Anti-Reflective Films: Spectroscopy and Ellipsometry of Porous Films

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Abstract:

The relationship between the index of refraction and the porosity of a material is that the index decreases with respect to the porosity. This property can be used to change the index of refraction of films which allows control of the reflection of the material. This is important because being able to control the reflection and thereby the transmission allows you to create anti-reflective or reflective films. There are two studies of porous films done in this thesis. First is the study of the relationship between the index of refraction and porosity of titanium oxide (titania) films using an ellipsometer. Second is examining aluminum phosphate (ALPO) films and determining the thickness and ALPO fraction of the film.

The titania films I created did not show the index of refraction to change with the porosity. The ALPO films were determined to be good anti-reflective films with percent reflectance less than ten percent over the visible spectrum. Each of the films showed reflectance of 4 percent or less at a constant wavelength of 550 nm. The three ALPO films studied differed by their thickness and their configuration of the films. A thick single sided film, a thin single sided film, and a double-sided thin film were the three configurations. The reflectance and thickness are determined using Scout, a modeling software made by Wolfgang Theiss, and used to fit the data using the Bruggeman model of effective medium approximation. The ALPO fraction is the percentage of ALPO to air bubbles in the films, while the thickness is the width of the film on a glass substrate. The thickness of the films is determined to be around 320 nm for the thick film, and around 120 nm for the thin films with fraction percentages around 70% as measured on the fiber optic spectrometer.

Table of Contents:

Table of Figures:

1 Introduction:

1.1 Motivation and Objectives:

Antireflective coatings have a major impact in all aspects of everyday life. These coatings can reduce glare on devices, allowing more light to enter solar cells, as well as many other applications in industry. Finding ways of creating better antireflective coatings allows better applications to be provided.

The research that has gone into antireflective films is extensive, and there are many ways of creating antireflective films including porous/patterned dielectrics or by introducing a gradient to the refractive index. For making porous films you add additional particles to reduce the index of refraction, and in this case the additional particles are air bubbles. In the gradient case you gradually reduce the index of the film to the index of air[1]. Another common way of making anti-reflective films is by layering dielectric films that introduce phase shifts to the light. This is most commonly used in sunglasses or regular glasses. Using nanoparticles one research paper showed that by loading the film created with varying concentrations of metal oxide nanoparticles the refractive index of the film was tuned from 1.46 to 1.54 using silica nanoparticle loadings, and from 1.54 to 1.95 using ceria nanoparticle loadings[2]. By combining the high and low refractive films in layers created an antireflective coating that was comparable to those produced using sol-gel and vacuum based techniques[2]. The sol-gel process can be used to create films with indices from 1.46 (SiO_2) to 2.4 (TiO_2) [3][4]. Other research into antireflective films has been done using thin films consisting of an array of SiO_2 nanorods. An SiO_2 film made with a nanorod layer was shown to have a refractive index of 1.08[5].

In this research I first determine the thickness and fraction of material of $AlPO_4$ (Aluminum Phosphate, ALPO) films, and second study the index of refraction for porous TiO_2 (titania) films by varying the surfactant[6]. The goal for the ALPO films was to make a film that is 100% transparent at 550 nm, which is the wavelength to which our eyes are most sensitive. The films were created in the lab of Dr. Keszler in the Oregon State Chemistry Department and were measured on the spectrometers in the OSU

Physics Department. The titania films were created by me in the lab of Dr. Keszler under supervision of Cory Perkins. These films were used to study how the index of refraction changes as you vary the porosity of the films. It is known that porosity decreases the index of refraction, and this research endeavors to confirm or disprove [7].

1.2 Background Optics:

When a beam of light passes through a transparent medium some of the light is reflected and some is transmitted. The power of the reflected and transmitted light is given by Fresnel's equations. Below is the solved equation for reflection:

$$R = \frac{I_r A \cos(\Theta_r)}{I_i A \cos(\Theta_i)} = \frac{I_r}{I_i} \quad . \qquad (1)$$

In *Equation 1* the reflectance is the reflected power over the incident power where A is area, $I_{r,I}$ is the intensity of the reflected or incident beams respectively, and theta is the angle of incidence, or the angle from the surface normal. The reflectance is the physical quantity measured on the spectrometers. The reflectance for a glass slide depends on the two interfaces with each interface adding four percent reflectance. Therefore, a glass slide has eight percent reflectance. By adding a dielectric film you induce a phase shift to one of the waves, and this phase shift can cause waves to cancel out and lower reflection.

1.3 Scout and Bruggeman Model:

Scout is an optical modeling program designed by Wolfgang Theiss. The greatest asset of Scout is that you have complete control over what you fit and how. For this experiment the basic template used by Ryan Lance was altered to fit the parameters used[10]. Instead of measuring the band gap, used in Lance's configuration, the configuration used was designed to fit the Bruggeman Model. Scout can be thought of as analogous to using simulations to determine the reflectance of porous materials[11]. This is because in Scout you enter in the data for the substances, 'create' your film or substrate, and then it uses data to determine what the reflectance should be for your model.

Reflectance data from ALPO films was fit using the Bruggeman model built into Scout. The Bruggeman model gives you the index of refraction for the material considering the porosity. It does this with *Equation 3* below:

$$(1-f)\frac{\varepsilon_M-\varepsilon_{eff}}{\varepsilon_M+2\varepsilon_{eff}}+f\frac{\varepsilon-\varepsilon_{eff}}{\varepsilon+2\varepsilon_{eff}}=0 \quad , \qquad (3)$$

The porous film is two separate materials; one labeled as the matrix material, and the other is the embedded particle. The matrix material is the material of which the film is created. The embedded particle are things like beads, air bubbles, or nanotubes. This is analogous to a sponge where you have the main sponge material with air embedded as pockets. In *Equation 3*, ε_m is the index of refraction for the matrix material, ε is the index of refraction for the embedded particle, and f is the volume fraction. In this study the Bruggeman model was used to determine the fraction of ALPO and the thickness of the film. This is done by using the index of refraction of ALPO of 1.54 and air of one [6].

2 Methods:

2.1 Titania:

2.11 Preparation of Films:

Films were prepared under supervision of Cory Perkins and meant to have varying degrees of porosity. The first step was making the solution of TiO_2 (titania). This was done via the chemical reaction of titania chloride and hydrogen peroxide. Note that below is not the complete chemical equation, only the part that applies to titania:

$$TiCl_{3(l)} + H_2O_{2(l)} \rightarrow TiO_{2(l)} \quad . \qquad (4)$$

The solutions were made to have a concentration of 1 mol/L, so by mixing 2.5 mL of each you would get a concentration of approximately 1 mol/L. The next step was adding the surfactant, Pluronic F-127, to control the porosity. The surfactant has both hydrophilic and hydrophobic components which, in aqueous solution create very small bubbles in the solution. The four samples made were 0%, 2.5%, 5%, and 10% surfactant by mass. After adding the surfactant to the four samples the films were ready to be spin coated. The silicon wafers that acted as the base for the films were cut into one-inch squares and placed in a sonicator for cleaning. The sonicator uses a slightly basic solution and sonic waves to sterilize the wafer to allow a clean film to be formed. After cleaning a wafer was placed on the spin coater, and a few drops of one of the samples is placed on it. The films were then spun at 3000 RPM for 30 seconds.

Once spin coated the films were separated by various annealing parameters. One film was only as deposited, one was placed only in the UV oven for 30 minutes, the rest were placed in the UV oven followed by an oven set at a specific temperature for one hour. The temperatures were 100ºC, 125ºC, 150ºC, 175ºC, 200ºC, 300ºC, 400ºC, 500ºC, and 600ºC for different films. Once the films were annealed, they were taken to the ellipsometer to have the thickness and index of refraction measured.

2.12 Ellipsometer:

The ellipsometer measures the index of refraction and the thickness of the films. The ellipsometer produces a beam of light that enters the material. This beam reflects off the surface of the material and reflects from the substrate the material is deposited on. The beams will constructively and destructively interfere depending on the relative phase of each light component and the light's wavelength. The beam passing through the material is delayed by the materials index of refraction and the thickness, thus is what the ellipsometer measures. In *Figure 1* you see the setup of the ellipsometer. The lamp is what produces the beam at three different angles. The detector matches the position of the lamp so that the angle between the lamp and the sample is equal to the angle between the detector and sample. The index of refraction is calculated based on the amplitude of data oscillations as well as the relative phases. The Oregon State Chemistry Department has a program called "Complete Ease" that connects with the ellipsometer and fits the data received with a model called "Cauchy on Tox @ 550 nm". This model uses Cauchy's equation which relates the index of refraction with the wavelength of light.

$$n(\lambda) = B + \frac{C}{\lambda^2} + \frac{D}{\lambda^4} + \cdots \quad , \qquad (5)$$

Equation 5 measures the index of refraction with constants related to the material and the wavelength with B, C, D, etc. being the constants that are based on the material. The model uses the Cauchy equation to calculate B, C, and D to determine the index of refraction at a constant wavelength of 550 nm. The wavelength used is arbitrary, but since 550 nm is in the visible light spectrum it is commonly used. The model changes the coefficients as well as the thickness to fit the experiment results. It uses mean squared error (MSE) between the model and experiment to determine if the fit is acceptable or not, and it changes the variables to minimize the MSE.

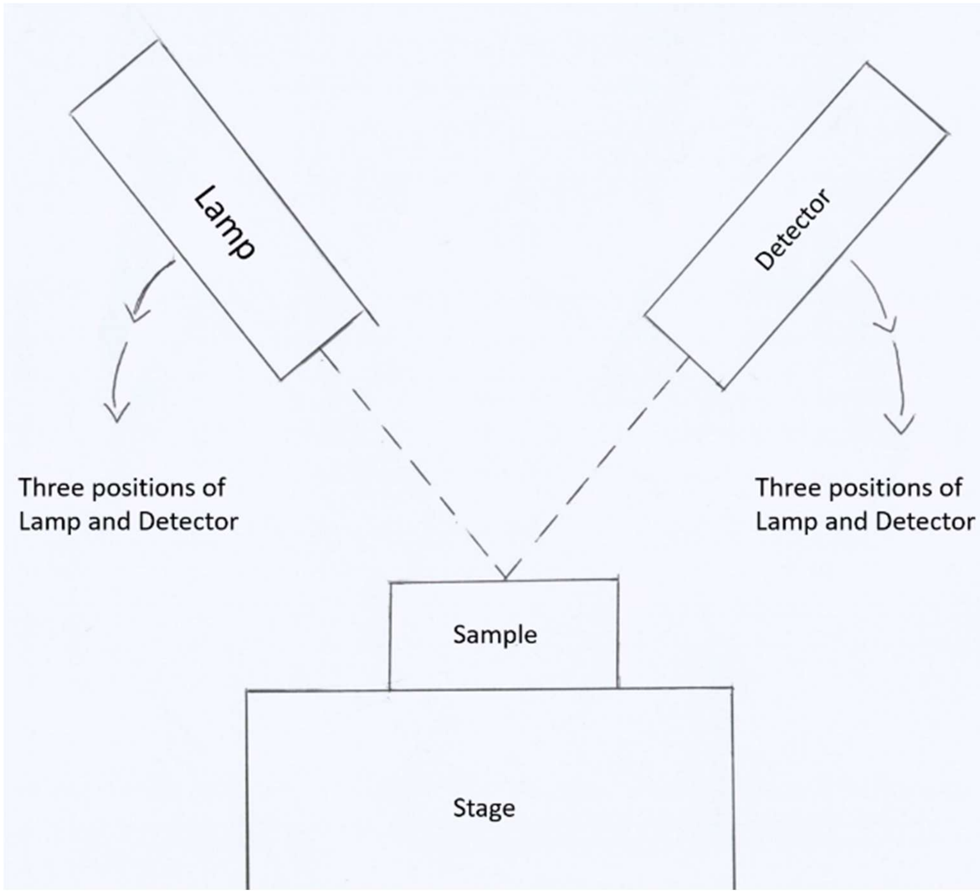

Figure 1: Schematic of ellipsometer. A laser is shined on your sample, and there are two reflections that are detected. One from the film itself, the second from the silicon disc the film is on. The ellipsometer has a program that detects the polarized light and the phase shift form the film and the silicon to determine the index of refraction as well as the thickness of the film.

2.2 ALPO:

The purpose of this experiment was to design a chemical film that had zero percent reflection at 550 nm. The films were made in Dr. Keszler's lab and provided to us to measure the reflection. The reflection was measured with two machines, the fiber optic spectrometer and the grating spectrometer. The data from these spectrometers was analyzed with an optics program called Scout. Spectroscopy has limits in that the precision of measurement depends on the concentration of the analyte[12]. Using two spectrometers to measure the thickness and ALPO fraction is a better method than only using one measurement[13]. This method is also similar to others used to determine the thickness and optical properties of thin films by looking at the reflection of thin films[14].

2.21 Fiber Optic Spectrometer:

The fiber optic spectrometer measures the reflection and transmission of a set of wavelengths. For this experiment the wavelength was the visible spectrum and a little past. To get more data and interesting graphs the wavelengths measured were roughly from 400 to 1000 nm. This is using the halogen lamp instead of the deuterium lamp. The spectrometer outputs a beam of white light from a lamp. The beam of light goes through a bifurcated fiber optic cable. The fiber optic directs the light through a lens and the sample is placed at the focal point of the lens. The beam of light then reflects and transmits through the sample, with the transmitted and reflected beams going through different bifurcated fiber optic cable. The spectrometer can only measure transmission or reflection at a single instance. To handle this the setup has cardboard blockers set on solenoids. These solenoids are connected to a toggle that allows you to block either the transmitted or reflected beam. While measuring the transmission the toggle will be switched to R where the solenoid has the cardboard blocking the fiber optic that collected the reflection. When you measure the reflection, you switch from R to T which blocks the transmitted light. When the beam is directed through the lens at the sample, the reflected beam goes back through the same lens. This then enters the second fiber optic cable and enters through the blocker. The transmitted and reflected beams are then connected to a second bifurcated fiber optic cable that then enters the spectrometer. The spectrometer records the data and sends it to a LabVIEW program which records and plots the data. This is shown in *Figure 2* where the lines are the fiber optic cables.

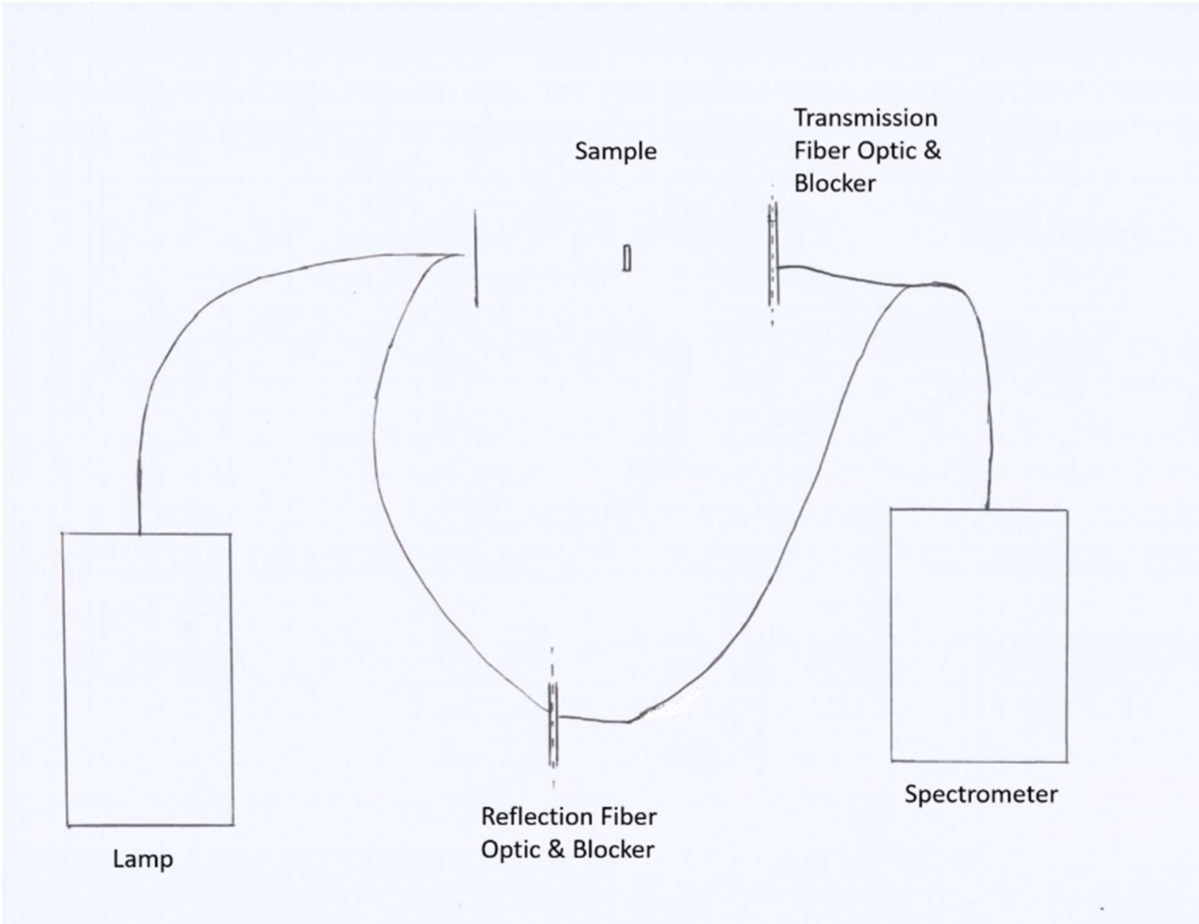

Figure 2: Schematic of fiber optic spectrometer: The lines are bifurcated fiber optic cables. The light comes from the lamp and hits the sample, some is transmitted, and some is reflected. The transmitted light goes through fiber optic cable to the spectrometer, where the reflected light goes back into the second part of the fiber optic cable. There are two settings that block either the transmitted or reflected light with a cardboard blocker, this allows the spectrometer to measure transmission and reflection separately.

2.22 Grating Spectrometer:

The grating spectrometer outputs singular wavelengths, instead of outputting white light. It does this by using a grating to separate the light into single wavelengths. The grating is set in a pair of monochromators to filter out all but one wavelength. This allows the spectrometer to determine the reflection and transmission at every wavelength in a provided set of wavelengths. For this experiment the set of wavelengths were from 250 nm to 1000 nm. The beam then enters a box designed to eliminate outside light. This beam goes through lenses and shutters to focus the beam down to a point so that when the beam reaches the detector the size of the beam is roughly the size or smaller than the detector window. This is done to ensure all the light goes through the sample and is then detected. The procedure for the grating spectrometer is as follows. You turn on the lamp, ozone eater, detector and the computer. The ozone eater collects and neutralizes the ozone to not harm the user. Allow the lamp to warm up for an hour because temperature fluctuations can warp the data creating anomalies. Allowing an hour for the lamp to warm up steadies these fluctuations. The next step is to measure the lamp and dark spectra. The lamp spectrum is the spectrum of light emitted by the lamp as the lamp goes through the set of wavelengths. The dark spectrum is the spectrum of "noise" or excess light in the box as measured by blocking the detector. The lamp and dark spectra are used to eliminate any noise or excess light that enters the box via *Equations 6* and *Equation 7*. After this you are ready to measure the transmission and reflection of your sample. You place your sample in the slot indicated by D in *Figure 3* and having the detector in position one. After measuring the transmission, move the detector to position two and ensure that the reflection of the sample does hit the detector window by rotating the sample. After running the program to measure the reflection you then save the data as an excel file and the LabVIEW program calculates the transmission and reflection of the sample. This is done with the equations for T and R:

$$T = \frac{I_T - I_{dark}}{I_{lamp} - I_{dark}} \quad , \tag{6}$$

$$R = \frac{I_R - I_{dark}}{I_{lamp} - I_{dark}} \quad . \tag{7}$$

Equations 6 and *Equation 7* show that to get the transmission or reflection you take the intensity of the transmission or reflection spectrum, subtract it from the intensity of the dark spectrum. This eliminates any noise that could be found in the sample. The denominator is the intensity of the lamp subtracted by the intensity of the dark. This gives a baseline that allows you to get solely the transmission or reflection.

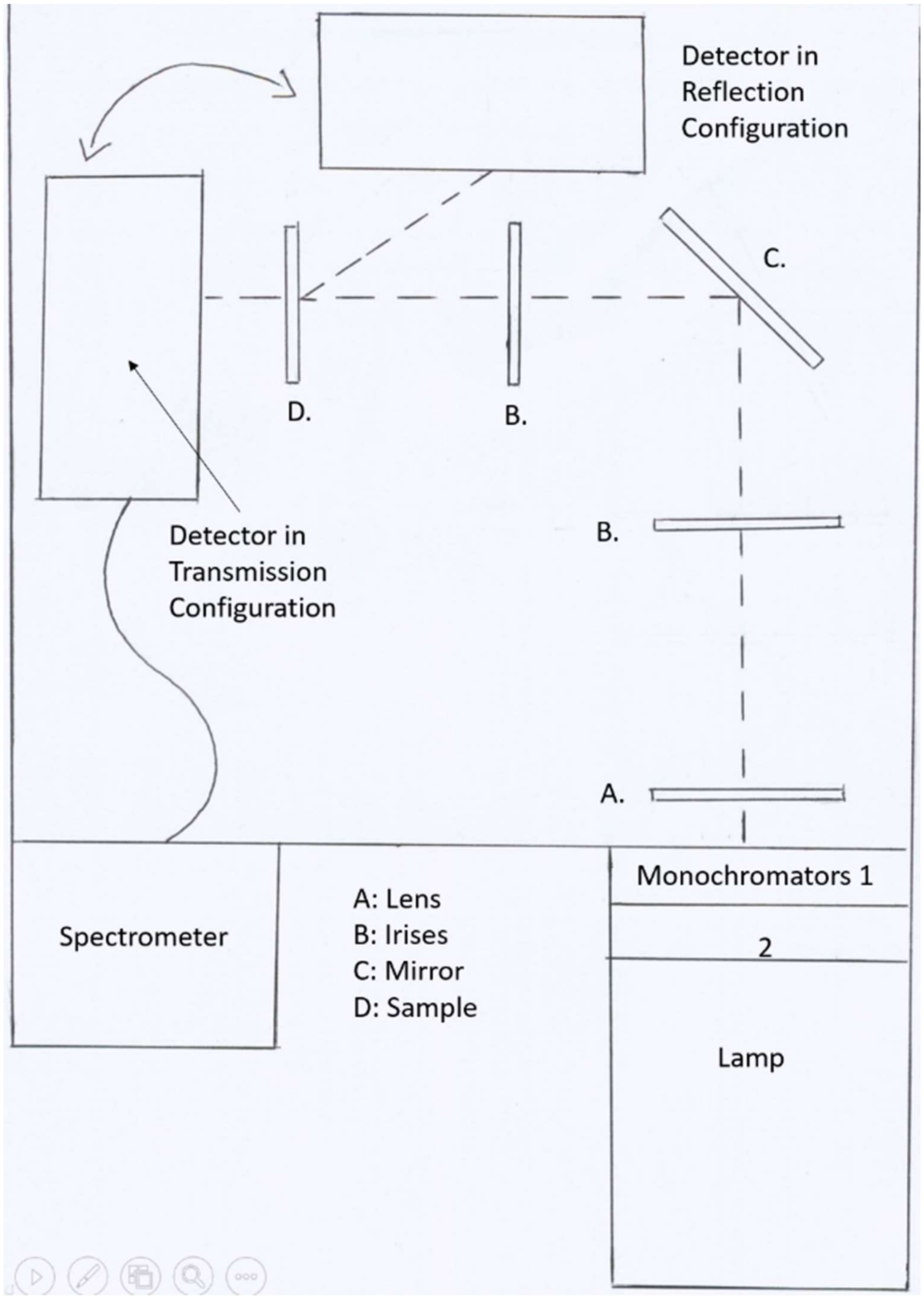

Figure 3: Grating spectrometer schematic. Everything but the lamp and monochromators are inside a box to block excess light to reduce noise. Lamp puts out white light which is filtered into a specific wavelength by the monochromators. The beam is directed through the sample and into the detector in either the transmission or reflection configuration.

3 Results and Discussion:

3.1 Titania:

The results from the titania films were not what was expected. The goal was to conclude that increasing porosity in titania films decreases the index of refraction. While individual points sometimes show this, the data overall showed slight increases in the index. Below is the data for 16 films with various degrees of porosity (as indicated by percentage of surfactant added) and annealed at various temperatures.

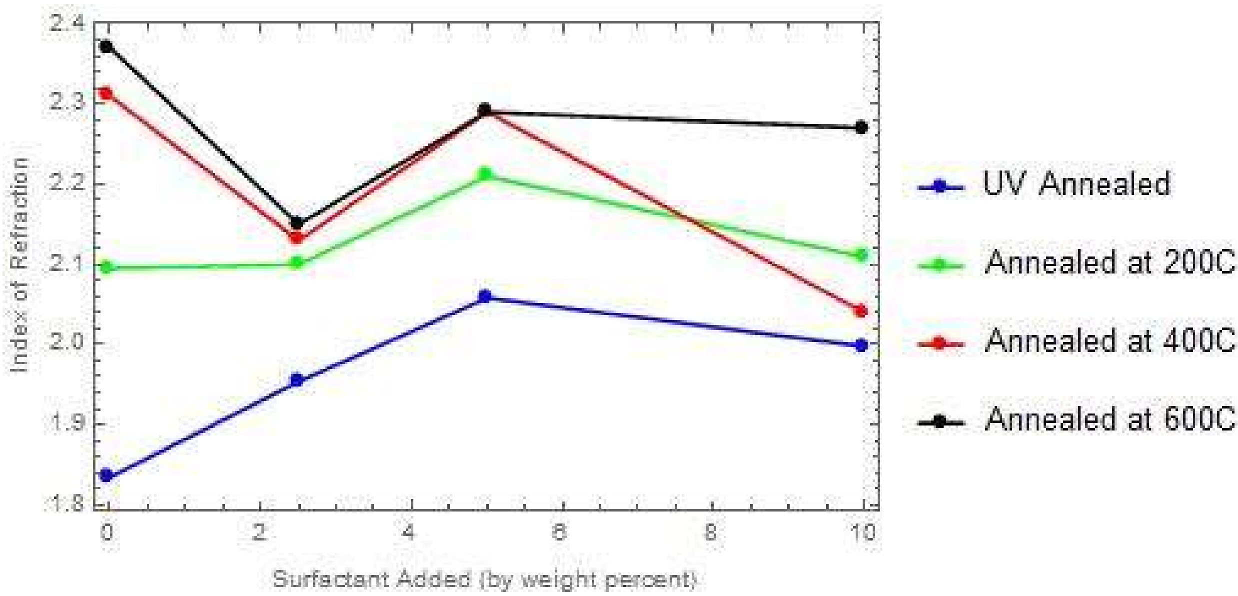

Figure 4: Index of refraction vs surfactant added annealed at various temperatures and the measured index of refraction for various percentages of surfactant added to solution.

Surfactant was added to create the porosity in the film, and thus the percent surfactant is proportional to porosity. We know that porosity should reduce the index of reactance of the film. However, as shown in *Figure 4* the results gathered are more inconclusive rather than showing the decrease in refraction index.

3.2 ALPO:

The results for the ALPO films are separated into two categories based on the spectrometer. As stated before, the fiber optic spectrometer doesn't give as accurate results since it deals with more noise than the grating spectrometer. The results for the three films fitted can be seen below. There were three films that were analyzed. Two single sided films, one with a known thickness of 320 nm and the other with unknown thickness. The third film was coated on both sides of the glass. These films are referred to hereafter as 320 nm thick film, AR film, and double-sided film respectively.

The 320 nm film shows promise for a small area, but as you can see it deviates from the fit after a wavelength of around 500 nm. There is some deviation from the fit and the experiment after 500 nm. The 320 nm film gave a measured thickness of 326.4 nm and a ALPO fraction of 55.6%. The MSE for this fit was 1.03×10^{-4}.

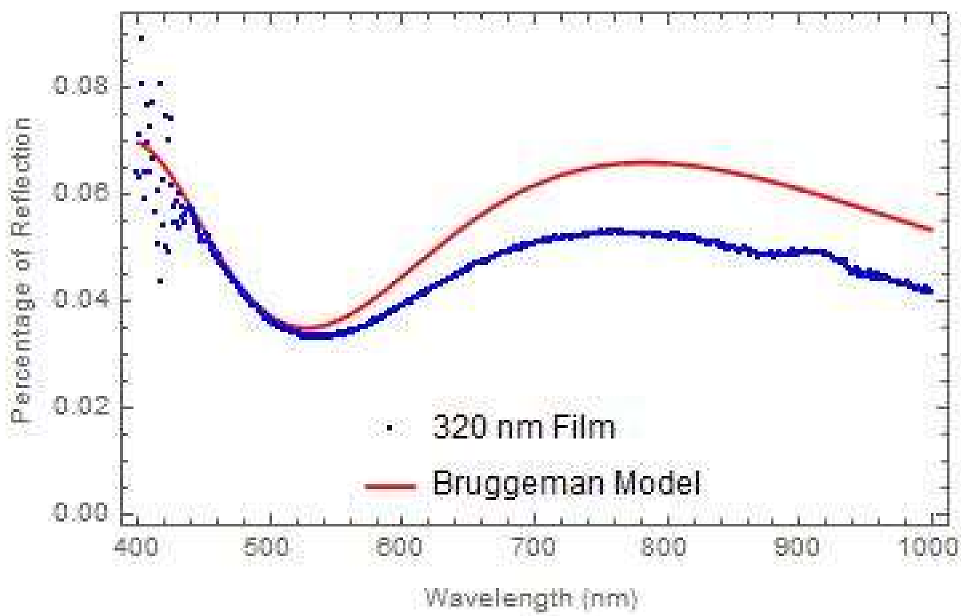

Figure 5: Reflection Fit for 320 nm Film: Intensity percentage vs wavelength for 320 nm thick ALPO Film on fiber optic spectrometer. This fit has an MSE of 1.03×10^{-4} with a thickness of 326.4 nm and ALPO fraction of 55.6 percent.

Meanwhile the double-sided film matches closely to the theory, while the AR film was offset. The double-sided film gave a thickness of 103 nm and 160 nm with ALPO fractions of 60.8% and 78.8% for the front and back films respectively.

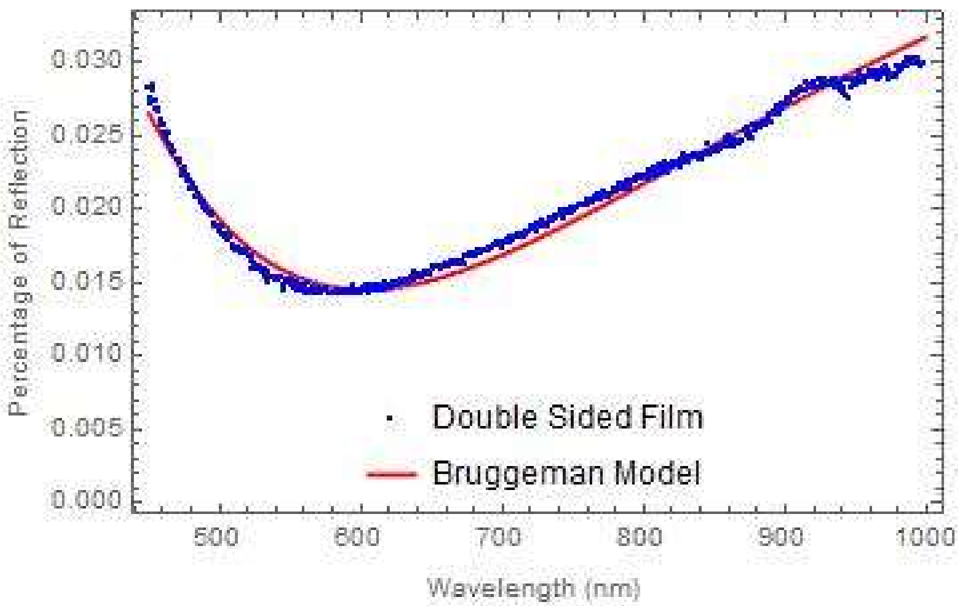

Figure 6: Reflection for Doubled Sided Film: Intensity percentage vs wavelength for doubled sided ALPO film on fiber optic spectrometer. This fit has an MSE of 4.84×10^{-7} with a thickness of 103 nm and 160 nm with ALPO fractions of 60.8% and 78.8% for the front and back films respectively.

The AR offset was reproducible as the spectrometer fits were always lower than the theory. The reason for this is unknown but could be due to absorption. However, as you'll see in Figure 9 the offset was present in measurements via both spectrometers. The AR film gave a thickness of 130.69 nm with an ALPO fraction of 55.75%. The MSE for this fit was 2.41×10^{-4}.

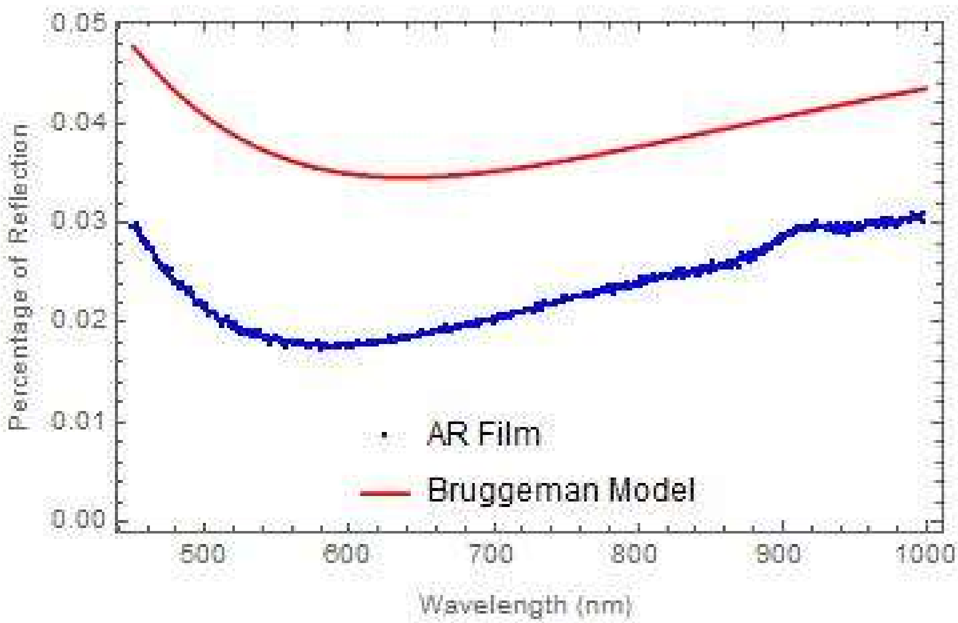

Figure 7: Reflection fit for AR Film: Intensity percentage vs wavelength for AR ALPO film on fiber optic spectrometer. This film has an MSE of 2.41×10^{-4} with a thickness of 130.69nm and 55.75% ALPO fraction.

From the above plots you can see that the fiber optic spectrometer gives decent measurements, but it does not match the fits very well. It also contains artifacts around 900 nm (artifacts are bumps or peaks in the graph that are known to not be there naturally and are caused by equipment or excess light). The MSEs show that the fits are approved, since they are low. Overall the percentage of reflection for all three films as measured on the fiber optic spectrometer are below four percent, which is lower than the percentage of reflection through a glass slide.

The fits for the grating spectrometer have lower MSE than the fits for the fiber optic spectrometer, which shows that the grating spectrometer is indeed the one to use for precise measurements. The 320 nm thick film is close to the theory; however, the AR film was offset. The double-sided film had the best fit as well as the best anti-reflection.

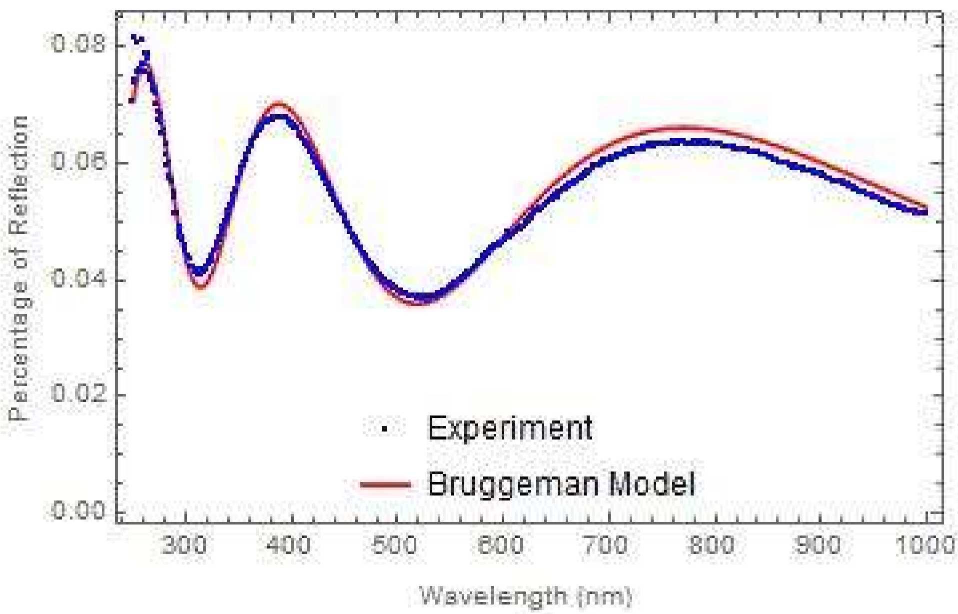

Figure 8: Reflection fit for 320 nm thick film: Intensity percentage vs wavelength for 320 nm thick ALPO film on grating spectrometer. This fit has an MSE of 8.11x10^{-5} with a thickness of 324 nm and an ALPO fraction of 75.83%.

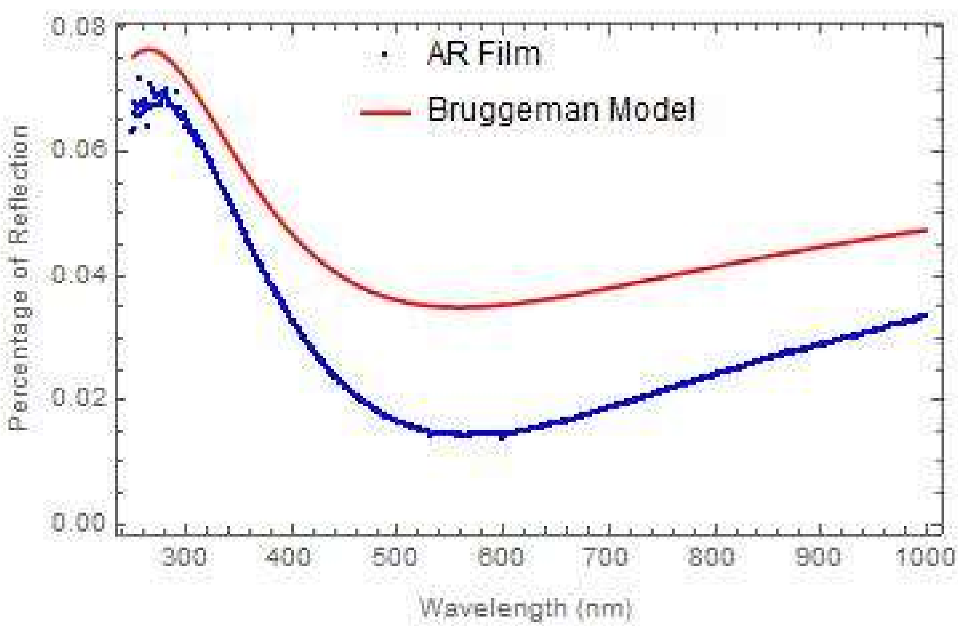

Figure 9: Reflection fit for AR Film: Intensity percentage vs wavelength for AR ALPO film on grating spectrometer. This fit has an MSE of 5.89x10^{-4} with a thickness of 113.64 nm and an ALPO fraction of 76.2%.

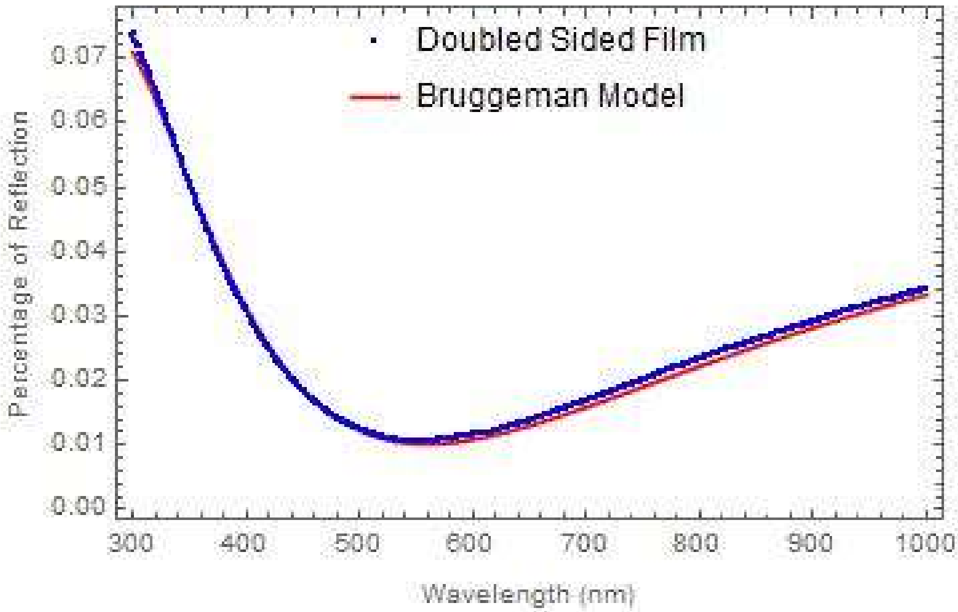

Figure 10: Reflection fit for Double Sided Film: Intensity percentage vs wavelength for double-sided ALPO film on grating spectrometer. This fit has an MSE of 5.54×10^{-6} with thickness 123.5 nm and 123.17 nm, and ALPO fractions of 73.2% and 72.3% for each film respectively.

As shown in the graphs above the reflectance in these films are low. The single sided film has a reflectance of around 4% at 550 nm. The AR film has a reflectance around 1.8% at 550 nm. The double-sided film has a reflectance of around 1% at 550 nm. This implies that the films are good antireflective (AR) coatings at that wavelength. Looking at the graphs in the visible spectrum you see that the wavelength is less than 8%. This shows that the ALPO films reduced the reflectance of plane glass.

The MSE for the grating spectrometer fits are either below or close to the MSE for the fiber optic spectrometer fits. The next step in analysis of the spectrometers is to look at the thickness and ALPO fraction for each film. The 320 nm thick film has a known thickness and was given. For the 320 nm thick film the grating spectrometer fit gave a thickness of 324 nm and the fiber optic spectrometer fit gave 326.3 nm. These are close to the known thickness of 320 nm, and the fraction percentages are 75.8% and 55.6%. These are very different by an order of 20% and is possibly due to the fiber optic spectrometer not matching the Bruggeman model after 500 nm. For the AR films the thickness as determined from the grating spectrometer is 113.6 nm and 130.7 nm for the fiber optic spectrometer. The ALPO fractions are 76.2% and 55.75% for the grating and fiber optic fits respectively. The grating spectrometer gave thicknesses for the two films on the double-sided sample to be 123.5 nm and 123.17 nm with ALPO fractions of 73.2% and 72.3% respectively. This is different to the fiber optic spectrometer fit which gave thicknesses for the two films to be 103 nm and 160 nm, with ALPO fractions of 60.8% and 78.8% respectively. The difference here is likely due to the nature of the spectrometers in question. Looking at the fits the grating spectrometer is always close to the model, with very little deviation after 600 nm. The fiber optic spectrometer crosses back and forth across the model, with an artifact around 900 nm. The main difference is that the grating spectrometer follows more closely to the model, and the fiber optic does not, which would explain the differences in values between the two.

As the films all reduced the reflectance of the glass slide they were good antireflective films. The double-sided sample reduced the reflectance to around one percent at 550 nm which is much lower than the eight percent in glass. The thick film reduced the reflectance to around four percent at 550 nm which is half the reflectance of glass. The AR film reduced the reflectance around 1.8% which is 6.2% less than glass. However, they did not meet the design goal of 0 reflectance at 550 nm. The two spectrometers gave similar fits for the three films, but the grating spectrometer showed better fits due to no artifacts and less noise.

4 Conclusion:

Porosity is one common way to create anti-reflective films, and this research has shown that porous anti-reflective films can be created to have very low reflectance. The two goals of this experiment were to show the relationship between porosity and the index of refraction using titania films, and to determine the thickness, ALPO fraction, and determine the viability of being anti-reflective for ALPO films.

The titania films were inconclusive in showing that the index of refraction decreases with the porosity. This is shown by the data in *Figure 4* that the index of refraction does not change very much for different surfactant percentages. Since the surfactant is the cause for the porosity, increasing the percentage of surfactant increases the porosity. The index of refraction decreases, but also increases over the four different surfactant percentages. The relationship should decrease linearly for the index of refraction as the porosity increases. This relationship was not proven with the designed experiment.

The ALPO films were shown to be good anti-reflective films due to having a reflectance of less than one percent in the visible spectrum. However, they did not meet the design goal of having zero reflectance at a wavelength of 550 nm, and this could be due to an error in design or manufacture. The two spectrometers used gave similar fits, with the double-sided film being the best antireflective film both in terms of error and reflectance. The 320 nm film was the next best fit for the two spectrometers, but the fiber optic spectrometer data was offset after a wavelength of 500 nm. The AR film in both spectrometers was offset, which could be due to absorption. The differences in the measurements between the spectrometers is due to offsets in the data with the fiber optic spectrometer. This shows that while the fiber optic spectrometer gives decent measurements the grating spectrometer is better for more precise measurements.

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