SELF-ASSEMBLY OF HYBRID MULTILAYER THIN FILMS AND INCORPORATION OF NONLINEAR OPTICAL PROPERTIES

by

GEOFFREY MARC LOWMAN

A THESIS

Presented to the Department of Chemistry
and the Honors College of the University of Oregon
in partial fulfillment of the requirements
for the degree of
Bachelor of Arts

June 1998

APPROVED:_____ [redacted]

Prof. Catherine J. Page

An Abstract of the Thesis of

Geoffrey Marc Lowman for the degree of Bachelor of Arts

in the Department of Chemistry to be taken June 1998

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A self-assembled multilayer thin film that combines metal-isocyanide functional groups with metal-phosphonate functional groups has been constructed. The self-assembly process allows for construction of a multilayer thin film based on covalent bonding interactions between layers of molecules. The analytical techniques of ellipsometry and x-ray photoelectron spectroscopy have shown that these films demonstrate fairly regular and predictable layer-by-layer growth. This multilayer system should exhibit nonlinear optical properties, due to the incorporation of a 4-aminophenylphosphonic acid molecule oriented noncentrosymmetrically in each full hybrid layer.

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INTRODUCTION

Since advent of the microchip, science has been striving for breakthroughs to make technology smaller and faster. As the dimensions of technology shrink, there arises a need for new and improved materials for use in the machines of tomorrow. It has been proposed that light energy (photons) will replace electricity (electrons) as the primary means of processing or transferring information[1]. One way that light energy may be applied to technology is through nonlinear optical (NLO) properties. It is hoped that the method of Self-Assembly (SA) or layer-by-layer growth can be utilized to produce thin films that incorporate NLO properties in such a way as to make them applicable as the basic components in the light energy powered devices of tomorrow.

To better explain this system, the following overview and terminology section will be used to define the vocabulary that may be unclear for those outside the field of chemistry. In the Materials and Methods section a detailed account of the molecules used in the hybrid system will be given, as well as their synthesis when applicable. Also, a detailed procedure for the self-assembly process will be presented along with an overview of analytical techniques used in this research. The Results and Discussion section will present and discuss data gathered from the analytical techniques discussed, as well as suggest some future directions for this research.

Self-assembly (SA) is a term given to the process in which two components in solution are attracted to one another via intermolecular forces into an extended system such as a thin film. Our ability to predict the way that certain molecules will interact with one another allows for control of the logical construction of ordered layers that are built layer-by-layer onto a silicon wafer. It is akin to putting the ingredients onto bread when making a sandwich; you know how they taste best and you rationally start with the mayonnaise and build up from there step by step.

To further illustrate the process of SA it is helpful to compare it with another widely used process for building layered molecular materials, known as the Langmuir-Blodgett[2] (LB) method. This method uses molecules that are amphiphilic, meaning that the head of the molecule is hydrophilic (water compatible), while the tail of the molecule is hydrophobic (water incompatible). The molecules are dissolved in a volatile solvent (meaning the solvent will evaporate quickly). A drop of this solution is dropped on a surface of water in a specially designed trough. When the solvent evaporates, a single layer of the molecule is left with the head oriented in the water and the tail pointing away from the water. The trough is then designed to mechanically compress the molecular layer to increase order. This molecular layer can then be transferred to a surface where successive layers are held together by weak molecular attractions (Van der Waals forces).

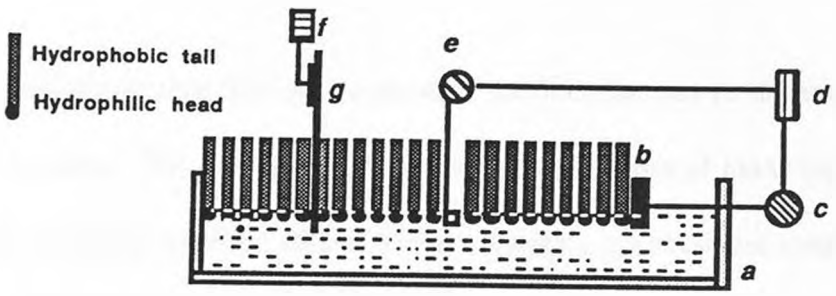


Figure 1.1 Diagram of a LB trough for deposition of molecules on solid substrates. a) the bath made of Teflon b) arm for compression of molecules c) motor that moves the compressor arm d) device that controls the pressure applied by compressor arm e) surface pressure monitor f) motor that raises and lowers the substrate g) a solid substrate[2].

The self-assembly process has been chosen over the LB method for many reasons. First, SA can allow the molecules in solution to choose their own orientation, therefore forming the most favorable orientations for the molecules in the layers. LB films are forced into a fairly stable orientation by compression, but do not form actual chemical bonds. LB films are held together by weak molecular attractions, whereas SA films are held together by actual covalent chemical bonds. Also, there are no special instruments, such as troughs, that are needed to employ the SA process, and a much wider range of molecules can be used in self-assembly, because there is no amphiphilic requirement of molecules in SA films. The last advantage of SA films are that the excess, non-bonded molecules that are left on the surface of the film after deposition can be washed off without affecting the bulk structure. This is due to the bulk structure's insolubility in water, organic solvents, and most mineral acids. For these reasons the SA process is gaining wider acceptance and is the primary research tool of the Page lab[3, 4] as well as other labs across the country[5, 6, 7].

A multilayer thin film is one possible product that can be developed using a self-assembly process. The thin film that is constructed consists of many layers of molecules built, layer-by-layer, onto the silicon wafer. A highly polished and cleaned silicon wafer is used, which has a thin native oxide layer. This surface is placed in a solution containing the molecule that will form the first layer of the thin film, called the anchor layer. This anchor layer will bond to the oxide layer and will point upward from the surface. The surface functionalities have now changed from the oxide layer on the silicon wafer to the

functionality that is present at the top of the anchor molecule. Successive layers of the film are formed in the same way, based on the functionalities that are present on the molecule that is on the top of the bulk structure. Predicting how the various

functionalities on the molecules interact allows for great control in the construction of the multilayer thin film. Each surface will have one functionality that will dictate the orientation of the successive layers through covalent chemical bonding.

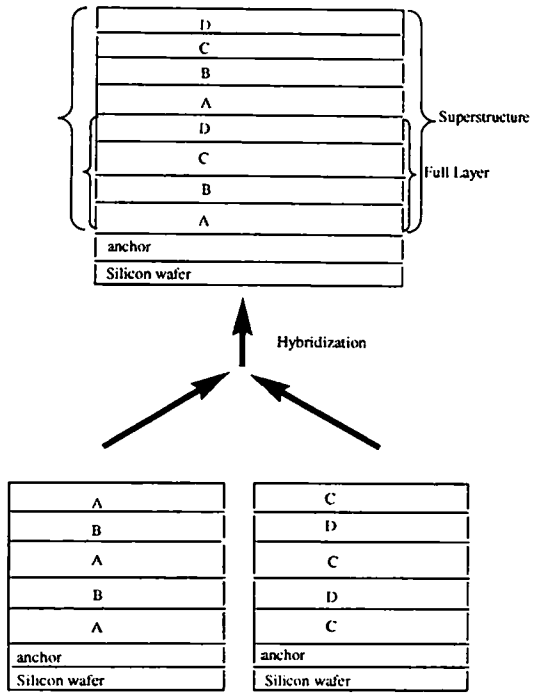


Figure 1.2 Diagram outlining the combination of two previously studied systems[3,4] into the hybrid process. The layers A, B, C, and D corresponding to the various molecules used in the hybrid system.

Building multilayers is much like being an architect at the molecular level. The chemist needs to know what purpose he/she is trying to serve in the design of the material, and the SA process allows for the choice of particular molecules that can exhibit the chosen properties. An architect must be sure that the design is rational and will stand the test of time. The chemist must be sure that the molecules bind in the predicted fashion and that the molecular design will remain in that configuration in order to exhibit the desired material properties as a bulk material. The stepwise SA process allows the sample to be analyzed after each layer is built. This analysis can include simply measuring the thickness of the molecular layers, or a more elaborate analysis of the molecules that are present throughout the sample and their relative ratios (see Materials and Methods section for a discussion of analytical techniques used). This information

can be used to alert the designer into any major problems in the construction process after any layering step.

The term "Hybrid" is used because this particular multilayer system combines the chemistry in two multilayer systems previously studied in the Page lab. Using a linking molecule that combines the functionalities of the two systems a hybrid system can be constructed. Any property of either of the two previous systems can be exhibited in the hybrid if desired, and can be controlled though the SA process through the substitution of particular molecules in the system. One other possible property that can be incorporated into films such as these is fluorescence for use in flat screen displays. As shown in figure 1, the hybrid system consists of a repeating unit, or full layer, of four molecules that are layered onto the anchor molecule. The full layers are then built one on top of each other to construct the bulk structure or superstructure.

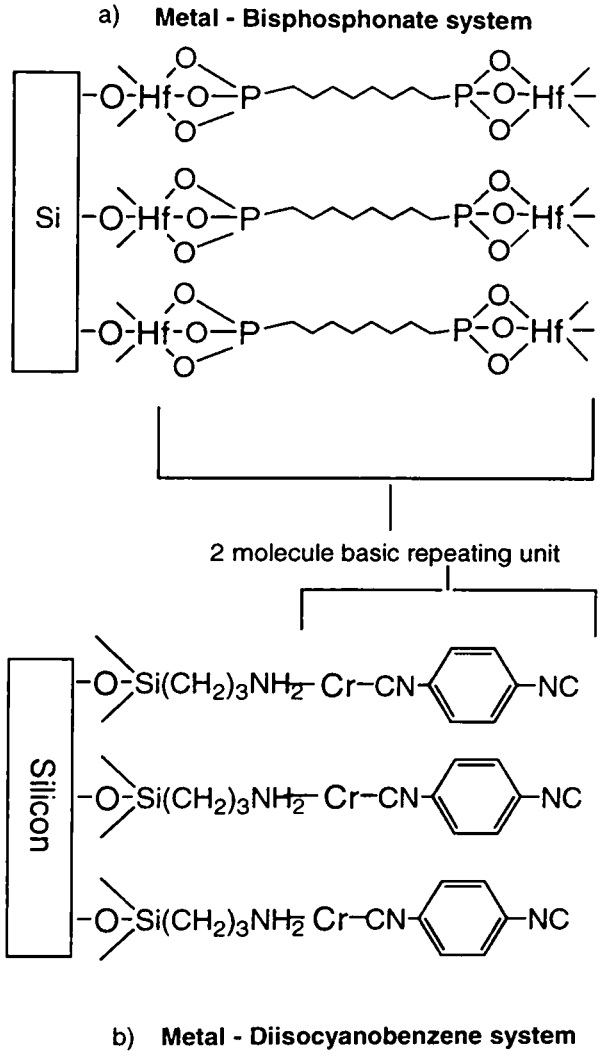


Figure 1.3 Diagram illustrating the molecular components of the two previous multilayer systems designed in the Page Lab[3,4].

Nonlinear optical (NLO) properties arise out of the interaction of light with matter to produce a light field of different wavelength or phase[2]. This property is incorporated into the system by the use of a specific molecule (4-aminophenylphosphonic acid; see materials section) which will give rise to second-order nonlinear optical properties. These

properties are by no means limited to this molecule, for nonlinear optical properties can be generated from any molecule that meet several criteria: The first of these is at the microscopic level, the molecule must be able to form a polarizable dipole when in the presence of an applied energy field. A dipole is best explained in simple terms as the electronic components of the molecule being polarized in one set direction. For this to occur the molecule must be made up of central atoms in which electrons are able to be polarized, or are free to orient themselves as the system changes. In the molecule used in this system the central atoms are in a conjugated pi system; here there are polarizable electrons. These electrons can orient themselves to give a dipole when an applied energy field is applied. The fact that these polarizable electrons are between electron donating and accepting groups means that these electrons will feel a pull from one direction and a push from the other. This uneven push-pull interaction is known as an anharmonic potential. For this reason, the dipole will always be formed in one direction. When an applied high-energy field interacts with this material it will interact with light in a different fashion than it would without the applied field.

The second criteria of a NLO material is that the material must be constructed in a way that the NLO molecules in each full layer are oriented with all of their dipoles pointed in the same direction; such an arrangement is noncentrosymmetric. It is easy to visualize the dipoles being centrosymmetric, or pointing to the same central point causing the dipoles to cancel (see Figure 1.3). Alignment of the dipoles is easily achieved using the SA process. The way that the molecules are layered one step at a time according to

functional groups allows only one orientation of the NLO molecule, meaning that the dipoles will always point in the same direction. Katz[5], Marks[8], and Corn[9] have shown that self-assembly can be used to produce nonlinear optical properties in thin films.

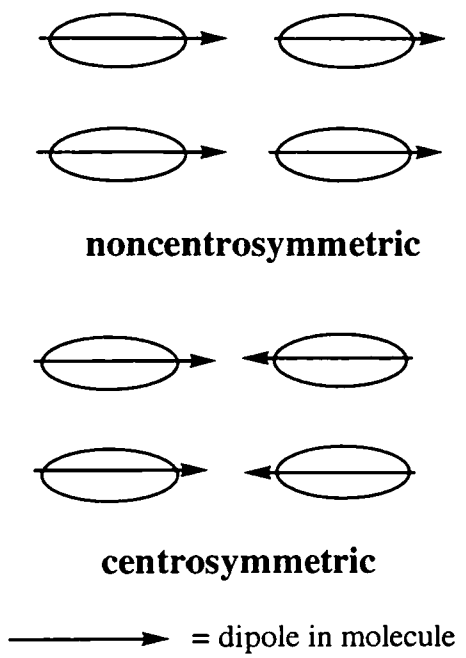


Figure 1.4 Diagram illustrating the molecular criteria that must be met by a material to exhibit nonlinear optical properties.

The incorporation of NLO properties in thin films leads back to the application of these films in the world of cutting-edge technology where light will someday replace electricity. Materials that can interact with light in two different ways, depending on the

presence of an applied energy field, could comprise some of the basic components of optoelectronic circuitry. For example, this type of material can form the basis of an on/off switch for light energy. Light that interacts with the material without the presence of an applied energy field will travel one direction (the "on" direction). When an energy field (another light source) is applied to the material, the index of refraction (a measure of the extent of refraction of light of a material) changes due to the formation of the dipoles in the NLO molecules, therefore rerouting the light to another destination (the "off" direction).

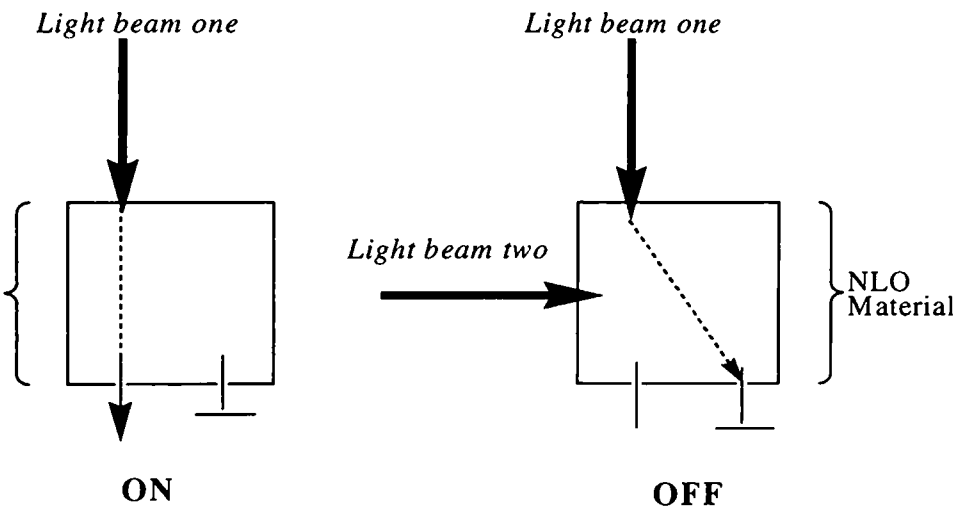


Figure 1.5 Diagram illustrating the application of an NLO material as an on/off switch for directing light energy.

MATERIALS AND METHODS

This section will guide the reader through the materials and procedures used in the synthesis and analysis of the hybrid multilayer thin films. This task cannot be accomplished without using the vocabulary of a chemist, but the overall process introduced in the previous section should be kept in mind while reading this section.

I. Materials

Zirconium (IV) acetylacetonate (acac) ($ZrC_{10}O_4H_{14}$, 98%) and 4-aminophenylphosphonic acid ($NH_2C_6H_4PO_3H_2$, 96%) were obtained from Aldrich and used as received. Chromium nitrate ($Cr(NO_3)_3 \bullet 9H_2O$) was obtained from Mallinckrodt Chemical Works and used as received. Marcus Helfrich of the Page Lab synthesized Isocyanodecylphosphonic acid according to figure 2.1.

3-aminopropyldimethylethoxysilane (3-APDES) was obtained from Gelest Inc. and used as received. Hafnium oxychloride octahydrate ($HfCl_2O \bullet 8H_2O$) was obtained from Teledyne-Wah Chang and used as received. All solvents were purchased through internal sources and used as received.

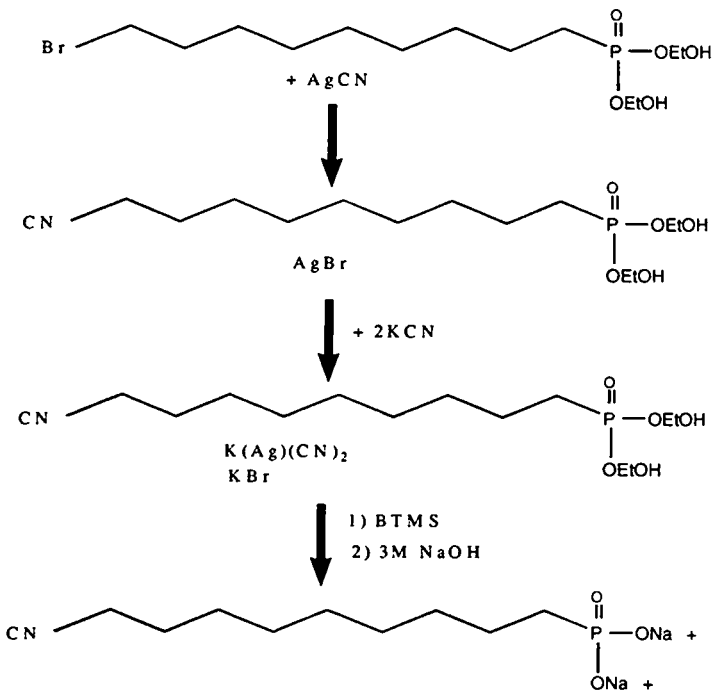


Figure 2.1 The synthesis scheme for the linking molecule (Isocyanodecylphosphonic acid)[10].

Polished (100) silicon wafers were obtained from Silicon Quest International. The substrate wafers were cleaned according to the following procedure: First, the wafers are placed in 1,4-trichloroethylene, which is stirred for 15 minutes. Then the wafers are pulled out and rinsed with ethanol and placed in 2-propanol and stirred for 15 minutes. Lastly, the wafers are rinsed with ethanol and placed in ultrapure water, deionized to a resistivity of 17-18 MΩ-cm with a Barnstead Nanopure II, and stirred for 15 minutes. The wafers are then rinsed with ultrapure water and dried with nitrogen.

II. Methods: The Anchoring Process

Both 3-aminopropyldimethylethoxysilane (3-APDES) and Hafnium oxychloride octahydrate were used as anchor molecules for the hybrid system. The procedures for anchoring with each molecule are shown in figure 2.2. The procedure for anchoring with

3-APDES involves the preparation of a 1:100 solution of 3-APDES in ethanol. The substrate is then immersed in the solution and refluxed on low heat overnight. After the anchoring

process the substrate is rinsed with ethanol and dried with nitrogen. The hafnium anchored substrates were prepared by Grace Ann Neff in the Page Lab. Substrates were placed in a 5mM Hafnium oxychloride octahydrate and water solution at 50° Celsius for three days, which results in a layer of Hafnium metal bound to the silicon substrate. The wafer was then removed, rinsed with water, and dried with nitrogen.

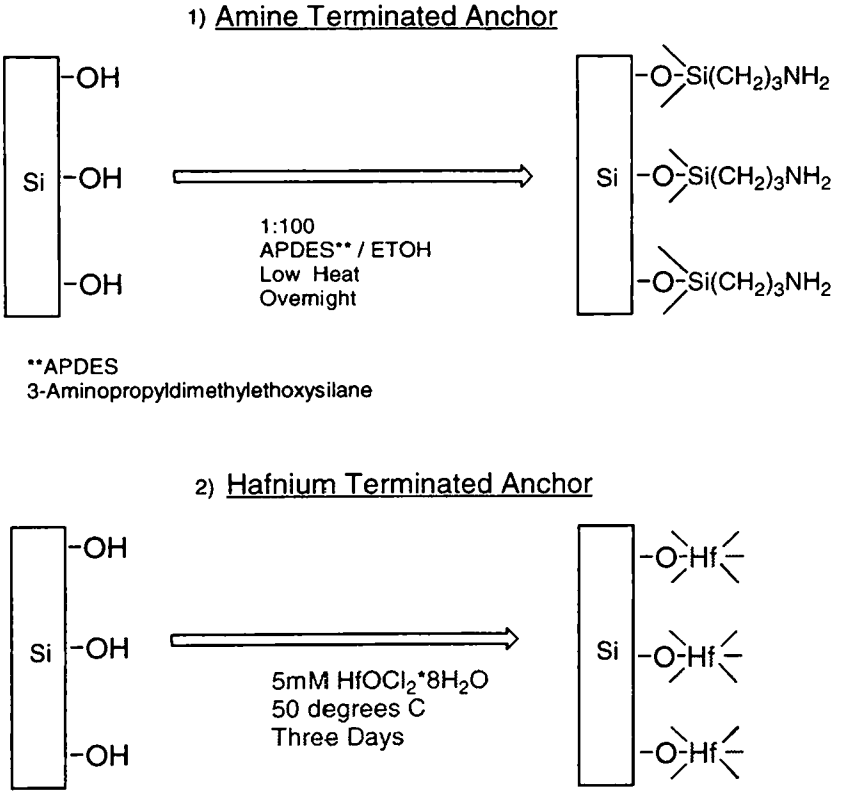


Figure 2.2 Diagram outlining the anchoring process, by showing the addition of the anchor molecule to a silicon wafer with a native oxide layer.

III. Methods: Multilayer Synthesis

The procedure for synthesis of hybrid multilayers differs slightly between the different anchoring schemes. These differences are only with respect to the order in which the layers are deposited, due to the different functionalities of the different anchor molecules. Figures 2.3 and 2.4 outline the multilayer synthesis procedures for each anchor molecule. Both procedures use the same multilayer components in the same concentrations, and the substrate remains in the layering solution for the same amount of time in both procedures.

When layering on a substrate with a 3-APDES anchor, the first layer that is bound is that of chromium ions. The substrate is placed in a 5mM solution of chromium nitrate in ultrapure water for three to four hours, which results in a layer of chromium ions (2) to be bound to the anchor surface. Next, the substrate is placed in a 5mM solution of isocyanodecylphosphonic acid (3) in ultrapure water/ethanol for two hours; this is the linking molecule that combines the functionalities of the previously studied diisocyanide and bisphosphonate multilayer schemes[3,4]. The third step is the layering of zirconium metal (4) from a 5mM solution of zirconium (IV) acetylacetonate in ethanol for three to four hours. The final step to form the first full layer is the addition of 4-aminophenylphosphonic acid (5) from a 5mM solution in ultrapure water. Rinsing the substrate with acetone to wash away any excess or unbound layering molecules from the functional surface, and then drying with nitrogen follow each step in the synthesis. When working from the Hafnium anchor the synthesis begins with the addition of a layer of 4-

aminophenylphosphonic acid, and then proceeds in the same manner with the addition of layers two through five in the same order.

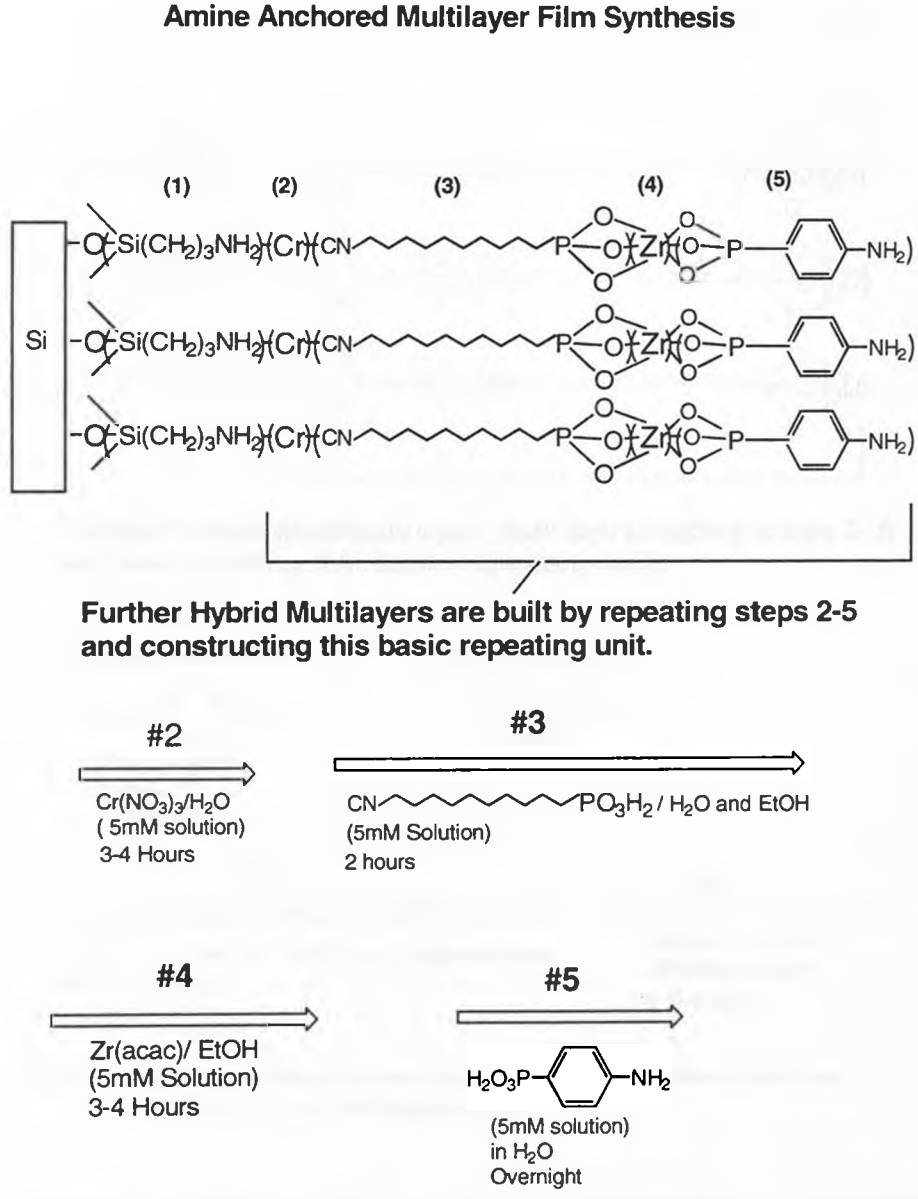


Figure 2.3 Diagram illustrating the procedure for self-assembled multilayer synthesis from a 3-APDES anchor.

Hafnium Anchored Multilayer Film Synthesis

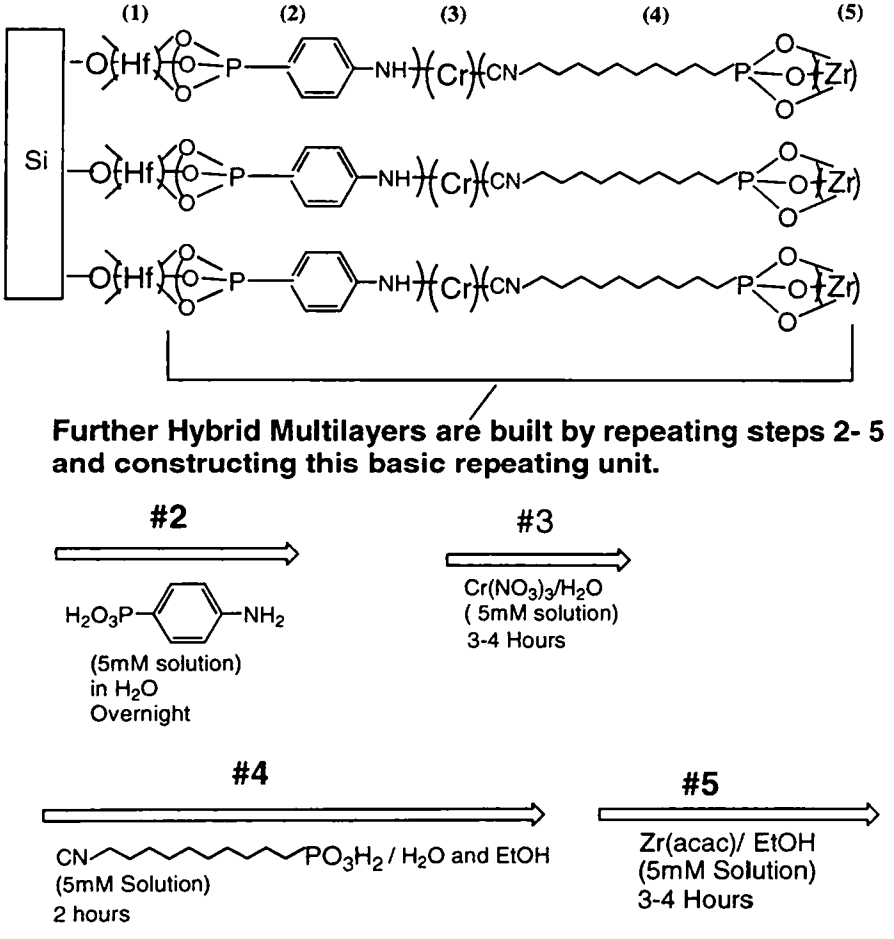


Figure 2.4 Diagram illustrating the procedure for self-assembled multilayer synthesis from a Hafnium anchor.

From a chemist's standpoint the actual process of self-assembly is not as involved as most syntheses, but analysis of these thin films by means of ellipsometry and x-ray photoelectron spectroscopy (XPS) is very time-consuming. After each step in the

synthesis procedure the thickness of the deposited layers on the substrate can be measured by a technique called optical ellipsometry. After a fairly uniform layer is constructed, and analyzed by ellipsometry, the film is analyzed by XPS which provides information on the elemental make-up and elemental ratios present in the film.

IV. Methods: Analytical Techniques

Optical ellipsometry can be used to determine the thickness of the thin films constructed by the self-assembly method. This method uses changes in the polarization state of light as it is reflected from a sample surface at a determined angle[11]. The specific kind of ellipsometer that is used in the Page Lab is known as a null type ellipsometer. Incident light is sent through a polarizer and a quarter wave plate (compensator) where the light becomes elliptically polarized before it is reflected from the film covered substrate at a known angle (70°). The light then is passed through another polarizer, called an analyzer, and a filter that removes all the light except that at a wavelength of 632.8 nm, which is then detected by a photomultiplier tube. The changes in the polarization state of the light which are caused by reflection through the thin film are measured by adjusting the angles of the polarizer and the analyzer until a null is produced at the photomultiplier tube. The angles of the polarizer and analyzer are measurable quantities P and A (with subscripts 1 and 2 for measurements made in different quadrants), which are used to calculate delta and Ψ according to the following mathematical relationships:

$$\Psi = (180 - A_2 + A_1)/2$$
$$\text{delta}_1 = | [P_1 \times 2] - 270 |$$
$$\text{delta}_2 = | [(P_2 - 180) \bullet 2] - 90 |$$
$$\text{delta} = (\text{delta}_2 + \text{delta}_1)/2$$

The calculated value of delta gives a measure of the phase change of the incident light and the calculated value of Ψ gives the corresponding change in amplitude. These values are then used to calculate a thickness for the sample film.

All optical ellipsometry data was obtained from a Rudolph Research Thin Film Ellipsometer, Type 43702-200E, using a tungsten filament incident light source filtered to 632.8 nm, at an incident angle of 70°. The parameters Ψ and delta were used in combination with estimated indices of refraction in a computer program (DAFIBM) provided with the Rudolph Ellipsometer to determine thickness. Figure 2.5 illustrates the basic components of an optical ellipsometer.

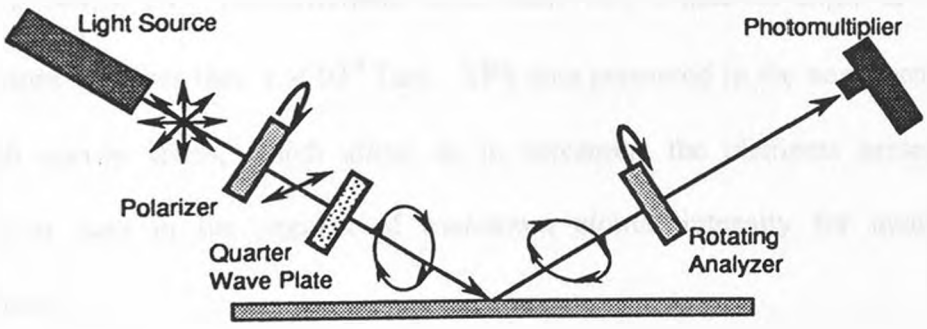


Figure 2.5 Diagram illustrating the basic components of an optical ellipsometer[12].

X-ray photoelectron spectroscopy (XPS) is the other primary analytical technique that was used to probe the molecular make-up of these thin films. XPS measures the binding energy of inner shell electrons, giving information about what atomic species are present near the surface of the sample[10]. The sample is exposed to monochromatic X-rays that cause inner shell electrons to be ejected from the sample. The kinetic energy of these ejected electrons are representative of their binding energies. The binding energy of electrons are characteristic for particular atoms, and therefore atomic species can be determined quantitatively. In addition to atomic identification, this method gives information about the oxidation states of the atoms present, as well as the atomic ratios within the film. Atomic ratios are very important when analyzing thin films for they are a reflection of the order within the film. This technique is inherently surface sensitive because the photoelectrons ejected have a mean-free path of only 20-50 angstroms.

All XPS measurements were made on a Kratos Analytical Axis HS High Performance XPS spectrometer operating at 13.5 kV using a monochromatic Al Kα X-ray source at 1482.6 eV. Measurements were made with a take-off angle of 90° and under a vacuum of better than 1×10^{-8} Torr. XPS data presented in the next section will include both survey scans, which allow us to determine the elements present, and multiplex scan data in the regions of maximum atomic intensity for quantitative elemental ratios.

V. Methods: Control Experiments

In order to develop the optimal procedure for synthesis of self-assembled hybrid multilayers, control experiments were developed to determine the effect of factors such

as temperature and choice of solvent for rinsing during the layering process. The procedures established on the two previous multilayer systems were the largest sources of information on developing a procedure for the hybrid system[3,4], but if any other factors could improve on these procedures they would be worth investigating. The first control experiment was designed to measure the effect of heating during the layering process. Two pieces of the same 3-APDES anchored silicon wafer were used for this experiment. One piece was labeled experimental (see results section, wafer 1503) and all layering was done in an oven at ~50°C. The second piece of the wafer was layered in the exact fashion of wafer 1503, but was layered in ambient laboratory conditions (see results section, wafer 1502). In this way a control was in place to determine the effect heating would have on the layering process.

The second control experiment was designed to determine whether the choice of solvent used to rinse the wafers after each layering step would effect the thickness of the layers. Like experiment one, two pieces of the same anchored silicon wafer were used in control experiment two. One piece was labeled experimental (see results section, wafer 1504) and was rinsed with the solvent present in the layering solution used in each step. The second piece of wafer was rinsed with acetone after each layering step (see results section, wafer 1505). In this way a control was in place to determine which solvent would more effectively remove all unbound molecules from the bulk structure. It was thought that unbound molecules would be better removed with solvents that the molecules are more soluble in, rather than the acetone solution. The data from both of

these control experiments as well as layering using the preceding procedure are given in the results section.

RESULTS AND DISCUSSION

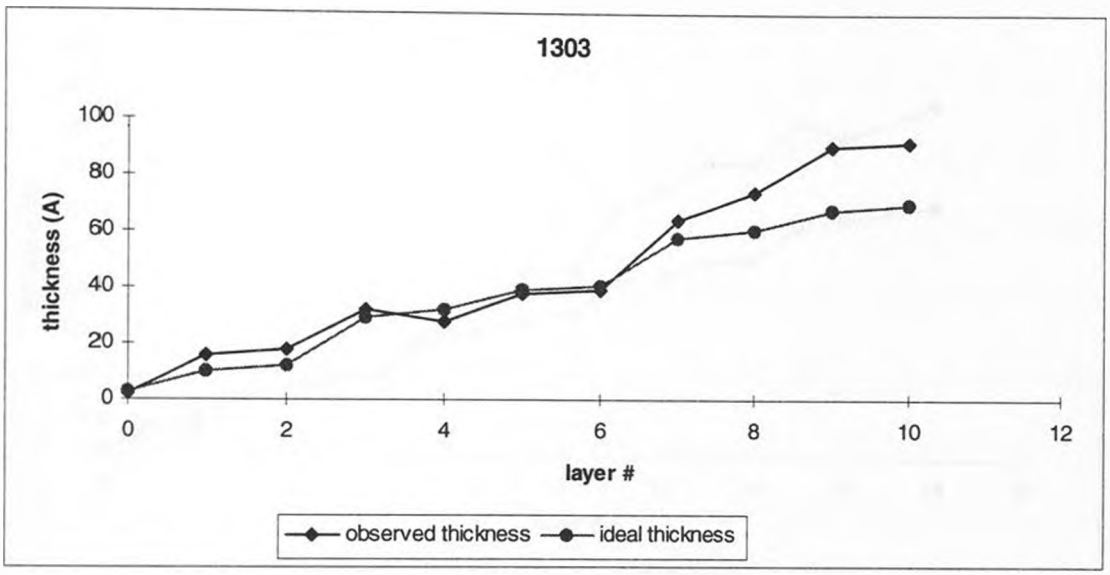
This section will be used to present and discuss growth and characterization data for the thin films that have been constructed using the SA technique. Data from the analytical techniques of ellipsometry and x-ray photoelectron spectroscopy is presented here, as is mass spectroscopy data from the IDPA linking molecule.

I. Ellipsometry Data

Ellipsometry data is presented in two forms in this section: 1) Thickness data showing ellipsometry measurements after each step in the layering process is presented, as is the ideal thickness at each step. Data is presented in plots of layer step versus thickness in angstroms. 2) Thickness data is also presented as thickness at each repeating unit in the layer process, or as each full hybrid layer is completed. Data is presented in plots of hybrid layer step versus hybrid layer thickness in angstroms. Data for the ideal thickness at each hybrid layer is also presented. The observed thickness data should give a linear relationship so a linear regression can be done to calculate average hybrid layer thickness for the film, as well information on the linearity of the relationship.

The first set of ellipsometry data is presented for wafers that were constructed using the hafnium anchor scheme. Wafers 1303 and 1304 were constructed from October to December, 1997. Data was analyzed using an index of refraction of 1.50.

a)



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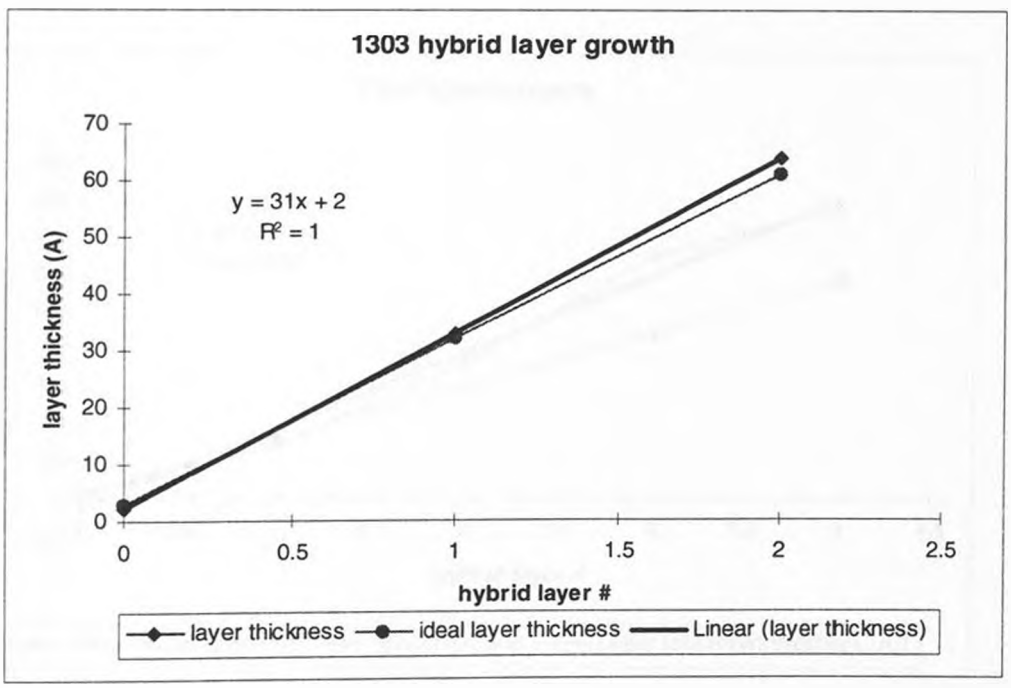
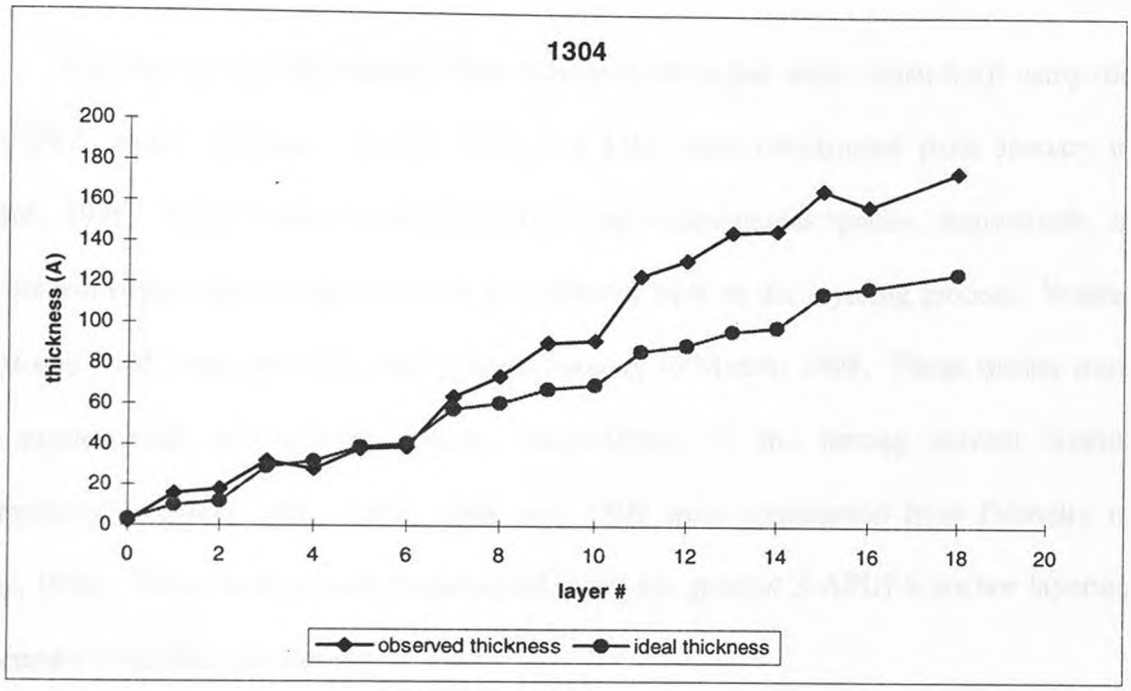


Figure 3.1 Ellipsometry data for wafer 1303: a) thickness in angstroms versus layer step number. b) Hybrid layer thickness versus hybrid layer number. The average hybrid layer thickness is 31 angstroms.

a)



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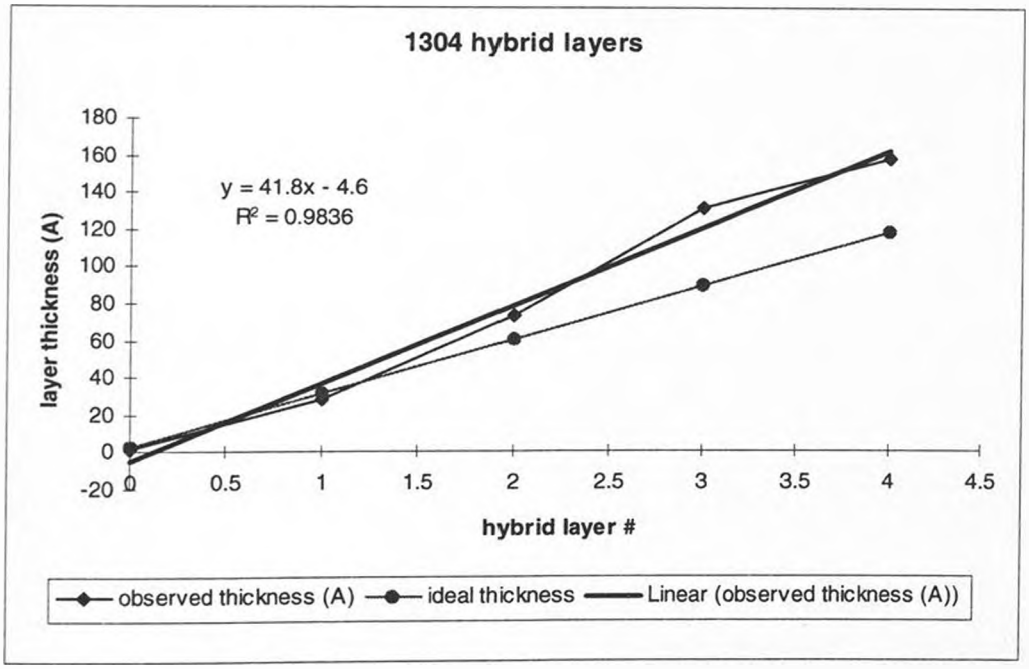
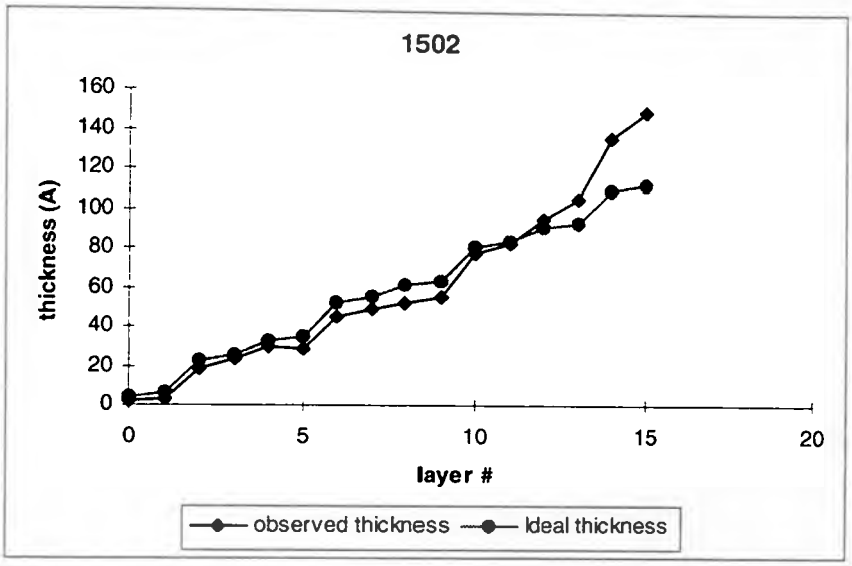


Figure 3.2 Ellipsometry data for wafer 1304: a) thickness in angstroms versus layer step number. b) Hybrid layer thickness versus hybrid layer number. The average hybrid layer thickness is 41.8 angstroms.

The next set of ellipsometry data represent films that were constructed using the 3-APDES anchor scheme. Wafers 1502 and 1503 were constructed from January to March, 1998. These wafers were the control and experimental species, respectively, in the control experiment designed to test the effect of heat on the layering process. Wafers 1504 and 1505 were also constructed from January to March, 1998. These wafers were the experimental and control species, respectively, in the rinsing solvent control experiment. Wafers 1506, 1507, 1508, and 1509 were constructed from February to May, 1998. These wafers were constructed using the general 3-APDES anchor layering procedure described previously.

a)



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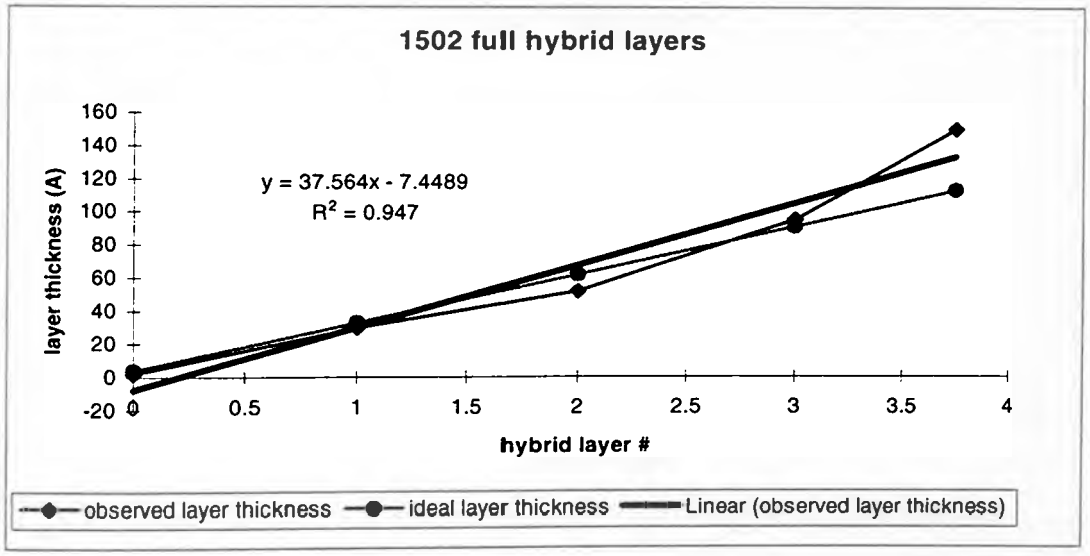
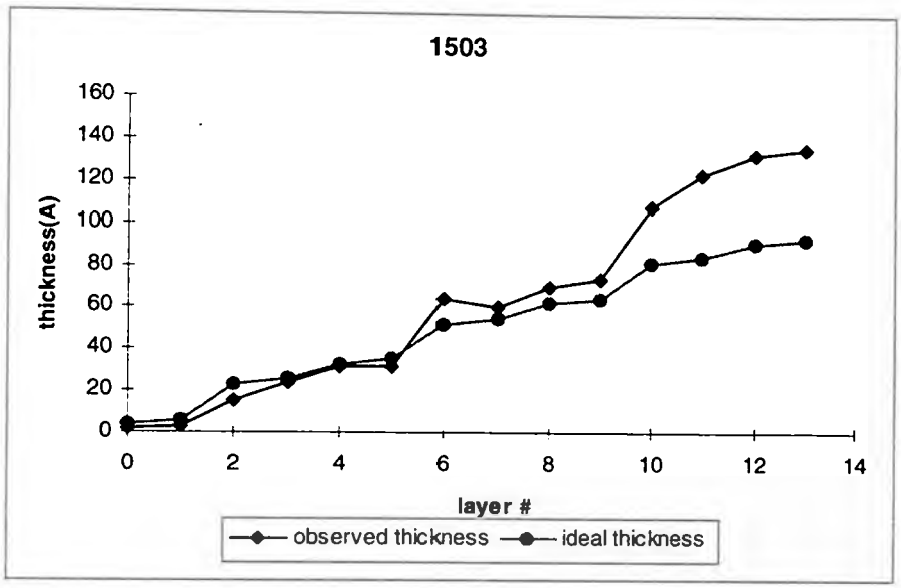


Figure 3.3 Ellipsometry data for wafer 1502, control species for the heating control experiment: a) Thickness in angstroms versus layer step number. b) Hybrid layer thickness versus hybrid layer number. The average hybrid layer thickness is 37.6 angstroms.

a)



b)

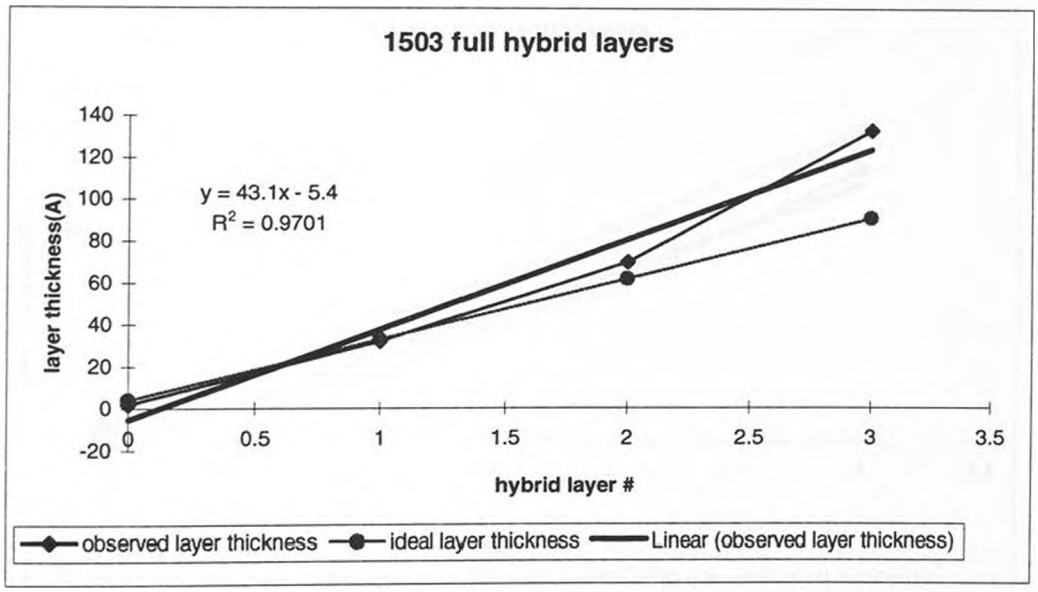
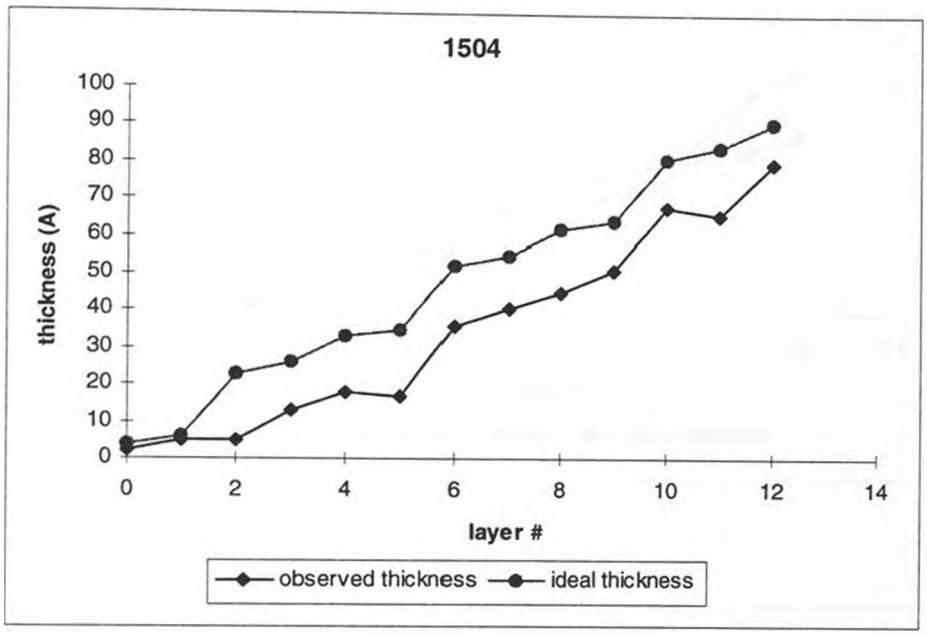


Figure 3.4 Ellipsometry data for wafer 1503, experimental species for the heating control experiment: a) Thickness in angstroms versus layer step number. b) Hybrid layer thickness versus hybrid layer number. The average hybrid layer thickness is 43.1 angstroms.

a)



b)

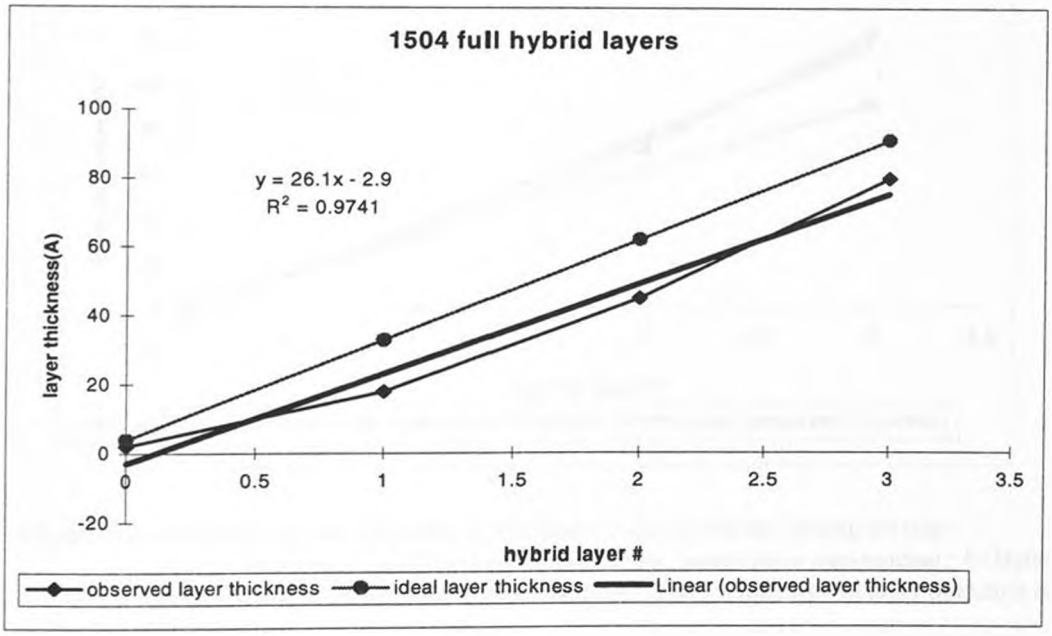
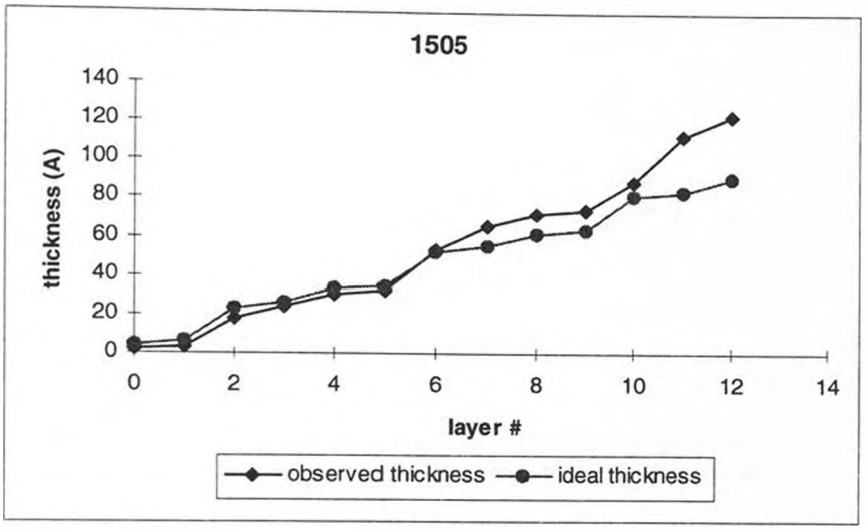


Figure 3.5 Ellipsometry data for wafer 1504, experimental species for the rinsing solvent control experiment: a) Thickness in angstroms versus layer step number. b) Hybrid layer thickness versus hybrid layer number. The average hybrid layer thickness is 26.1angstroms.

a)



b)

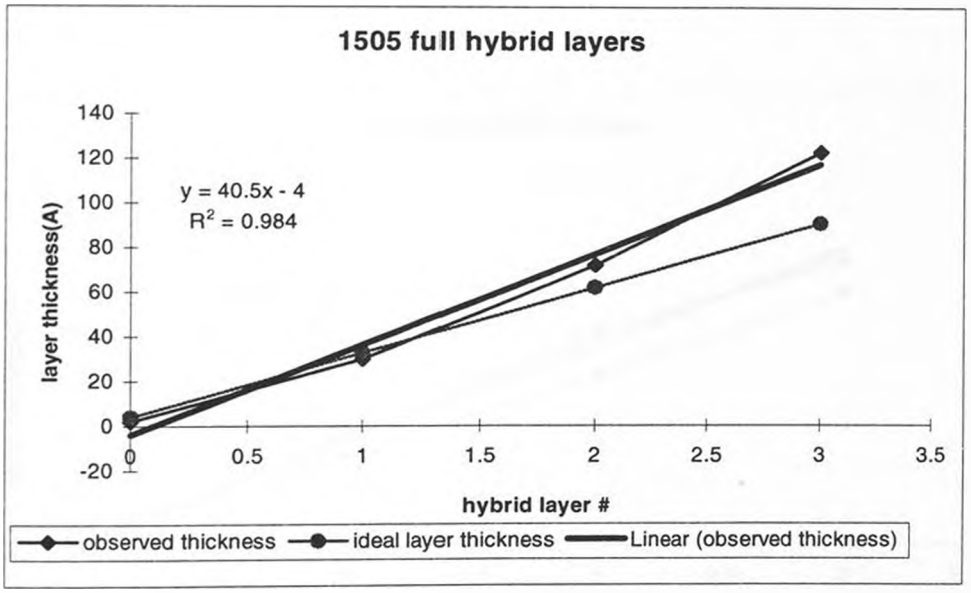
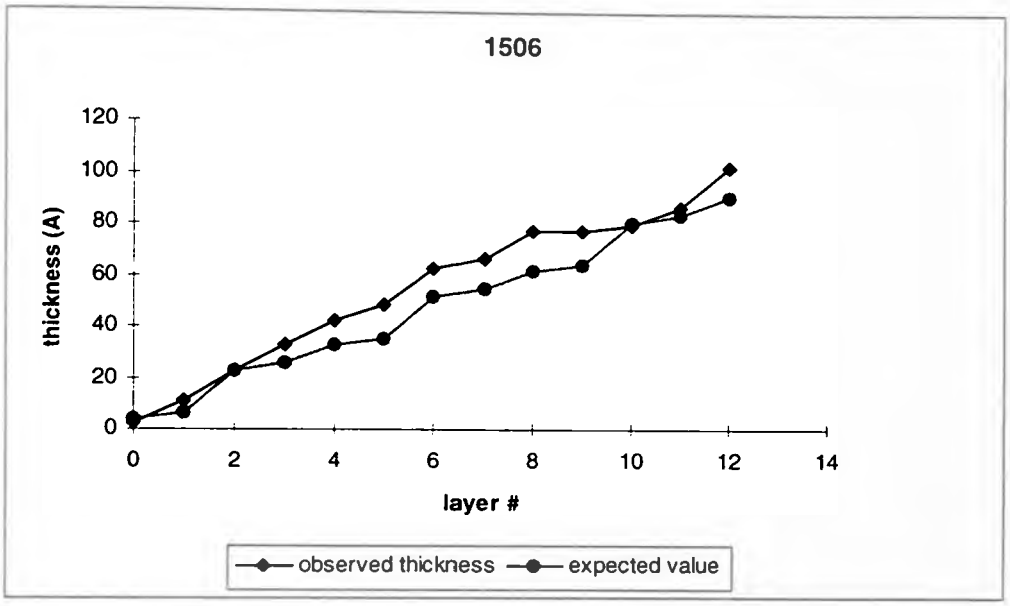


Figure 3.6 Ellipsometry data for wafer 1505, control species for the rinsing solvent control experiment: a) Thickness in angstroms versus layer step number. b) Hybrid layer thickness versus hybrid layer number. The average hybrid layer thickness is 40.5 angstroms.

a)



b)

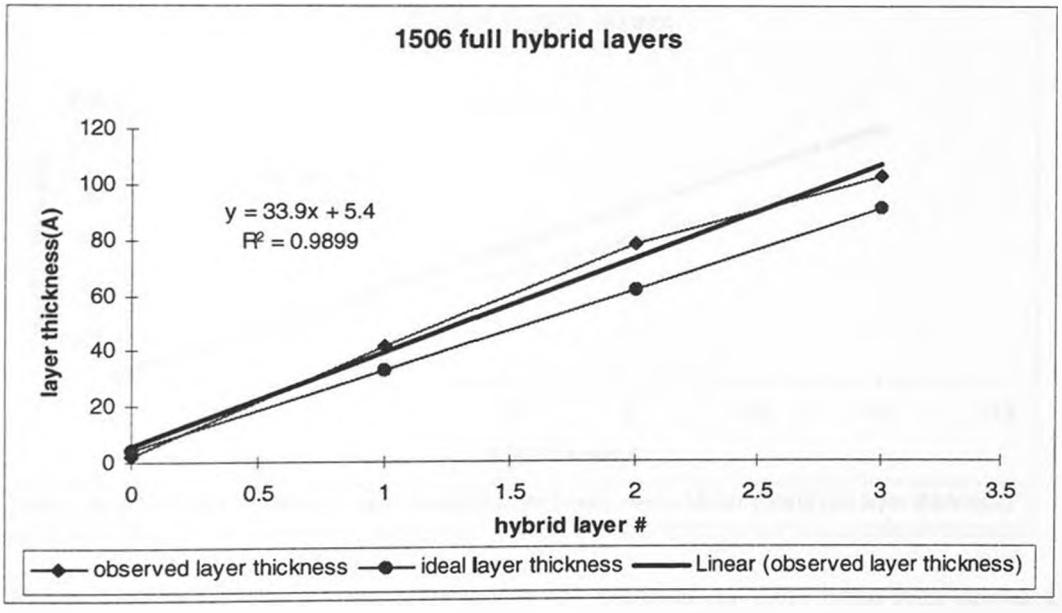
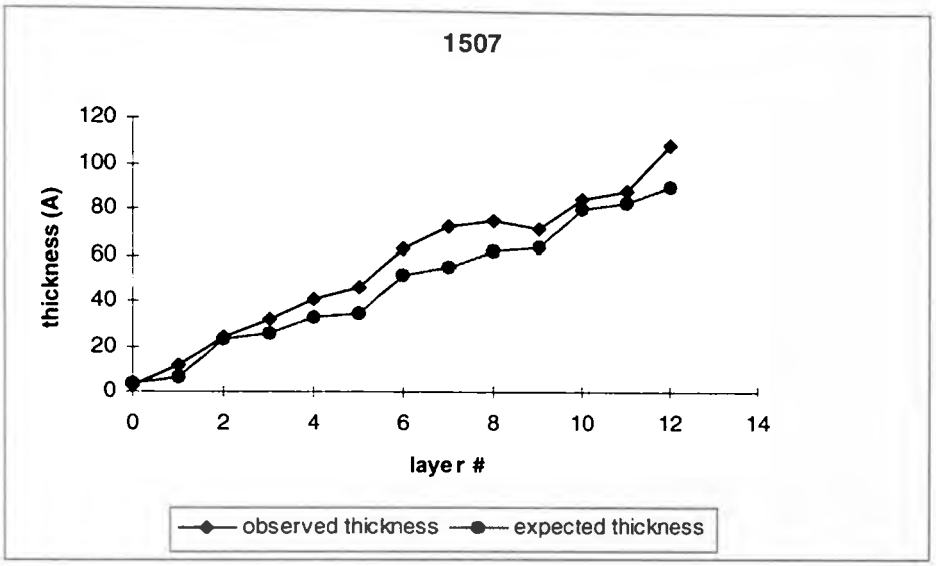


Figure 3.7 Ellipsometry data for wafer 1506: a) Thickness in angstroms versus layer step number. b) Hybrid layer thickness versus hybrid layer number. The average hybrid layer thickness is 33.9 angstroms.

a)



b)

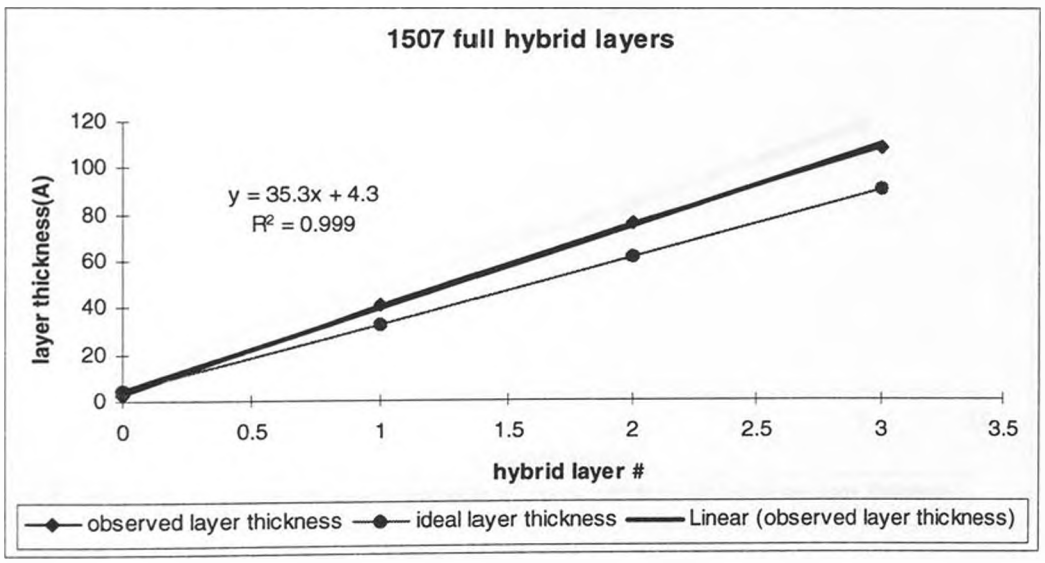
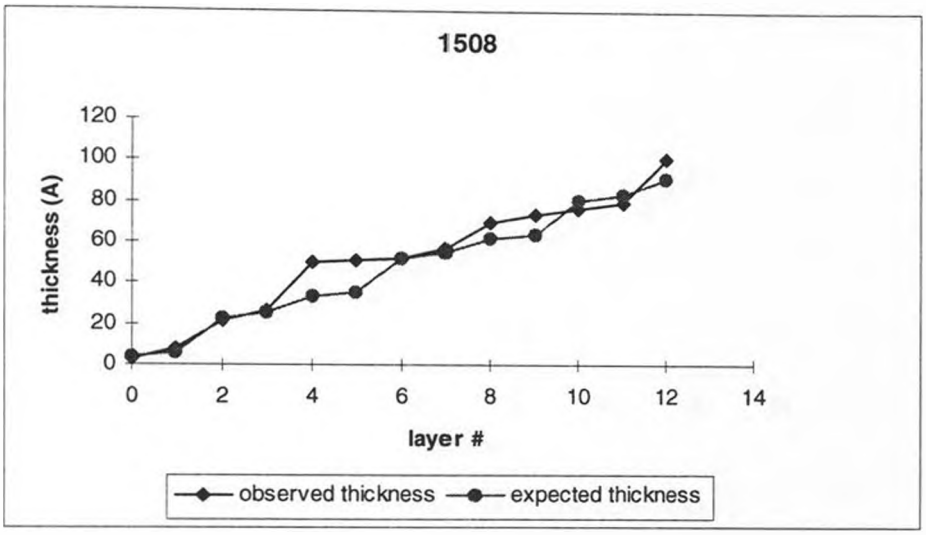


Figure 3.8 Ellipsometry data for wafer 1507: a) Thickness in angstroms versus layer step number. b) Hybrid layer thickness versus hybrid layer number. The average hybrid layer thickness is 35.3 angstroms.

a)



b)

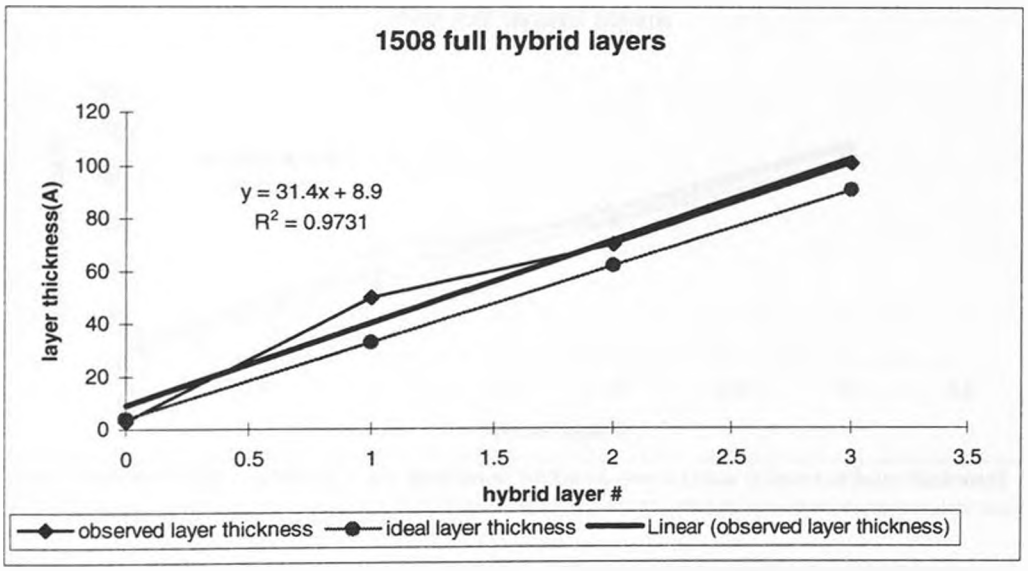
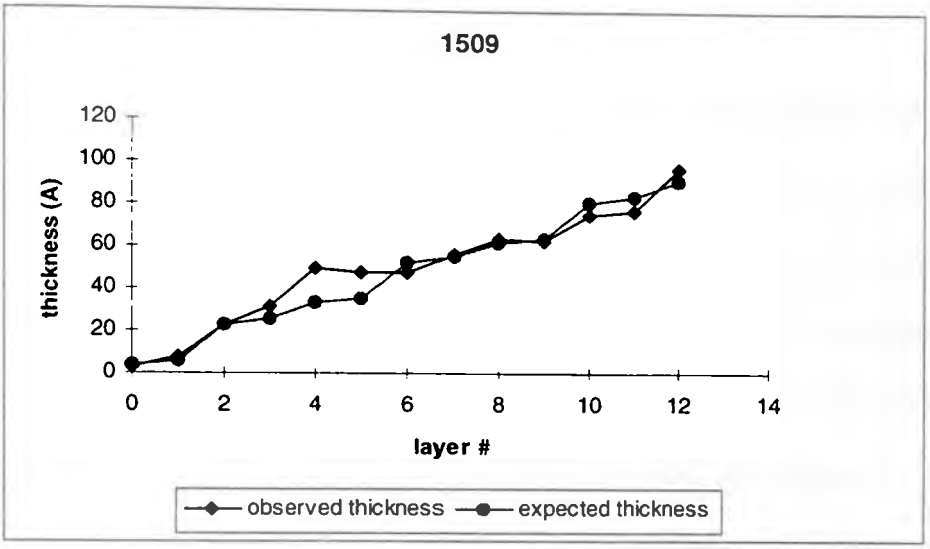


Figure 3.9 Ellipsometry data for wafer 1508: a) Thickness in angstroms versus layer step number. b) Hybrid layer thickness versus hybrid layer number. The average hybrid layer thickness is 31.4 angstroms.

a)



b)

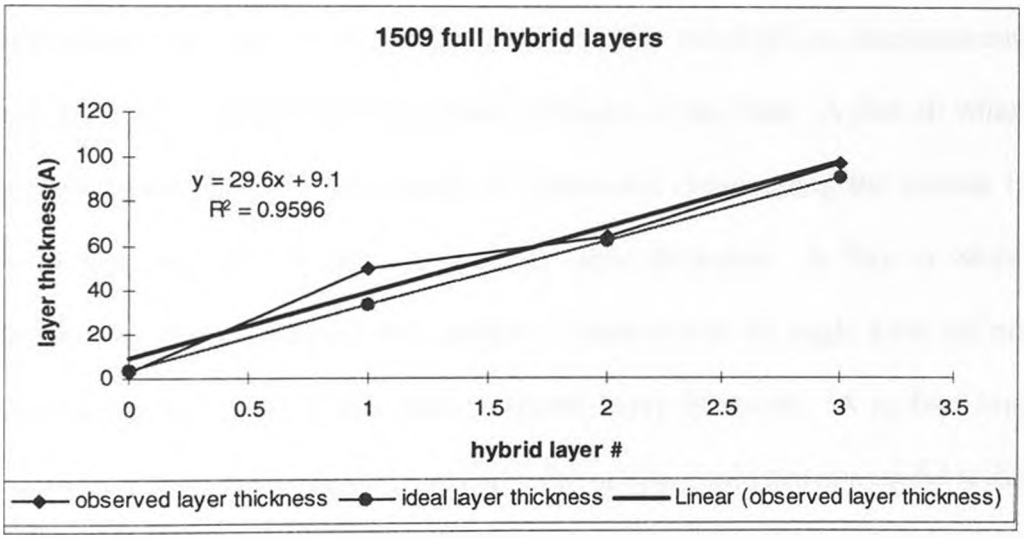


Figure 3.10 Ellipsometry data for wafer 1508: a) Thickness in angstroms versus layer step number. b) Hybrid layer thickness versus hybrid layer number. The average hybrid layer thickness is 29.6 angstroms.

II. Ellipsometry Conclusions

Ellipsometry data shows predictable growth with each molecule used in the hybrid system. The regularity of layer growth has been problematic, at times, for the IDPA linking molecule. The expected layer thickness for this molecule is approximately 17 angstroms. Observed layer thicknesses for IDPA have reached 25-30 angstroms. This fact raises the question of possible polymerization of this molecule. Research has shown the possibility of isocyanide ligands to polymerize under certain conditions[13,14].

The self-assembly process is equal parts technique and conditions. The minimized variability of layer thickness reflects the pursuit of optimal conditions and a refined procedure with which to construct the films. The variability in thickness can be a measure of the reproducibility of the surface coverage of the film. A film in which the molecules are densely packed will orient its molecules closer along the normal to the substrate surface, and give a more predictable layer thickness. A film in which the molecules are less densely packed will exhibit a considerable tilt angle from the normal to the substrate surface, and a less than predicted layer thickness. A surface imaging technique, such as near-field scanning optical microscopy, could prove a useful technique in observing surface coverage and film regularity[15].

Another problematic point found in this ellipsometry data is the divergence of observed thickness from predicted thickness as the films approach a thickness of approximately 100 angstroms. While the variability of thickness of IDPA layers does contribute to this effect, this trend may also be due to irregular bonding configurations between layered molecules as successive layers are added. The bonding diagrams

presented in the methods section were illustrations of the bonding in the system, and most likely do not reflect the regularity of the bonding within the true film. The possibility of cross-bonding between layers or side reactions with disassociated ligands in solution does exist, and could contribute to the divergence seen as the films reach a thickness of 100 angstroms.

Overall, the ellipsometry data shows that this system can be constructed and with fair predictability of layer thickness. More refinement of technique and optimization of layering conditions are needed to construct films with more consistent growth patterns. More testing of the IDPA linking molecule is also needed to determine how it transforms in solution, and how any transformations may affect its bonding patterns in this system.

III. Mass Spectroscopy Data

A mass spectroscopy analysis was done on two samples of the linking molecule IDPA; a solid sample and a sample dissolved in water. The inspiration for this analysis was the observed inconsistant growth at the IDPA layer step, as can be seen by inconsistant ellipsometry data. An analysis by mass spectroscopy will show various molecular weight segments of the original molecule, as well as any changes in molecular weight (added or subtracted) from the original molecule[16]. This experiment was designed to look for changes in the linking molecule when it is put into solution. One common transformation of isocyanide ligands is the formation of a formamide which results from addition of water across the carbon-nitrogen bond of the isocyanide.

Data is presented for both the solid sample and the solvated sample. Both samples were run at Oregon State University, by Brian Arbogast, on Feburary 12, 1998. The original molecule has a molecular weight of approximately 247 grams per mole, thus the formamide would have a molecular weight of approximately of 265 grams per mole.

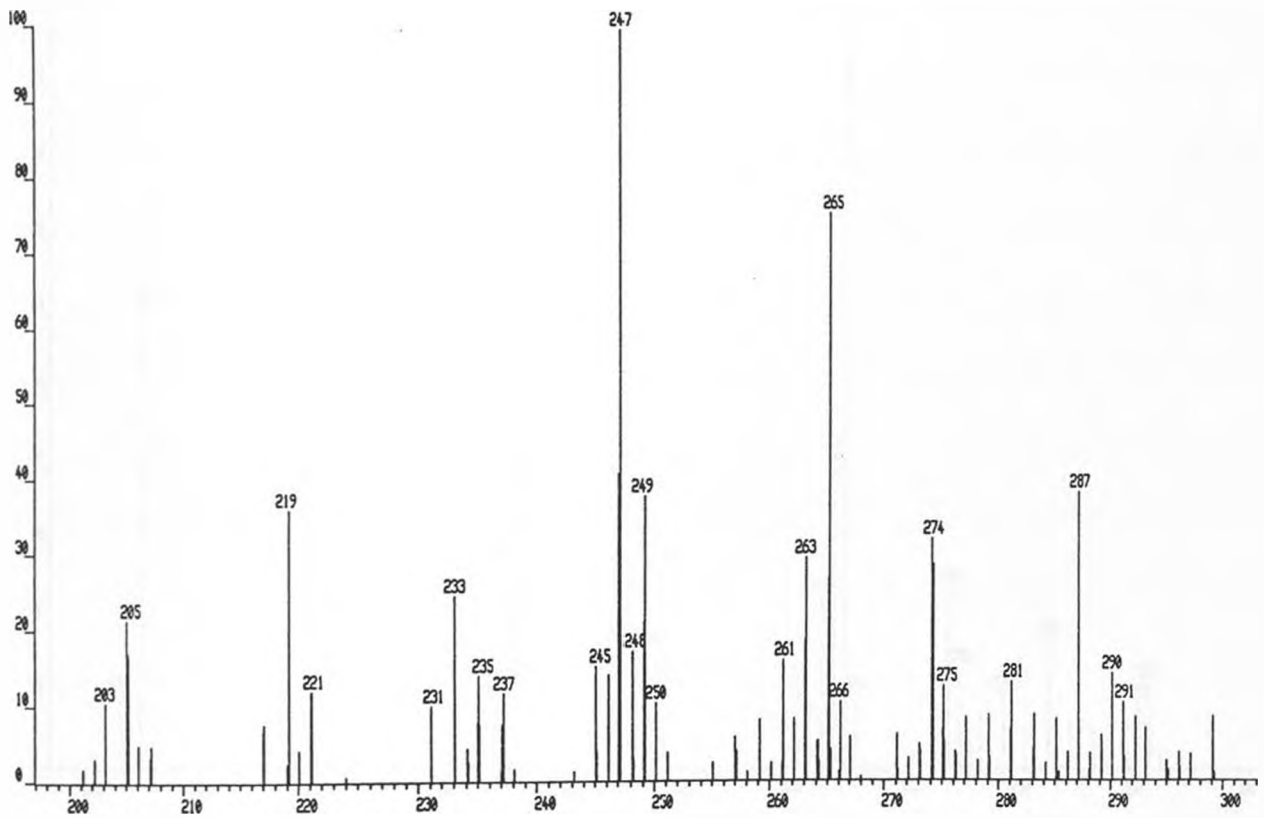


Figure 3.11 Mass spectroscopy data for the IDPA molecule in solid form. The original molecule is represented by the peak at 247g.

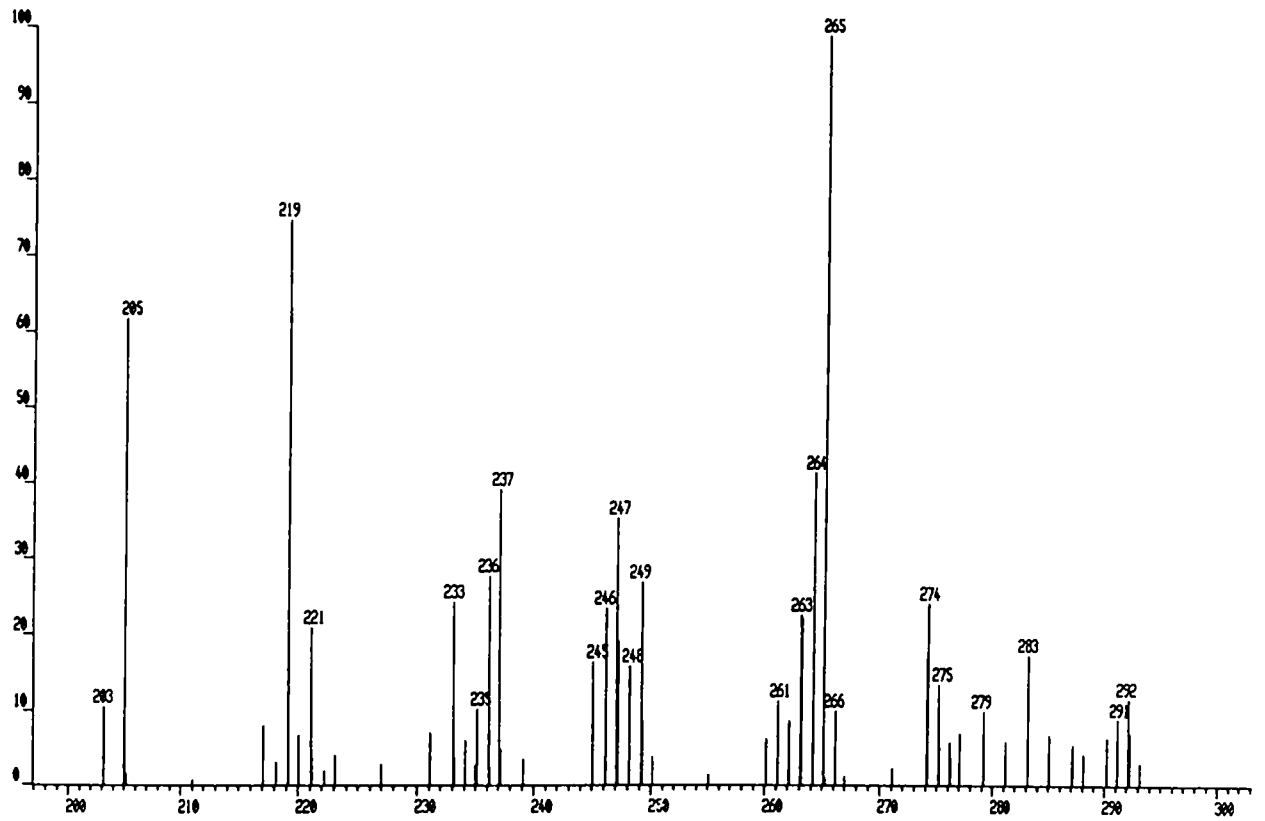


Figure 3.12 Mass spectroscopy of the IDPA molecule in water solution. Note the relative intensities of the original molecule at 247g and the peak at 265g which shows the addition of water to the original molecule forming a formamide.

IV. Mass Spectroscopy Conclusions

Mass spectroscopy was used to probe for transformations of the IDPA linking molecule in solution. It is clear that after only a short time (1-2 days) the formamide form of the IDPA molecule is the predominant species found in solution. In the future this molecule can be put through simple bonding tests using the technique of UV-Vis spectroscopy to determine the way in which the formamide form of the IDPA molecule bonds when incorporated into the hybrid system. The solution to the problem as of now is using fresh solutions of IDPA at each layer step, which causes the problem of supply of IDPA since it is a molecule that must be synthesized in the laboratory. The fresh solutions are made with a mixture of water and ethanol, in a 1:1 ratio, in hopes of lessening this transformation effect. We also plan to investigate the use of anhydrous aprotic solvents (such as DMF) as a possible route to making stable solutions by preventing hydration of the isocyanide functionality.

V. X-ray Photoelectron Spectroscopy Data

X-ray photoelectron spectroscopy data is presented for wafers 1502 and 1503. This data was collected in collaboration with Mike Ansell, a graduate student in the Page Lab. The data will consist of a survey scan of all the atomic species present close to the surface of the film, as well as more quantitative scans of particular elemental peaks of interest. Elemental peaks are presented along with corresponding ideal peak positions[17]. All peaks presented were referenced to the carbon peak at 284.5eV. This data will show which species are present in the film, along with their atomic ratios as discussed previously.

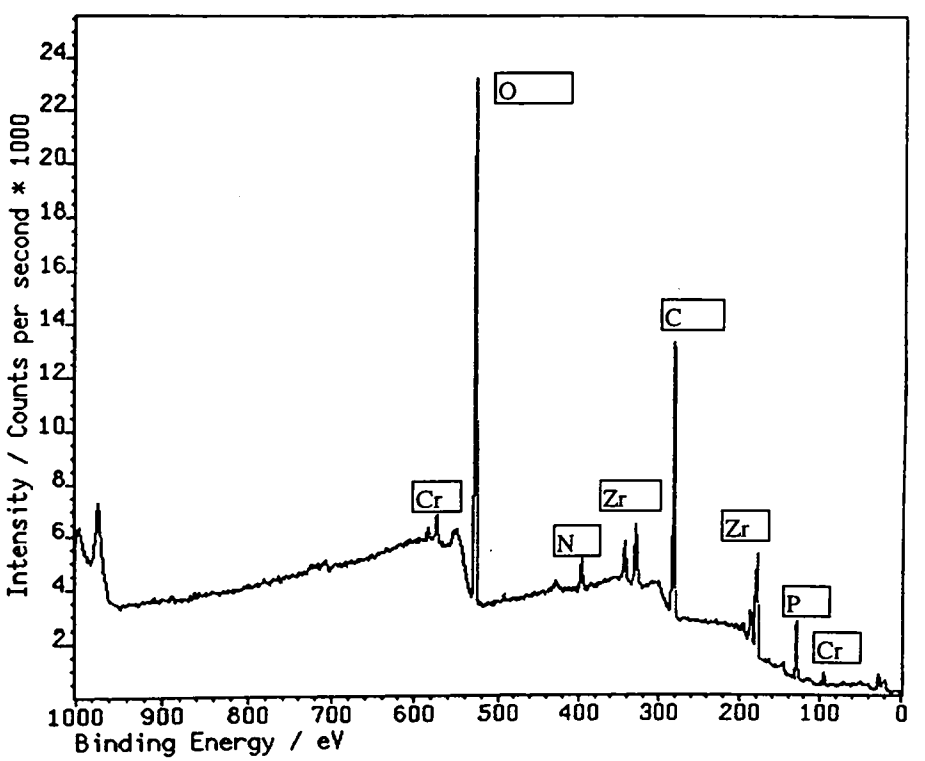
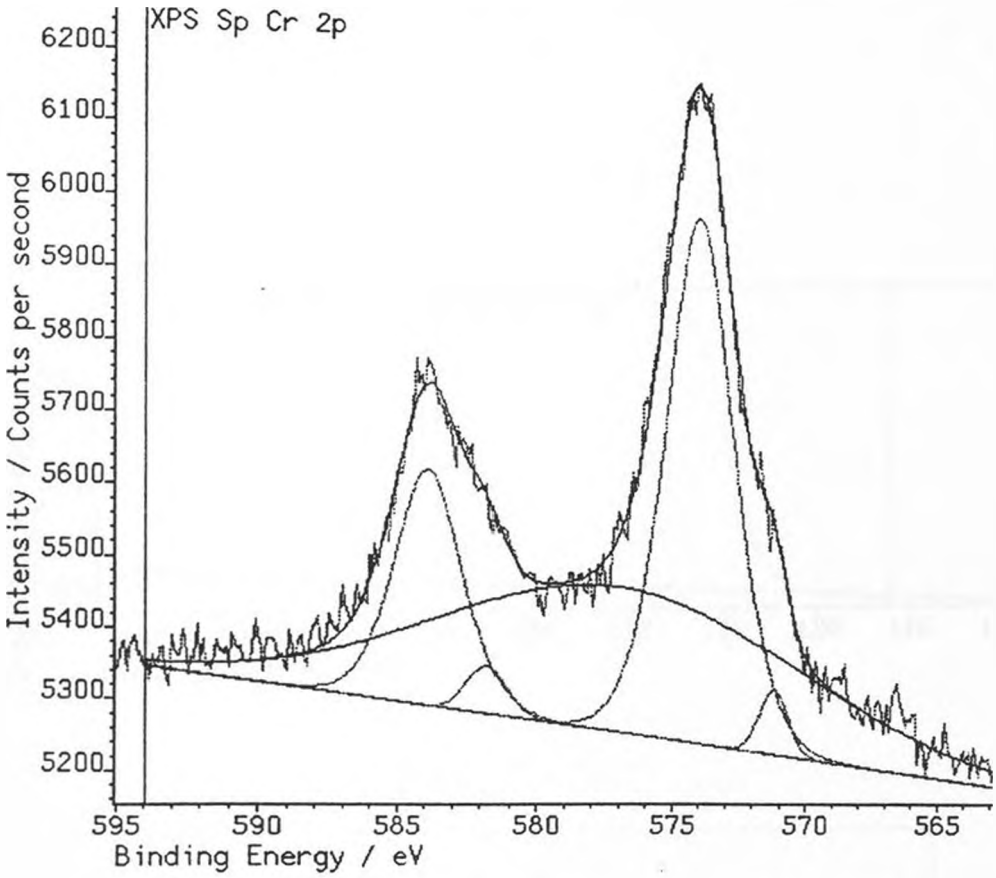


Figure 3.13 Survey XPS scan of wafer 1502 with atomic peaks identified. This scan was done with a pass energy of 80eV.

a)



b)

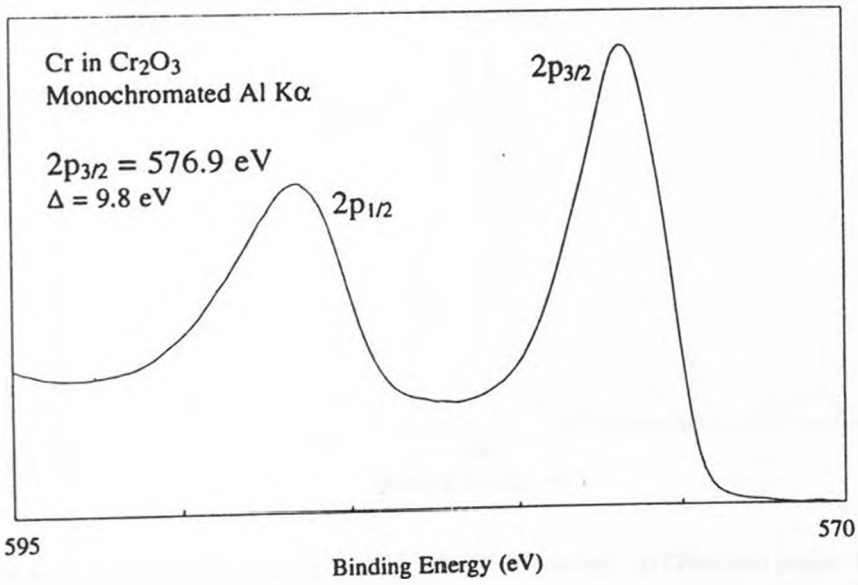
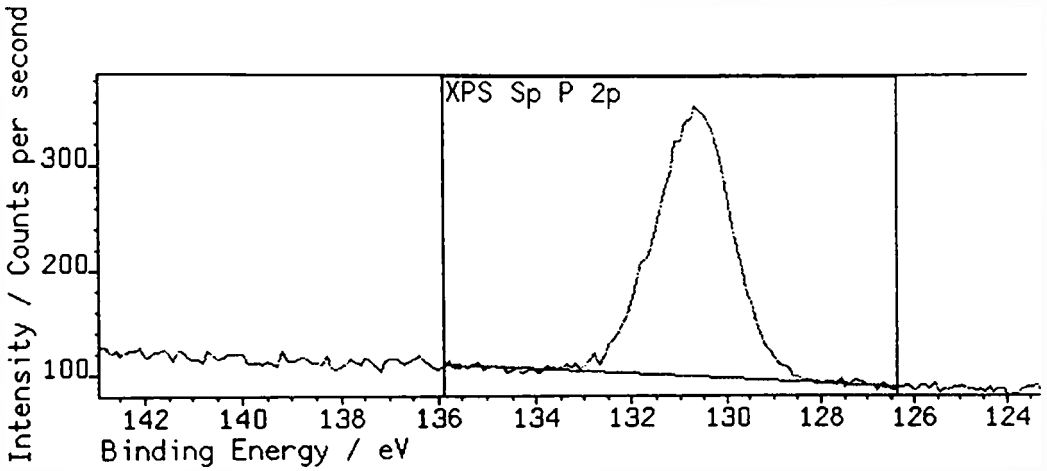


Figure 3.14 XPS data from wafer 1502 for the Cr 2p orbitals: a) Observed peak. b) Reference peak position. The presence of two peaks is due to spin-orbital splitting which gives a 1:2 ratio for p orbitals[17].

a)



b)

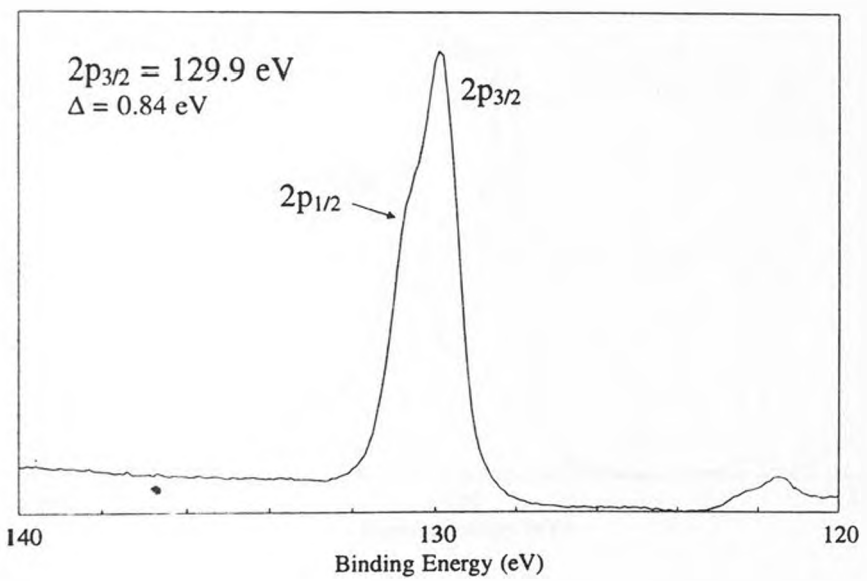
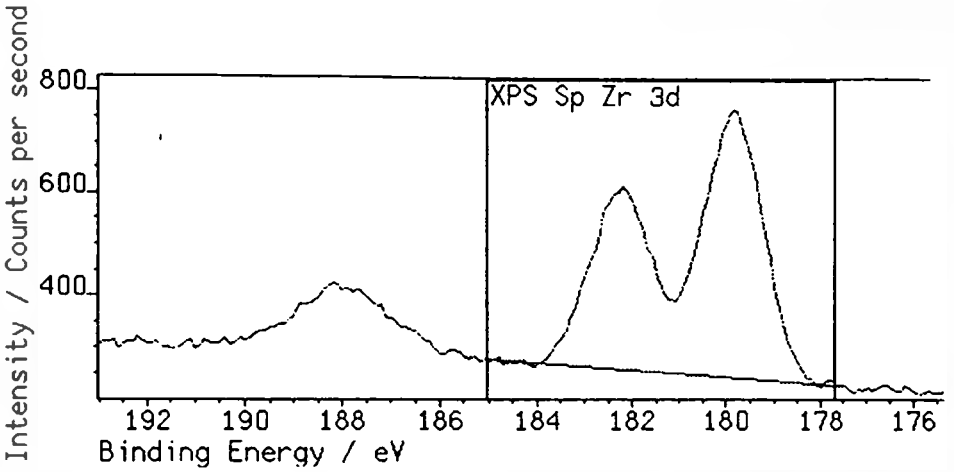


Figure 3.15 XPS data from wafer 1502 for the P 2p orbitals: a) Observed peaks. b) Reference peak position. Here the spin-orbital splitting results in an added feature on the left side of the phosphorus peak.

a)



b)

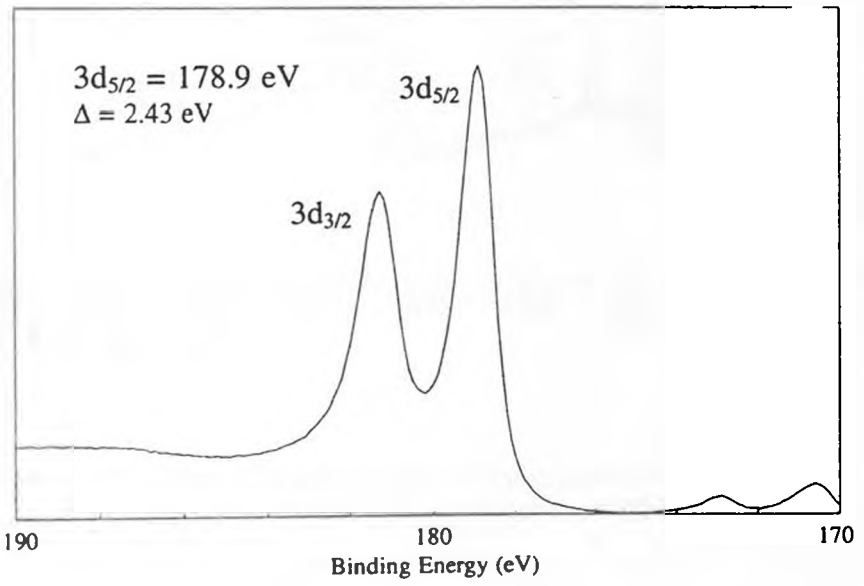


Figure 3.16 XPS data from wafer 1502 for the Zr 3d orbitals: a) Observed peaks. b) Reference peak positions. For the d orbitals the spin-orbital splitting is a 2:3 ratio which explains the splitting of this peak[17].

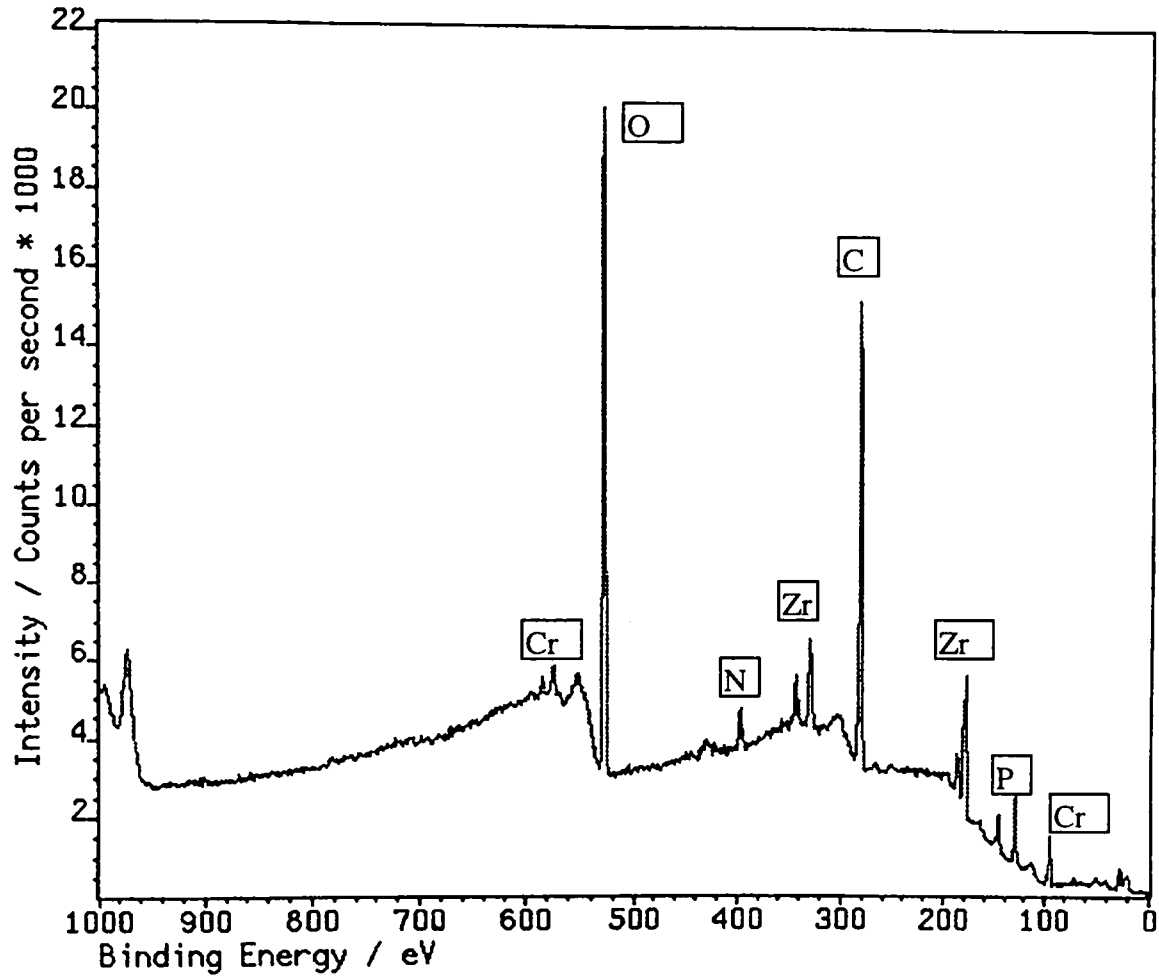
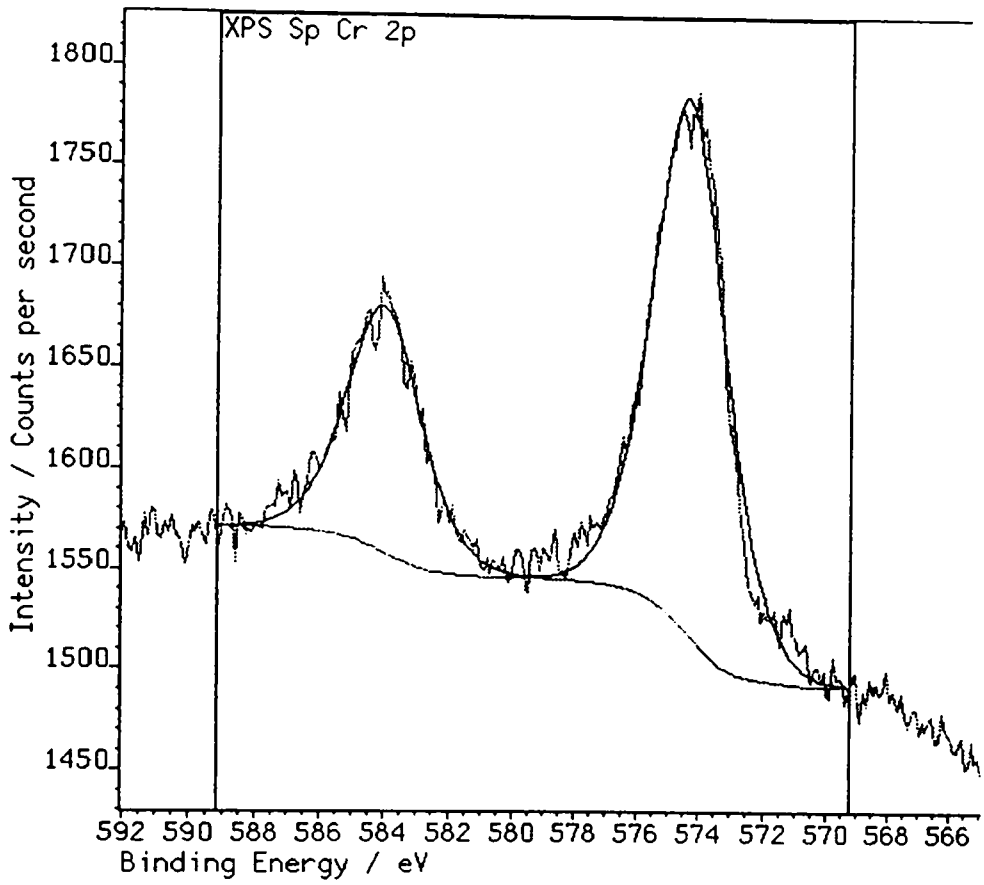


Figure 3.17 Survey XPS scan of wafer 1503 with atomic peaks identified. This scan was done with a pass energy of 80eV.

a)



b)

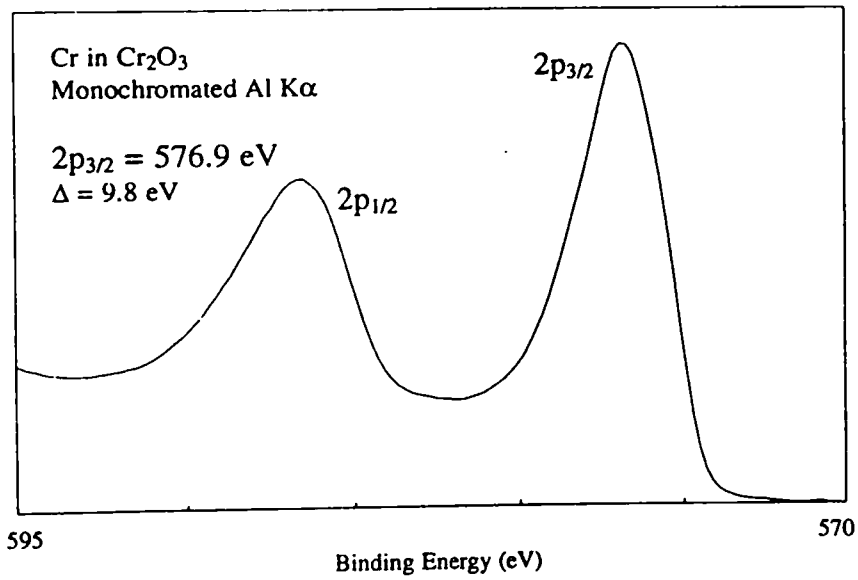
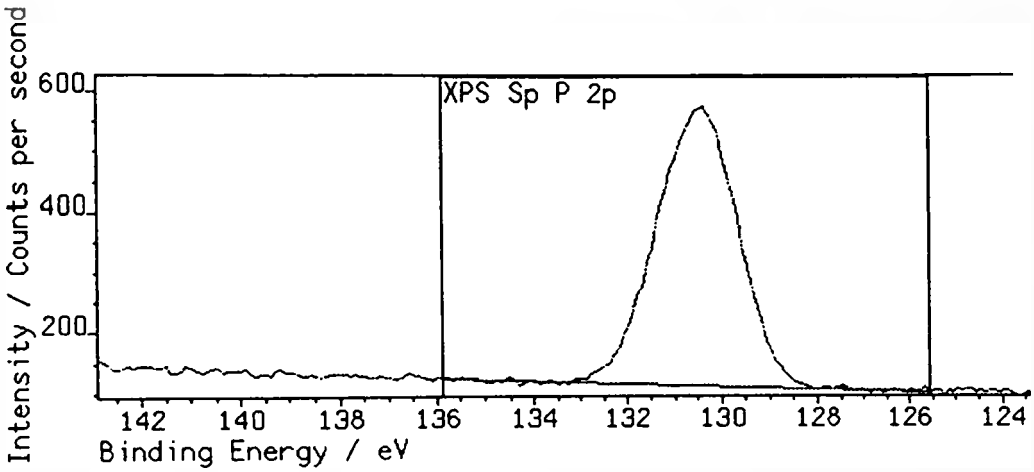


Figure 3.18 XPS data from wafer 1503 for the Cr 2p orbitals: a) Observed peak. b) Reference peak position. The presence of two peaks is due to spin-orbital splitting which gives a 1:2 ratio for p orbitals[17].

a)



b)

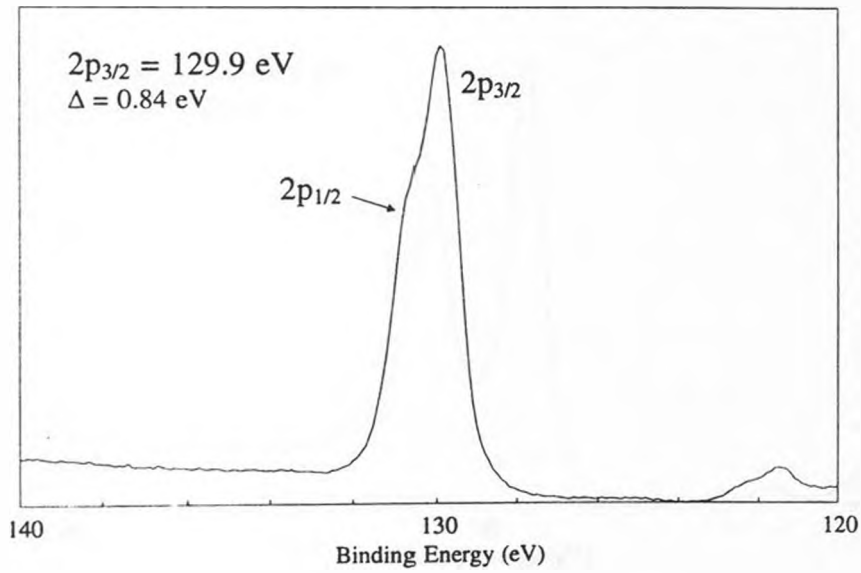
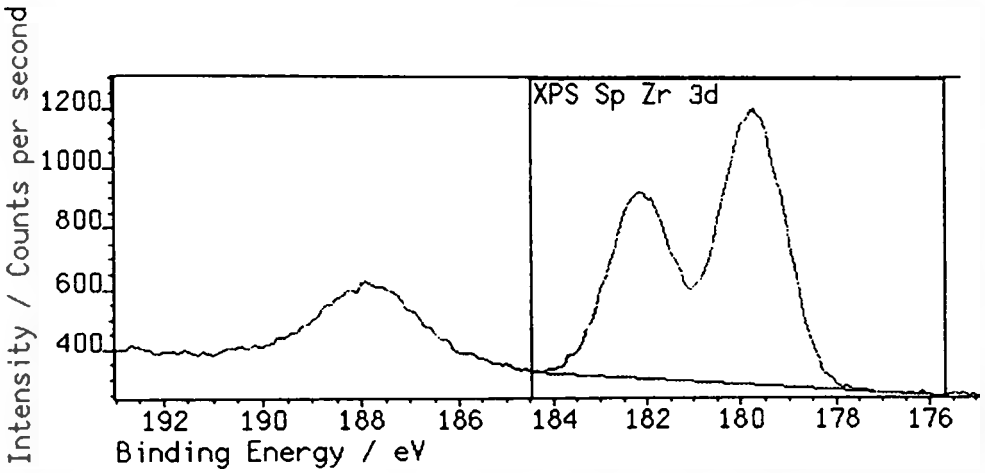


Figure 3.19 XPS data from wafer 1503 for the P 2p orbitals: a) Observed peaks. b) Reference peak position. Here the spin-orbital splitting results in an added feature on the left side of the phosphorus peak.

a)



b)

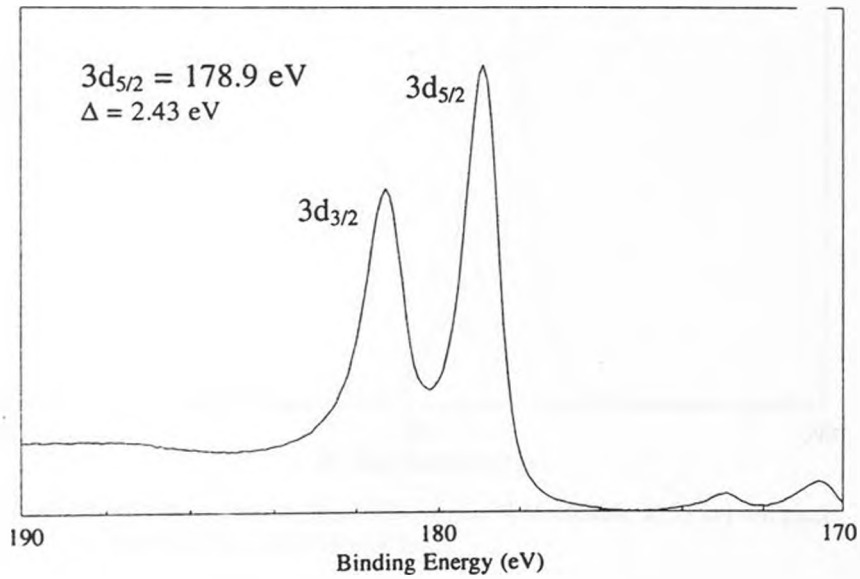
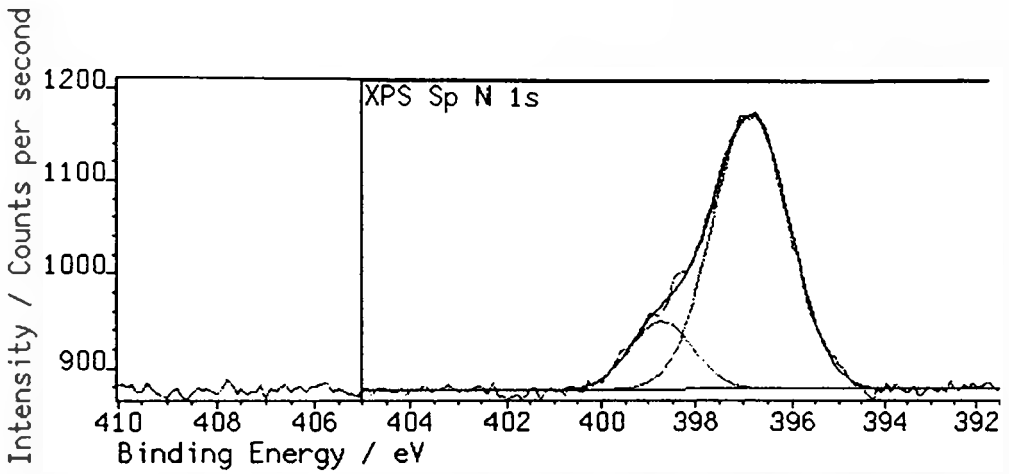


Figure 3.20 XPS data from wafer 1503 for the Zr 3d orbitals: a) Observed peaks. b) Reference peak positions. For the d orbitals the spin-orbital splitting is a 2:3 ratio which explains the splitting of this peak[17].

a)



b)

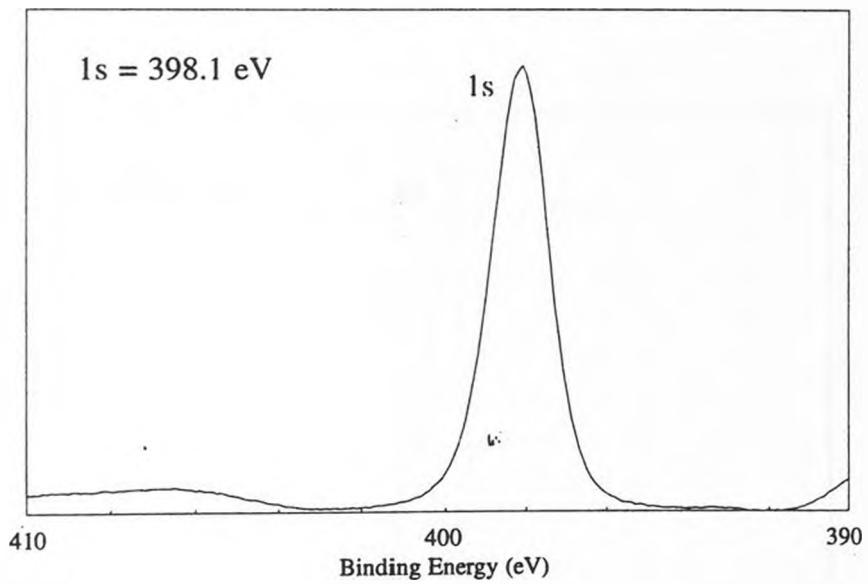
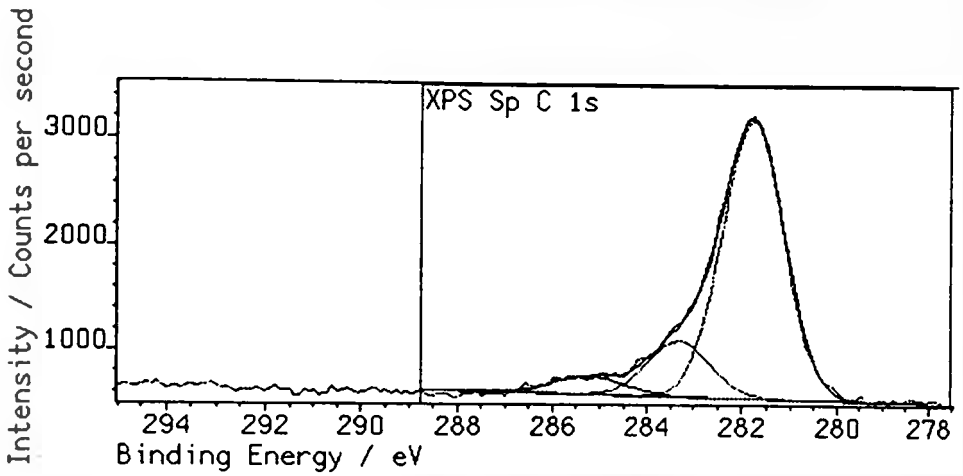


Figure 3.21 XPS data from wafer 1503 for the N 1s orbital: a) Observed peaks. b) Reference peak positions.

a)



b)

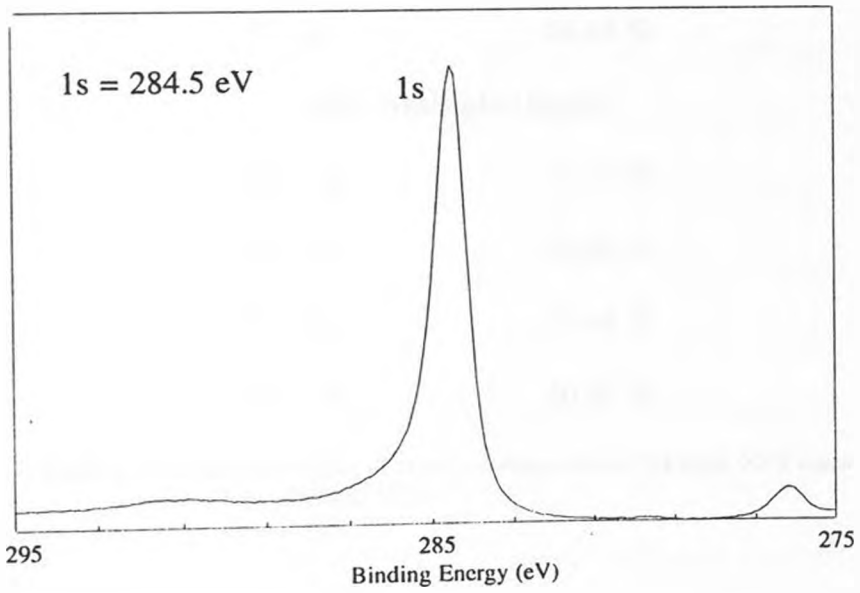


Figure 3.22 XPS data from wafer 1503 for the C 1s orbital: a) Observed peaks. b) Reference peak positions.

Atomic concentrations as determined by XPS

1502- Multiplex Scans

C – 1s	81.40 %
Cr – 2p	2.40 %
N – 1s	5.19 %
Zr – 3d	3.69 %
P – 2p	7.32 %

1502- Zr & P Scan

Zr – 3d	33.52 %
P – 2p	66.48 %

1503- Multiplex Scans

Cr – 2p	11.10 %
N – 1s	30.40 %
P – 2p	38.44 %
Zr – 3d	20.06 %

Table 3.1 Calculated values of atomic concentrations for three XPS scans of wafers 1502 and 1503.

VI. X-ray Photoelectron Spectroscopy Conclusions

The X-ray photoelectron spectroscopy data presented here is very promising for the development of this hybrid multilayer thin film system. All atomic species predicted in the system are present in the XPS survey scans for both wafers that were analyzed. The zirconium and phosphorus ratio is nearly exactly what we expect, and shows the strength of the interaction between zirconium and phosphonate functional groups. The calculated atomic concentrations for wafer 1502 show a nearly perfect ratio of phosphorus to zirconium at 2:1. Wafer 1503 also exhibits a phosphorus to zirconium ratio of nearly 2:1.

The chromium peaks for both samples show evidence of multiple oxidation states, probably resulting from the chromium (III) being reduced to chromium (I) in the film. Such a reduction could also play a role in the bonding of the IDPA linking molecule that subsequently binds to the chromium layer. Chromium to nitrogen atomic concentration ratios for wafer 1503 reflect the fact that too much IDPA is being deposited, showing nearly a 3:1 ratio, above the predicted 2:1 ratio. However, the chromium to nitrogen ratio for wafer 1502 is closer to 2:1. A future investigation using UV-Vis and IR spectroscopy should help elucidate the bonding patterns between the chromium and IDPA layers.

VI. Final Conclusions

The ability to self-assemble hybrid multilayer thin films that combine metal-isocyanide functional groups with metal-phosphonate functional groups has been demonstrated. The analytical techniques of ellipsometry and x-ray photoelectron spectroscopy have shown that these films demonstrate fairly regular and predictable layer-by-layer growth.

It is clear that this system has yet to be completely optimized in terms of the self-assembly procedure and experimental conditions. More work is needed in the analysis of the bonding between chromium and the IDPA linking molecule. Substitution of another metal, such as rhodium, is a viable alternative to the chromium layer which shows multiple oxidation states in XPS analysis. The variability of the layer thickness of the IDPA molecule raises questions of possible polymerization or molecular transformation. Mass spectroscopy data clearly shows transformation of the isocyanide group of the IDPA molecule into a formamide group when in water solution.

Future work on this system includes more work on the optimization of conditions and procedure, as well as testing the nonlinear optical properties of the thin films as they are constructed. Lisa Hommel, a graduate student in the Page Lab, has recently finished constructing a laser set-up capable of testing these properties using second harmonic generation. UV-Vis and infrared spectroscopy studies will aid in the determination of the exact bonding patterns of the IDPA linking molecule.

ACKNOWLEDGEMENTS

There are many people that I would like to thank for contributions to this thesis and my entire undergraduate career. I must begin with my family who has always provided encouragement in all of my pursuits, whether academic or otherwise. No major accomplishment in my life would have been possible without their love and support. I must also acknowledge the love and support of Teresa O'Neil, who has been closer to me than anyone throughout my final years of college. I am grateful for the opportunity given to me by Cathy Page. She does not hesitate to give undergraduates the opportunity to conduct research, and I believe this research will prove to be one of the biggest growth periods in my college career. I would also like to thank Jim Long and Joe Fracchia for their input into my thesis project. Rebecca Hamblin, of the Page Lab, has worked along side me on this project since day one. She has become a great friend, and I don't believe this work could have been done without her. Marcus Helfrich, of the Page Lab, has also become a good friend, as well as a good proof-reader. His knowledge of organic chemistry and music have helped me in many situations, as has his unique attitude towards optimism. Marcus and Mike Ansell both deserve thanks for direct contributions to this work. Marcus synthesized the IDPA linking molecule, and Mike helped me gather all XPS data presented in this thesis. In closing, I would like to thank the entire Page Lab for a great closing to my career at Oregon.

LITERATURE CITED

1)Dagani, R. *Chem. Eng. News.* **1996**, 22.

2)Ulman, A. *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly;* Academic Press, Inc.: San Diego, **1991**.

3)Ansell, M.A.; Cogan, E.B.; Neff, G.A.; von Roeschlaub, R.; Page, C.J. *Supramolecular Science* **1997**, 4, 21.

4)Zeppenfeld, A.C.; Fiddler, S.L.; Ham, W.K.; Klopfenstein, B.J.; Page, C.J. *J. Am. Chem. Soc.* **1994**, 351, 269.

5)Katz, H.E. *Chem. Mater.* **1994**, 6, 2227.

6)Hong, H.G.; Mallouk, T.E. *Langmuir* **1991**, 7, 2362.

7)Tillman, N.; Ulman, A.; Penner, T.L. *Langmuir* **1989,** 5, 101.

8)Yitzchaik, S.; Marks, T.J. *Acc. Chem. Res.* **1996,** 29, 197.

9)Hanken, D.G.; Naujok, R.R.; Gray, J.M.; Corn, R.M. *Anal. Chem.* **1997**, 69, 240.

10)Jackson, H.L.; McKusick, B.C. *Organic Syntheses Collective Volume IV*; John Wiley and Sons: New York, **1963**.

11)Ulman, A. *Characterization of Organic Thin Films*; Butterworth-Heinemann: Boston, **1995**.

12)Tompkins, H.G. *A User's Guide to Ellipsometry;* Harcourt Brace Jovanovich: Boston, **1993**.

13)Drenth, W.; Nolte, R.J.M. *Acc. Chem. Res.* **1979,** 12, 30.

14)Deming, T.J.; Novak, B.M. *J. Am. Chem. Soc.* **1993,** 115, *20*, 9101.

15)Weston, K.D.; Buratto, S.K. *J. Phys. Chem.* **1997,** 101, 5684.

16)Skoog, D.A.; Holler, F.J.; Nieman, T.A. *Principles of Instrumental Analysis*; Saunders College Publishing: Philadelphia, **1998**.

17)Wagner, C.D.; Riggs, W.M.; Davis, L.E.; Moulder, J.F.; Muilenberg, G.E. *Handbook of X-ray Photoelectron Spectroscopy;* Perkin-Elmer: Eden Prarie, MN, **1995**.