHz). MKS Baratron capacitance manometers are used to monitor the system pressure up to  $1.3 \times 10^4$  Pa. After introducing the samples into the vacuum system, the system is evacuated to a pressure of less than 2.6 Pa. Oxygen gas is then allowed to flow through the system, and an oxygen background is established by multiple pump-purge cycles with oxygen gas. Then, the oxygen pressure is allowed to stabilize around 33.3 Pa, at which point the chamber is isolated from the pump. An RF plasma is struck at 50 W forward power, and the samples are exposed to the plasma for five minutes. This treatment grows an oxide layer about 2 nm thick on the silicon surface. The samples are removed from the vacuum deposition system and etched again for ten minutes in concentrated HF, rinsed in copious amounts of deionized water, and dried under a stream of nitrogen. An additional oxygen plasma treatment is employed to re-grow an oxide layer. Treating the samples by this method “peels off” the uppermost layers of the crystal surface, revealing a clean, flat surface. This iterative cleaning method is repeated until inspection by contact angle and AFM indicate that a clean (contact angle  $< 5^\circ$ ), flat (RMS roughness  $\sim 0.2$  nm) surface has been obtained, but usually two iterations suffice.

### 11.4.3 Teflon Mold Fabrication

A teflon mold was fabricated and incorporated onto a silicon wafer. This mold consisted of a 4.0 inch diameter machined teflon disc (1/4” thick) consisting of multiple holes with an outer hole diameter of 1/4”. The teflon ring was attached to the silicon wafer surface and an inner teflon cylinder with an outer diameter of 1/8 ” was centered in each of the holes. The teflon disc and center cylinders were secured by applying a light layer of PDMS to both the disc and the cylinders. An illustration of the mold is shown in Figure 11.2. The mold

and silica unit was inserted into an aluminum pan for containment and placed in the furnace at 100 °C for 1-hour prior to utilization.

#### **11.4.4 PDMS Preparation**

GE RTV 615 Parts (a and b) were mixed according to the manufactures' instructions in a ratio of 10:1 by weight. The components were stirred for 3 minutes and then the mixture was pored over the teflon mold described in 11.2. Enough PDMS was applied to ensure that the entire mold would be completely submerged within the PDMS solution. The PDMS was also poured onto into an ZnSe ATR accessory to be utilized for FTIR analysis. The PDMS filled mold and ATR accessory were placed in the vacuum chamber previously described in section 11.4.2. The PDMS mixture was degassed under vacuum until the pressure was less than 10 mtorr.

Clean diced silicon squares were placed over each of the holes on the mold. Pressure was applied until the silica wafer laid flat against the mold. The silica wafer was initially applied at an angle which ensured that there would be no air entrapment between the silica and the diffusion cell. The PDMS mold structure and ATR accessory were cured either by placing in an oven for 1hr at (100 °C) and followed by room temperature for 24 hours or by leaving at room temperature for 24 hours. After curing the mold the silica squares are removed exposing a clean smooth surface. The wafer is then removed from the mold which exposes the individual diffusion cells which are still attached to the wafer. These cells are then removed by a gentle peeling and the center teflon cylinders are removed by applying a light pressure with a center punch.

#### **11.4.5 Deuterated Water Loading and Plasma Treatment for Device Sealing**

The PDMS Diffusion cells are placed on a clean piece of silicon and placed into the vacuum system. Placing the device on a clean piece of silicon allows for isolation of the plasma to the exposed surface (top). After introducing the samples into the vacuum system,

the system is evacuated to a pressure of less than 2.6 Pa. The samples are exposed to a 300 mtorr O<sub>2</sub> plasma for 30 seconds. The samples are immediately removed and a clean glass cover slip (6 mm diameter) is sealed on the plasma treated side of the sample. The sample is inverted (glass side down) and reintroduced into the vacuum chamber where it is exposed to a second round of plasma following the aforementioned procedure. Afterward, Deuterated water is syringe loaded in to the center chamber. The chamber is then sealed with a second clean glass cover slip. This addition of water and the final seal all occur within 5 minutes of removal of the diffusion cell from the plasma chamber. The PDMS that was molded into the ATR accessory is removed from the accessory and contact angle measurements are performed it is then placed upside down on a glass slide. The samples are exposed to a 300 mtorr O<sub>2</sub> plasma for 30 seconds. Upon removal from the vacuum system the PDMS is measured via contact angle analysis then placed back into the ATR accessory (plasma side down) and pressure clamped down into the accessory in order to maintain a consistent contact on the ZeSe crystal to allow for reproducibility in the FTIR measurements.

## **11.5 Analytical Techniques**

### **11.5.1 Contact Angle Analysis**

Water contact angle measurements are obtained by the sessile drop method on a Ramé-Hart model 200 automated goniometer (Ramé-Hart, Inc. Mountain Lakes, NJ) using DROPimage Standard software. Measurement error for this technique is  $\pm 2.0^\circ$ . The samples that were prepared for ATR/FTIR analysis were characterized for hydrophilic activity before and after after plasma treatments using contact angle measurements. Deionized water droplets were delivered on the PDMS surface by a calibrated syringe. The samples are then blown dry with dry nitrogen. Results showed that the PDMS as cured all had contact angles of around  $120^\circ$  which dropped to  $5^\circ$  after plasma treatment.

### 11.5.2 Fourier transform infrared (FTIR) spectroscopy

The PDMS films before and after plasma treatment were characterized using FTIR spectroscopy (PerkinElmer spectrum 2000 spectrometer) equipped with a deuterated triglycine sulfate detector. The samples were analyzed using horizontal attenuated total reflection (HATR) accessory, which consists of a steel plate with an attenuated total reflection (ATR) element sealed to it that rests on top of an optical alignment box. The optical alignment box contains two planar mirrors into focal mirrors which can be adjusted to focus the infrared beam on the incident face of the ATR Crystal. All spectra are recorded at room temperature at  $4.0\text{cm}^{-1}$  resolution with 284 co added scans. In this study, trapezoidal ZnSe and ATR elements are used ( $50 \times 20 \times 2 \text{ mm}^3$ ,  $45^\circ$  face angle) enabling acquisition of spectral data from 4000 to  $640 \text{ cm}^{-1}$ .

### 11.5.3 Thermogravimetric Analysis and Mass Spectroscopy

A schematic of the TGA Module used for this analysis is illustrated in Figure 11.3. The water filled PDMS diffusion cells are loaded into a TA Instruments Q-5000 IR. This system consists of an isolated thermo balance, an IR furnace, quartz sample chamber, purge inlets and outlets, and a capillary connection to a mass spectrometer. The thermo balance is maintained at  $40^\circ\text{C}$  in a well insulated, gas purged chamber isolated from the furnace by a water cooled plate. Evolved gas products are analyzed by a quadrapole mass spectrometer (Pfeiffer ThermoStar) via a heated transfer line. The technical specifications for this unit can be found in more detail on the manufacturers' website, but include a weighing accuracy of  $\pm 0.1\%$  and a weighing precision of  $\pm 0.01\%$ . The furnace consists of four symmetrically placed IR lamps with a quartz lined sample compartment that is a chemically inert and resistant to adsorption of off-gas products.

## 11.6 Results and Discussion

A gravimetric method was utilized for a direct determination of steady state water vapor diffusivity as influenced by curing methods and exposure temperature. Sample cells fabricated from PDMS, as illustrated in Figure 11.2, were loaded with liquid D<sub>2</sub>O and sealed following the methodology in section 11.4.5. Weight loss was monitored with TGA in conjunction with mass spectral observation of D<sub>2</sub>O vapor evolution with respect to time. The advantage of this method, is its simplicity, allowing for the continuous recording of sample weight change as a function of time and vapor activity. In addition, the arrangement allowed for water to be trapped inside the test device, allowing for a more representative comparison to the diffusion mechanism associated with microfluidic devices as opposed to membrane measurements.

Water transport can be described as a three-step process, starting with the absorption of water molecules to the interior surface of the polymer, diffusion through the polymer and as the third step, external surface desorption.

The transport phenomena is usually characterized by three quantities: diffusivity  $D$  ( $m^2/s$ ), solubility  $S$  ( $m^3/(m^3 \cdot Pa)$ ) and permeability  $P$  ( $m^2/(s \cdot Pa)$ ). Solubility is the molecular concentration  $C$  in the polymer near its surface divided by the partial pressure  $p$  ( $Pa$ ) of the molecules in the nearby gaseous phase, *i.e.* according to Henry's law:  $C = Sp$ . Permeability is the product of diffusivity and solubility  $P = DS$  [207]. The solubility limit of water in PDMS, which has been estimated in various experiments to be between 0.1 and 0.2 wt% at 300 K [208, 209].

The linear relation between the flux ( $J$ , which is the amount of molecules going through a unit area within the polymer matrix during a unit time) and the gradient of the concentration of these molecules ( $\Delta C$ ) is related by the first Ficks law: The permanent flux through the PDMS device is given by:

$$J = D \cdot A \cdot \left(\frac{\Delta C}{x}\right) \quad (11.1)$$

where  $D$  is the diffusion coefficient and  $C$  and  $x$  are the concentration within the fabricated system and external to the system and the wall thickness respectively. The PDMS test device design restricts diffusion to one dimension (radial direction) due to the utilization of glass seals on the top and bottom.

The diffusivity values were calculated based on assuming steady state. This assumption was validated by the linear weight loss measured for our test device. Water transport as limited to the radial direction is modeled with.

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (r D \frac{\partial C}{\partial r}) \quad (11.2)$$

Steady State Assumed

$$0 = \frac{\partial}{\partial r} (r \frac{\partial C}{\partial r}) \quad (11.3)$$

Thus simplified to

$$Q = \frac{2\pi D t (C_2 - C_1)}{\log \frac{b}{a}} \quad (11.4)$$

With  $Q$  = mass measured from TGA weight loss (mass difference in linear regime) ( $g$ )/ unit length in ( $m$ ),  $D$  ( $m^3/sec$ ),  $b$  and  $a$  = internal and external radius ( $m$ ),  $t$  = time for the weight loss interval ( $sec$ ) and  $C$  = concentration ( $g/m^3$ ).

The driving force of water transport is the difference between the partial pressures of water vapor on the interior and exterior sides. If the water vapor's partial pressure on both sides are different, a gradient of water concentration is established within the device. A schematic representation of the TGA system is shown in Figure 11.3. The external portion of the cell was maintained at a zero concentration by constantly sweeping a dry helium through the TGA-MS module. The balance assembly is isolated from the furnace and dry helium was continuously flowed through the module at 10 ml/min such that positive pressure was maintained (no moisture regression into balance chamber). Dry Helium was flowed into

the purge lines into the purge lines at a flow rate of 20.0 ml/min. The IR furnace is ramped at 10 °C/min to the selected temperature (75, 85, 95 °C) where it is held and weight loss is monitored with time. D<sub>2</sub>O resulting from vapor transport from within the PDMS Cell is monitored by mass spectroscopy. The experiment is allowed to proceed until there is no longer evident weight loss and the D<sub>2</sub>O concentration falls back to a zero baseline. An example of the data evolved is indicated in Figure 11.5, showing both weight loss and water evolution as a function of time at a temperature of 95 °C. The initial unsteady state start (ramping from ambient to temperature of interest) of vapor transport was ignored during calculations. The diffusivity calculations were performed on the data found in the linear region of weight loss. This linear region can be identified in Figure 11.5 following an initial transient period. The internal concentration was calculated based on the vapor pressure associated with water as a function of hold temperatures. The rate of vaporization was calculated and compared to the flux from the cell and was found to be 10000X higher than the diffusion rate from within the cell, thus indicating the rate controlling step was the vapor diffusion through the PDMS membrane.

The composition and morphology of a polymer play a significant role in determining transport properties. The factors having the greatest influence fall into two categories: those relating to the chemical composition and structure such as the degree of cross linking, and the degree of saturations. As well as those that involve heterogeneities in the polymer, such as orientation, crystallinity, and the presence of plasticizers and fillers [206]. The PDMS material presented lacks plasticizers or fillers and the test devices were formed in the absence of shearing such that orientational effects as assumed inconsequential. It has also been shown that when cured at room temperature that no preferential transport pathways exist in PDMS as commonly noted in heterogeneous polymers.

The data in Figure 11.6 show that regardless of the curing procedure as temperature increases water diffusivity increases. This increase is due to a higher chain mobility within the PDMS network as influence by increased thermal energy. The diffusion mechanism in

PDMS is described by the polymer’s ability to continually provide opportunities for permeants to progress through randomly generated voids “holes” [209]. Conformations of polymer chains change successively by the thermal motion, resulting in the fluctuation of the occupation volume of the chains and the formation of holes, which are effective transport channels allowing molecules to permeate easily. The plots in Figure 11.6 of the logarithm of the diffusion coefficient vs. the inverse absolute temperature follows a linear relationship confirming that no preferential transport pathways exist in PDMS despite the differing curing regimes.

In addition, the PDMS cell that was cured at a higher temperature had lower diffusivity values across all temperatures investigated. This result is consistent with increased chemical cross linking due to the higher curing temperature. This increase in cross linking has been shown contribute to a lowered chain segment mobility resulting from an increasing extent of saturation [210]. The decreased segment mobility results from conformational changes being limited by steric hinderences and ionic repulsions. These changes often limit the path of diffusion for molecules forcing a more tortuous path (often longer) due to a limited number of “holes” formed and thus lowering diffusivity.

Previously reported experimental water vapor diffusivity values at 300 K show a wide divergence. The equilibrium sorption and permeation studies of Barrie and Machin obtain a value of  $D = 4.0 \times 10^{-5} \text{ cm}^2/\text{s}$ . While Favre *et al.* obtained a diffusion constant of  $D \sim 10^{-4}$  [209]. For higher concentrations, aggregation effects can be significant in determining the transport coefficients for water in PDMS. Watson and Baron whose values is most often cited indicate a value of  $D = 2.0 \times 10^{-5} \text{ cm}^2$  ruling out the theory of water cluster formation. The values reported herein range from  $D = 1.0 \times 10^{-4} \text{ cm}^2$  to  $9.7 \times 10^{-4} \text{ cm}^2$  at between 348-368K and are in agreement with previously reported ranges.

The activation energy determines the magnitude of diffusion. The contribution of temperature as a driving force can generally be evaluated from determination of activation energy over a temperature range [211]. Temperature dependent diffusion coefficients have

been used to calculate the activation energies for the diffusion processes by using the equation  $D = D_0 e^{-E_a/RT}$ . Slope of the Arrhenius plot of  $\ln D$  vs.  $1/T$  ( $T$  in kelvin) Figure 11.7 provides the activation energies ( $E_d$ ). If we look at the activation energies for diffusion they can generally be explained by considering both the chemical affinity with PDMS and the molecular size of the penetrants. Barrie and Platt found that clustering of water molecules into dimers and trimers can lead to a 3-5-fold reduction in the measured diffusion constants. We feel this mechanism of clustering has been prevented with the PDMS test cells kept at high temperature, and thus diffusive species are expected to be only water monomers. Activation energies for the two different curing conditions (1) RT Cure vs (2) 100 °C(1hr) followed by 24 hr are calculated at 13.9 kJ and 9.8 kJ respectively. Watson and Baron calculated that the energy to generate voids of sufficient size to accommodate the water molecules within the PDMS (cured at 30 °C for 24 hrs) is 14.0 kJ/mol which is in close agreement with our experimental value for the RT Cure [212]. The activation energy for the higher cure condition was slightly lower and it is suspected that cross linking limits the available free volume “holes” such that less energy is required to start the diffusion process but, due to the tortuous path, the overall diffusivity is reduced as compared to the room temperature cure. In addition, the PDMS cured at the lower temperature will have a higher level of unsaturated bonds contributing to more hydrogen bonding with the diffusing molecules as compared to the higher cured case resulting in a higher activation energy.

FTIR analysis was performed to provide a comparison between the two curing regimes. No differences were noted as illustrated in Figure 11.4 in the FTIR spectra of the PDMS cells regardless of the curing procedure utilized. The data presented represent the PDMS devices post plasma treatment as it is known that plasma treatment causes surface activation and some modification of surface reactive groups.

## 11.7 Conclusion

It has been shown that the choice of curing scheme directly affects the water vapor diffusivity from within a PDMS cell. PDMS test devices cured at a higher temperature indicate a lower diffusivity and lower activation energy. This indicated that while less energy was needed to initiate diffusion a lower diffusivity value was obtained. It is suggested that increased cross linking contributes to a lowered chain segment mobility limiting the path of diffusion for molecules, forcing a more tortuous path due to a limited number of “holes” formed. FTIR analysis showed no obvious structural differences between the two curing temperatures. Because cross linking is shown to decrease molecular permeability, the choice of a curing regimen should be investigated by individual groups to ascertain the starting point for diffusivity improvements. This information will prove vital to discriminate between barrier layer improvement as compared to structural rearrangements caused by heating steps required for their attachment.

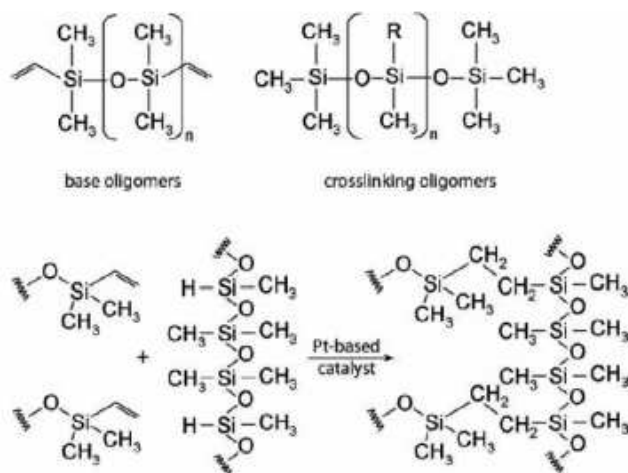


Figure 11.1: Reaction diagram of platinum catalyzed PDMS curing. The R group is either CH<sub>3</sub> or H.

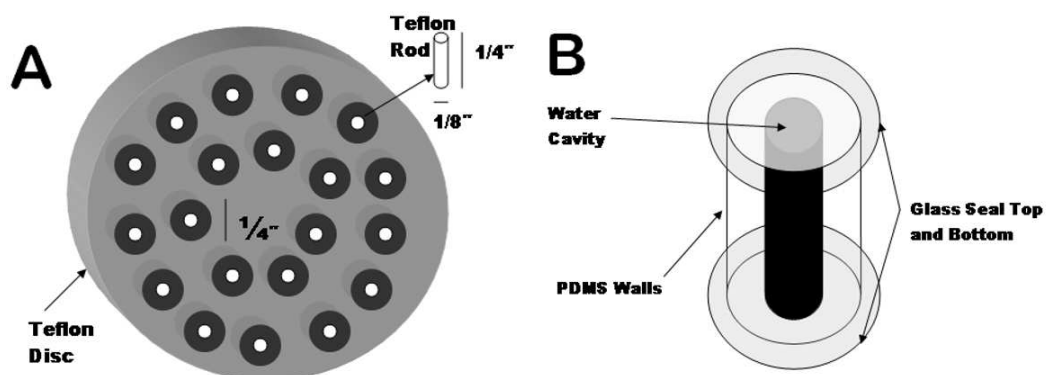


Figure 11.2: (A) Illustration of mold platform used for fabrication of the PDMS test devices and (B) PDMS diffusion cell.

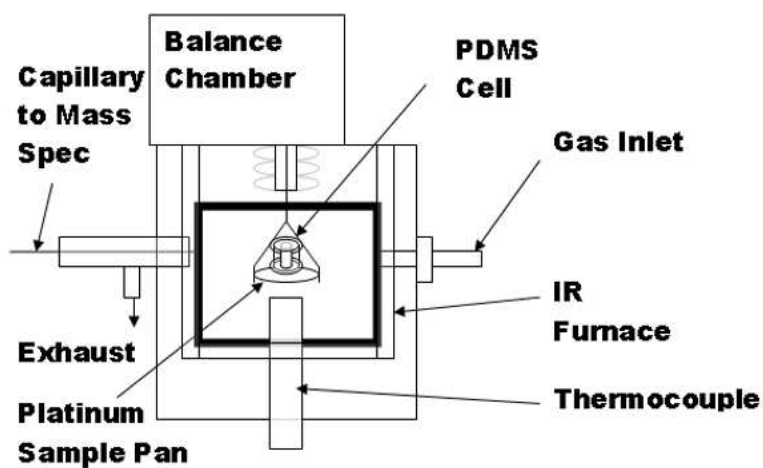


Figure 11.3: Representation of the gravimetric system utilized for this work.

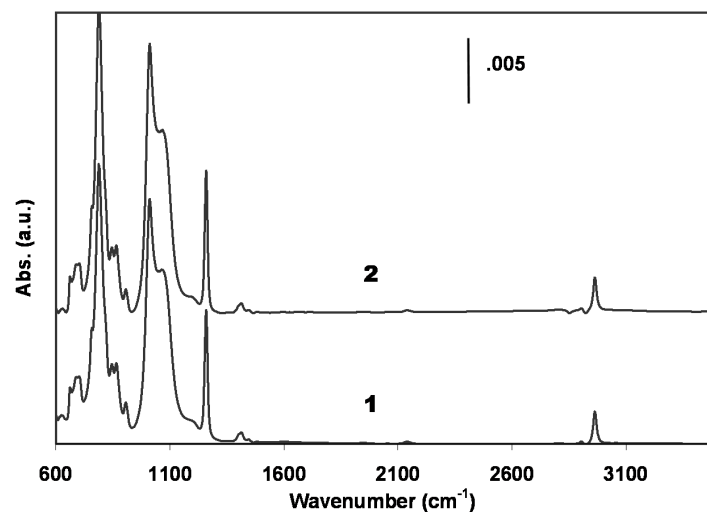


Figure 11.4: Representative FTIR spectra of PDMS (1) 24-hr room temperature cure after 30-sec oxygen plasma (2) 1hr at 100 °C followed by 24 hr room temperature cure after 30 sec oxygen plasma

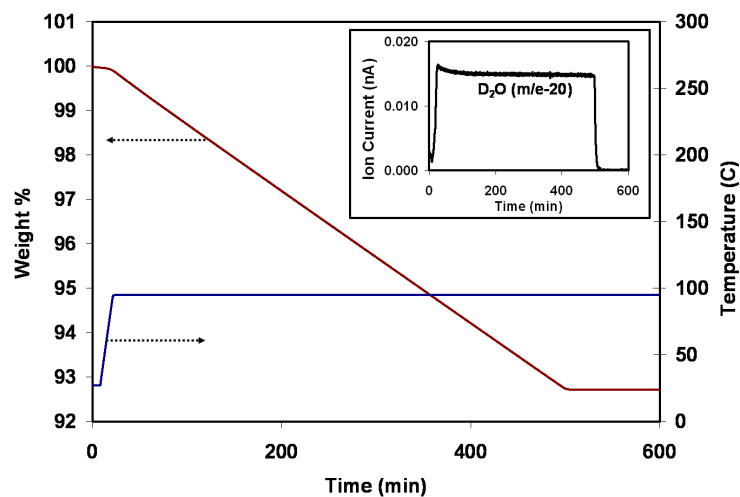


Figure 11.5: Example of data collected from TGA-MS experiments. Both weight loss and ion current are measured as a function of time. Ramp was 10 °C/min to 95 °C and held until until no observable weight loss.

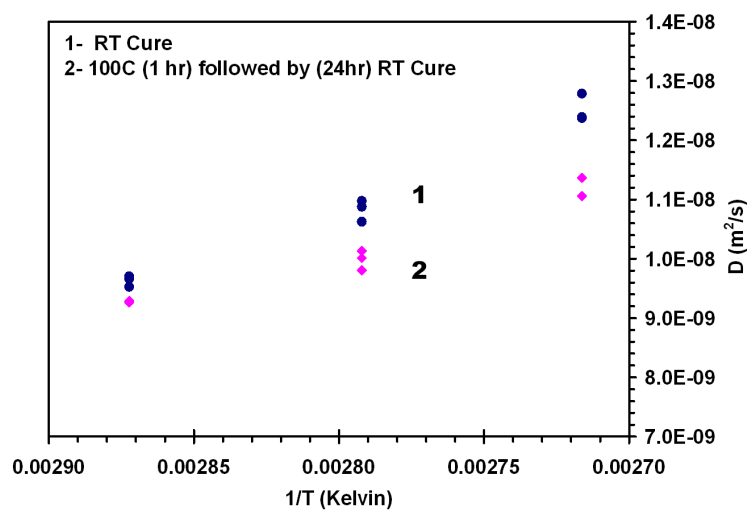


Figure 11.6: Diffusion coefficients as a function of temperature.

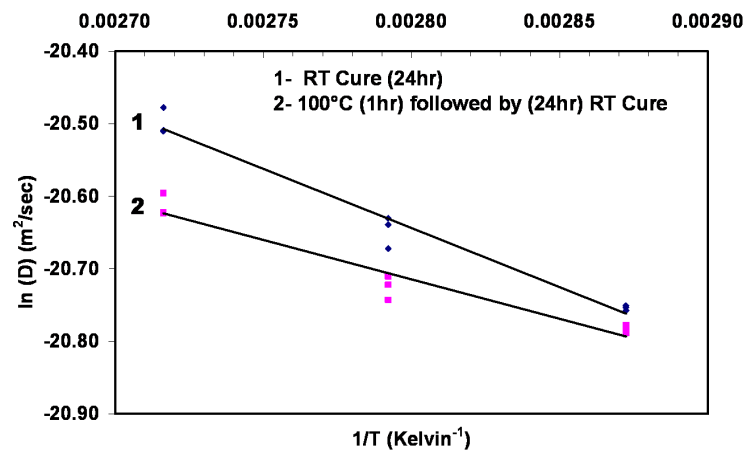


Figure 11.7: Data used to calculate activation energy.

## 11.8 Investigation of MVD silica Layers for Water Vapor Barrier Improvement

### Prior Work on Utilizing Silica layers on Polymer Surfaces- Implications toward utilization on PDMS

Research has shown thin transparent  $\text{SiO}_x$  barrier coatings deposited on polymer substrates exhibit a substantially reduced oxygen and water vapor permeability while maintaining stability in terms of reactivity, time and temperature. Such coatings possess highly desirable properties, such as transparency, recycle ability, and microwave use as demonstrated in their use for food packaging and biomedical applications. One of the benefits of these coatings lies in the flexibility by which they can be deposited on polymer surfaces. Thus far, sputtering, electron beam deposition, and plasma-enhanced chemical vapor deposition (PECVD) have all been utilized successfully to produce  $\text{SiO}_x$  coatings on polymer substrates [213–216]. Work done by Erlat *et al.* on PECVD  $\text{SiO}_x$  on polymer films has revealed a correlation between  $\text{SiO}_x$  morphology (including defects) and barrier performance [217]. Their group utilized phase-imaging atomic force microscopy and energy-filtered transmission electron microscopy to compare morphological and permeation results to identify some of the physical factors governing water vapor permeation through  $\text{SiO}_x$ -modified polymers. The focus of their research effort was on PET films. This research intend on depositing a Molecular Vapor Deposition (MVD) silica layer onto PDMS surfaces resulting in a stable reactive surface capable of sustaining much of the same chemistries associated with glass surfaces. Due to its controlled coverage and process tunability it is expected that this silica layer can provide the water barrier properties necessary for PDMS microfluidic devices. The surface roughness, surface activation procedure, coating thickness and uniformity of  $\text{SiO}_x$  coatings have been shown to be contributing factors affecting barrier performance on alternative polymer substrates. This work intends on exploring these factors on water vapor barrier improvement as related to MVD silica layers deposited on PDMS.

### 11.8.1 Results and Discussion

Different morphologies of silica layers were produced by controlling the design space associated with precursor dosing pressures. The morphologies and thicknesses were characterized via AFM and ellipsometry, and subsequent investigations when viable were performed on the TGA-MS to characterize the water diffusion as a function of morphology and thickness. If we consider a two layer structure, the total permeability is governed by the less permeable layer. In the case of an inorganic coating on a permeable polymer film, the permeability depends mostly on the permeability coefficient of the coating and on its thickness. The MVD silica coatings that were produced proved to be full of defects regardless of the deposition conditions. In addition the coating was susceptible to delamination if exposed to any type of compressive stress regardless of the surface activation procedure. This delamination occurred with gentle manipulation of the PDMS test cell and device sealing. Different thicknesses produced similar failures. A PDMS film with and without coating is illustrated in Figure 11.8. We were unable to produce a uniform film as deposited on PDMS surfaces regardless of the deposition conditions utilized. As a result, work was discontinued on this project.

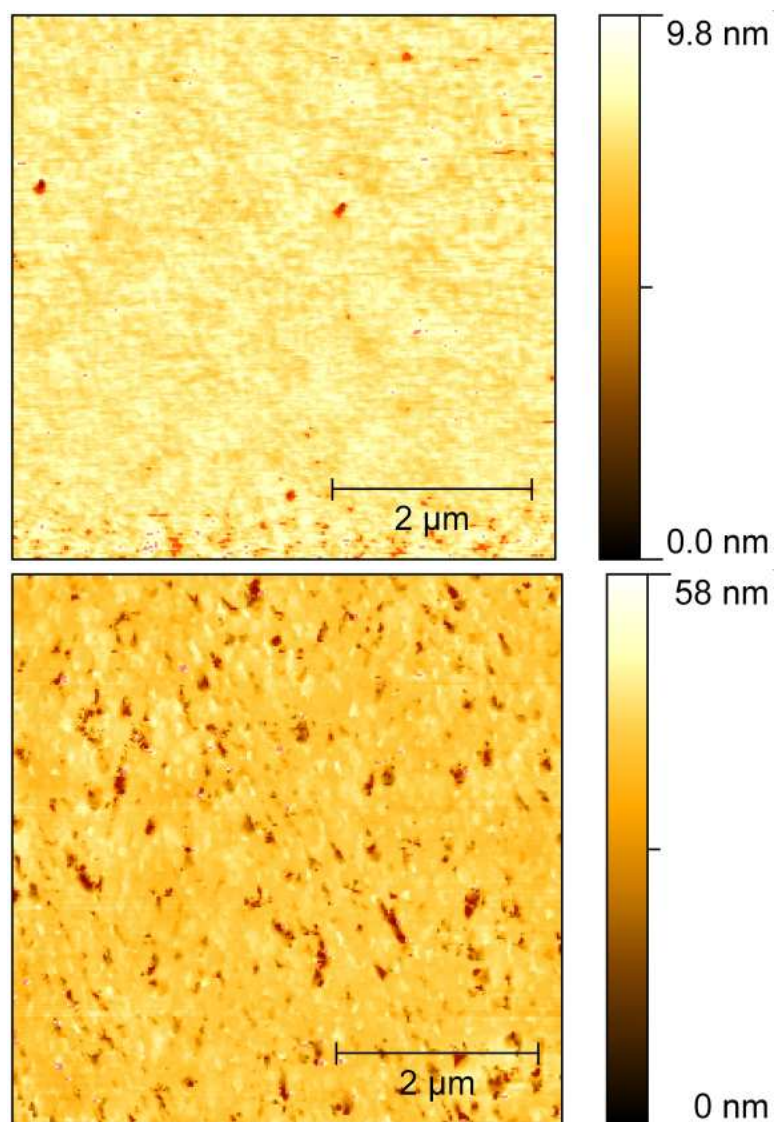


Figure 11.8: PDMS film (top), silica coated PDMS film (bottom).

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