Investigation of a Sol-Gel Coating Technique for Polarized ^{3}He Target Cells

A thesis submitted in partial fulfillment of the requirement
for the degree of Bachelor of Science with Honors in
Physics from the College of William and Mary in Virginia,

by

Jonathan Edward Mellor

Accepted for ____________________________

(Honors, High Honors, or Highest Honors)

____

Advisor: Dr. Todd D. Averett

____

Dr. Anne C. Reilly

____

Dr. Robert D. Pike

____

Dr. Keith A. Griffioen

Williamsburg, Virginia
April 2001

Contents

1. Abstract

Many nuclear physics experiments carried out at the Thomas Jefferson National Accelerator Facility require the use of glass cells filled with polarized ^{3}He gas. Currently a facility is in operation at William and Mary for the production of such cells. These target cells are made of aluminosilicate glass that is hand blown into a specific shape, and filled with ^{3}He, nitrogen and rubidium. The rubidium, which is optically pumped, is used to polarize the ^{3}He nuclei. The cells have to be made from aluminosilicate glass because it has a low porosity to ^{3}He, and its surface properties are desirable for high polarization. However, aluminosilicate glass is expensive and is difficult for glass blowers to work with, making the cells costly. It is also desirable to increase the maximum polarization of the ^{3}He, which is currently around 40%. An alternative would be to use Pyrex glass coated with a glass-like sol-gel coating, which should produce a better surface for achieving higher polarization and would be cheaper, and easier to manufacture. The goal of this research project is to develop a sol-gel coating technique for ^{3}He target cells and study the polarization characteristics of those cells. As a first step we tested sol-gel coatings on glass slides. This involved coating the slides and heating them to high temperatures in order to reduce the surface energy and increase the density of the coating. We have recently coated a cell with sol-gel, and filled it with ^{3}He. Its polarization characteristics are currently being studied.

2. Acknowledgments

I would like to thank several people, without whom this thesis would not have been possible.

First of all I would like to thank Dr. Bob Pike, who helped us understand sol-gel chemistry. Dr. Dennis Manos also helped us out a great deal by letting us use the DekTak throughout the year at the Applied Research Center in Newport News Virginia. I would also like to thank Amy Wilkerson for all of her help with the DekTak. She taught us how to use it, and was always happy to let us come over to make measurements.

Finally I would like to thank Dr. Todd Averett, who has always supported my research with enthusiasm. His countless hours of guidance and dedication have made my work possible. This thesis would not have been nearly as good without his relentless editing.

3. Introduction

A number of nuclear physics experiments at the Thomas Jefferson National Accelerator Facility study the spin-dependent properties of the neutron at the quark level using high-pressure, polarized ^{3}He target cells. Polarized ^{3}He can be used for such experiments in place of neutrons because the ^{3}He nucleus is primarily in the S-state, where the spins of the two protons are anti-aligned. Since any extra polarization of the protons can be corrected for using a model of the ^{3}He nuclear wavefunction, the neutron, which is unpaired, and is responsible for most of the ^{3}He spin, can be used to study the spin structure of the neutron.[1]

Special glass target cells are needed to contain the approximately 10 atm (at room temperature) of ^{3}He. These cells are specially designed so that the ^{3}He can be polarized and remain polarized for a long period of time. A schematic drawing of a target cell is shown in Figure 1. The upper pumping chamber allows the ^{3}He nuclei to be polarized via a hyperfine interaction with polarized rubidium atoms, which are optically pumped

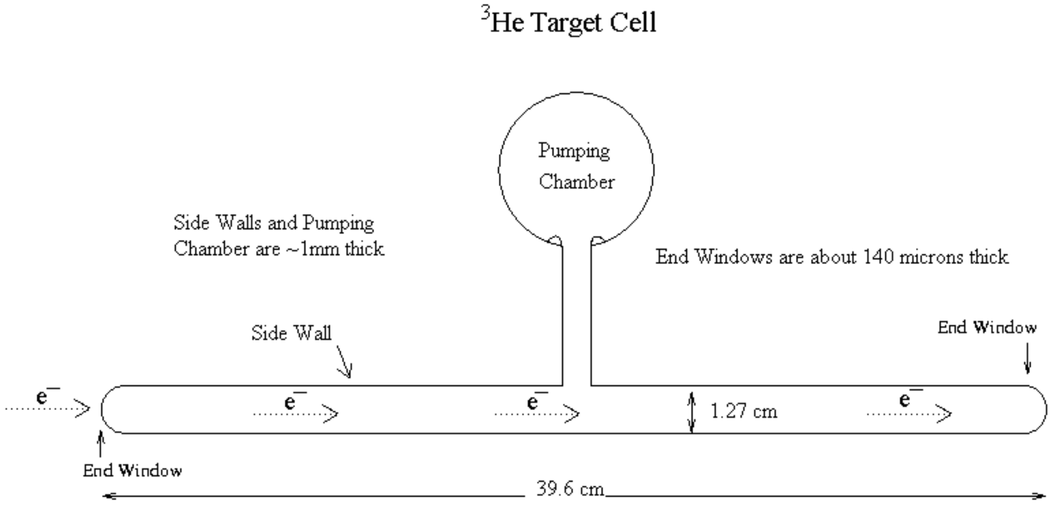


Figure 1. Schematic drawing of the target cell. The electron beam enters from the left, collides with the ^{3}He in the lower chamber, and the ejected particles are detected outside the cell. The top section is the where the Rb polarizes the ^{3}He through a hyperfine interaction.

by a laser. The upper chamber is surrounded by an oven, which vaporizes the rubidium, allowing it to interact with the ^{3}He. Rubidium remains in the upper chamber, while the polarized ^{3}He can travel down to the cooler lower chamber where it interacts with the electron beam that enters the cell through the end windows. Each end window is only about 130μm thick to minimize the interactions of the electron beam with glass. The rest of the glass walls are about 1mm think.

The dominant depolarization mechanism of the ^{3}He nuclei is the interaction with magnetic impurities during collisions with the cell walls. Alumnosilicate glass has been experimentally observed to reduce the depolarization effects better than other types of glass.[2] Each cell is blown by hand, out of General Electric type 180 glass, which is a type of aluminosilicate glass. However, the aluminosilicate glass used is difficult to work with, and is very expensive to buy.

The purpose of this honors research project will be to investigate sol-gel coatings that can be used to coat the walls of the cells. The sol-gel coating technique is an easy way to make high purity glass-like coatings at low temperatures. The sol-gel can then be used to coat Pyrex glass, in place of the aluminosilicate glass. Furthermore, the sol-gel coated cells may lead to improved lifetimes and higher polarizations due to its smooth, clean surface characteristics.

4. Background

4.1 Optical Pumping

It is difficult to polarize ^{3}He nuclei directly, so spin exchange with atomically polarized alkali metals is often used instead. Since alkali metals have only one outer shell electron they have an atomic spin of ½. Rubidium is used in these experiments because it can be polarized to nearly 100% by optical pumping with a laser diode array. A hyperfine interaction between the rubidium atom and the ^{3}He nucleus transfers the spin to the ^{3}He during binary collisions, which polarizes the ^{3}He. However, depolarization mechanisms limit even the best cells to polarizations of about 40%.

In order to optically pump the rubidium the cell is first placed in a magnetic field, which splits the magnetic sub-states. The rubidium is then optically pumped, as shown in Figure 2 (the effects of the Rb nuclear spin are ignored). With right circularly polarized light, electrons can only be excited from the $M = -½$ level. Although they can decay back into either state, they cannot be excited again from the $M = +½$ state, and eventually all of the atoms will be in the $M = + ½$ state. However, when the electrons decay radiatively back to the ground states they emit photons isotropically. These emitted photons can have any polarization and propagation direction, and can be reabsorbed by other rubidium atoms, giving the rubidium atoms the wrong polarization. Adding nitrogen to the cell allows the Rb to decay back to the ground state by collisions with the N_2 without photon emission. It has been found experimentally that the optimal pressures for the nitrogen and the ^{3}He are 60 torr and 7600 torr respectively at room temperature.[3]

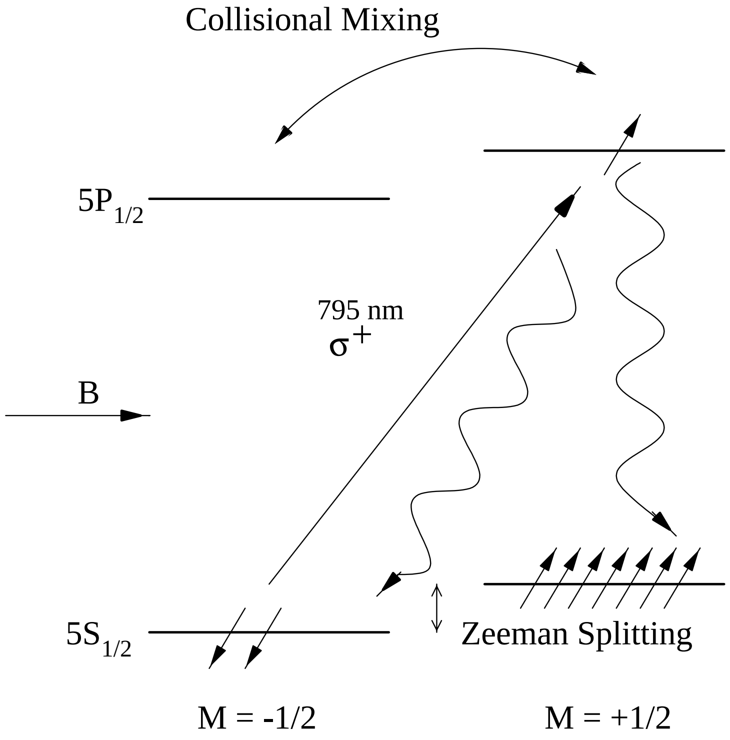


Figure 2. Optical pumping by circularly polarized light (ignoring effect of the Rb nuclear spin).

The Rb, in a hyperfine interaction between its atomic spin and the ^{3}He nuclear spin, polarizes the ^{3}He nucleus during collisions.[4] The polarization of the outer shell electron of Rb is transferred to the ^{3}He nucleus, and the Rb is quickly repolarized by the laser light. The ^{3}He polarization rate is described by the following differential equation:

$$\frac{dP_{He}(t)}{dt} = \gamma_{SE}\left(\left\langle P_{Rb}\right\rangle - P_{He}(t)\right) - \Gamma P_{He}(t) \tag{1}$$

Here $\left\langle P_{Rb}\right\rangle$ is the average Rb polarization (approximately 100%), P_{He} is the ^{3}He polarization, γ_{SE} is the spin exchange rate between the Rb and the ^{3}He, and Γ is the overall depolarization rate of the ^{3}He due to all possible depolarization mechanisms. The spin exchange rate γ_{SE} is given by the following equation:

$$\gamma_{SE} \propto k_{SE}\left[Rb\right] \tag{2}$$

Here $[Rb]$ is the density of Rb, and k_{SE} is the probability of a spin-exchange occurring. As is evident from this equation, γ_{SE}, and therefore the rate of ^{3}He polarization depends on the concentration of Rb; the higher the concentration, the higher the ^{3}He polarization rate. In practice, raising the temperature of the pumping chamber, thereby vaporizing more Rb and increasing the spin exchange rate, can produce higher polarization. However, this requires more laser power, which can become prohibitively expensive.

Equation (1) can be solved to provide the following result:

$$P_{He}(t) = \frac{\gamma_{SE}}{\gamma_{SE} + \Gamma} \langle P_{Rb} \rangle \left(1 - e^{-(\gamma_{SE} + \Gamma)t}\right) \tag{3}$$

It is easy to see that after a long time P_{He} will reach:

$$P_{He}^{\max} = \frac{\gamma_{SE}}{\gamma_{SE} + \Gamma} \langle P_{Rb} \rangle \tag{4}$$

In order to maximize the polarization it is necessary that $\frac{\gamma_{SE}}{\gamma_{SE} + \Gamma}$ be as large as possible. This can be done by making $\Gamma << \gamma_{SE}$. The depolarization rate, Γ, can be expressed equivalently as the relaxation time, $T \equiv 1 / \Gamma$, which should be as large as possible.

4.2 Depolarization

Depolarization can be controlled if special care is taken in the preparation of the cells. The relaxation time is determined by a number of different factors, some of which can, in theory, be accounted for.[1]

1) ^{3}He-^{3}He magnetic dipole relaxation can limit the relaxation time to $T_D \approx 84$ hours for our cells at 10 atm and to about $T_D \approx 280$ hours for cells at 3 atm.

2) Magnetic field gradients caused by inhomogeneous magnetic fields typically give $T_G \approx 1000$ hours.
3) Relaxation can occur due to beam ionization, which, for the Jefferson Lab beam, can be kept at a reasonable level by running at a beam current less than 15μA.
4) Relaxation time due to collisions with gas impurities depends on the amount of impurities in the cell and it typically not significant.
5) Interactions with paramagnetic impurities in the cell walls can cause a large magnetic dipole relaxation rate, with typical relaxation times of 40-60 hours.

In most experiments gas impurities and wall interactions are the largest contributing factors, and both can be controlled. Gas impurities are removed using filters during the cell filling.

The depolarization rate due to interactions with the wall can be diminished if proper care is taken in preparing the glass. Depolarization due to wall interactions is caused by paramagnetic impurities in the walls of the cell, which cause a large magnetic dipole relaxation rate. The ^{3}He can stick to the surface of the cell and exchange with other magnetic materials thereby losing its original spin. Also, ^{3}He can get trapped in micro-fissures in the glass, which increases the number of wall collisions.

Relaxation due to wall interactions has forced physicists and glass blowers to investigate many different types of glasses and preparation techniques, in order to find the most suitable one. It is also important to find glass that will have a low helium permeability to keep the helium from leaking, which is important for nuclear physics experiments when it is necessary to know exactly how many atoms are in the target cells.

Low helium permeability may also be correlated to an increase in polarization since a porous glass may increase wall collisions. It is also beneficial to have a smooth, clean glass with no impurities or micro-fissures to maximize polarization. Aluminosilicate glass has proven to be the best since it has a very low porosity to ^{3}He, loosing only 10% in 100 years compared to only 2 months for Pyrex.[3] Additionally, aluminosilicate glass provides a smooth clean glass surface with few imperfections. Most other types of glass have proven to be unsuitable for use in these cells. However, it is not completely certain why many other glasses, which are fairly non-porous, do not work as well. It is not clear whether it is due to surface contamination or it is actually inherent to the chemical structure of the material.

The disadvantages of the aluminosilicate glass that is currently used are that it is difficult to work with, and it is very costly. The glassblower must go through a labor-intensive routine of resizing and cleaning, in order to reduce both the micro-fissures and any contaminates.[5] Aluminosilicate glass has a steep viscosity curve, meaning the viscosity changes quickly as a function of temperature. It also has much higher melting and annealing temperatures when compared with Pyrex. Furthermore, the polarization lifetimes of the aluminosilicate cells could be improved. These difficulties have motivated the investigation of new techniques, such as sol-gel coatings, that can be used in the place of the aluminosilicate glass.

5. Sol-Gel Coatings

5.1 The Reaction

Sol-gel is a chemical synthesis technique for preparing glasses, gels and ceramic powders. For the purposes of this thesis it will serve as an easy way to make high purity glass in solution form at room temperature. In the sol-gel process a system of colloidal particles in a solution (sol) becomes a macroscopic material (gel), which is interpenetrated by a liquid. Once the liquid evaporates, a strong glass-like material remains. The basic sol-gel reaction, shown in Figure 3, consists of two chemical reactions that produce a thin film when the sol is applied to a substrate. The first is a hydrolysis reaction and the second is a condensation reaction. The hydrolysis reaction produces the sol, and then, in the condensation reaction, a macroscopic gel is formed on the substrate producing a thin film.

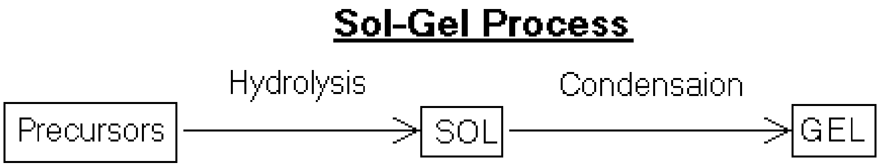


Figure 3. The basic sol-gel reaction.

This basic sol-gel reaction starts when the metal alkoxide $Si(OCH_2CH_3)_4$ (tetraethoxysilane, or TEOS) is mixed with H_2O and a hydrolysis reaction occurs. TEOS is used because it, along with other metal alkoxides, reacts readily with water. Ethanol is used as a solvent because water and alkoxides are immiscible. Providing there is sufficient water and a catalyst present, the hydrolysis reaction will be completed when all of the (OCH_2CH_3) groups are replaced by (OH):

$$Si(OCH_2CH_3)_4 + 4H_2O \rightarrow Si(OH)_4 + 4CH_3CH_2OH$$

producing a sol consisting of $Si(OH)_4$ (silicic acid) and CH_3CH_2OH (ethanol). Next, two partially hydrolyzed molecules can link together in a condensation reaction that liberates water:

$$2Si(OH)_4 \rightarrow (OH)_3Si—O—Si(OH)_3 + H_2O$$

As the reaction proceeds, the number of Si—O—Si bonds increases in a process called polymerization, which produces a macroscopic gel.[6] When producing thin films this gel is formed by rapid evaporation of the solvent.

Though not required, the addition of HCl as a catalyst greatly increases the normally slow reaction rate. Acidic conditions will make it likely that an alkoxide group will be protonated. This will withdraw electron density from the silicon atom, which will make it more electrophilic and it will therefore react more readily with water.[7]

5.2 Dip Coating

Initially, glass microscope slides were used to learn about the basic characteristics of the sol-gel coating solution. Once enough was learned through these trials the best coating solution was used on glass cells. The microscope slides were dip coated with the liquid sol-gel solution producing a thin layer of sol-gel on the surface. Dip coating microscope slides allows us to characterize the film surface using a thin film measuring device to be described in Section 6.1. Therefore understanding the dip coating technique will enable us to produce smoother, denser films for the real cells.

The dipping process is crucial to the properties of the final thin film. In Figure 4, one can see the steady-state deposition stage of the dip coating process.[8] The dilute, noninteracting, polymeric species of the sol-gel solution are concentrated onto the glass surface by gravitational draining, evaporation and more condensation reactions.

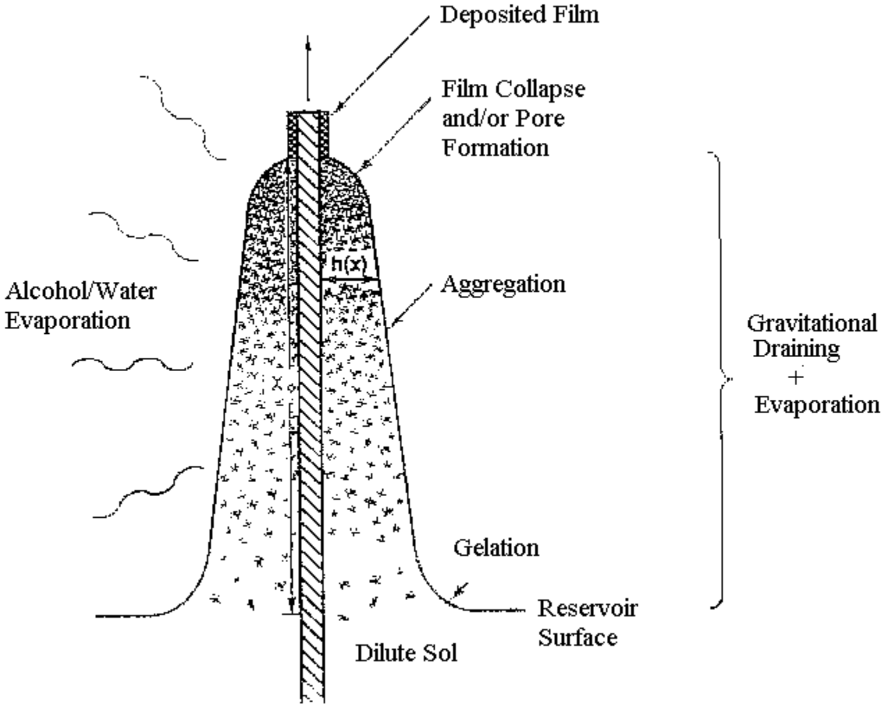


Figure 4. Schematic drawing of the withdrawal process. As the dilute sol is drawn upwards gravitational draining, and evaporation of both water and ethanol, combine to shrink the film into a gel. Once it has collapsed fully, a dense sol-gel thin film remains.[3]

This process increases the concentration by a factor of 20 or 30, which will drive the colloids, which were initially dilute, much closer together. As a result, the viscosity will increase because of the increasing colloid concentration and the continuing condensation reactions. Polymer growth during deposition leads to gelation, which is the point at which the condensing network is stiff enough to withstand gravity, yet is still filled with solvent and water. During the deposition stage there is a constant competition between condensation reactions and evaporation. The condensation reactions act to stiffen the structure while the evaporation compacts it. The entire process, including the aggregation, gelation and drying occurs within seconds for the dipped slides. This dip coating technique is similar to the technique that is used for the coating of the glass cell, since the cell coating involves filling up the cell with sol-gel and then pouring it back out. Therefore, understanding the dip coating technique is essential in order to make smooth coatings on the real cells.

5.3 Film Thickness

After gelation the film is under a tensile stress since it bonds to the substrate surface and then shrinks as it dries. This tensile stress can cause cracking in the film. However, cracking can be avoided if the film is less than a certain critical thickness. The thickness of the films is a result of many different variables that can be controlled. When the film is too thick the coherent force within the film will cause the film to shrink in the direction parallel to the substrate surface when it is later heated to drive out the remaining solvent and water. If this coherent force is too large the film will come off of the substrate surface causing cracking. For thinner films the bonding force prevents the shrinkage in the direction parallel to the surface, so the films shrinks perpendicular to the surface, resulting in a film that is strongly attached to the surface. The ideal thickness, obtained by one coating, should be between 0.1 and 0.45 μm.[9]

There are many factors that can affect the final film thickness including viscosity, dipping speed, and the H_2O/TEOS ratio. These factors can be adjusted so that the thickness of the film will be within range of ideal thicknesses, to produce a smooth, dense film.

The viscosity of the coating solution can affect the final thickness because the more viscous the solution, the more of it will "stick" to the substrate surface producing a thicker film, as is shown in Figure 5.[10] This plot shows that the final thickness increases with viscosity up to around 6 cP, where the resulting films had too many cracks. For this thesis the coating solution was had a viscosity of approximately 1.5-2 cP.

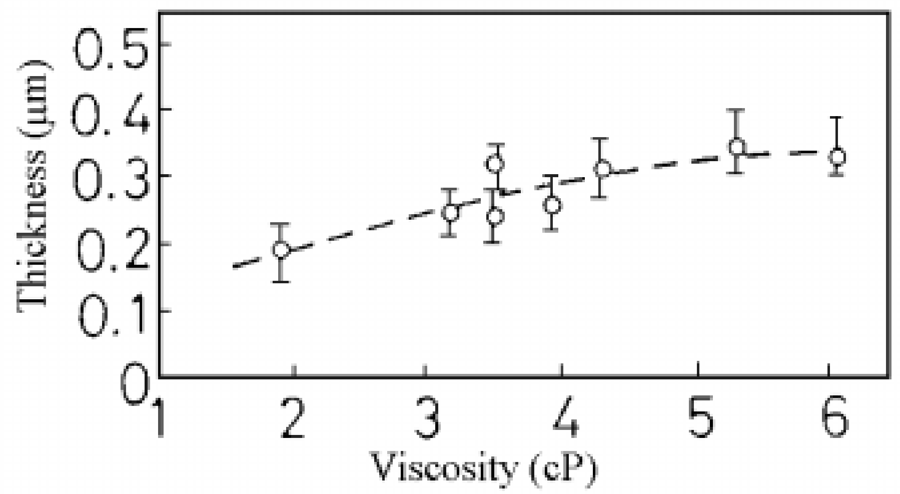


Figure 5. Thickness in microns vs. viscosity in cP for sol-gel thin films.[10]

One factor affecting the viscosity is the age of the solution. Studies have shown that the viscosity of the solution increases with time. This is a result of the fact that there will be a greater concentration of silicon-containing molecules because of evaporation of the solvent and the production of more hydrolyzed species as the reaction progresses ultimately yielding a higher density coating solution. It is therefore best to use as new a solution as possible.[11]

The H_2O/TEOS ratio can also affect the density of the final film, as shown in Figure 6.[12] The line with X's represents different H_2O/TEOS ratios with constant ethanol concentration. It is easy to see that the increasing H_2O/TEOS ratio increases the initial density of the films since they do not compact as much when they are heated to high temperature (line with solid circles). This is due to the fact that solutions with higher water content generally have higher hydrolysis reaction rates producing a more highly condensed polymer. Therefore, reducing the H_2O/TEOS ratio by adding more TEOS makes thicker films. This plot also shows, in the line in the upper right corner, with the open circles, that at constant H_2O/TEOS ratio the addition of ethanol makes thinner films.

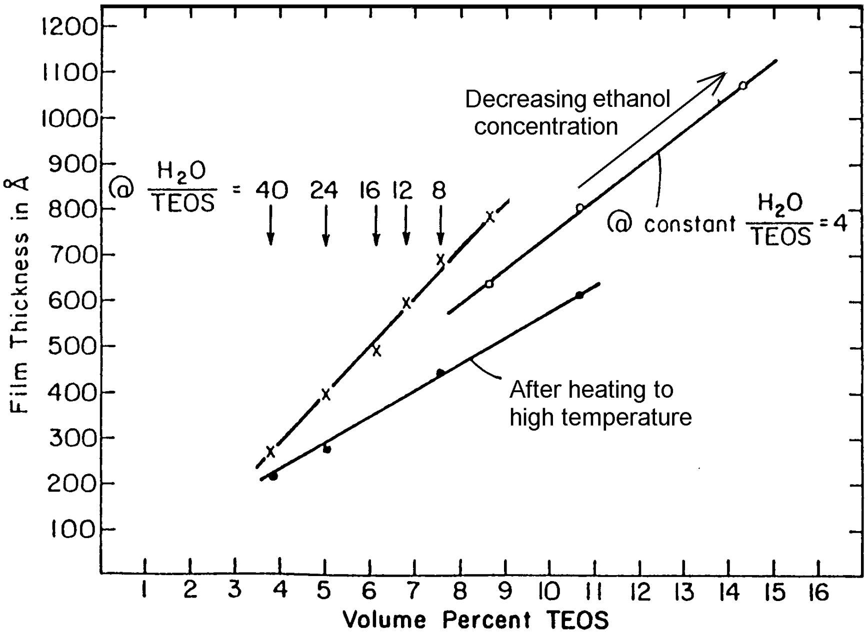


Figure 6. Film thickness vs. volume percent of TEOS. The film thickness increases for increasing volume percentages of TEOS when either the amount of H_2O or the ethanol is decreased. The line with the X's indicates the thickness variation when H_2O concentration is varied, and the line with the closed circles represents the thicknesses after heating to high temperature with varying H_2O concentration. The line with the open circles represents varying ethanol concentration.[12]

The withdrawal speed, as the slide is lifted from the sol-gel solution, affects the thickness of the coating. During the film deposition there are as many as six different forces that govern the final thickness of the film: (1) viscous drag upward on the liquid by the moving substrate, (2) force of gravity, (3) resultant force of surface tension in the concavely curved meniscus, (4) inertial force of the boundary layer liquid arriving at the deposition, (5) surface tension gradient, and (6) the disjoining or conjoining pressure (important for films less than 1μm thick).[13] Taking all of these forces into account the formula for the thickness is approximately:

$$h = c_1\sqrt{\frac{\eta U}{\rho g}} \tag{5}$$

Where h is the thickness, c_1 is the proportionally constant (about 0.8 for Newtonian liquids), U is the withdrawal speed, η is the viscosity, ρ is the density and g

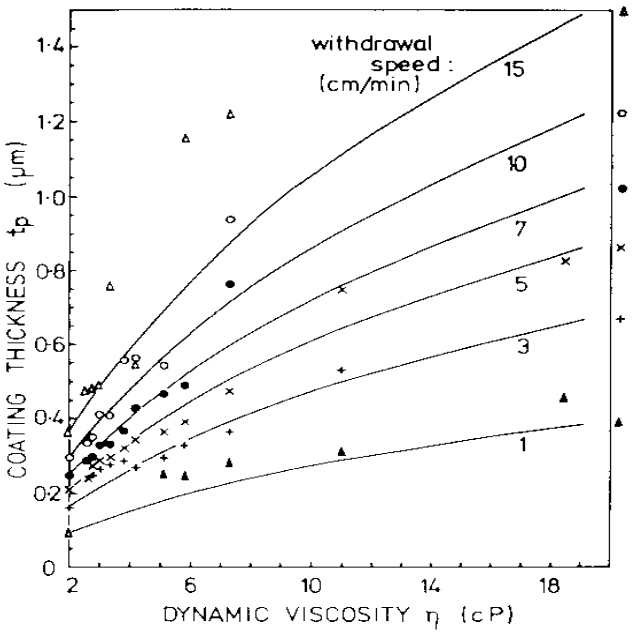


Figure 7. Thickness vs. viscosity and speed. Increasing the withdrawal speed increases the thickness, although for low viscosities the thickness variations are small.[14]

is the acceleration due to gravity.[9] Therefore the faster the withdrawal rate, the thicker the coating. It is estimated based on the work of Strawbridge and James[14], whose graph of thickness vs. withdraw rate is shown in Figure 7, that at the velocity we used, 3 cm/min, the coatings will be around 0.2 – 0.6 µm. This is crucial, since it is primarily the coating thickness that will determine whether or not the coating will crack, and this range of coating thicknesses should provide for mostly crack free coatings.

5.4 Sol-Gel Densification

Once coated, the film must be densified by heating the sol-gel thin film to high temperature in order to make a more compact and smoother surface. While the gel is shrinking, the gel network is continuously deformed and the remaining liquids are transported out of the film through pores. This produces stresses and strains in the shrinking gel. In order to make a pore-free ceramic the gel must be heated to high temperatures, which will collapse the pores and reduce the surface energy making the films as dense and as smooth as possible. Densification also has the added benefit of driving out organic residue.

Once the slides have been coated they are heated in an oven to the desired densification temperature, at a constant rate of approximately 120°C/hour. This slow heating rate helps to prevent cracks from forming in the film. This rate was determined by Klein et al.[15] to be the best to allow both the gel microstructure to collapse due to reduced viscosity and to allow the gases to escape. It is important that the heating rate not exceed 120°C/hour otherwise the film will likely crack. Once the slides have reached the desired temperature they are held there for one hour. Then the oven is turned off and the slides are allowed to cool down to room temperature overnight inside the oven.

The final densification temperature was determined largely from the work of Hsu et al., whose data is shown in Figure 8.[16] This is a plot of the fractional change in coating thickness for sol-gel films baked up to various temperatures. It is clear from the figure that after about 500°C the thickness does not change significantly. Therefore, 500°C is the temperature at which the film has fully densified. Based upon this work a densification temperature of 500°C was used to densify the coatings.

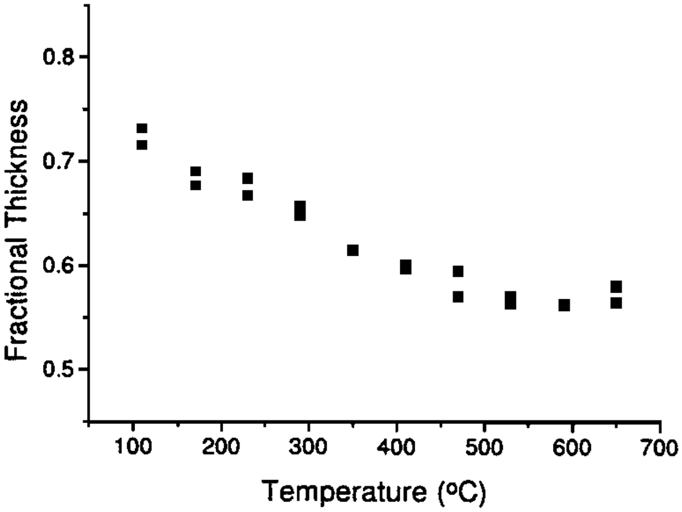


Figure 8. Change in fractional thickness as a function of densification temperature.[16]

6. Sol-Gel Application

The initial investigations of the sol-gel process consisted of coating microscope glass slides. Glass slides were used since they allowed the measurement of a profile of the film thickness using a DekTak apparatus located at the Applied Research Center in Newport News Virginia. These slides were first masked with tape (to assist in the accurate measurement by the DekTak), then dipped into the sol-gel solution, allowed to dry for a while, and finally densified at high temperature.

6.1 The DekTak

The DekTak is a device used to measure the thickness profile of thin films with a resolution of better than 0.01μm. It operates by determining the deflection of a fine tipped stylus as it moves across the surface of the sample. This profile is important since the smoothest possible coating is necessary to reduce wall interactions. The thickness of the film is also an indication of the degree of densification.

To measure a sample, the microscope slide is placed on the DekTak stage. The stylus then automatically comes down into place. Since the films are so thin and the slides tend to have varying flatness, they must first be leveled. This is only possible if there is a region without coating on either side of a coated region allowing two points of reference. The slides must therefore be masked with tape before being coated, as described in Section 6.2. Several successive passes of the stylus are needed to allow the operator to level the stage by adjusting a leveling screw. Once the slide is sufficiently leveled one more pass of the stylus makes a measurement of the thickness and a profile of the film. Since the slide can never be perfectly leveled, the DekTak software can be used to additionally level the data. The software is only capable of fitting the data to a straight line, which has proven to be a difficulty since many of the slides were warped to such a degree as to prevent an accurate measurement of the thickness.

6.2 Masking Technique

For proper operation, there can only be a small strip of coating on the slide with uncoated parts on either side of the small strip. This means that the slide must be masked so that it will only coat the proper areas. Ordinary clear packing tape was found to be the best for masking the slides. It provides a nice smooth edge and it can be cleanly removed after dipping.

Originally scotch tape was used to mask the slides. This was ineffective since the tape curled up on the edges during, and right after, dipping. This allowed some of the coating solution to run underneath the tape creating a rough edge. Next, aluminum tape was used, which was an improvement because it did not curl up during dipping. However, it was soon evident that it was not possible to fully remove the tape after dipping, leaving a sticky residue. The final tape tried was ordinary clear packing tape. This was very effective since it did not curl up during dipping and it was easily removed after dipping.

The first masking was horizontal as shown in Figure 10, but as the slides were removed, sol-gel bunched at the tape edges. This is seen in Figure 9, which is a DekTak scan of the coating thickness as a function of position along the slide. The solution to this problem is also shown in Figure 10, where the tape is applied vertically so that the solution can run off unobstructed. This proved to be a much better masking technique since it did not allow the solution to bunch up as much along the edges.

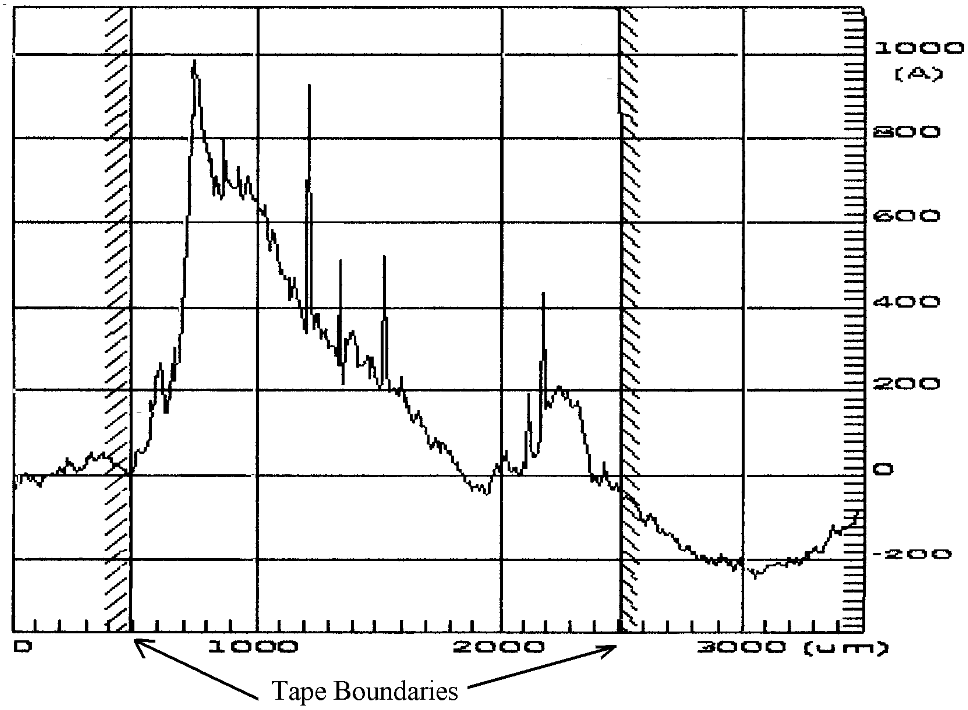


Figure 9. DekTak scan showing the film profile with horizontal units of μm and vertical units of Å. The coating is bunched up along the left side tape boundary.

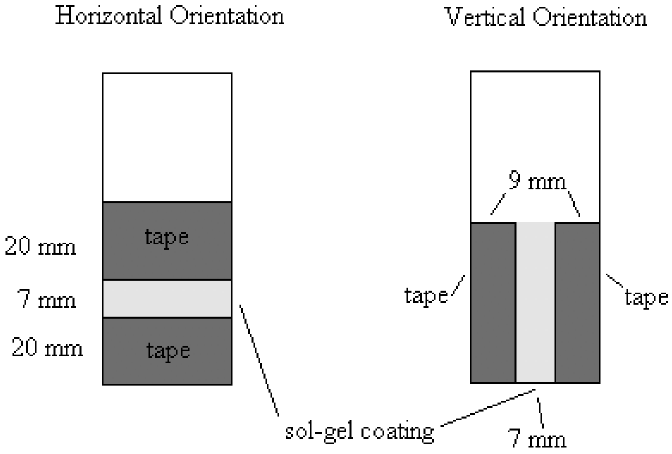


Figure 10. The different masking techniques.

The distance between the masked regions was another area that needed to be resolved. In order for the DekTak to work properly the slide must be carefully leveled. It is easier to level the slides over as short a distance as possible, therefore for leveling it is best to have a very narrow band of coating solution. However, the coating solution tends to get bunched up along the taped edges, so it is best to have a relatively large coated region in order to minimize the edge effects. The optimal coating distance proved to be about 7mm, which was a small enough region to be able to level for the DekTak yet large enough to minimize the edge effects in the middle.

The final coating issue that had to be resolved was the fact that originally the back sides of the slides were not masked at all. This left coating solution on the back side, which could have affected the DekTak measurements since the coating solution on the back may have contributed to some of the difficulty in leveling the slides. All subsequent slides were masked on their entire back side.

6.3 Sol-Gel Chemistry

The first step in the sol-gel synthesis process is to mix the solution. The components of the solution are measured using a graduated plastic pipette, and placed in an Erlenmeyer flask. A magnet stirrer mixes the solution at room temperature for several days in the flask to assure a homogeneous mixture. At all times the Erlenmeyer flask is sealed with Parafilm to prevent evaporation. Once the solution has been sufficiently stirred then the slides can be dipped.

For the majority of the first semester we followed the work of Hsu et al. in their work on sol-gel coatings.[16,17] Their solution, shown in Table 1, consists of aluminum nitrate nonahydrate ($Al(NO_3)_3 9H_2O$), water (H_2O), ethanol (CH_3CH_2OH) and TEOS ($Si(OCH_2CH_3)_4$). The aluminum nitrate was added to simulate the properties of the aluminosilicate glass. Before coating, this solution was diluted further with ethanol in a 1:7 ratio. They chose the composition because thin films are more resilient under compression so it is important that the thin film have coefficient of thermal expansion that is slightly smaller than that for the Pyrex. They argued that this would make the thin film less likely to crack during its multiple heating and cooling cycles. Therefore a molar composition of 20% alumina was chosen. This makes the coefficient of thermal expansion ~2.3×10^{-6} K^{-1}, which just below that of Pyrex, ~3.2×10^{-6} K^{-1}.

Composition (mole % Al_2O_3)	TEOS (mL)	$Al(NO_3)_3(9H_2O)$ (g)	Water (mL)	Ethanol (mL)
20%	11	9.2	6	66.9

Table 1. Sol-gel coating solution used by Hsu et al.

During our tests, this coating solution produced films that were not consistent with their measured thickness of 0.1μm and were not thick enough to be accurately measured using the DekTak apparatus. A typical example of a profile of a slide coated with this solution is shown in Figure 11. The background curvature of the slide itself makes it difficult to deduce the film thickness, but it is evident that the film is much less than 0.1μm. The possible cause of this problem is that the coating solution was diluted with too much ethanol, making the solution and therefore the final coating too thin.

Figure 11. Thickness profile of slide showing that the background curvature of the slide prevents an accurate assessment of the coating thickness.

The next solution tried was derived by Sakka et al. and is shown in Table 2.[18] It has been shown to form thin films on the order of 0.2μm using a procedure similar to ours. This solution has a molar concentration H_2O/TEOS = 11. It has a small amount of hydrochloric acid to catalyze the reaction, but does not contain any aluminum nitrate nonahydrate. The hydrochloric acid was in an aqueous solution that contained approximately 30% HCl and 70% water. We choose not to add any aluminum nitrate

TEOS (mL)	Water (mL)	Ethanol (mL)	HCl (mL)
23.4	29.7	23.0	0.9

Table 2. Sol-gel solution concentrations.

since we wanted to concentrate on getting the sol-gel technique to work and did not want to add any further complications.

This composition proved to be much better. It formed films that were thick enough to be accurately measured and were in the desired range of 0.1-0.45μm. An example of a typical film profile is shown in Figure 12. This slide was coated with the solution, but was not baked at all. It is very smooth, and is about 0.4 μm thick. However, when films of this concentration were coated they tended to crack when densified to high temperature. This is a significant problem since we want as smooth a surface as possible. An example of a cracked surface is shown in Figure 13. It is clear from this picture that a cracked surface will not allow for good polarization and cracking must be avoided when coating the real cells.

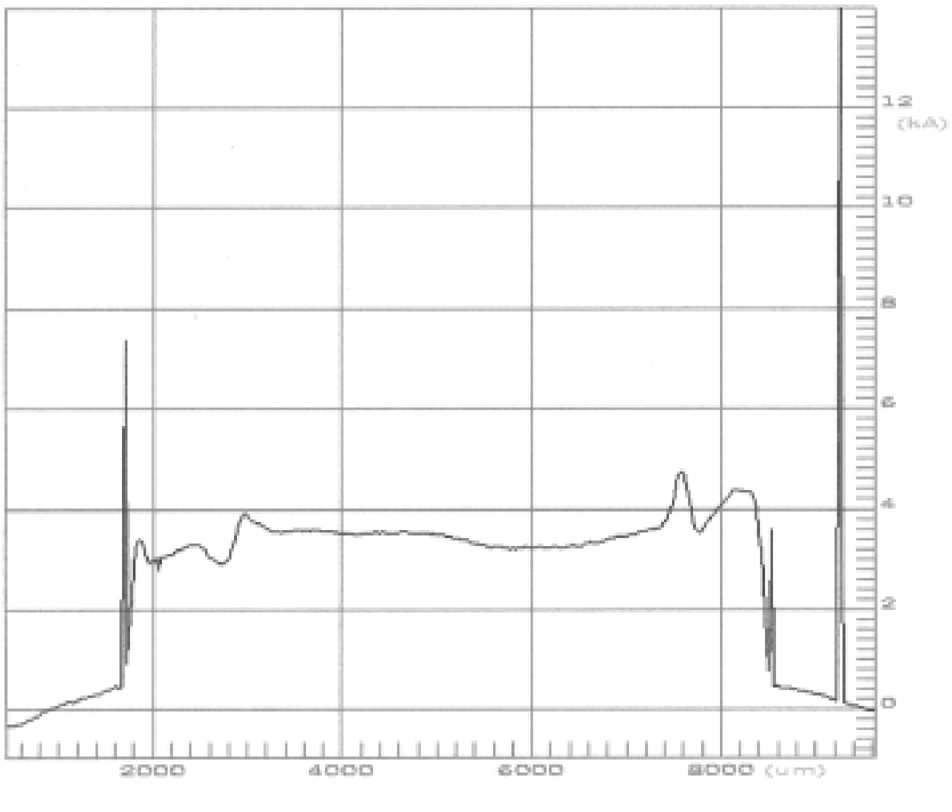


Figure 12. Unbaked slide shows even thickness of 0.4μm.

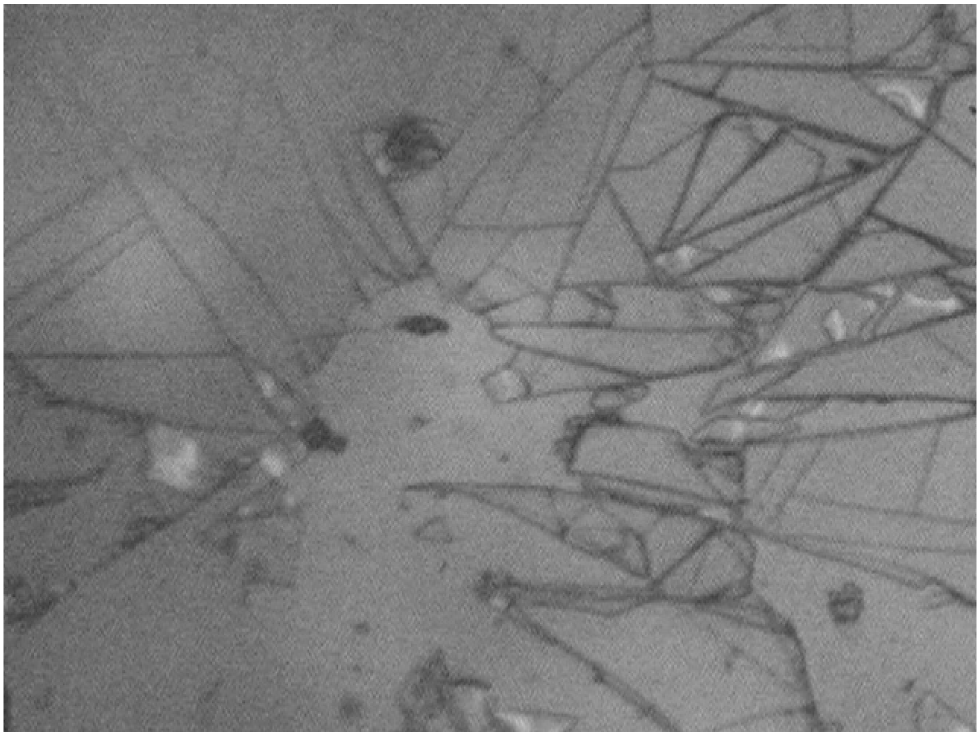


Figure 13. Cracked sol-gel surface under approximately 40X magnification.

Additional ethanol was added to the solution in Table 2 to reduce viscosity and prevent cracking. This was largely successful in that the cracking was eliminated except for regions close to the tape where excess solution tended to build up. Different quantities, between 4 and 144 ml, of ethanol were added to the solution in an attempt to create a non-cracking film that was thick enough to be measured. A couple of the thickness profiles are shown in Figures 14 and 15. All of these films were heated to 500°C. Notice the clear thinning of the films with increasing ethanol concentration. Figure 14, with 24 ml ethanol added, shows a fairly uniform surface of between 0.2 and 0.3 µm. The next one, with 84 ml of ethanol added, has almost no thickness at all, and it is hard to measure since the background curvature of the slide prevents an accurate assessment of the thickness. A coating solution with 20ml of additional ethanol was determined to be the best. It was a compromise between lack of cracking and adequate thickness. See appendix A for the complete procedure that will result in the best coatings.

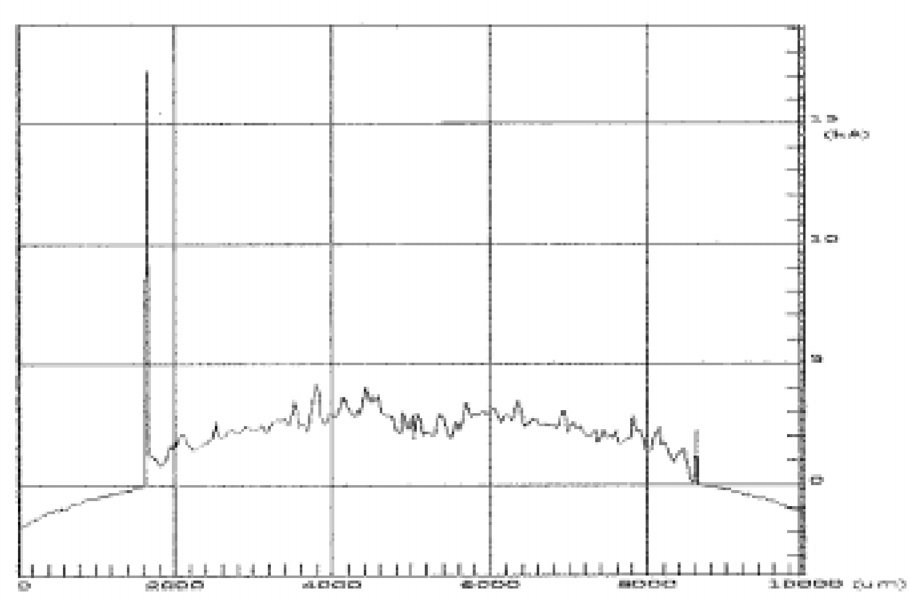


Figure 14. Thickness profile of slide with 24ml of ethanol added.

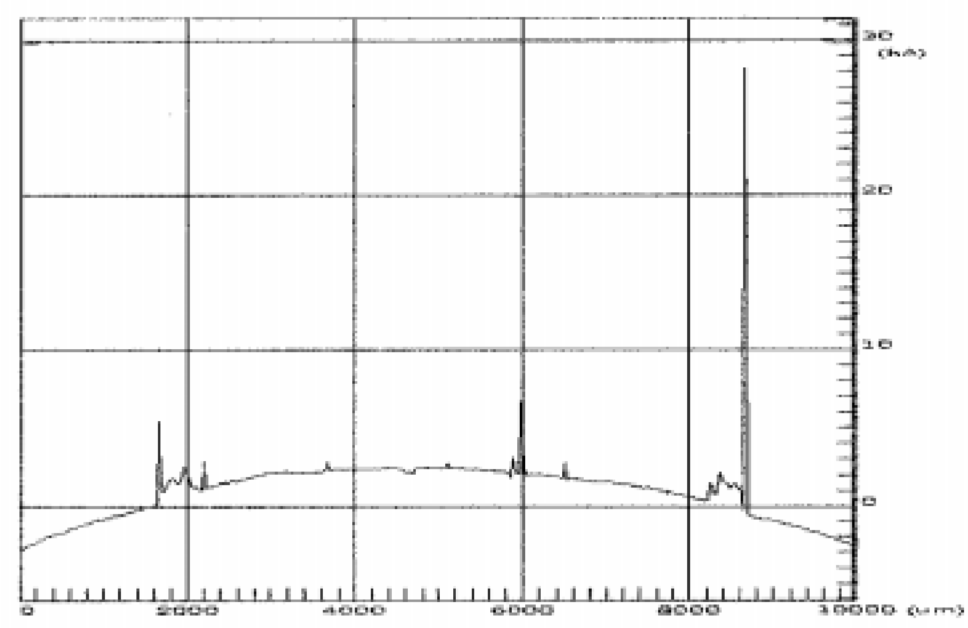


Figure 15. Thickness profile of slide with 84ml of ethanol added.

6.4 Dipping

After the slides were masked they were dipped in the coating solution using an apparatus consisting of a motor mounted on a stand with a string attached. The slide was attached to the string via a small piece of tape. It was then inserted by hand into the solution, and removed at a constant velocity by a motor at approximately 3 cm/min. This velocity, depending on the viscosity and other factors previously mentioned, would produce a film that was approximately 0.1-0.5 μm thick, which is within the optimal range of thicknesses.

This dipping method has proven to be quite reliable, however one has to be very careful both while inserting the slide and during its withdrawal. Careful attention is required because the sol-gel will stick immediately to any surface it touches, so the slides must be inserted cautiously to avoid producing an uneven coating.

6.5 Densification

After the slides were air-dried for a couple of hours they were baked in an oven. Initially the slides were dried overnight in the oven at 60°C to drive out any residual water and ethanol, further compacting the solution. This worked fine for the initial coating solution of Hsu et al. in Table 1. However, drying the coatings overnight severely cracked films made from the newer solution given in Table 2. It is unclear exactly how to interpret this finding. It is even more baffling since when the slides were baked up to 500°C directly there was little to no cracking.

In light of the drying problems, the later slides and cells were not dried overnight, but were rather densified immediately. To determine the proper densification temperature, and to see what physically happens to the sol-gel thin film as it is densified, slides were coated with the final solution chosen and were baked up to various temperatures ranging from 100 to 500 °C. Unfortunately the slides came out severely cracked, possibly since the solution was about a week old. However, some general results can be deduced by one slide that was not baked and one that was baked up to 500°C. Figure 16, which is a thickness profile for a slide that was unbaked, shows a relatively smooth surface that is about 0.2-0.3μm. The slide in Figure 17 was baked up to 500°C and clearly shows that it has been densified.

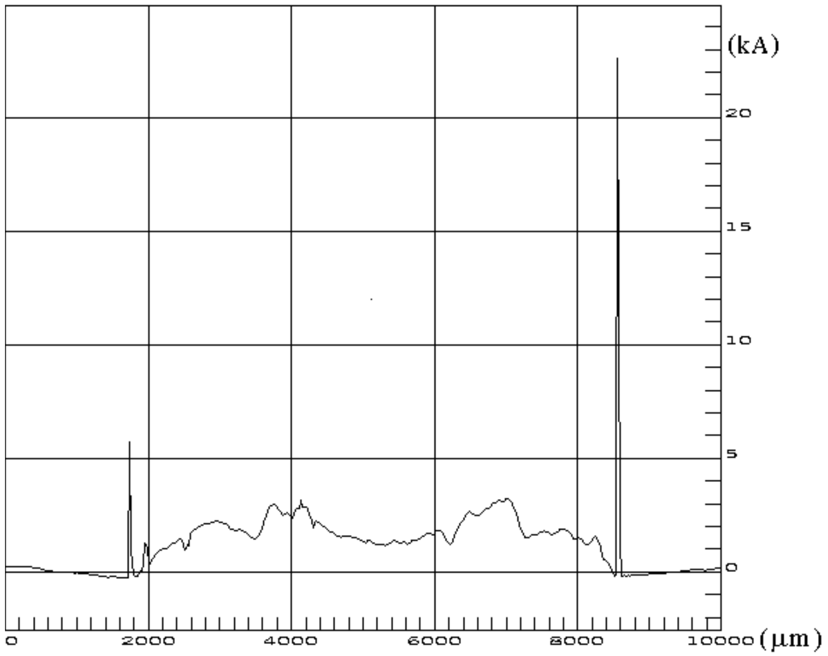


Figure 16. Sol-gel thickness profile for an undensified slide.

Although the background makes determining the thickness difficult, it is clear that it is less than 0.1μm thick. Evidently the sol-gel has reduced in thickness and become denser. However, it is not clear that densification made the surface any smoother. The densification process is important because this is what will make the sol-gel coating as dense as possible, which should lead to longer lifetimes.

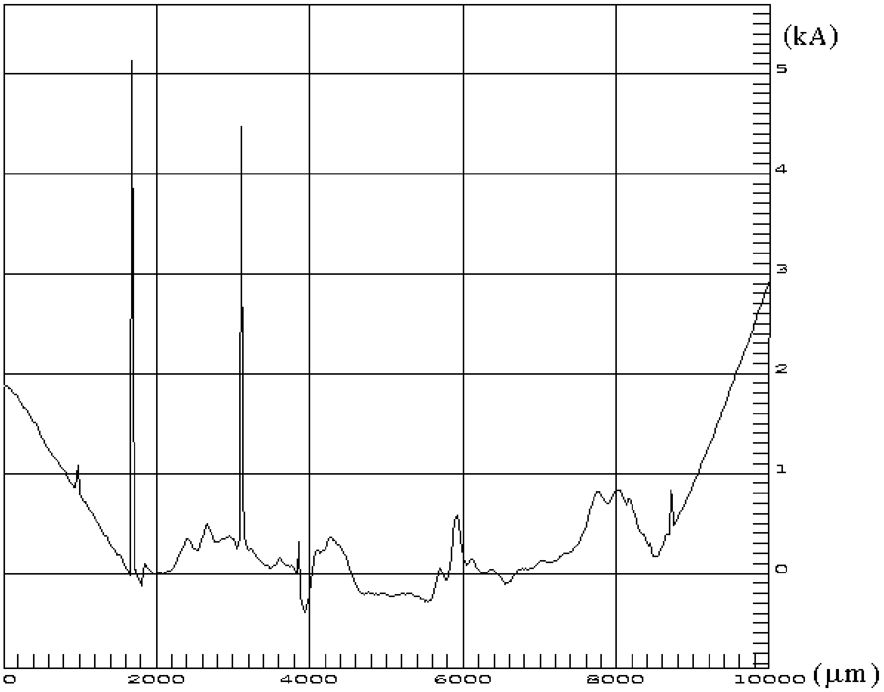


Figure 17. Sol-gel thickness profile for a slide densified to 500°C

7. Filling and Coating Test Cells

In order to test how well the sol-gel works, small cells were filled and sent to the polarized target lab of Korsch et al. at the University of Kentucky to have their polarizations and lifetimes measured. These small cells, shown in Figure 18 are 2 inches in diameter and are shown attached to a stringer, which is the long glass tube used to connect the vacuum system to the cells. The cell and the stringer are made entirely of Pyrex, but only the actual cells are coated with sol-gel.

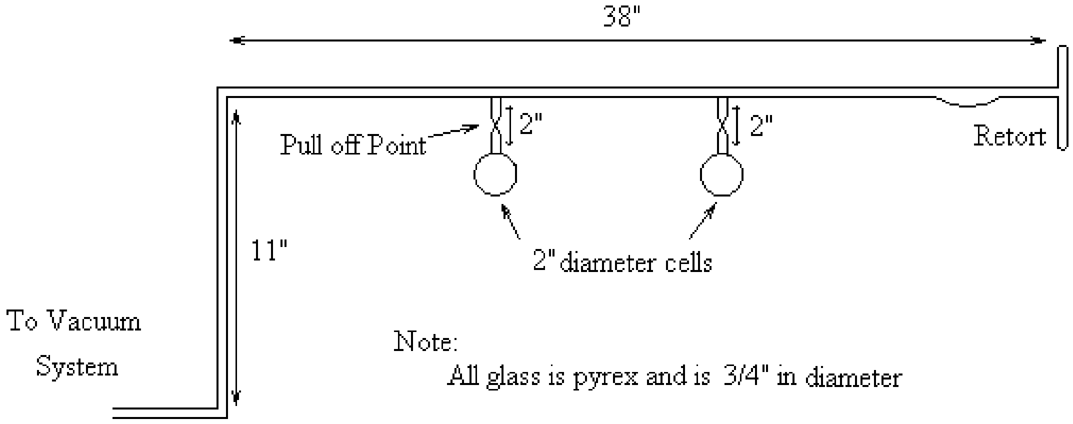


Figure 18. Stringer assembly with cells attached.

7.1 Coating the cell

The first step in filling the cells was to coat the cells with the sol-gel solution. This was done in much the same manner as the microscope slides. The coating solution was mixed as before using a coating solution consisting of the concentrations listed in Table 3, which was determined to be the best compromise between cracking and thickness. The cells initially came from the glassblower separate from the stringer, so

TEOS (mL)	Water (mL)	Ethanol (mL)	HCl (mL)
23.4	29.7	43.0	0.9

Table 3. Cell coating solution.

that they could be coated with sol-gel before being attached. The solution, once it was properly stirred, was put into the glass cell using a small syringe. It was filled to the top and allowed to sit for about 10 minutes. It was then dumped out. Since the small neck of the cell did not allow the solution to flow out freely a small tube had to be inserted into the cell to allow it to flow out properly. The cell was baked to 500°C to densify it. At all times it was held upside down in a specially designed holder. This allowed any excess solution to run out. Neither of the cells had any visible cracks on their spherical sections, although they both had some cracking in the neck of the cells. This was most likely due to excess sol-gel that built up in the neck as it was draining out. Cracking here should not lead to any depolarization since most of the neck was not attached to the final cell once it was attached to the stringer when the cells were separated from the stringer.

7.2 Filling the cell.

The cells were then filled using the ^{3}He cell production facility at William and Mary. The cell filling is a crucial part of the process since it can be a very important factor in the determination of the final relaxation rates. Therefore it is imperative that it is done carefully.

The cell filling facility is an ultra high vacuum system consisting of pumps, purifiers and gauges that allow the ^{3}He to pass from the ^{3}He gas cylinder to the cell. The vacuum is produced by a turbo-molecular pump, which is backed by a roughing pump.

These two main pumps are capable of achieving a vacuum of better than 10^{-9} torr. The high vacuum is an indication of the cleanliness of the system.

The cells, once coated, were fused onto the stringer, which is attached to the vacuum system. To purify the cells further of contaminants, they were baked at 470°C under high vacuum in an oven for six days. Before the baking, a Rb ampoule was opened and sealed into a retort that is on the far end of the stringer. A few days later the Rb was chased further down the stringer into a storage dip and the original retort was disconnected from the system. After six days the oven was removed and a small amount of Rb was chased down the stringer and into each cell. The cells were then each placed one at a time into liquid nitrogen dewars. The liquid nitrogen kept the cell at about 77 K so that the internal pressure of the cell was lower than the atmospheric pressure.

Once the cells were cold they were first filled with high-purity N_2 and then high-purity ^{3}He. These gases are contained in bottles at the far end of the vacuum system and passed through the system through purifiers by opening and closing the proper valves. Heated purifiers are used for the N_2 and ^{3}He because their purity is very important for high polarizations. The gas was then held in a manifold system, which includes a calibrated volume and a pressure manometer. With these devices the amount of gas that gets to the cell can be recorded. The final step was to be release the gas into the string and into the cells. Once the cells were filled they were sealed off and removed with a torch by melting the glass just above the spheres. This is possible, as the glass tubing will collapse since the pressure is greater outside the cell than inside. This produces a filled cell with no leakage. As the cells were brought back up to room temperature the pressure in the cells increased.[3]

7.3 Polarization Lifetimes

Since there is not currently a facility at William and Mary for measuring the polarization and lifetimes of the target cells we sent them to the University of Kentucky for testing. The testing of the cells consists of a "spin-up" period in which the ^{3}He is polarized by-spin exchange optical pumping and a "spin-down" period in which the ^{3}He is allowed to depolarize. While the ^{3}He is being polarized it is heated to ~180°C to vaporize the rubidium. It is also radiated with 795 nm light from a high power diode laser array. During the spin-down the cells stay at room temperature and the lasers are turned off while polarization is monitored using a nuclear magnetic resonance system. This will produce an exponentially decaying curve given by the following equation:

$$P = P_i \mathbf{e}^{-\Gamma t} \qquad (6)$$

where P is the polarization, P_i is the initial polarization, Γ is the depolarization rate and t is the time. The exponential decay indicates that the ^{3}He is becoming depolarized and it allows one to extract Γ.

To date, one of the coated Pyrex cells has been measured to have a lifetime of 58.5 hours, which is a reasonably long lifetime for a cell filled with 3 atm of helium. The full spin down curve, showing the polarization as measured in mV by the NMR system vs. time, is shown Appendix B. A similar uncoated Pyrex cell filled with 1.8 atm of ^{3}He and measured using the same system had a lifetime of 60 hours. This indicates that the sol-gel coating has increased the lifetime of the cell, although the wall interactions are still the dominant depolarization mechanism. The wall interactions are likely the dominant factor since ^{3}He-^{3}He magnetic dipole interactions contribute, for a cell at 3 atm, 280 hours to the depolarization. Other depolarization mechanisms including magnetic field gradients, and impurities should contribute lesser amounts to the depolarization. Therefore, it is likely the depolarization due to wall interactions still dominates the depolarization. However, it is surprising that the lifetimes for both the uncoated Pyrex cell and the coated Pyrex cell are similar, which could indicate that other systematic errors are contributing to the depolarization. Therefore, the 58.5 hour lifetime is likely a lower limit for the actual cell lifetime. The second cell has yet to be measured, however it will likely have a similar lifetime.

8. Future Research

Although a great deal has been accomplished this year there is still a tremendous amount of research that needs to be completed before these cells can be used in a real nuclear physics experiment.

One of the first priorities will be to do more work determining the best coating solution; one that will lead to the longest lifetimes. Since the concentration of the various chemical compounds in the sol-gel coating solution can be varied substantially, this ought to be done in order to determine the solution that makes the best coatings. Initially more needs to be learned about what makes the films crack when heated and how to prevent it. The various solutions that have proven to crack the least should be used to coat actual cells to determine the coating solution that leads to the longest lifetimes.

The surface quality of the sol-gel coating is another important aspect of the coating. In order to prevent the ^{3}He from getting trapped in any rough parts, or cracks in the surface it is necessary to make the surface as smooth as possible. The quality of the surface can be assessed using a scanning electron microscope. This will give us good indication of the surface quality to help determine the best coating solution possible.

One aspect that may lead to better lifetimes would be to simply dope the coating solution with aluminum nitrate, as done by Hsu et al.[16,17], so that the resulting glass layer will have some aluminum oxide in it like the alumnosilicate glass that is currently used. An alternative would be to use aluminum methoxide ($Al(OCH_3)_3$), which will also create sol-gel glass containing aluminum oxide. Either solution may work better because alumnosilicate glass has tended to yield longer lifetimes than similar Pyrex cells. Furthermore it would be interesting to see how permeable the sol-gel coating is to ^{3}He.

Uncoated Pyrex cells have been shown to be too permeable to ^{3}He and are therefore unacceptable for nuclear physics experiments where the exact ^{3}He density needs to be known.

It will also be interesting to see how the sol-gel coating is affected by radiation. The cells will be subjected to about 1-6 GeV of incident electron energy at 15μA from the beam at Jefferson Laboratory. It is not clear how the surface of the sol-gel will be affected by such radiation. Simply putting the cell into an electron beam for a period of time and then looking at the surface under a scanning electron microscope can assess the radiation damage to the sol-gel surface.

9. References.

---

[1] J.R. Johnson *et al.*, Nucl. Instr. Meth. **A356** (1995) 148.
[2] W.A. Fitzsimmons, L.L. Tankersley, and G. Walters, Phys Rev. **179** (1969) 156.
[3] J.L. Knowles, "Investigation of Techniques for Producing High Polarization ^{3}He Gas Targets", Senior Thesis, The College of William and Mary, (2000).
[4] M.V. Romalis, "Laser Polarized ^{3}He Target Used for a Precision Measurement of the Neutron Spin Structure," Doctoral Thesis, Princeton University (1997).
[5] H. Middleton, "Cell Production," Doctoral Thesis, Princeton University, (1994).
[6] J.C. Brinker and G.W. Scherer, *Sol-Gel Science* (Academic Press, New York, 1990), 2-4.
[7] K. Mauritz, "Sol-Gel Chemistry", http://www.solgel.com/educational/educframe.htm
[8] C.J. Brinker, A.J. Hurd, and K.J. Ward in *Ultrastructure Procesing of Advanced Ceramics*, eds. J.D. Makenzie and D.R. Ulrich (Wiley, New York, 1988), p. 223
[9] C.J. Brinker et al. J. Non-Cryst. Solids **147&148** (1992) 424.
[10] S.Sakka, K. Kamiya, K. Makita and Y. Yamamoto, J. Non-Crystalline Solids **63** (1984) 223.
[11] I. Strawbridge and P.F. James, J. Non-Cryst. Solids **86** (1986) 381.
[12] P.M. Glaser and C.G. Pantano, J. Non-Cryst. Solids **63** (1984) 209.
[13] L.E. Schriven in *Better Ceramics Through Chemistry III* eds. C.J. Brinker, D.E. Clark, and D.R. Ulrich (Mat. Res. Soc., Pittsburg, Pa., 1988), pp. 717—729.
[14] I. Strawbridge and P.F. James, J. Non-Cryst. Solids **82** (1986) 366.
[15] L.C. Klein, T.A. Gallo and G.J Garvey, J. Non-Cryst. Solids, **63** (1984) 23.
[16] M.F. Hsu, "A Study of Sol-Gel Coated Cells for Spin-Exchange Optical Pumping", Senior Thesis, Princeton University, (1999).
[17] M. F. Hsu, G. D. Cates, I. Kominis, I. A. Aksay and D.M. Dabbs, Appl. Phys. Lett., **77**, No. 13 (2000).
[18] S. Sakka, K. Kamiya, K. Makity and Y.Yamamoto, J. Non-Crystalline Solids **63** (1984) 223.

Appendix A.

The best sol-gel solution and coating procedure, which was developed experimentally throughout the year, is given below. The best chemical composition is shown in Table 4. Either this exact mixture or a proportional mixture may be used.

TEOS (mL)	Water (mL)	Ethanol (mL)	HCl (mL)
23.4	29.7	43.0	0.9

Table 4. Final coating solution.

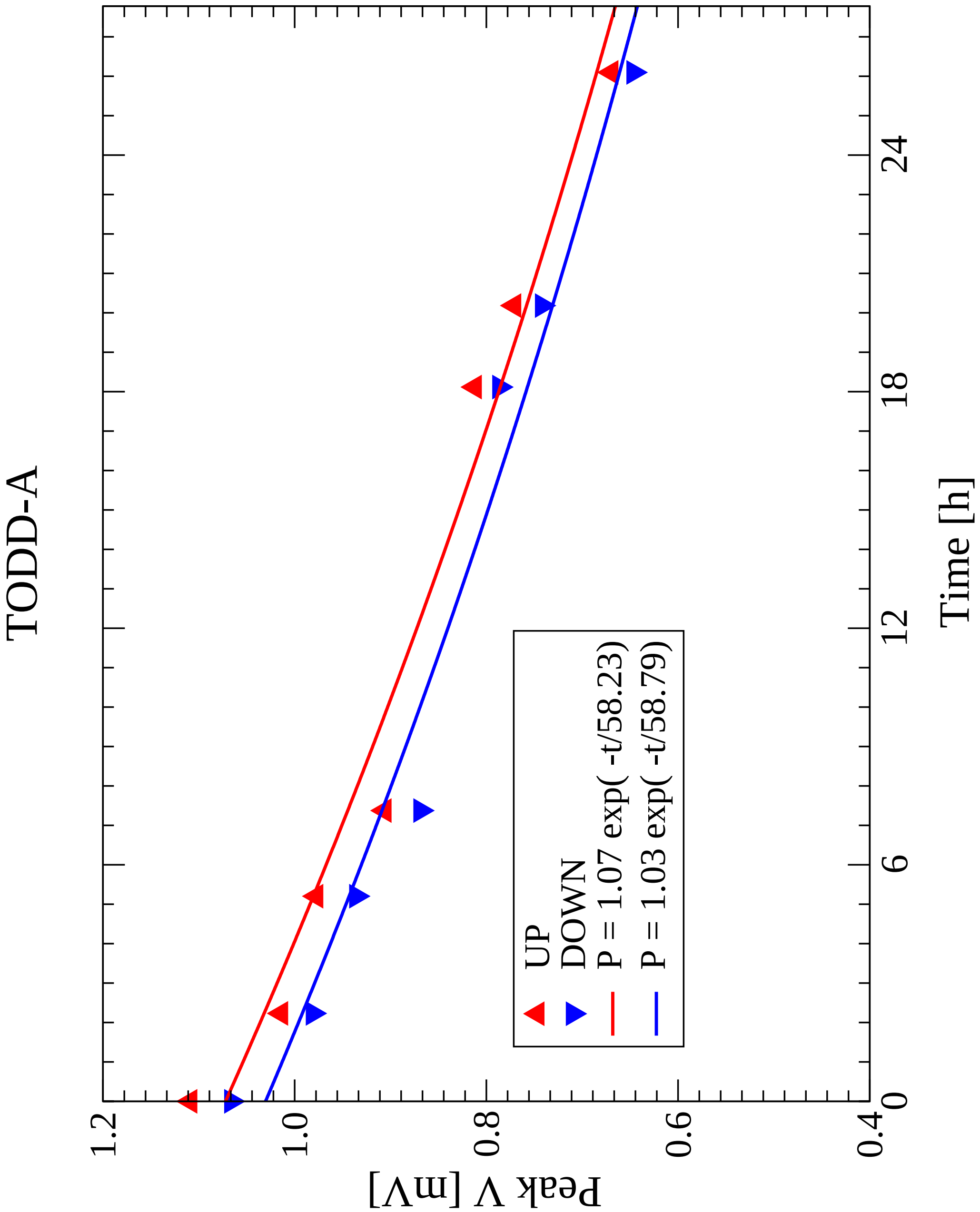
Each chemical is measured out carefully using a graduated plastic pipette into an Erlenmeyer flask. First the water is added followed by ethanol, TEOS and finally HCl. Immediately after the chemicals are mixed, the Erlenmeyer flask is covered with Parafilm to prevent evaporation. The mixture is allowed to mix at a medium speed for four days in the Erlenmeyer flask using a magnetic stirrer. It is best to mix it at a speed such that the solution does not excessively splash up onto the walls of the flask. It is important that the newest possible solution is always used since the older solutions tend to crack more during densification.

The slides are masked using ordinary clear masking tape as is shown in Figure 14. The tape is cut very carefully into strips that are 9mm wide by a razor. These strips are then carefully placed on the slide 7mm apart. The entire backsides of the slides are masked as well with a larger piece of tape. It is crucial that the tape be pressed down onto the slide to assure that sol-gel solution will not get underneath it during dipping. The masking is an important step since a poorly masked slide will not have sharp edges, which are necessary for the DekTak measurement.

Once the solution has mixed for four days it is then poured into a small beaker for dipping. The dipping mechanism consists of a motor mounted on a platform with a string attached to it. The string has a small piece of scotch tape attached to the end. The slide is attached to the string via the tape. It is then inserted by hand into the solution, the motor is then turned on and the slide is slowly withdrawn from the solution. After the slide has exited the solution it is immediately placed flat.

The slides are allowed to dry for a while in a clean environment. They are then put into an oven and baked up to the densification temperature, 500°C. The slides are placed on several blocks of insulation material so they will sit in the middle of the oven. The top block, upon which the slide rests, is covered with aluminum foil. It is also best to loosely cover the slides with aluminum foil while baking to keep them as clean as possible. The heating rate is critically important for producing crack-free films. The best heating rate is about 120 degrees per hour. At this rate it takes about 4 hours to get up to 500°C. This rate can either be programmed into a temperature controller or be done using a variable voltage supply. Either way, the voltage supply must be increased as the temperature increases. Once at full temperature, the slides must remain there for one hour. The oven is then turned off and they are allowed to cool inside the oven overnight. Once the slides have been densified their thicknesses are measured using the DekTak, which is described in Section 6.1.

Appendix B.


TODD-A
Peak V [mV]
1.2
1.0
0.8
0.6
0.4
Time [h]
0
6
12
18
24
UP
DOWN
P = 1.07 exp(-t/58.23)
P = 1.03 exp(-t/58.79)