FEASIBILITY OF ELLIPSOMETRIC SENSOR DEVELOPMENT FOR USE DURING PECVD SiO_x COATED POLYMER PRODUCT MANUFACTURING

A Thesis Presented to the Faculty of
California Polytechnic State University,
San Luis Obispo

In Partial Fulfillment of the Requirements for the Degree

Master of Science in Engineering,
with a Specialization in Materials Engineering

by

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September 2009

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for Use During PECVD SiO_x Coated Polymer
Product Manufacturing

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ABSTRACT

Feasibility of Ellipsometric Sensor Development for Use During PECVD SiO_x Coated Polymer Product Manufacturing

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Polymeric materials have provided pathways to products that could not be manufactured otherwise. A new technology which merges the benefits of ceramics into these polymer products has created materials ideally suited to many different industries, like food packaging. Nano Scale Surface Systems, Inc. (NS3), a company which coats polymers with ceramic oxides like SiO₂ through a process known as plasma enhanced chemical vapor deposition (PECVD), was interested in the feasibility of an in line measurement system for monitoring the deposited films on various polymer products. This project examined two different coated polymer products, polyethylene terephthalate (PET) beverage containers and biaxially oriented PET food packaging, commonly known as plastic wrap in an effort to determine the feasibility of an ellipsometry based measurement system for NS3's purpose.

Due to its extensive use in the semiconductor industry for monitoring films deposited on silicon, a measurement systems known as ellipsometry, adept at monitoring the thickness and refractive index of thin films deposited on various substrates, appeared to be an ideal system for the measurement of ceramic oxides deposited on various polymer substrates. This project set out to determine the feasibility of using an ellipsometry based measurement system to

monitor ceramic films, specifically silicon oxides (SiO_x), deposited on polymer products.

A preliminary experiment determined linearly polarized light could induce a discernible change in polarized light traversing a coated beverage container relative to an uncoated container. However, the experiment lacked repeatability due to the measurement apparatus' cheap setup, prompting the construction of a null (conventional) ellipsometer for further research. The curved surface of the beverage containers under study unnecessarily complicated the feasibility study so further research examined PECVD SiO_x on biaxially oriented PET instead.

Characterization of the PECVD SiO_x -PET material was divided into three experiments, with the first two analyzing the SiO_x film and PET substrate separately while the third analyzed them together. To assist with the characterization experiments, NS3 provided samples, both SiO_x coated and uncoated, of various deposition thicknesses on silicon and biaxially oriented PET substrates.

Null ellipsometry was used in conjunction with spectroscopic reflectometry to characterize the refractive index and thickness of the deposited films. The combined measurement systems found the refractive index of the deposited SiO_x films to be between 1.461 and 1.465. The measured thicknesses resulting from the two measurement systems coincided well and were usually 10-20 nm thicker than the predicted thicknesses by the deposition processing parameters. Abeles' method and monochromatic goniometry were attempted; however, the results had to be discarded due to irrecoverable errors discovered in the reflectance measurement. X-ray photoelectron spectroscopy (XPS) data provided by NS3 showed the deposited SiO_x films to be homogeneous with stoichiometries between 2.15 and 2.23.

Characterization of the uncoated biaxially oriented PET required numerous measurement systems. From spectroscopic transmission, birefringent anisotropy was discovered, intertwined with thickness variations in the PET foil. Goniometry measurements displayed distinct interference curves resulting from rear interface reflections interfering with front interface reflections from the PET sample. Subsequent goniometric models produced multiple solutions due to an unknown optical phenomenon, probably scattering, which degraded the reflection measurements. However, a combined measurement technique utilizing goniometry and differential scanning calorimetry (DSC) determined the refractive indices of the polymer to be $N_x = 1.677$, $N_y = 1.632$ and $N_z = 1.495$ with a thickness of $11.343\ \mu\text{m}$ and a volume fraction crystallinity of 35-41%. Utilizing the measured refractive indices, ellipsometric models produced only an adequate fit of the measured data due to the presence of depolarization caused by non-uniform PET thickness and scattering resulting from embedded microscopic crystallites. The majority of the error in the ellipsometric data was observed in the Δ measurement.

XPS measurements of SiO_x deposited on polypropylene (PP) provided by NS3 showed a heterogeneous interphase layer between the deposited oxide and the polymer substrate where the composition of the layer was continually changing. A similar region, which violates the homogeneous assumption the ellipsometric model relied on, was anticipated for the SiO_x -PET samples under investigation. The use of an effective medium approximation (EMA) to represent the interphase region was attempted, but failed to provide a decent model fit of the measured data. Depolarization and high optical anisotropy caused by the polymer substrate in combination with a heterogeneous interphase region and the effects of the deposited SiO_x layer all interacted to prevent

ellipsometric modelling of the null ellipsometry measurements conducted. Goniometry measurements were conducted on the thickest deposited SiO_x film (approximately 100 nm) which allowed for the refractive index of the film to be approximated through Abeles' method ($n = 1.46$); however the validity of this approximation was questionable given the presence of interference fringes resulting from interference between reflections at both the front and rear interfaces of the material.

From the experiments conducted, it was concluded that null ellipsometry with conventional ellipsometric models could not adequately measure a SiO_x film's refractive index or thickness when deposited on biaxially oriented PET. The reasons for the failure were interactions between multiple sources of error which led to both measurement errors and inaccurate model assumptions. Use of generalized ellipsometry, possibly with spectroscopic ellipsometry, may overcome the failures of conventional ellipsometry when studying this complex optical material.

Keywords: ellipsometry, polarized light, spectroscopic reflectometry, goniometry, SiO_2 , PECVD SiO_x , PET, response surface, model fitting, depolarization, sample tilt, crystallinity, DSC, Abeles method

ACKNOWLEDGEMENTS

I am grateful for the support I have received during this project, completion of the project would not have been possible otherwise. First of all, I would like to thank the following people and organizations for their technical support and guidance.

My thesis committee for the technical support on issues that arose during the project

- Dr. Richard Savage
- Dr. Linda Vanasupa
- Dr. Karen McGaughey

The individuals who assisted me in lab and with the design and development of the ellipsometer

- Richard Morrison
- Joe Denny
- David Caldwell

For the much needed support with editing and figure manipulation necessary for the writing of this thesis

- Kathrine Brooks
- Ivan Luk

General technical support whether physically (e.g. samples and equipment) or intellectually (e.g. figures)

- Nano Scale Surface Systems, Inc.
- The Global Association of Manufacturers of Polyester Film (AMPEF)
- Cal Poly Materials Engineering Department
- The Microsystems Technology Club

Secondly, while the technical support above was instrumental to this project, the non technical support I received allowed me to complete this project. Due to some unfortunate circumstances, I had to commute from Fresno, CA to San Luis Obispo, CA on a near weekly basis for nearly many months in order to finish the research presented in this project. Fortunately I have great friends, family and faith in Jesus Christ which kept me going during these difficult times. It is to my support structure that I credit the completion of this thesis and want to express my sincere gratitude.

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CHAPTER 1: Project History, Purpose and Scope

The project began as a preliminary, or proof-of-concept, experiment proposed by Nano Scale Surface Systems Inc. (NS3) to determine if polarized light could be used to detect 10-20 nm thick plasma enhanced chemical vapor deposition (PECVD) silicon oxide (SiO_x) gas barriers deposited on the inside of polyethylene terephthalate (PET) beverage containers (e.g. plastic water/soda bottles). Analysis of the preliminary experiment (Appendix A) showed statistical discrimination between coated and uncoated

containers could be accomplished with polarized light; however, the experimental measurement system used could not measure the film thickness.

Following the successful preliminary experiment, the scope of the project was expanded to determine the feasibility of polarized light based measurement systems for monitoring the SiO_x layer during SiO_x -polymer product manufacturing process. The project focused on the feasibility and pitfalls of developing a polarized light based quality control measurement system. An ellipsometer – a device that measures changes in polarization of light – was constructed as part of the project for the Cal Poly Materials Engineering Department.

Figure 1.1. The preliminary experiment sought to differentiate between coated and uncoated bottles (above right) through the use of polarized laser light (center).

CHAPTER 2: Material In Question

2.1. The Materials Studied

Fiber reinforced composites, like carbon fiber-epoxy composites used in airplanes, combine the high strength of ceramic fibers with the low density and ease of manufacturing of polymer matrices to produce products that may not otherwise be physically or economically feasible. Similarly, ceramic coated polymer materials, specifically SiO_x -polymer materials, combine the outstanding environmental resistance properties of SiO_2 with the associated polymer substrate benefits to form a unique material which is able to mitigate or reduce problems inherent to an uncoated polymer product. The material studied by this project consisted of a polymer substrate conformally coated with a ceramic film.¹ The film was chemically bound to the polymer through a definable “interphase” region which consisted of a mixture of both materials.

This project aims to study SiO_x -polymer, more specifically SiO_x deposited on biaxially oriented polyethylene terephthalate (PET*), with polarized light to determine the feasibility and pitfalls of using a polarized light based measurement system or sensor for monitoring the film characteristics (i.e. thickness, refractive index, etc.) following the deposition process during manufacturing.

2.2. Problematic polymers

The polymer class of materials constitutes a myriad of different polymers. For the sake of brevity, this report will focus on PET used in food packaging. Although the results and discussions presented apply beyond PET to other polymers used in food packaging, the validity of the material presented in this

* In the United States, this abbreviation is often PETE and has the polymer recycling number designation of 1; however, this report will use the more widely used abbreviation in literature, PET.

report may extend beyond the scope of food packaging to other industries which use similar materials, such as the biomedical industry.

Most food packaging from beverage containers to candy wrappers consists of polymer-based products. This extensive reliance on polymer based materials is due to their flexibility, great manufacturability, low density, chemical stability, resistance to fracture and impacts, and cost effectiveness.² However, despite these impressive qualities, polymers possess a few weaknesses which are pertinent to food packaging: chemical leeching, chemical interaction with foodstuff and gas permeation.

Though polymer packaging materials have been deemed safe for food contact by the United States Food and Drug Administration (FDA) for decades, recent studies have shown that the materials may be leeching toxic substances which exceed the allowed concentration levels of many different regulatory and scientific bodies, including the World Health Organization (WHO). A recent study conducted by researchers from Arizona State University discovered PET water bottles can leech antimony (Sb) – a mild toxin with largely unknown health effects³ that has been shown to cause cancer in female rats⁴ – into the water at greater concentrations than the maximum level recommended by the WHO.⁵ Concentrations of leached Sb exceeding the maximum recommended concentration levels can occur as a result of elevated temperatures (>60°C), long durations (>176 days), or a combination of the two (85°C for 1.3 days).⁶ Similar studies have also arrived at similar conclusions;⁷ however, these potentially unhealthful concentrations usually occur under specific conditions not typically found under normal operating conditions – such as elevated temperatures, long durations or specific pH levels. Despite leeching of potentially harmful chemicals into the food from the polymer, concentrations remain very low. The

general consensus of most studies was polymer containers pose little to no threat to human health. However, as will be discussed in the following sections, a method for mitigating the chemical transport problem has been devised and implemented.

Chemicals within polymer container materials are only part of the problem; absorption of food chemicals can lead to additional problems. Spaghetti sauce stains in a polymer food container, like a reusable Rubbermade®, are nearly impossible to remove, even after multiple washings. Container staining from food products results from the food adsorbing to the polymer surface or absorbing into the polymer material. A study which investigated the wetting properties of two polymer films, PET and low linear density polyethylene (LDPE), concluded the greater the wettability of a polymer surface (i.e. lower measured contact angles) the greater the interaction between foodstuff and polymer container.⁸ PET, a material with higher surface free energy than LDPE, was measured to have greater wettability properties than LDPE and subsequently greater possibly of chemical interaction with food materials.⁹ Another study investigated the absorption of different types of food simulants into polymer packaging materials. Comparing the absorption of six food simulates into two different polymer films, PET and polyamide (PA), the researchers concluded the amount of absorption depended greatly on the type of polymer as well as the type of food.¹⁰ These findings help to explain why some foods stain polymer packaging while others do not. Regardless, absorption and adsorption of food is a weakness of polymer-based food containers.

While many chemical substances pass both directions across the polymer-food interface as just described, smaller molecules, such as oxygen and other gases, are able to pass through the entire polymer material. Gas permeation

is a major problem for polymeric containers¹¹ of beverages and other foodstuff that can easily be oxidized or need to be carbonated; beer and orange juice are excellent examples. In order to preserve taste, brewers generally advise that no more than one part per million (ppm) of oxygen should be dissolved in the beverage during its shelf life, typically exceeding 120 days.¹² Likewise, vitamin C, a key nutrient in orange juice, will degrade in the presence of oxygen; the oxygen barrier properties of the beverage container is an important factor in preserving beverage freshness.¹³ The cause of gas permeation is gaps between the polymer material's molecular chains created during manufacturing which provide pathways for small gas molecules to diffuse through the material in either direction. While these gaps can be reduced through different processing techniques, such as crystallization, such technologies are limited by processing

Figure 2.1. Oxygen transmission measurements demonstrate how even SiO_x films as thin as 5 nm can significantly reduce gas diffusion rates, with 20 nm thick films being the ideal thickness for oxygen barrier applications. (Figure by author, measurement data courtesy of Nano Scale Surface Systems, Inc.)

conditions.¹⁴ However, gas barrier technologies have been developed to compensate for the shortfalls in PET manufacturing. Two technologies stand out: 1) the use of blended or stratified polymer layers instead of one homogeneous polymer layer and 2) coating the polymer surface with a ceramic or metal film. Blending of polymers effectively lessens the oxygen, as well as other gases,

diffusion rate.¹⁵ Likewise, metal and ceramic films will effectively reduce oxygen diffusion (Figure 2.1);¹⁶ however, metal films are not microwavable or optically transparent, like ceramic films.¹⁷

For a long time, interior (or food side) ceramic coatings that provide an effective barrier to all three food packaging problems described above were the most expensive barrier material that could be deposited on polymer containers. With regards to beverage containers, coating the inside of the containers was estimated to cost an additional \$28.92 (nearly a 55% cost increase) per thousand beverage containers produced.¹⁸ However Nano Coating Systems of Fremont, CA, announced in 2006 they had developed a system that could interior coat bottles for \$6.00 (roughly a 10% additional cost) per thousand bottles, making it one of the cheapest barriers available.¹⁹

2.3. The SiO_x-polymer solution

Before introduction of this interesting material can be accomplished, some nomenclature needs to be clarified. First, the term SiO_x is a general description of a silicon oxide (e.g. SiO₂) where x represents stoichiometry of the material. The process used to deposit the silicon oxide films studied by this project is known to produce non-stoichiometric oxides (i.e. stoichiometries where x is not an integer, like SiO_{1.8}). Therefore, some authors choose to round the stoichiometry to the nearest integer while others use the more general term SiO_x; this project will use the latter description of a silicon oxide film. Second, the term SiO_x-polymer refers to a polymer material (e.g. PET) which has been coated with SiO_x.

The application for SiO_x-polymer materials reaches far beyond food packaging because it combines the excellent chemical, mechanical and optical

Figure 2.2. Biaxially oriented PET covering freshly made brownies.

properties of SiO_2 without the disadvantages of bulk SiO_2 such as brittleness or weight. Despite the applicability of this hybrid material to many different products in a myriad of different industries, the focus of this project was on SiO_x coated biaxially oriented PET, a polymeric food packaging material commonly known as “plastic wrap” (Figure 2.1).

2.4.

Figure 2.3. The generalized chemistry involved in manufacturing PET.

2.5. How SiO_x-PET is manufactured

Like many other products, SiO_x-PET is not fabricated by one manufacturer but by many with each manufacturer responsible for a portion of the overall manufacturing process. For instance, Nano Scale Surface Systems, Inc.

Figure 2.4. Graphical representation of the biaxially oriented PET manufacturing process. (Reproduced with permission from AMPEF)²⁰

(NS3) is responsible for SiO_x coating of whatever materials their customers require coated. With regards to this project, NS3 coated the PET films for characterization, but did not manufacture the polymer films. As a result, processing parameters – such as draw ratios and drawing temperatures of the PET films, which will affect material properties such as crystallinity – were largely

Figure 2.5. SiO_x being deposited on the inside of a PET beverage container.
(Photograph courtesy of Nano Scale Surface Systems, Inc.)²²

unknown. The only information known about the substrate material was that it was biaxially stretched to produce the approximately twelve micrometer thick film.

In general, PET products begin as crude oil derivatives. One of two plasticizer, dimethyl terephthalate (DMT) or purified terephthalic acid (PTA), in combination with ethylene glycol (Figure 2.3) and other processing chemicals and parameters

are used in the polymerization process to produce PET resin.²¹ The resin is transformed into the desired product geometry through a multitude of different manufacturing processes such as extruding, injection molding, stretching, or blow molding to name a few. Once the product's net shape has been fabricated, NS3 receives the product to be coated with SiO_x . With regards to this project, biaxially oriented PET (see figure 2.4 for overview of the film manufacturing) was provided

Figure 2.6. The creation of SiO_x through the decomposition of HMDSO in a plasma with oxygen present.

to NS3, from which it was coated and samples were submitted for analysis.

Deposition of SiO_x was accomplished using plasma enhanced chemical vapor deposition (PECVD), a processing technique which chemically decomposes feed gases into the desired film material with a glow-discharge (plasma) at low partial pressures in a low vacuum (Figure 2.5). Silicon based gases such as hexamethyldisiloxane (HMDSO) or tetramethyldisiloxane (TMDSO) are decomposed in the presence of oxygen in a radio frequency (rf) plasma (Figure 2.6) to produce SiO_x .²³ The decomposed chemicals chemically bind themselves to the polymer substrate, forming an “interphase” region²⁴ consisting of part polymer and part SiO_x . Continual deposition on top of the interphase region produces a film whose thickness ranges from a few nanometers to a few micrometers, depending upon the application.

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CHAPTER 3: Characterization Techniques

3.1. Polarized Light

Light is an obvious feature of everyday life, and yet light's true nature has eluded us for centuries. Near the end of his life, Albert Einstein wrote, "All the 50 years of conscious brooding have brought me no closer to the answer to the question: What are light quanta?" We are today in the same state of "learned ignorance" with respect to light as was Einstein.¹

With all the achievements science has accomplished, it still fails to explain some of the most fundamental questions still posed by laymen and scientists alike, such as "What is light?" Possessing a split personality, light evades concise characterization. The duality principle is currently the best description of light: On one hand light behaves like a wave through its propagation behavior and through interference and diffraction phenomenon; however, on the other hand it acts like a particle, able to exchange energy with matter.² These different personalities of light have led to three different ways of describing the same photon: wavelength, photon energy and frequency. The optical measurement techniques used for this project utilize the wave properties of light – refraction, interference and wavelength – to characterize optical and physical properties of the SiO_x-PET samples.

Despite our "learned ignorance", there is much about the behavior of light that we know, like the vectorial nature of light known as polarization.³ For all types of vector waves including light, polarization refers to the behavior with time of one of the field vectors appropriate to that wave observed at a fixed point in space.⁴ Light, as it is commonly referred to, is an electro-magnetic

wave described using four electro-magnetic field vectors. However, with regards to polarized light, the electric field vector ($\mathbf{E}$) is chosen to define the state of polarization because when light interacts with matter, the electric force exerted on the electrons by the light wave is much greater than the magnetic force.⁵ More simply, polarized light is an electro-magnetic wave – although the electric portion only is typically used – with a defined phase and orientation at a specific point in time and space.

Figure 3.1. Definition of polarization directions: p-polarized plane is parallel to the plane of incidence (parallel to the paper) and s-polarized plane is normal to the p-polarized plane.

Before phase and orientation can be defined, the principle axes of a polarized wave must first be specified (Figure 3.1). Light is a three dimensional wave where the principle component of the wave vibrates parallel to the electric field vector, known as the p-wave (p for parallel). A transverse principle component wave vibrates

perpendicular to the electric vector, known as the s-wave (s for senkrecht, which means perpendicular in German⁶), to fully describe the electro-magnetic wave in three dimensions. Furthermore, z is typically used to describe the direction of propagation. By looking down the z-axis and tracing out the location of the wave onto the s-p plane as it propagates down the z-axis, the polarization ellipse can be constructed. The phase of a monochromatic wave (δ) is defined as the phase difference between the s and p waves. The orientation (ψ) is defined as the tangent of the s and p wave magnitudes.

Light comes in three levels of polarization: unpolarized, partially polarized,

Figure 3.2. Two orthogonal views demonstrating the effect phase difference and rotation have on the polarization ellipse with linear (red), elliptical (green) and circular (blue) polarized light portrayed.

and completely polarized. Partially polarized light occurs when a completely polarized beam becomes slightly depolarized, like reflecting off a rough surface, or fails to become completely polarized, like sunlight reflecting off water. All polarized light is considered to be elliptically polarized, as demonstrated with the polarization ellipse; however, there are two special forms which possess unique qualities. The first is linearly polarized light which is a monochromatic wave with no phase difference ($\delta = 0^\circ$). Its orientation is dependant on the relative s and p wave amplitudes. The second is circularly polarized light which has an orientation (Ψ) of 45° and a phase difference (δ) of 90° (Figure 3.2).

Unique polarization optics have been designed for producing a myriad of different polarizations; however, there are four basic polarization optics which can be combined to form more complex polarization filters, analyzers and instruments. The first is a linear polarizer, typically made of a dichroic film or birefringent prism, which takes light of any polarization and converts it to linear polarized light with an orientation parallel to the polarizer's transmission axis.

The second optic is a compensator which changes the phase between the s and p waves of the incoming light. For instance, depending upon the orientation of a special type of compensator known as the quarter-wave plate, the phase change of incoming elliptically polarized light can be changed up to 90°. The third

optic is a polarization rotator which utilizes the optical activity of a material – like quartz – or the unique optical anisotropy of a material – like twisted nematic cells, also known as liquid crystals – to cause a rotation in the orientation of an elliptically polarized beam as it passes through the optic. The final polarization optic is a depolarizer which changes the light's polarization from elliptical to random. A common material used in the kitchen, wax paper, can be used as a depolarizing optic.⁷

While different forms of polarized light contain certain qualitative properties, they would not be very useful unless those properties could be quantified mathematically. Two conventions exist for representing polarized light mathematically: Jones vector and Stokes vector matrix formalisms (Table 3.1).

TABLE 3.1. Jones and Stokes Vector Comparison

	Jones Vector	Stokes Vector
P-polarized light	$\begin{bmatrix} 1 \\ 0 \end{bmatrix}$	$\begin{bmatrix} 1 \\ 1 \\ 0 \\ 0 \end{bmatrix}$
S-polarized light	$\begin{bmatrix} 0 \\ 1 \end{bmatrix}$	$\begin{bmatrix} 1 \\ -1 \\ 0 \\ 0 \end{bmatrix}$

TABLE 3.2. Jones and Mueller matrix formalisms for two common polarization optics

	Jones Matrix	Mueller Matrix
Polarizer (θ = rotation)	$\begin{bmatrix} \cos^2(\theta) & \cos(\theta)\sin(\theta) \\ \cos(\theta)\sin(\theta) & \sin^2(\theta) \end{bmatrix}$	$\begin{bmatrix} 1 & \cos(2\theta) & \sin(2\theta) & 0 \\ \cos(2\theta) & \cos^2(2\theta) & \cos(2\theta)\sin(2\theta) & 0 \\ \sin(2\theta) & \cos(2\theta)\sin(2\theta) & \sin^2(2\theta) & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$
Retarder (θ = rotation) (δ = retardation)	$\begin{bmatrix} e^{i\delta}\cos^2(\theta) + \sin^2(\theta) & (e^{i\delta} - 1)\sin(\theta)\cos(\theta) \\ (e^{i\delta} - 1)\sin(\theta)\cos(\theta) & e^{i\delta}\sin^2(\theta) + \cos^2(\theta) \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos^2(2\theta) + \sin^2(2\theta)\cos(\delta) & (1 - \cos(\delta))\sin(2\theta)\cos(2\theta) & -\sin(2\theta)\sin(\delta) \\ 0 & (1 - \cos(\delta))\sin(2\theta)\cos(2\theta) & \sin^2(2\theta) + \cos^2(2\theta)\cos(\delta) & \cos(2\theta)\sin(\delta) \\ 0 & \sin(2\theta)\sin(\delta) & -\cos(2\theta)\sin(\delta) & \cos(\delta) \end{bmatrix}$

However, these matrices only describe the light entering or leaving an optical system. In order to represent optical components, Jones matrix and Mueller matrix formalisms (Table 3.2) were developed to work with the polarization vector matrix formalisms. The matrix representation of light allows the formulation of optical models for use to describe ellipsometric data. See Goldstein for a more in depth explanation of these matrix representations of polarized light.

3.2. Optical Properties of Materials

As light impinges on a material's surface, the vectorial components are altered due to the interaction of light's electric field vector with bound charges within the material.⁸ A consequence of this electromagnetic interaction is the altering of the light's velocity vector when it enters a material. In 1851, Armand Hypolite Louis Fizeau experimentally determined light had a lesser velocity in an optically dense medium than in a vacuum.⁹ However, the frequency of light, which is related to its energy (3.1), is unaffected when the light impinges upon a material surface.¹⁰ Thus, the wavelength of light (3.2) which is determined by light's velocity vector, must change its magnitude and direction to accommodate this change in velocity.

$$E = h \nu \quad (3.1)$$

$$\lambda = \frac{c}{\nu} \quad (3.2)$$

In the previous equations, E is energy in eV, h is Plank's constant, ν is frequency, c is the velocity of light in a vacuum, and λ is the wavelength. The change in velocity defines the material's refractive index (3.3).

Figure 3.3. Graphical representation of how refraction alters the vector of a beam of light as it traverses a material (left) which is the principle behind how photographic lenses work (right).

$$n_i = \frac{\lambda_{vac}}{\lambda_i} \quad (3.3)$$

$$\frac{\sin(\theta_1)}{\sin(\theta_2)} = \frac{v_1}{v_2} \quad (3.4)$$

Rearrangement of 3.3 with respect to refraction (3.4) leads to Snell's Law (3.5), named after Willebrord Snell who experimentally discovered the relationship in the early 17th century.¹¹

$$N_1 \sin(\theta_1) = N_2 \sin(\theta_2) \quad (3.5)$$

Much like religion, politics, and other areas of study, one of the interesting concepts of science is the interrelation of seemingly discrete areas – such as physics, chemistry and biology. A material's (or substance's) refractive index is a prime example. Thermal and electrical properties are linked in materials for which the electrons act as thermal carriers, like metals.¹² The refractive index is related to the electrical properties of a material through electromagnetism. Therefore, electrical and possibly thermal properties of a material could be

determined through the optical measurement of the material's refractive index.

The refractive index of a material is a function of its dielectric constant (3.6), a material property measuring the relative permittivity of a material (3.7):

$$N = \kappa^{\frac{1}{2}} \quad (3.6)$$

$$\kappa = \frac{\varepsilon}{\varepsilon_0} \quad (3.7)$$

where ε is the material electrical permittivity and ε_0 is the electrical permittivity of free space. The material's permittivity is derived from Maxwell's equations describing electromagnetic fields (3.8-3.11).¹³

$$\nabla \times \mathbf{H} = \mathbf{j} + \frac{\partial \mathbf{D}}{\partial t} \quad (3.8)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (3.9)$$

$$\nabla \cdot \mathbf{D} = \rho \quad (3.10)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (3.11)$$

By applying boundary conditions to Maxwell's equations, Azzam and Bashara derived the Fresnel equations for uniaxial and biaxial anisotropic materials,¹⁴ important equations for the study of polymers or crystalline materials with ellipsometry. The refractive index – or indices with regards to anisotropic materials – is related to the crystal structure of a material since crystallinity deals with the geometric arrangement of atoms and subsequently their electrons. For instance, metals with non-cubic crystal structures, like titanium, will be optically anisotropic, having orientation dependant refractive indices.

Optical anisotropy in transparent crystals, a phenomenon known as

refrindex, arises from the material possessing more than one refractive index. While studying a highly birefringent crystal known as calcite, Erasmus Bartholinus was credited in 1669 with the discovery of the birefringence optical phenomenon, sometimes referred to as double-refraction.¹⁵ However, Bartholinus could not provide a scientific explanation of calcite's optical behavior so it remained a scientific mystery for nearly 30 years until Christian Huygens' explanation – based on the revolutionary description of light as a wave – defined birefringence as two refractory waves.¹⁶ Birefringent materials, like calcite or quartz refract light differently depending upon crystal orientation. Trirefringence operates under the same idea of different material orientations possessing different refractive indices; however, a trirefringent material has three refractive indices instead of the two or one possessed by birefringence or isotropic materials.

No material is completely transparent, all materials absorb light. For instance, in the infrared spectrum, light absorption of specific wavelengths can be attributed to molecular bonding. This absorption of light by matter is a result of the extinction coefficient of the material's complex refractive index (3.12).

$$N = n - jk \quad (3.12)$$

The n term is the refractive index defined above, j is the imaginary unit and k is the extinction coefficient. If the material is thicker than a monochromatic light's maximum penetration depth (3.13), the material will appear opaque at that wavelength, λ .

$$D_p = \frac{\lambda}{4\pi k} \quad (3.13)$$

Through Beer's law (3.14), the extinction coefficient is related to absorption at a particular wavelength, which is particularly useful in many facets of science.

$$A = \frac{4\pi k}{\lambda} \ell = -\ln\left(\frac{I}{I_0}\right) \quad (3.14)$$

The absorption of a material relates the inverse maximum penetration depth ($1/D_p$) to the relative measured intensity (I/I_0) through the distance the light travels through the material (ℓ). Absorption will approach unity the closer the length traversed comes to the maximum penetration depth. Certain anisotropic materials will preferentially absorb light of one polarization. In some cases this leads to the beam emerging from the material to be linearly polarized, a phenomenon known as dichroism. Certain dichroic polymers make excellent linear polarizers – albeit not as good as calcite based polarizers – with an added advantage of being able to be formed into various geometries (e.g. polarized sunglasses).

As stated above, the refractive index is a constant; however, only at a specific wavelength. The change in refractive index is dependant on the material and how it interacts with light over a given spectrum of wavelengths (Figure 3.4). For

Figure 3.4. Dispersion curves for three common dielectric glasses demonstrating the continuously changing refractive index as a function of wavelength.

instance, in the visible spectrum the refractive index of dielectrics – materials with high dielectric constants which may also be transparent, like polymers and ceramic glasses – exhibit a common behavior known as dispersion. Being mathematically similar to a Lorentz oscillator from mechanics,¹⁷ dispersion models, like the Cauchy (3.15) or Sellmeier (3.16) models in the visible spectrum, have been derived to relate the change in wavelength to a change in refractive index. Such models are however limited to specific electro-magnetic spectrums.

$$n(\lambda) = C_0 + \frac{C_1}{\lambda^2} + \frac{C_2}{\lambda^4} \quad (3.15)$$

$$n(\lambda) = \left(1 + \sum_i \frac{B_i \lambda^2}{\lambda^2 - C_i} \right)^{\frac{1}{2}} \quad (3.16)$$

Polarization optics can be constructed from birefringent crystals like calcite (Figure 3.5). It is with these polarization optics that Fresnel was able to derive his polarization equations (3.17-3.20) in the mid 19th century which were validated later by electromagnetic field theory using Maxwell's equations.¹⁸

$$r_{01p} = \frac{N_1 \cos(\theta_0) - N_0 \cos(\theta_1)}{N_1 \cos(\theta_0) + N_0 \cos(\theta_1)} \quad (3.17)$$

$$r_{01s} = \frac{N_0 \cos(\theta_0) - N_1 \cos(\theta_1)}{N_0 \cos(\theta_0) + N_1 \cos(\theta_1)} \quad (3.18)$$

$$t_{01p} = \frac{2N_0 \cos(\theta_0)}{N_1 \cos(\theta_0) + N_0 \cos(\theta_1)} \quad (3.19)$$

$$t_{01s} = \frac{2N_0 \cos(\theta_0)}{N_0 \cos(\theta_0) + N_1 \cos(\theta_1)} \quad (3.20)$$

With the Fresnel equations, the refractive index of substrates and films could be determined as a function of polarization changes induced by a sample's interaction with the probing light.

3.3. Ellipsometry

The study of polarized light is generally referred to as ellipsometry. Similar to how a type of frozen dessert comes in the three main categories of ice cream, frozen yogurt and gelato yet consists of hundreds of unique flavors, ellipsometry comes in three broad categories out of which a myriad of different measurement systems have been developed. These categories are reflection, transmission – also known as polarimetry – and scattering.¹⁹ For example, the ellipsometer used on this project was designed to study both reflection and transmission ellipsometry and can assume the function of four different polarized light based measurement systems depending upon its component configuration. Despite the transmission capabilities of the ellipsometer, measurements were conducted exclusively on the reflected beam during this project.

Ellipsometry is an indirect type of measurement system requiring mathematical modeling of the measured data in order to determine the physical properties of the sample being measured. This is due to the measurement system only measuring the polarization change of the probing light, induced

Figure 3.5. Photograph of a HeNe laser beam traversing a Glan Thompson calcite polarizer where the ordinary wave (s) is reflected and the extraordinary wave (p) is transmitted.

through interaction with a sample. However, the Fresnel equations relate polarized light measurements to the refractive index of a material, allowing determination of optical parameters from the measured ellipsometric data.

A bare substrate's refractive index, complex or real, can be calculated directly (3.21) from the measurement of Δ and ψ , represented by ρ (3.22).

$$N_2 = N_0 \tan(\theta_0) \left(1 - \frac{4\rho}{(1 + \rho)^2} \sin^2(\theta_0) \right)^{\frac{1}{2}} \quad (3.21)$$

$$\rho = \frac{r_p}{r_s} = \tan(\psi) e^{j\Delta} \quad (3.22)$$

Where N_2 is the film free substrate's refractive index, N_0 is the superstrate medium's refractive index (typically 1 if measurements were taken in air, but can be drastically different if the sample were be submerged in another fluid), θ_0 is the angle of incidence and ρ is the ellipsometric measurement.

There are a multitude of different ways by which ρ could be measured; the technique used in this project was conventional (null) ellipsometry.

Figure 3.6. Two crossed linear film polarizers demonstrating the extinguishing of light as a result.

When the transmission axis (TA) of two polarizers are crossed (i.e. if rotated about the same axis, the TAs of the two polarizers would be 90° relative to each other), the transmitted light is extinguished (Figure 3.6). At this point, the relative angle between the two polarizers is known to be 90° , even if no angular measurements on either optic were made. It is this relationship that is the basis

of null ellipsometry. However, if the relative orientation of the two polarizers is not 90° , the light passing through will be attenuated with the intensity of the emerging light being a function of the relative angle between the polarizers. Near the null position, the intensity function becomes a quadratic (Figure 3.7), allowing for a fitted polynomial model (3.23) or position averaging to be used to determine the measured angular position of the null.

$$y = \beta_0 + \beta_1 x + \beta_2 x^2 + \varepsilon \quad (3.23)$$

Where the null position can be found by setting dy/dx (for the polynomial) to zero and solving for x (3.24) or averaging the position of two measurements of equivalent light intensity (3.25).

$$x_{null} = -\frac{\beta_1}{2\beta_2} \quad (3.24)$$

$$x_{null} = \frac{x_1 - x_2}{2} \quad (3.25)$$

When a probing beam of polarized light – whose polarization vector is known – interacts with a sample, a change in the phase and orientation of the beam will occur. Analysis of the reflected beam will determine the phase change, Δ (3.25), and orientation rotation, Ψ (3.26), induced by the material.

$$\Delta = \delta_i - \delta_r \quad (3.26)$$

$$\psi = \arctan\left(\frac{|r_p|}{|r_s|}\right) \quad (3.27)$$

From equation 3.26, if the phase of the incident beam is adjusted to equal the phase change induced by the material, the reflected beam will become linearly polarized (i.e. $\delta_r = 0$). If a linear polarizer is placed between the sample and a detector, known as an analyzing polarizer, or analyzer for short, the reflected beam can be extinguished. This allows the orientation and phase change to be determined through the orthogonal nature of crossed polarization.

Measurement of Δ and Ψ are accomplished with a measurement device called an ellipsometer, which comes in a variety of configurations depending upon the application. For this project, a multiple angle of incidence ellipsometer (MAIE) was used. The MAIE was configured to determine Δ and Ψ through the measurement of null conditions by utilizing a polarization generation arm, rotatable sample stage, and a polarization analyzing arm (Appendix C). The polarization generating arm, also known as the polarization state generator (PSG), consisted of a linear polarizer and a quarter waveplate compensator which worked together to produce any form of elliptically polarized light, from linear to circular. The sample was mounted on a rotation stage which allowed different incident angles to be measured. Finally, the analyzing arm consisted of a linear polarizer for analyzing the light reflected off the sample surface

and a detector to determine the null condition. For a fixed incident angle, the polarization change brought about by the sample can be calculated from the measured angles of the optical components when the null condition is achieved (3.29).

$$\rho = \tan(A) \frac{\tan(C) + \rho_c \tan(P - C)}{\rho_c \tan(C) \tan(P - C) - 1} \quad (3.29)$$

Where P, C, and A are the angular measurements of the polarizer, compensator, and analyzer and ρ_c is the complex relative transmittance of the compensator (for an ideal quarter-wave compensator, $\rho_c = -j$).

Materials with a film or films covering the substrate are more complex than bare substrates due to film thickness effects. Unfortunately, for film covered materials, the physical parameters – refractive index and film thickness – cannot be calculated directly as is the case with a bare substrate. Instead, a model based on the Fresnel equations must be fit to the ellipsometric measurements (3.30):

$$\rho = \left(\frac{r_{01p} + r_{12p}e^{-2j\beta}}{1 + r_{01p}r_{12p}e^{-2j\beta}} \right) \left(\frac{1 + r_{01s}r_{12s}e^{-2j\beta}}{r_{01s} + r_{12s}e^{-2j\beta}} \right) \quad (3.30a)$$

$$\beta = 2\pi \left(\frac{d_1}{\lambda} \right) (N_1^2 - N_0^2 \sin^2(\theta_0))^{\frac{1}{2}} \quad (3.30b)$$

Where ρ is the ellipsometric measurement, r_{01p} , r_{01s} , r_{12p} and r_{12s} are the Fresnel equations for s and p polarization directions, λ is the wavelength of light, d_1 is the film thickness and N_0 , N_1 , and N_2 are the complex refractive indices of the ambient, film and substrate. Suppose the physical parameters of the substrate and film were unknown, for instance a metal pacified by a thin oxide layer,

providing four to five unknown quantities (Figure 3.8). From linear algebra, a system of equations can only be solved if the number of independent equations is equal to or greater than the number of unknowns, otherwise an infinite number of solutions could be found for the unknown parameters. For each incident angle, or wavelength,

Figure 3.8. Cross section of a film covered material with the possible unknowns in parentheses.

one unique combination of Δ and Ψ will be measured, allowing for two physical parameters to be determined per measurement. Therefore, a minimum of two to three ellipsometric measurements at different incident angles would be needed in order to solve for all the unknown quantities in the film covered metal example. Even if the minimum number of ellipsometric measurements have been obtained, it is still possible to not find a solution. For example, when ellipsometrically testing very thin films, like native oxides, it is possible for parameters to be correlated with one another, leading to an infinite number of solutions. To help circumvent this problem, multiple wavelengths can be used to provide more optical information about the sample material. The use of wavelengths instead of or in addition to multiple incident angles will provide the necessary additional information required to find a solution. Unfortunately, the wavelength dependence of a material's refractive index or indices will further complicate any model which relies on spectroscopic measurements.

Multiple films on a substrate are not uncommon; however, the model presented with 3.30 is inadequate to describe a substrate with multiple films.

Azzam and Bashara devised a straightforward method for calculating a reflection model for a given number of films on a substrate by the matrix multiplication of a series of Jones matrices.²⁰

The models presented in 3.21 and 3.30 were for homogeneous isotropic materials only; however, if the material is homogeneous anisotropic, the model becomes a little more complicated. For a trirefringent film the Fresnel ellipsometric model (3.30) takes on a slightly different form (3.31).

$$\rho = \left(\frac{r_{01pp} + r_{12pp}e^{-2j\beta_p}}{1 + r_{01pp}r_{12pp}e^{-2j\beta_p}} \right) \left(\frac{1 + r_{01ss}r_{12ss}e^{-2j\beta_s}}{r_{01ss} + r_{12ss}e^{-2j\beta_s}} \right) \quad (3.31a)$$

$$\beta_p = 2\pi \left(\frac{d_1}{\lambda} \right) \left(\frac{N_{1x}}{N_{1z}} \right) (N_{1z}^2 - N_0^2 \sin^2(\theta_0))^{\frac{1}{2}} \quad (3.31b)$$

$$\beta_s = 2\pi \left(\frac{d_1}{\lambda} \right) (N_{1y}^2 - N_0^2 \sin^2(\theta_0))^{\frac{1}{2}} \quad (3.31c)$$

The Fresnel equations (3.17-3.20) are slightly different for a trirefringent material as well (3.32-3.35).

$$r_{01pp} = \frac{N_{1x}N_{1z} \cos(\theta_0) - N_0(N_{1z}^2 - N_0^2 \sin^2(\theta_0))^{\frac{1}{2}}}{N_{1x}N_{1z} \cos(\theta_0) + N_0(N_{1z}^2 - N_0^2 \sin^2(\theta_0))^{\frac{1}{2}}} \quad (3.32)$$

$$r_{01ss} = \frac{N_0 \cos(\theta_0) - (N_{1y}^2 - N_0^2 \sin^2(\theta_0))^{\frac{1}{2}}}{N_0 \cos(\theta_0) + (N_{1y}^2 - N_0^2 \sin^2(\theta_0))^{\frac{1}{2}}} \quad (3.33)$$

$$r_{12pp} = \frac{-N_{1x}N_{1z} \cos(\theta_2) + N_2(N_{1z}^2 - N_0^2 \sin^2(\theta_0))^{\frac{1}{2}}}{N_{1x}N_{1z} \cos(\theta_2) + N_2(N_{1z}^2 - N_0^2 \sin^2(\theta_0))^{\frac{1}{2}}} \quad (3.34)$$

$$r_{12ss} = \frac{-N_2 \cos(\theta_2) + (N_{1y}^2 - N_0^2 \sin^2(\theta_0))^{\frac{1}{2}}}{N_2 \cos(\theta_2) + (N_{1y}^2 - N_0^2 \sin^2(\theta_0))^{\frac{1}{2}}} \quad (3.35)$$

For models involving multiple incident angles, the measured ellipsometric parameters, Δ and Ψ , are plotted versus incident angle, θ_0 . Using a least squares model fitting technique which utilizes error functions,²¹ the measured data points for θ_0 vs. Δ and θ_0 vs. Ψ are fitted to the appropriate ellipsometric model to determine the desired optical parameters.

3.4. Supplemental Reflection Measurement Techniques

Just as a fingerprint is unique for every person, the polarization change resulting from interaction with a material surface is unique for every material. Examination of the θ_0 vs. Δ and θ_0 vs. Ψ plots provides insights into how the material interacts with light at a specific

wavelength. While a concise explanation of the plots is provided elsewhere,²² the following explanation will focus on two unique incidence angles used for material identification and optical characterization: the principle angle and the Brewster's angle. First, the principle angle is defined as the angle of incidence, for a specific wavelength, in which $\Delta = 90^\circ$. This is an important incidence angle

Figure 3.9. Reflection anatomy comparison between an absorbing substrate (Gold) and a non-absorbing substrate (Pyrex 7740) at $\lambda = 632.8$ nm.

because measurements conducted at or near the material's principle angle will be less influenced by measurement errors arising from the sample, measurement system or inaccurate model assumptions.²³ Second, the Brewster's angle is defined as the incidence angle which suppresses the reflection of p-polarized light.* Reflection suppression occurs with absorbing materials or film-substrate material systems while extinction occurs with non-absorbing materials (Figure 3.9). What makes the Brewster's angle unique for non-absorbing materials is its direct relation to the material's refractive index (3.36). For dielectric and other non-absorbing materials, the Brewster's angle and principle angle are the same whereas with absorbing materials, the two are different. Since the materials used in this project were non-absorbing (i.e. dielectrics), Brewster's angle measurements were used to determine the refractive index of an unknown dielectric as well as to validate the calibration of the ellipsometer (Appendix C). The major advantages of Brewster's angle measurements is speed and simplicity.

Figure 3.10. Reflection of three types of materials: non-absorbing, slightly absorbing and strongly absorbing.

$$\theta_B = \arctan\left(\frac{N_1}{N_0}\right) \quad (3.36)$$

A supplemental technique to Brewster's angle measurements is

* Suppression of s-polarized light and multiple Brewster's angles will occur with some film-substrate materials systems; however, such behavior was not observed in this project.

Figure 3.11. Reflection and transmission from a silicon dioxide sample as a function of incidence angle.

goniometry (not to be confused with the measurement technique that measures the contact angle of liquids on a material surface). By measuring the reflectance at different angles of incidence, goniometry is able to determine the optical characteristics of a material

(Figure 3.10). When a polarizer is used to linearly

polarize the light source in either the p or s directions, the Fresnel coefficients for the respective polarization orientation can be determined from the measured reflectance or transmission (3.37-3.40) from which the optical constants can be modeled (Figure 3.11).

$$R_p = |r_p|^2 \quad (3.37)$$

$$R_s = |r_s|^2 \quad (3.38)$$

$$T_p = \frac{N_1 \cos(\theta_1)}{N_0 \cos(\theta_0)} (|t_p|)^2 \quad (3.39)$$

$$T_s = \frac{N_1 \cos(\theta_1)}{N_0 \cos(\theta_0)} (|t_s|)^2 \quad (3.40)$$

When the incident angle is fixed at or near normal incidence and the reflection (or transmission) is measured for multiple wavelengths (i.e.

Figure 3.12. A reflection spectrum at normal incidence for a 815 nm SiO₂ film on Si.

spectroscopic reflectometry), the optical constants of the sample can be determined (Figure 3.12). The reflection at normal incidence is polarization independent for all isotropic materials and many anisotropic materials. However, if the material is birefringent, the polarization of the reflected beam becomes important. At normal incidence, the Fresnel equations simplify because $\theta_0 = 0$. If the sample has a film on its surface, a model (3.41) must be used to account for the phase change induced by the film. Since the measurement system spans multiple wavelengths, equations which adjust the refractive index for wavelength (3.15-3.16) must be used instead of constants for the refractive indices. The

procedure for model fitting of spectroscopic reflectometry is the same as ellipsometry, but with wavelength being adjusted instead of incident angle.

$$R = \left[\frac{r_{01} + r_{12}e^{-2j\beta}}{1 + r_{01}r_{12}e^{-2j\beta}} \right]^2 \quad (3.41a)$$

$$\beta = 2\pi \left(\frac{d}{\lambda} \right) N_1 \quad (3.41b)$$

It is worth noting that there is a measurement system which incorporates all the above mentioned measurement systems, called variable angle spectroscopic ellipsometry (VASE). Unfortunately, such measurement systems are quite expensive and data analysis is more complex; subsequently, use of a VASE system was not an option for this project.

Notes

- 1 Frank L. Pedrotti, Leno S. Pedrotti, and Leno M. Pedrotti, *Introduction to Optics*, (New Jersey: Pearson's Prentice Hall, 2007), 1-4.
- 2 Ibid.
- 3 Dennis Goldstein, *Polarized Light*, (New York: Marcel Dekker, Inc., 2003), 21.
- 4 R.M.A. Azzam and N.M. Bashara, *Ellipsometry and Polarized Light*, (Amsterdam: Elsevier Science B.V., 1987), 1.
- 5 Ibid.
- 6 See note 3, 137.
- 7 See note 3, 532.
- 8 See note 3, 448.
- 9 See note 3, xiii.
- 10 Raymond A. Serway, Rober J. Beichner and John W. Jewett Jr., *Physics for Scientists and Engineers with Modern Physics*, (United States: Thomson Learning, Inc., 2000), 1116-1118.
- 11 Ibid.
- 12 James P. Schaffer et al., *The Science and Design of Engineering Materails 2nd ed.*, (United States: WCB McGraw-Hill, 1999), 558.
- 13 See note 3,
- 14 See note 4, 340-358.
- 15 See note 3, 447.
- 16 Ibid.
- 17 Harland G. Tompkins and William A. McGahan, *Spectroscopic Ellipsometry and Reflectometry*, (New York: John Wiley and Sons, Inc., 1999), 26.
- 18 O.S. Heavens, *Optical Properties of Thin Solid Vilms*, (New York: Dover Publications, Inc., 1965), 49-51.
- 19 See note 4., 155.
- 20 See note 4., 332-340.
- 21 See note 4, 318-319.

22 See note 4, 295-298.

23 See note 17, 111.

CHAPTER 4: Statistical Background

4.1. Statistically designed experiments

In scientific research the way data is collected is just as vital as the way it is analyzed, for the former helps determine the latter. However, in most scientific and engineering curriculums, learning how to properly set up experiments is often overlooked. The purpose of statistically designed experiments is twofold: The first is to maximize the efficiency of the experiment by allowing the researcher to obtain the necessary data for analysis in the fewest runs. The second is to make sure the response being measured is what the researcher desires to study. A statistically designed experiment, commonly referred to as a design of experiment (DOE), utilizes available information about the subject, factors and anticipated response to determine how to best conduct the experiment.

When two factors are being used to determine an optimum response, a response surface DOE is particularly helpful. Two types of response surface designs were used in this project: a central composite design (CCD) and a Box-Behnken design. Both designs are analyzed the same way; the only difference is the way which they collect the data. Analysis of a response surface design is accomplished by fitting a quadratic function to each factor in addition to an interaction term between the factors (4.1):

$$y = \eta_0 + \sum_{i=1}^k \eta_i x_i + \sum_{i=1}^k \eta_{ii} x_i^2 + \sum_{i < j} \eta_{ij} x_i x_j + \varepsilon \quad (4.1)$$

Where η are the fitted coefficients, x_i and x_j are the experimental factors and ε is error. The fitted equation will produce a surface with one extreme point – a

Figure 4.1. A response surface model depicted graphically in 3D and as a contour plot.

maximum, minimum or saddlepoint depending on which is being sought – somewhere along the surface (Figure 4.1). Some statistical software packages, such as Minitab® and JMP®, contain profilers which use a numerical analysis routine, like the Newton-Raphson method, to determine the location of the extrema for the fitted model.¹ These profilers were incredibly helpful to this project in

the analysis of experiments.

Before a surface can be fitted, the data has to be collected. If two or more treatment factors exist, a CCD can be used. A CCD consists of four factorial points in combination with four axial points and a center point. However, if three

Figure 4.2. Graphical representations of the treatment level determinations for the two response surface DOEs used.

or more factors (i.e. treatments) exist, a Box-Bahnken design, which requires less runs than a CCD, can be used (Figure 4.2).

Regardless of the design, the levels of each factor are determined by coded units designated by the type of DOE the researcher chooses. The DOE is based on the predicted variance distribution and the experimental feasibility of the treatments. For instance, a rotatable DOE has its measurement points coded in such a way that the variance is the same for any point of equal distance from the design center, which is useful in minimizing experimental bias. Unfortunately, in this project experimental conditions prevented the use of a truly rotatable CCD for the null measurements, so a nearly rotatable design was used instead (Appendix B). In contrast, the Box-Behnken design, used during calibration, is inherently a rotatable design.

In order to conduct the experiment, the coded units are converted into real units by (4.2):

$$\xi_i = \Delta_i x_i + a_i \quad (4.2)$$

Where ξ_i is the real unit, Δ_i is the experimental divisions or standard deviations and a_i is an offset. Once all the responses have been measured, by convention, the model is fitted to the coded units and then converted to real units.² However, if the model is fitted to the real units directly (4.3), the same solution is reached, where the β s are the coefficients being fitted.

$$y = \beta_0 + \sum_{i=1}^k \beta_i \xi_i + \sum_{i=1}^k \beta_{ii} \xi_i^2 + \sum_{i < j} \beta_{ij} \xi_i \xi_j + \varepsilon \quad (4.3)$$

4.2. Comparison of statistical and numerical model fitting

Model fitting is an important part of statistical analyses; however, the anatomy of a fitted model is often overlooked. In order to determine if a model is a valid interpretation of the dataset, an analysis of variance (ANOVA) must be conducted. The premise behind an ANOVA is to determine if the model fit is significantly different than the mean of all the responses. In least squares regression, the sum of squared vertical deviations of the points from the model is minimized.³ The initial step is to determine the response's grand mean – the mean of all the response measurements. The following step is to iterate the model until the vertical deviations – also known as the sum of squares error (SSE) – are minimized. At that point, the model is fitting the data as best it can. ANOVA can then be used to determine how well the model fits the data. Appendix B provides an overview of the ANOVA table for a regression model.

With regards to the response surface model used extensively to determine the ellipsometer's null location, the model's validity was determined using $r^2(\text{adj})$ (4.4) which adjusts the measure of how much total response variance the model explains, also known as r^2 , for multiple factors. This provides a more accurate measure than r^2 of how well the model fit because it combines information about the variance explained with the number of variables used (factors, levels, blocks, etc.).⁴

$$r^2_{\text{adj}} = 1 - \left(\frac{\sum (y_i - \hat{y})^2}{\sum (y_i - \bar{y})^2} \right) \left(\frac{\text{df}_{\text{total}}}{\text{df}_{\text{error}}} \right) \quad (4.4)$$

In the preceding equation, y_i is the measured response, $\hat{y}$ is the model predicted response, $\bar{y}$ is the grand mean of all the response, and df_{total} and df_{error} are the degrees of freedom total and for error. While least squares is the statistical

approach to fitting a model to a data set, numerical techniques, like the Newton-Ralphson method (4.5), can also be used to fit models to datasets. However, for models involving complex numbers, numerical methods become quite complicated because taking derivatives of complex numbers is no trivial task.

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)} \quad (4.5)$$

Numerical methods iterate a model, $f(x_n)$, starting with an initial guess, x_0 , and ending at a termination criterion, which provides a solution, x_{n+1} . A termination criterion is a predefined condition determined by the researcher, such as gradients and objective changes. However, satisfaction of the termination criterion by itself does not imply the model has converged on an accurate solution.⁵ Models that are asymptotic or possess multiple solutions (e.g. such as local minimums) may satisfy the termination criterion even though the solution returned is not the correct one.

In order to circumvent the complications facing numerical method determination of best fit models involving complex numbers, like the models used in ellipsometry, Azzam and Bashara proposed conducting numerical methods on an error function which is related to the model and data.⁶ The simplest error function proposed is a least squares function (4.6) which measures the total sum of squares error of an ellipsometric model.

$$F = \sum_{i=1}^M \left[\left| \rho_i^m - \rho_i^c \right| \right]^2 \quad (4.6)$$

Numerical analysis is conducted on the error function to determine the set of parameters (i.e. the solution to the ellipsometric equation) that provides a

minimum in the error function. This approach is incredibly useful when trying to fit ellipsometric models to data measured at different incident angles.

Notes

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- 2 Douglas C. Montgomery, Design and Analysis of Experiments, (John Wiley and Sons, Inc., 2005), 406.
- 3 Alan Grafen and Rosie Hails, Modern Statistics for the Life Sciences, (Oxford: Oxford University Press, 2006), 23.
- 4 Ibid, 211.
- 5 Erwin Kreyszig, Advanced Engineering Mathematics 8th ed., (Danvers: John Wiley and Sons, Inc., 1999), 841-845.
- 6 R.M.A. Azzam and N.M. Bashara, Ellipsometry and Polarized Light, (Amsterdam: Elsevier Science B.V., 1987), 317-326.

CHAPTER 5: Experimental Procedures

5.1. Experimental Instrumentation

An ellipsometer is a device which measures the rotation (Ψ) and phase shift (Δ) of polarized light resulting from interaction with a sample. It accomplishes this by knowing the polarization state of the probing beam prior to its interaction with the sample and analyzes the polarization state of the reflected beam. Using standard optical components, a single wavelength ellipsometer was constructed on an optical breadboard. It was designed to allow reflectance and transmission measurements at multiple incidence angles in order to maximize its measurement capabilities. There are many types of ellipsometers with different optical

configurations; however, the type used for this project, conventional ellipsometry, determined Δ and Ψ through the measurement of the optics' rotation positions which extinguish the light incident on a light sensor, a position known as the null. The null settings for the polarizer and analyzer (the compensator

azimuth was held constant) were determined by constructing a response surface experiment around the suspected null settings of the optics. A series of light measurements were collected at the polarizer and analyzer settings defined

Figure 5.1. Contour plot demonstrating how the measurement points established by the DOE (black) allow for an efficient determination of the null position.

by the response surface DOE (Figure 5.1). The resulting data was fitted with a response surface model and the null position – which was the model’s optimum point, either a minimum or saddle point – was determined from the response surface model (see Figure 4.1). Similar response surface experiments were utilized during calibration of the ellipsometer (Appendix C).

One advantage of the custom built ellipsometer was its versatility, allowing it to be reconfigured for many different measurements, like Brewster’s angle, monochromatic goniometry and transmission measurements. Since the refractive index of a dielectric can be directly calculated from its Brewster’s angle, the ellipsometer was reconfigured to irradiate the sample’s surface with p-polarized light during Brewster’s angle experiments. A Pyrex® 7740 wafer was used as a standard by which to judge the validity of the PET measurements since the refractive index of Pyrex® 7740 is known ($n = 1.4711$)¹ at the wavelength used ($\lambda = 632.8$ nm). The Brewster’s position was determined by measuring the reflectance of p-polarized light at predetermined incident angles. A second order polynomial model was fitted to the data from which the Brewster’s angle was interpolated from the minimum point of the fitted statistical model (Appendix D).

Utilizing the Brewster’s angle phenomenon with dielectrics, a measurement procedure known as Abeles’ method can be used for determination of a film’s refractive index regardless of the underlying substrate.² At the film’s Brewster’s angle, a p-polarized probing beam will reflect off the film-substrate interface only. The magnitude of the resulting reflection is equal to the reflection from a film free material (Figure 5.2). The measured incidence angle at this reflection intersection is the Brewster’s angle of the film, from which the refractive index can be calculated from equation 3.36. Traditionally the method was constrained to transparent films on transparent substrates only;³ however, a

Figure 5.2. From goniometric measurements, Abeles' method can be used for the determination of a SiO_2 film grown on Si Brewster's angle ($\theta_B = 55.6^\circ$).

recent paper demonstrates that this method is also valid on weakly absorbing substrates, like silicon in the visible spectrum.⁴ If the refractive index of the substrate is well known, like silicon, the substrate's reflection can be calculated leaving only the film covered sample to be measured. However, if the refractive index of the substrate is not known, reflection measurements will be required of both the film and film free samples.

Since Brewster's angle measurements are thickness independent, they were a useful complement to monochromatic goniometry in the determination of the PET's refractive indices. A goniometer is a measurement system which measures the reflectance of a material as a function of incident angle (Figure

5.2). By polarizing the incident beam in the p or s directions, the magnitude of the Fresnel coefficient for that polarization can be determined, where v is p or s (5.1).

$$r_v = R_v^{\frac{1}{2}} \quad (5.1)$$

Thus, Ψ can be calculated (5.2) if the reflections in both the p and s directions are measured, making goniometry a complimentary technique to ellipsometry.

$$\Psi = \text{atan} \left(\frac{R_p^{\frac{1}{2}}}{R_s^{\frac{1}{2}}} \right) \quad (5.2)$$

If a material with a rear interface, like a transparent film or substrate, is measured, the rear interface reflections will interfere with reflections from the front interface producing observable interference fringes in the goniometric data (see film covered sample in figure 5.2). A model can be fit to the data (5.3) to determine the optical parameters of the material, where v is p or s.

$$R_v = \left[\frac{r_{01v} + r_{12v}e^{-2j\beta}}{1 + r_{01v}r_{12v}e^{-2j\beta}} \right]^{\frac{1}{2}} \quad (5.3a)$$

$$\beta = 2\pi \left(\frac{d_1}{\lambda} \right) (N_1^2 - N_0^2 \sin^2(\theta_0))^{\frac{1}{2}} \quad (5.3b)$$

Using the scripting capabilities of Mathcad®, a mathematical algorithm was constructed for determination of optical constants from the measured goniometric data (Appendix F). At the Brewster's angle of a transparent substrate, the reflectance is zero; therefore, Brewster's angle measurements are complimentary to goniometric measurements and models.

Reflectance measurements at normal incidence is commonly referred to as reflectometry. When these measurements are made over a range of wavelengths, it then becomes known as spectroscopic reflectometry. Such measurements were conducted for this project with a Filmetrics F20 spectroscopic reflectometer. Since the reflection is measured at normal incidence, the optical model describing the reflection behavior of the material simplifies significantly because the angular component of the model is eliminated (5.4); however, the refractive index of all materials will change as a function of wavelength, complicating the analysis of the reflectance measurements.

$$R = \left[\frac{r_{01} + r_{12}e^{-2j\beta}}{1 + r_{01}r_{12}e^{-2j\beta}} \right]^2 \quad (5.4a)$$

$$\beta = 2\pi \left(\frac{d}{\lambda} \right) N_1 \quad (5.4b)$$

How the refractive index changes can often be described by equations specific to a material class, like dispersion equations for dielectric materials, allowing for models which describe the material in question to be fit to the data. The F20 had a built in model fitting software package which made analysis of the measured reflectance convenient; however, correct model assumptions were required to achieve the best results (Appendix E).

At normal incidence, the transmission (or reflection) of p and s polarized light are the same, except if the material is birefringent (Figure 5.3). Since reflection of a dielectric material is very small and since reflection and transmission are related, spectroscopic transmission measurements were conducted to determine if a measurable difference between the two orthogonal polarizations could be measured using an apparatus constructed

in the lab (Appendix E).

The spectroscopic nature of the material was also investigated to determine if a dispersion relation common to dielectric materials, was present. An additional advantage of a spectroscopic measurement was the determination of film thickness through interference, since adjacent maxima or minima are directly related to film thickness (5.5).

Figure 5.3. P (solid) and s (dash) polarization reflectance for isotropic and anisotropic materials with the same Brewster's Angle.

$$d_f = \frac{\lambda_i \lambda_{i+1}}{2(n_i \lambda_{i+1} - n_{i+1} \lambda_i)} \quad (5.5)$$

Where d_f is the film thickness, λ_i and λ_{i+1} are the wavelengths of the adjacent extrema, n_i and n_{i+1} are the refractive indices at the respective extrema.

When the refractive index in three principle directions of a semi-crystalline polymer are averaged (5.6), the resulting average refractive index is directly related to its volume fraction of crystallinity (5.7).⁵

$$\bar{N} = \frac{N_x + N_y + N_z}{3} \quad (5.6)$$

$$\bar{N} = 4.654610^{-4}(X) + 1.5701 \quad (5.7)$$

In addition to this optical relation, the crystallinity of a semi-crystalline polymer is also related to the material's thermal properties (i.e. melting behavior); therefore, a Seiko Instruments DSC 6200 differential scanning calorimeter (DSC) was used to determine the crystallinity of uncoated PET samples using the First Law method.⁶

To assist in the ellipsometric model generation and fitting, x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) data was provided by NS3. A PHI Quantum 2000 XPS was used in conjunction with an argon ion mill for depth profile characterization while a Digital Instruments NanoScope AFM was used for determining surface roughness.

Figure 5.4. Overview of the experiments conducted.

5.2. Characterization Experiments

Apart from the experiments required for assembly, calibration and characterization of the ellipsometer, the project consisted of three interrelated experiments (Figure 5.4). The first was the characterization of the PECVD SiO_x film. This experiment consisted of two film deposition thickness levels (20 nm and 50 nm) on silicon with one replicate for each level and two uncoated control wafers. The measured response was the thickness and refractive index of the PECVD SiO_x film. The objective was to measure the film's refractive index and determine if it changed with deposition thickness. Measurement of film's thickness for each sample was of interest to determine how accurate the deposition parameters were at determining film thickness.

The second experiment was a multi-stage experiment designed to characterize the uncoated PET. Brewster's angle, monochromatic goniometry and DSC measurements were used in conjunction to determine the refractive indices and thickness of the uncoated PET sample. DSC measurements were conducted to verify the crystallinity of the PET sample. Spectroscopic transmission measurements were used to verify the existence of birefringence, optical dispersion, and PET thickness uniformity. Finally, null ellipsometry was used to verify that ellipsometric measurements were consistent with the other techniques.

The third experiment measured the ellipsometric change due to increasing SiO_x deposition thickness on PET. Four deposition levels were studied: 30nm, 50nm, 70nm and 100nm. Ellipsometry was attempted to determine the film thickness and refractive index of the SiO_x at the various levels. Goniometric measurements were made on the thickest deposited sample and compared to uncoated goniometric measurements.

5.3. Ellipsometric Model Fitting Procedures

Due to the complex nature of ellipsometric models, traditional statistical analysis of the data is difficult. Thus, a multi-step process was established to determine the best fit model and calculate basic model fitting statistics associated with those models. The first step was fitting a model to the measured data.

Once a null measurement was made, Δ , Ψ and ρ was calculated from (3.29). The Δ and Ψ responses were plotted vs. incident angle, θ_0 , similar to how Δ and Ψ are plotted verse wavelength in spectroscopic ellipsometry. Optimization of the ellipsometric model for the measured data was accomplished by a least squares method by minimizing a SSE error function (5.7).⁷

$$F = \sum_{i=1}^M \left[\rho_i^m - \rho_i^c \right]^2 \quad (5.7)$$

Some practitioners, like Azzam and Bashara, use a SSE based error function while others, like Tompkins, use the mean square error (MSE) or X^2 . While there is no difference between the SSE and MSE for use as an error function, there is a significant difference between SSE and X^2 error functions which is discussed in detail by Tompkins.⁸ The SSE based error function was used for model optimization in this project.

Once the best fit model has been determined, the parameters are placed in a statistical algorithm which compares the best fit model graphically and statistically to the measured data (Appendix F). The program outputs a graphical model and the model fitting statistics. The $r^2(\text{adj})$ statistic was used as a goodness of fit measure of the models to the data. A valid model had a $r^2(\text{adj})$ value around 0.9 or higher while the a poor fit was considered to be at least 0.5. Models that could not account for at least 50% of the data were determined

invalid.

The relationship between the measured ellipsometric parameters (Δ and Ψ) and the material parameters represented in the model can be illustrated through the scattering matrix, $\mathbf{S}$. The scattering matrix (5.9)⁹ is a 2x2 Jones matrix representation of reflected and transmitted light from stratified homogeneous layers of materials, which is similar to the more general Abeles matrix formalism.¹⁰

$$\mathbf{S} = \mathbf{I}_{01} \cdot \mathbf{L}_1 \cdot \mathbf{I}_{12} \cdot \dots \cdot \mathbf{L}_a \cdot \mathbf{I}_{ab} \quad (5.9)$$

Where $\mathbf{I}$ is a matrix representing the interface (5.10)¹¹ and $\mathbf{L}$ is a matrix representing a homogeneous layer (5.11).¹²

$$\mathbf{I}_{ab} = \left(\frac{1}{t_{ab}} \right) \begin{bmatrix} 1 & r_{ab} \\ r_{ab} & 1 \end{bmatrix} \quad (5.10)$$

$$\mathbf{L}_a = \begin{bmatrix} e^{j\beta} & 0 \\ 0 & e^{-j\beta} \end{bmatrix} \quad (5.11)$$

The measured ellipsometric parameter ρ is related to the scattering matrix, allowing multiple film models to be constructed through matrix multiplication of successive interface and layer matrices (5.12-5.13).

$$\rho_r = \left(\frac{\mathbf{S}_{21}}{\mathbf{S}_{11}} \right)_p \left(\frac{\mathbf{S}_{11}}{\mathbf{S}_{21}} \right)_s \quad (5.12)$$

$$\rho_t = \left(\frac{\mathbf{S}_{11s}}{\mathbf{S}_{11p}} \right) \quad (5.13)$$

Where $\mathbf{S}_{21}$ and $\mathbf{S}_{11}$ are elements of the scattering matrix and ρ_r and ρ_t are the measureable ellipsometric parameters for reflection and transmission

ellipsometry.

The models used to fit the ellipsometric data measured in the three experiments were derived using the scattering matrix method described by Azzam and Bahara.¹³ An algorithm was created to generate an SSE map from a predefined ellipsometric model over a defined range of model parameters (Appendix F). The SSE map was used to determine the optimized model through a series of iterations and data reduction steps which ultimately lead to a surface which could be modeled and a solution (i.e. minimum point or saddle point) found.

Notes

- 1 Joseph E. Gortych and Dennis G. Hall, "Fabrication of Planar Optical Waveguides by K⁺-Ion Exchange in BK7 and Pyrex Glass," *IEEE Journal of Quantum Electronics*. QE-22 (1986): 892.
- 2 O.S. Heavens, *Optical Properties of Thin Solid Films*, (New York, Dover Publications, Inc., 1965), 119.
- 3 Ibid.
- 4 Petre C. Logofătu, et al., "Abeles Method Revisited," *Applied Optics*. 45 (2006): 1120-1123.
- 5 Mukerrem Cakmak and James L. White, "Optical Properties of Simultaneous Biaxially Stretched Poly(Ethylene Terephthalate) Films," *Polymer Engineering and Science* (1989): 1534-1543.
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- 7 R.M.A. Azzam and N.M. Bashara, *Ellipsometry and Polarized Light*, (Amsterdam: Elsevier Science B.V., 1987), 317-326.
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- 9 See note 7, 336-337.
- 10 Valeri P. Tolstoy, Irina V. Chernyshova and Valeri A. Skryshevsky, *Handbook of Infrared Spectroscopy of Ultrathin Films*, (Hoboken: John Wiley and Sons, Inc., 2003), 44.
- 11 See note 7, 336-337.
- 12 Ibid.
- 13 Ibid.

CHAPTER 6: Experimental Results

6.1. SiO_x Film Characterization

SiO_x-PET materials are quite complex to analyze optically; therefore, each major component, the film and substrate, were characterized separately before being characterized together. The SiO_x film's thickness and refractive index were

Figure 6.1. Different oxide thicknesses can be observed from the reflected color of the PECVD SiO_x deposited samples: uncoated (top), 50nm SiO_x (middle), and 20nm SiO_x (bottom).

measured using multiple optically based measurement systems (e.g. ellipsometry, reflectometry, goniometry and Abeles' method) and its stoichiometry was determined using XPS. NS3 provided PECVD SiO_x coated silicon wafers of two thicknesses, estimated from the processing parameters to be 20 nm and 50 nm, for film characterization. Uncoated wafers were also provided for reference. Each thickness level consisted of one replicate, six wafers in all (Figure 6.1). The approximate thickness

of the oxide deposited on each sample was verified using a color chart.

Due to discrepancies in literature regarding the optical constants of silicon, characterization of the uncoated substrates was accomplished before analysis of the PECVD film. Determination of the refractive index and thickness of the

native oxide was accomplished with a very good model fit of the ellipsometric measurements ($r^2(\text{adj}) = 0.92991$). The determined refractive index of the two uncoated wafers ($n_{\text{si}} = 3.866$ and 3.877) showed good agreement with the refractive index of silicon in literature¹. However, the measured refractive index of the native oxides ($n_{\text{oxide}} = 1.639$ and 1.666) were higher than literature ($n_{\text{oxide}} = 1.46$ to 1.54). Therefore, the measured $n_{\text{oxide}} d_{\text{oxide}}$ (i.e. the oxide's pseudo thickness) was 2.80 nm and 3.08 nm which were consistent with literature.² There was an observed difference between the $n_{\text{oxide}} d_{\text{oxide}}$ measurements of the two uncoated samples; however, at $p = 0.0541$, this difference was not statistically significant. All the following models that assume a native oxide assumed the average of the measured values ($n = 1.663$ and $t = 1.83$ nm), not the literature values.

The optical measurement technique least sensitive to native oxides and interfacial effects was spectroscopic reflectometry, making it a good starting point for characterization of the PECVD SiO_x film. Determination of the deposited films' refractive indices and thicknesses was determined from spectroscopic models fitted to the normal

Figure 6.2. A spectroscopic reflectometry measurement (blue) for the 50 nm PECVD SiO_x sample with the fitted model superimposed (red).

reflectance datasets (Figure 6.2). The thickest deposited oxide samples (50 nm) resulted in measured oxide thicknesses of 69.9 ± 0.4 nm and 61.5 ± 1.7 nm. The corresponding measured refractive indices were 1.459 ± 0.003 and 1.461 ± 0.011 . The thinner deposited oxide samples had measured thicknesses of 28.63 ± 4.30 nm and 28.17 ± 5.96 nm with corresponding refractive indices of 1.465 ± 0.049 and 1.457 ± 0.022 , which are consistent with the thicker deposited PECVD films.

To verify the refractive index of the deposited oxide, Abeles' method was employed with the ellipsometer configured for goniometry measurements. Abeles' method measures the film's refractive index by determining the location when the reflection of the sample is the same as a film free sample. The thinner

Figure 6.3. The Brewster's angle for the 50 nm PECVD SiO_x sample was determined by finding the incident angle where the reflectances of the sample and uncoated silicon were equal.

the film, the more difficult it becomes to determine this location which subsequently leads to an increase in measurement error. Using optical constants for silicon stated in literature ($N_{\text{si}} = 3.871 - 0.018i$ at $\lambda = 632.8$ nm)³ with the goniometry measurements of the PECVD coated wafer, the measured Brewster's angle of the film was determined to be $56.23^\circ \pm 0.16^\circ$ (Figure 6.3). The

resulting refractive index was 1.495 ± 0.009 which was higher than the values measured by reflectometry. When a native oxide was assumed present – by measuring the difference between the uncoated and coated samples, instead of the difference between the coated sample and the theoretical reflection of

Figure 6.4. Cross sectional schematic of a model with a native oxide partition between the silicon substrate and the PECVD SiO_x film.

substrate (Figure 6.4), the modeled parameters were a little different. Allowing the substrate's refractive index to vary, the modeled results were $N_{Si} = 3.793 - 0.018i$, $N_{SiO_x} = 1.452$ and $t_{SiO_x} = 68.46$ nm with $r^2(\text{adj}) = 0.98064$. N_{Si} (Figure 6.5), used to determine model validity, was abnormally low which is indicative of systematic errors in the reflection measurement.

The ellipsometric results (Figure 6.6) found the measured refractive index to be consistent with the spectroscopic reflectometry measurements; however, like the goniometry measurements, the results were assumption dependant. With

uncoated silicon – the measured refractive index was 1.478 ± 0.027 (Appendix D).

A p-polarized ellipsometric model was fitted to the goniometer data to determine the film thickness for the measured reflectance (Appendix D). Assuming no underlying native oxide, the deposited film was determined to have a thickness of 67.82 nm and refractive index of 1.489 with $r^2(\text{adj}) = 0.89945$. However, when a native oxide was assumed to be present between the deposited film and

Figure 6.5. Goniometry data for the 50 nm PECVD SiO_x on Si sample with a two layer model fitted for optical parameter determination.

regards to the thickest sample measured, a single film model resulted in a refractive index of 1.487, while a model which assumes the presence of a native oxide resulted in a refractive index of 1.469. The discrepancy between the two model types only grew as the film thickness decreased. However, two interesting relations between measured refractive index and thickness were observed (Figure 6.7). The first was an inverse relation between total film thickness and the measured refractive index. A model representing this relation was fit to the data (6.1), where t was the thickness of the native oxide (t_{NO}) plus the deposited oxide (t_{PECVD}) and n_m was the modeled refractive index.

Figure 6.6. Measured ellipsometric points (black) and the resulting best fit models for each sample.

$$n_m = 1.4646793 + \frac{0.3664858}{t} \quad (6.1a)$$

$$t = t_{NO} + t_{PECVD} \quad (6.1b)$$

Such relations have been observed elsewhere when a detectable interface

Figure 6.7. A thickness vs. refractive index plot demonstrating how interfacial effects can influence the measured refractive index by ellipsometry.

between a silicon substrate and an oxide film is present.⁴ The fitted model predicted a refractive index of 1.465 for the PECVD SiO_x film which is similar to SiO₂ and consistent with the spectroscopic reflectometry measurements. The second observation was the increasing divergence of the single and double

layer models with decreasing film thickness, which is also indicative of interfacial effects.

The principle angles were determined for three samples measured at

Table 6.1. PECVD SiO_x Film Measured Properties Summary

		Reflectometer	Abelés' method	Goniometer	Ellipsometer	XPS
50nm Sample1	n	1.459 ± 0.003	1.478 - 1.495**	1.452* - 1.489	1.469* - 1.487	N/A
	d (nm)	69.89 ± 0.35	N/A	67.8 - 68.5*	65.9* - 66.5	
50nm Sample2	n	1.461 ± 0.011	N/A	N/A	1.469* - 1.492	N/A
	d (nm)	61.48 ± 1.74			60.1* - 61.2	
20nm Sample1	n	1.465 ± 0.049	N/A	N/A	1.479* - 1.523	N/A
	d (nm)	28.63 ± 4.30			26* - 27.5	
20nm Sample2	n	1.457 ± 0.022	N/A	N/A	1.51* - 1.536	N/A
	d (nm)	28.17 ± 5.96			23.3 - 23.9*	
Stoichiometry		N/A	N/A	N/A	N/A	2.1 - 2.2

(*) Includes the native oxide assumption

(**) Film free substrate calculated from literature and not measured

multiple incidence angles (indicated in Figure 6.6 by black vertical lines) resulting in $75.55^\circ \pm 0.16^\circ$ (uncoated Si), $74.08^\circ \pm 0.86^\circ$ (20nm PECVD SiO_x), and $68.37^\circ \pm 0.19^\circ$ (50nm PECVD SiO_x). The measured principle angles are consistent with the ellipsometric models that included a native oxide layer. A summary of the ellipsometric results for all the samples measured can be found in Table 6.1 along with the other measurement systems used to characterize the PECVD SiO_x films deposited on silicon.

Examination of the XPS data provided by NS3 for PECVD SiO_x on polypropylene (PP) showed the oxide stoichiometry to be slightly above the typical 2.0. The two samples analyzed had SiO_x film stoichiometries of 2.23 ± 0.02 and 2.15 ± 0.02 which did not vary significantly with depth (Figure 6.8), thus verifying the homogeneous isotropic

Figure 6.8. XPS depth profile, where zero is the film air interface, of two PECVD SiO_x samples demonstrating film homogeneity. (Figure by author with data courtesy of Nano Scale Surface Systems, Inc.)

assumption of the SiO_x films used by the optical measurement techniques above. The near 2.0 stoichiometries also verify why the measured refractive indices were very similar to fused silica (SiO_2). Trace amounts of carbon were present in the films, but the concentrations were < 1.0 at% for all depths measured, excluding interfaces.

Optical microscopy was also conducted and found pinholes in the film near the approximate region of testing (Figure 6.9). These film defects, which

Figure 6.9. An optical micrograph showing the presence of film inhomogeneties like pinholes and surface organic containments in the near area of optical measurements.

ranged in diameter from less than a micron to around 10 microns across, were sparsely scattered throughout the film. The presence of such defects may have affected the measured refractive indices for the film; however, no defects were found in the area of measurement. The presence of surface containments was also observed; however, none were observed in the region of testing.

6.2. Uncoated PET Characterization

Literature suggests axially stretched, whether uniaxially or biaxially, PET will exhibit some type of optical anisotropy, either birefringence or trirefringence.⁵ Therefore, multiple measurement systems were utilized to characterize the optical anisotropy of the uncoated PET film provided by NS3.

At normal incidence, a trirefringent material will exhibit two different

Figure 6.10. Averaged spectroscopic transmission measurements conducted at normal incidence with two orthogonal polarizations incident on the sample, the difference between the polarizations demonstrates the material is trirefringent.

reflection (or transmission) amplitudes depending upon the polarization of the incident light whereas a birefringent material will have only one reflectance amplitude for both polarization directions (see figure 5.3). Utilizing this phenomenon, spectroscopic transmission at normal incidence was measured to determine the anisotropy of the material. A statistically significant difference between the p and s polarizations was observed, verifying the existence of trirefringence (Figure 6.10). A dispersion relationship, common among dielectric materials, was also observed. The calculation of optical constants is dependant on the absolute measurement of transmission (or reflection); consequently, determination of the optical constants from the measured transmission data was not attempted because the interference “envelops” were degraded by an unknown optical phenomenon, probably depolarization or scattering, inherent to the material, measurement system or both.

Figure 6.11. Measured reflection of p-polarized light at 1° incident angle increments between 30° and 85°.

Before goniometry analysis could be conducted, measurement of the effective Brewster's angle was determined. Although the Brewster's angle of the material was found to be 60.39° (+/- 0.17°), this angle does not directly correlate to a refractive index as it does in isotropic materials. To determine the directionally

dependant refractive indices, the Brewster's angle measurement experiment was used in conjunction with the p-polarized reflection spectrum measured.

Examination of the measured p-polarized reflection spectrum led to the

observation of interference fringes, resulting from to rear interface reflections inherent to transparent materials (Figure 6.11 and 6.12). These fringes were a function of the optical constants and thickness of the material. Determination of the film thickness was attempted on both reflection spectrums (Figure 6.12); however, the

Figure 6.12. Measured reflection of p-polarized light at 1° incident angle increments between 30° and 85°.

maximum amplitudes of the interference fringes were attenuated by an optical phenomenon inherent to the material, preventing an accurate least squares regression model fit. Through analysis, periodic combinations of film thickness and refractive index were discovered to provide a local best fit model to the interference fringes. These fringe fits were conducted for the p and s polarization reflection spectrums (Appendix D) and compared against the measured Brewster's angle to reduce the number of possible optical model parameter combinations; however, a number of parameter combinations still remained. A relation between the film thickness (in nm) and the principle refractive indices was discovered through the following expression (6.2):

$$d_{\text{PET}} = 8471.14N_Z + 5235.27N_Y - 3249.87N_X - 4418.58 \quad (6.2)$$

Analysis of the interference fringes from the s-polarized goniometry measurements led to a similar relation for N_Y and d (6.3); however, since N_Y wasn't known, the exact thickness and other refractive indices could not be determined.

$$d_{\text{PET}} = 8982.89N_Y - 3355.06 \quad (6.3)$$

Polymers are semi-crystalline materials consisting of both crystalline and amorphous phases. The crystallinity of the polymer is defined as the volume fraction of crystalline particles in the material matrix. It has been found that polymer crystallinity is related to the average refractive index, density and thermal properties of the material.⁶ Utilizing this relation, the optical model parameters were further trimmed to include only parameter combinations with average refractive indices less than completely crystalline PET ($n = 1.6486$) and greater than completely amorphous PET ($n = 1.575$).⁷

To determine the actual crystallinity of the PET sample, a DSC measurement was conducted; however, the polymer failed to reach a completely molten state within the temperature measurement range (50 to 300 °C), making the calculation of the material's crystallinity very difficult. A post T_m amorphous baseline was assumed to be a constant

Figure 6.13. DSC measurement of uncoated PET for crystallinity determination.

heat capacity of 1.029 J/g°K, based upon comparisons of the measured DSC data with literature.⁸ Extrapolation of the PET thermal plot to the anticipated

Figure 6.14. Schematic of laser reflection at the air-PET interface with the plane of incidence parallel to the x and z axes.

completely molten position was conducted (Figure 6.13) and the crystallinity was determined through the First Law method.⁹ The resulting crystallinity was estimated at 36-41% with a resulting N_{ave} of 1.601-1.604. Comparisons of the measured DSC thermal plot to those provided in literature shows distinct

features inherent to medium crystallinity semi-crystalline polymer, including multiple melting peaks¹⁰ and a high melting point, 261°C.¹¹

Assuming a homogeneous anisotropic material (Figure 6.14), the resulting combination of Brewster's angle measurement, goniometry and DSC led to the determination of the following optical parameters: $N_x = 1.677$, $N_y = 1.632$, $N_z = 1.495$ and thickness = 11.343 μm , with the measured refractive indices being consistent with literature.¹² However, since the DSC measurement failed to reach a molten state, the crystallinity may have been overestimated, leaving two other possible solutions: $N_{\text{ave}} = (1.598, 1.6)$ and crystallinity = (31, 34) %.

Figure 6.16. Response surface model (red) interpolating the solution by minimizing the SSE grid (black).

Figure 6.15. The optimized model of ellipsometric measurements (Δ and Ψ) conducted on uncoated PET.

The optical constants derived from the above experiments were used to fit an ellipsometric model to the measured data (Figure 6.15). Single (graphically represented in Figure 6.14) and double layer models were fit to the data with the additional layer comprising of a Bruggeman EMA consisting of 50%

air and 50% N_{ave} of the polymer ($N_{EMA} = 1.289$) to account for scattering effects. Error function optimization resulted in an acceptable fit ($r^2(\text{adj}) = 0.62334$) of a two layer model (EMA layer on top of the PET layer). The modeled thickness for the PET was 11.174 μm accompanied by an EMA thickness of 8.1 nm (Figure 6.16). The effective Brewster's angle determined from the ellipsometric measurements was $60.36^\circ \pm 0.70^\circ$ which coincides with the measured effective Brewster's angle above.

Figure 6.17. Contrary to how it may appear, the depolarization never occurred at the same incident angle; however, the rotational difference between the nulls affected and unaffected by depolarization were as small as 0.1° .

The largest discrepancy between the fitted models and measured data was found in Δ which suggests the presence of depolarization.¹³ Depolarization

Figure 6.18. An AFM scan of blow molded PET demonstrating variation in surface height which, in combination with the rear surface, could lead to influential thickness variations.

is known to cause errors in the measured ellipsometric data, particularly in null ellipsometry.¹⁴ The depolarization detected in the characterization of uncoated PET was approximated through the measurement of the residual light striking the photo

Figure 6.19. Shifting of the interference fringes in the measured Ψ s is indicative of PET thickness differences at different locations on the same sample.

thickness uniformity of the PET. Not only did the thickness vary within the laser probing area which led to depolarization, but also between various locations on the sample (Figure 6.19). This was confirmed with interference fringe analysis of transmission measurements at normal incidence with unpolarized light (Figure

sensor at the null position at multiple incident angles (Figure 6.17). The cause of the depolarization may be thickness non-uniformities within the measured area (Figure 6.18).

An observed discrepancy in the goniometer and ellipsometric data demonstrated the lack of

Figure 6.20. A demonstration of thickness non-uniformity in the uncoated PET sample can be observed through unpolarized light transmission measurements at normal incidence.

Figure 6.22. Low power optical micrograph of uncoated PET.

6.20). The thickness variation ranged from no variation to a few hundred nanometers depending upon the relative location of the measurement points. The non-uniform thickness is not surprising given the manufacturing process of the

Figure 6.23. Qualitative depth profile (top) of stacked images (bottom) shows small particulates contained on the surface and within the PET sample.

PET samples; however, this could pose serious problems to any reflection, transmission or ellipsometric measurement system developed to monitor SiO_x deposition on such polymer products.

Macro photography showed small particulates within the material were scattering the incident laser light (Figure 6.21). This scattering may have contributed to depolarization and was probably the main reason the transmission and goniometry measurements had reduced amplitudes. Optical microscopy confirmed the presence of these micro particles (Figure 6.22). Using a digital photography technique known as *frame stacking*, a qualitative depth profile was created from multiple optical micrographs. From the stacked frames, it was observed that these particles existed inside the material; however, they appear to primarily reside near the surfaces (Figure 6.23).

6.3. SiO_x -PET Characterization

Although ellipsometric models were fit to the measurements on uncoated PET, the best fit was not a very good representation of the measured data. Problems fitting ellipsometric models were only confounded by the addition of the SiO_x layer. Despite the response

Figure 6.24. An ellipsometric plot of the best fit model to the 50 nm PECVD SiO_x -PET sample demonstrates the difficulty in fitting this complex optical material.

surface models providing very good interpolations of the null positions ($r^2(\text{adj}) > 0.995$) (Appendix B), a model could not be produced that adequately fit the measured ellipsometric data (Figure 6.24). Models consisting of up to five layers were attempted with various Bruggeman EMAs, but a combination of model parameter correlations, lack of data and inefficient model fitting capabilities doomed the model fitting process. The layers used in the model were assumed to be homogeneous; however, the XPS data showed the interface region to be inhomogeneous.

Examination of the compositional depth profile provided by the XPS data for $\text{SiO}_x\text{-PP}$ shows a large region between the two materials where the

composition is constantly changing from one material to the other (Figure 6.25). A similar region is also observed in the XPS depth profile of SiO_x on blow molded PET bottles (Figure 6.26). A similar region was expected for SiO_x on biaxially oriented PET.

Since the refractive index is linked to material composition, the continually changing composition within the interphase region means the material interface is inhomogeneous. With the polymer substrate being anisotropic, it is unknown if all or part of the interphase region is also anisotropic. Models were attempted which consisted of Bruggeman EMAs; however, fitting of such models

Figure 6.28. Ellipsometric surface with constant thickness contours (CTC) for a SiO_2 (film thickness between 600 and 720 nm) on Si demonstrating a discernable pattern of measured data.

Figure 6.27. The resulting compilation plot of all the ellipsometric measurements collected show no discernable pattern other than uncoated PET.

was prohibitive due to the number of parameters being fit and the lack of unique points (i.e. measurements at different incident angles).

Although ellipsometric models describing the optical construction of the material could not be fitted to the measured data, the different SiO_x film thicknesses led to measurable differences

Figure 6.29. Comparisons of the measured reflection at different incident angles shows the change in reflection induced by the deposited film.

Figure 6.30. Magnified view of the approximate Brewster's angle of the deposited film.

in both Δ and Ψ (Figure 6.27). However, there is no readily observable pattern to the data and how it changes as a function of film thickness like there is in SiO_2 on Si (Figure 6.28). A measurable difference in reflectance was observed as well (Figure 6.29); however, reflectance measurement techniques like Abeles' method are

difficult due to interference

caused by rear interface reflections. It appears as though the Brewster's angle for the deposited film was approximately 55.4° (Figure 6.30) which corresponds to an approximate film refractive index of 1.45. Had the reflected s-polarized light been measured, Ψ could have been calculated from the goniometer measurements and an observable pattern may have emerged; unfortunately those measurements were not

conducted and will have to be prorogued to future research.

Notes

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CHAPTER 7: Discussion of Results

7.1. The Use of Response Surface DOEs for Null Determination

The use of model profilers, included in statistical software packages like JMP®, with response surface experimental analyses made null determination very simple and accurate. Although more time consuming than averaging the positions of two equivalent light measurements on either side of the null, response surface interpolations are less prone to erroneous measurements and are easier to troubleshoot than the position averaging method. An additional advantage of response surface experiments for null determinations is the estimation of depolarization. Since the response surface analysis models the light measurement as a function of ellipsometric components' positions, it allows for the calculation of sample depolarization by the crossed polarizer method. This can be useful for determining the optical behavior of a material since sample depolarization is directly linked to the measured null and subsequently the calculation of Δ and Ψ .¹

The light measurements used in the response surface modeling for determination of the null can also be used to calculate Δ and Ψ through a technique known as photometric ellipsometry.² These measurements could be used in conjunction with null (conventional) ellipsometry to provide a measure of variance and to improve model fitting; however, photometric ellipsometry was not employed by this project due to time constraints.

Estimation of the variance in the response (i.e. the light measured) is possible using the response surface method, which is useful in depolarization measurements. However, the real measurement of interest is the variance of the treatments (i.e. the analyzer and polarizer positions) because that will determine

the variance in the calculated Δ and Ψ parameters. In order to estimate the variance in those parameters from a response surface model, the model has to be inverted with the response becoming the treatment and the treatments becoming the responses.³ Unlike linear models, this is not a trivial process and although associated with this project, inverting response surface models was a little outside the project scope and subsequently has been left to future research.

7.2. The PECVD SiO_x Film on Silicon Experiment

Prior to the measurement and analysis of the PECVD SiO_x films, the uncoated control wafers were measured by ellipsometry. Analysis of the ellipsometric data showed a consistently higher than bulk refractive index for the native oxide, but a silicon refractive index that was in line with literature. Since the refractive index of silicon is well known, it was used as a measure of validity for all the optical measurements made on silicon. The measured refractive index of the uncoated silicon samples coincided with the measurements found in literature.⁴ The higher than bulk refractive index is typical for native oxide measurements due mainly to the surface topography of the silicon surface.⁵ The measured native oxide's refractive index ($n = 1.663$) was situated between measurements made by Lukes ($n = 1.54$)⁶ and Hebert ($n = 1.894$)⁷ for thin oxides on silicon with null ellipsometry at $\lambda = 632.8$ nm. The validity of the interface roughness explanation for the higher than bulk refractive index measurements was further enhanced by measurements which found the refractive index of thin SiO₂ films to decrease with decreasing film thickness.⁸

Despite the native oxide's refractive index dependence on the interface topography between the oxide and the silicon substrate, adsorbed atmospheric contaminants can also alter the measurement. McCrackin showed that

layers of water as thin as 0.4 nm adsorbed on a gold film can be measured using null ellipsometry.⁹ Methods for removal of these adsorbed layers have been developed. Plasma and heat are two effective means to clean a surface;¹⁰ however, neither were used for this project. With regards to oxide characterization on silicon, elevating the temperature could cause the native oxide to grow thicker or a deposited oxide to change refractive index through annealing. Plasma treating was decided against because it would be ineffectual due to the measurement speed of the ellipsometer constructed being slower than the adsorption rate of airborne contaminants. With regards to PET and SiO_x-PET neither technique could be used because it would irreversibly alter the polymer chemistry, thus affecting the optical measurements of the material. Although slight errors may have been induced by presence of airborne contaminants, the overall influence would have been small compared to other factors like roughness at the material interfaces.

Interfacial roughness and film inhomogeneities violate the ellipsometric model assumption of homogeneous layers. Creation of an effective medium approximation (EMA)¹¹ converts an inhomogeneous layer into a homogeneous layer through interpolation of optical constants (Figure 7.1). The measured refractive indices of the native oxides on the uncoated samples are examples

native oxides measured were a mixture of silicon and silicon oxide, a Maxwell-Garnett EMA (7.1) would interpret the layer to consist of 86.5% SiO₂ with Si particles occupying the remaining 13.5%, assuming native oxide refractive index (N = 1.663) was N_{EMA}, SiO₂ (N = 1.46) was N_h and Si (N = 3.871 - 0.018j) was N_i.

$$\frac{N_{\text{EMA}}^2 - N_h^2}{N_{\text{EMA}}^2 + 2N_h^2} = f_i \frac{N_i^2 - N_h^2}{N_i^2 + 2N_h^2} \quad (7.1)$$

In reality, the native oxide is not a SiO₂ film with embedded Si particles, but a more complex structure. The space between the bulk silicon and a thermal SiO₂ film, like a native oxide, was found to contain a physical interface with silicon protrusions into the oxide layer and a chemical layer consisting of various silicon oxides as an intermediate layer between the Si protrusions and the SiO₂ film, discovered by Irene using atomic force microscopy (AFM) and spectroscopic immersion ellipsometry (SIE).¹² A similar interface was measured by Jellison, while studying thermal SiO₂ films ranging in thickness from 3 nm to 325 nm with spectroscopic ellipsometry, using a Bruggeman EMA (7.2) with f_{Si} = 0.5.¹³

$$f_{\text{Si}} \frac{N_{\text{Si}}^2 - N_{\text{EMA}}^2}{N_{\text{Si}}^2 + 2N_{\text{EMA}}^2} + (1 - f_{\text{Si}}) \frac{N_{\text{SiO}_2}^2 - N_{\text{EMA}}^2}{N_{\text{SiO}_2}^2 + 2N_{\text{EMA}}^2} = 0 \quad (7.2)$$

Subsequently such Bruggeman EMAs have been successfully employed to account for surface roughness¹⁴ and interphase region¹⁵ effects on ellipsometric measurements.

At normal incidence, transparent films with thicknesses greater than zero reduce the reflectance of light from the silicon sample (Figure 7.1). Utilizing this relation, the film's thickness can be determined if the refractive indices of the film and substrate are known.¹⁶ However, if the refractive index is not known,

the thickness and refractive index can be calculated if the normal reflectance is measured over a range of wavelengths. Typically the Filmetrics' reflectometer used for these measurements was only accurate to film thicknesses of approximately 100 nm. However, alterations to the measurement procedure from provided by Filmetrics allowed for accurate measures of the refractive index of transparent films on silicon down to the thin films region (Appendix E). The greatest source of error in the operation of the reflectometer was found to be in the baseline measurement procedure.

The measured reflectance of a sample measured by the Filmetrics F20 spectroscopic reflectometer was not the actual reflectance from the sample, but

the relative reflectance to a baseline material – typically uncoated silicon. Dust and other particulate matter which may adsorb to the surface of the standard will cause deviations in the baseline measurement

which influence the actual reflectance

measurement (Figure 7.2). It was found that if the baseline was verified prior to the sample measurement, this error could be significantly reduced. Further reduction of measurement error was accomplished by baselining – the baseline measurement process – prior to each sample measurement. Although slow, this technique randomized the error associated with the baselining procedure which allowed it to be averaged out during sample measurement analysis.

Since spectroscopic reflectometry is an indirect measurement system, like ellipsometry or goniometry, a model had to be fitted to the measured reflectance in order to determine the optical parameters of the material. This model fitting process could also induce error if not done correctly. Spectroscopic reflectometry utilizes the same model as ellipsometry to fit the measured reflectance data.*

However, at normal incidence there is no difference between the p and s polarizations – accept with regards to some anisotropic materials – so either

* This is because the measured reflectance and the material's Fresnel coefficients are directly related by $R = r^2$.

Figure 7.3. Poor baseline measurements will lead to extreme variation in the measured reflectance of the data.

equation could be used to calculate the refractive index and thickness of the measured sample.

Using numerical methods, the model fitting algorithm utilized by the F20 converges on a solution under a set of constraints specified by the operator. Typically, the more constrained the model the less complex the fitting procedure; however, it may also lead to inaccurate models or solutions that are not physically possible, due to the influence of measurement errors. In order to measure the PECVD films, a two layer model was used with only the native oxide refractive index and thickness constrained; the other four parameters (n_{Si} , n_{SiO_x} , k_{Si} and t_{SiO_x}) were allowed to vary. Allowing the refractive index of silicon to vary provided the model fitting program the latitude necessary to compensate for measurement errors while also providing a measure of model validity. The data used in the model fitting process was also limited to a 500 - 800 nm wavelength range to reduce measurement error associated with the extreme ends of the measured spectra and because the validity of the Cauchy equation is limited to wavelengths longer than approximately 500 nm (Appendix E).¹⁷ The modeled refractive index for silicon did deviate from the commonly quoted range ($3.865 - 0.018i$ to $3.882 - 0.019i$)¹⁸ for the samples measured, but the deviations were very small (typically $\delta n < 0.01$ and $\delta k < 0.01$). Small deviations in silicon's modeled refractive index verified the modeled parameters for the PECVD SiO_x layer. Interestingly, there was no difference in resulting model of the PECVD SiO_x layer without a native oxide assumed present. This was probably due to the negligible reflectance effects of a native oxide on reflectometry in the visible spectrum¹⁸ and the measurement systems inability to discriminate between the two films. Because of this, the measured thicknesses were overestimated by the native oxide's approximate thickness.

The refractive index measured by Abeles' method should have been the most accurate of the measurement systems used because it was independent of the substrate's refractive index and the film's thickness. However, reflectance errors inherent to the measurement system's baselining procedure caused Abeles' method to overestimate the film's refractive index. The overestimation was evident when comparing the measured refractive index to the refractive index measured by spectroscopic reflectometry.

A goniometry (ellipsometry based) model (7.3) was fitted to the measured reflectance data since from the model, thickness in addition to refractive index could be determined utilizing the same the model fitting procedure as ellipsometry (Appendix F).

$$R_p = \left[\frac{(r_{01p} + r_{12p}e^{-2j\beta_1}) + (r_{01p}r_{12p}e^{-2j\beta_1})r_{23p}e^{-2j\beta_2}}{(1 + r_{01p}r_{12p}e^{-2j\beta_1}) + (r_{12p} + r_{01p}e^{-2j\beta_1})r_{23p}e^{-2j\beta_2}} \right]^2 \quad (7.3)$$

Two models were fit to the PECVD SiO_x measured reflectance data, the first assumed no native oxide was present between the silicon substrate and the deposited SiO_x film while the second model assumed the presence of a native oxide with the same parameters as the native oxides measured on the uncoated wafers.

For the first model, the only unconstrained parameters modeled were the thickness and refractive index of the PECVD SiO_x film. The resulting refractive index was consistent with the Abeles' method measurements and the thickness was consistent with spectroscopic reflectometry. However, a pattern in the residual plot called into question the model's validity. In an attempt to fit a more valid model, the second model, assuming the native oxide presence, was also less constrained. Similar to the spectroscopic reflectometry models, the modeled

Figure 7.4. Residual plot for the best fit goniometric model of the reflectance measurements.

refractive index of the silicon substrate was used as a measure of validity since it is well known and doesn't vary much. The resulting best fit model produced a residual plot that would be expected of a valid fit (Figure 7.3); however, although the model fitted to the data was valid, the data itself was not valid.

The modeled refractive index of the silicon substrate was abnormally low, an indication of reflection measurement error, most likely associated with the baseline measurement procedure. A systematic error or set of errors had reduced the reflection amplitudes by approximately 0.33% to 0.84% depending upon the measured incidence angle. Although the reflectance error was not great, it was a measureable amount which adversely affected the model fitting and interpretation. The modeled refractive index for the SiO_x layer was subsequently lower than the refractive index measured by spectroscopic reflectometry due to the errors in the reflectance data.

Since the goniometry reflection measurements were determined relative to a 100% transmission in air baseline measurement, any fluctuation in the baseline directly affected the reflection measurement. Two baseline measurements were taken, one before and one after each sample; however, analysis of the baseline measurements showed a measureable shift. Linear interpolation between the two baseline measurements was used to compensate for this deviation; however, the error caused by the faulty baseline was only reduced not

eliminated because the error was not linear, but a function of other sources of error (e.g. environmental conditions). Subsequently, the errors in the goniometric measurements prevented the use of the Abeles' method and goniometric models from being valid measures of the PECVD SiO_x film's refractive index.

Null ellipsometry is a very sensitive measurement technique capable of sub-nanometer resolution under certain conditions.²⁰ Although ellipsometry's greatest strength is its sensitivity to thin layers, this can also cause major problems. Nanoscopic structures not detectable by other techniques, like interfacial roughness, and very thin films, like sub-nanometer adsorbed layers and intermediate films, will influence the ellipsometric measurement. This sensitivity to interfacial effects was encountered during PECVD SiO_x on Si.

Utilizing a two-zone measurement scheme with multiple incidence angle ellipsometry, the influence of the interfaces between the materials (ie. native oxide, silicon substrate and PECVD oxide) led to errors in the modelled refractive index for the deposited oxide. From the XPS measurements, the composition of the film was constant; however, a distinct relation between the modeled film thickness and refractive index from the ellipsometric data was observed. A reciprocal function of thickness vs. measured refractive index was fitted to the measurements resulting from the multiple incidence angle models (i.e. Sample 1 for the three film thicknesses) which included the presence of a native oxide. A similar relation between thickness and measured refractive index was observed by Hebert when studying thin thermal SiO_2 films on silicon with ellipsometry and tunneling current oscillations.²¹ The predicted refractive index of the PECVD SiO_x film absent of interfacial effects (Figure 7.5) was estimated from the fitted thickness reciprocal model to be 1.645 which was consistent with the spectroscopic reflectometry measurements ($n = 1.461$), a measurement system

which is insensitive to interfacial effects and films thinner than 5 nm (see Figure 7.2). Further evidence of interfacial effects and the presence of a native oxide was the

growing discrepancy between the single film ellipsometric model and the model which included a native oxide.

The use of multiple incident angle measurements and the fitting of a model to those measurements allowed a more accurate estimation of the optical parameters to be obtained. However, construction of 95% confidence intervals about the ellipsometric modeled parameters was not conducted due to the complex nature of the multiple angle of incidence ellipsometric models fits. Such estimations of variance from an ellipsometric model would greatly reduce the number of measurements needed by not requiring as many replicate measurements; however, this was left to further research to determine.

Confidence intervals about the spectroscopic reflectometry measurements were constructed using multiple measurements on the same sample, a method known as point by point analysis. However, point by point analysis could easily be conducted on spectroscopic reflectometry because its faster measurement and analysis times could collect more measurements in a given period of time than the ellipsometer. If the ellipsometric measurements were analyzed with a point by point analysis instead of as a function of incidence angle, then a measure of parameter variance could be calculated. However, a point by point

Figure 7.5. As the length scale of the film thickness becomes much larger than the length scale of the interfacial effects (e.g. surface roughness), the film begins to behave more ideally and its thickness and refractive index can be modeled more accurately.

analysis is more prone to errors in the incidence angle which can cause major errors especially for the thinner films. This was observed when comparing Sample 1 and Sample 2 in figure 6.7. The experiment was designed to use one measurement sample (Sample 1) to determine the optical parameters via a multiple angle of incidence model and use the other measurement sample to determine if a significant difference in deposited thickness and refractive index between the samples existed by comparisons at one angle of incidence (70°) (see figure 6.6).

The measured refractive index for both ellipsometry and spectroscopic reflectometry was slightly higher than fused silica (SiO_2) ($n = 1.457$).²² This deviation probably resulted from the slightly higher stoichiometric composition of 2.1-2.2 suggested from the XPS data. It is not uncommon for PECVD films to be non-stoichiometric (i.e. have stoichiometry other than 2.0)²³ given the deposition of SiO_x from an organic silicate feed gas, like HMDSO, at low temperature. Elements, such as carbon, which are contained in the plasma as a result of feed gas decomposition, can be incorporated into the film which would result in changing its composition. For this reason, many literature sources cite the material as silicon oxide (SiO_x) because a Si to O ratio of 2.0 does not necessarily correspond to a stoichiometric oxide²⁴ when deposited by PECVD. Analysis of the XPS depth profile shows the composition of the SiO_x film does not change significantly until it reaches the interface region, thus satisfying the homogeneous layer assumption for thickness and refractive index calculations by ellipsometry, reflectometry and goniometry.

7.3. Discussion of PET Characterization

The stretching and crystallization processing steps in the manufacturing of PET films cause the material to become optically anisotropic. The bidirectional stretching leads to the complex birefringent nature of the material which will pose a serious challenge to any manufacturing sensor or measurement system developed. To characterize the complex optical structure of biaxially oriented PET, a multi-step process was employed.

To determine if the material was birefringent, as was expected given the nature of its processing, spectroscopic transmission measurements were conducted at normal incidence. Each sample provided by NS3 had one flat side, presumably from the side of the roll of PET, which was used for orientation. The beam was polarized in two orthogonal directions – later determined to be the p and s directions – to determine the presence of a statistically significant change in transmission which is inherent to birefringent materials. The resulting statistical analysis of the transmission data determined a measureable difference between the polarizations leading to the conclusion that the material was birefringent. From the transmission differences, the s and p polarization directions were established.

A dispersive relation of the transmission data, with the material's refractive indices being higher at the shorter wavelengths than the longer ones, was observed which confirmed the assumption that the material was a dielectric. Although the refractive index and material thickness might have been determined through fitting equations 3.31 through 3.35 to the data, it was not attempted because of the increased complexity inherent to the refractive index being a function of wavelength. Interference envelop measurements have been proposed²⁵ for the determination of the material's refractive index independent of

the film thickness; however, degradation of the interference peaks and variation in the measured reflectance magnitude (as seen in Figure 6.16) prevented good estimations of the optical constants.

Pseudo-thickness calculations ($n_{\text{PET}}d_{\text{PET}}$) were calculated from the interference extrema of the unpolarized transmission measurements in the longer wavelengths. From these measurements, the thickness of the PET sample was determined to not be constant and would actually vary greatly within a small area on the same sample. The refractive indices associated with each polarization could have been approximated from the interference extrema analysis, but limitations on the polarizers prevented the use of longer, more useful, wavelengths (i.e. $\lambda > 800\text{nm}$).

At the Brewster's angle of a dielectric material, the p-polarization of any polarized light source will be suppressed which leads the material to act as a polarizer. By polarizing the incident beam in the p direction, extinction of the beam will occur when the incident angle equals the Brewster's angle. Since the Brewster's angle is a function of the isotropic material's refractive index, the refractive index can be directly calculated. Measurement of a material's Brewster's angle is independent of the material's thickness, making it a good starting point for characterization. However, for birefringent materials a Brewster's angle will exist, but it will not be directly linked to the material's refractive index like with an isotropic material.

Monochromatic goniometry, which is similar to Brewster's angle measurement, measures the reflectance of the material as a function of incident angle. The measured reflectance of a dielectric material by a goniometer whose incident beam is p-polarized will have a minimum at the material's Brewster's angle. This relation between goniometry and Brewster's angle measurements

allowed the two complimentary techniques to be used in determining the optical constants of a dielectric material. Unlike Brewster's angle measurements, goniometry is thickness dependant when rear interface reflections are present due to interference.

One of the most troublesome problems encountered by this project was the presence of reflections from the rear interface. Such reflections turn a material which may be considered a substrate into a film with well defined interference fringes. Despite the presence of rear interface reflections complicating the measurement analysis it was also a source of information. The interference fringes seen in the goniometer and spectroscopic transmission data were a function of the material's refractive index and thickness. This relation was utilized in the determination of the optical constants of the PET sample tested.

The Fresnel equations for a trirefringent substrate can be used to calculate the refractive index of the material from the goniometer data because, as stated earlier, reflectance is directly related to the Fresnel coefficients (equations 3.37 and 3.38). However, if rear interface reflections are present, the material's thickness must be taken into account, leading to a more complex model (3.31-3.35). Iteration of the optical model for p-polarized data could be conducted to determine the optical parameters and the solution checked against the measured Brewster's angle. Unfortunately, attenuation of the measured reflectance caused by scattering meant a best fit model could not be fit because the resulting solution would be a refractive index which was not physically possible for the material. It was discovered that periodic best fit solutions of the interference fringes could be used to narrow the possible combinations of optical parameters (N_x , N_y , N_z and d) to a few that were physically possible. It was from these local solutions that the relation between the principle direction refractive indices was

Figure 7.6. Thickness vs. refractive index plot showing how the three principle refractive indices and the PET thickness are related; N_y was the only refractive index with a direct relation to the PET thickness..

determined (Figure 7.6).

Through analysis of the reflection for each polarization, a series of solutions was determined. With semi-crystalline polymers, like biaxially oriented PET, an interesting relation between the average refractive index of the three refractive indices with the volume fraction of crystallinity exists.²⁶ Utilizing this relation, the list of possible solutions was further limited

to those that were physically possible between quoted amorphous ($N_a = 1.575$) and crystalline ($N_c = 1.6486$) average refractive indices** for biaxially oriented PET,²⁷ leaving 19 different combinations. Fortunately, because the crystallinity is directly proportional to the average refractive index (7.4), the crystallinity was measured to reduce the possible optical parameter combinations to one.

$$V_c = \frac{\bar{N}_a - \bar{N}}{\bar{N}_a - \bar{N}_c} \quad (7.4)$$

Where N_c is the average refractive index of a completely crystalline polymer, N_a is the average refractive index of a completely amorphous polymer, and V_c is the volume fraction of crystallinity. Typically the average refractive index is measured by a Abbe refractometer with the prism aligned in the machine direction (MD),

** It should be noted the published refractive indices are for a sodium D line ($\lambda = 589.3\text{nm}$); however because of the dispersion relation of dielectrics, the refractive index does not differ much from 589.3nm to 632.8nm; however, the refractive index at 632.8nm will be lower.

transverse direction (TD) and normal direction (ND); however, since it was unknown which direction the machine direction was for the samples provided, the plane of polarization (p-polarization) was aligned parallel to the sample edge (Figure 7.7). From the resulting refractive index measurements it appears the N_{MD} was N_x , N_{TD} was N_y and N_{ND} was N_z . Polymer crystallinity can be measured through multiple means, such as density measurements;²⁸ however, another relation between the crystallinity and thermal behavior of a polymer was used to verify the crystallinity using a DSC.

The DSC measurement of the uncoated PET sample exhibited odd thermal behavior. First, the melting endotherm was much larger than anticipated from the literature review which led to the premature ending of the DSC experiment. This required an estimation of the amorphous heat capacity and extrapolation of the heating curve, both of which reduce the accuracy of the crystallinity measurement. Second, the material displayed multiple melting peaks, common for PET,²⁹ in addition to heat induced crystallization. Analysis of the DSC data using the First Law method (a detailed description

Figure 7.7. Uncoated PET mounted with the edge of the sample at the top of the mount and oriented such that it is parallel to the plane of incidence.

of this method can be found in literature)³⁰ the crystallinity was determined to be between 35% and 40%, corresponding to only one combination of optical parameters. Consequently, the resulting N_x and N_y for the PET samples measured were consistent with measurements made on biaxially oriented PET with the WANTED spectrogoniometry method by Martinez-Anton and Bernaieu.³¹

The refractive indices determined through the auxiliary measurement systems were used to fit the ellipsometric data. By optimizing the ellipsometric equations with the previously determined refractive indices, the thickness of the PET sample was determined, at that measurement point. However, optimization of the ellipsometric data was a challenge due to the presence of rear interface reflections. A front side Bruggeman EMA was used to simulate depolarization due to scattering when a single film model did not sufficiently model the data. Capable of explaining only 64% of the measured data, the best fit model consisted of only an EMA on the front surface. Model fitting of thick anisotropic polymer films has been accomplished with spectroscopic ellipsometry by assuming the front interface consists of a coherent film while the polymer material and rear interface consists of incoherent layers.³² However, only low anisotropic polymers films (e.g. polycarbonate) have been successfully modeled this way; highly anisotropic materials, such as biaxially oriented PET, can not be measured with ellipsometry because depolarization, anisotropy and scattering effects interact to prevent the modeling of n and k .³³

A comprehensive study on the effect of depolarization on null (conventional) ellipsometry concluded depolarization has a significant effect on Ψ as it approaches 0° ,³⁴ which for dielectric materials is the Brewster's angle. The presence of depolarization near the measured Brewster's angle of the PET samples and the drastically reduced Ψ measurements, approximately 2° - 5° ,

compared to the goniometer data is consistent with the study's findings. Two possible sources of the measured depolarization were sample thickness variation and scattering effects.

Thickness variation was measured for the PET sample. Given the magnitude of the measured differences, small variations in the sample thickness in the area of the probing beam spot (between 1 and 200 mm² depending upon angle of incidence) is a probable assumption. Such thickness variations within the area measured by the beam of light leads to depolarization through the superposition of multiple reflections, each a different phase, which get integrated by the detector to produce an abnormally high signal.³⁵ The angular dependence of the measured depolarization in conjunction with the AFM measurements of surface height variation over an area smaller than the beam spot size adds validity to this depolarization source. Generalized ellipsometry utilizing a Muller matrix representation of the ellipsometric system can be used to correct the effects of depolarization;³⁶ however, no such correction exists for null ellipsometry.

The second plausible source of depolarization is through scattering. Traditionally depolarization resulting from scattering is a result of a very rough surface; however, scattering caused inside the plane of the material can produce the same effect. Superposition of incoherent waves of scattered light by different parts of the sample lead to depolarization of the analyzing beam.³⁷ Optical microscopy found nano particles, believed to be crystalline PET,³⁸ within and on the surface of the polymer material. Macro photography discovered that these particles were the source of light scatter observed in the reflected and transmitted beams. Use of a traditional surface roughness EMA has been shown to be effective in compensating the model for the depolarization effects of the scattered

light.³⁹ This was the basis for the single EMA layer being integrated into the ellipsometric model.

The front side EMA which was the result of the best fit model accounted for the depolarization caused by scattering. Point by point comparison of the model to the measured data shows the greatest deviation occurs in Δ . Such deviations are probably due to depolarization caused by the non-uniform thickness of the PET sample.

To mitigate the depolarization caused by rear surface reflections, techniques such as rear surface abrasion⁴⁰ and index matching fluid immersion⁴¹ could have been employed. However, since this was a feasibility study of ellipsometric sensors, such techniques were decided against because those ideal situations would probably not be available in an industrial environment.

7.4. Characterization of PECVD SiO_x-PET

With the uncoated PET sample, the ellipsometer struggled to adequately measure the sample's refractive indices and thickness; however, it utterly failed when trying to measure SiO_x-PET. Similar to the uncoated PET measurements, the minimum amount of data had been collected so a model could be fit, but an insufficient amount of data was collected to fit a model that provided useful information about the material being studied. However, unlike the uncoated sample, it is unknown if null ellipsometry is even capable of undertaking the incredibly difficult task of measuring SiO_x films on PET. A model was attempted on the 50 nm SiO_x deposited sample so information from the XPS data may be used to assist in the fitting process; however, the best fit model could only explain 14% of the measured data, far too low to provide useful information about the sample.

Despite having to compensate for depolarization, whose existence was demonstrated with the uncoated PET measurements, the ellipsometer had to contend with two additional material layers: a homogeneous SiO_x film and a heterogeneous “interphase” region between the SiO_x and PET. As determined by measuring PECVD SiO_x on silicon, the deposited films were uniform in refractive index and homogeneity; therefore the addition of these layers to the ellipsometric model should not have been that complicated. However, the region between the polymer and the SiO_x film, where the film was chemically bound to the polymer, makes SiO_x -polymer materials difficult to measure ellipsometrically. From the XPS compositional profile data for SiO_x -PP and SiO_x -PET, it is obvious this region is constantly changing its composition as a function of depth, as the material transitions from ceramic to polymer. Inevitably, this continual change in composition also caused a continual change in the refractive index. The changing composition was not the only factor effecting the refractive index in this region, possible cross-linking and densification resulting from interaction of vacuum ultraviolet light (VUV), emitted by the plasma during the deposition process, with the polymer probably contributed to the interphase refractive index modifications.⁴² Although, this cross-linking and densification may result from normal deposition by PECVD, some practitioners utilize VUV to improve adhesion of the ceramic films to the polymer surface;⁴³ however, it is unknown if NS3 plasma treated the polymer prior to SiO_x deposition.

It has been shown that a Bruggeman EMA can adequately represent this region on a slightly anisotropic polymer (polycarbonate),⁴⁴ but as discussed in the previous section, what is possible on a slightly anisotropic material may not be feasible on a highly anisotropic material like PET. Studying SiN on PET, it was shown a Bruggeman EMA consisting of PET, SiN and voids could

produce a decent model fit of the measured spectroscopic data; however, the model appeared to diverge quite a bit in the longer wavelengths.⁴⁵ The SiN on PET study also failed to mention anisotropy of any type for the PET or the interphase region and also failed to state how the PET was processed (e.g. biaxially oriented, blow molded, extruded, cast, etc.); information which could have important consequences on the ellipsometric models. A calculated EMA containing voids does not necessarily contain pockets of material absence within the modeled layer, but voids are often used to adjust the refractive index of the EMA layer.⁴⁶

Attempts to fit models to the measured data including an interphase region failed to provide a sufficient fit from which physical interpretation of the measured sample could be drawn. Several attempts at interphase modeling were conducted; of the attempts, some defined the interphase layer with an EMA while others allowed the effective refractive index to vary. Typically, the models fit the thicknesses and constrained the refractive indices of the layers. The most liberated model constrained only the refractive index of the PET and SiO_x layers; however, an optimum solution was not found due to an insufficient amount of data to prevent parameter correlation. The model fitting process was also a constraint on what models could be fitted. Although models consisting of up to five layers were attempted, it was found that too many variable parameters prevented the fitting process from working properly.

The fitting process (Appendix F) consisted of an algorithm constructed in Mathcad® for the calculation of a sum of squares error (SSE) grid from a given set of model parameters. While theoretically capable of an innumerable number of variable parameters, the practical limit was around four. The SSE grid calculation program produced spreadsheets which could be opened and

manipulated by any program capable of evaluating spreadsheets. However, the size of the spreadsheet increased exponentially as the number of parameters increased or the deviations between SSE steps decreased. The limiting factor in the model fitting process was the size of the spreadsheet that could be constructed and analyzed, the approximate limit was around one million rows of data. The model fitting process was similar to solid model finite element analysis (FEA) where the SSE grid acts as the mesh for the model. With FEA, the solid model is broken up into small elements which are analyzed locally and then combined with the other elements to simulate a global affect of stress, strain or other engineering property of interest. The smaller the mesh elements, the more accurate the FEA; however, the larger the computational burden. Similarly, the SSE grid produced more accurate results when the deviations between grid points were small; however, the smaller the grid point deviations, the larger the SSE spreadsheet produced. Most of the fitted models consisted of SSE grids between 50,000 and 500,000 rows with the latter being indicative of the more complex models.

Analysis of the data produced by the SSE calculation program was accomplished with JMP® statistical software. An error function, which was the total sum of squares error for the model, was used to determine the optimum model for the measured data set. Minimization of the error function produced the optimal solution. Since the error function behavior was quadratic,⁴⁷ a second order response surface model could be fit to the error function data from which an optimum solution could be found. For example, if only two parameters were being modeled (e.g. film refractive index and thickness), the resulting surface would be three dimensional (Figure 7.8). However, more than two variable parameters prevents graphical representation of the entire surface in three

Figure 7.8. A SSE grid showing how optimization of the error function will lead to a best fit solution.

dimensions, but does not prevent the fitting of a response surface model.

Numerical analysis algorithms like Newton's method and Levenberg-Marquardt are often employed to optimize ellipsometric data via an error function.⁴⁸ However, it was found that for the biaxially oriented PET samples such optimization algorithms would struggle to produce

good fits due to the multiplicity of solutions. The above mentioned algorithms are designed to find an optimum point (e.g. maxima, minima or saddle point) for a given function. Examination of the SSE grid shows many such "solutions" which the algorithms would inevitably converge upon depended greatly on the seed value (Figure 7.9). The multiple solution problem was only encountered with the PET samples and never with any absorbing substrate or thick transparent isotropic substrate (e.g. Pyrex 7740), probably due to the length scale of those samples. The presence of multiple solutions also results from interference due to rear surface reflections.

Despite not being able to fit an ellipsometric model to the measured SiO_x -PET data, a measureable difference in Δ and Ψ for the different film thicknesses was observed. The implications of this observation are polarized light base sensors could possibly be developed for SiO_x -PET (or more general, SiO_x -polymer) products; however, further experimentation is needed.

A major problem worth noting was encountered during calibration of the ellipsometer, sample tilt. A fixed sample tilt causes the plane of incidence

to change as a function of incidence angle, significantly complicating the measurement of Δ and Ψ . This affects not just the incidence angle measurement, but the angular measurement of all the ellipsometric components (polarizer, compensator and analyzer). If multiple incidence angles are used in the analysis of a material, careful characterization of all the

Figure 7.9. An SSE grid plot demonstrating the presence of multiple solutions which could erroneously affect an automatic model fitting algorithm.

errors must be accomplished in order to achieve good results. Literature does a good job identifying and explaining the effects of all the sources of error, except sample tilt. This is probably because commercial grade ellipsometers feature tilting sample stages which allow easy physical correction of this error. Many techniques were proposed for the measurement of the sample tilt angle using the ellipsometer under normal conditions with a dielectric sample;⁴⁹ however, these techniques were developed so physical adjustment of the sample stage could be made during calibration only. No post measurement adjustment was proposed to compensate for sample tilting except for one literature source.⁵⁰ However, the correction proposed was limited to very small tilt angles ($\theta_t \ll 1^\circ$) and was unable to correct for the larger tilt angles encountered by this project ($0.5^\circ < \theta_t < 1^\circ$). Due to budgetary constraints, sample mounting tilt adjustment was never incorporated into the design of the ellipsometer constructed for this project; as

such, a system for adjusting the measurement data during the calculation of Δ and Ψ was developed to correct for this error following the measurement process (Appendix C).

7.5. Implications on measurement system and sensor design

The use of ellipsometry in a manufacturing measurement system for SiO_x -polymer materials is feasible; however many factors, which were encountered by this project, must be addressed during the development of such a system.

- Sample tilting
- Backside reflections
- Beam scattering resulting from polymer microstructure
- Anisotropy of the polymer and possibly the interphase region
- The heterogeneous interphase region between the SiO_x layer and the polymer substrate
- Optical parameter correlations
- Measurement speed

The plane of incidence of polarized light is a function of the material's geometry and positioning. Tilting of the sample will cause the plane of incidence to change, resulting in significant measurement errors if not corrected. In a laboratory environment, sample tilt is typically of little concern because it can be physically corrected during calibration; however, on an assembly line such geometrical errors can easily be caused by the machinery operating under normal conditions (e.g. vibrations) which may prevent physical correction of such errors. Therefore, measurement and correction of the sample error during the ellipsometric measurement process may need to be dealt with during the development of an ellipsometric measurement system.

When measuring transparent materials, such as PET, backside reflections must be taken into consideration, otherwise erroneous results will be collected. Backside reflections computationally turn a substrate material into film, bringing the thickness of the material into the equation. Measurement of transparent materials means thickness variations could lead to depolarization effects. Correction of such effects can only be accomplished with generalized ellipsometry using the Muller matrix notation. Back side reflection mitigation techniques do exist, like the use of focusing optics with pickoff apertures for use with thicker films or active signal filters,⁵¹ which could be developed to eliminate or reduce the error induced by the measurement of transparent polymer substrates.

The presence of polymer crystallites may induce scattering of the measurement system's probing beam. While depolarization of such scattering can be corrected using an EMA, reflection or photometric ellipsometric measurement systems may be severely affected by the attenuation of the reflected or transmitted beam. While ellipsometers of various configurations could be employed,⁵² the configuration that is developed will need to take scattering into consideration if the material contains polymer crystallites or other light scattering particles within its matrix.

Anisotropy could be a serious developmental hurdle by preventing the use of some ellipsometric configurations or requiring special arrangement of the measurement system relative to the material being monitored. However, anisotropy may also provide unique measurement capabilities, like polymer crystallinity monitoring, which may allow SiO_x-polymer products to be better tailored for the desired application. Unfortunately anisotropy may also complicate the ellipsometric measurement of the material, not only through a geometric

constraint, but also by interacting with other sources of error to convolute or prevent their correction. Generalized ellipsometry utilizing the Berreman matrix formalism may be required for such complex materials.

Characterization and analysis of a material is dependant upon the amount of data collected because this affects how the material can be modeled. Unfortunately this project failed to collect enough data to sufficiently model the materials being investigated. Because a model of sufficient validity wasn't fitted to the measured data for SiO_x -PET, it remains unknown if single wavelength ellipsometry is capable of measuring such a complex material given the multitudinous factors (e.g. anisotropy, scattering, backside reflections, heterogeneous interphase region, etc.) which affect the measurement system. Complex materials, such as biaxially oriented PET, might best be analyzed with a spectroscopic solution which has been successfully employed in the measurement of SiO_2 -polymer materials and transparent polymers with rear interface reflections.

The experiments conducted by this project consisted of static subjects; however, in a manufacturing environment static measurements may not be possible. Therefore, some of the problems, like depolarization due to non-uniform polymer thickness, will be compounded in a dynamic measurement environment and should be taken into consideration during measurement system development.

Finally, construction of a binary sensor for detecting the presence of an oxide layer is much easier than development of a measurement system. As demonstrated by this project, discrimination of oxide layers is possible with ellipsometry. Sensor fidelity is dependant upon the incidence angle, wavelength and polarization of the sensing beam (in addition to the electronics used). As

with an ellipsometric measurement system, there are a myriad of different optical configurations, both reflection and transmission, which can be incorporated in the sensor development.⁵³

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CHAPTER 8: Conclusions and Recommendations

This project set out to determine if polarized light based measurement systems (i.e. ellipsometry) could be used in an industrial environment for quality control purposes during the manufacturing of SiO_x -polymer products. It has been shown that it might be possible to create sensors for film detection with a material as complex of SiO_x -PET; however, the possibility of creating measurement systems for quantifying the thickness and optical properties of deposited films remains unknown.

From the three experiments setup to characterize SiO_x -PET with ellipsometry, eight major pitfalls were encountered which must be addressed during development of a polarized light based sensor or measurement system for SiO_x -polymer products: rear interface reflections associated with transparent substrates, substrate optical anisotropy, changing plane of incidence due to a tilted sample, depolarization and scattering, measurement speed and measurement environment. Of the listed problems, rear interface reflections and optical anisotropy will probably be the most difficult to deal with, as they were with this project. The single wavelength null ellipsometer constructed for testing SiO_x deposited on biaxially oriented PET may not have been capable of characterizing the material system due to the extreme complexity associated with SiO_x -PET; however, generalized ellipsometry, which was not attempted, may prove successful.

What led to the demise of the ellipsometric models for SiO_x -PET was not one factor, but the interaction of multiple factors creating an extremely complex optical material (i.e. rear interface reflections with scattering, depolarization, optical anisotropy and a heterogeneous interphase region). While many possible

solutions exist, for instance the use of a spectroscopic measurement system, the success of such solutions depends largely upon the materials being measured. Biaxially oriented PET is a complex material to measure with ellipsometry because of its transparency and high anisotropy; however, ellipsometry may be feasible with an isotropic or opaque polymer substrate. Future studies should focus on sufficiently characterizing the uncoated polymer substrate prior to studying more complex coated material systems, like SiO_x -PET; incomplete characterization of the PET substrate by this project was where the majority of measurement problems were encountered.

Optical measurements of polymer crystallinity has traditionally been done using an Abbe refractometer; however, this project has shown that ellipsometry can be used for this measurement as well. Unfortunately, time and material constraints prevented further research into this relation; as such, comparisons with XRD, DSC, FTIR and density measurements of various polymers is recommended to further explore this concept.

Since not all product geometries are planar like biaxially oriented PET, researching the feasibility of ellipsometry on curved polymer surfaces may prove beneficial to companies which utilize non planar geometries in their products. The preliminary experiment conducted by this project determined it is possible to measure SiO_x within a polymer container with polarized light; however, the experiment was far from conclusive. If ellipsometry can be used to monitor SiO_x deposited within a non planar polymer container or more generally on a non-planar surface, the benefit would reach well beyond the polymer beverage container industry.

Despite good results, manually measuring the null positions was a very time consuming task and if the ellipsometer is to be used more widely

in by the Materials Engineering Department at Cal Poly, this measurement time will need to decrease. Investigating a combined photometric and null measurement technique for determination of Δ and Ψ through the response surface method proposed and utilized by this project could assist in speeding up the measurement process. However, photometric ellipsometry requires an accurate measure of the intensity of light incident on the light sensor. While capable of intensity measurements, the current electronics used in the collection, amplification and digital conversion of the light sensor signal need to be redesigned to improve reliability. Related to the ellipsometer electronics, automation of one or more of the rotational mechanisms is needed to improve measurement speed. On average, a two-zone measurement by the response surface method took 40-60 minutes to conduct; automation could reduce that time to 2-3 minutes or less, making the system more useful for more projects. Regardless of whether automation of the optical components is done, the software used in the calculation of the ellipsometric parameters, ellipsometric model fits and statistical calculations needs to be recoded to make it more user friendly. Finally, redesign of the sample mounting system is very necessary. Although accurate measurements were possible with a fixed, but measured, sample tilt, elimination of the tilt through a redesigned sample mount will greatly simplify the analysis process and improve accuracy.

One of the most useful instruments used in this project was the goniometer. As spectroscopic reflectometry can measure film thickness and refractive index from reflection measurements at normal incidence by varying the wavelength measured, goniometry can do the same by varying the incidence angle at a constant wavelength. Unfortunately, the current goniometer cannot measure refractive index dispersion and the spectroscopic reflectometer cannot

measure dielectric substrates. Construction of a spectrogoniometer may prove very beneficial given the number of optical projects being taken on by students working in the microfabriaction laboratory at Cal Poly, like PDMS waveguides, where refractive index and possibly thickness measurements are crucial.

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APPENDIX A: Proof of Concept Experiment

In the Spring of 2007, a set of experiments were conducted to determine if polarized light could detect the presence of a SiO_x film deposited on the inside of a polymer beverage container. Nano Scale Surface Systems, Inc. provided a number of samples with different coating thicknesses and bottle types to be tested. The experiments conducted were designed to be a full factorial experiments; however, they were conducted as a split-plot experiments. Since the original analysis was for full factorial experiments, reanalysis of the data, presented at the end of this appendix, was conducted to determine the validity of the original conclusions and add any additional information which may have been discovered.

A.1. The Original Report

Investigating the Optical Properties of Transparent Polymeric Beverage Containers Utilizing
Polarized Light

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Abstract

Interior coated silicon oxide (SiO_x) films are being employed as vapor barriers for polymeric containers. As a portion of a larger project developing a thickness measurement technique of the vapor barriers, three experiments using light sources of different polarization states were used to test the assumption of optical homogeneity of the polymeric containers. Two fixed effects variables were used as predictors for the measured intensity, measurement point and bottle type. The optical homogeneity assumption was rejected using a general linear model (GLM) routine with a Bonferroni adjustment at $\alpha = 0.05$ for the polymeric container designs tested. The current measurement system was able to differentiate containers with film thicknesses as thin as 200 Å from uncoated containers, but better resolution was hampered by precision problems with the measurement system.

Introduction

Polymeric containers are becoming the container of choice for many applications, beverages in particular. The cost effectiveness of polymers with respect to other comparable materials, like aluminum, is one of the major reasons behind this trend. Although polymeric containers are superior to other materials in many applications, they contain one major flaw ... permeability. Gases dissolved in liquids, such as carbon dioxide in sodas or beer, can diffuse through the polymeric barrier of the container and escape to the outside environment. The effect of such diffusion is a reduced shelf life for products which spoil or "go flat" as a result of gas translation. The development of vapor barriers for polymeric containers was in direct response to the diffusion problem.

Vapor barriers are materials that have been integrated into the container design to block or inhibit the diffusion of gas molecules in and out of the container. An interior silicon oxide (SiO_x) coating is an example of a specific vapor barrier design integrated into a polymeric container design and is the vapor barrier design investigated in this report.

The SiO_x glass film is deposited on the inner surface of a polymeric container at an approximate thickness of 100 Å (10 nm). Adhesion of the film to the polymeric substrate is accomplished through plasma enhanced chemical vapor deposition (PECVD). Control of external plasma parameters allow PECVD to open up a chemical pathway to precisely control the polymerization and deposition process of a decomposed volatile organo-silicon precursor (Grunier *et al*, 2006, p. 4564), like hexamethyldisiloxane, in the presence of oxygen on a polymeric substrate. The SiO_x film, which is created through the precursor decomposition in the presence of oxygen, is chemically bonded to the polymeric substrate through the creation of an interphase region during the PECVD process. The interphase region is loosely defined as the intermediate region between two contacting solids, which is distinct in structure and properties from either of the contacting phases (Sobrinho *et al*, 1998, p. 121).

Understanding the scale and physical properties of the vapor barrier / polymeric container system is difficult. With regards to scale, a vapor barrier with a thickness of approximately 100 Å on a polymeric substrate whose thickness is approximately 1.0 mm, the average thickness of a polymeric container, is analogous to a piece of printer paper, like this report is written on, laid on top of a three story building. Similarly, a single sheet of paper has different physical properties than the bulk material it came from; the vapor barrier film also has different physical properties, like flexibility, that is not observable in the bulk material. The difference in physical properties of a film from its bulk material allows the vapor barrier to give with the polymer container when the container has an external load acting on it. Therefore, the chemical bonding of the vapor

barrier to the polymeric container and the unique physical properties of materials on the nano-scale keep the SiO_x film from breaking and flaking off into the product the container is holding.

Each bottle is produced by a blow molding process and should have approximately the same geometries for a given design. Production line rates of the SiO_x coated bottles are between 10,000 and 20,000 bottles per hour, however, currently no “in line” vapor barrier thickness measurement technique is available to measure the thickness of a film within the produced container. The purpose of the experiments outlined in this report is to act as a supplement in the development of an “in line” vapor barrier thickness measurement technique.

Samples of uncoated, single coated and double coated containers were used to predict the properties of the population of containers produced. The population of the experiment was defined as all the containers of two specific bottle designs produced with and without the vapor barriers.

Review of Literature

On February 9, 2006, Nano Coating Systems LLC., announced the development of a new, cost effective process for plasma coating plastics with SiO_x (Molinaro, 2006; Omnexus.com, 2006). Up until that time, interior plasma coating was the most expensive vapor barrier design available (Knights, 2000). The new process made plasma coating on the interior of bottles more competitive while maintaining numerous advantages. Polymer bottles have been found to leech chemicals, although most aren't harmful, into the liquid which they contain (Biscardi & et al, 2003). An interior SiO_x coating prevents polymer

leeching while preserving the product through inhibiting gas diffusion. “According to John Felts (personal communication, February 2, 2007), President and CEO of Nano Scale Surface Systems Inc, the SiO_x film does not interfere with current recycling technologies and is FDA approved.” While this impressive technology is poised to integrate itself throughout the beverage container market, one problem remains: there is no way to measure the film deposited in the containers after they have been produced. Due to production constraints, this can be accomplished optically.

Very little literature exists about optical techniques for measuring thin films on curved surfaces and none exist for measuring through a container. A technique developed for measuring a very small point (Holzapfel, Neuschaefer-Rube, & Wirth, 2003) could be used to measure inside the container, but design constraints eliminate its use for application on this project. Therefore, due to the lack of literature and the need for a measurement technique, this project seeks to satisfy both.

Experimental methods

To investigate the optical effects due to the polymer container and vapor barrier, polyethylene terephthalate (PETE) bottles and interior coated SiO_x vapor barriers were analyzed with linear and circular polarized light sources. A sample of six uncoated containers, ten single coated containers, and one double coated container were taken out of the population of containers produced – courtesy of John Felts. Unfortunately one coated and one uncoated container were damaged and could not be used, thus only nine coated and five uncoated containers were tested.

The sample of fifteen containers consisted of two bottle designs, clear and transparent blue. Four clear and eleven blue containers were tested in all. The uncoated containers were a control group which was tested against the other two groups, coated and double coated. The samples were tested utilizing a blocking design.

The experiment utilized a linear polarized helium-neon (HeNe) laser as the light source. The laser propagated through the center of the sample so the effect geometry would have a minimized effect on the polarization state of the transmitted beam. The transmitted beam then passed through a linear polarizer whose orientation was orthogonal to the polarization produced by the laser to completely extinguish the transmitted beam if there was no interaction between the light and the sample. The light that passed through the linear polarizer was collected by a fiber optic cable which was attached to a spectrometer. The spectrometer measured the light intensity in the form of counts for a fixed integration time, 10 ms. The measurement was outputted to a computer for analysis (Figure 1,2). The intensity of the measured light corresponded to the change in polarization state of the beam as it interacted with the sample. Circular polarized light was produced by placing a circular polarizer in between the laser output and the sample.

Figure 2. Experimental set up for samples tested with linear polarized light.

Figure 3. Experimental set up for samples tested with circular polarized light.

The samples were measured using the same process regardless of bottle design. Each sample had five measurement points per half side of the bottle. Therefore, ten measurement points were located all the way around the bottle. In theory, the direction of light propagation should have little or no effect on the light as it passes through the sample. Therefore, the points on the opposite side of the bottle should be the same. The measurement points were the same for all bottles which were located approximately 5° , 45° , 90° , 135° , and 175° counterclockwise from the bottle seam (Figure 3). The repeated measurements of each measurement point, twice per sample, tested the repeatability of the measurement process. The removal and replacement of the sample every ten measurements tested the reproducibility of the measurement process.

Figure 3. Cross-sectional view of the container and a schematic representation of the laser passing through the sample at the different measurement points.

The location on the bottle where the laser was to measure was determined through by the arc length of a circle (1). Although it is known that the cross section of the container is elliptical, the differences between the major and minor diameters were so small that they could not be measured accurately, therefore it was assumed to be circular and the arc length was approximated using the major diameter which was measured from seam to seam. The arc length for each measurement angle was marked on the side of each container as a reference point in the measurement process.

$$arclength = \frac{\pi \theta D}{360} \quad (1)$$

The data was analyzed using the general linear model (GLM) routine in the statistical analysis software package Minitab®. The response variables were the intensity and the wavelength of the maximum peak. The intensity was measured three ways: integrating the area under the peak from 630 – 637 nm, using a pseudo bandpass filter¹ which measured the area under the curve from 632 – 634 nm, and measuring height of the maximum peak. The explanatory variables in the model were measurement point, bottle type, repeatability, and reproducibility.

In an attempt to simplify the analysis process, the measured data was broken up into different analysis blocks and models were constructed for each block (Figure 4). The statistical models included random effects to analyze the variance in the data caused by the measurement system. With the random effects included in the model allowed for the estimation of the precision affected by repeated measurements and reproduced experiments on the response.

¹ No physical bandpass filter was used, but the area under the resulting peak was measured ± 1 nm from the specified wavelength on the laser. This was done to investigate the precision effects of integration the entire peak and how a bandpass filter might affect the measurement system.

Figure 4. Measurement data analysis process flowchart.

Results

As outlined in figure 4, the experimental data was broken down into smaller analysis blocks.

Unfortunately due to time constraints, only three of the four blocks of experimental data were measured. The block not measured was blue tinted bottles analyzed using circular polarized light. Also, due to short comings in the experimental design, the experiment of blue bottles analyzed with linear polarized light was not conducted in a balanced manner, resulting in analysis complications. Fortunately, the two analysis blocks for the clear bottles produced useful models.

Blue bottles measured with linear polarized light

The experiment was designed to be balanced and the corresponding experimental measurements were conducted accordingly. Two replications of five measurements, repeated once per bottle were conducted on five different bottles. Of the five bottles, there were three different bottle types: uncoated, coated, and double coated (Table I).

Table I. Breakdown of the balanced experimental design.

Bottle Type	Bottles per type	Measurement locations per half bottle	Bottle halves measured per replication	Measurement Replications	Total Measurements
Uncoated	1	5	2	2	20
Coated	3	5	2	2	60
Double Coated	1	5	2	2	20

Measurements were taken according to the balanced design, but one coated bottle acted completely different from the there two. The outlier bottle had little or no interaction with the light while the other two had a significant amount of interaction. The lack of interaction by the outlier bottle with the linearly polarized input light may have artificially skewed the data (Figure 5). Elimination of the bottle reduced the skew and eliminated the influence of the outlier measurements on the dataset (Figure 6). However, effects on the analysis was unknown so two datasets were modeled, one with and one without the outlier bottle.

Figure 5. Marginal plot displaying the intensity frequency for each measurement point.

Figure 6. Marginal plot displaying the effect the outlier bottle had on the data distribution.

The model tested on all analysis blocks of the measurement data (Figure 4) modeled the effect of two fixed effects variables, bottle type (BT) and measurement point (Meas Pt), their interaction (BT*Meas Pt), and the effect random effects variables, repeatability and reproducibility, on the measured response. The models were constructed using a Bonferroni adjustment at $\alpha = 0.05$.

Analysis of the resulting models of the response measurements led to the rejection of the models due to ANOVA assumption violations. The standardized residuals revealed a violation of the independence and normality assumptions required by an ANOVA model (Appendix A). The skewness and possible loss of independence was due, in part, to the large difference between response measurements. In an effort to reduce the magnitude of the response measurements and produce a valid model, the log of the response measurements was taken. Response measurements of zero or less could not have the log taken of them, so those data points were thrown out of the model. The corresponding measurements for the three dependant response outputs produced three valid models (Table II) which did not violate the required ANOVA assumptions (Figure 7). Interestingly, there was no significant difference between the two different datasets since the zero values from the outlier bottle were thrown out because the log could not be taken of them.

Figure 7. A 4-in-1 residual plot for the GLM of the log peak response. This 4-in-1 residual plot is approximately identical to the 4-in-1 plots produced by the GLMs of log overall response and log refined response.

Table II. General linear model of the log of each response (Overall, refine, and peak).

Factor	Type	Levels	Values
BT	fixed	3	Coated, Double, Uncoated
Meas Pt	fixed	5	1, 2, 3, 4, 5
Replicate	random	2	1, 2
Repeat	random	2	1, 2

Analysis of Variance for Log Overall, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
BT	2	1.6586	1.5185	0.7593	2.97	0.058
Meas Pt	4	3.9507	3.9503	0.9876	3.86	0.007
Replicate	1	0.1852	0.1246	0.1246	0.49	0.488
Repeat	1	0.6643	0.5430	0.5430	2.12	0.150
BT*Meas Pt	8	5.6037	5.6037	0.7005	2.74	0.011
Error	68	17.4034	17.4034	0.2559		
Total	84	29.4660				

S = 0.505898 R-Sq = 40.94% R-Sq(adj) = 27.04%

Analysis of Variance for Log Refined, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
BT	2	1.6333	1.4906	0.7453	3.06	0.053
Meas Pt	4	3.9506	3.9457	0.9864	4.05	0.005
Replicate	1	0.1484	0.0965	0.0965	0.40	0.531
Repeat	1	0.6604	0.5448	0.5448	2.24	0.139
BT*Meas Pt	8	5.1346	5.1346	0.6418	2.64	0.014
Error	68	16.5482	16.5482	0.2434		
Total	84	28.0754				

S = 0.493311 R-Sq = 41.06% R-Sq(adj) = 27.19%

Analysis of Variance for Log Peak, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
BT	2	1.4277	1.3080	0.6540	3.39	0.039
Meas Pt	4	3.2160	3.4122	0.8530	4.42	0.003
Replicate	1	0.1451	0.0990	0.0990	0.51	0.476
Repeat	1	0.5852	0.4780	0.4780	2.48	0.120
BT*Meas Pt	8	4.1231	4.1231	0.5154	2.67	0.013
Error	68	13.1130	13.1130	0.1928		
Total	84	22.6101				

S = 0.439134 R-Sq = 42.00% R-Sq(adj) = 28.36%

Clear bottles measured with linear polarized light

Although the experimental design for this experiment was balanced, the actual measurements were not. Unfortunately, a few of the measurement points were skipped during the two days of measurements which caused the design to lose its orthogonality.

Similar to the transparent blue container experiment, the unadjusted measurements violated the required ANOVA assumptions. The log of the response measurements was taken to promote normality and independence of the responses measured. The result was a model that reasonably fit the ANOVA assumptions, but had a slight skew in the residual distribution. Although analysis of the residuals showed a slight skew, it was determined that the departure from normality was not enough to reject the models (Figure 8). Therefore, a model for each measured response was created (Table III).

Figure 8. A 4-in-1 residual plot for the peak residual values of the GLM produced for the log of the peak response.

Table III. Fitted GLMs for clear containers analyzed with linear polarized light.

Factor	Type	Levels	Values
BT	fixed	2	Coated, Uncoated
Meas Pt.	fixed	5	1, 2, 3, 4, 5
Reproduce	random	8	1, 2, 3, 4, 5, 6, 7, 8
Repeat	random	2	1, 2

Analysis of Variance for Log Over, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
BT	1	2.4716	2.7617	2.7617	12.95	0.000
Meas Pt.	4	5.6541	5.3764	1.3441	6.30	0.000
Reproduce	7	0.8866	0.9692	0.1385	0.65	0.715
Repeat	1	1.6212	1.6429	1.6429	7.71	0.006
BT*Meas Pt.	4	11.4336	11.4336	2.8584	13.41	0.000
Error	262	55.8604	55.8604	0.2132		
Total	279	77.9275				

S = 0.461744 R-Sq = 28.32% R-Sq(adj) = 23.67%

Analysis of Variance for Log Refine, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
BT	1	2.3946	2.7515	2.7515	13.51	0.000
Meas Pt.	4	5.4668	5.4998	1.3749	6.75	0.000
Reproduce	7	0.4232	0.5426	0.0775	0.38	0.913
Repeat	1	1.9069	1.9269	1.9269	9.46	0.002
BT*Meas Pt.	4	11.1397	11.1397	2.7849	13.67	0.000
Error	262	53.3648	53.3648	0.2037		
Total	279	74.6960				

S = 0.451312 R-Sq = 28.56% R-Sq(adj) = 23.92%

Analysis of Variance for Log Peak, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
BT	1	1.9397	2.1891	2.1891	13.27	0.000
Meas Pt.	4	4.4555	5.2600	1.3150	7.97	0.000
Reproduce	7	0.7085	0.7535	0.1076	0.65	0.712
Repeat	1	1.3038	1.3198	1.3198	8.00	0.005
BT*Meas Pt.	4	8.1626	8.1626	2.0406	12.37	0.000
Error	262	43.2202	43.2202	0.1650		
Total	279	59.7903				

S = 0.406156 R-Sq = 27.71% R-Sq(adj) = 23.02%

Clear containers measured with circular polarized light

The experimental design for analyzing the clear containers with circular polarized light was identical to the design for analyzing clear containers using linear polarized light. Fortunately for

this experiment, the response measurements were collected in a balanced manner. The measured response values behaved and were adjusted for the same as the previous two experiments. However, problem with the measurement system not evident in the previous two experiments affected the measured results of this experiment. Due to some immeasurable factor, probably vibration, the measured response decreased over time (Figure 9). To counteract the effect of the response decrease on the model, the run order (Run) was included in the model (Table IV). A slight curve in the random residual distribution on the residuals vs. fitted values plot (Figure 10) led to the questioning of the ANOVA assumption of independence. However, it was deemed that the slight order of the residuals was not enough to declare a violation of the ANOVA assumption of independence.

Figure 9. A graphical representation of the response with respect to time demonstrating the time dependant error mechanism within the measurement system.

Table IV. ANOVA output for GLMs of clear containers measured with circular polarized light.

Factor	Type	Levels	Values
BT	fixed	2	Coated, Uncoated
Meas Pt.	fixed	5	1, 2, 3, 4, 5
Reproduce	random	4	1, 2, 3, 4
Repeat	random	2	1, 2

Analysis of Variance for log OM, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Run	1	0.73954	0.58204	0.58204	43.68	0.000
BT	1	0.03744	0.03382	0.03382	2.54	0.113
Meas Pt.	4	0.24393	0.28035	0.07009	5.26	0.001
Reproduce	3	0.01795	0.01863	0.00621	0.47	0.707
Repeat	1	0.05080	0.05006	0.05006	3.76	0.055
BT*Meas Pt.	4	0.13488	0.13488	0.03372	2.53	0.043
Error	140	1.86551	1.86551	0.01333		
Total	154	3.09005				

S = 0.115434 R-Sq = 39.63% R-Sq(adj) = 33.59%

Term	Coef	SE Coef	T	P
Constant	3.56913	0.02160	165.27	0.000
Run	-0.001287	0.000195	-6.61	0.000

Analysis of Variance for log RM, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Run	1	2.62049	2.17822	2.17822	63.67	0.000
BT	1	0.05495	0.04600	0.04600	1.34	0.248
Meas Pt.	4	0.64843	0.78927	0.19732	5.77	0.000
Reproduce	3	0.02661	0.02832	0.00944	0.28	0.843
Repeat	1	0.13861	0.13634	0.13634	3.99	0.048
BT*Meas Pt.	4	0.46688	0.46688	0.11672	3.41	0.011
Error	140	4.78969	4.78969	0.03421		
Total	154	8.74566				

S = 0.184965 R-Sq = 45.23% R-Sq(adj) = 39.76%

Term	Coef	SE Coef	T	P
Constant	3.16197	0.03460	91.38	0.000
Run	-0.002490	0.000312	-7.98	0.000

Analysis of Variance for log P, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Run	1	5.78196	5.09284	5.09284	89.78	0.000
BT	1	0.01620	0.00912	0.00912	0.16	0.689
Meas Pt.	4	1.05449	1.28598	0.32150	5.67	0.000
Reproduce	3	0.01913	0.02238	0.00746	0.13	0.941
Repeat	1	0.24546	0.24214	0.24214	4.27	0.041
BT*Meas Pt.	4	0.93159	0.93159	0.23290	4.11	0.004
Error	140	7.94139	7.94139	0.05672		
Total	154	15.99023				

S = 0.238168 R-Sq = 50.34% R-Sq(adj) = 45.37%

Term	Coef	SE Coef	T	P
Constant	2.93931	0.04456	65.97	0.000
Run	-0.003807	0.000402	-9.48	0.000

Figure 10. One of three similar resulting 4-in-1 residual plots produced by the GLM for the measured response.

Discussion

Analysis of variance

In any measured system, there will be some amount of variance. The degree to which the response or responses vary depend upon the precision of the measurement instrument or system. A Gage R & R study, a reproducibility and repeatability study, was conducted on the measurement system to determine the amount of variance in the responses caused by the measurement system. According to the Gage R & R study, the measurement system accounted for all of the variance produced, 99.64% (Appendix B). Since all the variance produced is due to the measurement system, the 54 – 77% of variance that could not be accounted for by the models was the result of immeasurable error due to the measurement system.

The amount of responses that could be explained by the models ranged from 23 – 45%, which was the adjusted sums of squares, $r^2(\text{adj})$ (Table I,II,III). The resulting low $r^2(\text{adj})$ values and all the variance being produced by the measurement system means the measurement system is imprecise. Improvements in the precision of the measurement system will drastically improve the prediction power of the system and the subsequent GLMs it produces. Although the $r^2(\text{adj})$ values were low, very useful information was taken from the ANOVA tables.

The measurement point fixed effect variable (Meas Pt) and its interaction with bottle type was consistent throughout the three experiments. With p-values no higher than 0.043, and with total degrees of freedom no less than 84, it is reasonable to conclude that there is a statistically significant difference between measurement points, regardless of bottle type. The non-homogeneous optical properties concluded from the previous statement add complexities to the project and rejects the assumption that the optical properties are the same regardless of container location. The significant interaction term between bottle type and measurement point states that there is a statistical difference between identical locations on the two different bottle types. While the rejection of the optical homogeneity assumption added complexities to the project, the interaction between the bottle types and measurement points could prove useful in the development of a reliable measurement system.

The bottle type fixed effect variable (BT) provided mixed information. The three different experiments resulted in three different conclusions involving a significant difference between the bottle types. In the transparent blue containers measured with linear polarized light experiment, the difference in bottle types was found to be significant. This is due to the use of three different bottle types: uncoated, coated, and double coated. Since the double coated bottle had a SiO_x film that was twice as thick as a single coated bottle, the interaction with the light was greater. The greater interaction would result in a larger difference between the responses for the double coat

and the responses for the uncoated. This larger difference is what led to the statistical significance of the bottle type measurements. Therefore, it is reasonable to conclude that a double coated bottle can be detected using the current measurement system. However, the other two experiments state that there is no statistical difference between the bottle types. In the clear container experiments, only two bottle types were used: coated and uncoated. Unfortunately, the lack of a double coated sample for the clear container experiments did not allow for the comparison of the clear container experiments with the transparent blue container experiment. However, the advantage of the clear container experiments is the pair-wise comparison which can be made between the two bottle types. Since the p-values were non-significant in the experiment utilizing circular polarized light and were mixed in the experiment utilizing linear polarized light, it is reasonable to conclude that a single coated bottle cannot be differentiated from an uncoated bottle using the current measurement system. A more precise system may overcome this obstacle.

The measurement system

The measurement system was proven to be imprecise in the previous section; however, the reason for this is unknown. Analysis of a time vs. measurement plot (Appendix C), produced to analyze the sources of error in the measurement system, indicates that the measurement system can be significantly influenced by small, sharp vibrations. Bumping or usage of the drawers under the counter with which the measurement system operates, bumping the counter, and loading, unloading and rotating the sample produced measurable differences in the measurement system. Unfortunately, many of these sources of error are random and do not constitute a measurable trend which can be statistically accounted for. A more robust measurement system would be needed to endure these sources of error which occur naturally in the course of measurement process.

Light Sources

There were two light sources used in the measurement of the different bottle types and bottle designs: linear and circular polarized light. The statistical conclusions produced by the GLM routine in Minitab® for each experiment allowed for inferences to be made as to what kind of interaction was taking place between the bottle and the polarized light. Analysis shows that circular polarized light has a less statistical effect on the measurement of bottle type. This means that bottles of different types, coated and uncoated, tend to affect the polarized light more by rotation and less by phase change. What was hoped for, but not accomplished in these experiments, was the phase shift could be statistically significant. According to ellipsometry, the difference in light phase shift between the substrate induced phase shift and the phase shift measured of a coated substrate is the phase shift due to the film or coating. It is this phase shift in the polarized light that allows for the calculation of film thickness. A more precise measurement system may allow for a statistical difference between coated and uncoated bottles to be measured with both circular and linear polarized light sources.

Conclusions

In order to investigate the optical homogeneity of the polymeric containers, both transparent blue and clear, two light sources were used. The conclusion from all three experiments was that the assumption of optical homogeneity of the bottles was invalid. The rejection of the optical homogeneity assumption further complicates the task of designing a vapor barrier measurement system. However, it was determined that a double coat, approximate thickness of 200 Å, could be detected using linear polarized light. Resolution greater than 200 Å was rejected due to the inability of the measurement system to differentiate between single coated and uncoated bottles.

It was hoped that a statistical difference between coated and uncoated container types would be found, but such a conclusion could not be made with the current measurement system.

The precision of the measurement system was also investigated. The variance in the measured responses was almost entirely due to the measurement system. Therefore, a better measurement system design should improve the precision and allow for more reliable and conclusive statistical models to be constructed.

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Appendix A

Results from fitting a general linear model to the measurements with the outlier bottle included in the modeled measurement data.

Factor	Type	Levels	Values
BT	fixed	3	Coated, Double, Uncoated
Meas Pt	fixed	5	1, 2, 3, 4, 5
Replicate	random	2	1, 2
Repeat	random	2	1, 2

Analysis of Variance for Overall, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
BT	2	59591403	59591403	29795702	8.50	0.000
Meas Pt	4	23361488	60921128	15230282	4.34	0.003
Replicate	1	333622	333622	333622	0.10	0.758
Repeat	1	6292071	6292071	6292071	1.79	0.184
BT*Meas Pt	8	97328141	97328141	12166018	3.47	0.002
Error	83	291008269	291008269	3506124		
Total	99	477914993				

S = 1872.46 R-Sq = 39.11% R-Sq(adj) = 27.37%

Analysis of Variance for Refined, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
BT	2	17887048	17887048	8943524	8.71	0.000
Meas Pt	4	6799699	18113396	4528349	4.41	0.003
Replicate	1	13948	13948	13948	0.01	0.907
Repeat	1	2013845	2013845	2013845	1.96	0.165
BT*Meas Pt	8	29589960	29589960	3698745	3.60	0.001
Error	83	85192958	85192958	1026421		
Total	99	141497458				

S = 1013.12 R-Sq = 39.79% R-Sq(adj) = 28.19%

Analysis of Variance for Peak, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
BT	2	5470545	5470545	2735272	8.87	0.000
Meas Pt	4	2110919	5525810	1381452	4.48	0.003
Replicate	1	4942	4942	4942	0.02	0.900
Repeat	1	697392	697392	697392	2.26	0.136
BT*Meas Pt	8	8881806	8881806	1110226	3.60	0.001
Error	83	25605495	25605495	308500		
Total	99	42771098				

S = 555.428 R-Sq = 40.13% R-Sq(adj) = 28.59%

Analysis of residual 4-in-1 plot shows violation of ANOVA assumptions. First, the independence assumption violation is identified by the clumping of residuals rather than random scatter in the Residuals Versus the Fitted Values plot. Second, the normality assumption violation was identified by the skewed histogram plot and curved normal probability plot.

Results from fitting a general linear model to the measurements with the outlier bottle omitted.

Factor	Type	Levels	Values
BT	fixed	3	Coated, Double, Uncoated
Meas Pt	fixed	5	1, 2, 3, 4, 5
Replicate	random	2	1, 2
Repeat	random	2	1, 2

Analysis of Variance for Overall, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
BT	2	26987194	26987194	13493597	3.60	0.033
Meas Pt	4	30011977	55597348	13899337	3.71	0.009
Replicate	1	287640	287640	287640	0.08	0.783
Repeat	1	9513032	9513032	9513032	2.54	0.116
BT*Meas Pt	8	87559045	87559045	10944881	2.92	0.008
Error	63	236159079	236159079	3748557		
Total	79	390517967				

S = 1936.12 R-Sq = 39.53% R-Sq(adj) = 24.17%

Analysis of Variance for Refined, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
BT	2	8082625	8082625	4041312	3.67	0.031
Meas Pt	4	8784919	16486181	4121545	3.74	0.009
Replicate	1	7605	7605	7605	0.01	0.934
Repeat	1	3013208	3013208	3013208	2.73	0.103
BT*Meas Pt	8	26711149	26711149	3338894	3.03	0.006
Error	63	69452032	69452032	1102413		
Total	79	116051538				

S = 1049.96 R-Sq = 40.15% R-Sq(adj) = 24.96%

Analysis of Variance for Peak, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
BT	2	2443041	2443041	1221521	3.72	0.030
Meas Pt	4	2760122	5075611	1268903	3.86	0.007
Replicate	1	2868	2868	2868	0.01	0.926
Repeat	1	1038540	1038540	1038540	3.16	0.080
BT*Meas Pt	8	7958072	7958072	994759	3.03	0.006
Error	63	20710063	20710063	328731		
Total	79	34912705				

S = 573.351 R-Sq = 40.68% R-Sq(adj) = 25.62%

Analysis of the 4-in-1 residual plot corresponding to the above data displays ANOVA assumption violations. The violations are the same as the dataset with the bottle outlier, but are less pronounced.

Appendix B

Results from the Gage R & R study:

Gage R&R

Source	VarComp	%Contribution (of VarComp)
Total Gage R&R	125766	99.64
Repeatability	125741	99.62
Reproducibility	24	0.02
Container	24	0.02
Part-To-Part	452	0.36
Total Variation	126218	100.00

Source	StdDev (SD)	Study Var (6 * SD)	%Study Var (%SV)
Total Gage R&R	354.635	2127.81	99.82
Repeatability	354.600	2127.60	99.81
Reproducibility	4.941	29.65	1.39
Container	4.941	29.65	1.39

Gage R&R (ANOVA) for Intensity Peak

Gage name: Measurement System Analysis
Date of study: 6-7-2007

Reported by: Daniel Helms
Tolerance:
Misc:

Appendix C

6/7/2007

AvaSoft 6.2 Avantes - SINsimulation

Appendix D

Background in data transformation and additional information and graphical representation of the raw data collected and the log transformation.

A logarithm of base ten or log for short is a transformation which reduces large numbers to more manageable sizes. An additional advantage of the log transformation is the corresponding linear or lower order relation which results, making analysis of data with multiple order ranges easier (2,3). Equation 4 demonstrates the log transformation of 100.

$$\log_b(x) = y \quad (2)$$

$$x = b^y \quad (3)$$

$$\log_{10}(100) = 2 \quad (4)$$

The following is a series of graphical representations of the data, both raw and transformed, to further explain what the model from Table IV is interpreting.

Figure 19. A scatterplot of all the data, including the location and bottle type, over the course of the experiment.

Figure 20. The raw data has been broken down into bottle type (BT) and measurement point (Meas Pt.) for better variance analysis.

Figure 21. A plot of all the data after a log transformation.

Figure 22. Transformed data broken down by bottle type and measurement point.

A.2. Redefinition of Measurement Apparatus

The explanation of the measurement apparatus and the theory behind its use may have been a little convoluted in the original report, so the following will attempt to clarify any ambiguities. The measurement system was designed to detect any interactions between the probing beam of linear or circular polarized laser light and the sample by measuring the percent transmittance through a crossed polarizer (Figure A.1). If there was an interaction, like a phase change, the percent transmission would increase.

Figure A.1. Schematic of the measurement system setup.

A.3. Experimental Data Reevaluation

Reevaluation of the results was accomplished by statistically analyzing the original data. However, unlike the original report which evaluated the raw counts measured, the reevaluation converted the counts to percent transmission by dividing the measured counts by a control (henceforth referred to as a baseline) which was the maximum counts measured before and after each sample (A.1).

$$T = \frac{C_{\text{meas}}}{C_{\text{max}}} \times 100 \quad (\text{A.1})$$

Where T is percent transmission, C_{meas} is the sample measurement in counts and C_{max} is the baseline measurement in number of counts. By converting the

Figure A.2. Peak measurement drift over the course of the experiment, normalized to the first baseline measurement.

measurements to transmission through the ratiometric baseline conversion shown in equation A.1, much of the variance caused by measurement drift was accounted for (Figure A.2). Linear interpolation between the baseline measurements was used to estimate the baseline at each measurement point, further reducing the variance due to errors in the

transmission measurement.

Data reduction was also utilized to reduce the variance in the measured data prior to statistical evaluation. Measurements taken near the bottle seam (measurement points 1 and 5) were discarded because these were the most erroneous measurements due to poor repeatability. Similarly, since the measurements were taken over the course of a few days with the measurement

Figure A.3. Schematic of the experimental setup with the bottle type whole plots and the nested split plot measurement positions.

parameters varying (e.g. spectrometer integration times, peak measurements, etc.) from day to day and because the days were not blocked correctly, all but

Figure A.4. The statistical output for the proof of concept reevaluation showing a statistical difference between the double coated sample and the uncoated sample.

denoted with a prime (45', 90' or 135'). In theory, the measurements on both sides of the bottle should coincide for each angular measurement; however, they were kept separate to account for any measurement error.

the most recent measurements were discarded. The samples left were from the first experiment discussed in the initial report (blue bottles analyzed with linear polarization). Of the samples measured, two suffered from missing measurements and were subsequently discarded. The remaining data consisted of three coating levels (uncoated, single coat and double coat) each represented by a single bottle with six measurement points per bottle (3 per side) with each measurement replicated once (Figure A.3). The measurement points were renamed to 45, 90 and 135 for the approximate counter-clockwise angular rotation from the bottle seam each measurement was taken at. The measurements collected on the opposite side of the bottle were

Although the experiment was conducted as a full factorial, the way the measurements were collected actually made it a split-plot experiment. In layman's terms, a split-plot experiment is an experiment – known as a split plot – nested within another experiment – known as a

Figure A.5. One way ANOVA plot of the measured transmission at 135 and 135' measurement points.

whole plot. The whole plot for this experiment was a completely randomized experiment (CR) of the coating levels and the split plot was an experiment which measured each measurement point sequentially (see Figure A.3). The statistical analysis output (Figure A.4) demonstrated discrimination between

Figure A.6. An overlay plot showing the measured transmission for the different measurement points and bottle types.

the double coated and uncoated bottles is possible; however, there was not a statistical difference between the coated and uncoated bottles. Although, it should be mentioned that the difference between the coating thicknesses was only significant at one rotation, 135 and 135' (Figure A.5). The difference

between the measurements on either side of the bottle varied significantly for measurements made at angular rotations 45° and 90° about the bottle for all three samples (Figure A.6).

A.4. Proof of Concept Experiment Reevaluation Conclusions

Reevaluation of the original data provided models with significantly better fits, $r^2(\text{adj}) > 0.8$ opposed to $r^2(\text{adj}) < 0.3$; however, no new information can be deduced. The report's conclusion that polarized light can detect thin SiO_x films deposited on the inside of a polymeric beverage container was verified; however, further research is needed to investigate geometric effects on polarization because this conclusion was only valid at one bottle rotation.

APPENDIX B: Overview of Statistics

A basic outline of the scientific method is:

- 1) Question or problem in need of a solution arises
- 2) Hypothesis regarding a solution to the problem or question is devised
- 3) Experimentation is conducted to test hypothesis validity
- 4) Analysis of the experimental data
- 5) Conclusion regarding hypothesis validity

It is by this method that engineers and scientists evaluate problems and develop solutions. While steps one and two are rather intuitive, those following are not. It is in the experimentation, analysis and conclusion steps that statistics plays a very large role. The following is an overview of the statistics used in the experimental designs and analyses used with this project.

B.1. Experimental Design

As discussed in some depth in Chapter 4, this step in the problem solving process is often given little thought; however, a good experimental design can save both time and money by reducing excessive experimentation. This project used the entire gambit of experimental designs from simple to complex. The following is a brief description of the experimental designs used, for more information regarding this subject consult Montgomery.

The simplest experimental design is known as a completely randomized (CR) design. This design consists of no special experimental setup except the randomization of the run order in which the treatments are tested. The reason

for the randomization is to reduce systematic error which may skew the data. Randomization was not done for the preliminary experiment (Appendix A) and subsequently the measured data was skewed as the experiment progressed. Although the error was correctable in this case, sometimes it isn't because of lack of information or correlating factors.

The next experimental design utilized was a randomized complete block (RCB) design. This experimental design is useful if sources of experimental error are known or suspected (e.g. parameters unique to a particular day, such as temperature, could be a source of error if the experiment spans multiple days). Multiple RCB experiments were setup during this project; however, most were not analyzed as such due to complexities associated with the analyses (e.g. ellipsometric models).

The previous experimental designs are used primarily for a single treatment with multiple levels; however, if multiple treatments also exist, a factorial design might be the best choice. Factorial experimental designs make efficient use of the different treatment combinations, reducing the amount of experimentation needed for meaningful results. There are numerous factorial designs (e.g. full, fractional, 2^k , 3^k , etc.) each used for a different experimental need. The simplest is a full factorial where all level combinations of the treatments are examined. Full factorial experiments were attempted in the proof of concept experiments (Appendix A); however, they were accidentally conducted as a split-plot designed experiments.

When an experiment is conducted within an experiment, it is known as a split plot experimental design. Many times a split plot experiment may look exactly like another experimental design with only the experimental procedures (i.e. treatment combination run order) differing between the two.

The final experimental design, response surface, was utilized the most by this project. When optimization is concerned, this is the usually the best experimental design to use. Treatment level combinations are chosen to produce the optimum prediction variance distribution in the analysis model.

B.2. Statistical Analysis of Experimental Data

The reason statistically designed experiments are important in setting up experiments is they help determine how the measured response is analyzed. However, before an analysis technique can be chosen, characterization of the type of data, whether categorical or continuous, for the treatment(s) and the measured response must be determined. Fortunately the response for all the experiments conducted during this project were continuous; however, many times the treatments consist of a mixture of categorical and continuous variables. To analyze experiments which involve different data types for treatment variables, an analysis technique known as the general linear model (GLM) must be used.*

Statistics analyzes datasets by fitting models to them. ANOVA, least squares regression and GLM are all different types of statistical models which can be used to analyze experimental data. If all the treatments levels are categorical, an ANOVA routine can be used to determine if the measured continuous response at the different treatment levels are significantly different from one another. A regression routine fits continuous treatment levels to the measured continuous response. It is from such a routine that linear, quadratic or other continuous mathematical models are fitted to measured datasets. Finally, GLM and some least squares regression routines combine both the ANOVA and

* Of the statistic software packages which offer mixed data type regression model fitting routines, only some actually refer to them as a GLMs. For instance Minitab, the statistical software package primarily used at Cal Poly, refers to such models as GLMs while JMP, the primary statistical software package used for this project, makes no distinction between the regression routines.

regression routines to fit a model containing both continuous and categorical treatments (e.g. analysis of regression data with blocking).

B.3. Least Squares Model Fitting Procedure Overview

In order to fit a model to a measured dataset, an iterative procedure known as least squares regression must be conducted. First, the model, which could be as simple as a linear model (B.1) or something more complex, is defined.

$$\hat{y} = \beta_1 x + \beta_0 \quad (\text{B.1})$$

Where the β terms are coefficients which the regression routine is seeking to determine, y is the response variable and x is the treatment variable. Thus the minimum number of data points is the same as the number of coefficients being fit; however, in order to do a statistical analysis on the data, more than the minimum number of points is required.

Once a model has been defined, the model fitting routine proceeds to minimize the sum of squares error (SSE) through the testing of numerous models with different model coefficient combinations until the model of best fit for the measured data is achieved. Upon completion of the SSE minimization, the model fitting statistics can be calculated. An example of this process can be observed with the fitting of light measurements (response) as a function of analyzer position (treatment) (Figure B.1).

Categorical treatments can be added to a regression model through a logical (i.e. an if statement) summation which acts as an intercept offset (B.2) or a slope offset (B.3), depending upon whether the continuous and categorical data interact.

$$\hat{y} = \beta_1 x + n + \beta_0 \quad (\text{B.2})$$

$$\hat{y} = (\beta_1 + n)x + \beta_0 \quad (\text{B.3})$$

Where y , x and β are the same as equation B.1; however, the n term represents the categorical variable (e.g. a blocking variable).

B.4. Using Response Surface DOEs to Find the Null Condition

As discussed in Chapter 3, the ellipsometric parameters ψ and Δ can be determined from the position of the optical components at the null condition. With a linear polarized beam incident on a polarization analyzer (i.e. another polarizer), the amount of light transmitted through the analyzer was measured as a function of analyzer azimuth. From these measurements a quadratic relation was observed near the null condition (see figure 3.7). Since the null position – the position of minimum light flux – was the parameter of interest, a CCD response surface DOE could be established around the suspected null azimuth positions of the optical components to find the optimum azimuth for each optical component.

While azimuth measurements of degree fractions were possible, such measurements were found, through experimentation, to be less accurate when

compared to whole degree measurements. Small errors within the vernier scales in addition to small errors in the mounts' degree markings, both manufacturing defects, had a more significant

affect on fractional degree measurements than whole degree measurements (Figure B.2). Therefore, any DOE set up for null azimuth determination of the optical components was constrained to the use of integers (i.e. whole degree measurements) for rotational measurements. Unfortunately, due to the integer only constraint, a rotatable CCD could not be performed since the coded axial points could not be 1.414. However, recall equation 4.2:

$$\xi_i = \Delta_i x_i + a_i \quad (4.2)$$

where Δ_i is the deviation between measurement points ξ_i . If Δ_i were chosen such that it was divisible by two (i.e. 2°, 4°, 6°, etc.), then the coded axial points could be 1.5; sufficiently close to a rotatable design to minimize variance discrepancies between two measurement points equidistant from the center of the design.

The number of center point replicates used determines the prediction variance profile for the model fitted to the data. Too few center points adversely affect the prediction variance distribution, leading to an inverse relation

Run Order	CodeP	CodeA	Polarizer	Analyzer	Light Measurement	Temperature
1	-1.5	0	-177	47	0.0772	22.29
2	0	0	-171	47	0.0029	22.84
3	-1	-1	-175	43	0.0609	22.31
4	-1	1	-175	51	0.092	23.11
5	0	-1.5	-171	41	0.0877	22.33
6	0	0	-171	47	0.0029	22.75
7	0	1.5	-171	53	0.1274	22.86
8	1	-1	-167	43	0.1035	22.23
9	1	1	-167	51	0.1274	22.99
10	0	0	-171	47	0.0026	22.83
11	1.5	0	-165	47	0.1353	22.49

Figure B.3. Screenshot of the response surface DOE table in JMP® with the resulting responses measured.

Figure B.4. A contour plot of actual measurements (black) made during ellipsometric testing of an Au sputtered Si wafer.

between prediction model precision and measurement speed. For null determination, the optimum number of center point replicates was determined to be two when measured in a systematic order like figure B.3. Although some of the measurements are confounded with the previous measurement, it was found that completely independent measurements only increased measurement time with no variance reduction benefit. Temperature was an uncontrollable variable which was found to influence the measurement system, thus

Figure B.5. JMP output for null position determination.

requiring simultaneous measurement so the error it caused could be accounted for during analysis.

The data shown in figure B.3 was for a null measurement conducted on a thick sputtered gold layer on a silicon wafer – essentially acting like a gold substrate to the ellipsometer. Optimization of the response surface model fit to the data (Figure B.4) produces an optimum point at a polarizer setting of -171.85° and an analyzer setting of 46.43° (Figure B.5). Although the model also produces a prediction of the response, this is normally of little interest, with the exception of depolarization measurements. Temperature can be added to the model to account for the error caused by the temperature dependence of the measurement system; however, this error was normally negligible.

APPENDIX C: Ellipsometer Construction and Use

C.1. Ellipsometer Construction Overview

The general construction of a null (conventional) ellipsometer contains the following components: a light source, polarizer, compensator, analyzer

Figure C.1. Operational schematic of the ellipsometer constructed for this project.

and detector (Figure C.1).

The light source used was a helium neon (HeNe) gas laser which lases at a near monochromatic wavelength of 632.8 nm (Figure C.2). To ensure the light intensity following the polarizer remained as

close to constant as possible, a quarter waveplate compensator was inserted between the HeNe laser and rotated 45° relative to the laser polarization to produce circular polarized light (Figure C.3). A linear film polarizer with a high extinction coefficient (10,000:1) was used for the polarizer (Figure C.4); an

Figure C.2. The HeNe laser light source used to make ellipsometric measurements, with an attached linear film polarizer.

Figure C.3. Quartz quarter waveplate used to produce circular polarized light between the linearly polarized HeNe laser (right) and the polarizer (left).

Figure C.4. The polarizer optic used to define the orientation of the polarized light incident on the sample.

optic which determines the orientation of the polarized light produced by the polarization state generator (PSG). To adjust the phase of the polarized light produced by the PSG, a quarter wave quartz compensator was used with its fast axis azimuth fixed near 45° (Figure C.5). The samples measured were mounted to a rotation stage by a sample mount constructed specifically for standard 100 mm diameter wafers (Figure C.6). Reflections from the sample were analyzed with a linear polarizer which was identical to the polarizer in the PSG (Figure C.7). Finally, the amount of light which passed through the analyzer was measured with a silicon photodiode detector

Figure C.5. Quartz quarter waveplate compensator used to define the phase difference between the p and s waves of the polarized light incident on the sample surface.

Figure C.6. Custom built sample holder designed specifically for 100 mm diameter wafers.

(Figure C.8) which sent a signal to the ellipsometer's electronics where it was amplified and digitized (Figure C.9). With the above described components in their respective mounts, configured in a polarizer-compensator-sample-analyzer (PCSA) arrangement and properly aligned, the ellipsometric measurements conducted for this project were carried out.

Figure C.7. Analyzer with photodiode sensor assembly behind.

Figure C.8. Photodiode sensor featured a depolarization diffusing filter (wax paper) in front (top) and sat in a housing which allows for easy alignment with the reflected beam.

Figure C.9. The ellipsometer electronics which measured the light detected by the photodiode sensor and logged temperature during an experiment.

C.2. Circular Polarized HeNe Laser Construction and Alignment

1. Assemble the sample stage and laser mount and attach to the optical breadboard
2. Mount the HeNe laser in the laser mount and rotate the empty sample mount for transmission measurements
3. Assemble apertures whose height is coincident with the polarizer mounts
4. Place apertures of equal height on either side of the sample mount,

- with one aperture between the laser and the sample mounts
5. Align the laser beam with the apertures by repositioning and adjusting the laser mount until the beam traversed both apertures
 6. Mount the Pyrex 7740 sample and rotate the sample to an incidence angle of 56°
 7. Secure a linear film polarizer to the laser; however, rotate the polarizer's transmission axis until it is parallel with the polarization produced by the laser (as indicated on the laser casing) prior to securing
 - This is to help improve the polarizer's linear polarization and to reduce reflections by working in concert with the quarter wave compensator to produce circular polarization in both directions
 8. Rotate the laser within its mount until the intensity of the reflected beam is at its minimum, then secure the laser within its mount
 - The polarization of the laser is approximately in the p-plane of the sample, thus defining the p-polarization plane
 9. Remove the Pyrex 7740 sample and insert and align the first quarter wave compensator
 10. Insert and align the polarizer and its mount
 11. Assemble the detector and the ellipsometer electronics and align the detector with the laser beam following the second aperture
 12. Once all the components are aligned in the straight through configuration, rotate the quarter wave compensator until circular polarization is incident on the polarizer
 - Circular polarization can be determined by measuring the amount of light that passes through the polarizer at different

polarizer azimuths; circular polarized light will occur when the measurements at different polarizer azimuths are the same

- The compensator used was a quartz quarter waveplate; it was found to be slightly absorbing, creating a different measurement along its fast and slow axis

13. If truly circular polarization cannot be achieved, measurement of the error in the resulting photometric measurements must be characterized and a correction factor created to minimize the effects of this error (Figure C.10)

C.3. Alignment of the Optics and Their Mounts

The alignment of the optics was rather straight forward, with the probing laser beam coaxially aligned with the center of the optics and normal to the optics' sides. This was accomplished with the help of the cage system components and apertures.

Figure C.10. Photometric measurements made at different polarization azimuths (blue) with the associated correction function (green) and corrected light measurements (red).

Although alignment was straight forward the handedness of the optic mounts was not. Due to the use of standard optical components, the optical mounts could only be purchased in one rotational orientation (right handed). For ease of use, the optical mounts

Figure C.11. The direction of the optical mounts were flipped on the polarization generation side (right), making the measurements left handed.

housing the optics which manipulate the light prior to the sample (i.e. the PSG) were flipped, converting all the flipped mount measurements to a left handed rotational measurement system (Figure C.11). For example, if the polarizer and analyzer were aligned with their transmission axes parallel, both optical mount measurements would be the same if both were right handed. However, a 30° measurement made on the analyzer mount (a right handed measurement) corresponded to a 330° measurement on the polarizer mount. Therefore, all the measurements made on the polarizer and compensator had to include a negative sign in order to keep them in the right handed coordinate system.

C.4. Measurement and Correction of Sample Tilting

In the following calibration procedures, correction for sample tilting becomes important. When a sample is tilted off its ideal axis of rotation, not only is an error induced in the measured angle of incidence, but a substantial error is created in the measurement of the polarizer, compensator and analyzer. This is due to the plane of polarization becoming a function of incidence angle. The

source of the sample tilt was determined to be caused by the wafer holder's friction fit design. The tilt error was generally between 0.5° and 1.5°, but varied from sample to sample. Thus tilt measurements must be made for all samples measured using that sample holder. Redesign of the sample holder with the ability to correct this source of error will greatly simplify the measurement process.

Figure C.12. Aperture plate being used to measure sample tilt.

Figure C.13. Rotational error measurement prior to sample measurements.

Sample tilt error was measured easily with an aperture placed between the last optic in the PSG and the sample. With the aperture coaxially aligned with the laser beam, the sample was rotated until the reflected beam was directly above the aperture. The distance between the aperture and where the reflecting beam struck the aperture plate was measured (Figure C.12)

along with the distance between the sample surface and the aperture plate. The angle of tilt was determined by calculating the tangent (C.1).

$$\theta_t = \arctan\left(\frac{d_a}{d_s}\right) \quad (C.1)$$

Where d_a is the measured distance between the aperture and the reflected beam

incident on the aperture plate and d_s is the distance between the aperture plate and the sample.

Error in the rotational measurement was also determined by measuring the angular rotation (Figure C.13) during sample tilt measurements. By subtracting any offset – there was a 10° rotational offset for the setup used for this project – the amount of error in the rotational measurement caused by mounting the sample can be determined.

A novel approach to correcting the error caused by sample tilting was devised using three dimensional vector algebra. The following Mathcad worksheet was used to determine the correction factors for the incidence angle, polarizer, compensator and analyzer.

Determination of the tilt induced error with a tilted sample

$$\phi := 1.3\text{deg}$$

Measured tilt angle

$$\theta_e := 0.1\text{deg}$$

Measured rotational error

$$\theta_m := 50\text{deg}$$

Measured Angle of Incidence

Calculation of Actual AOI and Sample Tilt Error

$$\theta := 2\pi - (\theta_m - \theta_e)$$

$$\text{IP}_V := \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

Input Vector

$$\text{Ro}_X := \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(\phi) & -\sin(\phi) \\ 0 & \sin(\phi) & \cos(\phi) \end{pmatrix}$$

$$\text{Ro}_Z := \begin{pmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\text{OP}_V := (\text{Ro}_X \cdot \text{Ro}_Z \cdot \text{IP}_V) \rightarrow \begin{pmatrix} \sin(49.9\text{-deg}) \\ \cos(1.3\text{-deg}) \cdot \cos(49.9\text{-deg}) \\ \sin(1.3\text{-deg}) \cdot \cos(49.9\text{-deg}) \end{pmatrix}$$

$$\text{OP}_V = \begin{pmatrix} 0.765 \\ 0.644 \\ 0.015 \end{pmatrix}$$

Output Vector

$$\theta_0 := \arccos\left(\frac{\text{IP}_V \cdot \text{OP}_V}{\sqrt{\text{IP}_V \cdot \text{IP}_V} \sqrt{\text{OP}_V \cdot \text{OP}_V}}\right)$$

$$\theta_0 = 49.912\text{ deg}$$

Actual Angle of Incidence

$$\text{Z}_V := \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

$$\text{Z}'_V := \text{OP}_V \times \text{IP}_V$$

$$\varepsilon_t := \arccos\left(\frac{Z_V \cdot Z'_V}{\sqrt{Z_V \cdot Z_V} \cdot \sqrt{Z'_V \cdot Z'_V}}\right)$$

$$\varepsilon_t = 1.094 \text{ deg}$$

AOI Error vs Measured AOI Calculation

```

Tilt := for D ∈ 0 .. 90
|
|   θ ← 2π - D · (π / 180)
|
|   RoX ← ( 1   0   0 )
|         ( 0  cos(φ) -sin(φ) )
|         ( 0  sin(φ)  cos(φ) )
|
|   RoZ ← ( cos(θ) -sin(θ)  0 )
|         ( sin(θ)  cos(θ)  0 )
|         ( 0      0      1 )
|
|   OPV ← RoX · RoZ · IPV
|
|   γ ← arccos( ( IPV · OPV ) / ( √(IPV · IPV) · √(OPV · OPV) ) )
|
|   TiltD,0 ← D
|
|   TiltD,1 ← γ · (180 / π)
|
|   TiltD,2 ← TiltD,1 - TiltD,0
|
Tilt

```

Component Error vs Measured AOI Calculation

```

Error := for D ∈ 0 .. 90
    θ ← 2 · π - ⌊ D · (π / 180) ⌋
    Z ← ⎡ 0 ⎤
        ⎢ 0 ⎥
        ⎣ 1 ⎣
    RoX ← ⎡ 1 0 0 ⎤
        ⎢ 0 cos(ϕ) -sin(ϕ) ⎥
        ⎣ 0 sin(ϕ) cos(ϕ) ⎦
    RoZ ← ⎡ cos(θ) -sin(θ) 0 ⎤
        ⎢ sin(θ) cos(θ) 0 ⎥
        ⎣ 0 0 1 ⎦
    OPV ← RoX · RoZ · IPV
    Z'V ← OPV × IPV
    ε ← acos ⎡ ZV · Z'V ⎤
        ⎢ √ZV · ZV · √Z'V · Z'V ⎥
    ErrorD,0 ← D
    ErrorD,1 ← ε · (180 / π)
Error

```

C.5. Polarizer and Analyzer Mount Calibration and Verification

Calibration of the polarizer (P) and analyzer (A) measurement mounts was accomplished using the principle angle method¹ on a thick gold sputtered silicon wafer, with the gold layer sputtered sufficiently thick to exceed the penetration

Response Light Measurement

Summary of Fit

RSquare	0.999951
RSquare Adj	0.999862
Root Mean Square Error	0.000199
Mean of Response	0.018647
Observations (or Sum Wgts)	15

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	9	0.00400022	0.000444	11252.38
Error	5	0.00000020	3.95e-8	Prob > F
C. Total	14	0.00400042		<.0001*

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	3	1.975e-7	6.5833e-8	Prob > F
Pure Error	2	0	0	
Total Error	5	1.975e-7		Max RSq 1.0000

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.0369875	0.002445	15.13	<.0001*
Incident Angle	-0.000687	1.757e-5	-39.14	<.0001*
Polarizer	-2.188e-5	1.757e-5	-1.25	0.2682
Analyzer	9.375e-6	1.757e-5	0.53	0.6164
(Incident Angle-56)*(Incident Angle-56)	0.0020297	6.464e-6	313.98	<.0001*
(Incident Angle-56)*(Polarizer+90)	-4.687e-6	6.211e-6	-0.75	0.4844
(Polarizer+90)*(Polarizer+90)	0.0000125	6.464e-6	1.93	0.1110
(Incident Angle-56)*(Analyzer-90)	-2.656e-5	6.211e-6	-4.28	0.0079*
(Polarizer+90)*(Analyzer-90)	-4.688e-5	6.211e-6	-7.55	0.0006*
(Analyzer-90)*(Analyzer-90)	-9.375e-6	6.464e-6	-1.45	0.2067

Response Surface

Coef	Incident Angle	Polarizer	Analyzer	Light Measurement
Incident Angle	0.0020297	-4.687e-6	-2.656e-5	-0.000687
Polarizer		0.0000125	-4.688e-5	-2.188e-5
Analyzer			-9.375e-6	9.375e-6

Solution

Variable	Critical Value
Incident Angle	56.167341
Polarizer	-89.75396
Analyzer	89.647823

Solution is a SaddlePoint

Predicted Value at Solution 0.0012381

Figure C.14. The results for the Box-Behnken calibration verification experiment.

depth of the probing beam, thus causing the gold layer to behave as a gold substrate. A slight variation on the procedures stated in literature was used with a central composite designed experiment being used to find the absolute null instead of the iterative process proposed in literature.

Verification of the P and A calibration was accomplished using a technique similar to method 2 proposed by Azzam and Bashara.² At the Brewster's angle of a dielectric material, in this case Pyrex 7740, a minimum light measurement will occur. Special configuration of the ellipsometer for Brewster's angle measurement (e.g. like fixing P or A

1 R.M.A. Azzam and N.M. Bashara, *Ellipsometry and Polarized Light*, (Amsterdam: Elsevier Science B.V., 1987), 380-385; Frank L. McCrackin et al., "Measurement of the Thickness and Refractive Index of Very Thin Films by Ellipsometry (short title)," *Journal of Research of the National Bureau of Standards – A Physics and Chemistry*. 67A (1963): 367-370.

2 R.M.A. Azzam and N.M. Bashara, *Ellipsometry and Polarized Light*, (Amsterdam: Elsevier Science B.V., 1987), 383.

to 90°) was not needed. Instead, a Box-Behnken experiment was set up around the null positions for the three components varied: the polarizer (P), the analyzer (A) and the incidence angle (AOI). Since the positions of all three components are known for a properly calibrated ellipsometer ($P = -90^\circ$, $A = 90^\circ$ and $\text{AOI} = 55.79^\circ$), comparisons with the measured angles (Figure C.14) was used to determine the error left in the ellipsometer after calibration.

C.6. Compensator Alignment

The compensator was aligned to the polarizer and analyzer by setting the polarizer to -45° and nulling the analyzer in a straight through configuration with all samples removed (the position of the analyzer was recorded for additional information about the relation between the polarizer and analyzer). The compensator was positioned between the polarizer and the sample mount and was aligned to the laser beam. The compensator was rotated so the compensator's fast axis was aligned with the polarizer. This was accomplished by taking a series of measurements around -45° and fitting a quadratic model to the measured data. The point of lowest light measurement occurred when the fast axis of the compensator and polarizer were aligned. The compensator was rotated and fixed at the point where it was aligned with the polarizer.

C.7. Ellipsometric Measurement Procedures

1. Mount the sample to the sample mount
2. Place an aperture between the compensator and the sample
3. Rotated the sample until the reflected beam is directly above the aperture
4. Measure the distance between the reflected beam and aperture and

between the aperture and the sample surface and calculate the sample tilt

5. Measure the error in the rotational measurement (do not rotate the sample between measuring the sample tilt and rotational error)
6. Upon completion of rotational and tilt error measurements, remove the aperture and rotate the sample to the desired incident angle; adjust the sample position using the translation stage if needed
7. Remove the analyzer and place two apertures in the detector housing
8. Align the reflected beam between the two apertures then secure the detector to the optical breadboard
9. Secure the analyzer flush with the detector housing and coaxially with the reflected beam
10. Open the LabVIEW software written for the ellipsometer electronics so light measurements can be collected
11. Begin taking measurements

C.8. Pyrex 7740 Verification Experiment

The correction factors resulting from all the calibration experiments were $P_c = -0.579^\circ$, $A_c = 0.020^\circ$, $C_c = -0.288^\circ$ and $AOI_c = 0^\circ$. These correction factors were used to adjust measured data to account for the errors in the mounting of the measurement optics. Although there was a measureable difference between the actual and the measured incidence angle in experiments like the Box-Behnken verification experiment, the variability was not consistent, possibly caused by inconsistencies in the rotational error determination during sample tilt measurements. Therefore a standard correction factor for the incidence angle measurements was omitted.

To ensure the correction factors determined from the calibration experiments were valid, the ellipsometric measurements were taken at multiple angles of incidence with all the optical components in place (PCSA). The result was a measured refractive index of 1.469 ± 0.009 . The advantage of measurements made at multiple angles of incidence is the determination of the Brewster's angle from the measurement data. The Brewster's angle was determined from the data to be $55.81^\circ \pm 0.09^\circ$ which corresponds to a refractive index measurement of 1.472 ± 0.005 . Both measurements include the actual refractive index of Pyrex 7740 of 1.4711, thus confirming proper calibration of the ellipsometer.

C.9. Au-Si Verification Experiment

Measurement of the gold film's refractive index was accomplished with the ellipsometer. Unfortunately, the film measured was as sputtered so direct comparison to literature measurements was difficult since the processing of the film will directly affect its refractive index. The measured refractive index was $n_{\text{Au}} = 0.205 \pm 0.011$ and $k_{\text{Au}} = 3.181 \pm 0.008$ with a measured principle angle of $73.91^\circ \pm 0.03^\circ$. Although the real part of the refractive index (n) of the Au film was slightly higher than what was stated in literature, this discrepancy was probably due to film stress since the film had yet to be annealed. Film stress and defects, which reduce electrical conductivity, associated with an amorphous metal film is known to increase the real part of the refractive index.³

Creation of a crystalline gold standard wafer is recommended since gold is an excellent material for calibration verification due to its insensitivity to errors

³ O.S. Heavens, *Optical Properties of Thin Solid Films*, (New York: Dover Publications, Inc., 1965), 49-51.

in angle of incidence measurements near its principle angle.⁴ Such a standard could be used for control measurements with other measurement systems (e.g. XRD, XRF, spectroscopic reflectometry, four point probe, ellipsometer) to ensure consistency when multiple measurement systems are used for material analysis.

C.10. Thermal SiO₂-Si Verification Experiment

Verification of the ellipsometer performance was evaluated on a non-absorbing substrate (Pyrex 7740), an absorbing substrate (thick Au film on Si) and finally with a thick transparent film on an absorbing substrate (SiO₂ on Si). The results from the measurements of thermally grown SiO₂ on Si were compared against measurements made by the Filmetrics F20 spectroscopic reflectometer on the same sample.

Figure C.15. The measured SiO₂-Si sample with a visible thickness gradient.

The ellipsometric measurements were conducted at one angle of incidence ($\theta = 69.93^\circ$) with the corresponding ellipsometric measurements: $\Delta = 80.68^\circ \pm 0.16^\circ$ and $\Psi = 42.90^\circ \pm 0.09^\circ$. These measurements correspond to a film refractive index of $n_{\text{SiO}_2} = 1.452 \pm 0.001$ and thickness of $d_{\text{SiO}_2} = 675 \pm 1.4$

⁴ Russev, Stoyan C. Russev, Jean-Pierre Drolet and Daniel Ducharme. "Standards for Which the Ellipsometric Parameter Ψ Remains Insensitive to Variations in the Angle of Incidence." *Applied Optics* 37, no. 25 (1998): 5912-5922.

nm. The spectroscopic reflectometer measured the SiO₂ layer on the Si wafer to have a refractive index of $n_{\text{SiO}_2} = 1.450 \pm 0.002$ and thickness of $d_{\text{SiO}_2} = 681.9 \pm 2.2$ nm. A thickness gradient in the SiO₂ film was observed (Figure C.15) which would cause thickness discrepancies between the measurement systems if the positions measured were slightly different.

C.11. Custom Ellipsometric Components

Since the ellipsometer used was not a commercial system, but rather a compilation of components from various parts suppliers, there were a few components which could not be purchased and had to be constructed. Those components were the sample mount, electronics and software. There were two types of software written for the operation of the ellipsometer, the first was a LabVIEW® program written to operate the electronics via an analog to digital (A/D) converter (Figure C.16). The second set of software was written to calculate Δ and Ψ from the ellipsometric measurements and relate them to physical quantities, these algorithms are discussed in detail in Appendix F.

The electronics designed and constructed for ellipsometric measurements relied on a National Instruments A/D data acquisition device (DAQ) for voltage measurements at specific measurement points (Figure C.17). The voltages measured related to two different circuits designed to measure the amount of light detected by the silicon photodiode sensor and the temperature of the ambient air.

The first circuit was a temperature measurement circuit which used the change in resistance of a thermistor to determine the ambient air temperature; however, the thermistor used had a large time constant. Although it worked and a correlation between the measurements and the ambient temperature was

observed with it, a thermistor with a smaller time constant will provide a better measure of the ambient temperature. The second circuit was a pre-amplification circuit, utilizing a LM741CN op-amp to amplify the signal produced by the silicon photodiode sensor. The amplified signal (voltage) helped improve the measurements made by the DAQ with its programmable gain amplifier (PGA).

A vertical sample mount is rather unusual for most modern ellipsometers, as such, finding a prefabricated mount was not possible. A mount for a 100 mm wafer was designed and fabricated (Figure C.18). It was secured to a 90° angle bracket by a friction fitting (Figure C.19).

Figure C.16. LabVIEW code written for light measurement and temperature logging.

Figure C.17. Schematics for the electronics used in the construction of the ellipsometer.

Figure C.18. Machine drawing for the fabrication of the sample mount.

Figure C.19. Machine drawing for the sample mount aligner which secures the wafer holder to the 90° angle bracket.

APPENDIX D: Goniometer Configuration and Use

D.1. Goniometer Setup

The goniometer utilized the same platform as the ellipsometer, with a slightly different configuration (Figure D.1). The compensator was removed

Figure D.1. Configuration schematic of the goniometer utilizing a polarization filter for beam intensity attenuation.

and the analyzer was placed between the polarizer and sample (Figure D.2). The polarization orientation of the light incident on the sample was determined by the orientation of the analyzer. The polarizer orientation attenuated the amount of light that was incident on

the sample, which was important for preventing sensor saturation when making relative reflectance measurements. The same operational software (LabVIEW) was used for making the light measurements as the ellipsometer; however, the analysis software (Mathcad) was different (Appendix F).

Figure D.2. Photograph of the goniometer used for reflectance measurements by thesis project.

D.2. Goniometry Measurement Procedures

1. With the sample removed and the detector secured in the straight through position, a baseline measurement is taken
2. Mount the sample and rotate the sample to the desired angle of incidence and take a light measurement
3. Repeat step 2 until all the measurements have been made
 - A more time consuming, but more accurate method involves taking a baseline measurement between each sample measurement (i.e. repeat steps 1 and 2 instead of just step 2)
4. After all the sample measurements have been collected, take another baseline measurement
5. In the measurement spreadsheet, reflectance is calculated by dividing the sample measurement by the baseline measurement
 - Linear interpolation for the baseline between the two measurements may improve the accuracy of the reflectance measurements

D.3. Abeles' Method for Refractive Index Determination of a Film

From the reflectances measured with the goniometer, the film's refractive index can be determined, if the light incident on the sample surface is p-polarized and the film is transparent (i.e. has a zero extinction coefficient, like dielectrics). At the film's refractive index, the measured reflectance will be equal to a film free sample; therefore, film covered and film free samples must be measured.

The film's Brewster's angle is determined by subtracting the measured reflectances of the two samples from each other. The point where there is no difference is the film's Brewster's angle. The amount of error in the measurement

can be estimated by fitting a model to the difference measurements as a function of incidence angle (Figure D.3). Although the refractive index can be measured from one set of goniometry measurements, multiple sets of measurements is recommended for best results.

Figure D.3. Determination of the PECVD SiO_x film's Brewster's angle from goniometry data collected on the coated and uncoated samples.

Appendix E: Spectroscopic Reflectometry and Transmission Measurement Procedures

E.1. Spectroscopic Reflectometry Measurements

Spectroscopic reflectometry is an important measurement technique given its speed and accuracy. The Filmetrics F20 spectroscopic reflectometer was shown to be capable of measuring films as thin as 28 nm with a fair degree of precision. However, since the F20 is a relative reflectivity measurement system which relies on a measurement baseline to determine the actual reflectance of a material, very accurate baseline measurements are required to measure thin films. The following is the measurement procedure used to measure the 20 nm and 50 nm PECVD SiO_x films deposited on silicon.

1. Allow the light source to warm up for at least 30 minutes before beginning testing
2. Following the standard measurement procedures, take a baseline measurement on the silicon standard wafer; however, be sure to measure a position on the wafer that is free of any visible defect (e.g. dust)
3. Once the baseline measurement is complete (silicon reflectance and dark noise subtraction), model the silicon standard's reflectance and refractive index
 - In the "Edit Structure" window, check "n" and "k" for the substrate under the "Layers" tab
 - Under the "Options" tab, limit the model to wavelengths between 475 nm and 950 nm, this is to eliminate errors associated with

diffraction grating within the measurement system

- Also under the “Options” tab, verify the reported refractive index wavelength is 632.8 nm
- Under the constraints tab, the ranges of n or k may need to be expanded in order for the model to converge, also change the GOF to 0.99

4. Verify the model results

- Tolerance for n is 3.86 to 3.89, resulting models with n values outside this range need to have the baseline measurement conducted again
- Tolerance for k is 0 to 0.03
- Another check of the validity is the reflectance at 632.8 nm, if it is near 0.3472 than the baseline measurement is valid

5. Once the model results are validated, proceed to measure the desired sample

Reflectometry, like ellipsometry, is a model dependant measurement system. Therefore, measurement of the samples reflection is only the first step, modelling the reflection to determine the optical parameters of interest (i.e. 0 index and thickness) is required. To measure thin oxides on silicon, a modelling procedure contrary to the one provided by Filmetrics was used.

6. With the reflectance measurements complete, select the optical model to be fit to the data (Figure E.1) with an anticipated thickness value inserted

- The anticipated thickness acts as a seed value for the model

Figure E.1. A screenshot of the Filmetrics frontend software package demonstrating the model designation for the measurement of a 50 nm oxide on silicon.

fitting program from which it iterates the model until one with a sufficiently high goodness of fit (GOF) statistic is found

- Although the Filmetrics procedure states the optical constants of the film and substrate should not be modeled if the film thickness is less than approximately 200 nm, by checking them the model fitting algorithm is less constrained and able to account for any errors in the reflectance measurement
- Although the refractive index of silicon is well known, it is treated as a variable in the model so to act as a measure of

model validity, similar to how it was used to verify the baseline measurement

- For films with thicknesses greater than approximately 100 nm, modeling the substrates refractive index is no longer needed, but still recommended for the same reasons stated above

7. Select “Measure” to run the model

- Models resulting in a substrate refractive index within the range given in step 4 are considered valid
- Models which return a substrate refractive index outside the range stated in step 4 are indicative of significant reflectance measurement error (i.e. surface particulate matter, warped wafer or other source of reflectance error) and the model must be discarded and the reflectance measurement repeated (step 5)
- Failure of models to converge are typically due to poor reflectance measurements (repeat step 5 to remedy) or are too constrained; if too constrained, adjust the ranges on n and k under the “Constraints” tab or uncheck k for the substrate under the “Layers” tab
- Modelling of the extinction coefficient of silicon is not necessary since it plays little role in the reflectance of light off a silicon surface at normal incidence and is usually correlated with the thickness of an overlying oxide

8. Upon successful modeling of the reflectance measurement, rebaseline the measurement system (i.e. return to step 1) before making another measurement

- Although the Filmetrics software allows for continual

measurements to be collected, these measurements are not independent of each other and therefore should not be treated as individual measurements

- Remeasurement of the baseline is not essential, but removal of the sample is in order to make the measurements independent and a valid statistical measure of variance
- Repeating the baseline procedure between measurements is an error reduction technique which is recommended, especially for thin films since small errors have a larger affect on the modeled parameters of thin films than thicker ones

E.2. Spectroscopic Transmission for Transparent Materials

Although the Filmetrics F20 is an excellent measurement tool, it is limited to materials which reflect a decent amount of light at normal incidence. Unfortunately, this makes measurements of dielectrics near impossible since the normal reflectance of most dielectrics is less than 10%, leading to small signal to noise ratios in the reflectance measurements. The F20 does have a transmission mode; however, it requires a special attachment which the lab at

Figure E.2. The spectroscopic transmission measurement setup.

Cal Poly does not have. Therefore, a spectroscopic transmission measurement system was constructed from a tungsten arc lamp, fiber optics and an Ocean Optics UV-Vis spectrometer (Figure E.2). The samples were placed in a sample holder which included columnising optics to ensure efficient transfer of light through the sample holder. Polarization of the spectroscopic light source was accomplished using a linear film polarizer situated before the sample in the optical train (Figure E.3).

The transmission procedure was straight forward, utilizing the transmission measurement wizard in the spectrometer software. Although the spectrometer software normalizes the measurement data to air, a baseline measurement was taken prior to each sample for noise reduction purposes. The transmission measurements made on the sample were divided by the baseline measurements to reduce any errors induced by the transmission measurement process.

Multiple measurements were taken for each sample; however, the position of each measurement was not exactly the same as the previous. As discovered later, the thickness of the PET samples was not constant and varied from measurement to measurement. Averaging the measurements did not eliminate

Figure E.3. Linear film polarizer used to polarize the light incident on the PET sample.

this variation, but rather destroyed the interference fringes (as seen in figure 6.10). When the film polarizer was used, due to the lack of an antireflection coating on the polarizer, errors caused by parasitic reflections further degraded the interference fringes. Finally, the polarizers used sharply decreased their polarizability at wavelengths 800 nm and greater, limiting the usefulness of the spectroscopic transmission measurements.

Although transmission measurements were conducted on all the sample provided by NS3, only the uncoated samples provided any useful information for this project.

APPENDIX F: Model Fitting Programs

F.1. Model Generation

The optical measurement systems utilized in this project were all indirect type measurement systems. What was actually measured, reflectance and polarization change, was of little interest; however, from optical models, these measurements could be converted into a more useful information, like refractive index and thickness measurements. A series of Mathcad worksheets were programed to generate models for the extraction of refractive index and thickness parameters from the optical measurements. Although many of these worksheets were programed, they consisted of the same basic structure.

All global variables are defined at the beginning by the user (i.e. refractive indices, thicknesses, incidence angles, etc.). The model is then iteratively calculated using a for loop with the calculated values output to a table. Some of the programs automatically write the table to a .csv file for upload by a graphic program that supports spreadsheets while others just graph the data within the worksheet.

The following is an example of the model generation programs used by this project. I apologize for the format, but Mathcad 11 doesn't export well.

Ellipsometric Curve Generator (Classic)

Parameters

$$\lambda := 632.8$$

$$N_0 := 1$$

$$N_1 := 1.454$$

$$N_2 := 3.88 - 0.018j$$

$$\theta_0 := 69.9 \text{ deg}$$

$$d := 700$$

Model parameters defined by the user

Thickness Calculator

$$\theta_1 := \arccos \left[\sqrt{1 - \left(\frac{N_0}{N_1} \cdot \sin(\theta_0) \right)^2} \right]$$

$$\theta_1 = 40.231 \text{ deg}$$

$$\theta_2 := \arccos \left[\sqrt{1 - \left(\frac{N_1}{N_2} \cdot \sin(\theta_1) \right)^2} \right]$$

$$\theta_2 = 14.006 + 0.066i \text{ deg}$$

$$r_{01p} := \frac{N_1 \cdot \cos(\theta_0) - N_0 \cdot \cos(\theta_1)}{N_1 \cdot \cos(\theta_0) + N_0 \cdot \cos(\theta_1)}$$

$$r_{01p} = -0.209$$

$$r_{12p} := \frac{N_2 \cdot \cos(\theta_1) - N_1 \cdot \cos(\theta_2)}{N_2 \cdot \cos(\theta_1) + N_1 \cdot \cos(\theta_2)}$$

$$r_{12p} = 0.355 - 1.901i \times 10^{-3}$$

$$r_{01s} := \frac{N_0 \cdot \cos(\theta_0) - N_1 \cdot \cos(\theta_1)}{N_0 \cdot \cos(\theta_0) + N_1 \cdot \cos(\theta_1)}$$

$$r_{01s} = -0.527$$

$$r_{12s} := \frac{N_1 \cdot \cos(\theta_1) - N_2 \cdot \cos(\theta_2)}{N_1 \cdot \cos(\theta_1) + N_2 \cdot \cos(\theta_2)}$$

$$r_{12s} = -0.545 + 1.733i \times 10^{-3}$$

$$t_{01p} := \frac{2 \cdot N_0 \cdot \cos(\theta_0)}{N_1 \cdot \cos(\theta_0) + N_0 \cdot \cos(\theta_1)}$$

$$t_{01p} = 0.544$$

$$t_{01s} := \frac{2 \cdot N_0 \cdot \cos(\theta_0)}{N_0 \cdot \cos(\theta_0) + N_1 \cdot \cos(\theta_1)}$$

$$t_{01s} = 0.473$$

$$t_{12p} := \frac{2 \cdot N_1 \cdot \cos(\theta_1)}{N_2 \cdot \cos(\theta_1) + N_1 \cdot \cos(\theta_2)}$$

$$t_{12p} = 0.508 + 1.643i \times 10^{-3}$$

$$t_{12s} := \frac{2 \cdot N_1 \cdot \cos(\theta_1)}{N_1 \cdot \cos(\theta_1) + N_2 \cdot \cos(\theta_2)}$$

$$t_{12s} = 0.455 + 1.733i \times 10^{-3}$$

Calculation
of the Fresnel
coefficients


```

Data := [ for t ∈ 0, 1 .. d
  [
    
$$\delta \leftarrow \left[ \left( \frac{2 \cdot \pi}{\lambda} \right) \cdot t \cdot N_1 \cdot \sqrt{1 - \left( \frac{N_0}{N_1} \cdot \sin(\theta_0) \right)^2} \right]$$

    
$$\rho_{rp} \leftarrow \frac{r_{01p} + r_{12p} \cdot e^{-2j\delta}}{1 + r_{01p} \cdot r_{12p} \cdot e^{-2j\delta}}$$

    
$$\rho_{rs} \leftarrow \frac{r_{01s} + r_{12s} \cdot e^{-2j\delta}}{1 + r_{01s} \cdot r_{12s} \cdot e^{-2j\delta}}$$

    
$$\rho_r \leftarrow \frac{\rho_{rp}}{\rho_{rs}}$$

    
$$\rho_{tp} \leftarrow \frac{t_{01p} \cdot t_{12p} \cdot e^{-j \cdot \delta}}{1 + r_{01p} \cdot r_{12p} \cdot e^{-2j \cdot \delta}}$$

    
$$\rho_{ts} \leftarrow \frac{t_{01s} \cdot t_{12s} \cdot e^{-j \cdot \delta}}{1 + r_{01s} \cdot r_{12s} \cdot e^{-2j \cdot \delta}}$$

    
$$\rho_t \leftarrow \frac{\rho_{tp}}{\rho_{ts}}$$

    
$$\Delta_r \leftarrow \text{atan2}(\text{Re}(\rho_r), \text{Im}(\rho_r)) \cdot \left( \frac{180}{\pi} \right)$$

    
$$\psi_r \leftarrow \text{atan}(|\rho_r|) \cdot \left( \frac{180}{\pi} \right)$$

    
$$\Delta_r \leftarrow \Delta_r + 360 \text{ if } \Delta_r < 0$$

    
$$\Delta_t \leftarrow \text{atan2}(\text{Re}(\rho_t), \text{Im}(\rho_t)) \cdot \left( \frac{180}{\pi} \right)$$

    
$$\psi_t \leftarrow \text{atan}(|\rho_t|) \cdot \left( \frac{180}{\pi} \right)$$

    Datat,0 ← t
    Datat,1 ← Δr
    Datat,2 ← ψr
    Datat,4 ← Δt
    Datat,5 ← ψt
    Datat,3 ← ρr
    Datat,6 ← ρt
  ]
Data

```

Calculation of the ellipsometric parameters from the defined optical parameters

Data and Graphical Output

Data =

	0	1	2
0	0	179.281	10.721
1	1	176.473	10.734
2	2	173.675	10.764
3	3	170.895	10.812
4	4	168.142	10.877
5	5	165.422	10.959
6	6	162.741	11.057
7	7	160.107	11.171
8	8	157.524	11.3
9	9	154.996	11.444
10	10	152.527	11.601
11	11	150.119	11.772
12	12	147.775	11.955
13	13	145.497	12.15
14	14	143.284	12.356
15	15	141.137	12.572

**Numerical
and graphical
outputs**

F.2. Model Fitting Process

Since the optical measurements conducted were quite complex, it was difficult to anticipate the best measurement position prior to experimentation. Therefore, model generation programs, like those briefly described above, were used in the design of the experiments to help anticipate the measured response of a material. However, once the material was measured, the generated models proved to be inadequate for determination of the optical parameters. A model fitting program was needed.

Using least squares regression on a predefined error function, the ellipsometric, and goniometric, models were optimized to the measured data. The general model fitting process:

1. The measured data was uploaded to the worksheet as a .csv or text data file type
2. The measurement correction factors measured during calibration were inserted and calculation of the corrected measurements with their associated ellipsometric parameters was conducted
3. The calculated ellipsometric parameters were output to a table and a text file for use both within the worksheet and by outside programs capable of manipulating spreadsheets (e.g. for graphing)
4. The model fitting algorithm was very similar to the model generation programs; however, the model fitting algorithm included an error function for model optimization
5. A SSE grid was constructed from a range of parameters decided upon by the user and output to a table and text file
6. The text file containing the SSE grid was uploaded to a statistics

software package (JMP®) from which it was analyzed to determine the model that best fit the measured data

7. Through a series of data reduction and modelling steps, the SSE grid eventually was reduced to a surface which could be modeled and an optimum point could be achieved (see figure 6.16)

Although this method was more cumbersome than a numerical method, like Newton-Raphson or the gradient method, which would converge on a solution automatically, it allowed the researcher to examine the SSE grid prior to optimization. It was through this intermediate step that led to the discovery of multiple solutions for some samples, a situation where an automatic optimization method could converge on the wrong solution. A hybrid method which examines the SSE grid prior to optimization by a numerical algorithm would be ideal for many applications; however, time constraints prevented this method from being pursued; subsequently, such a model fitting method will have to be deferred to future research.

A model fitting worksheet was created for each sample measured; however, the following examples are just two of those worksheets used. The first was used to optimize the data for the thickest PECVD SiO_x film deposited on silicon. The second was the model used to analyze the ellipsometric measurements on biaxially oriented PET.

PECVD SiO₂ on Si Model Fitting Program

data :=
150 nm Coating AOI Modelling.TX

Measurements := 11

counter := Measurements - 1

Previously measured or known parameters

$$\varepsilon_A := -0.420 \text{deg}$$

$$\varepsilon_P := -0.0625 \text{deg}$$

$$\varepsilon_C := 0.131 \text{deg}$$

$$\varepsilon_{AOI} := -0.04213 \text{deg}$$

$$N_0 := 1$$

$$\lambda := 632.8$$

$$C_{13m} := -45 \text{deg}$$

$$a_y := 0.9969$$

$$a_x := 1$$

$$\phi := -90 \text{deg}$$

$$\rho_c := \left(\frac{a_y}{a_x} \right) \cdot e^{j \cdot \phi}$$

$$N_{IPV} := \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

$$Z_V := \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

The compensator is slightly absorbing, but still acts as a quarter waveplate. The absorbance makes it act as a weak polarizer in addition to a phase retarder. The calculation of r_c corrects for the slight absorbance.

```

p_data := for row ∈ 0 .. counter
|
|   A1m ← datarow,3 ·  $\left(\frac{\pi}{180}\right)$ 
|   A3m ← datarow,5 ·  $\left(\frac{\pi}{180}\right)$ 
|   P1m ← datarow,4 ·  $\left(\frac{\pi}{180}\right)$ 
|   P3m ← datarow,6 ·  $\left(\frac{\pi}{180}\right)$ 
|   θt ← datarow,1 ·  $\left(\frac{\pi}{180}\right)$ 
|   θe ← datarow,2 ·  $\left(\frac{\pi}{180}\right)$ 
|   θm ← datarow,0 ·  $\left(\frac{\pi}{180}\right)$ 
|   θ ← 2 · π − (θm − θe + εAOI)
|   θNt ←  $\frac{\theta_t}{2}$ 
|   RoNX ←  $\begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(\theta_{Nt}) & -\sin(\theta_{Nt}) \\ 0 & \sin(\theta_{Nt}) & \cos(\theta_{Nt}) \end{pmatrix}$ 
|   RoNZ ←  $\begin{pmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix}$ 
|   NVsample ← (RoNZ · RoNX · NIPV)
|   θ0 ←  $\arccos\left(\frac{N_{IPV} \cdot N_{Vsample}}{\sqrt{N_{IPV} \cdot N_{IPV}} \cdot \sqrt{N_{Vsample} \cdot N_{Vsample}}}\right)$ 
|   Z' ← NVsample × NIPV
|   εt ←  $\arccos\left(\frac{Z_V \cdot Z'}{\sqrt{Z_V \cdot Z_V} \cdot \sqrt{Z' \cdot Z'}}\right)$ 
|   A1 ← A1m + εA + εt
|   A3 ← π − (A3m + εA + εt)
|   P1 ← P1m − εt + εP
|   P3 ← (P3m − εt + εP) −  $\frac{\pi}{2}$ 
|   C13 ← C13m − εt + εC
|   A13 ←  $\frac{\pi}{2} - \frac{A_1 + A_3}{2}$ 
|   P13 ←  $\frac{P_1 + P_3}{2}$ 
|

```

$\rho \leftarrow \tan(A_{13}) \cdot \frac{(\tan(C_{13}) + \rho_c \cdot \tan(P_{13} - C_{13}))}{\rho_c \cdot \tan(C_{13}) \cdot \tan(P_{13} - C_{13}) - 1}$	
$\Delta \leftarrow \begin{cases} \Delta \leftarrow \arg(\rho) \\ \Delta \leftarrow \Delta + 2 \cdot \pi \text{ if } \Delta < 0 \end{cases}$	
$\psi \leftarrow \text{atan}(\rho)$	
$\rho_{\text{data}_{\text{row},0}} \leftarrow \theta_0 \cdot \left(\frac{180}{\pi} \right)$	
$\rho_{\text{data}_{\text{row},1}} \leftarrow \rho$	
$\rho_{\text{data}_{\text{row},2}} \leftarrow \Delta \cdot \left(\frac{180}{\pi} \right)$	
$\rho_{\text{data}_{\text{row},3}} \leftarrow \psi \cdot \left(\frac{180}{\pi} \right)$	
$\rho_{\text{data}_{\text{row},4}} \leftarrow A_{13} \cdot \left(\frac{180}{\pi} \right)$	
$\rho_{\text{data}_{\text{row},5}} \leftarrow P_{13} \cdot \left(\frac{180}{\pi} \right)$	
ρ_{data}	ρ_{data}

$$N_3 := 3.871 - 0.018i$$

$$N_2 := 1.46$$

$$t_2 := 1.83$$

$$N_1 := 1.45$$

$$\text{range} := 0.04$$

$$\text{range}_{n2} := 0.4$$

$$\text{div} := 0.001$$

$$\text{div}_{n2} := 0.001$$

$$t_{\text{range}} := 6$$

$$t_{\text{div}} := 0.2$$

$$\text{int}_{n2} := \frac{\text{range}_{n2}}{\text{div}_{n2}}$$

$$d := \frac{t_{\text{range}}}{t_{\text{div}}}$$

$$\text{int}_{n2} = 400$$

$$t_{\text{offset}} := 63$$

$$\text{int} := \frac{\text{range}}{\text{div}}$$

$$\text{int} = 40$$

$$\text{calc} := \text{int} \cdot [(d + 1)(\text{int}_{n2} + 1)] + \text{int}_{n2} \cdot (d + 1) + d$$

$$\text{calc} = 5.0967 \times 10^5$$

```

Model := Model0,0 ← "Film Refractive Index"
Model0,1 ← "EMA Refractive Index"
Model0,2 ← "Film Thickness"
Model0,3 ← "EF(F)"
Model0,4 ← "EF(G)"
for count ∈ 0, 1 .. int
  N1 ← N1 + count·div
  for RI ∈ 0 .. intn2
    N2 ← N2 + RI·divn2
    for num ∈ 0, 1 .. d
      t1 ← num·tdiv + toffset
      rows ← count[(d + 1)(intn2 + 1)] + RI·(d + 1) + num + 1
      for row ∈ 0, 1 .. counter
        θ0 ← ρdatarow,0 · (π / 180)
        Δm ← ρdatarow,2 · (π / 180)
        ψm ← ρdatarow,3 · (π / 180)
        ρm ← ρdatarow,1
        θ1 ← acos[√(1 - (N0 / N1) · sin(θ0))2]
        θ2 ← acos[√(1 - (N0 / N2) · sin(θ1))2]
        θ3 ← acos[√(1 - (N0 / N3) · sin(θ0))2]
        r01p ← (N1 · cos(θ0) - N0 · cos(θ1)) / (N1 · cos(θ0) + N0 · cos(θ1))
        r01s ← (N0 · cos(θ0) - N1 · cos(θ1)) / (N0 · cos(θ0) + N1 · cos(θ1))
        r12p ← (N2 · cos(θ1) - N1 · cos(θ2)) / (N2 · cos(θ1) + N1 · cos(θ2))
        r12s ← (N1 · cos(θ1) - N2 · cos(θ2)) / (N1 · cos(θ1) + N2 · cos(θ2))
        r23p ← (N3 · cos(θ2) - N2 · cos(θ3)) / (N3 · cos(θ2) + N2 · cos(θ3))

```


$$\begin{aligned}
r_{23s} &\leftarrow \frac{N_2 \cdot \cos(\theta_2) - N_3 \cdot \cos(\theta_3)}{N_2 \cdot \cos(\theta_2) + N_3 \cdot \cos(\theta_3)} \\
\delta_1 &\leftarrow \left[\left(\frac{2 \cdot \pi}{\lambda} \right) \cdot t_1 \cdot N_1 \cdot \sqrt{1 - \left(\frac{N_0}{N_1} \cdot \sin(\theta_0) \right)^2} \right] \\
\delta_2 &\leftarrow \left[\left(\frac{2 \cdot \pi}{\lambda} \right) \cdot t_2 \cdot N_2 \cdot \sqrt{1 - \left(\frac{N_0}{N_2} \cdot \sin(\theta_0) \right)^2} \right] \\
\rho_{rp} &\leftarrow \frac{\left(r_{01p} + r_{12p} \cdot e^{-2j \cdot \delta_1} \right) + \left(r_{01p} \cdot r_{12p} + e^{-2j \cdot \delta_1} \right) \cdot r_{23p} \cdot e^{-2j \cdot \delta_2}}{\left(1 + r_{01p} \cdot r_{12p} \cdot e^{-2j \cdot \delta_1} \right) + \left(r_{12p} + r_{01p} \cdot e^{-2j \cdot \delta_1} \right) \cdot r_{23p} \cdot e^{-2j \cdot \delta_2}} \\
\rho_{rs} &\leftarrow \frac{\left(r_{01s} + r_{12s} \cdot e^{-2j \cdot \delta_1} \right) + \left(r_{01s} \cdot r_{12s} + e^{-2j \cdot \delta_1} \right) \cdot r_{23s} \cdot e^{-2j \cdot \delta_2}}{\left(1 + r_{01s} \cdot r_{12s} \cdot e^{-2j \cdot \delta_1} \right) + \left(r_{12s} + r_{01s} \cdot e^{-2j \cdot \delta_1} \right) \cdot r_{23s} \cdot e^{-2j \cdot \delta_2}} \\
\rho_c &\leftarrow \frac{\rho_{rp}}{\rho_{rs}} \\
\psi &\leftarrow \text{atan}\left(\left|\rho_c\right|\right) \\
\Delta &\leftarrow \arg(\rho_c) \\
\text{SSE}_{\text{row},0} &\leftarrow \left(\left|\rho_m - \rho_c\right|\right)^2 \\
\text{SSE}_{\text{row},1} &\leftarrow \left(\Delta - \Delta_m\right)^2 \\
\text{SSE}_{\text{row},2} &\leftarrow \left(\psi - \psi_m\right)^2 \\
\text{Model}_{\text{rows},0} &\leftarrow N_1 \\
\text{Model}_{\text{rows},1} &\leftarrow \text{Re}(N_2) \\
\text{Model}_{\text{rows},2} &\leftarrow t_1 \\
\text{Model}_{\text{rows},3} &\leftarrow \sum \text{SSE}^{(0)} \\
\text{Model}_{\text{rows},4} &\leftarrow \sum \text{SSE}^{(1)} + \sum \text{SSE}^{(2)}
\end{aligned}$$

Model

	0	1	2	3	4	5
0	70	1.114	0	118.891	-92.509	61.389
1	74	1.114	0	119.909	-101.104	60.295
2	75	1.114	0	120.218	-103.328	59.778
3	75	1.114	0	120.126	-103.297	59.768
4	76	1.114	0	120.734	-105.475	59.256
5	80	1.114	0	123.652	-114.255	56.273
6	70	1.043	0	118.725	-92.5882	61.284
7	65	1.043	0	61.031	-173.242	119.084
8	56	1.2	0	58.034	-159.59	122.098
9	70	1.309	0	118.93	-92.583	61.264
10	70	1.199	0	118.855	-92.458	61.282

	0	1	2	
0	69.9588576694	877+0.5450724697i	84.3157244303	
1	73.9586484913	849+0.5239989499i	66.9721434628	
2	74.9585975817	876+0.5130376354i	62.5145364201	
3	74.9585975817	881+0.5124279403i	62.563603406	
4	75.9585471475	858+0.5015478995i	58.2431997534	
5	79.9583494424	817+0.4287901627i	40.5908610375	
6	69.9587357857	883+0.5442079835i	84.0913619166	
7	64.9589788092	889+0.5380195071i	103.3364190242	
8	55.9599923477	887+0.4684269264i	130.6350823473	
9	69.9592336995	815+0.5465006391i	84.1190664162	
10	69.9590141391	831+0.5458782274i	84.3968879406	

olution Surface (S1).de

Model

	0	1	2
0	"Film Refractive Index"	"EMA Refractive Index"	"Film Thickness"
1	1.45	1.46	63
2	1.45	1.46	63.2
3	1.45	1.46	63.4
4	1.45	1.46	63.6
5	1.45	1.46	63.8
6	1.45	1.46	64
7	1.45	1.46	64.2
8	1.45	1.46	64.4
9	1.45	1.46	64.6
10	1.45	1.46	64.8
11	1.45	1.46	65
12	1.45	1.46	65.2
13	1.45	1.46	65.4
14	1.45	1.46	65.6
15	1.45	1.46	65.8

Ellipsometric Model Fitting Program (Uncoated PET)

data := Uncoated PET.T;

Measurements := 15

counter := Measurements - 1

data =

	0	1	2	3
0	56	0.93	0.35	82.375
1	57	0.88	0.16	87.045
2	58	0.87	0.35	86.758
3	58	0.88	0.25	86.295
4	58	0.72	0.2	86.289
5	59	0.77	0.3	86.658
6	60	1.09	0.16	88.087

Previously measured or known parameters

$\varepsilon_A := 0.02 \text{deg}$

$\varepsilon_P := -0.579 \text{deg}$

$\varepsilon_C := -0.288 \text{deg}$

$\varepsilon_{AOI} := 0 \text{deg}$

$$N_{IPV} := \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$Z_V := \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

$N_0 := 1$

$\lambda := 632.8$

$C_{13m} := -45 \text{deg}$

$a_y := 0.9969$

$a_x := 1$

$\phi := -90 \text{deg}$

$$\rho_c := \begin{pmatrix} a_y \\ a_x \end{pmatrix} \cdot e^{j \cdot \phi}$$

The compensator is slightly absorbing, but still acts as a quarter waveplate. The absorbance makes it act as a weak polarizer in addition to a phase retarder. The calculation of r_c corrects for the slight absorbance.

Rho calculation program

$\rho_{data} :=$ for row $\in 0 \dots \text{counter}$

$$A_{1m} \leftarrow \text{data}_{\text{row},3} \cdot \left(\frac{\pi}{180} \right)$$

$$A_{3m} \leftarrow \text{data}_{\text{row},5} \cdot \left(\frac{\pi}{180} \right)$$

$$P_{1m} \leftarrow \text{data}_{\text{row},4} \cdot \left(\frac{\pi}{180} \right)$$

$$P_{3m} \leftarrow \text{data}_{\text{row},6} \cdot \left(\frac{\pi}{180} \right)$$

$$\theta_t \leftarrow \text{data}_{\text{row},1} \cdot \left(\frac{\pi}{180} \right)$$

$$\theta_e \leftarrow \text{data}_{\text{row},2} \cdot \left(\frac{\pi}{180} \right)$$

$$\theta_m \leftarrow \text{data}_{\text{row},0} \cdot \left(\frac{\pi}{180} \right)$$

$$\theta \leftarrow 2 \cdot \pi - (\theta_m - \theta_e + \varepsilon_{AOI})$$

$$\theta_{Nt} \leftarrow \frac{\theta_t}{2}$$

$$R_{NX} \leftarrow \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(\theta_{Nt}) & -\sin(\theta_{Nt}) \\ 0 & \sin(\theta_{Nt}) & \cos(\theta_{Nt}) \end{pmatrix}$$

$$R_{NZ} \leftarrow \begin{pmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$N_{V\text{sample}} \leftarrow (R_{NZ} \cdot R_{NX} \cdot N_{PV})$$

$$\theta_0 \leftarrow \arccos \left(\frac{N_{PV} \cdot N_{PV}}{\sqrt{N_{PV} \cdot N_{PV}} \cdot \sqrt{N_{V\text{sample}} \cdot N_{V\text{sample}}}} \right)$$

$$Z' \leftarrow N_{V\text{sample}} \times N_{PV}$$

$\rho_{data} =$

	0	1	2
0	55.651	-0.124+0.014i	173.523
1	56.841	-0.04+0.033i	219.585
2	57.651	-5.437·10 ⁻³ +0.066i	94.683
3	57.751	-6.715·10 ⁻³ +0.075i	95.087
4	57.801	-6.043·10 ⁻³ +0.076i	94.554
5	58.701	-0.033+0.049i	123.857
6	59.842	-0.018+6.11i·10 ⁻³	161.179
7	60.751	-3.75·10 ⁻³ -0.024i	261.223
8	61.584	0.016+0.01i	32.031
9	61.901	0.026+2.504i·10 ⁻³	5.406
10	61.651	0.022+5.326i·10 ⁻³	13.364
11	61.751	0.025+2.78i·10 ⁻³	6.238
12	63.701	0.145-7.812i·10 ⁻³	356.913
13	66.751	0.191-0.011i	356.626
14	69.901	0.178+7.344i·10 ⁻³	2.363

$$\begin{aligned}
\varepsilon_t &\leftarrow \arccos\left(\frac{Z_V \cdot Z'}{\sqrt{Z_V \cdot Z_V} \sqrt{Z' \cdot Z'}}\right) \\
A_1 &\leftarrow A_{1m} + \varepsilon_A + \varepsilon_t \\
A_3 &\leftarrow \pi - (A_{3m} + \varepsilon_A + \varepsilon_t) \\
P_1 &\leftarrow P_{1m} - \varepsilon_t + \varepsilon_p \\
P_3 &\leftarrow (P_{3m} - \varepsilon_t + \varepsilon_p) - \frac{\pi}{2} \\
C_{13} &\leftarrow C_{13m} - \varepsilon_t + \varepsilon_C \\
A_{13} &\leftarrow \frac{\pi}{2} - \frac{A_1 + A_3}{2} \\
P_{13} &\leftarrow \frac{P_1 + P_3}{2} \\
\rho &\leftarrow \frac{\tan(A_{13}) \cdot (\tan(C_{13}) + \rho_c \cdot \tan(P_{13} - C_{13}))}{\rho_c \cdot \tan(C_{13}) \cdot \tan(P_{13} - C_{13}) - 1} \\
\Delta &\leftarrow \begin{cases} \Delta \leftarrow \arg(\rho) \\ \Delta \leftarrow \Delta + 2 \cdot \pi \text{ if } \Delta < 0 \end{cases} \\
\psi &\leftarrow \operatorname{atan}(|\rho|) \\
\rho_{\text{data}_{\text{row},0}} &\leftarrow \theta_0 \cdot \left(\frac{180}{\pi}\right) \\
\rho_{\text{data}_{\text{row},1}} &\leftarrow \rho \\
\rho_{\text{data}_{\text{row},2}} &\leftarrow \Delta \cdot \left(\frac{180}{\pi}\right) \\
\rho_{\text{data}_{\text{row},3}} &\leftarrow \psi \cdot \left(\frac{180}{\pi}\right) \\
\rho_{\text{data}_{\text{row},4}} &\leftarrow A_{13} \cdot \left(\frac{180}{\pi}\right) \\
\rho_{\text{data}_{\text{row},5}} &\leftarrow P_{13} \cdot \left(\frac{180}{\pi}\right)
\end{aligned}$$

ρ_{data}

..Elipsometric Measurements.de

ρ_{data}

Model Fitting Algorithm

$N_3 := N_0$

$N_{2x} := 1.677$	$\text{range}_x := 0$	$\text{div}_x := 0.01$	$\text{intx} := \frac{\text{range}_x}{\text{div}_x}$	$\text{intx} = 0$
$N_{2y} := 1.632$	$\text{range}_y := 0$	$\text{div}_y := 0.01$	$\text{inty} := \frac{\text{range}_y}{\text{div}_y}$	$\text{inty} = 0$
$N_{2z} := 1.495$	$\text{range}_z := 0$	$\text{div}_z := 0.01$	$\text{intz} := \frac{\text{range}_z}{\text{div}_z}$	$\text{intz} = 0$

$N_1 := 1.289$

$t_{\text{offset}} := 14.75 \cdot 10^3$	$t_{\text{range}} := 500$	$t_{\text{div}} := 1$	$d := \frac{t_{\text{range}}}{t_{\text{div}}}$	$d = 500$
$t_{\text{front}} := 0$	$t_{\text{frange}} := 80$	$t_{\text{fdiv}} := 0.1$	$d_f := \frac{t_{\text{frange}}}{t_{\text{fdiv}}}$	$d_f = 800$

$\text{runs} := \left[d_f \cdot [(\text{intz} + 1) \cdot (\text{inty} + 1) \cdot (\text{intx} + 1) \cdot (d + 1)] + \text{intz} \cdot [(\text{inty} + 1) \cdot (\text{intx} + 1) \cdot (d + 1)] + \text{inty} \cdot [(\text{intx} + 1) \cdot (d + 1)] + \text{intx} \cdot (d + 1) + d + 1 \right]$

$\text{runs} = 4\,013 \times 10^5$

```

Model :=
Model0,0 ← "N1x"
Model0,1 ← "N1y"
Model0,2 ← "N1z"
Model0,3 ← "PET Thickness"
Model0,4 ← "Front Film Thickness"
Model0,5 ← "EF(F)"
Model0,6 ← "EF(G)"
Model0,7 ← "SSE(Delta)"
Model0,8 ← "SSE(Psi)"
for tf ∈ 0 .. df
| d1 ← tfront + tf·tdiv
| for n2z ∈ 0 .. intz
| N2z ← N2z + n2z·divz
| for n2y ∈ 0 .. inty
| N2y ← N2y + n2y·divy
| for n2x ∈ 0 .. intx
| N2x ← N2x + n2x·divx
| for t ∈ 0 .. d
| d2 ← t·tdiv + toffset
| rows ← tf[(intz + 1)·(inty + 1)·(intx + 1)·(d + 1)] + n2z·[(intx + 1)·(d + 1)] + n2x·(d + 1) + t + 1
| for row ∈ 0, 1 .. counter
| θ0 ← ρdatarow,0 ·  $\frac{\pi}{180}$ 
| Δm ← ρdatarow,2 ·  $\left(\frac{\pi}{180}\right)$ 
| ψm ← ρdatarow,3 ·  $\left(\frac{\pi}{180}\right)$ 
| ρm ← ρdata

```

$$\begin{aligned}
& \theta_1 \leftarrow \arccos \left[\sqrt{1 - \left(\frac{N_0}{N_1} \cdot \sin(\theta_0) \right)^2} \right] \\
& \theta_3 \leftarrow \arccos \left[\sqrt{1 - \left(\frac{N_0}{N_3} \cdot \sin(\theta_0) \right)^2} \right] \\
& r_{01p} \leftarrow \frac{N_1 \cdot \cos(\theta_0) - N_0 \cdot \cos(\theta_1)}{N_1 \cdot \cos(\theta_0) + N_0 \cdot \cos(\theta_1)} \\
& r_{01s} \leftarrow \frac{N_0 \cdot \cos(\theta_0) - N_1 \cdot \cos(\theta_1)}{N_0 \cdot \cos(\theta_0) + N_1 \cdot \cos(\theta_1)} \\
& r_{12pp} \leftarrow \frac{N_{2x} \cdot N_{2z} \cdot \cos(\theta_1) - N_1 \cdot \sqrt{N_{2z}^2 - N_1^2 \cdot \sin(\theta_1)^2}}{N_{2x} \cdot N_{2z} \cdot \cos(\theta_1) + N_1 \cdot \sqrt{N_{2z}^2 - N_1^2 \cdot \sin(\theta_1)^2}} \\
& r_{23pp} \leftarrow \frac{(-N_{2x} \cdot N_{2z} \cdot \cos(\theta_3)) + N_3 \cdot \sqrt{N_{2z}^2 - N_3^2 \cdot \sin(\theta_3)^2}}{N_{2x} \cdot N_{2z} \cdot \cos(\theta_3) + N_3 \cdot \sqrt{N_{2z}^2 - N_3^2 \cdot \sin(\theta_3)^2}} \\
& r_{12ss} \leftarrow \frac{N_1 \cdot \cos(\theta_1) - \sqrt{N_{2y}^2 - N_1^2 \cdot \sin(\theta_1)^2}}{N_1 \cdot \cos(\theta_1) + \sqrt{N_{2y}^2 - N_1^2 \cdot \sin(\theta_1)^2}} \\
& r_{23ss} \leftarrow \frac{-N_3 \cdot \cos(\theta_3) + \sqrt{N_{2y}^2 - N_3^2 \cdot \sin(\theta_3)^2}}{N_3 \cdot \cos(\theta_3) + \sqrt{N_{2y}^2 - N_3^2 \cdot \sin(\theta_3)^2}} \\
& \beta_1 \leftarrow \left[\left(\frac{2 \cdot \pi}{\lambda} \right) \cdot d_1 \cdot \sqrt{N_1^2 - N_0^2 \cdot \sin(\theta_0)^2} \right] \\
& \beta_{2p} \leftarrow \left[\left(\frac{2 \cdot \pi}{\lambda} \right) \cdot d_2 \cdot \left(\frac{N_{2x}}{N_{2z}} \right) \cdot \sqrt{N_{2z}^2 - N_0^2 \cdot \sin(\theta_0)^2} \right] \\
& \beta_{2s} \leftarrow \left[\left(\frac{2 \cdot \pi}{\lambda} \right) \cdot d_2 \cdot \sqrt{N_{2y}^2 - N_0^2 \cdot \sin(\theta_0)^2} \right] \\
& l_{01s} \leftarrow \begin{pmatrix} 1 & r_{01s} \end{pmatrix}
\end{aligned}$$

$$\begin{aligned}
& \left(\begin{array}{cc} r_{01s} & 1 \\ 1 & r_{01p} \end{array} \right) \\
I_{01p} & \leftarrow \left(\begin{array}{cc} 1 & r_{01p} \\ r_{01p} & 1 \end{array} \right) \\
I_{12pp} & \leftarrow \left(\begin{array}{cc} 1 & r_{12pp} \\ r_{12pp} & 1 \end{array} \right) \\
I_{23pp} & \leftarrow \left(\begin{array}{cc} 1 & r_{23pp} \\ r_{23pp} & 1 \end{array} \right) \\
I_{12ss} & \leftarrow \left(\begin{array}{cc} 1 & r_{12ss} \\ r_{12ss} & 1 \end{array} \right) \\
I_{23ss} & \leftarrow \left(\begin{array}{cc} 1 & r_{23ss} \\ r_{23ss} & 1 \end{array} \right) \\
L_1 & \leftarrow \left(\begin{array}{cc} e^{j\beta_1} & 0 \\ 0 & e^{-j\beta_1} \end{array} \right) \\
L_{2p} & \leftarrow \left(\begin{array}{cc} e^{j\beta_{2p}} & 0 \\ 0 & e^{-j\beta_{2p}} \end{array} \right) \\
L_{2s} & \leftarrow \left(\begin{array}{cc} e^{j\beta_{2s}} & 0 \\ 0 & e^{-j\beta_{2s}} \end{array} \right) \\
S_{3p} & \leftarrow I_{01p} \cdot L_1 \cdot I_{12pp} \cdot L_{2p} \cdot I_{23pp} \\
S_{3s} & \leftarrow I_{01s} \cdot L_1 \cdot I_{12ss} \cdot L_{2s} \cdot I_{23ss} \\
R_{3p} & \leftarrow \frac{S_{3p1,0}}{S_{3p0,0}} \\
R_{3s} & \leftarrow \frac{S_{3s1,0}}{S_{3s0,0}} \\
\rho_{rp} & \leftarrow R_{3p}
\end{aligned}$$

```

 $\rho_{rs} \leftarrow K_{3s}$ 
 $\rho \leftarrow \frac{\rho_{rp}}{\rho_{rs}}$ 
 $\psi \leftarrow \text{atan}(|\rho|)$ 
 $\Delta \leftarrow \arg(\rho)$ 
 $\psi_{\text{mean}} \leftarrow \text{mean}(\rho_{\text{data}}^{(3)})$ 
 $\Delta_{\text{mean}} \leftarrow \text{mean}(\rho_{\text{data}}^{(2)})$ 
 $\text{SSE}_{\text{row},0} \leftarrow (\Delta_{\text{m}} - \Delta)^2$ 
 $\text{SSE}_{\text{row},1} \leftarrow (\psi_{\text{m}} - \psi)^2$ 
 $\text{SSE}_{\text{row},2} \leftarrow (|\rho_{\text{m}} - \rho|)^2$ 
Model_rows,0  $\leftarrow N_{2x}$ 
Model_rows,1  $\leftarrow N_{2y}$ 
Model_rows,2  $\leftarrow N_{2z}$ 
Model_rows,3  $\leftarrow d_2$ 
Model_rows,4  $\leftarrow d_1$ 
Model_rows,5  $\leftarrow \sum \text{SSE}^{(2)}$ 
Model_rows,6  $\leftarrow \sum (\text{SSE}^{(0)} + \text{SSE}^{(1)})$ 
Model_rows,7  $\leftarrow \sum \text{SSE}^{(0)}$ 
Model_rows,8  $\leftarrow \sum \text{SSE}^{(1)}$ 
Model

```

Model Fit Solutions.

Model

	0	1	2	3	4
0	"N1x"	"N1y"	"N1z"	"PET Thickness"	"Front Film Thickness"
1	1.677	1.632	1.495	$1.475 \cdot 10^4$	0
2	1.677	1.632	1.495	$1.475 \cdot 10^4$	0
3	1.677	1.632	1.495	$1.475 \cdot 10^4$	0
4	1.677	1.632	1.495	$1.475 \cdot 10^4$	0
5	1.677	1.632	1.495	$1.475 \cdot 10^4$	0
6	1.677	1.632	1.495	$1.476 \cdot 10^4$	0
7	1.677	1.632	1.495	$1.476 \cdot 10^4$	0
8	1.677	1.632	1.495	$1.476 \cdot 10^4$	0
9	1.677	1.632	1.495	$1.476 \cdot 10^4$	0
10	1.677	1.632	1.495	$1.476 \cdot 10^4$	0
11	1.677	1.632	1.495	$1.476 \cdot 10^4$	0
12	1.677	1.632	1.495	$1.476 \cdot 10^4$	0
13	1.677	1.632	1.495	$1.476 \cdot 10^4$	0
14	1.677	1.632	1.495	$1.476 \cdot 10^4$	0
15	1.677	1.632	1.495	$1.476 \cdot 10^4$	0

Model =

E.3. Goniometric Model Fitting

Since p-polarized reflection was needed for Abeles method measurements, it made sense to make a few extra measurements and then fit the goniometric model to the data. The model fitting process was the same as with ellipsometry with the notable exception of the model and the data the model was being fit to.

The model fitting method is identical to the one used for fitting the ellipsometric models, with the notable exception of the measured data. The following is an example of the goniometric model fitting programs utilized by this project.

P-Polarized Goniometry Measurements of PECVD SiO_x-Si

Measurements := 55
 counter := Measurements - 1
 data := 10nm SiO₂-Si.TX1

Rho calculation program

```

Rdata := for row ∈ 0 .. counter
    θ0 ← datarow,0
    Rp ← datarow,1
    rp ← √Rp
    Rdatarow,0 ← θ0
    Rdatarow,1 ← Rp
    Rdatarow,2 ← rp
Rdata
    
```

	0	1	2	3
0	84.08	0.506	1.014	0.332
1	83.08	0.451	0.904	0.328
2	82.08	0.402	0.807	0.318
3	81.08	0.364	0.73	0.309
4	80.08	0.329	0.66	0.294
5	79.08	0.294	0.589	0.274
6	78.08	0.267	0.535	0.257
7	77.08	0.247	0.495	0.243
8	76.08	0.226	0.453	0.225
9	75.08	0.22	0.441	0.219
10	74.08	0.203	0.408	0.201
11	73.08	0.186	0.374	0.18
12	72.08	0.178	0.358	0.167

data =

N_{1g} := 1.47

N_{3g} := 3.845 - 0.018j

d := 50

range₁ := 0.04

div₁ := 0.001

range₃ := 0.045

div₃ := 0.001

range_d := 25

div_d := 0.25

int1 := $\frac{\text{range}_1}{\text{div}_1}$

int3 := $\frac{\text{range}_3}{\text{div}_3}$

intd := $\frac{\text{range}_d}{\text{div}_d}$

	0	1	2
0	84.08	0.506	0.711
1	83.08	0.451	0.671
2	82.08	0.402	0.634
3	81.08	0.364	0.603
4	80.08	0.329	0.573
5	79.08	0.294	0.542
6	78.08	0.267	0.516
7	77.08	0.247	0.497
8	76.08	0.226	0.475

Rdata =

N₂ := 1.663

d₂ := 1.83

int1 = 40

int3 = 45

intd = 100

$\text{rows}_{\text{total}} := \text{intd} \cdot (\text{intl} + 1) \cdot (\text{int3} + 1) + \text{intl} \cdot (\text{int3} + 1) + \text{int3}$

$\text{rows}_{\text{total}} = 1.905 \times 10^5$

```

Model := | Model0,0 ← "n1"
          | Model0,1 ← "n2"
          | Model0,2 ← "Thickness"
          | Model0,3 ← "SSE (Reflection)"
          | Model0,4 ← "SSE (Fresnel)"
          | for t ∈ 0 .. intd
            |   d1 ← d + t · divd
            |   for n1 ∈ 0 .. intl
            |     | N1 ← N1g + n1 · div1
            |     | for n3 ∈ 0 .. int3
            |     |   N3 ← (N3g + n3 · div3)
            |     |   rows ← t · (intl + 1) · (int3 + 1) + n1 · (int3 + 1) + n3 + 1
            |     |   for row ∈ 0, 1 .. counter
            |     |     | θ0 ← Rdatarow,0 ·  $\left(\frac{\pi}{180}\right)$ 
            |     |     | Rpm ← Rdatarow,1
            |     |     | rpm ← Rdatarow,2
            |     |     | θ1 ←  $\arccos \left[ \sqrt{1 - \left( \frac{N_0}{N_1} \cdot \sin(\theta_0) \right)^2} \right]$ 
            |     |     | θ2 ←  $\arccos \left[ \sqrt{1 - \left( \frac{N_1}{N_2} \cdot \sin(\theta_1) \right)^2} \right]$ 
            |     |     | θ3 ←  $\arccos \left[ \sqrt{1 - \left( \frac{N_0}{N_3} \cdot \sin(\theta_0) \right)^2} \right]$ 
            |     |     | r01p ←  $\frac{N_1 \cdot \cos(\theta_0) - N_0 \cdot \cos(\theta_1)}{N_1 \cdot \cos(\theta_0) + N_0 \cdot \cos(\theta_1)}$ 
            |     |     | r12p ←  $\frac{N_2 \cdot \cos(\theta_1) - N_1 \cdot \cos(\theta_2)}{N_2 \cdot \cos(\theta_1) + N_1 \cdot \cos(\theta_2)}$ 
            |     |     | r23p ←  $\frac{N_3 \cdot \cos(\theta_2) - N_2 \cdot \cos(\theta_3)}{N_3 \cdot \cos(\theta_2) + N_2 \cdot \cos(\theta_3)}$ 
            |     |     | δ1 ←  $\left[ \left( \frac{2 \cdot \pi}{\lambda} \right) \cdot d_1 \cdot \sqrt{N_1^2 - N_0^2 \cdot \sin^2(\theta_0)} \right]$ 
            |     |     | δ2 ←  $\left[ \left( \frac{2 \cdot \pi}{\lambda} \right) \cdot d_2 \cdot \sqrt{N_2^2 - N_0^2 \cdot \sin^2(\theta_0)} \right]$ 

```

$$\begin{aligned}
& \rho_p \leftarrow \frac{\left(r_{01p} + r_{12p} \cdot e^{-2j\delta_1}\right) + \left(r_{01p} \cdot r_{12p} + e^{-2j\delta_1}\right) \cdot r_{23p} \cdot e^{-2j\delta_2}}{\left(1 + r_{01p} \cdot r_{12p} \cdot e^{-2j\delta_1}\right) + \left(r_{12p} + r_{01p} \cdot e^{-2j\delta_1}\right) \cdot r_{23p} \cdot e^{-2j\delta_2}} \\
& R_p \leftarrow \left(|\rho_p|\right)^2 \\
& r_p \leftarrow |\rho_p| \\
& SSE_{row,0} \leftarrow \left(R_{pm} - R_p\right)^2 \\
& SSE_{row,1} \leftarrow \left(r_{pm} - r_p\right)^2 \\
& Model_{rows,0} \leftarrow N_1 \\
& Model_{rows,1} \leftarrow Re(N_3) \\
& Model_{rows,2} \leftarrow d_1 \\
& Model_{rows,3} \leftarrow \sum SSE^{(0)} \\
& Model_{rows,4} \leftarrow \sum SSE^{(1)}
\end{aligned}$$

Model

Model =

	0	1	2	3
0	"n1"	"n2"	"Thickness"	"SSE (Reflection)"
1	1.47	3.845	50	0.121
2	1.47	3.846	50	0.121
3	1.47	3.847	50	0.121
4	1.47	3.848	50	0.121
5	1.47	3.849	50	0.121
6	1.47	3.85	50	0.121
7	1.47	3.851	50	0.121

RI and thickness fit data

Model

E.4. Model Fitting Statistics

Although an optimum model may be found for a given set of measurements, it did not necessarily mean the model was a good fit of the data. To determine model validity, a statistical analysis worksheet was written to compare the measured data to the model both graphically and statistically. From these worksheets, the validity of the models constructed for this project were determined. The following two examples are statistical worksheets constructed for ellipsometric and goniometric models.

Ellipsometric Model Validation Program

Parameters

$\lambda := 632.8$

Measurement := 11

data := Calculated Values (S1).da

$N_0 := 1$

Unknown := 2

$N_1 := 1.469$

n := Measurement

$N_2 := 1.663$

p := Unknown

$N_3 := 3.871 - 0.018j$

data =

	0	1	2
0	69.959	0.054+0.545i	84.316
1	73.959	0.223+0.524i	66.972
2	74.959	0.267+0.513i	62.515
3	74.959	0.266+0.512i	62.564
4	75.959	0.31+0.502i	58.243
5	79.958	0.5+0.429i	40.591
6	69.959	0.056+0.544i	84.091

$t_1 := 65.9$

$t_2 := 1.83$

Thickness Calculator

```
Film := for count ∈ 0 .. 9000
    row ← count + 1
     $\theta_0 \leftarrow \frac{\text{count}}{100} \cdot \left( \frac{\pi}{180} \right)$ 
     $\theta_1 \leftarrow \arccos \left[ \sqrt{1 - \left( \frac{N_0}{N_1} \cdot \sin(\theta_0) \right)^2} \right]$ 
     $\theta_2 \leftarrow \arccos \left[ \sqrt{1 - \left( \frac{N_0}{N_2} \cdot \sin(\theta_1) \right)^2} \right]$ 
     $\theta_3 \leftarrow \arccos \left[ \sqrt{1 - \left( \frac{N_0}{N_3} \cdot \sin(\theta_0) \right)^2} \right]$ 
     $r_{01p} \leftarrow \frac{N_1 \cdot \cos(\theta_0) - N_0 \cdot \cos(\theta_1)}{N_1 \cdot \cos(\theta_0) + N_0 \cdot \cos(\theta_1)}$ 
     $r_{01s} \leftarrow \frac{N_0 \cdot \cos(\theta_0) - N_1 \cdot \cos(\theta_1)}{N_0 \cdot \cos(\theta_0) + N_1 \cdot \cos(\theta_1)}$ 
     $r_{12p} \leftarrow \frac{N_2 \cdot \cos(\theta_1) - N_1 \cdot \cos(\theta_2)}{N_2 \cdot \cos(\theta_1) + N_1 \cdot \cos(\theta_2)}$ 
     $r_{12s} \leftarrow \frac{N_1 \cdot \cos(\theta_1) - N_2 \cdot \cos(\theta_2)}{N_1 \cdot \cos(\theta_1) + N_2 \cdot \cos(\theta_2)}$ 
     $r_{23p} \leftarrow \frac{N_3 \cdot \cos(\theta_2) - N_2 \cdot \cos(\theta_3)}{N_3 \cdot \cos(\theta_2) + N_2 \cdot \cos(\theta_3)}$ 
```

$$\begin{aligned}
r_{23s} &\leftarrow \frac{N_2 \cdot \cos(\theta_2) - N_3 \cdot \cos(\theta_3)}{N_2 \cdot \cos(\theta_2) + N_3 \cdot \cos(\theta_3)} \\
\delta_1 &\leftarrow \left[\left(\frac{2 \cdot \pi}{\lambda} \right) \cdot t_1 \cdot N_1 \cdot \sqrt{1 - \left(\frac{N_0}{N_1} \cdot \sin(\theta_0) \right)^2} \right] \\
\delta_2 &\leftarrow \left[\left(\frac{2 \cdot \pi}{\lambda} \right) \cdot t_2 \cdot N_2 \cdot \sqrt{1 - \left(\frac{N_0}{N_2} \cdot \sin(\theta_0) \right)^2} \right] \\
\rho_{rp} &\leftarrow \frac{\left(r_{01p} + r_{12p} \cdot e^{-2j \cdot \delta_1} \right) + \left(r_{01p} \cdot r_{12p} + e^{-2j \cdot \delta_1} \right) \cdot r_{23p} \cdot e^{-2j \cdot \delta_2}}{\left(1 + r_{01p} \cdot r_{12p} \cdot e^{-2j \cdot \delta_1} \right) + \left(r_{12p} + r_{01p} \cdot e^{-2j \cdot \delta_1} \right) \cdot r_{23p} \cdot e^{-2j \cdot \delta_2}} \\
\rho_{rs} &\leftarrow \frac{\left(r_{01s} + r_{12s} \cdot e^{-2j \cdot \delta_1} \right) + \left(r_{01s} \cdot r_{12s} + e^{-2j \cdot \delta_1} \right) \cdot r_{23s} \cdot e^{-2j \cdot \delta_2}}{\left(1 + r_{01s} \cdot r_{12s} \cdot e^{-2j \cdot \delta_1} \right) + \left(r_{12s} + r_{01s} \cdot e^{-2j \cdot \delta_1} \right) \cdot r_{23s} \cdot e^{-2j \cdot \delta_2}} \\
\rho_c &\leftarrow \frac{\rho_{rp}}{\rho_{rs}} \\
\psi &\leftarrow \text{atan}\left(\left|\rho_c\right|\right) \\
\Delta &\leftarrow \arg(\rho_c) \\
\text{Film}_{\text{row},0} &\leftarrow \theta_0 \cdot \left(\frac{180}{\pi} \right) \\
\text{Film}_{\text{row},1} &\leftarrow t_1 \\
\text{Film}_{\text{row},2} &\leftarrow \Delta \cdot \left(\frac{180}{\pi} \right) \\
\text{Film}_{\text{row},3} &\leftarrow \psi \cdot \left(\frac{180}{\pi} \right) \\
\text{Film}_{0,0} &\leftarrow \text{"Incident Angle"} \\
\text{Film}_{0,1} &\leftarrow \text{"Thickness"} \\
\text{Film}_{0,2} &\leftarrow \text{"Delta"} \\
\text{Film}_{0,3} &\leftarrow \text{"Psi"} \\
\text{Film} &
\end{aligned}$$

```

Stat := for row ∈ 0 .. n - 1
|
|    $\theta_0 \leftarrow \text{data}_{\text{row},0} \cdot \left( \frac{\pi}{180} \right)$ 
|    $\Delta_m \leftarrow \text{data}_{\text{row},2} \cdot \left( \frac{\pi}{180} \right)$ 
|    $\psi_m \leftarrow \text{data}_{\text{row},3} \cdot \left( \frac{\pi}{180} \right)$ 
|    $\rho_m \leftarrow \text{data}_{\text{row},1}$ 
|    $\theta_1 \leftarrow \arccos \left[ \sqrt{1 - \left( \frac{N_0}{N_1} \cdot \sin(\theta_0) \right)^2} \right]$ 
|    $\theta_2 \leftarrow \arccos \left[ \sqrt{1 - \left( \frac{N_0}{N_2} \cdot \sin(\theta_1) \right)^2} \right]$ 
|    $\theta_3 \leftarrow \arccos \left[ \sqrt{1 - \left( \frac{N_0}{N_3} \cdot \sin(\theta_0) \right)^2} \right]$ 
|    $r_{01p} \leftarrow \frac{N_1 \cdot \cos(\theta_0) - N_0 \cdot \cos(\theta_1)}{N_1 \cdot \cos(\theta_0) + N_0 \cdot \cos(\theta_1)}$ 
|    $r_{01s} \leftarrow \frac{N_0 \cdot \cos(\theta_0) - N_1 \cdot \cos(\theta_1)}{N_0 \cdot \cos(\theta_0) + N_1 \cdot \cos(\theta_1)}$ 
|    $r_{12p} \leftarrow \frac{N_2 \cdot \cos(\theta_1) - N_1 \cdot \cos(\theta_2)}{N_2 \cdot \cos(\theta_1) + N_1 \cdot \cos(\theta_2)}$ 
|    $r_{12s} \leftarrow \frac{N_1 \cdot \cos(\theta_1) - N_2 \cdot \cos(\theta_2)}{N_1 \cdot \cos(\theta_1) + N_2 \cdot \cos(\theta_2)}$ 
|    $r_{23p} \leftarrow \frac{N_3 \cdot \cos(\theta_2) - N_2 \cdot \cos(\theta_3)}{N_3 \cdot \cos(\theta_2) + N_2 \cdot \cos(\theta_3)}$ 
|    $r_{23s} \leftarrow \frac{N_2 \cdot \cos(\theta_2) - N_3 \cdot \cos(\theta_3)}{N_2 \cdot \cos(\theta_2) + N_3 \cdot \cos(\theta_3)}$ 
|    $\delta_1 \leftarrow \left[ \left( \frac{2 \cdot \pi}{\lambda} \right) \cdot t_1 \cdot N_1 \cdot \sqrt{1 - \left( \frac{N_0}{N_1} \cdot \sin(\theta_0) \right)^2} \right]$ 
|    $\delta_2 \leftarrow \left[ \left( \frac{2 \cdot \pi}{\lambda} \right) \cdot t_2 \cdot N_2 \cdot \sqrt{1 - \left( \frac{N_0}{N_2} \cdot \sin(\theta_0) \right)^2} \right]$ 
|    $\rho_{rp} \leftarrow \frac{\left( r_{01p} + r_{12p} \cdot e^{-2j \cdot \delta_1} \right) + \left( r_{01p} \cdot r_{12p} + e^{-2j \cdot \delta_1} \right) \cdot r_{23p} \cdot e^{-2j \cdot \delta_2}}{\left( 1 + r_{01p} \cdot r_{12p} \cdot e^{-2j \cdot \delta_1} \right) + \left( r_{12p} + r_{01p} \cdot e^{-2j \cdot \delta_1} \right) \cdot r_{23p} \cdot e^{-2j \cdot \delta_2}}$ 

```

$$\begin{aligned}
\rho_{rs} &\leftarrow \frac{\left(r_{01s} + r_{12s} \cdot e^{-2j \cdot \delta_1}\right) + \left(r_{01s} \cdot r_{12s} + e^{-2j \cdot \delta_1}\right) \cdot r_{23s} \cdot e^{-2j \cdot \delta_2}}{\left(1 + r_{01s} \cdot r_{12s} \cdot e^{-2j \cdot \delta_1}\right) + \left(r_{12s} + r_{01s} \cdot e^{-2j \cdot \delta_1}\right) \cdot r_{23s} \cdot e^{-2j \cdot \delta_2}} \\
\rho &\leftarrow \frac{\rho_{rp}}{\rho_{rs}} \\
\psi &\leftarrow \text{atan}(|\rho|) \\
\Delta &\leftarrow \arg(\rho) \\
\rho_{\text{mean}} &\leftarrow \text{mean}(\text{data}^{\langle 1 \rangle}) \\
\Delta_{\text{mean}} &\leftarrow \text{mean}(\text{data}^{\langle 2 \rangle}) \\
\psi_{\text{mean}} &\leftarrow \text{mean}(\text{data}^{\langle 3 \rangle}) \\
\text{SSE}_{\text{row}, 0} &\leftarrow \left(|\rho_m - \rho|\right)^2 \\
\text{SSE}_{\text{row}, 1} &\leftarrow \left(\Delta_m - \Delta\right)^2 \\
\text{SSE}_{\text{row}, 2} &\leftarrow \left(\psi_m - \psi\right)^2 \\
\text{SSR}_{\text{row}, 0} &\leftarrow \left(|\rho_m - \rho_{\text{mean}}|\right)^2 \\
\text{SSR}_{\text{row}, 1} &\leftarrow \left(\Delta_m - \Delta_{\text{mean}}\right)^2 \\
\text{SSR}_{\text{row}, 2} &\leftarrow \left(\psi_m - \psi_{\text{mean}}\right)^2 \\
\text{Stat}_{0,0} &\leftarrow \text{"EF(F)"} \\
\text{Stat}_{1,0} &\leftarrow \text{"Delta"} \\
\text{Stat}_{2,0} &\leftarrow \text{"Psi"} \\
\text{Stat}_{0,1} &\leftarrow \sum \text{SSE}^{\langle 0 \rangle} \\
\text{Stat}_{1,1} &\leftarrow \sum \text{SSE}^{\langle 1 \rangle} \\
\text{Stat}_{2,1} &\leftarrow \sum \text{SSE}^{\langle 2 \rangle} \\
\text{Stat}_{0,2} &\leftarrow \sum \text{SSR}^{\langle 0 \rangle} \\
\text{Stat}_{1,2} &\leftarrow \sum \text{SSR}^{\langle 1 \rangle} \\
\text{Stat}_{2,2} &\leftarrow \sum \text{SSR}^{\langle 2 \rangle} \\
\text{Stat}_{0,3} &\leftarrow \sqrt{\frac{\sum \text{SSE}^{\langle 0 \rangle}}{n - p}}
\end{aligned}$$

$$\begin{aligned}
 \text{Stat}_{1,3} &\leftarrow \sqrt{\frac{\sum \text{SSE}^{(1)}}{n-p}} \left(\frac{180}{\pi} \right) \\
 \text{Stat}_{2,3} &\leftarrow \sqrt{\frac{\sum \text{SSE}^{(2)}}{n-p}} \left(\frac{180}{\pi} \right) \\
 \text{Stat}_{0,4} &\leftarrow \frac{\sum \text{SSR}^{(0)}}{\sum \text{SSE}^{(0)} + \sum \text{SSR}^{(0)}} \cdot \left(\frac{n-p}{n-1} \right) \\
 \text{Stat}_{0,5} &\leftarrow n \\
 \text{Stat}_{0,6} &\leftarrow p \\
 \text{Stat} &
 \end{aligned}$$

.\20S1.dæ

Film

$$\text{Stat} = \begin{pmatrix} \text{"EF(F)"} & 2.12626 \times 10^{-4} & 0.59881 & 4.86056 \times 10^{-3} & 0.89968 & 11 & 2 \\ \text{"Delta"} & 2.97908 \times 10^{-4} & 6.51805 \times 10^4 & 0.32964 & 0 & 0 & 0 \\ \text{"Psi"} & 5.75488 \times 10^{-5} & 9.50932 \times 10^3 & 0.14488 & 0 & 0 & 0 \end{pmatrix}$$

Goniometric Model Validation

Parameters

$\lambda := 632.8$

Measurement := 55

data := .50nm SiO2-Si.TX

$N_0 := 1$

Unknown := 2

$N_1 := 1.444$

n := Measurement

$N_2 := N_1$

p := Unknown

$N_3 := 3.787 - 0.018j$

$t_1 := 71.5$

$t_2 := 0$

data =

	0	1	2
0	84.08	0.506	1.014
1	83.08	0.451	0.904
2	82.08	0.402	0.807
3	81.08	0.364	0.73
4	80.08	0.329	0.66
5	79.08	0.294	0.589

Film := for count ∈ 0..9000

*

```

row ← count + 1
 $\theta_0 \leftarrow \frac{\text{count}}{100} \cdot \left( \frac{\pi}{180} \right)$ 
 $\theta_1 \leftarrow \arccos \left[ \sqrt{1 - \left( \frac{N_0}{N_1} \cdot \sin(\theta_0) \right)^2} \right]$ 
 $\theta_2 \leftarrow \arccos \left[ \sqrt{1 - \left( \frac{N_0}{N_2} \cdot \sin(\theta_1) \right)^2} \right]$ 
 $\theta_3 \leftarrow \arccos \left[ \sqrt{1 - \left( \frac{N_0}{N_3} \cdot \sin(\theta_0) \right)^2} \right]$ 
 $r_{01p} \leftarrow \frac{N_1 \cdot \cos(\theta_0) - N_0 \cdot \cos(\theta_1)}{N_1 \cdot \cos(\theta_0) + N_0 \cdot \cos(\theta_1)}$ 
 $r_{01s} \leftarrow \frac{N_0 \cdot \cos(\theta_0) - N_1 \cdot \cos(\theta_1)}{N_0 \cdot \cos(\theta_0) + N_1 \cdot \cos(\theta_1)}$ 
 $r_{12p} \leftarrow \frac{N_2 \cdot \cos(\theta_1) - N_1 \cdot \cos(\theta_2)}{N_2 \cdot \cos(\theta_1) + N_1 \cdot \cos(\theta_2)}$ 
 $r_{12s} \leftarrow \frac{N_1 \cdot \cos(\theta_1) - N_2 \cdot \cos(\theta_2)}{N_1 \cdot \cos(\theta_1) + N_2 \cdot \cos(\theta_2)}$ 
 $r_{23p} \leftarrow \frac{N_3 \cdot \cos(\theta_2) - N_2 \cdot \cos(\theta_3)}{N_3 \cdot \cos(\theta_2) + N_2 \cdot \cos(\theta_3)}$ 
 $r_{23s} \leftarrow \frac{N_2 \cdot \cos(\theta_2) - N_3 \cdot \cos(\theta_3)}{N_2 \cdot \cos(\theta_2) + N_3 \cdot \cos(\theta_3)}$ 

```

$$\begin{aligned}
\delta_1 &\leftarrow \left[\left(\frac{2 \cdot \pi}{\lambda} \right) \cdot t_1 \cdot N_1 \cdot \sqrt{1 - \left(\frac{N_0}{N_1} \cdot \sin(\theta_0) \right)^2} \right] \\
\delta_2 &\leftarrow \left[\left(\frac{2 \cdot \pi}{\lambda} \right) \cdot t_2 \cdot N_2 \cdot \sqrt{1 - \left(\frac{N_0}{N_2} \cdot \sin(\theta_0) \right)^2} \right] \\
\rho_{rp} &\leftarrow \frac{\left(r_{01p} + r_{12p} \cdot e^{-2j \cdot \delta_1} \right) + \left(r_{01p} \cdot r_{12p} + e^{-2j \cdot \delta_1} \right) \cdot r_{23p} \cdot e^{-2j \cdot \delta_2}}{\left(1 + r_{01p} \cdot r_{12p} \cdot e^{-2j \cdot \delta_1} \right) + \left(r_{12p} + r_{01p} \cdot e^{-2j \cdot \delta_1} \right) \cdot r_{23p} \cdot e^{-2j \cdot \delta_2}} \\
\rho_{rs} &\leftarrow \frac{\left(r_{01s} + r_{12s} \cdot e^{-2j \cdot \delta_1} \right) + \left(r_{01s} \cdot r_{12s} + e^{-2j \cdot \delta_1} \right) \cdot r_{23s} \cdot e^{-2j \cdot \delta_2}}{\left(1 + r_{01s} \cdot r_{12s} \cdot e^{-2j \cdot \delta_1} \right) + \left(r_{12s} + r_{01s} \cdot e^{-2j \cdot \delta_1} \right) \cdot r_{23s} \cdot e^{-2j \cdot \delta_2}} \\
\rho_c &\leftarrow \frac{\rho_{rp}}{\rho_{rs}} \\
\psi &\leftarrow \text{atan}\left(\left|\rho_c\right|\right) \\
\Delta &\leftarrow \arg\left(\rho_c\right) \\
\text{Film}_{\text{row}, 0} &\leftarrow \theta_0 \cdot \left(\frac{180}{\pi} \right) \\
\text{Film}_{\text{row}, 1} &\leftarrow t_1 \\
\text{Film}_{\text{row}, 2} &\leftarrow \Delta \cdot \left(\frac{180}{\pi} \right) \\
\text{Film}_{\text{row}, 3} &\leftarrow \psi \cdot \left(\frac{180}{\pi} \right) \\
\text{Film}_{\text{row}, 4} &\leftarrow \left(\left|\rho_{rp}\right| \right)^2 \\
\text{Film}_{0, 0} &\leftarrow \text{"Incident Angle"} \\
\text{Film}_{0, 1} &\leftarrow \text{"Thickness"} \\
\text{Film}_{0, 2} &\leftarrow \text{"Delta"} \\
\text{Film}_{0, 3} &\leftarrow \text{"Psi"} \\
\text{Film}_{0, 4} &\leftarrow \text{"Rp"} \\
\text{Film} &
\end{aligned}$$


```

Stat := for row ∈ 0 .. n - 1
    θ0 ← datarow,0 ·  $\left(\frac{\pi}{180}\right)$ 
    Rpm ← datarow,1
    θ1 ←  $\arccos\left[\sqrt{1 - \left(\frac{N_0}{N_1} \cdot \sin(\theta_0)\right)^2}\right]$ 
    θ2 ←  $\arccos\left[\sqrt{1 - \left(\frac{N_0}{N_2} \cdot \sin(\theta_1)\right)^2}\right]$ 
    θ3 ←  $\arccos\left[\sqrt{1 - \left(\frac{N_0}{N_3} \cdot \sin(\theta_0)\right)^2}\right]$ 
    r01p ←  $\frac{N_1 \cdot \cos(\theta_0) - N_0 \cdot \cos(\theta_1)}{N_1 \cdot \cos(\theta_0) + N_0 \cdot \cos(\theta_1)}$ 
    r12p ←  $\frac{N_2 \cdot \cos(\theta_1) - N_1 \cdot \cos(\theta_2)}{N_2 \cdot \cos(\theta_1) + N_1 \cdot \cos(\theta_2)}$ 
    r23p ←  $\frac{N_3 \cdot \cos(\theta_2) - N_2 \cdot \cos(\theta_3)}{N_3 \cdot \cos(\theta_2) + N_2 \cdot \cos(\theta_3)}$ 
    δ1 ←  $\left[\left(\frac{2 \cdot \pi}{\lambda}\right) \cdot t_1 \cdot N_1 \cdot \sqrt{1 - \left(\frac{N_0}{N_1} \cdot \sin(\theta_0)\right)^2}\right]$ 
    δ2 ←  $\left[\left(\frac{2 \cdot \pi}{\lambda}\right) \cdot t_2 \cdot N_2 \cdot \sqrt{1 - \left(\frac{N_0}{N_2} \cdot \sin(\theta_0)\right)^2}\right]$ 
    ρrp ←  $\frac{\left(r_{01p} + r_{12p} \cdot e^{-2j \cdot \delta_1}\right) + \left(r_{01p} \cdot r_{12p} + e^{-2j \cdot \delta_1}\right) \cdot r_{23p} \cdot e^{-2j \cdot \delta_2}}{\left(1 + r_{01p} \cdot r_{12p} \cdot e^{-2j \cdot \delta_1}\right) + \left(r_{12p} + r_{01p} \cdot e^{-2j \cdot \delta_1}\right) \cdot r_{23p} \cdot e^{-2j \cdot \delta_2}}$ 
    Rpc ←  $\left(|\rho_{rp}|\right)^2$ 
    Rmean ← mean(data(1))
    SSErow,0 ←  $\left(|R_{pm} - R_{pc}|\right)^2$ 
    SSRrow,0 ←  $\left(|R_{pm} - R_{mean}|\right)^2$ 
Stat0,0 ← "SSE(R)"
Stat0,1 ←  $\sum SSE^{(0)}$ 
Stat0,2 ←  $\sum SSR^{(0)}$ 
Stat0,3 ←  $\sqrt{\frac{\sum SSE^{(0)}}{n - n}}$ 

```

$$\begin{aligned}
& \sum SSR^{(0)} \\
Stat_{0,4} & \leftarrow \frac{\sum SSR^{(0)}}{\sum SSE^{(0)} + \sum SSR^{(0)}} \cdot \left(\frac{n-p}{n-1} \right) \\
Stat_{0,5} & \leftarrow n \\
Stat_{0,6} & \leftarrow p \\
Stat
\end{aligned}$$

$$\begin{aligned}
residual := & \text{for } row \in 0 \dots n-1 \\
& \theta_0 \leftarrow data_{row,0} \cdot \left(\frac{\pi}{180} \right) \\
& R_{pm} \leftarrow data_{row,1} \\
& \theta_1 \leftarrow \arccos \left[\sqrt{1 - \left(\frac{N_0}{N_1} \cdot \sin(\theta_0) \right)^2} \right] \\
& \theta_2 \leftarrow \arccos \left[\sqrt{1 - \left(\frac{N_0}{N_2} \cdot \sin(\theta_1) \right)^2} \right] \\
& \theta_3 \leftarrow \arccos \left[\sqrt{1 - \left(\frac{N_0}{N_3} \cdot \sin(\theta_0) \right)^2} \right] \\
& r_{01p} \leftarrow \frac{N_1 \cdot \cos(\theta_0) - N_0 \cdot \cos(\theta_1)}{N_1 \cdot \cos(\theta_0) + N_0 \cdot \cos(\theta_1)} \\
& r_{12p} \leftarrow \frac{N_2 \cdot \cos(\theta_1) - N_1 \cdot \cos(\theta_2)}{N_2 \cdot \cos(\theta_1) + N_1 \cdot \cos(\theta_2)} \\
& r_{23p} \leftarrow \frac{N_3 \cdot \cos(\theta_2) - N_2 \cdot \cos(\theta_3)}{N_3 \cdot \cos(\theta_2) + N_2 \cdot \cos(\theta_3)} \\
& \delta_1 \leftarrow \left[\left(\frac{2 \cdot \pi}{\lambda} \right) \cdot t_1 \cdot N_1 \cdot \sqrt{1 - \left(\frac{N_0}{N_1} \cdot \sin(\theta_0) \right)^2} \right] \\
& \delta_2 \leftarrow \left[\left(\frac{2 \cdot \pi}{\lambda} \right) \cdot t_2 \cdot N_2 \cdot \sqrt{1 - \left(\frac{N_0}{N_2} \cdot \sin(\theta_0) \right)^2} \right] \\
& \rho_{rp} \leftarrow \frac{\left(r_{01p} + r_{12p} \cdot e^{-2j \cdot \delta_1} \right) + \left(r_{01p} \cdot r_{12p} + e^{-2j \cdot \delta_1} \right) \cdot r_{23p} \cdot e^{-2j \cdot \delta_2}}{\left(1 + r_{01p} \cdot r_{12p} \cdot e^{-2j \cdot \delta_1} \right) + \left(r_{12p} + r_{01p} \cdot e^{-2j \cdot \delta_1} \right) \cdot r_{23p} \cdot e^{-2j \cdot \delta_2}} \\
& R_{pc} \leftarrow \left(|\rho_{rp}| \right)^2 \\
& residual_{row+1,0} \leftarrow \theta_0 \cdot \left(\frac{180}{\pi} \right) \\
& residual_{row+1,1} \leftarrow R_{pm} - R_{pc}
\end{aligned}$$

```

residual_0,0 ← "Incidence Angle"
residual_0,1 ← "R residual"
residual

```

Stat = ("SSE(R)" 2.67044×10^{-4} 0.34878 2.24467×10^{-3} 0.98073 55 2)

Film =

	0	1	2	3	4
0	"Incident Angle"	"Thickness"	"Delta"	"Psi"	"Rp"
1	0	71.5	180	45	0.17
2	0.01	71.5	180	45	0.17
3	0.02	71.5	180	45	0.17
4	0.03	71.5	180	45	0.17
5	0.04	71.5	180	45	0.17
6	0.05	71.5	180	45	0.17
7	0.06	71.5	180	45	0.17

residual =

	0	1
0	"Incidence Angle"	"R residual"
1	84.08	$4.653 \cdot 10^{-3}$
2	83.08	$2.051 \cdot 10^{-3}$
3	82.08	$-5.818 \cdot 10^{-4}$
4	81.08	$1.058 \cdot 10^{-3}$
5	80.08	$4.733 \cdot 10^{-4}$
6	79.08	$-4.662 \cdot 10^{-3}$
7	78.08	$-5.678 \cdot 10^{-3}$
8	77.08	$-3.185 \cdot 10^{-3}$
9	76.08	$-5.124 \cdot 10^{-3}$
10	75.08	$5.475 \cdot 10^{-3}$
11	74.08	$2.702 \cdot 10^{-3}$
12	73.08	$-2.185 \cdot 10^{-3}$
13	72.08	$-2.588 \cdot 10^{-4}$
14	71.08	$1.045 \cdot 10^{-3}$
15	70.08	$4.39 \cdot 10^{-4}$

.\Stat fit.da

Film

.\Fit residuals.cs

residual