PHOTOPATTERNING IN THIN FILM MULTILAYERS

by
Andrea Sieg

Honors College Thesis
Date submitted: April 19, 1999

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ABSTRACT

Title: PHOTOPATTERNING IN THIN FILM MULTILAYERS

Layer-by-layer assembly of multilayer thin films allows controlled growth of multiple layers in the direction perpendicular to the substrate. To control growth in the lateral direction, we are investigating patterning planar surfaces using UV lithography. Patterning is accomplished via UV-initiated phosphonation of an aryl iodide monolayer on a silicon wafer. Thorough analysis of this experiment using ellipsometry and X-ray photoelectron spectroscopy (XPS) provides insight into the photochemistry that takes place on the surface. The main conclusions presented in this Honors College thesis are the results of various control experiments. These include developing predictable monolayer growth, establishing bonds which are UV-stable, finding an optimal solvent for the photochemistry, and optimizing the time necessary for the photopatterning reaction.

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I. INTRODUCTION AND BACKGROUND

One of the greatest achievements of the human mind is the development of technology. Technology has built airplanes, launched people into outer space, designed computers, and created microwaves. Many of these applications are relatively large scale. However, the focus of the future is how to put as much information as possible into the smallest possible space. Various devices from cellular phones to calculators have decreased in size over the years as they have increased in performance capabilities. As technology continues to narrow its physical scope, its potential scope continually expands. Today, researchers are developing technology on a molecular scale. One expanding field in atomic scale research deals with structures built up of molecular layers. These types of layers are referred to as thin films.

Thin film chemistry is different from the concept of chemistry as mixing substances in test tubes to get a desired product. Test tube chemistry is generally done on a macroscopic scale, and the results are readily visible to the chemist. Thin film chemistry is microscopic. Molecular layers can be built up on the surface of a substrate, creating thin films. These films are so thin that they are invisible to the naked eye, and even to the average microscope.

There are many practical applications for thin films. They can be used in reverse phase chromatography, as chemical resists, and chemical sensors.[1,2] Since the chemist has control over the way these films are built up, any number of desired properties can be incorporated into these films.

The thin films of interest in this Honors College thesis are termed Self Assembled Multilayers (SAMs) and have been a topic of interest to many researchers in the past few

years.[3,4,5,6,7,8,9,10] SAMs are thin films that are constructed in a controlled manner by sequentially depositing molecular monolayers onto the surface of a substrate. Just as bonds are made and broken in solution to form molecules in synthetic reactions, these reactions will also take place on the surface of a substrate. A substrate that has specific properties allows a suitable molecule to bind to its surface. This project focuses on silicon wafer substrates that have a native silicon dioxide (SiO_2) layer on their surfaces, or glass slides that are composed of SiO_2. The electron density surrounding the oxygen allows a metal ion, namely hafnium, to covalently bind to the substrate's surface, forming a monolayer. Binding hafnium to the surface of a substrate is one way of functionalizing that substrate. This functionalization is depicted in Figure 1:

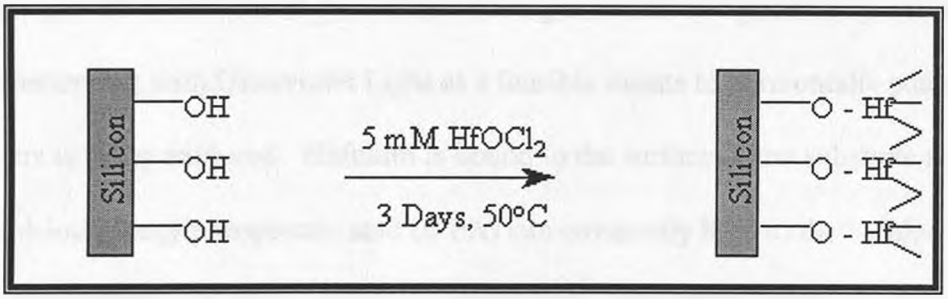


Figure 1. Functionalizing a Silicon Substrate

The surface of the film is now terminated with hafnium. Hafnium has a strong affinity for molecules with a great electron density, making it possible to bind another molecule with a phosphonic acid group. This molecule is decylbisphosphonic acid (DBPA). Repeating this procedure leads to multilayers of molecules on the surface of the original substrate. Figure 2 depicts the scheme to build these multilayers:

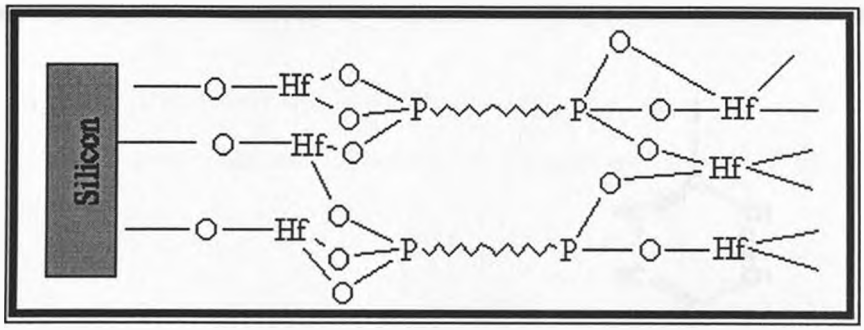


Figure 2. Multilayers with Hafnium and Decylbisphosphonic Acid

This process is termed self-assembly, and one or more multilayers can be referred to as a thin film.

Self-assembly has been well characterized for the growth of Hafnium-DBPA thin films.[8,9] In Dr. Catherine Page's laboratory at the University of Oregon, controlling multilayer growth in the lateral dimension is being researched. Specifically, investigation of photopatterning with Ultraviolet Light as a feasible means to horizontally pattern multilayers is being explored. Hafnium is bound to the surface of the substrate as before, and now 4-iodophenylphosphonic acid (IPPA) can covalently bind to the hafnium through the phosphonate group creating a monolayer. The surface of the monolayer will now consist of carbon-iodine bonds. This monolayer scheme is shown in Figure 3:

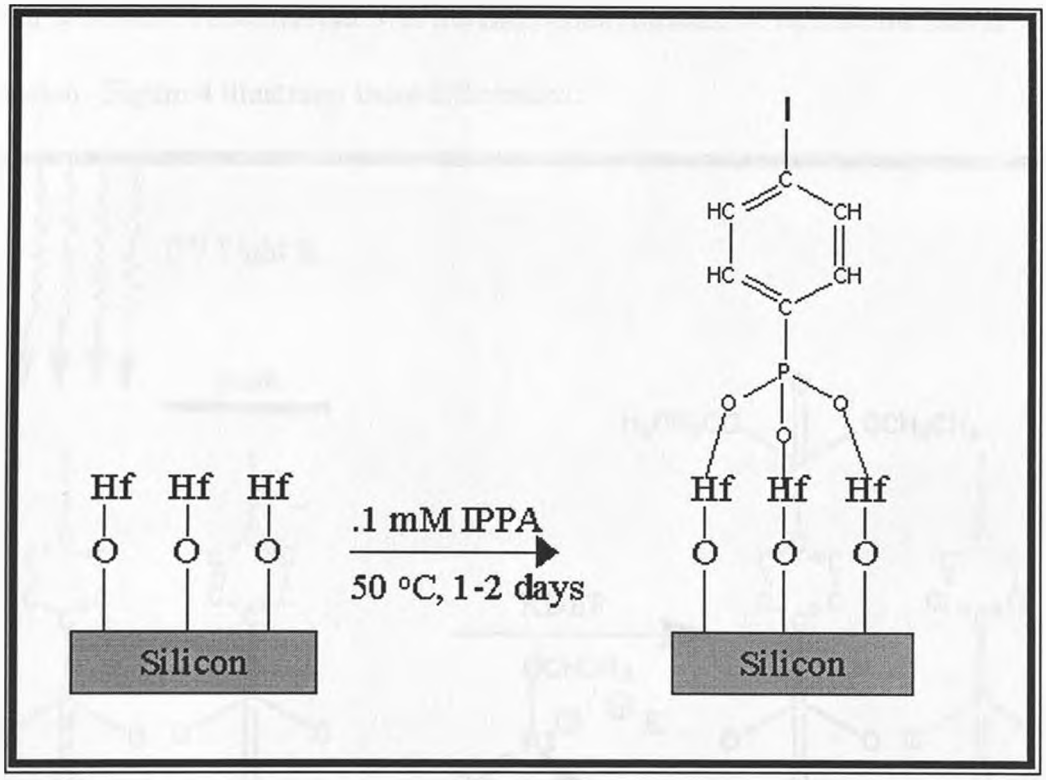


Figure 3. Creating a Monolayer with IPPA

The thin film's surface now has a unique property. The C-I bond at the surface is susceptible to cleavage at a wavelength of 280 nanometers (or smaller).[11] If the substrate is exposed to UV light, the C-I bond will theoretically dissociate.[12,13] This exposure is done under a solution containing another molecule that can form a UV-stable bond where the C-I bond was broken. In this way, the surface of the film can be chemically altered by UV light.

The term used to describe this technique is photolysis. A mask can be used to cover part of the surface so photolysis will only occur on a desired portion of the film's surface. This will result in different properties of the surface of the film in a lateral dimension. In Dr. Page's laboratory, much work has been done to control the perpendicular growth of a film to the substrate. With photopatterning chemistry, the

amount of control a chemist has over the film would increase to include the lateral dimension. Figure 4 illustrates these differences:

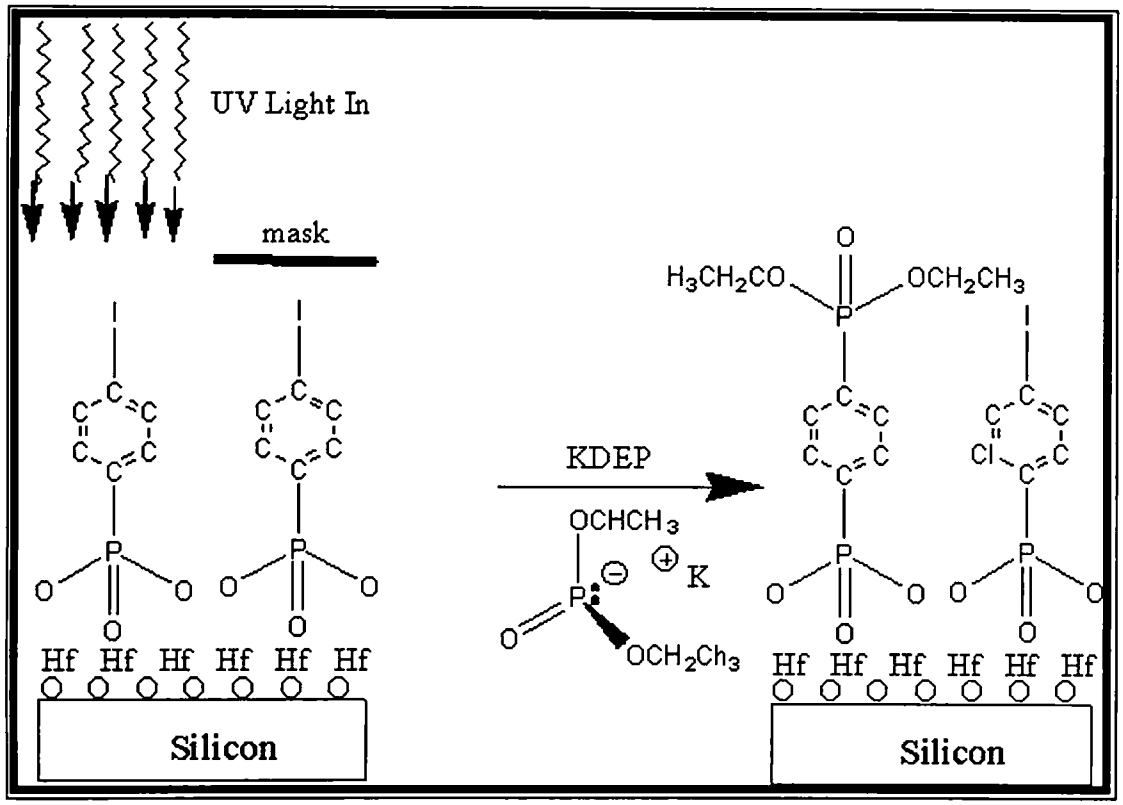


Figure 4. Photolysis Scheme; Final Product has Two Different Functionalities

The film surface of the monolayer could be altered in such a way that a "chemical" design would be produced on the surface. The top view of one simple example is given by Figure 5:

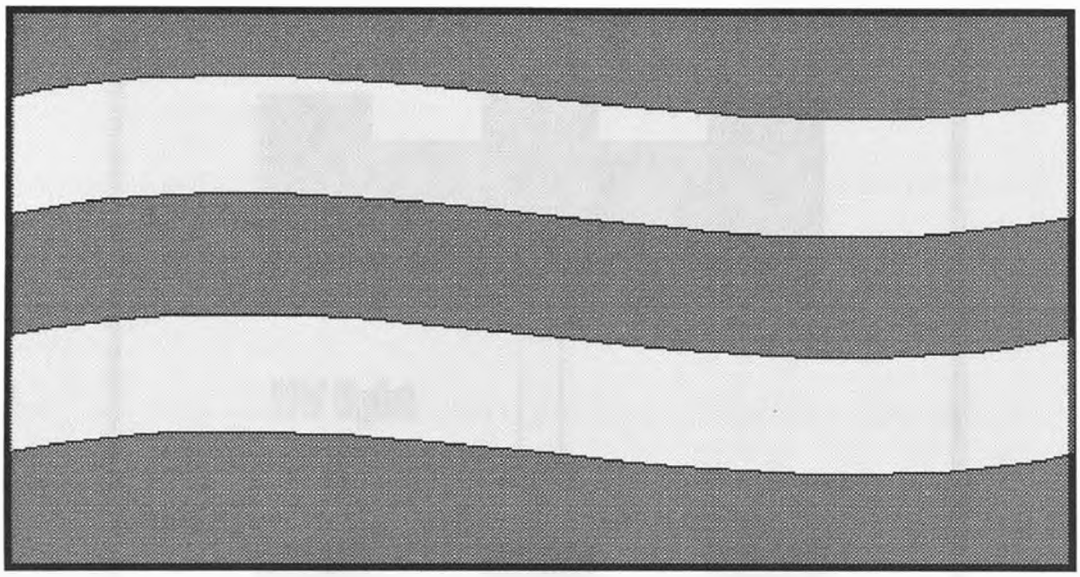


Figure 5. Top View of a Potential Pattern on the Surface of a SAM

In this example, the portion of the surface that was not exposed to UV light is denoted by the silver color. The yellow denotes the portion of the surface that was exposed to UV light. The different colors represent the different surface properties of the film. Figure 6 denotes the entire process from a side view perspective:

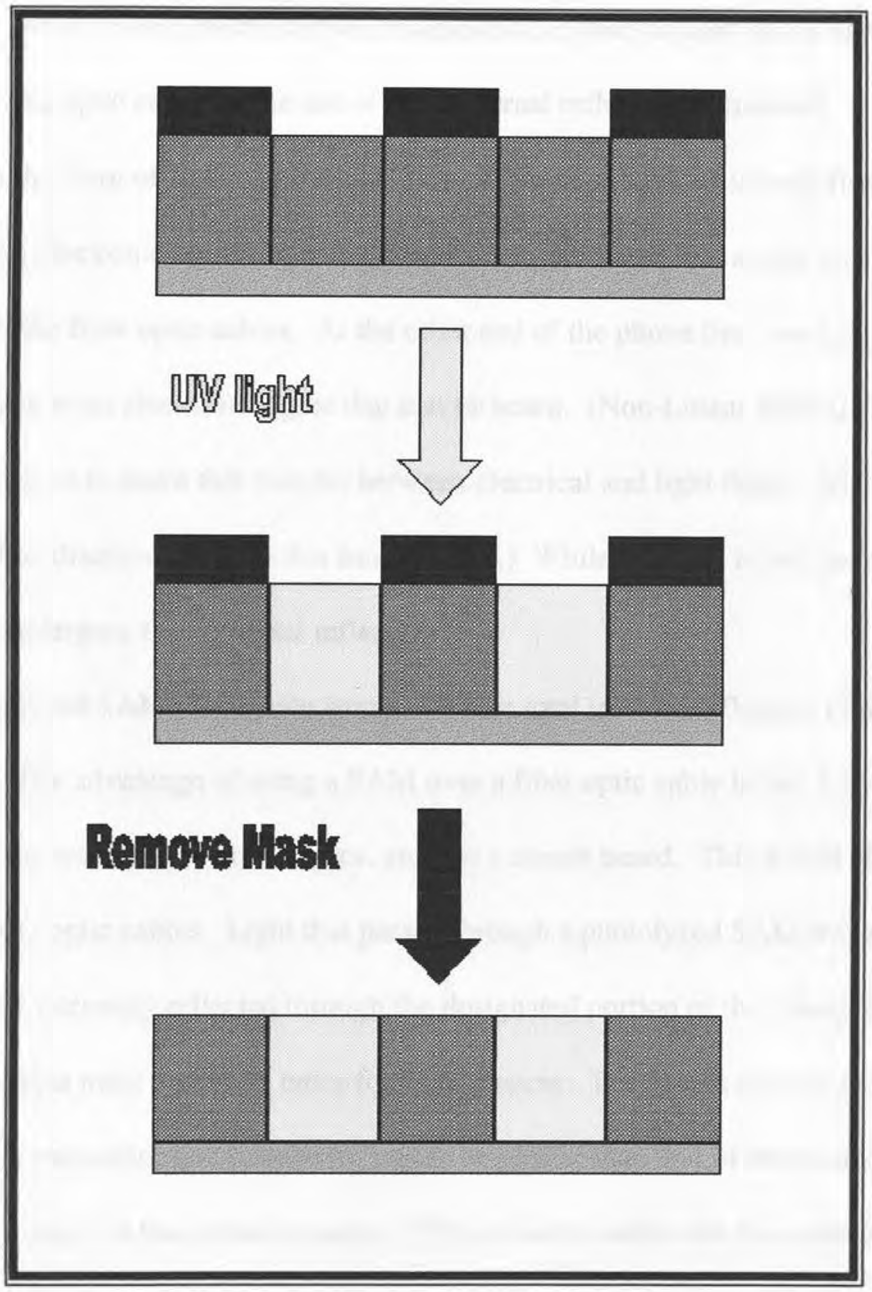


Figure 6. Side View of Photolysis Process on a SAM

In this figure, the black rectangles represent a mask that can be manually placed on and removed from the SAM. The blue boxes are the original thin film, which is altered when exposed to UV light. Notice that only the portions of the SAM that were not blocked by the mask were altered. The turquoise rectangle represents the silicon wafer or glass slide.

SAMs could be used to transfer information in the form of light much like a fiber optic cable. Fiber optic cables make use of total internal reflection to transmit information in the form of light. One application of fiber optic cables is long distance phone calls. An electronic signal from the telephone is translated into a light signal that travels through the fiber optic cables. At the other end of the phone line, the light signal is translated back to an electronic signal that can be heard. (Non-Linear Optical (NLO) multilayers are used to make this transfer between electrical and light fields. NLO properties will be discussed later in this Introduction.) While the light is within the fiber optic cable, it undergoes total internal reflection.

A photolyzed SAM waveguide would also use total internal reflection (TIR) to transmit light. The advantage of using a SAM over a fiber optic cable is that SAMs could be used to put the waveguides on a surface, such as a circuit board. This would eliminate the need for fiber optic cables. Light that passes through a photolyzed SAM waveguide would be totally internally reflected through the designated portion of the waveguide.

Two criteria must be met in order for TIR to occur. The first is that the index of refraction of the transmitting substance (n_1) must be greater than that of the second substance, n_2 ($n_1 > n_2$). If this criterion is met, TIR can occur within the first substance. The second criterion, however, is that light must hit the interface between substances one and two at or greater than some critical angle, θ_c. The θ_c is specific to the two adjoining substances. It is determined by a derivative of Snell's Law, Equation 1:[14]

$$\text{Sin } \theta_c = n_2/n_1 \qquad [1]$$

Total internal reflection is illustrated by Figure 7:

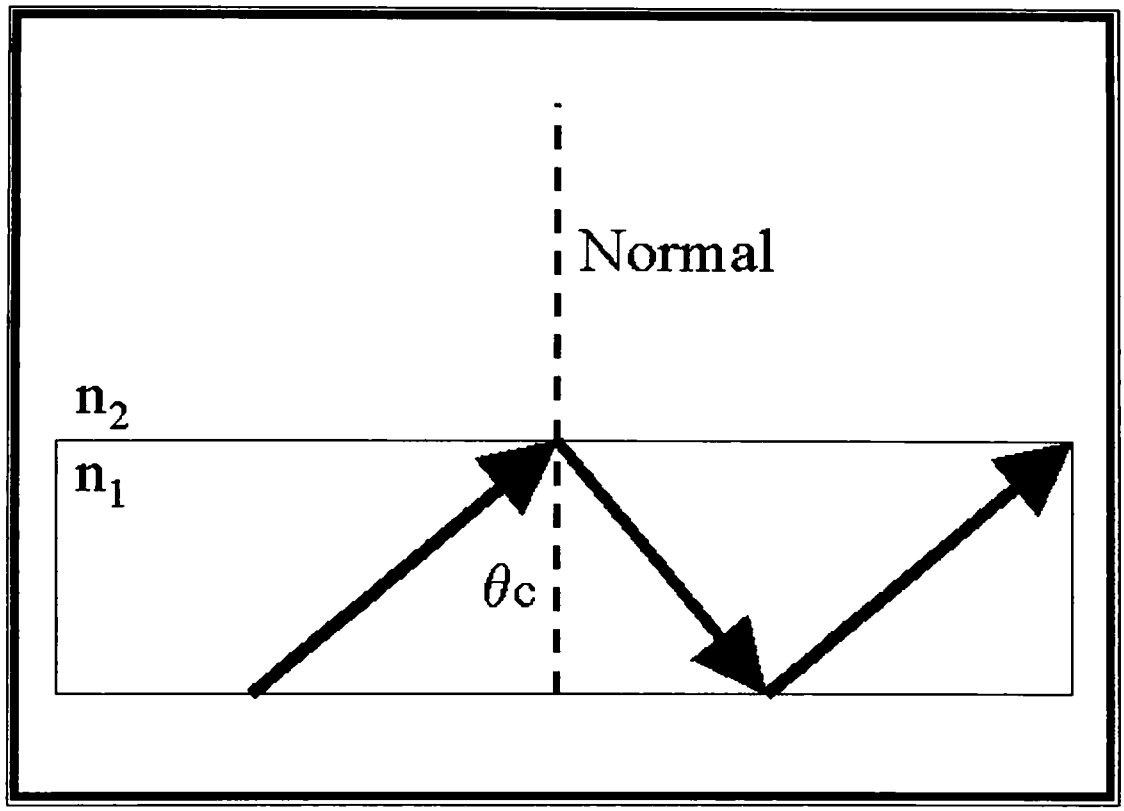


Figure 7. Total Internal Reflection

The two adjoining substances in Figure 7 are the yellow rectangle and the white background, which could be air. Since the index of refraction of substance one is greater than that of substance two ($n_1 > n_2$) when light hits the interface at the critical angle, θ_c, it will be totally internally reflected as was shown in Figure 7.

Figure 8 illustrates how a photolyzed SAM can act like a waveguide using TIR:

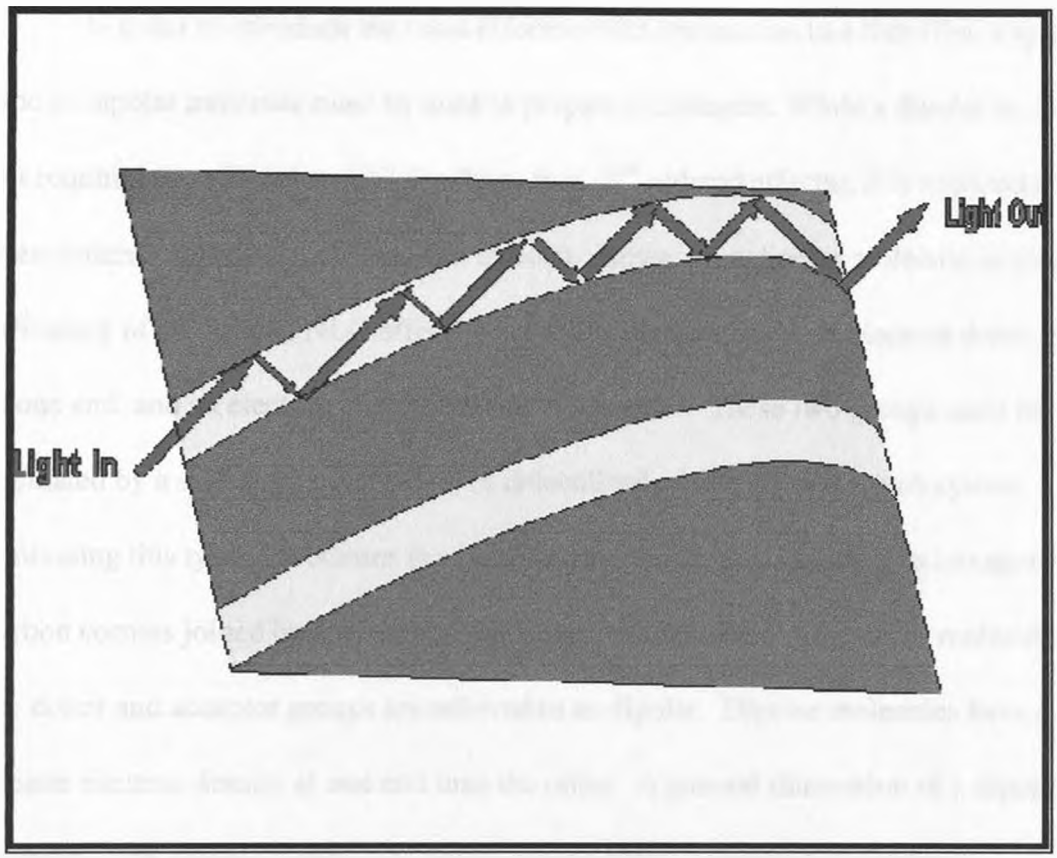


Figure 8. A Potential Waveguide: Total Internal Reflection of Light in a SAM

The red arrows represent light, and the rest of the diagram is like Figure 5. Care must be taken to ensure that the index of refraction of the yellow substance is greater than the blue, and that light hits the yellow-blue interface at or above the critical angle, θ_c.

Waveguides can be used to direct light in various optically controlled devices. One major interest for waveguide technology would be to direct light in all-optical computers.[15] SAMs can also be used for optical switches, another major requirement in all optical computers. In order for a SAM to be used as an optical switch, specific molecules must be incorporated into the SAM. These molecules must have Non-Linear Optical (NLO) properties.

In order to introduce the most effective NLO properties to a thin film, a specific type of dipolar molecule must be used to prepare multilayers. While a dipolar molecule is not required for odd-ordered NLO effects (e.g., 3rd ordered effects), it is required for even-ordered effects (e.g. 2nd ordered effects). However, a dipolar molecule increases the efficiency of all ordered NLO effects. This molecule must have an electron donor group at one end, and an electron acceptor group at the other. These two groups must be separated by a system of polarizable, or delocalized, electrons. One such system containing this type of electrons is a benzene ring that is represented by a hexagon with carbon corners joined by alternating single and double bonds. In general, molecules with the donor and acceptor groups are referred to as dipolar. Dipolar molecules have a greater electron density at one end than the other. A general illustration of a dipolar molecule that would be sufficient for NLO properties is depicted in Figure 9:

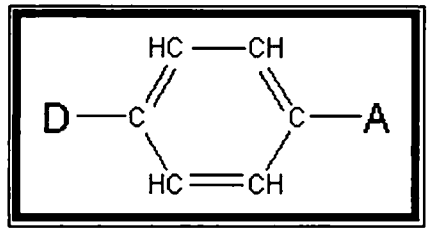


Figure 9. Dipole Schematic

"D" stands for the electron donor end of the molecule, and "A" for the acceptor end. The polarizable electron system includes the benzene ring. The arrow points in the direction of the greatest electron density. When a strong optical field, such as a laser, is applied, however, a higher order oscillation occurs. The donor and acceptor groups dominate this intense oscillation, and the electron density at the acceptor end will increase. This causes

a stronger dipole in the molecule, and actually changes some properties of that molecule. One property that is changed is the molecule's index of refraction.

An example of an NLO molecule is para-amino-phosphonic acid (APPA) which is under current investigation in the Page Lab. APPA is shown in Figure 10:

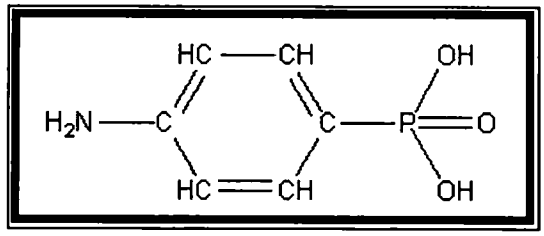


Figure 10. Aminophenylphosphonic Acid

APPA can be covalently bound to a hafnium-functionalized SAM in the same manner as IPPA through the phosphonic acid functional group. Thus the APPA molecules will all bind in the same direction on the surface. This molecule is dipolar because the phosphonic acid group is an electron acceptor and the amine is an electron donor. The dipole increases because electron s can be polarized more towards the phosphonic acid group than the amine when interacting with a strong oscillating electric field, such as light. It also is separated by a polarizable benzene ring. This combination leads to potential NLO properties in APPA.

When all the APPA molecules bind in one direction on the film, all the dipoles will line up in the same direction. This is important so the adjoining dipoles do not cancel each other out. When a low intensity light beam shines through the material the light will pass through at a certain angle, according to the index of refraction. (Note that the information light is the low intensity light. The intensity must be low so that the light alone does not change the index of refraction.) Then when a laser is passed through the

NLO film at the same time as the low intensity light, all the dipoles will strengthen in the same direction, and the bulk film will experience a change in index of refraction. The low intensity light will pass through the NLO material at a different angle. This is further illustrated by Figure 11 in the form of an optical switch:

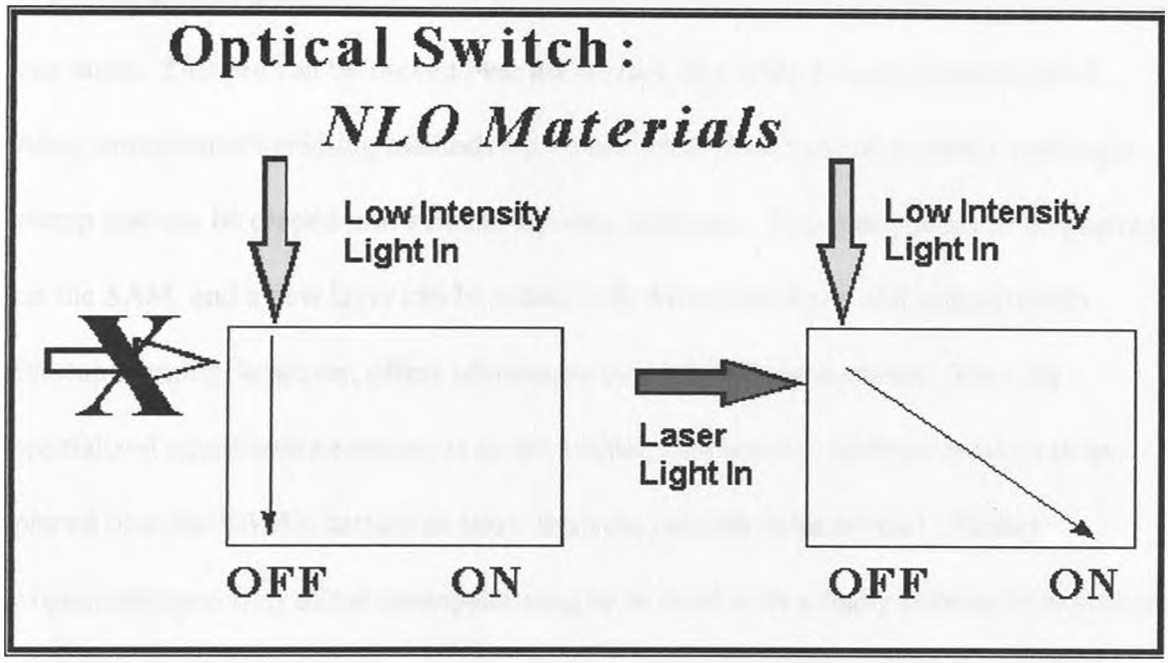


Figure 11. Optical Switch Using NLO Materials

Notice that on the left, only low intensity light enters the material. The light then travels through the material to a position that can be considered "off." On the right, an additional laser bean enters the material. The NLO molecules will then oscillate to create a stronger dipole, and the index of refraction changes. Thus, the low intensity light travels out of the material to a position that can be considered "on." This could potentially form the basis of optical signaling in all-optical computers.[15] While electronic computers use 0 and 1 bytes to process all their information, optical computers could use on and off as their binary code. NLO materials are also used to translate

binary code. NLO materials are also used to translate between optical and electronic signals as was mentioned in the discussion about fiber optics cables.

Photopatterning is not the only method to pattern SAMs.[16] One alternate method is electron beam lithography, where a fine beam of electrons etches the surface. Another is scanning probe lithography. This involves a very sharp pin whose tip is on the order of one atom. This pin can be moved over the surface of a SAM to trace patterns into it. Also, microcontact-printing methods have been used. This method involves creating a stamp that can be dipped into suitable layering solutions. This wet stamp can be pressed on the SAM, and a new layer can be added only where the stamp and surface touch. Photopatterning, however, offers advantages over all of these methods. The only specialized equipment necessary is an ultraviolet light source. Intricate masks can be placed over the SAM's surface to allow intricate patterns to be created. Further experimentation may allow photopatterning to be done with a finely pointed laser source. Both UV light sources and laser sources are more accessible and less expensive than electron beam and scanning probe lithography equipment. Photopatterning should prove to be a very precise method of patterning, and this is an advantage over the microcontact stamping method. The solution can easily soak around the edges of the stamp, leading to an ill-defined edge between the stamped area and the non-stamped area. Thus, photopatterning has many potential advantages over these other patterning methods.

The overall goal of this Honors College Thesis project is to begin developing the chemistry that will make photopatterning possible. The procedure follows the illustration in Figure 4, and will be discussed in the Experimental section. It is important to recognize that this chemistry is not yet completely characterized. Developing a procedure

that produces the desired results, and makes efficient use of time and materials is a long, tedious process. Therefore, the bulk of this thesis is devoted to the experimental procedures used, and the analysis of the results obtained. Despite the slow pace of research, however, this project has been continually motivated by the endless possibilities pending its success.

II. EXPERIMENTAL

Functionalizing Silicon Wafers

Polished (100) silicon wafers were purchased from Silicon Quest International, and were cleaned in the laboratory. All solvents were purchased from the Aldrich Chemical Company unless otherwise specified. Cleansing involved soaking the wafer for twenty minutes each in two solvents: first trichloroethylene, then 2-propanol. The wafer was then rinsed with ultrapure water. A Barnstead Nanopure II deionizes this water to a resistivity of 17-19 MΩ-cm. The wafer is dried with flowing Nitrogen gas, cut with a diamond tip pen and labeled. It is then analyzed using Ellipsometry for the thickness of its native oxide layer (See Analysis Techniques on page 28).

A 5 milli-molar (mM) solution of hafnium oxychloride octahydrate ($HfOCl_2 \bullet 8H_2O$) in ultrapure water was made. $HfOCl_2$ was donated by Teledyne Wah Chang Company in Albany and used as received. Wafers are soaked in this solution in a heating oven at a constant temperature of 50°C. After three days, they are removed from the solution, rinsed with ultrapure water for 15-20 minutes and dried with flowing N_2 gas. The Silicon wafers are then analyzed to assess the growth of a hafnium layer on the surface using Ellipsometry. Wafers that have a monolayer of hafnium are called functionalized wafers.

Functionalizing Glass Slides

GlassMicro Slides were purchased from Corning Glass Works. Cleansing was performed in the following manner: 20-minute soak in trichloroethylene, 20-minute soak in 2-propanol, 20-minute rinse with ultrapure water. The slides were then soaked in a

solution of 70% sulfuric acid and 30% hydrogen peroxide for approximately 2-3 hours. This was followed by another 20-minute rinse in ultrapure water.

Glass is functionalized in the same manner as silicon wafers. However, some glass slides were functionalized with zirconium rather than hafnium. (These two metals are tetravalent ions and can be interchanged with no effects on film growth.) The zirconium solution consisted of an aqueous 5 mM of zirconium oxychloride octahydrate ($ZrOCl_2 \bullet 8H_2O$) which was also donated by Teledyne Wah Chang Company. After the glass slide is functionalized, it cannot be easily analyzed using Ellipsometry because glass is transparent.

Binding the Experimental Molecule

After the functionalization process, the substrate is ready to bind molecular layers. This process consists of binding specific molecules or ions one by one to the surface of the substrate until a repeating unit is established. The repeating unit is referred to as one layer, and sequential growth of more than one layer produces a multilayer. In order to limit the experimental variables, however, only one layer is bound to study the photolysis chemistry.

Photolysis is possible only after binding an ultraviolet-light-sensitive molecule to the surface of the substrate (See Photolysis on page 26). The molecule chosen was 4-iodophenylphosphonic acid (IPPA) Figure 12:

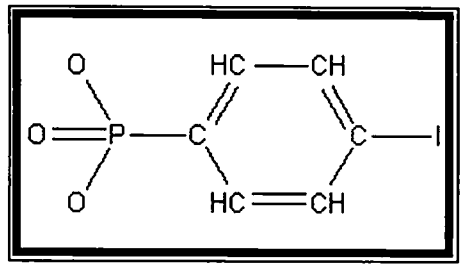


Figure 12. 4-Iodophenylphosphonic Acid

This molecule was chosen for two reasons. It has a phosphonic acid terminus that will bind to hafnium or zirconium, and the carbon-iodine (C-I) bond on the other end is known to dissociate under UV light at wavelength approximately 280 nanometers.[11] (Note that since this is a relatively simple molecule it is assumed that the C-I bond is the only weak link.) Thus, in the presence of this wavelength of light, the C-I bond will dissociate, leaving the possibility of binding a different molecule to the terminus of the molecule.[12,13]

The synthesis of IPPA was done with the help of Elizabeth Hommel using a procedure that was adapted from a preparation of 4-bromoaniline by Grummit, et.al.[17] This synthesis is depicted in Figure 13:

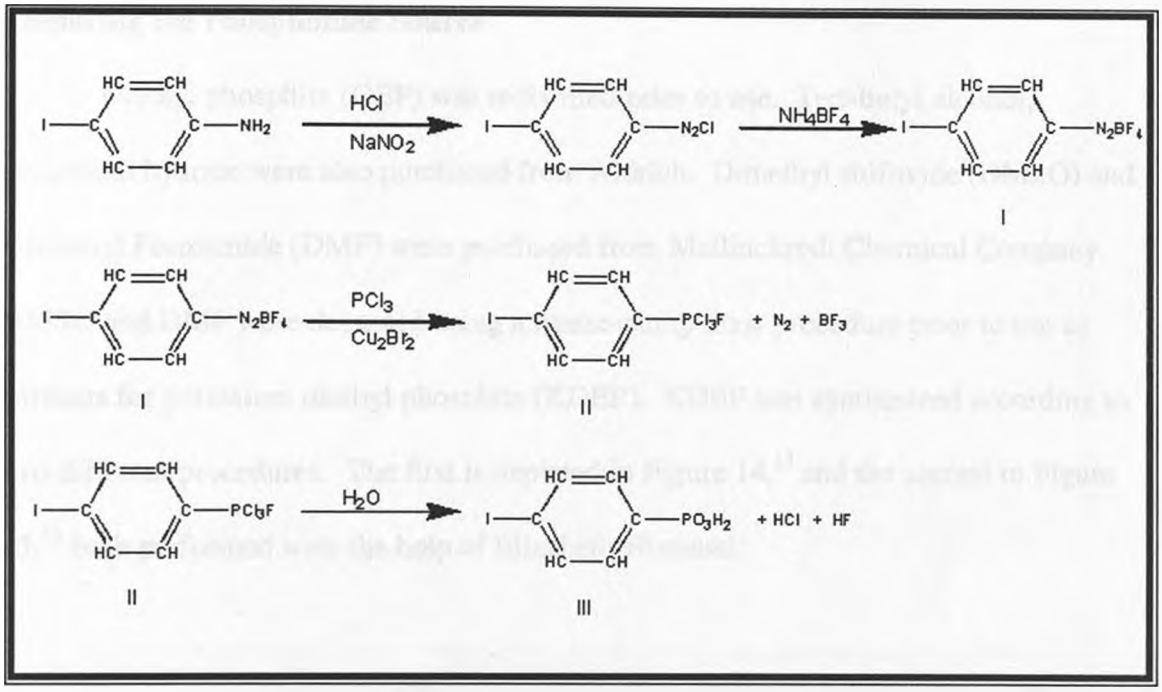


Figure 13. Synthesis of 4-Iodophenylphosphonic Acid

The layering process for IPPA is similar to the functionalization process. A functionalized wafer or glass slide is soaked in a 1 mM solution of IPPA in 50% 200 proof ethanol and 50% water for one to two days at 50 °C (See Figure 2).

After soaking, the substrate is removed from the IPPA solution, rinsed for five minutes with flowing 200 proof ethanol and fifteen minutes with ultrapure water, then dried with nitrogen gas. Silicon wafer substrates are analyzed using Ellipsometry to determine the film thickness of the IPPA layer. A small piece of either the silicon wafers or the glass slides are analyzed at this point using X-ray Photoelectron Spectroscopy (XPS) to establish that the expected elements are present. (See Analysis Techniques on page 28.)

Preparing the Phosphonate Source

Diethyl phosphite (DEP) was redistilled prior to use. Tert-butyl alcohol, potassium hydride were also purchased from Aldrich. Dimethyl sulfoxide (DMSO) and Dimethyl Formamide (DMF) were purchased from Mallinckrodt Chemical Company. DMSO and DMF were degassed using a freeze-pump thaw procedure prior to use as solvents for potassium diethyl phosphite (KDEP). KDEP was synthesized according to two different procedures. The first is depicted in Figure 14,[11] and the second in Figure 15,[13] both performed with the help of Elizabeth Hommel:

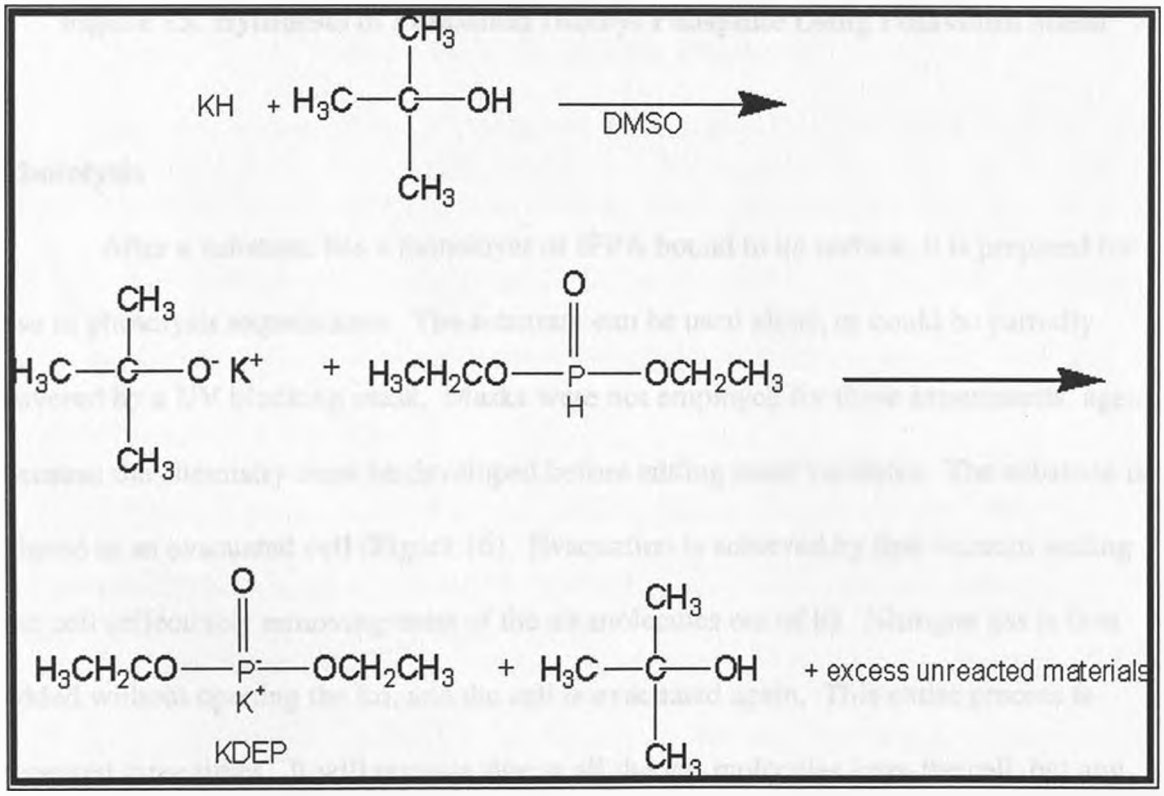


Figure 14. Synthesis of Potassium Diethyl Phosphite Using Potassium Hydride

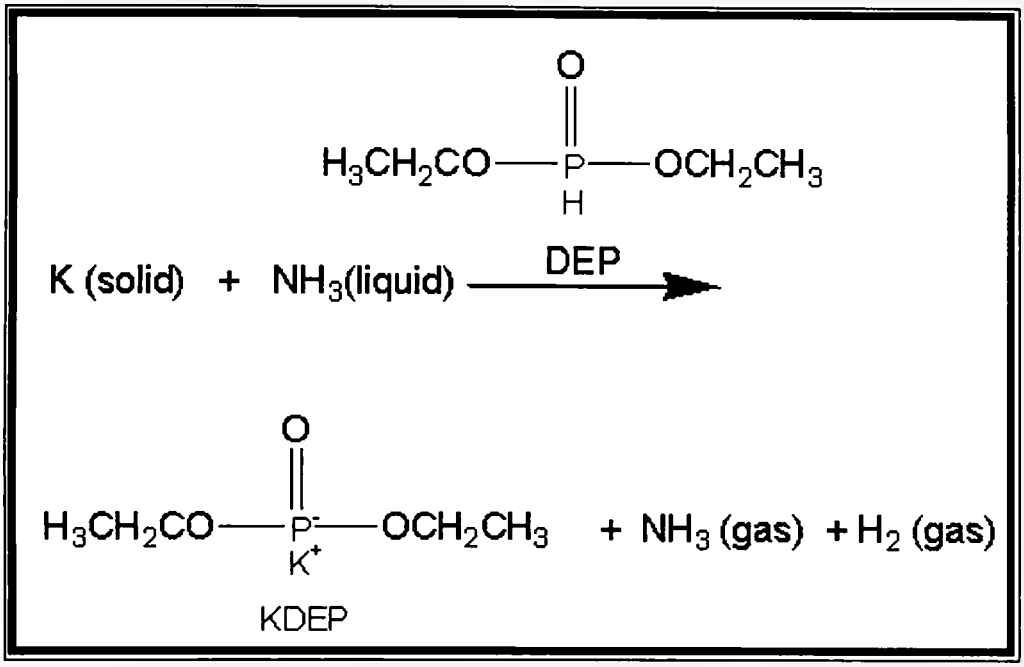


Figure 15. Synthesis of Potassium Diethyl Phosphite Using Potassium Metal

Photolysis

After a substrate has a monolayer of IPPA bound to its surface, it is prepared for use in photolysis experiments. The substrate can be used alone, or could be partially covered by a UV blocking mask. Masks were not employed for these experiments, again because the chemistry must be developed before adding more variables. The substrate is placed in an evacuated cell (Figure 16). Evacuation is achieved by first vacuum sealing the cell (effectively removing most of the air molecules out of it). Nitrogen gas is then added without opening the lid, and the cell is evacuated again. This entire process is repeated three times. It will remove almost all the gas molecules from the cell, but any that remain should only be nitrogen gas. This is done in order to remove as much oxygen from the cell as possible since photolysis in the presence of oxygen would remove the entire monolayer. The cell used for photolysis is shown in Figure 16:

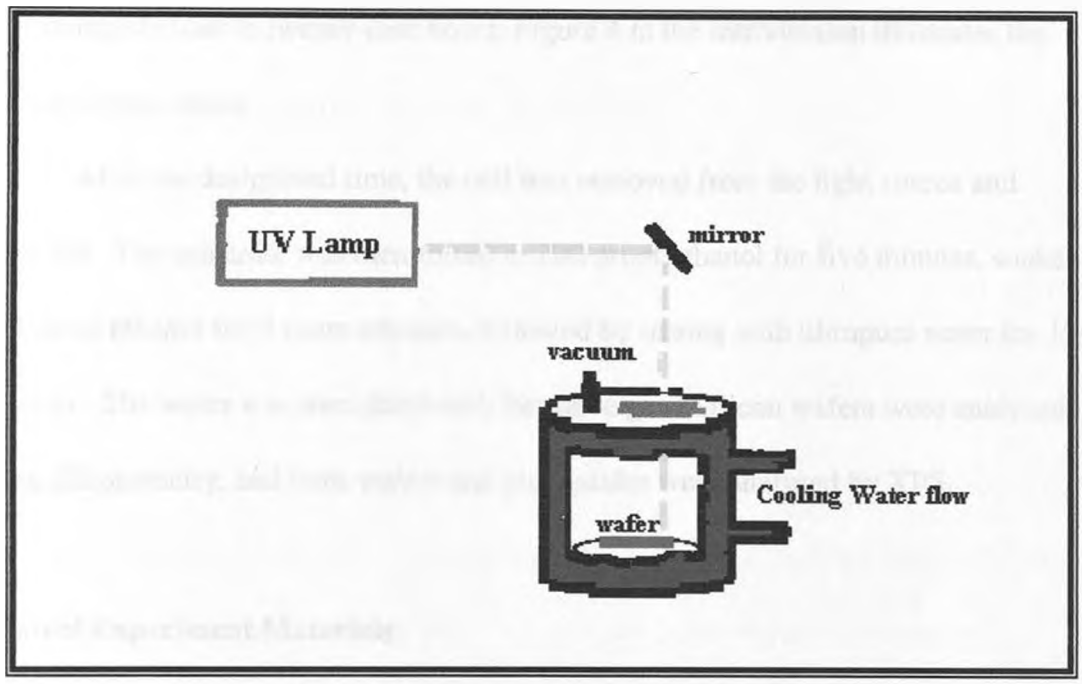


Figure 16. Cell Used for Photolysis[11]

Several solutions of potassium diethyl phosphite (KDEP) in DMSO or DMF were prepared as specified in Section D. The concentrations ranged from 500 to 50 mM. The desired solution for each experiment was placed under nitrogen gas (N_2) and transferred via syringe to the evacuated cell. Approximately 8-10 milliliters of solution was required to cover the substrate completely.

The cell was then attached to a circulating water bath, and placed in direct exposure to ultraviolet light. A silver coated mirror provided by the University of Oregon's Shared Laser Facility was used to reflect the UV light onto the substrate. The UV light source used was a Model 6136, Serial 207, 200 watt Mercury Arc Lamp purchased from the Oriel Corporation. The light passed through a 3 inch deionized water filter prior to hitting the substrate. The substrate was exposed to UV light for

approximately four to twenty-four hours. Figure 4 in the Introduction illustrates the photolysis procedure.

After the designated time, the cell was removed from the light source and unsealed. The substrate was then rinsed in 200 proof ethanol for five minutes, soaked in 200 proof ethanol for 5 more minutes, followed by rinsing with ultrapure water for 15-20 minutes. The wafer was then dried with Nitrogen gas. Silicon wafers were analyzed using Ellipsometry, and both wafers and glass slides were analyzed by XPS.

Control Experiment Materials

Bromodecylphosphonic acid (BDPA) was synthesized in the Page laboratory. A 5 mM solution of BDPA in 200 proof ethanol was prepared. Functionalized silicon wafers that were layered with BDPA soaked in the 5 mM solution for four hours in an oven that was at 61°C. Since this was a control experiment, this temperature was used to ensure that the molecule would bind. It does not reflect optimization efforts.

Acetonitrile (CH_3CN) was purchased from the Aldrich Chemical company, and also de-gassed by the freeze-pump thaw procedure. This is also an aprotic, polar solvent that had the potential for use as a solvent for KDEP. Hoz and Bunnett (1977)[12] reported using this solvent for KDEP, and so it was assumed to be suitable. Solubility tests proved, however, that this KDEP was not soluble in acetonitrile. (Dr. Catherine Page has suggested that perhaps the literature source was using acetonitrile that had excess water in it, which would aid the solvation process.)

A 0.2 mM solution Phenylphosphonic acid (PPA) was prepared in 200 proof ethanol. A 0.1 mM solution of PPA was prepared using 50% of the 0.2 mM solution in ethanol,

and 50% ultrapure water. In order to deposit a monolayer of PPA, the substrate was soaked in the 0.1mM solution for 24-48 hours at 50°C.

Analysis Techniques

Ellipsometry and X-ray Photoelectron Spectroscopy (XPS) techniques were used in order to determine film thickness, uniformity, and composition. The purpose of this section is to give a brief overview of each technique. Two different Ellipsometers were used during the course of these experiments. The first was a Rudolph Research Thin Film Ellipsometer, Type 43702-200E. The data collected was analyzed using the DAFIBM program the Rudolph company provided to obtain thickness. The second Ellipsometer used was a J.A. Woollam Company, Inc. M-44™ Ellipsometer. The XPS used was a Kratos Analytical Axis HSI spectrometer.

An arc lamp source emits elliptically polarized light within the Ellipsometer.[18] This light is aimed onto a wafer. The light then travels through the film, reflects off the substrate, and exits the film. Since the film has a different index of refraction than air, the light's polarization changes. These changes can be measured to give average film thickness. Ellipsometry does not, however, give information regarding surface composition of the film. Figure 17 illustrates Ellipsometery:

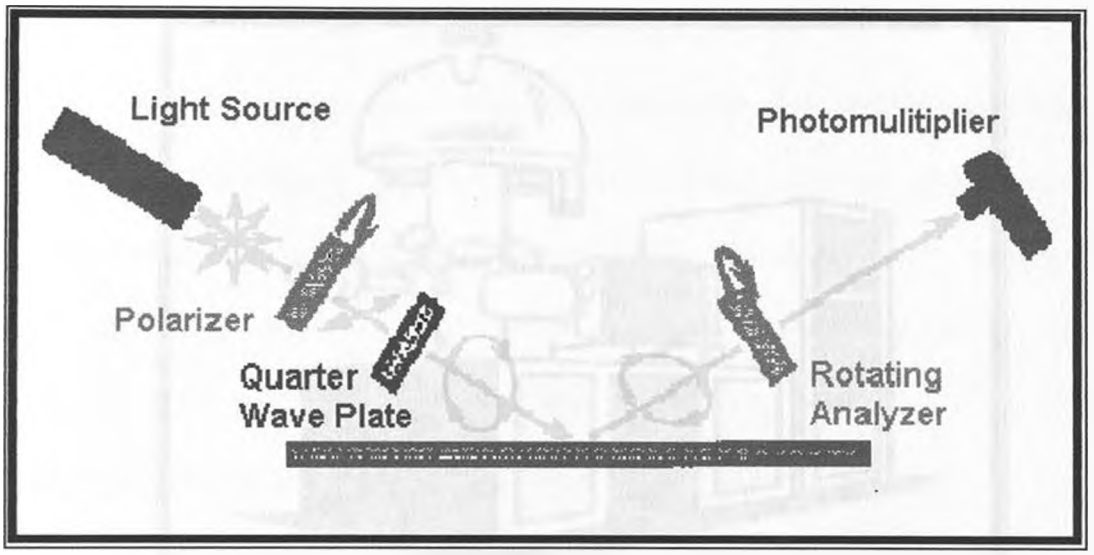


Figure 17. Ellipsometery

X-ray Photoelectron Spectroscopy provides highly accurate composition data as deep as 50 Angstroms (1 Angstrom is 10^{-10} meters). High energy X-rays bombard the surface of the film and interact with molecules on the surface. Some of the electrons in these molecules are ejected from their parent atoms with a specific velocity particular to specific elements. This velocity is measured, and manipulated through a series of functions to positively identify and quantify different elements present in the film.[19] Figure 18 illustrates the XPS used:

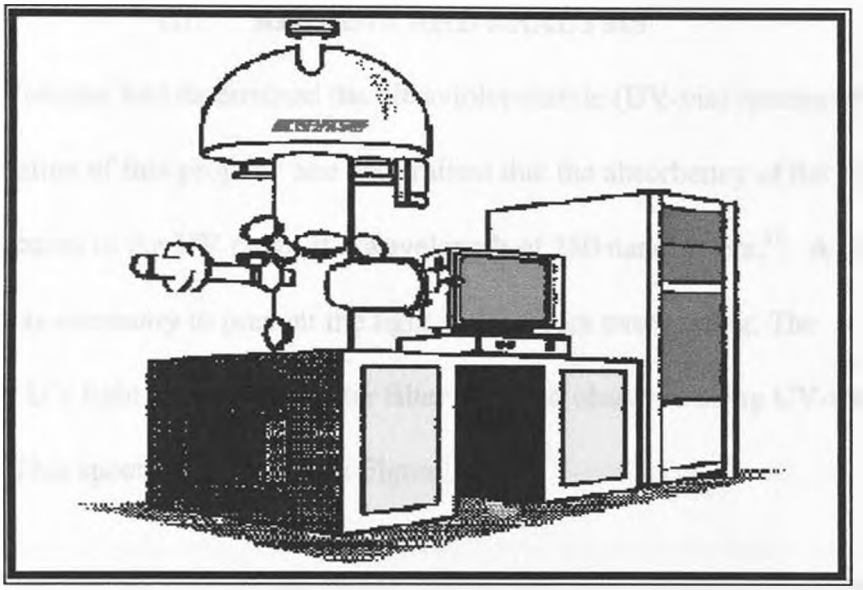


Figure 18. X-ray Photoelectron Spectrometer

XPS is essential to this experiment. Before and after photolysis, XPS is used to analyze the surface composition of the silicon wafer or glass slide. Before photolysis the hafnium: phosphorus: iodine ratio should be approximately 1:1:1 (See Figure 2.8). After photolysis the iodine should be replaced by DEP, but nothing else should be altered on the surface. This would give an XPS ratio of approximately Hf:P:I of 1:2:0. Comparing the data from before and after photolysis helps to determine the efficiency of the experiment.

III. RESULTS AND ANALYSIS

Elizabeth Hommel had determined the ultraviolet-visible (UV-vis) spectra of IPPA prior to the timeline of this project. She determined that the absorbency of the carbon-iodine bond occured in the UV range at a wavelength of 280 nanometers.[11] A water column filter was necessary to prevent the light source from overheating. The transmission of UV light through the water filter was also observed using UV-vis spectroscopy. This spectrum is shown in Figure 19:

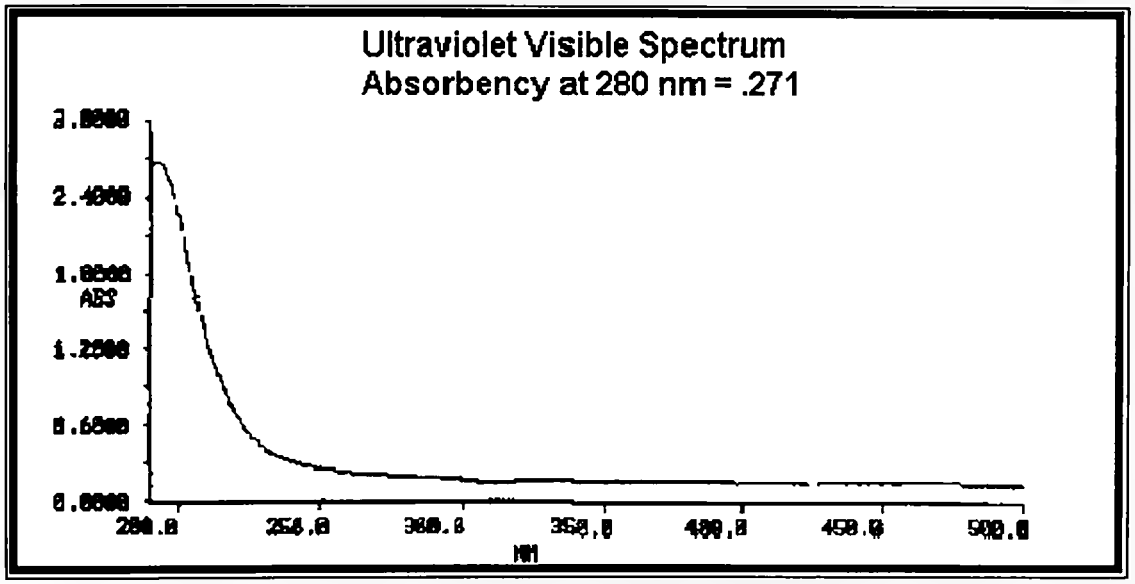


Figure 19. UV-Visible Spectrum of Water Filter in Photolysis

The absorbency (A) at 280 nanomethers is .271. Percent transmission (%T) from is given by the following Equations 2 and 3:[20]

$$A = - \log \%T \qquad [2]$$

$$10^{-A} = \%T \qquad [3]$$

By these equations, the percent transmittance of the water filter at 280 nanometers of light is 53.6 % transmitted. Based on this data, it was concluded that no additional filter was needed to block the incoming ultraviolet light before it irradiated the surface.

It was also necessary to prove that the ultraviolet light did not cleave bonds that were assumed stable to UV cleavage. A control experiment was performed to test this assumption. A hafnium-functionalized silicon substrate was put into a solution of 5 mM bromo-decyl phosphonic acid for four hours. Figure 20 illustrates this molecule:

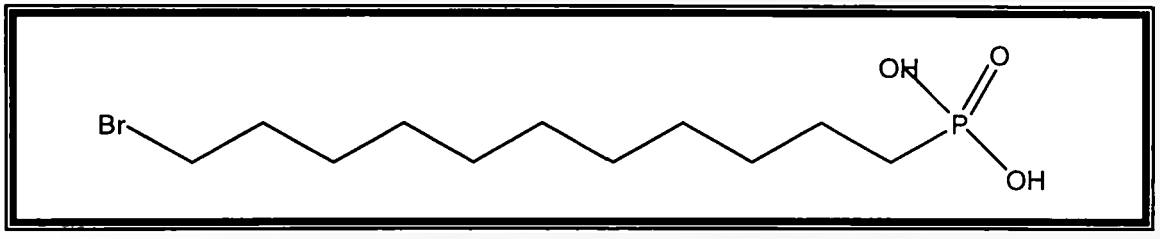


Figure 20. Bromodecylphosphonic Acid

Ellipsometry was used to characterize the thickness of the thin film before and after BDPA was added. The substrate with BDPA was photolyzed in ethanol open to the atmosphere for two hours. Before and after photolysis the substrate was analyzed with Ellipsometry. The results are graphed in Figure 21:

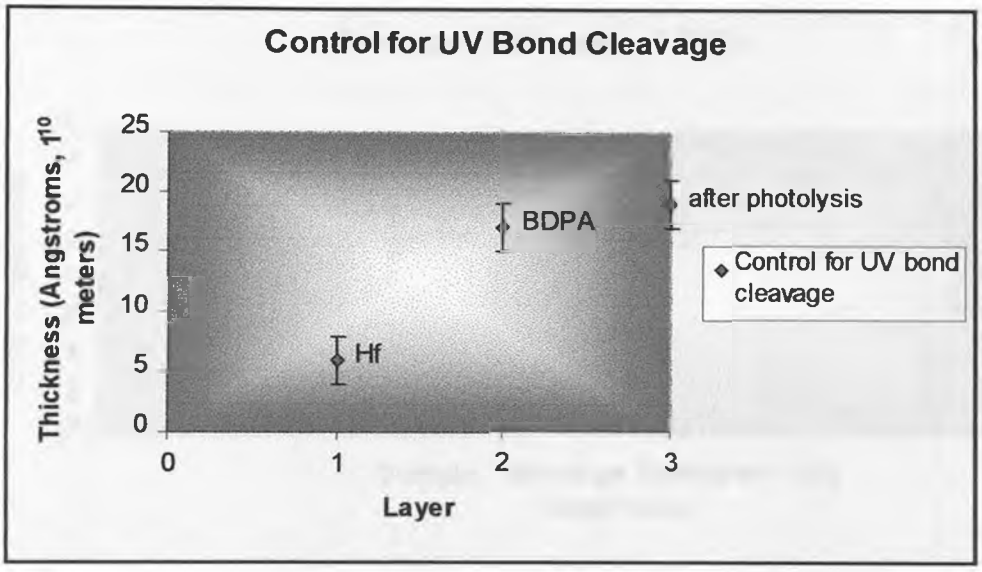


Figure 21. Control for UV Bond Cleavage

Notice that the thickness of the thin film both before and after the photolysis were the same to within the estimated error from Ellipsometry, ± 2 Angstroms. This experiment leads to the conclusion that when a photolysis experiment was done in solution, the UV light does not cleave any bonds assumed to be UV-stable. Since the experiment was done open to the atmosphere, it also suggests that the films under study are probably not as susceptible to UV photooxidation as was originally thought.

To begin development of photopatterning, each sample that is photolyzed has a layer of a metal (hafnium or zirconium) followed by a subsequent layer of IPPA. Figure 22 graphs the average experimental thickness of the IPPA layer from Ellipsometry results:

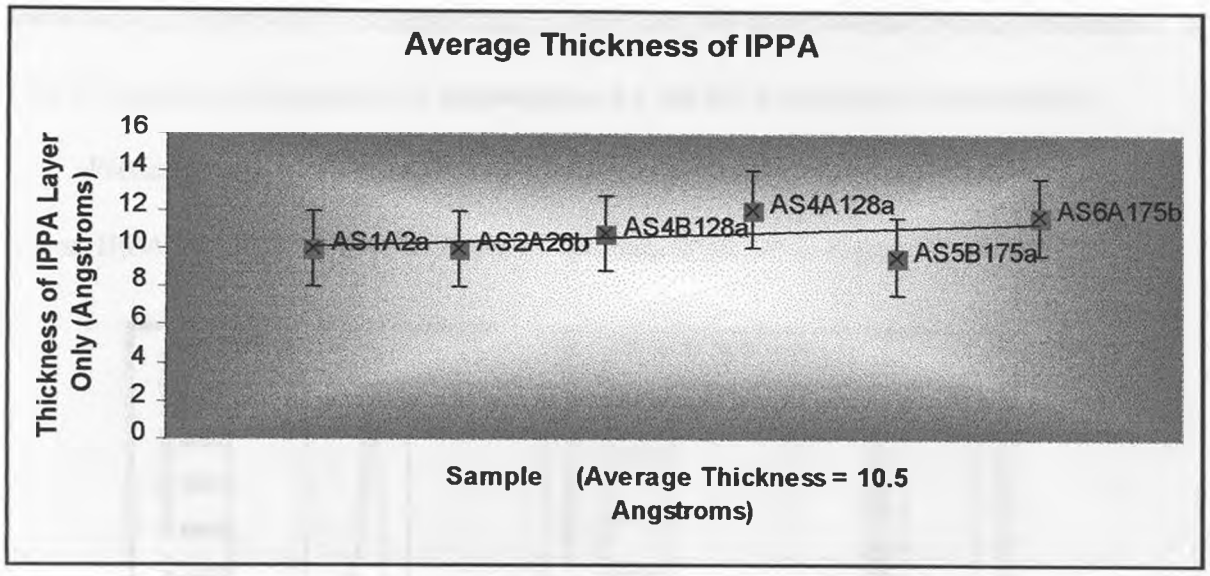


Figure 22. Average Thickness of IPPA

The average thickness taken from a handful of data collected over the past two years gives an average value for the thickness of IPPA to be approximately 10.5 Angstroms. This is reasonable considering the average sums of the average diameters of iodine, benzene, and diethyl phosphite, and the bonds made between them. The molecular modeling program Spartan was used to estimate the length of IPPA, and the O-Hf bond. The length determined by Spartan for the IPPA molecule is 8.5 Angstroms. This, however, only includes half the diameter of the iodine. Iodine's covalent radius is approximately 1.4 Angstroms.[21] (The covalent radius measures the distance from the center of iodine to the center of another atom it is bound to.) Half of this length corresponds to the radius of iodine. Thus the length of IPPA is 9.2 Angstroms. However, the oxygen-hafnium bond must also be considered. Winn considers a "typical atomic interaction length" to be 2 Angstroms (Reference 22, page 399). If this is the bond length for oxygen and hafnium, then the entire IPPA molecule bound to hafnium

should be approximately 11.2 Angstroms. Therefore, the epxerimental average thickness of 10.5 Angstroms determined by ellipsometry for the IPPA monolayer is reasonable.

Preliminary X-ray Photoelectron Spectroscopy (XPS) was taken of silicon wafers with an IPPA monolayer. One example of this data is shown in Figure 23:

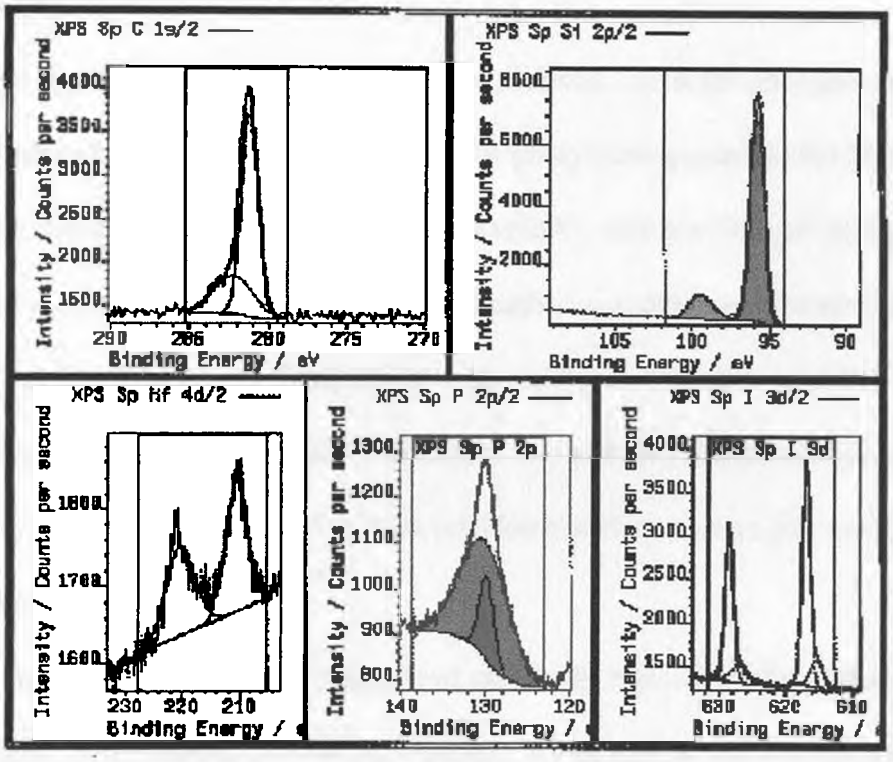


Figure 23. XPS of Hf-IPPA on a Silicon Wafer

The colored areas in Figure 23 are those that warrant analytical attention. In the top right spectrum, there are two silicon peaks. The taller of these is from the the silicon in the wafer, and the shorter is from the silicon in the thin layer of silicon dioxide. The silicon peak has a plasmon peak, much like a shadow peak, characteristic of atoms in a bulk material that have electrical conductivity. Silicon's plasmon peak occurs at 20 electronVolts (eV, which is a measure of energy) higher than its incidental peak. Unfortunately, this plasmon peak coincides with the phosphorus 2p peak shown in the

bottom middle spectrum. The blue area represents (although is not exactly equal to) the silicon plasmon peak. The red area represents the area that is due to phosphorus alone. The purple outlined peak represents the sum of these two peaks. This sum is the number that is used when ratios are calculated to determine the relative elemental composition of the thin film.

Due to the interference from the silicon plasmon line in the phosphorus peak, it is very difficult to fully characterize the amount of phosphorus present in the IPPA monolayer. Because this project's focus is to explicitly characterize the chemistry necessary for photopatterning, it is not scientifically satisfactory to determine results based on indefinite numbers. While it was important to use the silicon wafers to help determine that IPPA was successfully binding to the susbtrate (Ellipsometry data) a different system must be used to avoid the interference of the silicon plasmon line with the phosphorus peak.

Glass slides, composed completely of silicon dioxide, solve the silicon plasmon line dilemma. Since silicon dioxide is insulating, the silicon in this material does not have a plason line, and the interference problem is avoided completely. XPS data for a glass slide functionalized with hafnium followed by a monolayer of IPPA is shown in Figure 24:

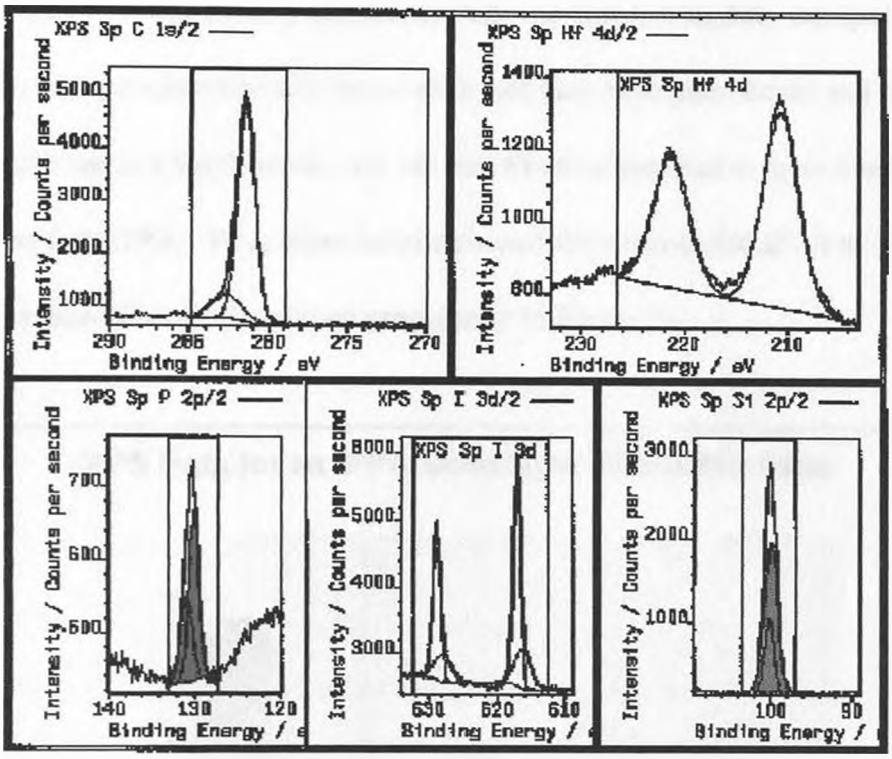


Figure 24. XPS of Hf-IPPA on a Glass Slide (SiO_2)

Notice that in Figure 23, silicon has a single peak, the blue area, that corresponds to the silicon dioxide. There is no plasmon line coincidental with the phosphorus peak, so the entire area in red is due to phosphorus only.

The data for Figure 24 was analyzed to obtain the results in Figure 25:

Element	ΣAtomic Conc	Ratio:Hafnium
Silicon	33.92	8.90
Hafnium	3.81	1.00
Phosphorus	2.62	0.69
Iodine	2.77	0.73

Figure 25. XPS Data of Hf-IPPA Monolayer

Since silicon is present in large amounts (considering that the substrate is largely composed of it) the large ratio of silicon:hafnium is reasonable. Phosphorus and iodine have a 1:1 ratio to one significant digit, and given an average experimental error of

approximately ± .05, that ratio is also reasonable. At first it is slightly unexpected to see that hafnium is approximately 40% more abundant than both phosphorus and iodine. However, hafnium is a single atom, and can therefore be assumed to have a smaller cross-section than IPPA. Thus more hafnium would be needed than IPPA to cover the same surface area. This data is shown graphically in Figure 26:

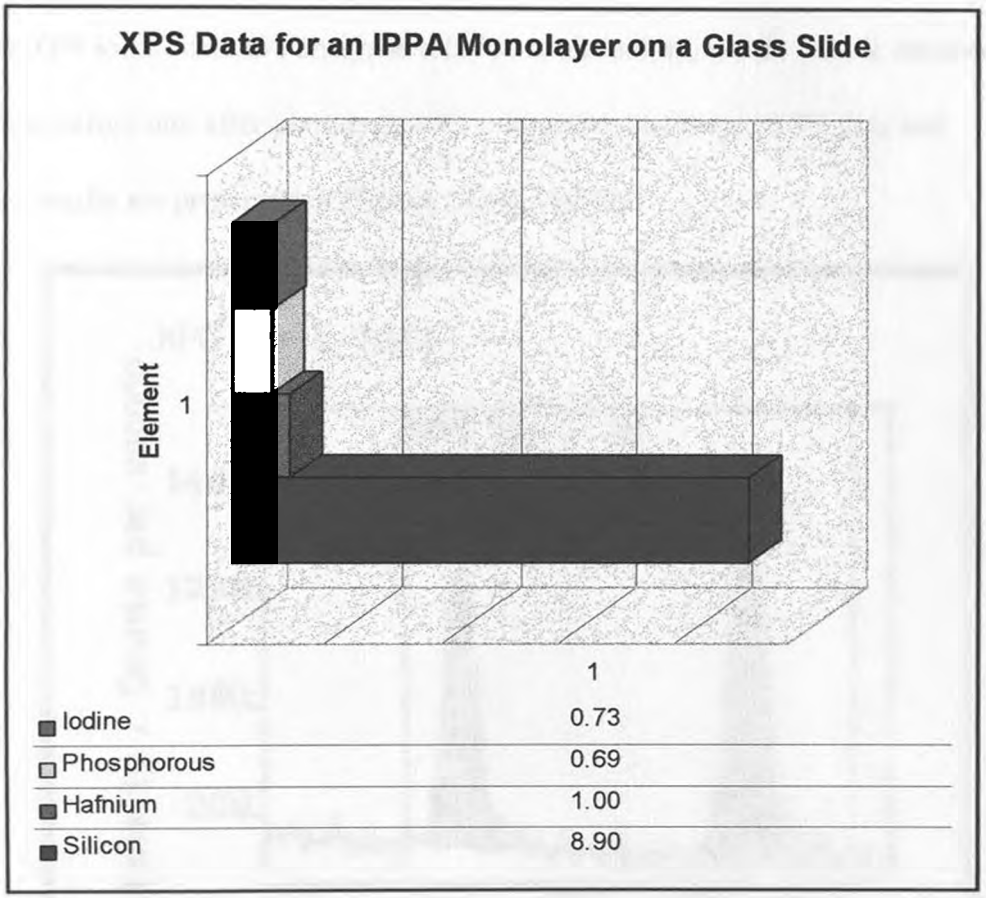


Figure 26. Graphical XPS Data of Hf-IPPA Monolayer

Another control reaction was performed to determine the necessity of making potassium diethyl phosphite salt (KDEP) from diethyl phosphite (DEP) which is a liquid that is readily available from the Aldrich Chemical company. In KDEP the phosphonic acid is a negative ion, counterbalanced by the positive potassium ion. In DEP, however,

no ion is present. This negative charge on the phosphorus may have something to do with the actual mechanism of the reaction during photolysis. If not, however, experimentally it would be desirable to avoid making KDEP in the first place.

In order to make this determination, IPPA was bound to a glass substrate functionalized with zirconium. This substrate in the photolysis cell was covered in DEP, vacuum sealed, and irradiated with UV light for 23 hours and 20 minutes. The before and after XPS iodine data are analyzed relative to zirconium, whose atomic concentration is the same before and after photolysis within experimental error. XPS data and graphical results are presented in Figures 27a-b, and 28:

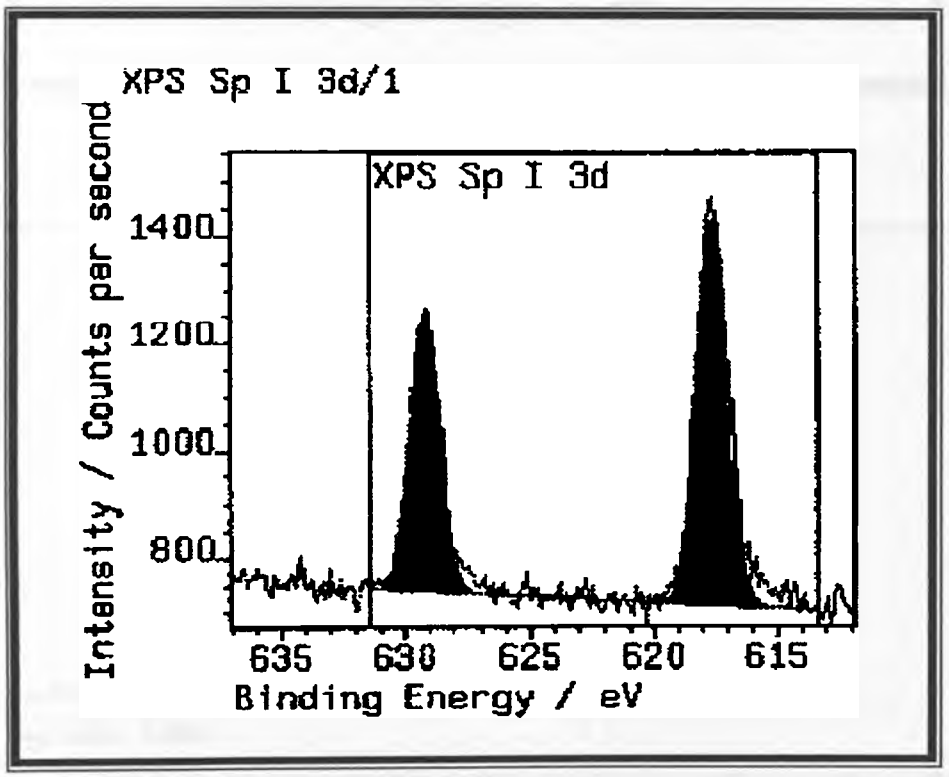


Figure 27a. XPS of Iodine Before Photolyzing in DEP

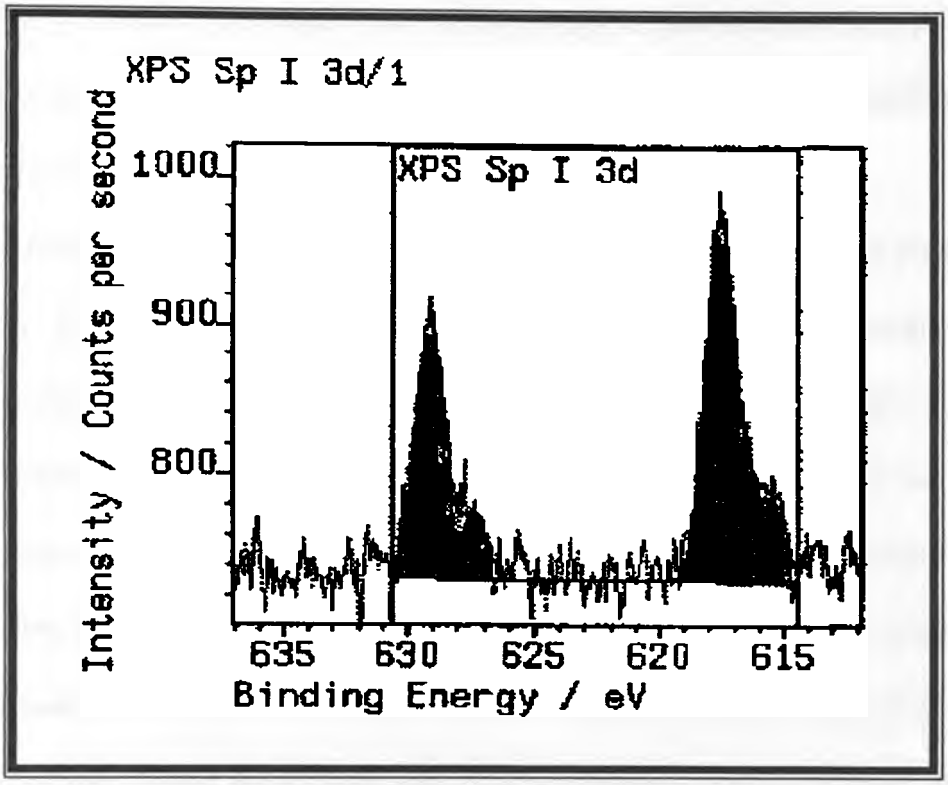


Figure 27b. XPS of Iodine After Photolyzing in DEP

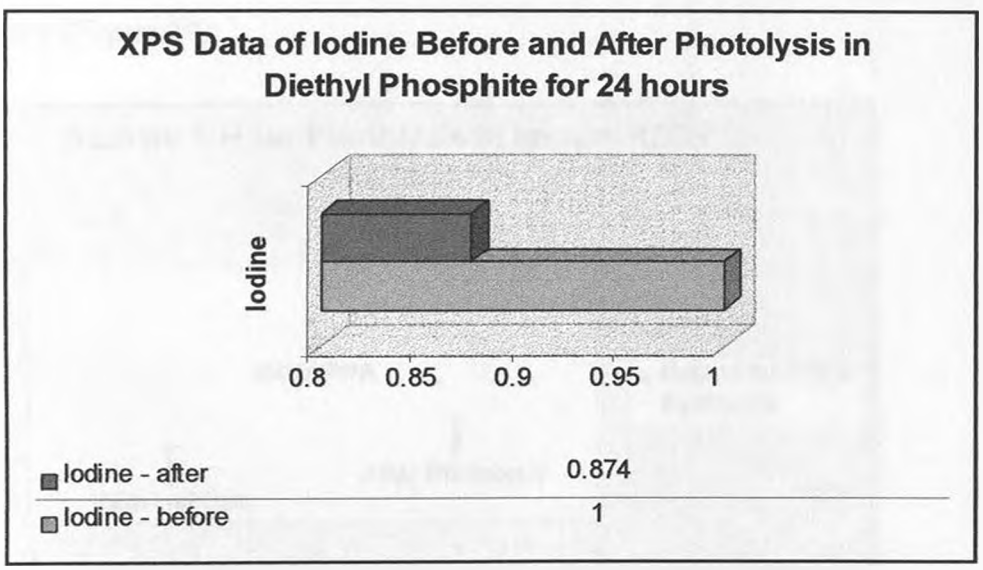


Figure 28. Graphical Representation of Iodine XPS Data

The amount of iodine present on the substrate after photolysis only decreased by about 13%. The phosphorus concentration remained approximately unity (not depicted). The

conclusion drawn is that DEP alone is not strong enough to remove iodine from the surface and replace it with the phosphonate ester group. Using a solution of KDEP is concluded to be necessary.

The first experimental method of synthesizing a solution of KDEP was presented in Figure 14. It involved multiple synthetic steps and was air sensitive, so it could not be purified to isolate the KDEP. The solvent used was dimethyl sulfoxide (DMSO) which is polar and aprotic, meaning that it has no available hydrogen atoms. If DMSO was capable of donating a hydrogen atom, it could compete with the phosphonate ester ion for the binding site on the benzene ring after the carbon-iodine bond had been cleaved. The KDEP solution was transferred via cannula wire into the evacuated photolysis cell to cover the substrate. When this solution was used to photolyze a silicon substrate with hafnium and IPPA for just one hour, the following thickness data was obtained by Ellipsometry (Figure 29):

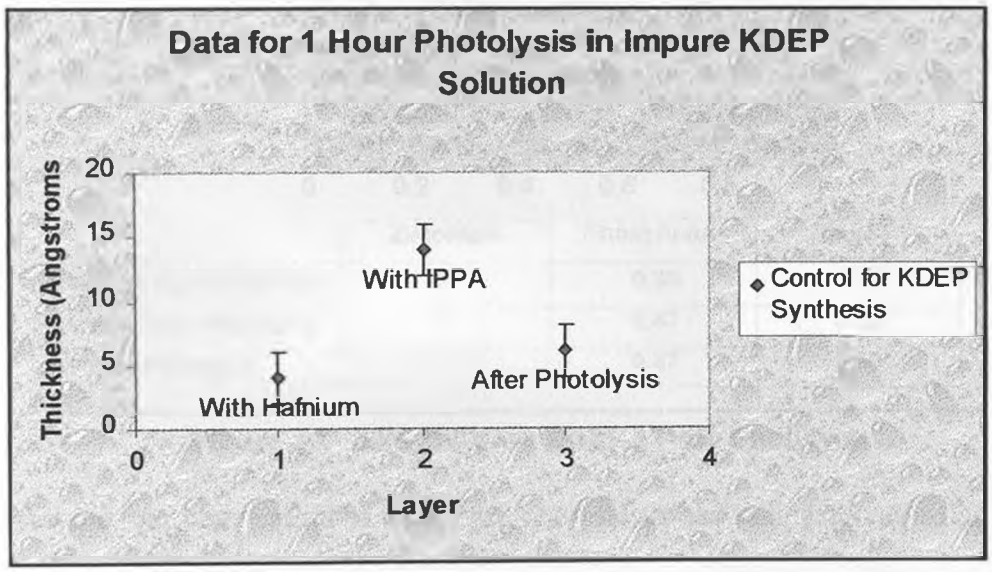
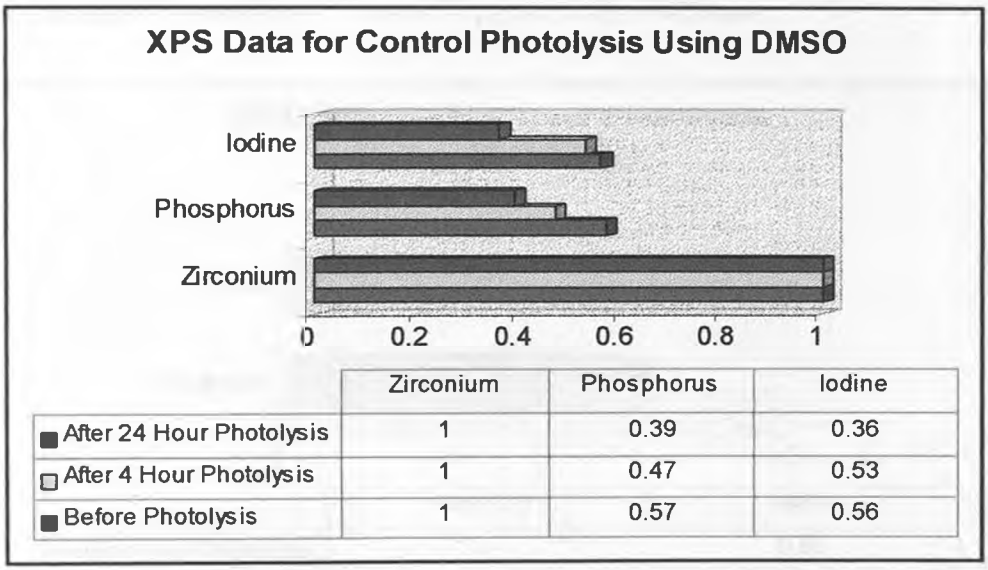


Figure 29. Photolysis Thickness Data from Impure KDEP

The functionalizataion with hafnium step gives a layer 4 Angstroms thick. When IPPA is added, the thickness is 14 Angstroms, a 10 Angstrom growth, which is about average. After photolysis, however, the Ellipsometery shows that the thickness decreased 8 Angstroms. The photolysis was only done for one hour, but still the solution was harsh enough to cleave nearly the entire IPPA monolayer. The three things in this solution that could be responsible are the KDEP, the solvent (DMSO) and the excess impurities from the reaction.

In order to determine if DMSO was too harsh, a glass slide with IPPA was photolyzed in DMSO alone. Two control experiments were performed, one for four hours, and the other for twenty-four hours. The XPS data for these experiments gave the following data (Figure 30):



	Zirconium	Phosphorus	Iodine
After 24 Hour Photolysis	1	0.39	0.36
After 4 Hour Photolysis	1	0.47	0.53
Before Photolysis	1	0.57	0.56

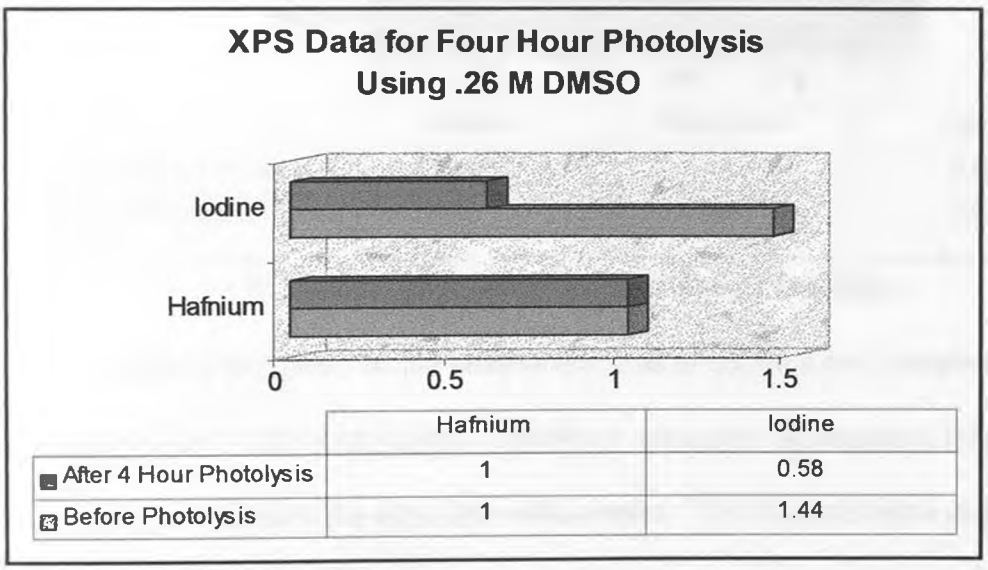
Figure 30. XPS Data for DMSO Only Photolysis

After the four hour period of time, both phosphorus and iodine decreased in concentration by a relatively small amount. The concentration of zirconium remained the same. After twenty-four hours, however, both iodine and phosphorus concentrations

decreased significantly. This suggests that DMSO removes some of the IPPA molecule over time, and that it may not be a suitable solvent for a 24 hour photolysis. If, however, photolysis is possible in only four hours, DMSO should be adequate.

The four hour time required for photolysis was investigated using a solution of KDEP in DMSO. In order to eliminate the excess impurities altogether, a different synthetic route to KDEP was used (Figure 15). This route does not have any side products, and the solvent, liquid ammonia (NH_3) is evaporated after the reaction is completed.

A silicon wafer with hafnium and IPPA was photolyzed for four hours in .26 M solution of KDEP in DMSO. Because of the interference between the plasmon line from the wafer's silicon and the phosphorus peak, only hafnium and iodine data were able to be adequately quantified. Figure 31 presents this XPS data:



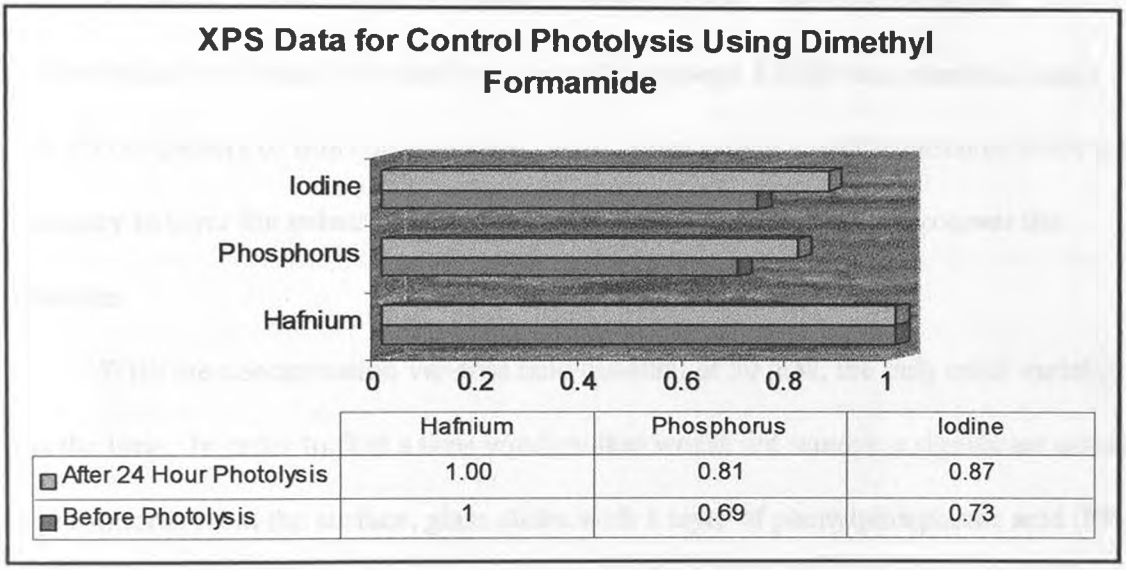
	Hafnium	Iodine
After 4 Hour Photolysis	1	0.58
Before Photolysis	1	1.44

Figure 31. XPS Data for KDEP in DMSO

Since there is still iodine present after the photolysis, it can be concluded that four hours of this concentration of KDEP in DMSO is not sufficient for photolysis to be completed.

It had already been concluded that if the reaction requires up to twenty-four hours, DMSO is not a suitable solvent (See Figure 30). Thus, a new solvent needed to be considered.

The new solvent chosen was dimethyl formamide (DMF). This solvent is also polar and aprotic, and was used by Reference 13. Thus it should be a good solvent for photolysis. As a control experiment, a hafnium functionalized glass slide layered with IPPA was photolyzed in pure DMF for 24 hours. The before and after XPS data is shown as Figure 32:



	Hafnium	Phosphorus	Iodine
After 24 Hour Photolysis	1.00	0.81	0.87
Before Photolysis	1	0.69	0.73

Figure 32. XPS Data for DMF Only Photolysis

Figure 32 suggests that the relative amounts of hafnium and phosphorus actually inceased after the 24 hour photolysis. However, after error propagation, the values can actually be determined to be experimentally similar. The details of error propagation will be included as Appendix 1, but the results are shown below in Figure 33:

Experiment	Element	Ratio to Hf	Error
Before Photolysis	Hafnium	1.00	0.08
	Phosphorus	0.69	0.06
	Iodine	0.73	0.06
After 24 Hour Photolysis	Hafnium	1.00	0.06
	Phosphorus	0.81	0.06
	Iodine	0.87	0.05

Figure 33. Error Propagation for DMF Only Control Photolysis

Since this solvent appeared suitable for this reaction, the next step was to determine a specific concentration of KDEP to be used in this solvent. A 50 mM solution of KDEP was used as the standard concentration. The reason that this concentration was initially decided upon was that enough KDEP was present to make over 200 milliliters of this concentration. Also, since only a 1 mM solution of IPPA was necessary to layer the substrate, 50 mM should be more than adequate to cover the substrate.

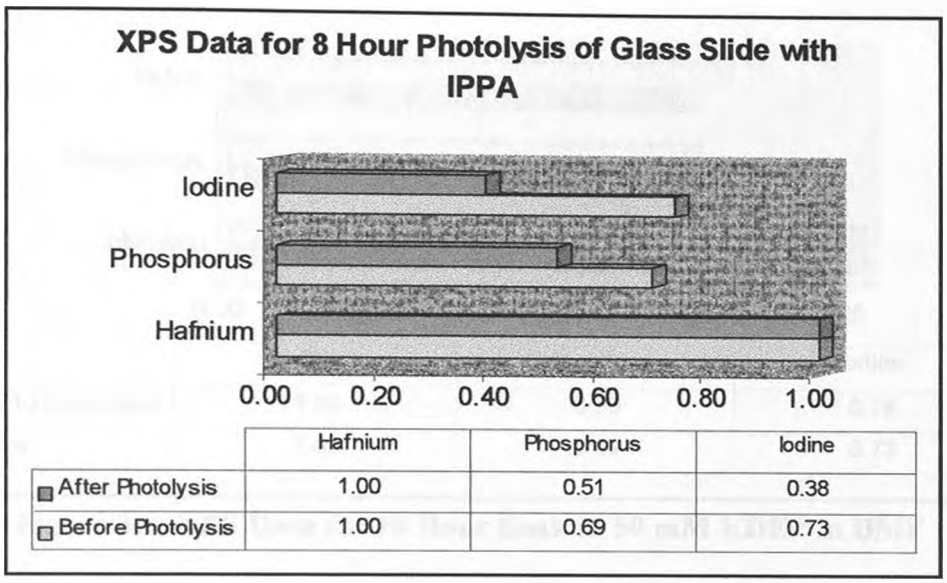
With the concentration variable held constant at 50 mM, the only other variable was the time. In order to find a time window that would not remove a significant amount of phosphorus from the surface, glass slides with 1 layer of phenylphosphonic acid (PPA) were used for control. Initially, a slide with 1 layer of PPA was photolyzed for 24 hours in an evacuated cell. The XPS data showed that this time period was too long. The amount of phosphorus relative to hafnium decreased beyond experimental error. The same photolysis was then done for 12 hours, which again proved too long, and finally for 8 hours. Figure 34 presents these results:

Experiment	Element	Ratio to Hf	Error
Before Photolysis	Hafnium	1.00	0.06
	Phosphorus	0.43	0.05
After 24 Hour Photolysis	Hafnium	1.00	0.06
	Phosphorus	0.33	0.05
After 12 Hour Photolysis	Hafnium	1.00	0.05
	Phosphorus	0.27	0.04
After 8 Hour Photolysis	Hafnium	1.00	0.06
	Phosphorus	0.28	0.04

Figure 34. Results of Experiments with 50 mM KDEP in DMF on PPA

Figure 34 shows that 24, 12, and 8 hours of photolysis in 50 mM KDEP cleaves too much phosphorus from the surface. However, it had been previously established from Figure 31 that 4 hours was not enough time for photolysis to occur. Although that experiment was done using 0.26 M KDEP in DMSO, it still provides useful information. The experiment for Figure 31 was much more concentrated than the 50 mM being used in the experiments for Figure 34. Therefore, it is reasonable to assume that four hours at a lower concentration would definitely not be enough to successfully remove all of the iodine from the surface.

Despite the fact that 0.05 M of KDEP in DMF was somehow cleaving the hafnium-Phosphorus bond, another photolysis was done at this point using a monolayer of IPPA. This experiment was done in order to determine if 8 hours was enough to dissociate the carbon-iodine bond. A glass slide was irradiated with UV light for 8 hours in 50 mM KDEP in DMF and analyzed using XPS. The results of that experiment are presented in Figure 35:

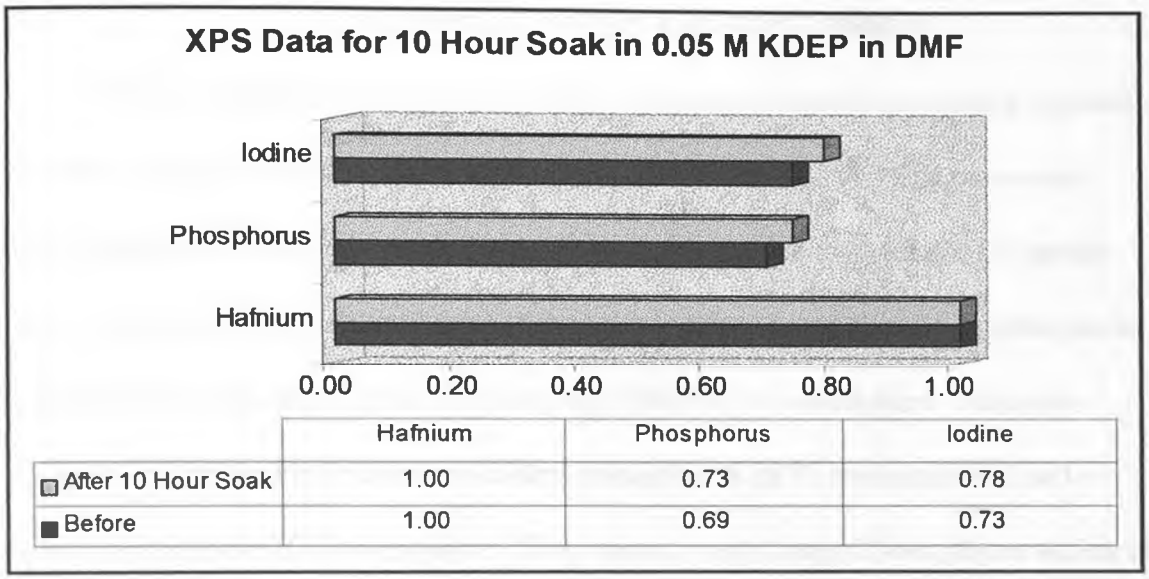


	Hafnium	Phosphorus	Iodine
After Photolysis	1.00	0.51	0.38
Before Photolysis	1.00	0.69	0.73

Figure 35. XPS for 8 Hour Photolysis in 50 mM KDEP in DMF

This data asserts that iodine is still present after the 8 hour photolysis. The relative amounts of iodine and phosphorus have decreased, as opposed to the expected decrease in iodine and increase in phosphorus. It is known from the data presented in Figure 33 that phosphorus from PPA is cleaved when photolyzed in 50 mM KDEP in DMF for 8 hours. Therefore, if iodine from IPPA is still present after this time, the photolysis will not work under these parameters.

The last control experiment that will be presented in this thesis was done in order to determine if the UV light plays a role in cleaving the hafnium-Phosphorus bond, or if it is the KDEP solution alone that was responsible for that cleavage. A glass slide with a monolayer of IPPA was placed in the photolysis cell, which was then evacuated. The 50 mM solution of KDEP in DMF was added to the cell, and the cell was then placed in the dark to soak for 8 hours. The XPS results of this experiment are presented as Figure 36:



	Hafnium	Phosphorus	Iodine
After 10 Hour Soak	1.00	0.73	0.78
Before	1.00	0.69	0.73

Figure 36. XPS Data for 10 Hour Soak in 50 mM KDEP in DMF

The data from Figure 36 indicates that the 50 mM KDEP solution in DMF does not alone have an adverse affect on the IPPA molecule bound to the substrate. This suggests that some how the combination of the UV light and the KDEP solution is partially removing the entire IPPA or PPA molecule from the surface.

IV. CONCLUSIONS AND DISCUSSION

Much progress has been made in defining the experimental parameters required for the overall goal of photopatterning in thin film multilayers. Physical parameters, namely the water filter, were considered. A control was done to check for UV-stable bonds. 4-Iodophenylphosphonic acid (IPPA) deposition was verified, and photolysis was originally investigated using diethyl phosphite (DEP) in the liquid form. Next, two methods for synthesizing potassium diethyl phosphite (KDEP) were explored, and a suitable solvent for KDEP was found. The substrate was changed from silicon wafers to glass slides for more efficient analysis using XPS. Time issues were addressed with a phenyl-phosphonic acid (PPA) monolayer control and the effect of the KDEP solution with or without light was examined.

The water filter through which the ultraviolet light passes was verified to have 53.6% transmittance at the desired wavelength, 280 nanometers. Thus, the need for an additional filter was eliminated. A control experiment was done using a BDPA monolayer that forms the same bond between hafnium and the phosphonic acid that IPPA does. This experiment determined that the hafnium-phosphonate bond was stable under UV light.

The UV-susceptible molecule, IPPA, was verified to bind to the surface of a functionalized substrate in a repeatable, predictable manner. This was determined using Ellipsometry to measure the thickness of the IPPA monolayer. A molecular modeling program supported these thickness results.

Photolysis was initially investigated by simply irradiating a substrate with an IPPA monolayer in an evacuated cell containing liquid DEP. XPS data confirmed that

DEP alone would not replace iodine after the carbon-iodine bond was cleaved. Therefore, two synthetic routes to making KDEP were investigated. The first involved an air-sensitive reaction that was unable to be purified prior to use.[11] This impure solution was found to remove the entire IPPA molecule after irradiation with UV light. The second synthetic route was reported to yield KDEP in its pure salt form,[13] and this product was used in all further experimentation.

Once the KDEP salt was made, a suitable solvent for it was needed. Dimethyl sulfoxide (DMSO) was the first solvent to be considered, since it was used in the first KDEP synthetic route and was used in two literature sources for replacing a carbon-iodine bond with a carbon-phosphonate bond under UV light cleavage.[12,13] Although DMSO successfully dissolved KDEP, preliminary X-ray photoelectron spectroscopy (XPS) data from photolysis on a silicon substrate determined that four hours in a solution of KDEP in DMSO was not sufficient to perform the required chemistry.

The type of substrate was switched from silicon wafers to glass slides to make XPS data analysis less complicated. Although glass slides could not be analyzed using Ellipsometry, they were better suited for XPS. By eliminating the semiconducting silicon, however, the silicon plasmon peak that coincides with the phosphorus peak was also eliminated. Analyzing glass slides reduces the error in calculating the relative phosphorus content from the phosphorus (2p) line.

Glass slides were then used for all solvent control experiments. When a 24 hour irradiation time for DMSO was investigated, it proved to remove some of the IPPA monolayer, and was discarded as a potential solvent. The next solvent considered was acetonitrile. Consideration of this solvent was discussed in the Experimental section,

where it was specified that despite a literature reference[12] acetonitrile did not dissolve KDEP. Dimethyl formamide, however, was found to dissolve KDEP and also was determined using XPS not to affect the IPPA monolayer after a 24 hour irradiation time.

Time was the next variable to be considered for the photopatterning scheme. For a four-hour photolysis time of a silicon wafer in a solution of KDEP in DMSO, the XPS data showed that a significant amount of iodine remained on the surface. Since DMF was checked for a 24-hour block of time, the time window from 4-24 hours was considered. A monolayer of PPA was used in the control photolysis experiments in order to concentrate on the hafnium-phosphonic group bond in the KDEP solution. Three times were investigated, 24 hours, 12 hours, and 8 hours, none of which gave satisfactory results. Significant amounts of phosphorus were lost each time.

With the time window decreased to less than 8 hours, a new question was raised. Since 4 hours had not worked to remove all of the iodine before, it was questioned whether 8 hours would. Therefore, despite the results of the 8 hour PPA photolysis, an 8 hour IPPA photolysis was done in KDEP. This too proved futile, as there was still a significant amount of phosphorus removed from the substrate, and a significant amount of iodine still present.

In order to determine if it was the KDEP solution alone, or the interaction between the KDEP solution and the UV light that was cleaving the hafnium-phosphonate bond, an 8 hour soak of a glass slide was done under photolysis conditions without the UV light. The results asserted that the KDEP solution alone was not removing the molecule from the surface. From the results of the DMF-only photolysis control experiments, it is known that neither the solvent nor the UV light alone removes the

molecule from the surface. Therefore it can be concluded that somehow the combination of UV light on the KDEP solution is causing the experiment to go awry.

All of the experiments tried so far have not given successful photolysis results. These results suggest that several future experiments be performed.

In order to ensure that the KDEP and UV light combination is not affecting the silicon dioxide-hafnium bond, a photolysis on a hafnium-functionalized substrate could be performed for 8 hours. XPS data could be taken of this substrate both before and after photolysis, and atomic concentrations could be directly compared. If, however, the problem does not lie in the silicon dioxide-metal bond, an alternate explanation must be proposed.

The next control experiment to be performed must determine how the KDEP solution attacks IPPA. One such experiment would be to photolyze a solution of IPPA powder in the KDEP solution for at least 8 hours. Traditional synthetic analyses such as Nuclear Magnetic Resonance (NMR) for both hydrogen and phosphorus nuclei, and Infrared Spectroscopy (IR) could be done in order to determine what changed in the IPPA molecule. For example, perhaps the UV light alters the phosphonate salt, and creates a new radical that attacks the carbon-phosphonate bond.

In order to contain this experiment, it could potentially be run in a UV transmitting NMR tube. The solution of IPPA and KDEP could be made in deuterated DMF, flame sealed, and analyzed by NMR. Then photolysis could be performed directly onto the NMR tube, which could be analyzed again afterwards. In this manner, the only variable that would be changing the experimental conditions before and after photolysis would be the UV light. After the NMR was performed, the tube could be broken open,

and the solvent evaporated off. Then a separation of the KDEP salt and the former IPPA could be done, and the former IPPA molecule could also be analyzed using IR. If it is determined that the KDEP and UV light combination is harmful to the IPPA molecule, a new phosphonate source, or a new UV-susceptible molecule should be considered for these photopatterning experiments.

In principle, the approach to photopatterning SAMs, and the motivation behind this approach remain intact. In practice, it is always a struggle to develop the chemistry necessary to successfully carry out good ideas in the chemical world. This thesis presents a significant advance down the experimental path towards the ultimate goal of photopatterning in thin film multilayers.

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VII. APPENDIX

Error Propagation

Excel spreadsheets were used to propagate error for XPS data. The basic format is the same for all data collected, so only one sample will be described here. Figures A-1 and A-2 present the numerical data for error propagation of XPS data for ASG1Aa and ASG1Ad, respectively. These were a monolayer of IPPA on a hafnium functionalized glass slide before photolysis, and after an 8-hour photolysis under 50 mM KDEP in DMF.

ASG1Aabefore photolysis												
Molecule	Raw Area	Sensitivity Factor	Scaled Area	ΔScaled Area	Total Area	ΔArea	Atomic Conc.	ΔAt. Conc.	At. Conc. %	ΔAt Conc%	Ratio to Hf	ΔRatio to Hf
Carbon	1029.00	0.60	1712.15	85.61	11266.22	485.31	0.57	0.03	56.88	2.92	14.93	0.68
	5742.00	0.60	9554.08	477.70								
Silicon	3513.00	0.70	5032.95	251.65	6717.77	265.37	0.34	0.02	33.92	1.64	8.90	0.41
	1176.00	0.70	1684.81	84.24								
Hafnium	2363.00	5.25	450.18	22.51	754.43	27.17	0.04	0.00	3.81	0.17	1.00	0.06
	1590.00	5.23	304.25	15.21								
Phosphorus	335.00	1.00	336.01	16.80	518.56	19.12	0.03	0.00	2.62	0.12	0.69	0.06
	182.00	1.00	182.55	9.13								
Iodine	3935.00	18.00	218.62	10.93	550.10	14.86	0.03	0.00	2.78	0.11	0.73	0.05
	2812.00	17.70	158.87	7.94								
	1813.00	18.02	100.60	5.03								
	1276.00	17.72	72.00	3.60								
TOTALS					19807.07	554.33						

Figure A-1. Error Propagation for ASG1Aa

ASG1Adafter photolysis												
Molecule	Raw Area	Sensitivity Factor	Scaled Area	ΔScaled Area	Total Area	ΔArea	Atomic Conc.	ΔAt. Conc.	At. Conc. %	ΔAt Conc %	Ratio to Hf	ΔRatio to Hf
Carbon	5754.00	0.60	9574.04	478.70	14204.66	531.75	0.59	0.03	59.19	2.70	18.98	0.84
	2783.00	0.60	4630.62	231.53								
Silicon	4433.00	0.70	6351.00	317.55	8375.36	333.29	0.35	0.02	34.90	1.66	11.19	0.50
	1413.00	0.70	2024.36	101.22								
Hafnium	2273.00	5.25	433.03	21.65	748.51	26.79	0.03	0.00	3.12	0.14	1.00	0.06
	1649.00	5.23	315.48	15.77								
Phosphorus	218.00	1.00	218.66	10.93	383.15	13.68	0.02	0.00	1.60	0.07	0.51	0.05
	164.00	1.00	164.49	8.22								
Iodine	2102.00	18.00	116.77	5.84	286.29	7.81	0.01	0.00	1.19	0.05	0.38	0.04
	1486.00	17.70	83.95	4.20								
	872.00	18.05	48.32	2.42								
	661.00	17.75	37.25	1.86								
TOTALS					23997.97	628.34						

Figure A-2. Error Propagation for ASG1Ad

The XPS data was the raw area under the peak and the sensitivity factor. The experimental error is 5% of the raw area. The equations for the remaining headings and totals are as follows (Equations A-1 – A12):

$$\text{Scaled Area} = \text{Raw Area}/\text{Sensitivity Factor} \quad [A\text{-}1]$$

$$\Delta\text{Scaled Area} = [A\text{-}1]*.05 \quad [A\text{-}2]$$

$$\text{Total Area} = \Sigma[A\text{-}1] \quad [A\text{-}3]$$

$$\Delta\text{Area} = (\Sigma[A\text{-}1]^2)^{1/2} \quad [A\text{-}4]$$

$$\text{Totals (Total Area)} = \Sigma([A\text{-}3]) \text{ for all elements} \quad [A\text{-}5]$$

Totals (ΔArea) = $(\Sigma([A\text{-}3]^2)^{1/2}$ for all elements) [A-6]

Atomic Conc. = [A-3]/[A-5] where [A-3] is specific to the element [A-7]

ΔAt.Conc. = $\sqrt{((1/[A\text{-}5])^2*([A\text{-}4]^2) + (-[A\text{-}3]/([A\text{-}5]^2)^2*([A\text{-}6]^2))}$ [A-8]

At. Conc. % = [A-7]*100% [A-9]

ΔAt. Conc. % = [A-9]*100% [A-10]

Ratio to Hf = $[A\text{-}9]/[A\text{-}9]_{Hf}$ [A-11]

ΔRatio to Hf = $\sqrt{((1/[A9]_{Hf})^2*([A\text{-}9]^2) + (-[A\text{-}9]/([A\text{-}9]_{Hf}^2)^2*([A\text{-}9]_{Hf}^2))}$ [A-12]

Atomic Conc. stands for atomic concentration, At. Conc. % stands for atomic concentration percent, and a Δ in front of an equation represents the error for that calculation.