

TEMPERATURE PROGRAMMED DESORPTION STUDY OF DODECANETHIOL  
SELF-ASSEMBLED MONOLAYERS ON Ag

THESIS

Presented to the Graduate Council of  
Texas State University-San Marcos  
In Partial Fulfillment  
of the Requirements

for the Degree

Master of SCIENCE

by

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San Marcos, Texas  
May 2009

TEMPERATURE PROGRAMMED DESORPTION STUDY OF DODECANETHIOL  
SELF-ASSEMBLED MONOLAYERS ON Ag

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## **ACKNOWLEDGEMENTS**

I would like to thank my mother, and my father for the love and support throughout my life, education and accomplishing this document. I would also like to thank my loving husband, Jose Nava, for being my daily rock and support throughout the past two years of pursuing my master's. I cannot put into words how I feel that you all can see me graduate with my master's. The journey has been long and challenging, but having you all in my corner gave me the strength I needed to carry on to the end.

I also want to thank Carl and Heike for their guidance and time in my master's education. Your efforts went beyond the classroom in helping me make my thesis possible. The experience was a blast working in the lab and always finding something to laugh about with Heike. These are memories I will carry wherever life takes me.

Lastly, I would like to thank all my classmates for being so supportive. Especially, Nick, Chris, Nick, Rob, Jennifer and Gabe, you have all become like brothers and sister to me throughout the years. All through our bachelors, and here now finishing our master's, it is something we have all worked extremely hard for, and now we can enjoy the outcome. The long nights and endless homework sessions were long and hard, but the journey was made a little brighter sharing it with all of you. I wish you all love, happiness and abundant blessings wherever life takes you.

This manuscript was submitted on April 21, 2009.

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## **ABSTRACT**

### **TEMPERATURE PROGRAMMED DESORPTION STUDY OF DODECANETHIOL SELF-ASSEMBLED MONOLAYERS ON Ag**

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May 2009

**SUPERVISING PROFESSOR: CARL VENTRICE JR**

The desorption kinetics of dodecanethiol self-assembled monolayers grown on Ag films has been studied using temperature programmed desorption. The Ag films were grown on Si(100) substrates by physical vapor deposition in a high vacuum system. The self-assembled monolayers have been grown either in solution or by vapor deposition in ultra high vacuum. The direct detection of dodecanethiol by the residual gas analyzer gives a complex spectrum due to multiple cracking fragments that are produced during

the ionization of the molecule. The temperature programmed desorption measurements indicate that desorption of the self-assembled monolayer occurs in a two-stage process: dissociation of the alkane chain followed by desorption of the sulfur from the surface. Alkane chain fragments are observed to desorb over a range of about 100°C to about 220°C, and the desorption of sulfur is observed starting around 200°C. Analysis of the relative coverage of the self-assembled monolayers was performed by measuring the areas under the pressure versus time curves. These results show that the saturation coverage is similar for both the vapor deposited and the solution grown self-assembled monolayers.

## CHAPTER 1

### INTRODUCTION

There has been relatively little work done on the use of silver (Ag) as a substrate for the growth of self-assembled monolayers (SAM); however, the interest in Ag as a substrate for SAM growth has increased in the last few years. Different techniques have been used to analyze SAM growth on Ag such as fourier transform infrared spectroscopy (FTIR), raman spectroscopy, scanning tunneling microscopy (STM), low energy electron diffraction (LEED), and Moiré patterns [1].

STM has been used to image the surface of untreated Ag(111) surfaces in ambient conditions, and these results reveal that the surface has atomically flat terraces [1]. Samples treated with sulfides from aqueous solution form single crystalline adlayer domains with diameters on the order of 10nm. Images for air-metal interface show that the self-assembly of alkanethiols and dimethyl sulfide results in hexagonal adsorbate structure. Moiré patterns formed between the sulfide adsorbate and the silver substrate which was analyzed to improve the determination of adlayer lattice constants measured by STM [1].

STM topographs have revealed depressions on the films which have been identified as substrate vacancy islands generated by chemical erosion during a self-assembly process [1]. Thermal annealing of hexane and octadecanethiol on Ag(111) has

been done with hopes to improve quality of such films. Alkanethiol monolayers on silver are subject to oxidation; unlike alkanethiol monolayers on gold, which are more stable against contaminants. The island formation on silver compared to pits on gold surfaces suggests that a larger amount of material is getting displaced on silver than for gold [2]. The islands are a possible outcome of domain boundary etching. It is suggested that substrate-molecule and intermolecular interactions have a dominant role at different stages of the formation of a SAM [3].

There have been studies using time of flight secondary ion mass spectrometry (ToF-SIMS) of dodecanethiol monolayers on Ag substrate. This technique was used to do chemical analysis on all mass peaks within the mass to charge ratio range of 0 to 2000 amu of this long chain molecule. The results of the analysis show that on dodecanethiol form a dense high coverage phase on the Ag surface. There were fragments of hydrocarbon which dominated the secondary ion emission spectra. There were also sulfur fragments in the range of 150 to 700 amu, but a significant peak was observed at 201 amu [24].

Other than work of Ag with long-chain alkanethiols, there have been studies of adsorption of methanethiol ( $\text{SCH}_3$ ) to determine the adsorption geometry of the sulfur (S) head atoms, which is crucial for understanding the growth of SAMs. These were measured using a normal-incidence X-ray standing wave technique, (NISXW). This study shows relationship between the structural parameters determined in NISXW and the number of simple adsorption structures. The data indicated that the formation of SAMs induced reconstruction of the outermost layer of the substrate [4].

The approach taken for the study of this paper was to expand on the thermal properties of a self-assembled monolayer of dodecanethiol on silver. Encompassing the study of desorption of molecular species of dodecanethiol for multiple samples prepared the same way. In return, by finding the peak temperature for the respective species, their activation energies could be calculated.

## CHAPTER 2

### EXPERIMENTAL

#### 2.1 ULTRA HIGH VACUUM

An ultra-high vacuum (UHV) system is a chamber in which the base pressure is  $10^{-9}$  Torr or lower. To achieve this vacuum within our system, there is a turbo molecular pump, a titanium sublimation pump, an ion pump, and a rotary vane pump that backs the turbo pump [21]. There is a pumping sequence used for this chamber to reach the aforementioned pressure range. First, the rotary vane pump is turned on for about five minutes to reach a pressure of  $10^{-3}$  Torr. Since the rotary vane pump can contaminate the UHV with back streaming oil, a zeolite trap is used to prevent this from happening. Next, the turbo molecular pump is started. This pump is very clean, efficient, and can pump both reactive and inert gases. The chamber pressure should be about  $10^{-6}$  Torr before turning on the ion pump. The ion pump is primarily used to pump gases such as  $H_2O$ ,  $CO$ ,  $CO_2$ ,  $N_2$ ,  $O_2$ , etc. Since the molecule being pumped is captured primarily by reacting with the titanium pumping elements, this pump does not pump inert gas atoms very well at all. These pumps together will only get the chamber to a pressure of about  $10^{-8}$  Torr. To attain the base pressure for UHV, the chamber is baked at about  $150^\circ C$  for at least 24 hours. This process allows trapped water and other molecules on the surfaces

of the chamber and instruments within the chamber to desorb and be removed by the turbo molecular pump and ion pump. Once UHV has been achieved, the titanium sublimation pump can be used. This pump works by flashing a fresh layer of pure titanium on the walls of the pump, and the titanium layer then reacts with gases such as  $H_2$ ,  $H_2O$ , and  $O_2$ . This pump is only flashed once a day for about one and a half minutes to give the chamber a fresh layer of titanium, which can react with the residual gases in the chamber.

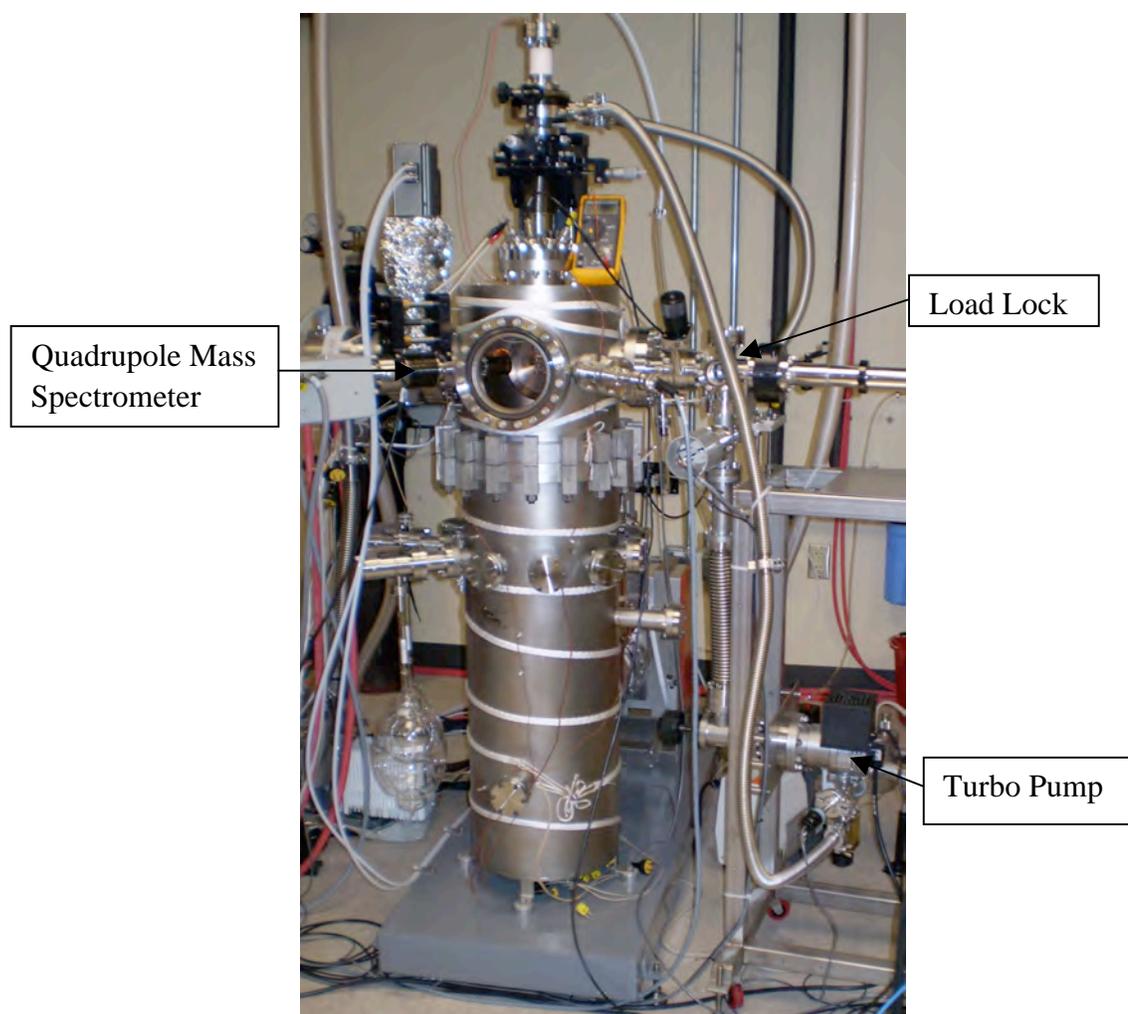


FIGURE 1: The Front view of the UHV chamber. This system was used in this experiment. The main components of this frontal view is the quadrupole mass spectrometer, the load lock where the sample is transferred into the main chamber, and the turbo pump that pumps down the load lock to maintain a pressure around  $10^{-7}$  Torr.

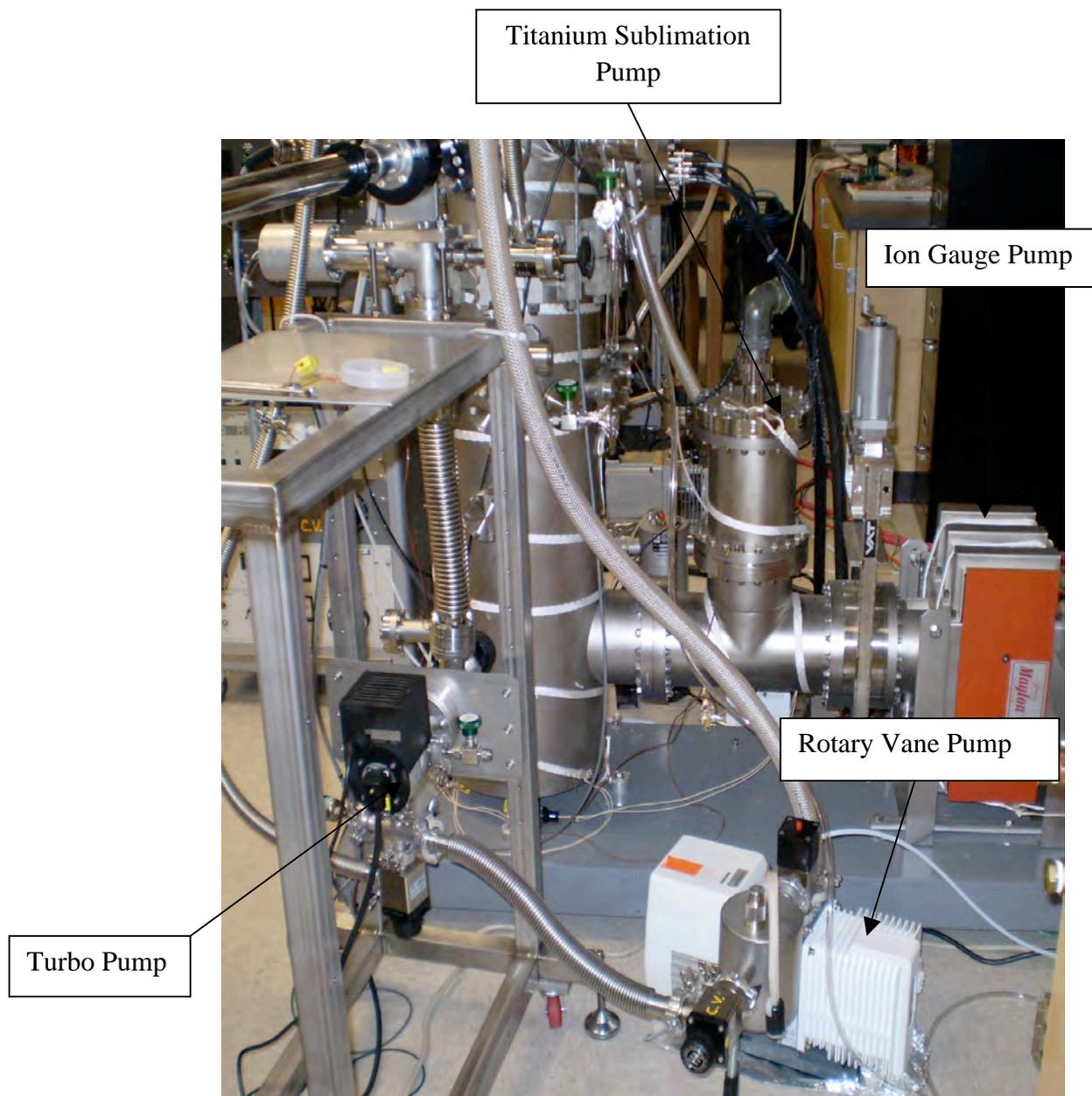


FIGURE 2: The Back view of the UHV chamber and the pumping system. This system was used in the experiment. This side of the system consists of a titanium sublimation pump, a ion gauge pump, a rotary vane pump, and the back view of the turbo pump mentioned in Figure 1.

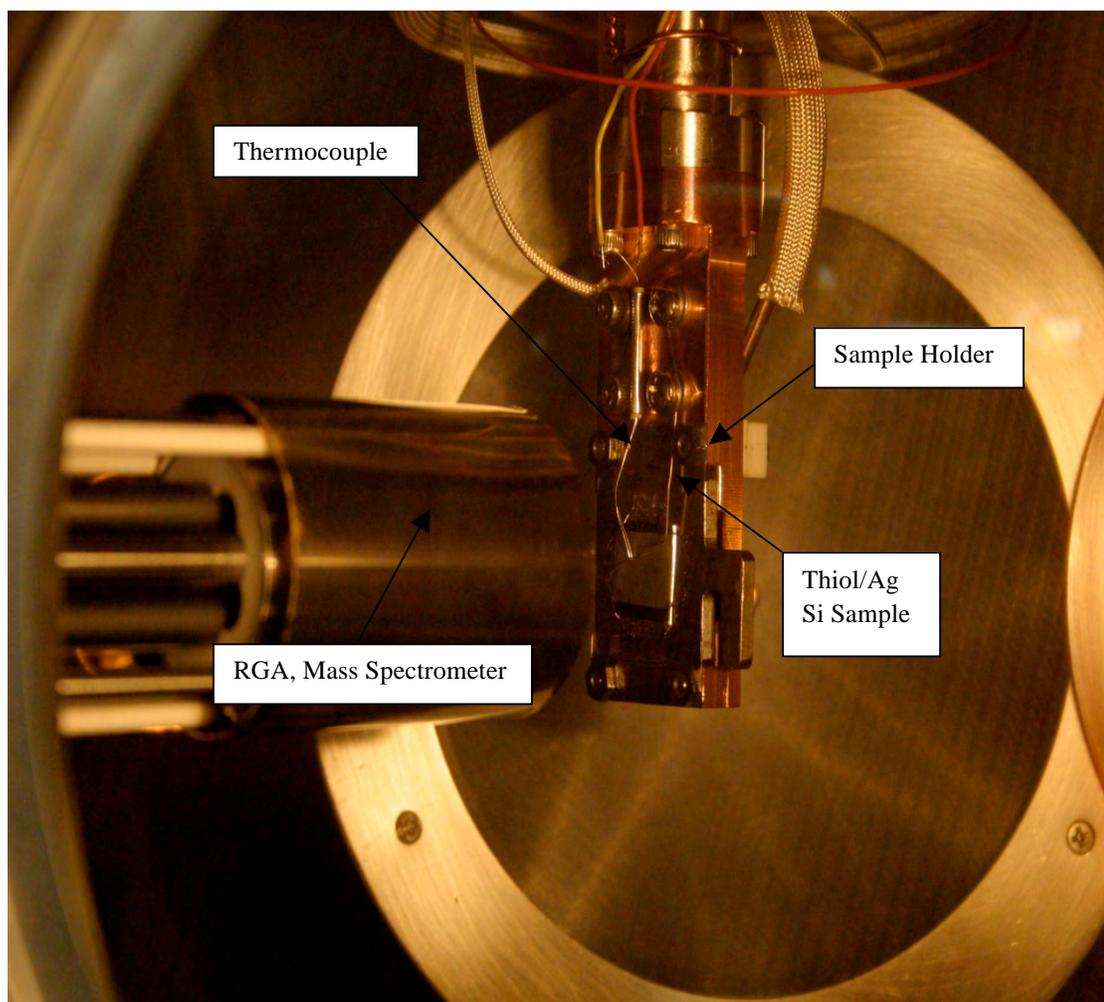


FIGURE 3: Temperature Programmed Desorption System consisting of a Hiden 200 amu RGA, a molybdenum sample holder with a self-assemble monolayer of dodecanethiol grown on a thin film of silver on silicon substrate, and a thermocouple mounted on a tungsten spring to read the temperature on the surface of the sample.

## 2.2 TEMPERATURE PROGRAMMED DESORPTION

Temperature programmed desorption (TPD) is a powerful surface science technique that provides information about species present on a surface and their reactions on a surface [21]. The molecules that are attached to a surface are thermally excited by raising the temperature of the surface at a programmed rate, while monitoring the desorbing gas molecules with a mass spectrometer. The increase in temperature causes the rate of desorption, and corresponding partial pressure, to rise until there is a reduced amount of that species left on the surface, at which point the partial pressure will drop. This forms a peak on the pressure versus temperature plot. The shape of the peak gives information about the desorption kinetics. In addition, the area under the pressure versus time curve is proportional to the molecular coverage [8].

The principle behind TPD is that the adsorbed molecule desorbs when the thermal energy of the molecule exceeds the activation energy associated with the bond between the adsorbate and the surface [7]. Notably, the product molecules are desorbed and detected only after they have adsorbed and been in contact with the surface. The desorption rate can be described using the Polanyi-Wigner equation as follows:

$$r(\theta) = -\frac{d\theta}{dt} = \nu(\theta)\theta^n \exp\left[-\frac{E(\theta)}{RT}\right] \quad [3.1]$$

where  $r(\theta)$  is the rate of desorption,  $\theta$  represents the surface coverage,  $t$  is the time,  $\nu$  is the pre-exponential factor,  $n$  is reaction order,  $E(\theta)$  is the activation energy,  $R$  is the gas constant, and  $T$  is the temperature. The kinetics of the material is governed by the reaction order,  $n$ , which is typically 0, 1, or 2 [7]. Zero order kinetics results from desorption of a multilayer of an adsorbate. First order kinetics is the direct desorption of

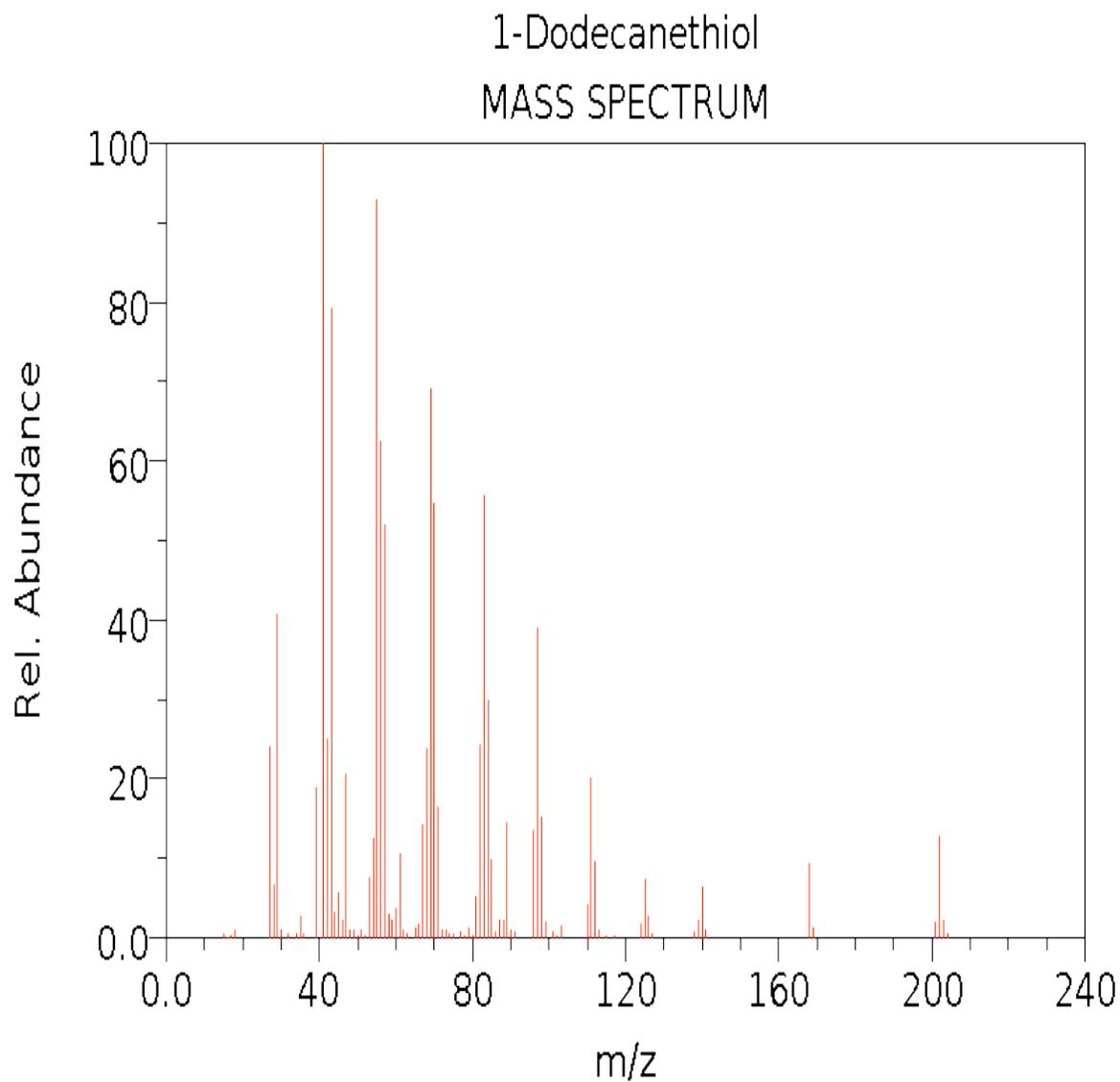
submonolayers of an adsorbate. Second order kinetics results from desorption of a gas molecule that must first undergo a recombination. For instance, oxygen adsorption on some surfaces results in dissociation of the oxygen molecule into oxygen atoms. If the oxygen desorbs molecularly, the individual oxygen atoms must first migrate to another oxygen atom before it can desorb as an O<sub>2</sub> molecule.

### 2.3 MASS SPECTROMETER

During TPD a quadrupole mass spectrometer monitors the molecular desorption on the surface. A quadrupole spectrometer must first ionize the gas molecules so that they can be accelerated into the quadrupole region, which is used to measure the mass to charge ratio ( $\frac{m}{e}$ ) of the molecule. The ionization is achieved by extracting electrons from a hot filament. A radio frequency (RF) potential is applied to a set of four rods, which creates a quadrupole field that is used to select ions with a specific mass to charge ratio. The ions are collected at the other end of the four rods using either a Faraday cup or a secondary electron multiplier (SEM). The ultimate pressure of the Faraday cup is  $\sim 10^{-9}$  Torr and the SEM is  $\sim 10^{-13}$  Torr. The ion beam is composed of ionized molecules and molecular fragments with different masses and net charges that are separated into a spectrum that gives the measure of partial pressure versus a mass to charge ratio ( $\frac{m}{e}$ ). The ( $\frac{m}{e}$ ) is used to describe ions in mass spectrometry. There can be multiple ( $\frac{m}{e}$ ) for a particular molecule due to multiple ionizations of the molecule or due to the mass spectrometer breaking the molecule into fragments, which is called “cracking of

molecules". An example of molecular cracking is shown in Figure 2 for the molecule dodecanethiol, which is the molecule used in this study to grow our self-assembled monolayers (SAMs). The ionization does not occur by electron capture. Instead, positive ions are produced. As the electron passes close to the molecule the negative charge repels and distorts the electron cloud. This causes kinetic energy to be transferred from the moving electron to the electron cloud of the molecule [10]. Cracking patterns are well documented and are unique for each molecule, which allows mass spectrometry of a sample. Mass spectrometry can be used to determine the structure and chemical properties of a molecule, identify unknown species, and quantify known species.

The dodecanethiol molecule has an atomic mass unit of 202. In Figure 4, the cracking pattern for the gas phase of dodecanethiol can be seen. Using a quadrupole mass spectrometer, the dodecanethiol molecule is ionized into fragments of smaller mass, which are accelerated by a quadrupole potential down the four rods, and are detected at the other end of the spectrometer as a mass to charge ratio. It is noticeable that a lot of the thiol molecule is broken into smaller pieces of alkane fragments such as  $C_3H_5$ ,  $C_3H_7$ ,  $C_2H_5$  and sulfur fragments such as SH,  $SH_2$ , and S just to name a few. At the end of the spectrum there is a smaller signal for 202 amu which indicates there is only a small amount of dodecanethiol left.



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

FIGURE 4: NIST Dodecanthiol Mass Spectrum of mass to charge ratio cracking patterns[6]. The following cracking patterns were picked for the LABVIEW program to monitor;  $C_3H_7$ ,  $C_3H_5$ ,  $C_2H_5$ ,  $SH_2$ ,  $SH$ , and  $S$ .

## 2.4 ACTIVATION ENERGY

The activation energy,  $E_a$ , is the minimum energy required for a reactant to overcome before a chemical reaction can occur. It can be determined by measuring the temperature shift of the maximum of the pressure versus temperature plot of a chemical species as a function of heating rate [7]. It is assumed that there is a uniform substrate temperature, and that the activation energy is independent of the coverage. A linear temperature ramp function,  $T_0 + \beta t$ , is substituted into the Polanyi-Wigner equation, differentiated with respect to time,  $t$ , and then set to zero to find the maximum of the pressure versus temperature plot. The following expressions are obtained [8],

$$\frac{E_a}{RT_p^2} = \frac{\nu}{\beta} e^{-\frac{E_a}{RT_p}} \quad [4.1]$$

and

$$\frac{E_a}{RT_p^2} = 2 \frac{\theta_0}{\beta} \nu e^{-\frac{E_a}{RT_p}} \quad [4.2]$$

where  $n = 1$  and  $n = 2$ . The desorption equation for first and second order kinetics can be written as follows

$$\ln \left( \frac{T_p^2}{\beta} \right) = \frac{E_a}{RT_p} - \ln \left( \frac{E_a}{\nu \beta} \right) \quad [4.3]$$

and

$$\ln \left( \frac{T_p^2}{\beta} \right) = \frac{E_a}{RT_p} - \ln \left( \frac{2\nu R \theta_0}{E_a} \right). \quad [4.4]$$

Therefore, the activation energy can be determined by plotting  $\ln \left( \frac{\tau_p^2}{\beta} \right)$  as a function of  $\frac{1}{\tau_p}$  [7]. This method of determining the activation energy is called the Redhead method [9]. The analysis of second order kinetics is rather difficult because the intercept depends on the coverage of the adsorbate [10].

## 2.5 THIN FILM DEPOSITION OF SILVER

The use of thin films of metals is indispensable in much of today's technology. Research in deposition of films is moving faster than ever before with improved properties. The importance of thin films is the ability to characterize the films in terms of their chemical composition and structure [21].

The thin film deposition chamber that was used in this study can reach a vacuum of up to  $10^{-7}$  Torr. This vacuum chamber has similar components to the UHV chamber, such as a turbo molecular pump, a rotary vane pump, and the pressure is measured via an ion gauge. As with the UHV chamber, the rotary vane pump is first run for about 5 minutes. The rotary pump by itself only gets the chamber up to  $10^{-3}$  Torr. The turbo pump is turned on next. This process brings the deposition chamber to  $\sim 10^{-7}$  Torr after about 12 hours, which is the desired pressure for deposition of thin films. Once vacuum is reached, a current meter is clamped onto one of the conductors for the crucible heater to monitor the current reading going through the crucible heater filament.

The material to be evaporated is placed into an aluminum oxide ceramic crucible which is heated by a tungsten filament to a point where the vapor pressure is sufficient to

create the desired deposition rate (typically between  $10^{-5}$  and  $10^{-2}$  Torr). The vapor will condense on the substrate surface and form a thin film of a desired thickness [11].

To determine the deposition rate and film thickness, an Inficon XTM/2 quartz crystal microbalance was used. It is designed with a Modelock measurement system that continuously tests the monitor crystal, which is piezoelectric, for a resonance at a fundamental frequency. As the metal is deposited on the quartz crystal, the natural frequency of the system will change. This system tests and analyzes the phase frequency relationship of the crystal, which provides an intelligent link between the quartz crystal and the instrument [19]. The XTM/2 has a frequency resolution of 0.1 Hertz in 250 milliseconds, and it accurately displays rate resolutions as small as 0.01 Angstroms.

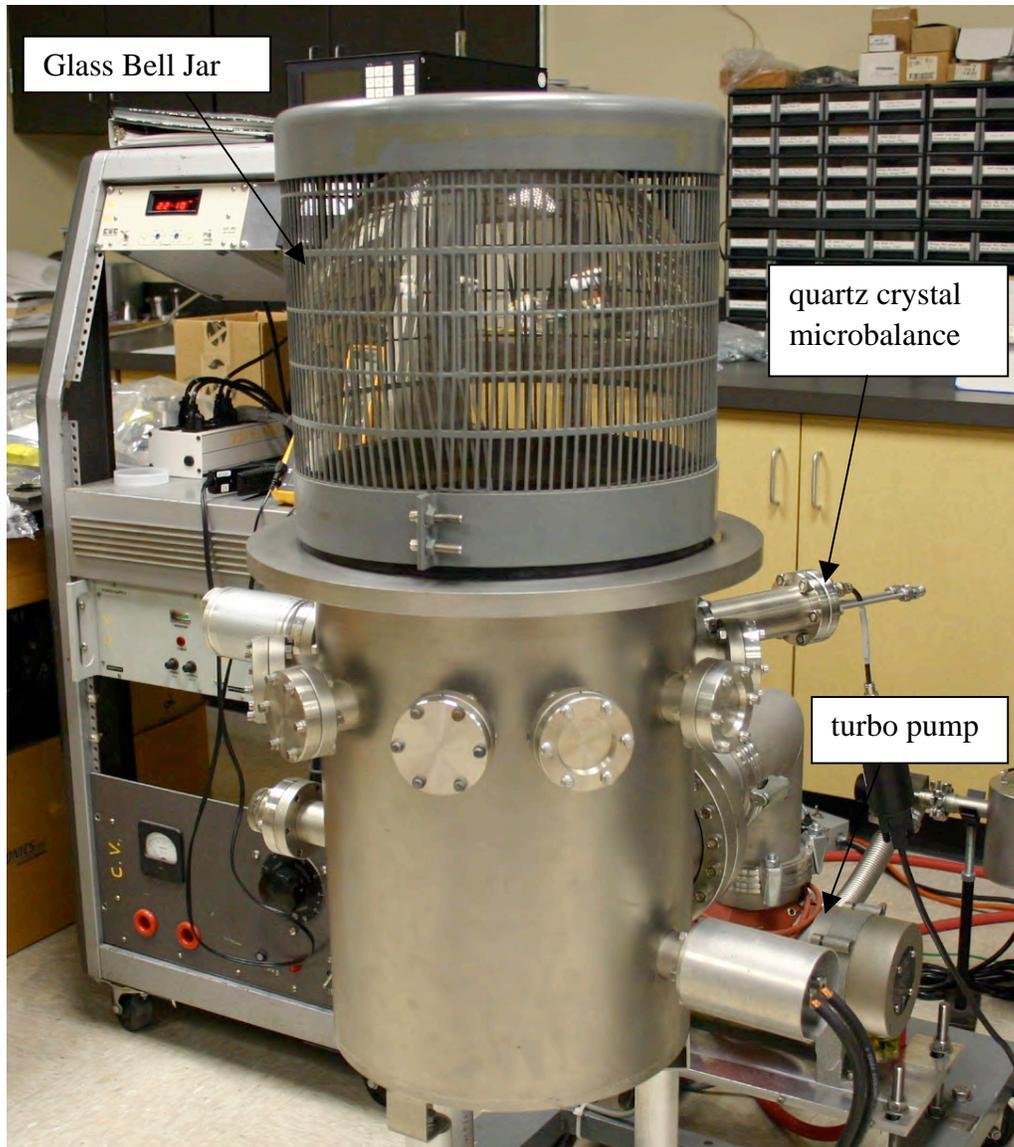


FIGURE 5: Thin Film Deposition Chamber .This is where the film of silver is evaporated and adsorbed on the surface of the Si(100). The glass bell jar seals the top of the chamber and protects the inside from contaminants. The quartz crystal microbalance is used to measure the rate of deposition and the thickness of the thin film. The turbo pump is used to pump down the chamber and maintain a pressure of about  $10^{-7}$

## 2.6 PREPARATION OF SELF-ASSEMBLED MONOLAYERS

The substrate used in this experiment was Si(100) on which a thin film of silver is grown using evaporative deposition in a vacuum chamber. The primary reason that Si is chosen as the substrate is because it is desired to incorporate SAMs into conventional silicon-based microelectronics. Most previous studies have used Au films, have been shown to have a strong interaction with the Si surface and can result in interdiffusion into the Si. Whereas, Ag has shown to have a weaker interaction. This is due to the energy gap between orbital 4d and 5s for Ag such that only the orbital interaction between the orbital 5s and Si dangling bonds at the surface can occur [12].

Silicon pieces about 0.5 x 0.5 inches are cut from a silicon Si(100) wafer. The pieces are placed in a beaker with acetone, and then placed in an ultra sonic cleaner for 15 minutes. Next, the samples are put into another beaker with methanol, which is also put into the ultra sonic cleaner for 10 minutes. Hereafter, the samples are mounted onto the sample holder that goes in the thin film deposition chamber. The power dial of the Ag source is gradually increased in increments of 5 A. The starting current is 20 A, which is timed for 2 minutes using a stop watch. Each increment is held for 2 minutes before ramping up. At 40 A the chamber shutter is opened to see if deposition has begun. The Inficon Deposition monitor XTM/2 is used to display the deposition rate in Å per second, and the film thickness in Å. The shutter remains open until the desired thickness is reached, and then it is closed [19]. Then the current is ramped down slowly to avoid cracking of the crucible due to sudden change in the temperature around it. The ramp down is performed in 5 A increments, holding each for 2 minutes. At about 10 A, the

power supply can be completely turned off, as well as the ion gauge, and the Inficon deposition monitor. The chamber and Ag source is allowed to cool down before venting and opening to take out the samples. This takes about 15 minutes.

Once the samples are removed, and they are mounted onto a sample holder that will be used in the UHV chamber for TPD analysis. The sample holder has dimensions of 0.9 x 1.20 x 0.10 inches. It was made of pure molybdenum and has a beveled hole in the center with a diameter of 0.38 inch. This hole allows the heating filament to heat the sample without having to conduct through the molybdenum holder. The Si substrate is attached to the Mo holder using 0.010" Ta wires spotwelded to the holder. For solution grown SAMs, the dodecanethiol solution is prepared. In a small beaker, 100 ml of Ethanol is poured in followed by 25  $\mu\text{L}$  of dodecanethiol. This amount of chemical is taken from its bottle using a calibrated capillary tube which is calibrated to hold only 25  $\mu\text{L}$ . This concentration results in 1 millimolar dodecanethiol solution. Two samples are prepared simultaneously; therefore, two beakers of the solution are prepared each time. Each sample is placed in a beaker of solution while the time is recorded. After a minimum of 24 hours, one sample is taken out and rinsed in ethanol. Then it is placed in the load lock of the UHV and pumped for at least 4 hours to achieve a pressure in the  $10^{-7}$  Torr range. It is then transferred into the UHV chamber. It is important to note that most samples were left in solution within 40 and 46 hours.

Samples were also prepared using vapor deposition. These samples were prepared the same way as previously described up to the thin film deposition. Once the thin film is grown, the sample is removed from the deposition chamber and placed into the load lock that is connected to the main UHV chamber. Here the sample sits for about

two hours until the pressure in the load lock is about  $10^{-7}$  Torr. The right-angle valve between the load lock and the mini-turbo pump is closed and the valve to the dodecanethiol is opened fully to expose the sample to the vapor. The vapor pressure of dodecanethiol is about  $10^{-2}$  Torr at room temperature. After about 1 hour, the valve to the miniturno pump is opened, and the load lock is pumped overnight with the turbo pump to allow the pressure to recover to the  $10^{-7}$  Torr range before inserting into the UHV chamber.

## **CHAPTER 3**

### **RESULTS**

#### **3.1 TPD OF SOLUTION GROWN SAMPLES**

A total of fourteen solution grown samples were measured for this research project. The computer programs used for the TPD measurements were written by Nicholas Clark using LABVIEW [20]. A program was written to ramp the temperature of the sample at a given heating rate, and the temperature verses time of the sample was stored in a file. A second program records partial pressure versus time so that the pressure verses temperature plots can be generated by linking the two time profiles. Eight masses were picked according to the gas phase spectrum in Figure 2. The purpose of the TPD measurements on these SAMs is to find the activation energy for the desorbing molecules of dodecanethiol and to determine whether there is direct desorption of dissociative desorption.

##### **3.1.A. HEATING RATE #1: 50 °C/min**

The first two samples were ran at a heating of 50°C/min. They were prepared as described above. Sample 1 was left in solution for 44 hours. Once taken out of solution,

it was rinsed in ethanol, and then transferred into the UHV chamber. The eight masses measured for this sample were 15, 16, 32, 33, 34, 41, 43 and 64 amu. TPD was performed on this sample for 8 minutes reaching a final temperature of 400°C. Sample 2 was done the same way, and was left in solution for 46 hours. However, the last two masses were different from the first, 15, 16, 32, 33, 34, 41, 43, 54 and 109 amu. The dominant peaks apparent on both plots, sample 1 and 2, were for masses 41 and 43 amu. However, the temperatures of the maxima of the peaks were shifted by around 90°C from each other. Two more samples were run at this same heating rate, Sample 14 and 15. The eight masses for these two were 15, 16, 29, 32, 33, 34, 41, and 43 amu. Sample 14 was left in solution for 46 hrs, and sample 15 was in for 29 hrs. The time each sample was left in solution was purposely done to see if the peaks would differ in magnitude and temperature. The same two peaks were dominant in these two graphs, 41 and 43 amu, but a third mass became noticeable in the process, 29 amu. However, the inconsistency in the temperature for each peak from sample to sample continued.

There was also a notable desorption of sulfur and sulfur/hydrogen components that was consistent in these samples. Such fragments were masses 34 (SH<sub>2</sub>), 33 (SH) and 32 (S), which desorbed at a temperature that was around 90°C higher in temperature than the alkane fragments. The temperature range was about 220°C to 260°C for these sulfur components. For sample #1, which is shown in Figure 4, the peak temperature of these masses was around 220°C. It is notable that the sulfur molecule is activated at this range since the peaks for all of the corresponding sulfur molecules start desorbing at the same temperature. However, just like the other masses, the temperatures for the peaks of each sample are inconsistent.

The inconsistency of the peak temperature from one sample to another of the same heating rate made it very difficult to calculate an accurate activation energy. One similarity was found, the peak for mass 43 amu was generally the largest peak found for all samples. Instead of finding the activation energy, the area under the curve was solved for peak of mass 43 for each sample. By comparing the area under the pressure verses time curve for each sample, the relative coverage of dodecanethiol before desorption could be determined.

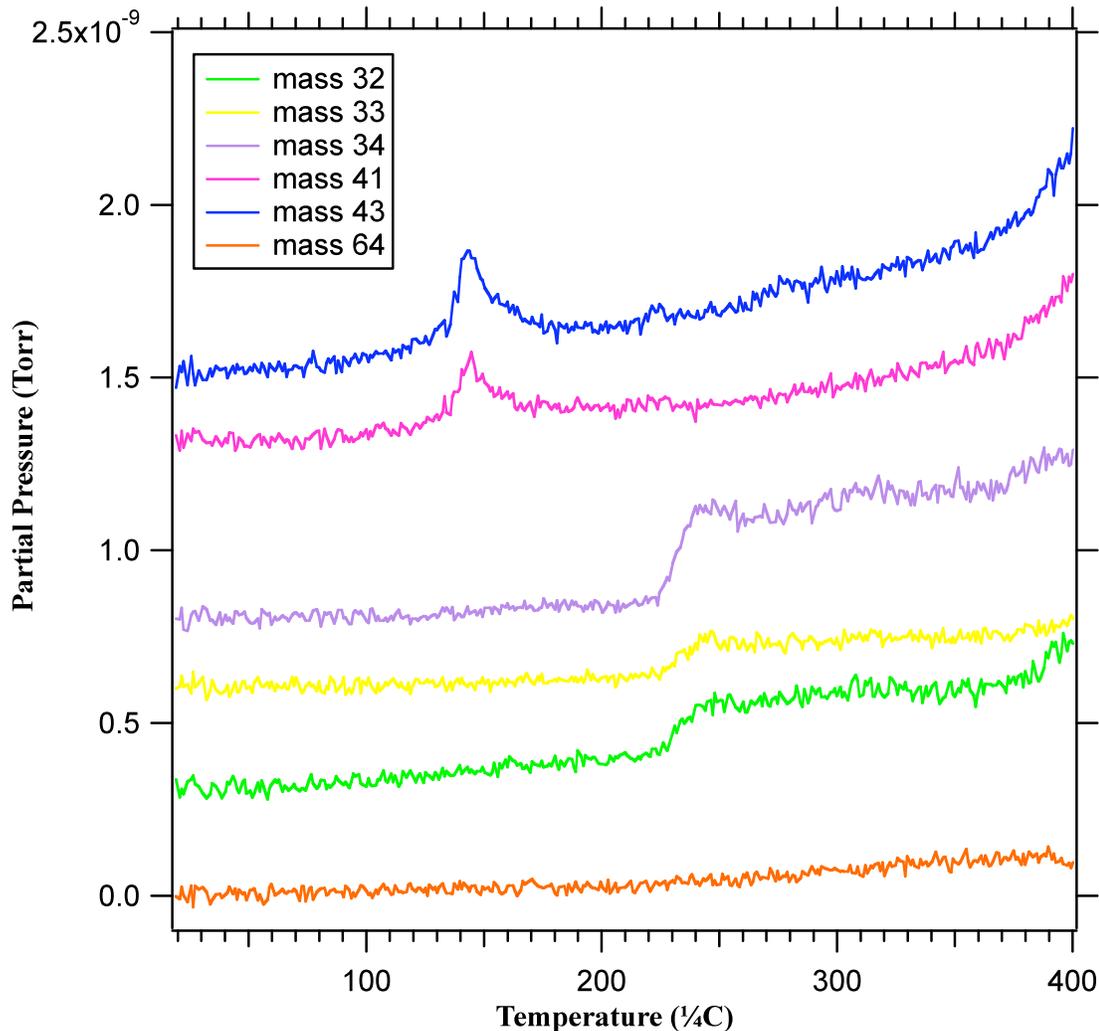


FIGURE 6: Offset TPD plot of  $\text{C}_{12}\text{H}_{26}\text{S}$  SAM on Ag/Si(100) Sample# 1:  $R_H = 50^\circ\text{C}/\text{min}$ .

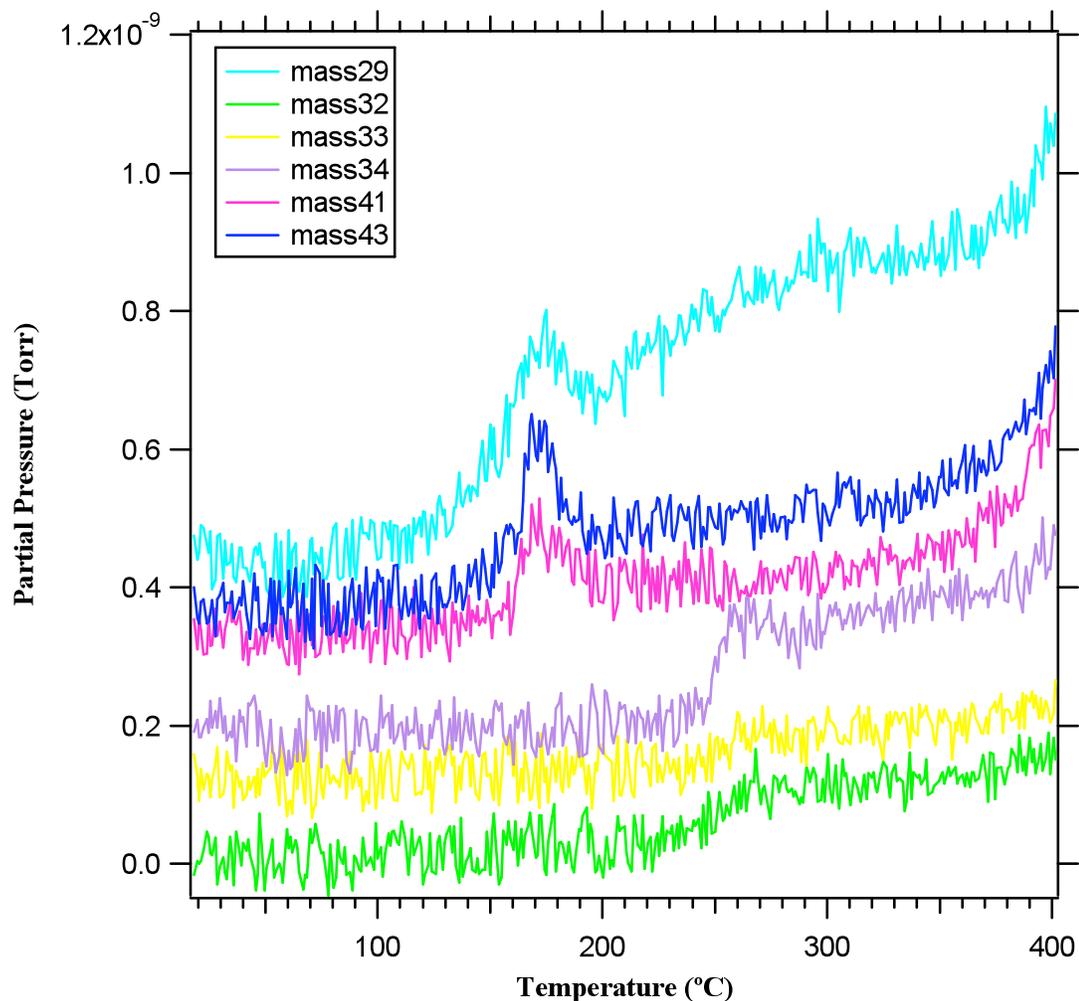


FIGURE 7: Offset TPD plot of  $C_{12}H_{26}S$  SAM on Ag/Si(100) Sample# 15:  $R_H = 50^\circ C/min$ .

### 3.1.B. HEATING RATE #2: $25^\circ C/min$

TPD was done on 4 samples at  $25^\circ C/min$  heating rate. These samples were prepared in solution as previously described. The time in solution varied from one sample to another. The time range was from 24 hrs up to 43 hrs. For this set of samples the eight masses used were the same for each, 15, 16, 29, 32, 33, 34, 41, and 43 amu. The time set for the temperature ramp was 16 minutes, ending at a maximum temperature of  $400^\circ C$ .

The peaks that were noticeable in this set were mass 43( $C_3H_7$ ), 41( $C_3H_5$ ) and 29( $C_2H_5$ ).

These masses form an alkane group. They lined up considerably in the plots, but the temperature for the peaks shifted from sample to sample. For sample #10, the peak was at around 100°C, for sample #12 it was at about 120°C, and for sample #13 it was at about 190°C. There were also noticeable peaks for the sulfur components such as 34(SH<sub>2</sub>), 33(SH), and 32(S). These peaks came off at higher temperature as before, and remain consistent with the temperature at which desorption was activated for all three. Their peak temperature was around 260°C. The temperature range for these masses was around 210°C to 260°C which is a wider range than the previous heating rate. Notice in Figure #7, mass 32 and 33 have very low signals compared to Figure 6 where they are better defined. Mass 34 has a dominant peak in Figure 6, but very low signal in Figure 7. Again, the inconsistency in temperature made it very difficult to calculate an accurate activation energy.

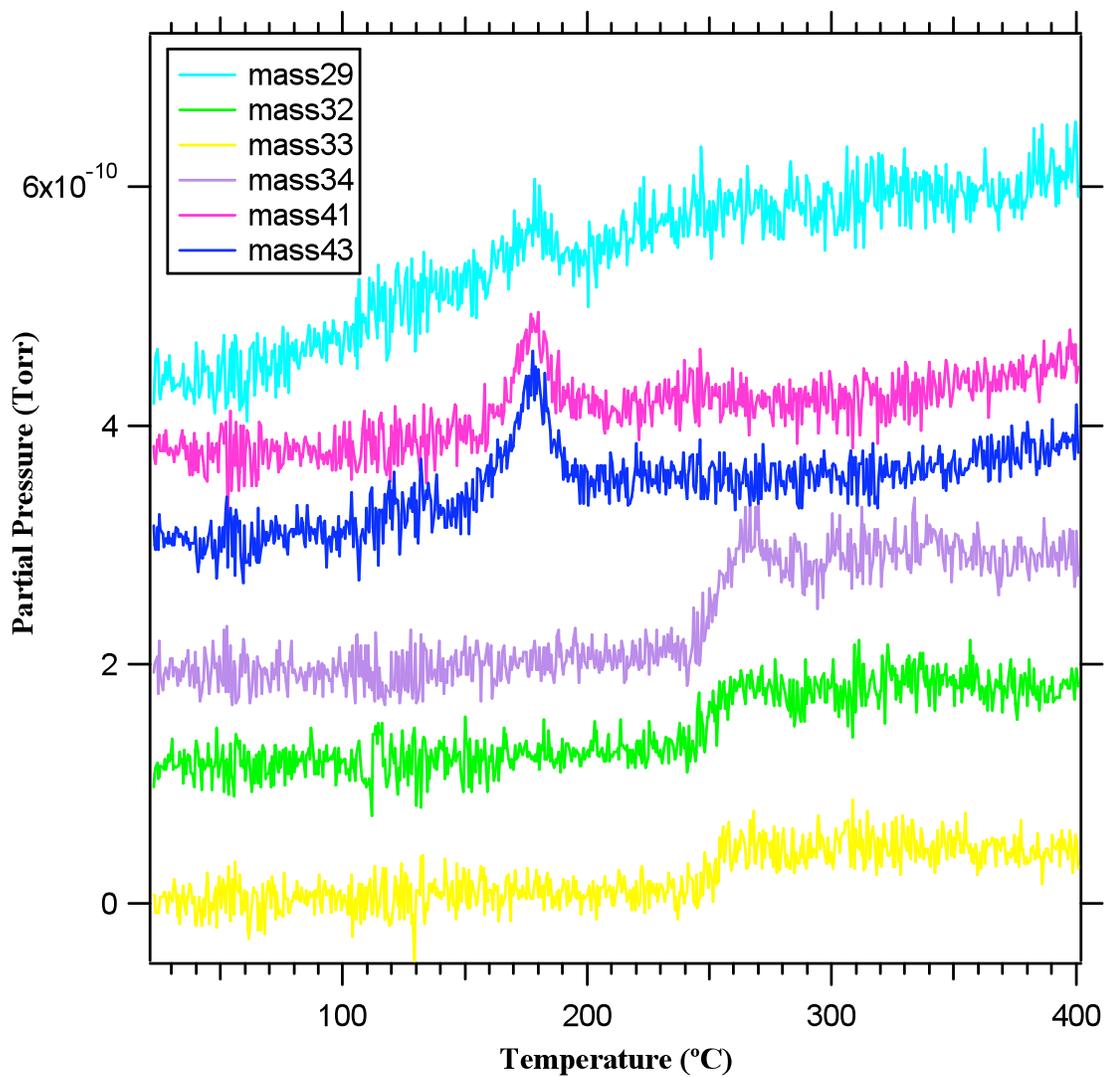


FIGURE 8: Offset TPD plot of  $C_{12}H_{26}S$  SAM on Ag/Si(100) Sample #13. The dominant peaks  $C_3H_7$ ,  $C_3H_5$  and  $C_2H_5$  desorb at around  $190^\circ C$ .

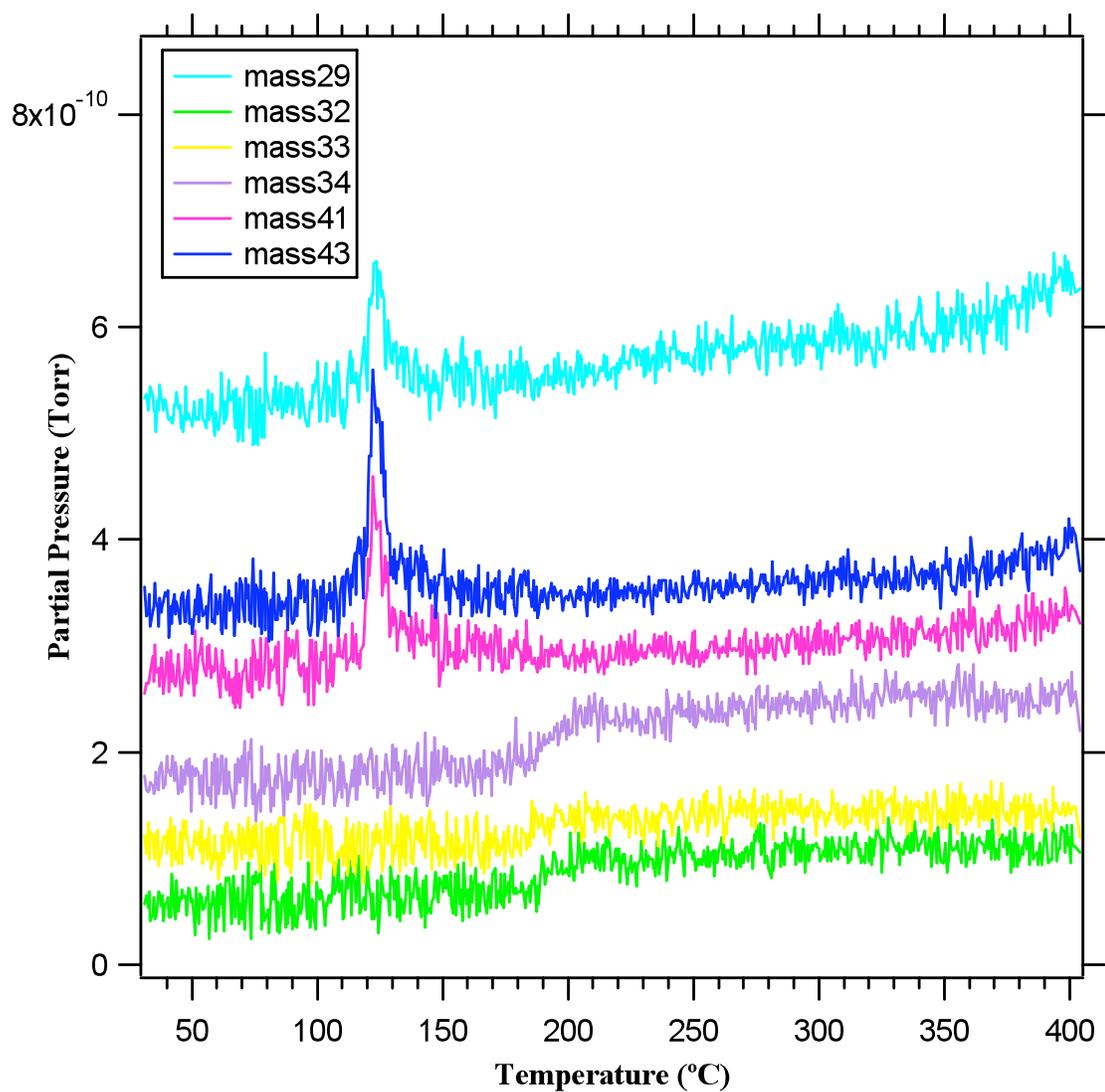


FIGURE 9: Offset TPD plot of Ag/Thiol SAM Sample #12. Peaks desorb at around 120°C.

### 3.1.C. HEATING RATE 3: 10 °C/min

The four samples that were run at this heating rate were prepared the same as before. Again, there was variation in the time the samples were in solution, between 26 to 45 hours. The same three sulfur components were dominant in these samples with

variation in peak temperature, as Figure 8 and 9 show. For this heating rate, the sulfur components are barely noticeable compared to the alkane fragments. The peaks for the sulfur group of masses 34(SH<sub>2</sub>), 33(SH), and 32(S) are at about 190°C which is a lower peak temperature than the previous heating rate. However, their signal is also lower than they were previously. Again, the inconsistency made it very difficult to calculate the activation energy for any of the masses.

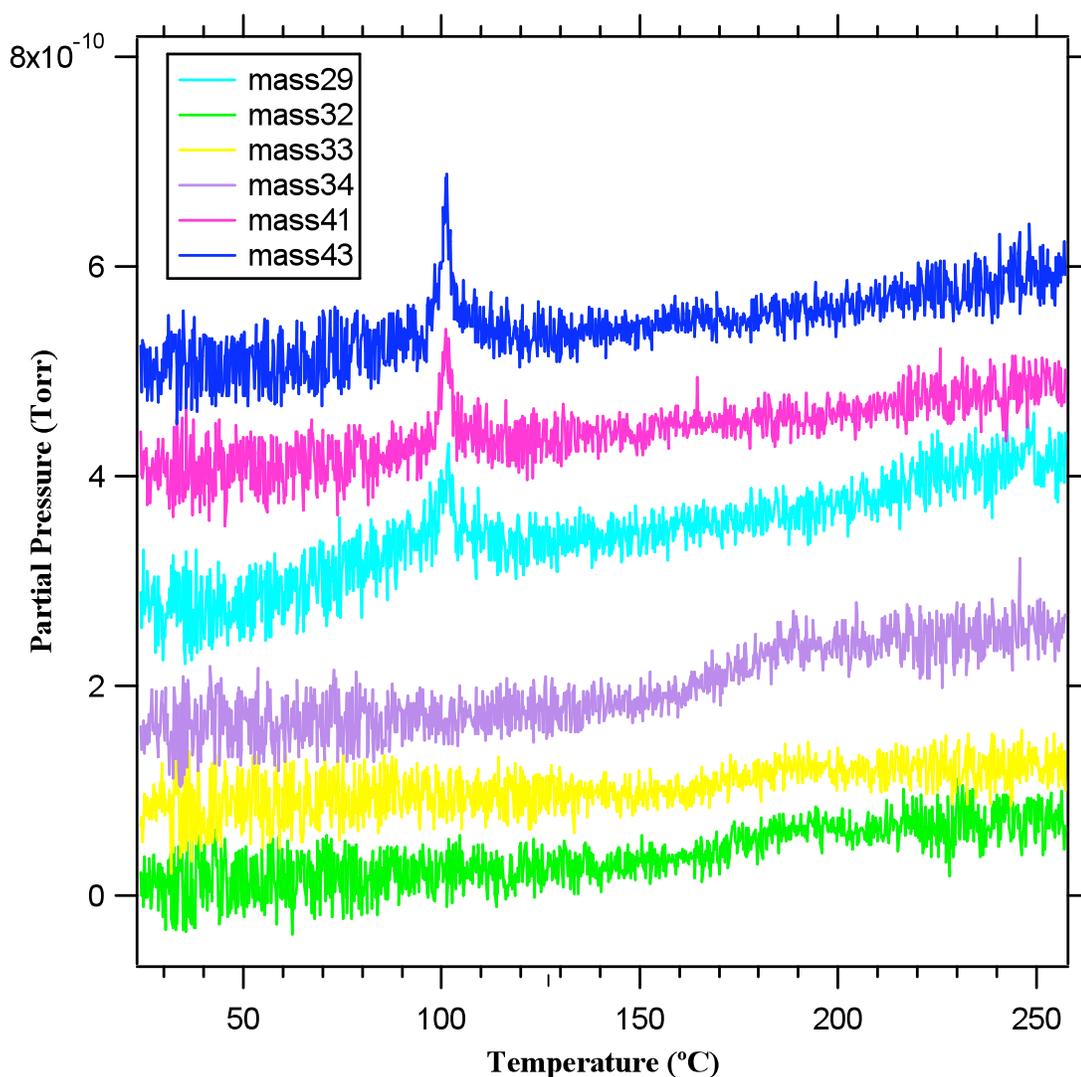


FIGURE 10: Offset TPD plot of Ag/Thil SAM Sample #16  $R_H = 10^\circ\text{C}/\text{min}$ .  $\text{C}_3\text{H}_7$ ,  $\text{C}_3\text{H}_5$  and  $\text{C}_2\text{H}_5$  desorb at about  $100^\circ\text{C}$ .

### 3.2 VAPOR GROWN

There was also a study of samples where the SAMs were grown by vapor deposition. These samples were run at a heating rate of 25°C/min for 16 minutes. The eight masses studied on these samples were 15, 16, 32, 33, 41, 43, 108, and 140 amu. A total of three samples were vapor grown. Similar to solution grown, there were inconsistencies in the peak temperature for each sample. For sample #5, the dominant peaks were alkane fragments such as 41(C<sub>3</sub>H<sub>5</sub>) and 43(C<sub>3</sub>H<sub>7</sub>) amu, and these were the first components to desorb at about 110°C. At higher temperature, sulfur components such as 32(S) and 33(SH) amu came off, about 220°C. For sample #3, the peaks came off at very low temperatures compared to any other sample. This was due to overheating of the sample and problems with the temperature ramp. The alkane fragments desorb at about 55°C, and the Sulfur fragments barely came off at around 120°C.

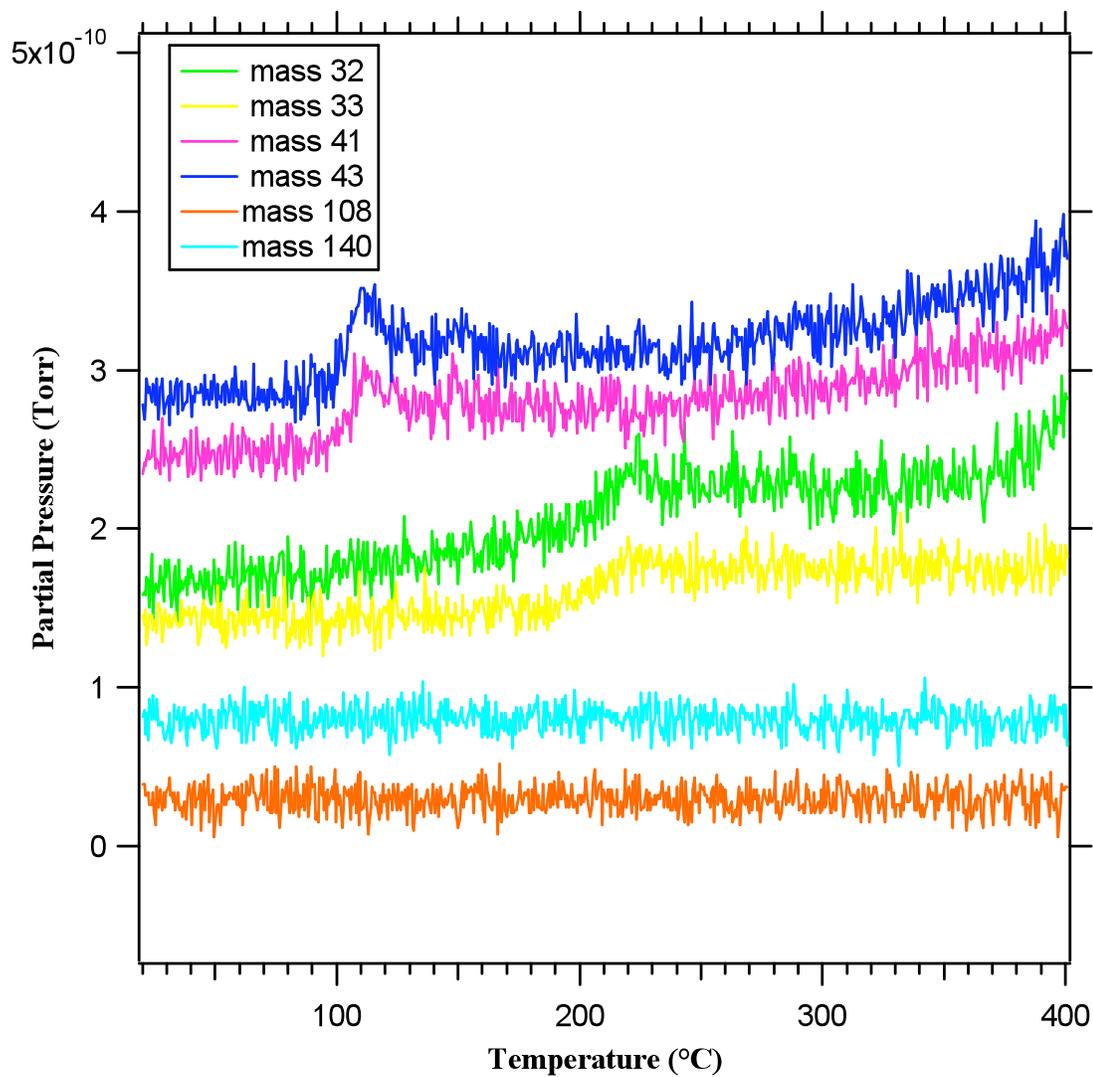


FIGURE 11: Offset TPD plot of Vapor grown Sample #5 :  $R_H = 25^\circ\text{C}/\text{min}$ . The desorption pattern is similar to solution grown cracking pattern. The fragments of 41 and 43 amu coming off at around  $110^\circ\text{C}$ , a similar range of some solution grown samples.

## CHAPTER 4

### DISCUSSION

There were a few changes in parameters with hopes to correct the inconsistency in the peak temperature. Three different sample holders were used. The first holder had a hole with a diameter of 0.38 inches. A second holder was machine with a hole of 0.5 inches in diameter. This exposed more of the sample surface to the heating filament which created a better direct contact between the two. There was no noticeable change to the consistency of the value of the peak temperature of any of the desorption components. The third holder was a solid holder. The idea behind this change was to attain an even distribution of heat through out the sample at a linear rate. However, the heat transfer rate through the holder was too low to perform TPD.

Another variation in parameters was in the position of the mass spectrometer with respect to the sample. The mass spectrometer is on a linear translator with 2 inches or 50 millimeters (mm) of travel. The 50mm mark being at the end of the translator inside the UHV chamber where it meet with the sample. The first samples were run having the mass spectrometer at 45 mm. This position was changed after the sample #3 measurement due to problems with the temperature ramp. The mass spectrometer seemed to be too close to the thermocouple at this position. The next position of the mass spectrometer that was held consistent for all the other samples was at 43 mm.

Another possible cause for inconsistent peak temperatures could be due to shifts of the thermocouple spring. The same thermocouple spring was used for all the samples, so possible wear and tear of the thermocouple could have caused poor contact with the sample as the process went on. Another contributing factor to poor thermocouple readings was that Ag got deposited on the thermocouple itself. There were visible scratch marks on a few samples that indicated the thermocouple was in contact with the surface. This indicated that Ag was on the thermocouple, and this would affect the thermal readings of the sample. Possible problems in the sample preparation that were not evident to the naked eye could have also altered any consistency.

A possible contamination of samples in the process of transfer from solution into the transfer chamber could also cause a change in the saturation coverage and/or a change in the activation energy for desorption. The lack of a more controlled environment could have exposed the samples to many contaminants. Although there was inconsistency with the peak temperature for all the cracking patterns in the samples, the activation energy for mass 43,  $C_3H_7$ , was calculated. This mass was chosen since it was consistent in all the samples, and a bigger cracking pattern of dodecanethiol than the others that were present. Its temperature range was generally between  $100^{\circ}C$  and  $190^{\circ}C$ . There were several masses that were measured to see which had strong signals and which had did not in order to narrow the group down. All masses measured in this experiment are below in Table 1.

Due to inconsistencies with the peak temperature in all the samples, an area analysis was done to each. The principal for this analysis was to find if all the peaks had the same area coverage which would help determine the phase of the dodecanethiol

monolayer. The “lying down” phase is when there is low coverage which causes the molecular backbone to lie down. The monolayer coverage phase is just the opposite, when there is high coverage causing the molecules to form standing up. It is notable that the standing up phase grows about 500 times slower than the lying down phase which grows almost immediately in gas deposition [15]. The areas for each solution grown samples and the average area for each heating rate are shown in Table 2.

The process of temperature programmed desorption starts with a self-assembled monolayer of dodecanethiol on Ag as shown in Figure 13. Then heat is added to the surface of this monolayer causing desorption of dodecanethiol which breaks off into alkane fragments first at about 150°C. Next, the sulfur fragments desorb off the surface around 220°C leaving silver on the substrate. The silver dewets on the Si(100) substrate which is seen as a rough and discolored by the naked eye.

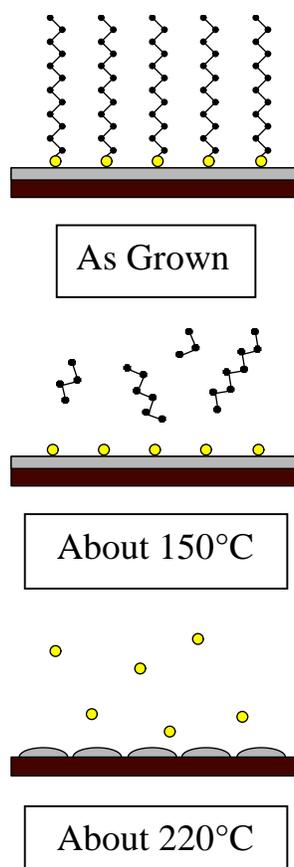


FIGURE 12: Thermal Desorption of Dodecanethiol. Description of the desorption pattern that starts at  $\sim 150^{\circ}\text{C}$ . At  $\sim 240^{\circ}\text{C}$  all of the self assembled monolayer has been desorb, sulfur (S, yellow dots) being the last to come off, and the Ag film dewetts on the substrate. Dewetting is the breaking apart of a thin liquid film on a substrate forming droplets [14].

TABLE 1. Masses and chemical compound. The masses and their compound for the cracking patterns that were measured in this experiment.

MASS	COMPOUND
15	CH <sub>3</sub>
16	CH <sub>4</sub>
29	C <sub>2</sub> H <sub>5</sub>
32	S
33	SH
34	SH <sub>2</sub>
41	C <sub>3</sub> H <sub>5</sub>
43	C <sub>3</sub> H <sub>7</sub>
64	SO <sub>2</sub>
108	Ag
140	AgS

TABLE 2. Area Analysis. Area Analysis of Solution grown samples in their respective heating rate. The area analysis was done in IGOR, a graphing program.

<b>Heat Rate</b>	<b>Sample</b>	<b>Area</b>	<b>Average Area</b>	<b>RGA Position</b>
<b>SOLUTION</b>				
50 C/min	1	5.06E-09	5.26237E-09	41
	2	7.84E-09		41
	12	4.67E-09	4.07358E-09	43
	13	3.47E-09		43
25 C/min	10	4.41E-09	4.80948E-09	43
	12	5.41E-09		43
	13	4.61E-09		43
10 C/min	9	3.09E-09	4.76752E-09	43
	6	3.87E-09		43
	16	3.44E-09		43
	18	2.84E-09		43
	17	1.06E-08		43
<b>VAPOR</b>				
25 C/min	3	4.02E-09	4.06341E-09	45
	4	3.79E-09		41
	5	4.38E-09		43

The areas for the samples within heating range were more consistent than expected. Considering all the shifts with the peaks and temperature, the areas had the same order of magnitude. For the 50°C/min heating rate, two of the samples were measured with the mass spectrometer at 43mm, resulting in low average area coverage, around  $4.07e^{-9}$ . The other two were measured having the mass spectrometer further from the sample at 41mm. These two had higher average area coverage, about  $5.26e^{-9}$  which would reflect in wider peaks taking longer to heat up. This would prove logical considering it was further from the sample. For the 25°C/min heating rate, the three samples were ran with the mass spectrometer in the same position, 43mm, and the average area coverage here was around  $4.809e^{-9}$ . This was higher than the average area for the previous samples at the same position. This would agree when considering the heating rate is slower such that it took longer to heat up causing higher area coverage. The last heating rate was 10°C/min for which the average area coverage was about  $4.767e^{-9}$ . This being consistent with the magnitude of the other areas, and noting that there were more samples ran for this rate. Also, the coverage area for the vapor grown samples, 25°C/min, was about  $4.06e^{-9}$  which was very close to the result for the 50°C/min heating rate samples at the same position, 43mm or 7mm from the samples.

A last attempt to correlate the results from this experiment was done through plotting points of mass 34 and 43 to find an activation energy. The activation was calculated by finding the peak temperature for mass 43 and 34 from each sample. Plot the natural log of peak temperature squared over heating rate versus inverse peak temperature. The slope of this line is the activation energy over universal gas constant, and from this you can solve for the activation energy. The plot below, Figure 10, clearly

shows the inconsistencies of the data that makes an accurate activation energy very difficult to calculate. It was done to show the results of the experiment.

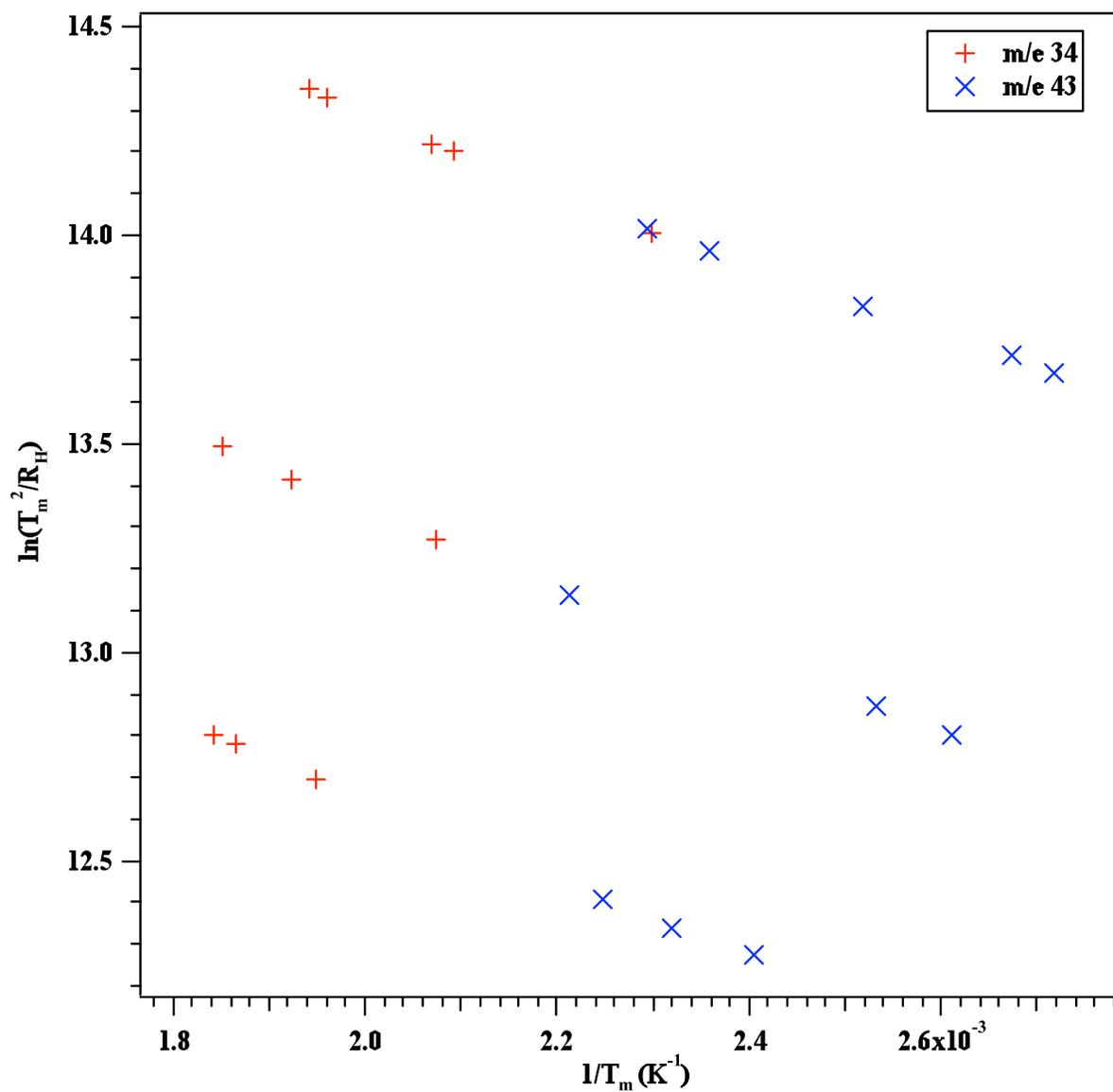


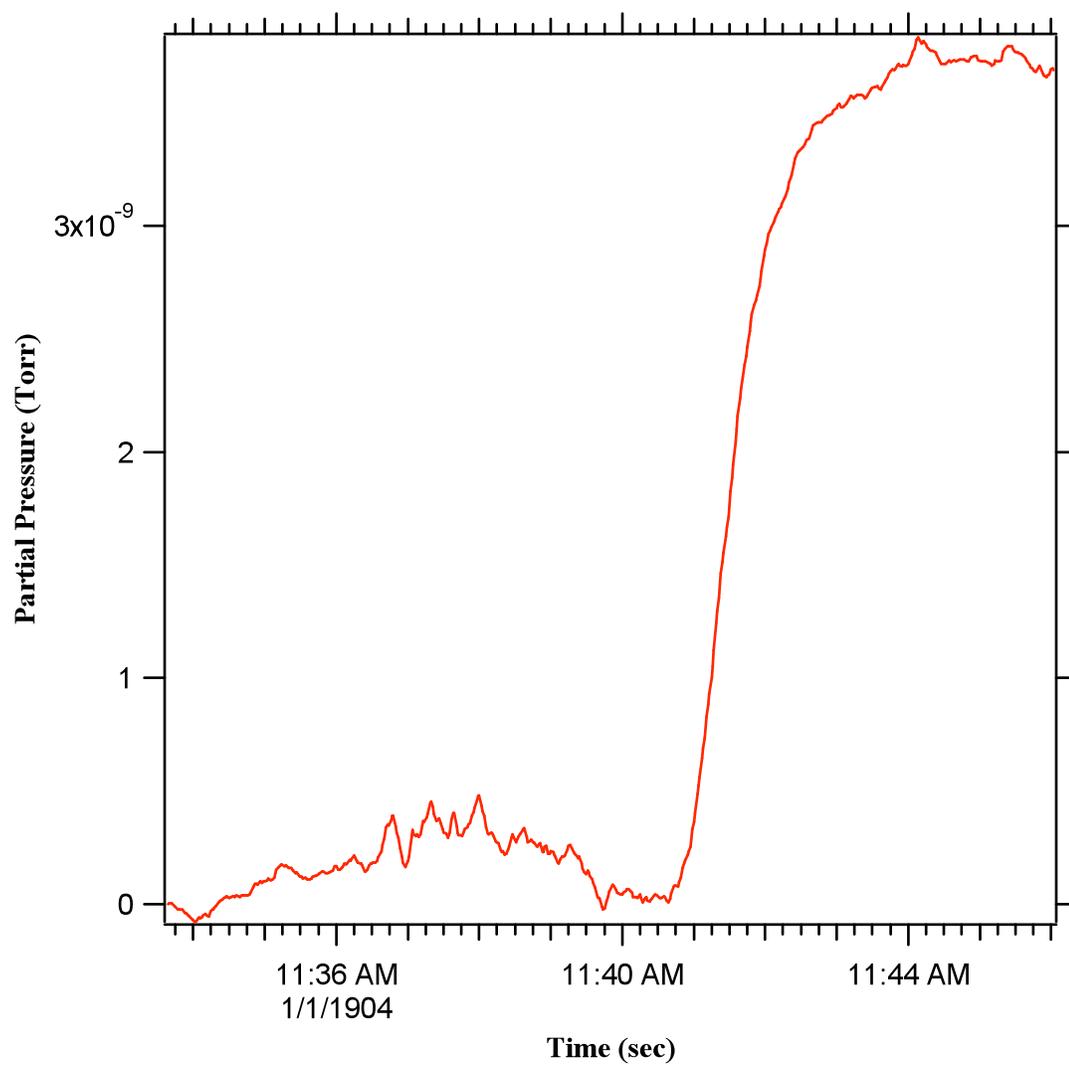
FIGURE 13: Activation Energy for  $C_3H_7$  and  $SH_2$ , the sliding thermocouple contact may have caused inconsistent peak temperature for similar sample preparation and heating rate. Therefore, activation energy determination was not possible.

## **CHAPTER 5**

### **CONCLUSION**

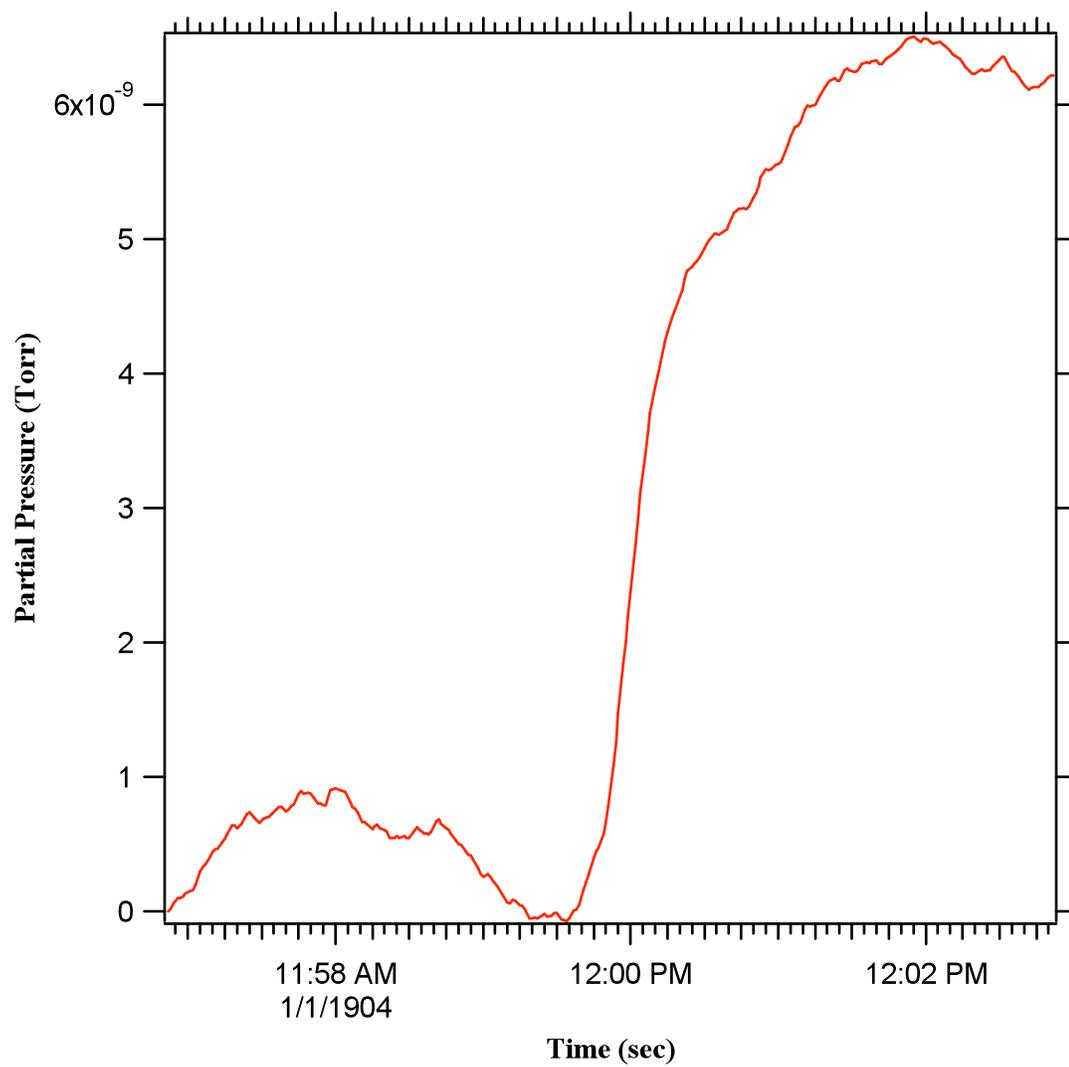
TPD of self-assemble monolayers of dodecanthiol has shown promise as a field of continual research. Thermal desorption has proven true to the simple theory of adding energy to molecules will cause excitation and desorption into the surroundings. Our results show that the desorption of dodecanethiol is a two step process: desorption of the alkane chain of the thiol molecule followed by desorption of sulfur and sulfur/hydrogen components. Because of poor thermal contact between the thermocouple spring and the Ag film, there were inconsistencies in the measure of the sample temperature during the TPD measurements. Therefore, it was not possible to estimate an activation energy for this molecule on the Ag surface. A future direction for this research might be to mount a thermocouple directly on a single crystal of Ag and do all dosing in the UHV chamber since this would avoid the use of a sliding thermocouple contact.

## APPENDIX A



Area analysis plot for Sample #4 for heating rate of 25°C/min.

## APPENDIX B



This is the area analysis for sample #15 at a heating rate of 50°C/min.

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## VITA

Simona Rieman Nava is the youngest daughter of Robert and Myra Rieman. She was born in La Ceiba, Honduras on June 12, 1981. She was raised on the Island of Roatan off the north coast of Honduras in the Caribbean Sea.

Simona went through home school for kindergarten and first grade. She then attended a private elementary school, Seventh Day Adventist Bilingual School, in French Harbour, Roatan. She was transferred to Roatan Bilingual School to complete middle school and high school from which she graduated in June 1999. She then moved to Austin, Texas where she attended ACC and later transferred to Texas State University-San Marcos. In May 2007, she graduated with a Bachelor of Science in Physics, and started the master's program in Physics the Fall of the same year. She will graduate with a Master of Science in Physics in May 2009.

Simona has already started to work for Syracuse Research Corporation in San Antonio. She plans to continue her education through this company and obtain a Ph.D. in Electrical Engineering at the University of Texas San Antonio.

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