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# TUNABLE NANOSTRUCTURE ANTI-REFLECTIVE COATINGS

by

ERIK ROBERT BRINLEY  
B.S. University of Toledo, 2003

A thesis submitted in partial fulfillment of the requirements  
for the degree of Master of Science  
in the Department of Materials, Mechanical, and Aerospace Engineering  
in the College of Computer Science and Engineering  
at the University of Central Florida  
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## ABSTRACT

Research was conducted on broadband, anti-reflective coatings for fused silica and chalcogenide substrates in the infrared region of light. Using chemical preparation to create nano-porous through nano-particle based sol-gel solutions, the alteration of optical properties including refractive index and optical thickness was conducted. The nano-particles can modify the coating surface to allow only zero-order diffracted wave propagation reducing scattering while a partially graded profile of refractive index due surface evaporation lessened the precise phase relations of typical homogeneous coatings. My study of silica and titania sol-gel, and hybrid mixtures of the two were used to obtain the optical properties of the materials. The choice of experiments were rooted in theoretically calculated values, and parameters were selected based on quarter wavelength thickness and square root of refractive index theories of destructive cancellation of rebound waves for reduction of reflection. The fused silica system required anti-reflection in the region of 1.0-1.6 micrometer wavelength of the near-infrared. The base, uncoated transmission in this region is ~91%. A maximum transmission of 98% and no less than 97.3% over the entire region of interest was achieved. The chalcogenide system required anti-reflection in the regions of 1.0-1.6 and 3.5-5.0 micrometers of the near- and mid-infrared. The base, uncoated transmission of these regions is 61.9%. A maximum of 95% transmission was achieved for the 1.0-1.6 region and 87% for the 3.5-5.0 region. Solutions and coatings were characterized by Scanning Electron Microscope, Atomic Force Microscopy, X-ray Photoelectron Spectroscopy, particle size, elipsometry, UV-Vis-NIR, and FTIR to reveal the science behind the development and synthesis of nano optical coatings.

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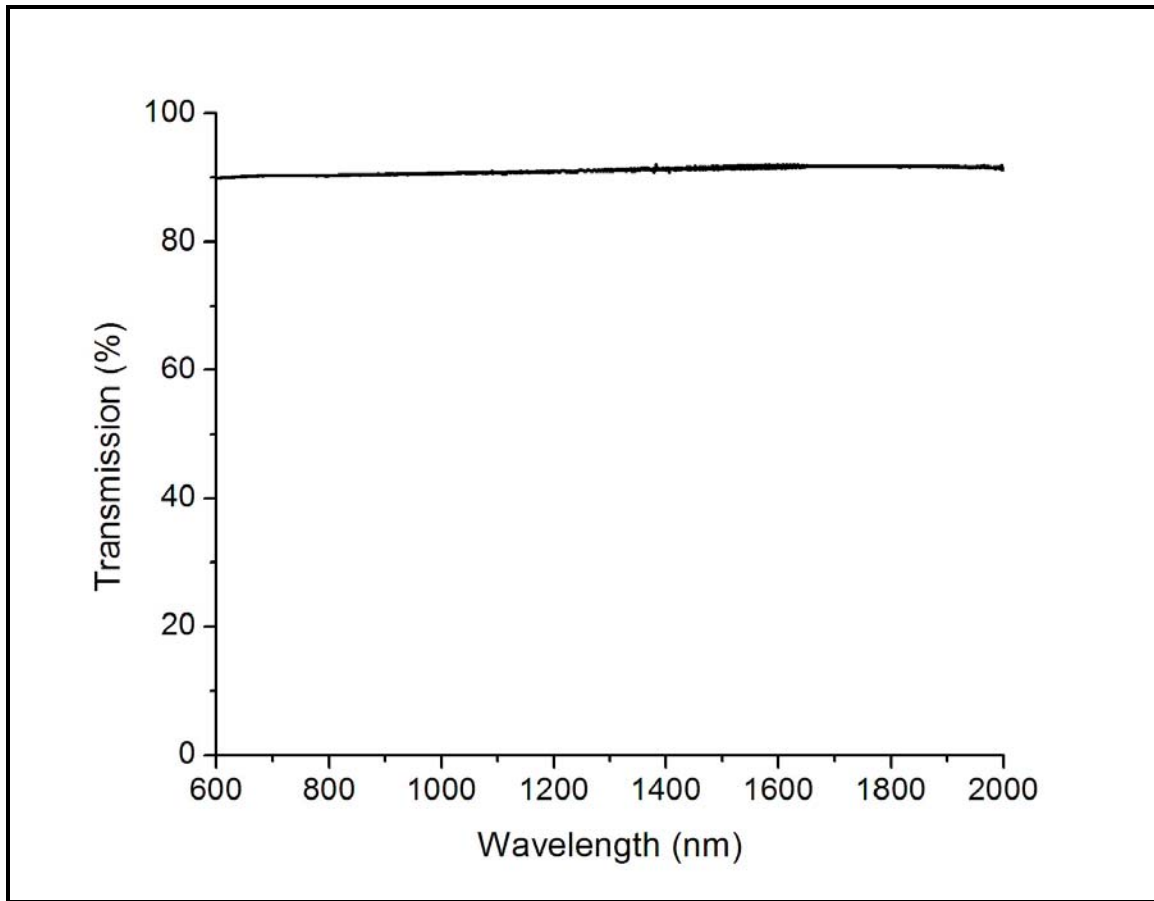
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## INTRODUCTION

Anti-reflective coatings have been used for many years to reduce reflection off the surface of transparent materials. Examples of this can be found in many applications such as solar cells, windshields for cars, and glazing for windows applications including cathode ray tubes, windows, and glasses<sup>1</sup>. The advantages of retaining this light lost can be seen in energy bills in the case of solar cells, efficiency of operation of cathode ray tubes, or general comfort in glasses.

Much research has been conducted on sol-gel coatings for use as an anti-reflective coating fused silica glass. It can be found in application as windows in a house or a car window. A unique property of the fused silica type of glass is its base (uncoated) transmission of approximately ninety percent of the light in the visible spectrum, of normal incidence to its surface [Figure 1]. Later I will discuss the angles away from normal and other regions of the electromagnetic spectrum more relevant to this research. This transmission allows for an acceptable amount of light to pass through a sheet of this glass without extra coatings or processing. This, however, is not ideal and even in a common application, such as eye glasses, a slight reduction in transmission can hinder sight, so it is a goal that every effort be made to increase transmission of optical glass in a low cost and effective manner.



**Figure 1: Transmission spectra of Fused Silica (uncoated)**

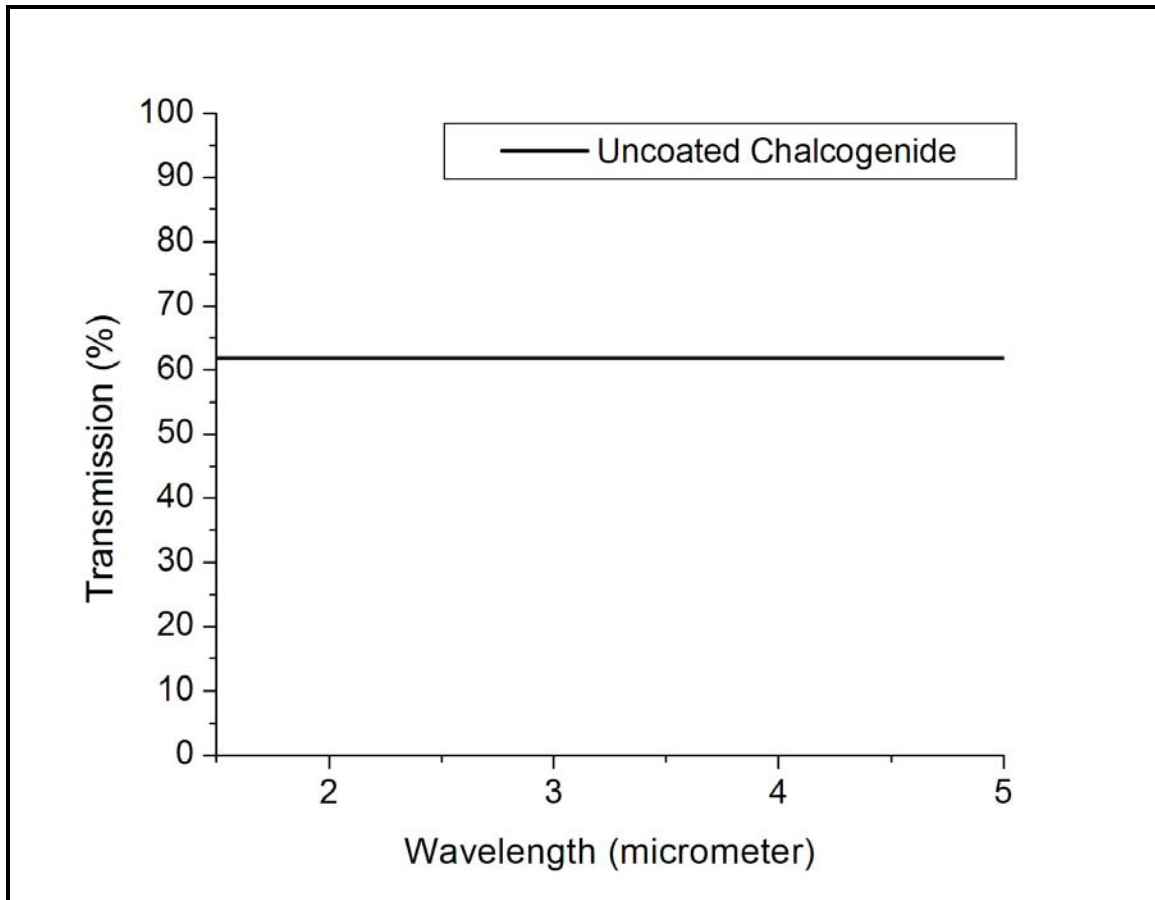
The loss of transmission is either absorbed or reflected and discussion in the section entitled “Anti-reflective Theory” will display the equations and concepts that prove this. In the case of fused silica, the absorbance of visible and infrared light is negligible leaving reflectance as the reason for scattering the 9-10 percent of light missing in the transmission spectra. With the application of an anti-reflective coating designed specifically for this type of glass and the particular wavelengths of light incident, above 99% transmission is possible in the visible spectrum<sup>1 2 3</sup>.

The second material of interest to this research is a type of glass called chalcogenide. Chalcogenide glasses are non-oxide glasses made up of group IV & VI elements, group II & VI elements, or other combinations thereof and have semi-conducting properties<sup>4 5</sup>. Of interest to this research is their transmission throughout the infrared region while other research focuses on the materials unique non-linear refractive index<sup>6 7</sup>. Further, such materials have high chemical stability<sup>7</sup>. Common applications of this unique glass substance include night vision systems and thermal imaging. Both applications exploit the excellent transmission of the chalcogenide glass throughout the infrared region of light<sup>8</sup>. Most studies found in literature are concerned only with the mid-infrared transmission of the chalcogenide glass. In many cases, this is most important range and also the best for transmission properties. Lacking is a low cost method of improving the transmission characteristics of chalcogenide glass in the near-infrared region, such as 1064nm for CO<sub>2</sub> lasers.

With the fused silica, the base transmission was adequate and the material has been used for many years' in common everyday applications. In the case of chalcogenide glass the base transmission is quite different. Shown in Figure 2, the base transmission in the near- and mid-infrared regions of light is very low at around 62%. The range of interest of this anti-reflective coating has been extended beyond that of fused silica from the near-infrared into the mid-infrared due to the superior non-absorption of light in these regions. Although this has been accepted at first and in recent years alleviated in the mid-infrared region, the method of fixing this difficulty still remains expensive and hard to implement on diverse chalcogenide shapes and sizes. Although the diverse shapes and sizes are not a primary objective of this research, in developing a solution for decreasing the cost off creation and application of anti-reflective



coatings on chalcogenide substrates, these issues are tangentially remedied. As the coating technique is solution based, different shapes can easily be accommodated.



**Figure 2: Transmission spectra of Chalcogenide (uncoated)**

Although a more detailed comprehensive discussion of the anti-reflective theory is found later in this paper, an introduction into the theory reveals the fundamental difference in the basic optical properties between fused silica and chalcogenide glass, while showing that the creation of optimal anti-reflective coatings are intrinsically similar between these two materials.

The increase of transmission is because of the reduction of light lost due to reflection. To make an anti-reflective layer for one specific wavelength requires that the layer have a certain thickness and refractive index. The coating must follow the formula  $n_{\text{coating}} = (n_{\text{substrate}})^{1/2}$  for the

coating refractive index<sup>9</sup>. The proper combination of these creates out of phase reflections that rebound from the medium. In general, a single quarter-wavelength coating with a refractive index that is the square root of the substrate is used to achieve full transmission<sup>10</sup>. Multi-layer coatings can be used to expand the properties of a single layer, among many layers. Using this theory, many layers of different thicknesses and refractive indices are layered to allow for different wavelengths<sup>9</sup>.

Current anti-reflective coating techniques are limited to two broad categories. The first involves the creation of a coating that has very high transmission for a certain wavelength of light. This technique is very useful for applications that use particular wavelengths of light, as in lasers. The second type is termed broad-band coatings. Some of the techniques used to create these functional coatings include multilayer coatings (MLC), sub-micron structures, and sol-gel derived anti-reflective (anti-reflective) coatings.

The multilayer coatings are extremely effective for transmission across a large range of wavelengths. The drawbacks of multilayer techniques are their intrinsic, complicated nature. The challenge is to maintain coating thickness while minimizing defects as each successive layer has an exponential chance of defect and defect propagation from a previous layer. Further, multilayer coatings can be mechanically less strong when compared to singular layers, given similar materials and process parameters<sup>11</sup>. Multi-layer coatings of where each layer is a different material have not been applied to this research, however a description of multi-layer theory and multi-layer coatings of the same material have been discussed thoroughly and applied, respectively.

The second type of broadband coating uses sub-wavelength structures in such a way that light scattering at the surface of the coating is minimized and transmission is therefore maximized<sup>2</sup>. By creating a structure that is smaller than the wavelength of the incident light the “...only the zero-order diffracted wave propagates” acting like a thin film<sup>2</sup>. The use of this has been limited as sub-wavelength structures for visible regions would need to be of diameters approximately 100-250 nano-meters (nm). If this is attempted the surface would have to be processed using expensive, difficult, and time consuming techniques such as lithography or other patterning methods. The theory is that the surface features larger than the wavelength of the light creates scattering.

The third general type of broadband coating is sol-gel derived anti-reflective coatings. Being the easiest to apply, they show the most potential in broadband applications. Unlike MLCs, single layer sol-gel coatings are very mechanically sound and are simple to create with minimal defects. Also, are vaguely similar to sub-micron structured anti-reflective techniques, sol-gel derived anti-reflective coatings can be created in such a way to mimic the function of sub-wavelength structures through the use of nano-structured networks and nanometer sized particles, affecting both the refractive index and the light scattering of the coating. The particles at the surface of the coating reduce the local average refractive index due to the voids of air between surface particles. Or in other words, the sub-wavelength structures are inherent to the sol-gel process although not to the extent (depth of the channel created) to which sub-wavelength structures can be created. This comparison to sub-wavelength structures is not entirely applicable except in

certain preparations due to the deep nature of sub-wavelength structures and the relatively shallow nature of sol-gel derived anti-reflective coatings.

One of the most common sol-gel materials is  $\text{SiO}_2$  (silica) due to its extremely low refractive index of 1.42. Compared to its pure, bulk form fused silica with a refractive index of 1.52, the refractive index of acid catalyzed sol-gel silica is one of the lowest refractive index materials. The creation of another material soon after sol-gel silica was magnesium fluoride with a refractive index of 1.38 in bulk form. Sol-gel solutions and coatings of magnesium fluoride have been created, but the advent of another preparation of sol-gel silica, the basic form, made Magnesium Fluoride less useful for anti-reflective coatings. It should be noted that acid catalyzed sol-gel silica was still used in the formation of anti-reflective coatings on chalcogenide glass in this research while the basic was used on fused silica. The alternative preparation of sol-gel silica, using basic rather than acidic catalysis allowed for the formation of a sol-gel coating with some of the lowest refractive index values ever seen at 1.20-1.22. Further discussion of sol-gel silica is presented in the subsequent sections.

As mentioned above the refractive index of fused silica of 1.52 and a transmission of 90% on a 1.2mm sample without an applied coating in the visible spectrum (300-900nm). The chalcogenide substrate, with a refractive index of 2.7-2.5 @ 1000-5000nm, respectively and a base transmission of 62% requires the use of different materials for coating with higher refractive indices. In fact, according to the square root of refractive index theory stated above, a refractive index of 1.6-1.65 is needed for the coating material. There are some materials that can satisfy this directly such as other chalcogenide materials; however they cannot be applied using the

simple sol-gel method. To combat this and retain the cost effective and ease of coating premise of this research, a hybrid combination of two well known sol-gel materials was developed. Using the high refractive index of sol-gel derived  $\text{TiO}_2$  (titania) in its amorphous form, with a refractive index of 1.91-2.2 depending on preparation and the acid catalyzed sol-gel derived silica, with a refractive index of 1.41, the appropriate combination of the two can create any refractive index between the two. Based on the discussion above, the appropriate constituent amounts and preparation methods required to create the desired refractive index for the anti-reflective coating on chalcogenide glass. Presented in following sections is the characterization proof, and procedural steps required to make this hybrid sol-gel solution and coating.

After the preparation of the sol-gel solutions it was necessary to coat the substrates. The two techniques that are commonly used for anti-reflective sol-gel coatings are spin coating and dip coating. Both methods were tried, but dip coating was chosen and spin coating was not applied to this research, but would be sufficient for the homogeneous, defect free, controlled thickness coatings important to this research. The latter, dip coating, uses a controlled dipping mechanism, which lowers and raises the substrate material to be dipped into the sol-gel solution.

As a final introduction to our research goals, we seek to achieve our goals of anti-reflective coatings on both fused silica and chalcogenide substrates without the application of heat or its equivalent energy in any other form beyond the chemistry of the sol-gel solution preparations. Sol-gel coating are typically coated then subjected to heat in a furnace to densify the coatings and remove unwanted organic and water species, and create stronger linkage between layers<sup>12</sup>. Due to the thermal instability of the amorphous chalcogenide substrate material the research was

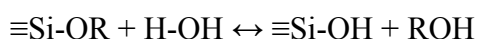
conducted on the premise that no introduction of heat energy was to be applied to either the coating or the substrate. Since the research was already focused on overcoming the issues associated with the no heat procedure, I decided to pursue the same no heat solution to the anti-reflective coating on the fused silica substrate.

## SOL-GEL AND ITS CHEMISTRY

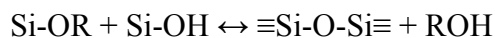
A sol-gel coating is a porous version of the bulk solid typically used. It can be created using room temperature synthesis through chemical means. The basic procedure includes hydrolysis, condensation of a precursor, and the final formation of the porous network consisting of either nano-porous coatings formed from spaces within the network or the spaces between nano-particles that are linked together<sup>13</sup>. Typically this procedure is followed by a heat treatment called 'calcining' to densify the coating, remove organic material and water, and further strengthen the network, however this is not done in the present research. An example formulation showing the reaction steps and the chemical bonding is referenced from literature as this process is very well known. Shown is the formulation of silica sol-gel, but similar procedures are used for the titania with an alternative precursor and a slight reduction in acid as the titania acts as its own catalyst.

Beginning with tetraethoxysilane (TEOS) for the precursor<sup>13</sup>:

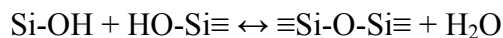
(i) Hydrolysis



(ii) Alcohol condensation



(iii) Water condensation



From this procedure different end products can result that have drastically different applications. Possibilities include xerogel coatings, wet gel coatings, uniform particle coatings, or ceramic fibers. Figure 3 shows a diagram of two different possible coating end products by two different processing methods<sup>14</sup>. The first creates a dense film by the entanglement of linear polymer chains of the particles which form into a nano-porous network. The second, network of uniform particles, creating a porous film is created by the basic preparation of the silica sol-gel where individual particles are allowed to grow in sufficient size that they remain individual particles after coating and drying. In this case, there is increased porosity in the coating, lowering the refractive index.

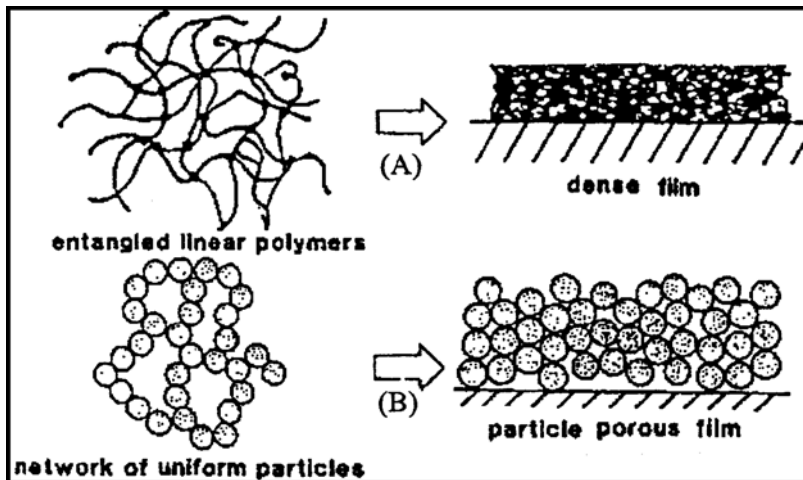


Figure 3: Dense and porous coatings by sol-gel method<sup>14</sup>

Another parameter of great importance is the time of each reaction stage and the amount of time needed for proper sol-gel aging. Aging is a term that means the time it takes the solution to reach the meta-stable gel state that is best for coating and also infers the completion of the chemical reaction, if the appropriate stoichiometry is followed. This proper aging can be as fast as 12 hours as in the case of Titania



prepared by water limited preparation and 5 hours in the case where heat is added as additional energy to the reaction stages or as long as 10 days in the case of the acid-base two step process<sup>14</sup>. After proper aging, if the sol is kept in an enclosed environment free from additional heat and excess humidity, the titania sol can remain indefinitely in this meta-stable state.

## SOL-GEL COATING TECHNIQUES

There are many variations of the main coating techniques that are used to obtain better coatings either in thickness homogeneity or to reduce defects, but all spawn from three main techniques. They consist of dip coating, spin coating, and the spraying of xerogels. Each has advantages and disadvantages as all are widely used. I will discuss two of the three showing the general principles, advantages/disadvantages, and application in anti-reflective coatings.

Dip coating consists of preparing sol-gel solutions, referred to as a 'sol', and dipping the substrate into a bath of the sol. Dip coating machines have the capability to change speeds, control sol solution temperature, reduce vibrations both internal and external, and some can even apply a heat treatment or drying procedure upon completion of the dip. These features have grown from the years of experimental research that has shown the factors which play a key role in the successful coating of sol-gel solutions by dip coating.

For dip coating, the equation of coating thickness,  $h$ , as a function of substrate speed,  $U$ , is shown as

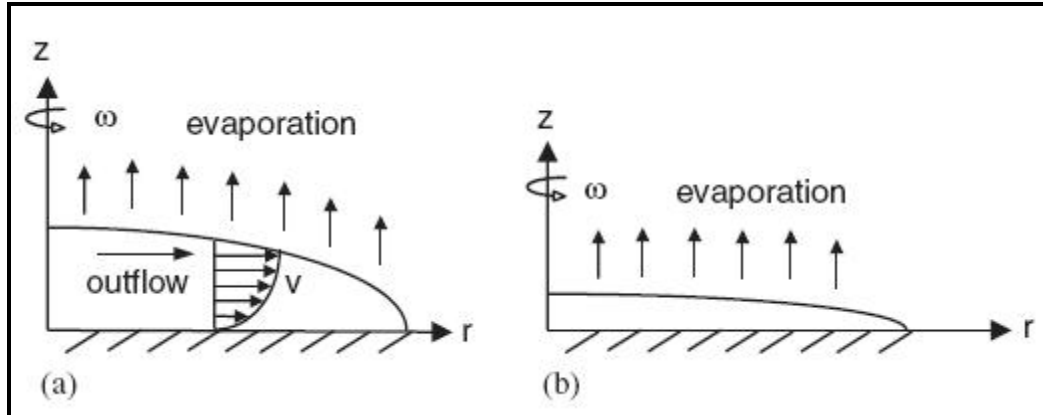
$$h = 0.944(N_{ca})^{1/6}(\eta U / \rho g)^{1/2}$$

“Where  $\eta$  is the viscosity,  $\rho$  is the density,  $g$  is the acceleration due to gravity and  $N_{ca}$  is the capillary number, defined as  $N_{ca} = \eta U / \sigma$  ( $\sigma$  is surface tension).”<sup>13</sup> This equation displays the important parameters that can be changed during creation of the sol-gel and the amount of aging allowed. The substrate speed was kept constant in our experimentation at 8.5 cm/min and the solution was preparation was kept the same. The exact aging time of 24 hours was found to be

the best by visual inspection of the coating showing no major visual defects, optical microscope inspections to verify cracks were not forming upon drying, and UV-Vis spectroscopy transmission spectra to show smooth interference patterns typical of good coatings.

Spin coating consists of placing a substrate material on a chuck attached to a rotating disc. This underside of the chuck is connected to vacuum to hold the sample so that the sample can be spun from 500-10,000 RPM for effective coatings. Today's spin coating machines feature isolated chambers backfilled with dry air or nitrogen, vibration dampening mechanisms, and automated dispensing of solutions from one or more syringe applicators. This whole system is designed in such a way to control the amount of solution that is applied to a substrate, precisely control spin speed, to create homogeneous coatings. A unique advantage of spin coating is its homogenous coating thickness due to the dynamics of the solution as it is applied to a spinning substrate. The sol-gel is added drop-wise onto the center of the spinning substrate and the sol-gel solution is pulled towards the outside. Excess is thrown off the edges and for a given speed and viscosity a maximum layer thickness is achieved.

The model of the spin coating process is below:



**Figure 4: Spin coating diagrams (a) the outward flow of liquid (b) the evaporation due to spinning velocity**

The detailed equations that govern spin coating are not shown because spin coating is not used in this research. However, the use of spin coating would be an adequate approach for applying homogeneous layers of multi-layer coatings and would be a further venture of this research if continued.

## ANTI-REFLECTIVE THEORY

### ***Single Wavelength***

There are certain guiding principles for single wavelength anti-reflective coatings that can be used to ascertain the appropriate coating materials and thicknesses necessary the best possible transmission. Single wavelength coatings are called this because their best anti-reflection is a narrow peak at a certain wavelength. Although this single layer coating can create an interference pattern in its transmission spectra with multiple minima and maxima, it is still ideal for only one wavelength. Other wavelengths that have maxima in the interference spectra will most likely have more reflection, if only slightly, than the wavelength for which the coating is tuned. This is particularly important for coatings systems where transmission values of 99% or better are the requirements.

The first principle of single wavelength coatings is the quarter wavelength theory. The single layer coating must be a quarter the thickness of the incident wavelength of light which anti-reflection is wanted<sup>10</sup>. This is due to the reflection of the waves of a certain wavelength. If the reflected wave can be destructively cancelled by the incoming wavelength then the total transmission would be 100%. This is of course not possible due to absorption in even the best materials.

The second principle of single wavelength coatings is the square root of refractive index. The refractive index, being the speed of light through a medium as compared to the speed of light in a vacuum, is the second important part of the two principles. Each property, refractive index and

thickness, must be controlled in order to attain a high transmission optical quality coating. This principle simply states that the refractive index of the coating material, matched with the quarter wavelength thickness would be the square root of the refractive index of the substrate which it is applied.

A final note before broadband theory is the justification of the second principle. As mentioned previously, the refractive index is an important part of an anti-reflective coating. In specific, it is one of the major difficulties in creating anti-reflective coatings for chalcogenides. Chalcogenides are known for their high refractive indices<sup>15</sup>. In this case, the chalcogenide used had a refractive index close to 2.7 at 1000nm. Focusing on a refractive index of 2.7, the closest approximation of the glasses index of refraction averaging out dispersion effects, an attempt was made to fine tune a sol-gel blend to the aforementioned square root refractive index value, of ~1.64. This will be discussed further in the section entitled “Chalcogenide Glass.” To further express the concept we take a coating with a refractive index of 1.50 and create the Fresnel amplitude reflection coefficient (r). The equation and coefficient would be,  $r = \frac{n_1 - n_2}{n_1 + n_2}$ , for each

interface, where  $n_1$  and  $n_2$  are the refractive index values of each of the two medium in the system. We use  $n_1=1.0$  for air and  $n_2=1.50$  for the coating in the first instance of the equation, and in a separate instance of the Fresnel equation using  $n_1=1.50$  for the coating and  $n_2=2.7$  for the substrate. Doing the calculations, it can be theorized that the optimal coating obtainable for this refractive index is 0.7% reflectance for the exact coating thickness needed for destructive interference of the reflected light waves. This number does not take into account surface roughness, coating inconsistencies, or thickness variations.

## ***Broadband Theory of Sol-gels***

The particular application for this research for anti-reflective coatings requires that the coating be capable of broad-band anti-reflective use. In a narrow-band anti-reflective coating, a single wavelength is used as a target goal for maximum transmission. The rules for creation of an anti-reflective coating are applied and other wavelengths of incident light, other than the target, are neglected. In broad-band anti-reflective coatings, a range of wavelengths of incident light will be the target of the coating. Prior to sol-gel technology, to be considered a broad-band anti-reflective coating, the coating had to make use of multiple coatings of different refractive index. This process is both complicated and less mechanically stable than its single coating counterpart. As a solution to this difficulty we use the unique properties of sol-gel coatings and their broad-band anti-reflective nature to our advantage in order to use a single coating (this term includes 2 or 3 layers of the same coating material to obtain the appropriate thickness) to create the broad-band nature. Sol-gel coatings derive their refractive index from a combination of nano-scale particles and the voids (air) between them creating a scaffolding or skeleton which coatings both solid and empty spaces. The refractive index is then the average of the refractive index of the two different mediums, the sol-gel material, and air, making the combined refractive index lower than the sol-gel material. This alone can allow control over the refractive index of the final coating. The second characteristic that leads to the broad-band nature is the size of the nano-scale particles. There is research into an anti-reflective technique using structures designed at a sub-wavelength, of incident light, scale that the scattering properties promote the transmission of the incident light discussed above. The sol-gel coatings take advantage of this because the nano-particles can act as these sub-wavelength structures at the surface of the coating depending on size and porosity. Finally, the third characteristic that leads to the broad-band nature is the

porosity at the bottom or middle of the coating as it is compared to the top of the coating. Inside the coating the refractive index is an average of the RIs as described above, but at the top of the coating the porosity is increased due to the manner in which sol-gel coatings dry. Because the sol-gel coatings are created at room temperature and then dried by evaporation, the surface evaporation causes the removal of more of the organic material. Although the coating is fully devoid of the solvent after drying, some residual material remains inside the coating, making the refractive index higher on the bottom and inside, if only slightly, than the top. Again, this broadband characteristic is dependent on the properties of individual preparation of sol-gels. Graded index coatings and their feasibility when created appropriately and purposefully with sol-gel methods will be discussed in the final section of the thesis, but it has been documented in literature that graded index coatings are not critically dependent on precise phase relations of typical interference coatings.



## ***Single Layer Experimental Requirements***

The first substrate, fused silica, has a refractive index of 1.52 @ 550nm and 1.46 @ 1000nm. Both are relevant because the dispersion of a material, or the change of its refractive index with increasing or decreasing wavelengths of incident light, becomes a factor in determining the appropriate material for the chosen range of anti-reflection. Since this is a single layer solution, even with the use of sol-gels and their previously discussed broadband nature, a specific wavelength of greatest transmission must be chosen. For reasons described later we choose 550nm as a starting point at the beginning of the research and 1000nm as the final goal of the anti-reflective coating. The use of 550nm as a starting point allows for minimal alteration of the sol-gel solution while allowing us to confirm the experimental results of the theoretical understanding. The range for each will be approximately 1-2% loss due to reflection over a 100nm, or greater, in each direction from the chosen value.

The quarter wavelength thickness at 550nm is 137.5nm and for 1000nm is 250nm thickness. These values, along with the correct refractive indices, will combine to achieve transmissions of 99% or greater on fused silica substrates. The coatings are applied by dip coating and will therefore be applied to both sides of the substrate. Since they are applied to both sides, values of 99% are possible. If one side were coated and the other not with a fused silica substrate, the reflection from the uncoated side would be ~4%, making the total possible transmission no more than 96%. This is the justification for the use of dip coating as a one step process for creating two sided coatings of exactly the same material and thickness.

The refractive index values, due to dispersion, change between the two wavelengths. At 550nm the refractive index is 1.52, making the ideal square root refractive index 1.233. This is far

below the stated values of the acid catalyzed silica sol-gel and the magnesium fluoride sol-gel materials. For values this low we must look toward base catalyzed silica. At 1000nm the refractive index is 1.46, making the ideal refractive index 1.21. Again, it is to our advantage to use basic catalyzed silica.

For the chalcogenide substrate has a refractive index of 2.7 @1333nm and 2.5 @4000 nm. Typical dispersion in the infrared region of light is negligible, but in the case of the chalcogenide the dispersion was considerable. In response to this we chose a value between the two ends of the curve as a value for the refractive index in order to minimize the negative effects of the large slope of the dispersion curve. For reasons described later the ranges of interest for the anti-reflective coating on the chalcogenide substrate are 1000-1600nm and 3500-5000nm. The goal was to increase the transmission in each of these regions simultaneously with a single anti-reflective coating. Since the use of only single layer coatings are possible, it is necessary to use two different maximums centered over each of the regions. The two wavelengths shown above were chosen for that reason and it is that reason that the refractive indices are shown. By choosing the maxima to be at these locations it is possible to create one coating with the appropriate thickness and nearly the optimal refractive index for both ranges.

The quarter wavelength formulation for the chalcogenide substrate is more complicated to account for the two different maxima goal. Using a quarter and three-quarter wavelength of the incident light, according the quarter wavelength theory, the two maxima of the transmission spectra will lie at 1333nm ( $3/4$  wavelength of 1000nm) and 4000nm ( $1/4$  wavelength of 1000nm). This was not by chance and, due to the tendency of the maximum peaks in sol-gel coatings to broaden at higher wavelengths, the range of the first peak will be smaller than that of

the second. If tuned with the appropriate process parameters, the smaller first range of 1000-1600 being only 400nm and the larger second range of 3500-5000 being 1500nm, it is possible to create a single layer broadband coating to increase the transmission over the entirety of each range.

The refractive index, as with the  $\frac{1}{4}$  wavelength, is a concern with the chalcogenide and becomes complicated. The material for the anti-reflective coating of the fused silica was straight forward as there was a sol-gel material and preparation to create the desired refractive index. As it is, there are materials that will satisfy the square root of refractive index for the chalcogenide coating. The difficulty lies in their cost and possible preparation by sol-gel method. Other chalcogenide glasses can be laid down in a coating by other processing methods such as Chemical Vapor Deposition (CVD), but this goes against the goal of this research. First, CVD is more expensive than dip coating requiring vacuum chambers, stages, and power supplies. Second, CVD and other process that lay down layers by deposition usually deposit on a flat surface and falter with curved or oddly shaped substrates. Dip coating can alleviate this by coating equally well on curved or flat surfaces as long as they all exit normal to the surface of the sol. Finally, materials such as chalcogenides are expensive to create and more rare than the sol-gel materials chosen for this research. This discussion validates the choice of dip coating over other application techniques.

The refractive index of the chalcogenide substrate is a range from 2.5-2.7 over the wavelengths of interest, of which I chose 2.6 as a midpoint for the basis of choosing the appropriate coating material. The square root of this index is 1.612 and, aside from the expensive aforementioned materials, is not a value that is easily obtained with one sol-gel material or process. To combat

this, a hybrid sol-gel solution was created using two well known sol-gel materials. The first, acid catalyzed silica discussed above and the other is acid catalyzed titania. The refractive index of acid silica sol-gel is 1.41 and the refractive index of titania is 1.91-2.2 based on preparation<sup>16,17,18</sup>. The values quoted in literature at 2.0 and above are at wavelengths far lower than are subjected to the substrates with these coatings. As such, even the value of 1.91 is unattainable using the current procedures because in preparation of sol-gel solutions at this refractive index, densification and removal of organic material plays a key role in raising the value. At the wavelengths we need, up to 5000nm, the refractive index of titania that is possible using a no heat procedure is 1.75. Both of these refractive indices are static over the near- and mid-infrared region. To obtain the 1.612 index that the theory predicts a 1:1 mixture of the two sol-gel materials should provide a refractive index that is the average of the two at 1.58. This is not exactly the refractive index, but is close enough that the deviance from the ideal predicted is negligible.

### ***The Multi-Layer, Same Material Solution***

The dip coating process is dependent upon factors such as viscosity, dip speed, and surface tension. Each of these can be altered to create different coating thicknesses, but each has a limit to the extent it can be modified. For our applications, single layer coatings cannot provide adequate thickness for the infrared regions. Because of this it is necessary to apply multiple dip coatings of the same sol-gel onto the same substrate to, in essence, build up the layer thickness. In the case of the fused silica, the ideal coating thickness was 137.5 nm which could be created with two layers. In the case of the chalcogenide substrate, the 1000nm was much thicker and in the present research was not obtained. Coatings that approached this value were obtained and the results displayed for the fused silica are proof of the concept, while the results obtained for the chalcogenide are substantially better than are to be expected for a slightly less than adequate coating thickness. The success of the fused silica coating system and the important understanding gained from the chalcogenide coating system are of equal benefit to the present research and the scientific community.

## RESULTS: FUSED SILICA

### ***Infrared Region***

A main focus of this research was to create a coating, sol-gel derived, that would aid in the maximum transmission of light at certain wavelengths of interest. Three such wavelengths, 1500nm, 3500nm, and 5000nm, were pursued. These three wavelengths represent well used wavelengths of the near infrared region. With a coherent light source such as lasers it is possible to transmit large amounts of data over vast distances at the speed of light. Further, this technology can be used as targeting systems and remote sensing applications. The current limitations of this technology for laser systems are the losses due to reflections. This can be overcome by the application of anti-reflective coatings. In addition, the robustness of the lens can be increased by decreasing reflectance for many common laser wavelengths ranging from the near-infrared to the mid-infrared. The increased absorbance of fused silica at wavelengths above 3000nm makes it less useful and therefore anti-reflection in this region is not attempted. However, the range of 1000-1500nm is possible and is the focus of the research.

### ***Preparation of Sols***

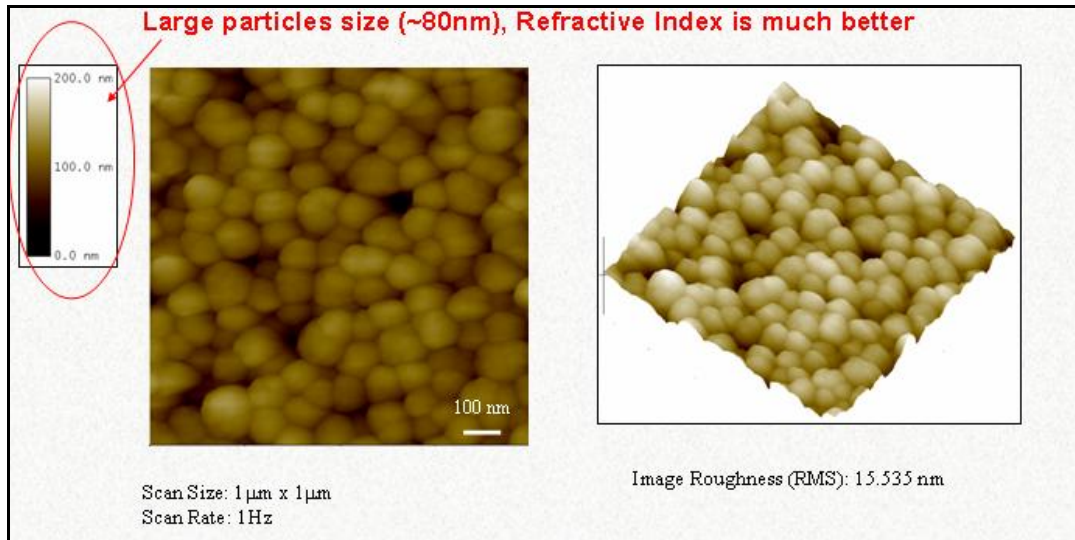
The acidic silica sol-gel is created with equal parts Tetraethoxysilane (TEOS) (+99%) and Ethanol (anhydrous, 85%) at 90mL apiece. The sol reaction utilizes 10mL of nitric acid for hydrolysis and 10mL of deionized water, added drop wise, for water condensation. The sol is then covered, to prevent evaporation, and left for aging for 24 hours.

### ***Dipping Procedure***

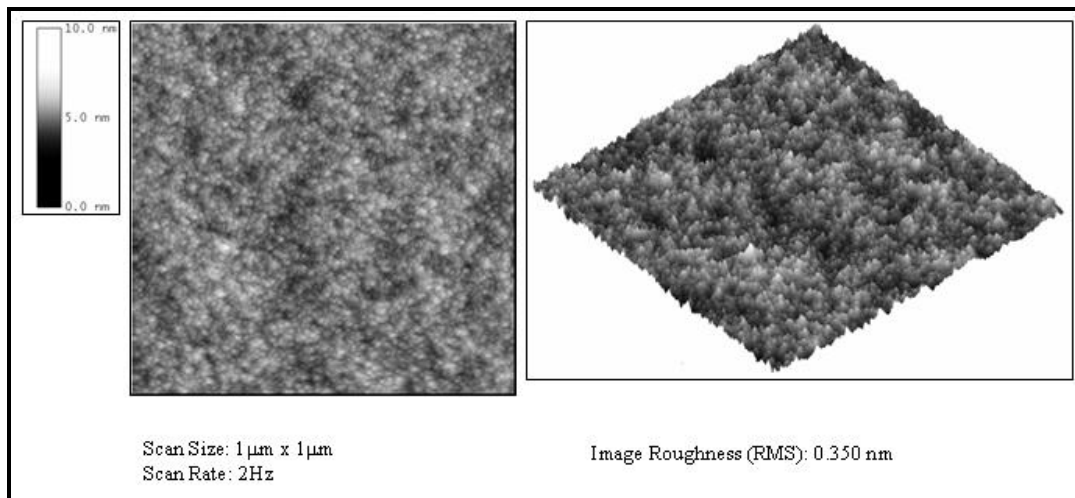
A dip coating instrument (KSV Instruments, Ltd. Dip Coater) was used to control vibrational effects and to increase the homogeneity of the film thickness. The rate used for withdrawal was 85 mm/min. At this rate, inconsistencies due to surface tension were avoided. For coating the glass slides the instrument was equipped with a standard gripping mechanism. Held on an angle so that the corner of the slides was facing downward, the surface tension that can create waves within the coating was avoided. The slides were cleaned prior to coating with iso-propanol, and then dried with compressed air.

### ***Optimal Refractive Index***

To meet the requirements of the anti-reflective theory silica sol-gel material was used. With two preparation methods, catalyzed either by acid or base with refractive index of 1.41 and 1.22, respectively, silica was the ideal for low refractive index substrates. The base catalyzed method creates highly branched clusters which cause the formation of particles. The voids between the particles reduce the refractive index of the coating. By creating larger the particle, thus large voids between them the refractive index could be lowered. By creating a homogeneous particle size of 80nm, shown in Figure 5, the necessary refractive index of 1.202 is achieved. This is compared to the 5nm particles size of acid catalyzed silica sol-gel coating shown in Figure 6, with a refractive index of 1.41.



**Figure 5: The AFM image shows the homogeneous particle size in the sol-gel coating. The material is base catalyzed silica sol-gel coated by dip coating method. The size range shown is not indicative of the actual size. The particle size has been calculated to be 80nm  $\pm$ 5nm. The large size allows for more space between particles creating a lower Refractive Index of 1.202.**

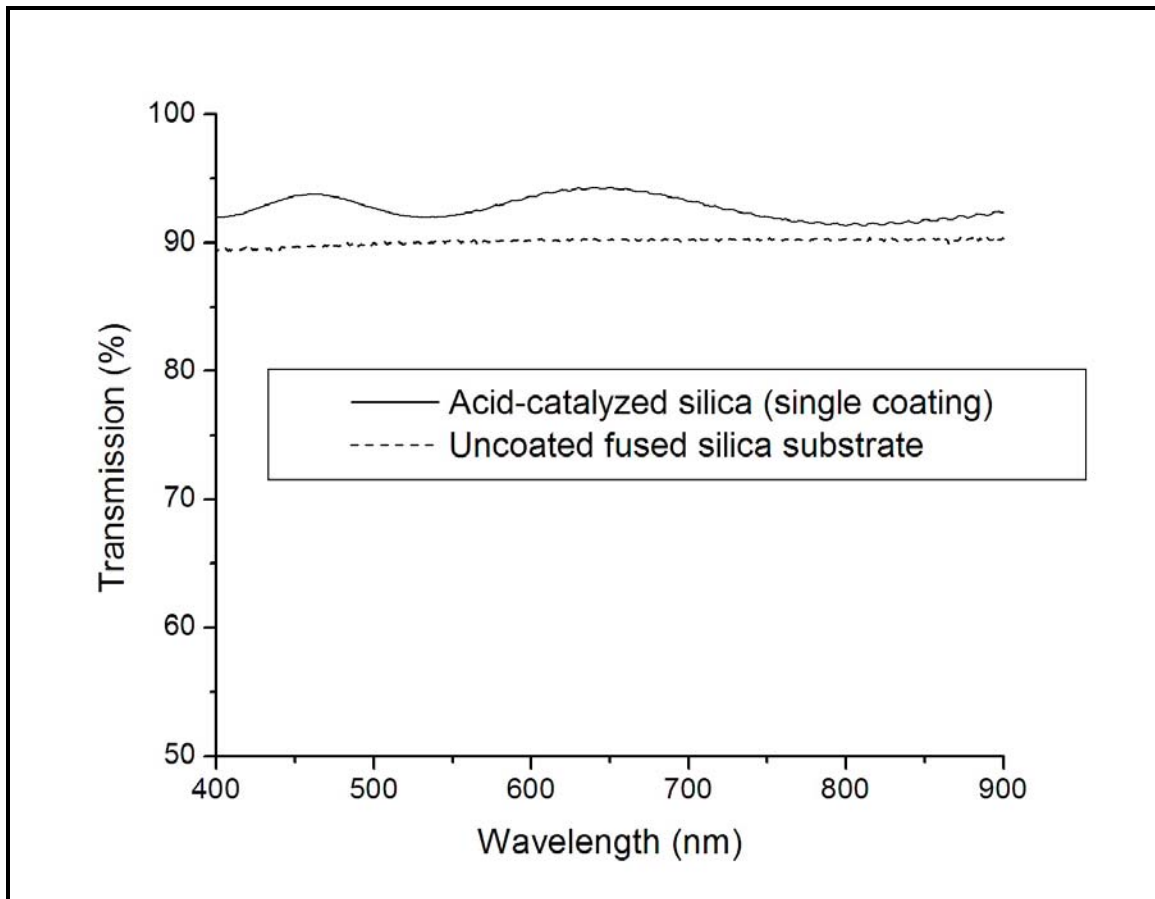


**Figure 6: The AFM image shows the homogeneous particle size in our sol-gel coating. Material is acid catalyzed silica sol-gel coated by dip coating method. The size range shown is not indicative of the actual size. The particle size has been calculated to be 5nm. The small size decreases porosity which in turn increases Refractive Index to 1.41.**



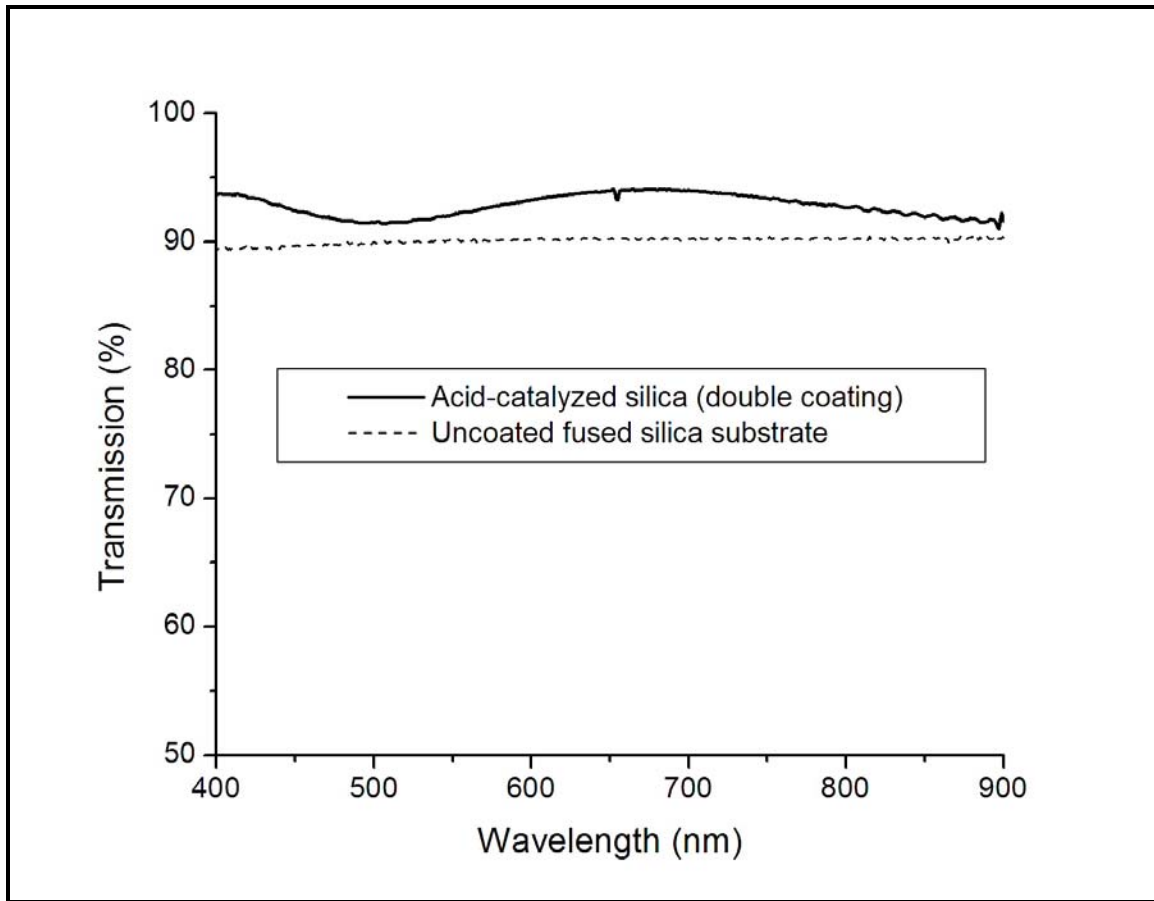
## Transmission

The uncoated transmission spectrum of fused silica, Figure 1, shows 9-10% loss of transmission due to reflection, 4-4.5% on each side of the substrate. The first attempt at a coating was an acid silica coating. Figure 7 shows the interference pattern common to a single layer and indicative of a coating that is too thin for a 550nm wavelength.



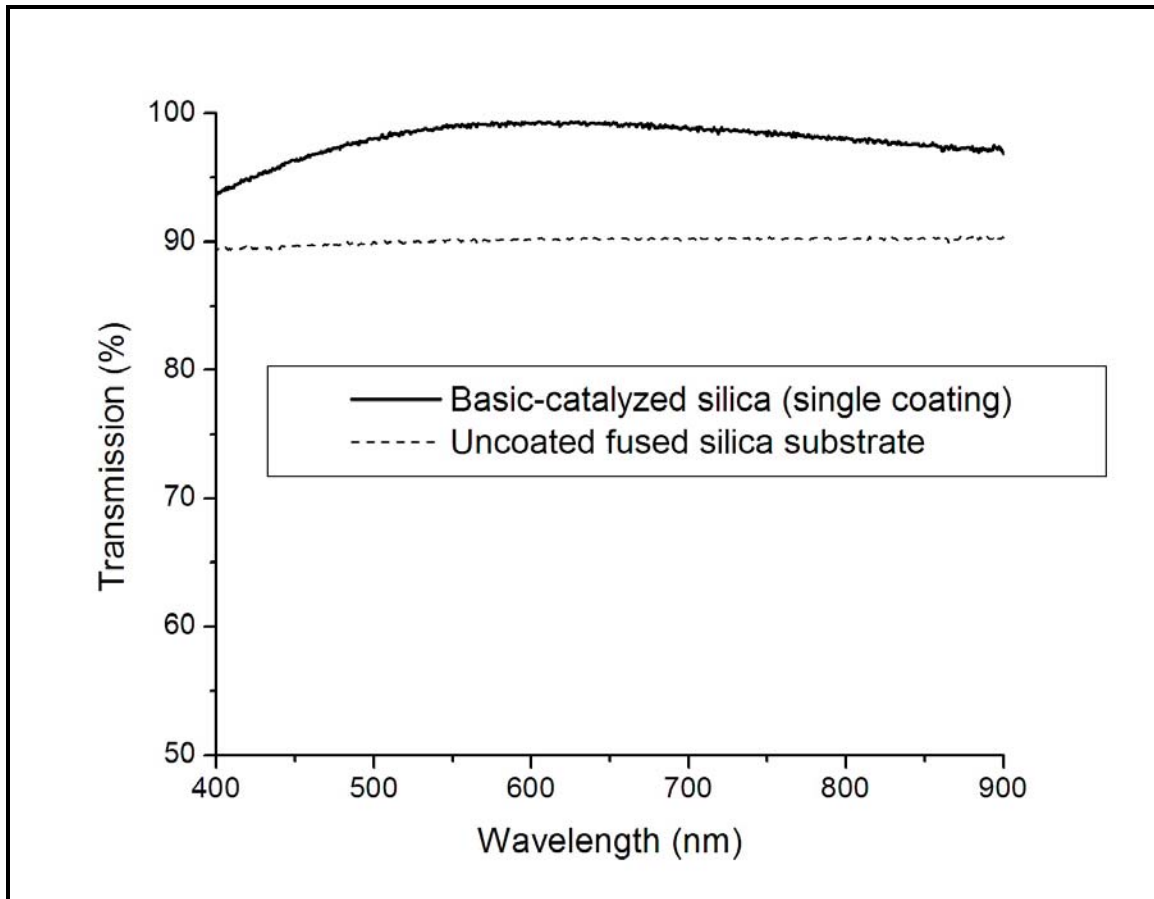
**Figure 7: Acid-catalyzed silica (single layer) compared to uncoated**

Figure 8 shows a lesser interference pattern due to a thicker coating of two layers of acid silica on fused silica. These spectra, Figure 7 & 8, were used as tools for understanding how the optical properties could be interpreted from the transmission spectra.



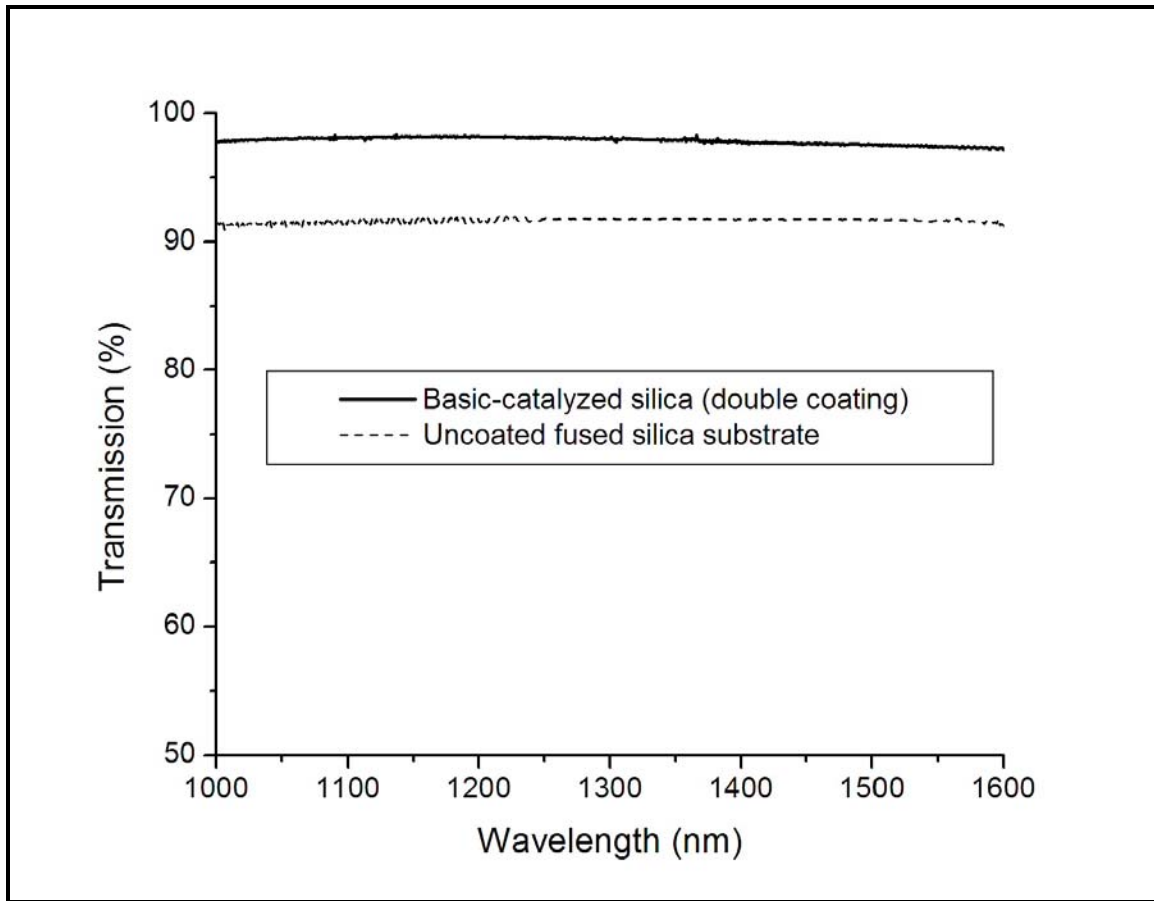
**Figure 8: Acid-catalyzed silica (single layer) compared to uncoated**

It was not until after this confirmation that the first basic silica experimentation was conducted. The first trials of basic silica provided all the verification of concept that was needed for the research that was to follow. Figure 9 shows a single layer coating of basic silica on fused silica substrate.



**Figure 9: Base-catalyzed silica (single layer) compared to uncoated**

The excellent transmission at 550nm indicates that the refractive index was appropriate for that wavelength and that the coating thickness was 137.5nm thick. Further, the broadband nature can be realized with the nano-particle effect. Following this trial and several confirmations of it, a two layer coating of the base silica was done in an attempt to increase the wavelength of optimal transmission while retaining the excellent anti-reflective qualities. Figure 10 is a two layer basic silica coating on a fused silica substrate.



**Figure 10: Base-catalyzed silica (double layer) coating compared to uncoated**

The two layer basic coating shown in Figure 10 illustrates the broadband nature of sol-gel coatings with a maximum transmission of 98% at 1100nm and no less than 97.1%. This coating system is 275nm thick as is indicated by the maximum transmission at 1100nm and the quarter wave theory. The refractive index value has changed slightly with the addition of another layer, revealed by the 98% rather than 99% transmission. The values of 1.20 and 1.21 are difficult to achieve even with nano-particle based silica sol-gel coatings, but the accomplishment of 98% is considered a success for the research goals.

## RESULTS: CHALCOGENIDE GLASS

### ***Infrared Region***

A main focus of this research was to create a coating, sol-gel derived, that would aid in the maximum transmission of light at certain wavelengths of interest. Three such wavelengths, 1500nm, 3500nm, and 5000nm, were pursued. Some common applications such as low cost optics by molding of chalcogenide glass<sup>1</sup>, photo-darkening<sup>19</sup>, or the use of chalcogenides for microbiological function used in early tumor diagnosis with the aid of specialized sensors capable of recording infrared signals of bio-molecules<sup>20</sup>.

### ***Preparation of Sols***

As mentioned above, it was necessary for a hybrid sol-gel to be created to obtain the appropriate refractive index. The hybrid sol-gel is created in a multiple step process combining the two different components after aging. The silica sol-gel is acid catalyzed and described above in the “Fused Silica” section. The second part of the hybrid sol-gel is the titania. Components of the titania sol include 12mL of titanium (IV) isopropoxide (97%), 170mL of 2-Propanol (Grade GC, 99.7%), and 1mL of DI water. The Isopropoxide is added to the propanol to avoid premature hydrolysis reactions. After mixing of these two, the water is added. The two components are then combined into one large container after appropriate aging cycles.

This mixture is stirred to ensure proper combination of the two constituents described elsewhere (S. Seal, E. Brinley, L. Kramer, E. Braunstein – A composite sol-gel hybrid optical coating for

IR applications (Patent Pending, 2005)). The two individual sols are clear in color and devoid of emulsion before combination. After mixing, the solution becomes a mild yellow color. This yellow color will not affect the final coating due to the extremely thin nature of the coating.

### ***Dipping Procedure***

The aged sols, both Silica and Titania, were tested individually on fused silica glass slides. The film consistencies were confirmed through both visual observation and optical microscope. The solutions were viewed for consistency and confirmed to be free of particulates or premature gelation. Further confirmation was achieved by a test coating to observe any visible imperfections. After the verification of acceptable aging times was completed, the two sols were mixed and stirred. The coating was done promptly following mixing to avoid gelation. The coatings done on chalcogenide glass were carried out in room temperature conditions.

The same KSV Instruments dip coating equipment was used for the dipping of chalcogenide substrates as was used for Fused Silica. The speed was still 8.5cm/min to avoid inconsistencies. For coating the glass slides the instrument was equipped with a standard gripping mechanism. However, for the chalcogenide glass, of circular design, nearly 0.5 cm thick, it was necessary to fashion a holding ring of platinum wire. The glass slides and chalcogenide glass samples were cleaned prior to dipping in order to ensure a consistent coating surface. The cleaning procedure consisted of a rinsing in xylene and then application of methanol to remove water, finally followed by compressed air for a pristine surface.

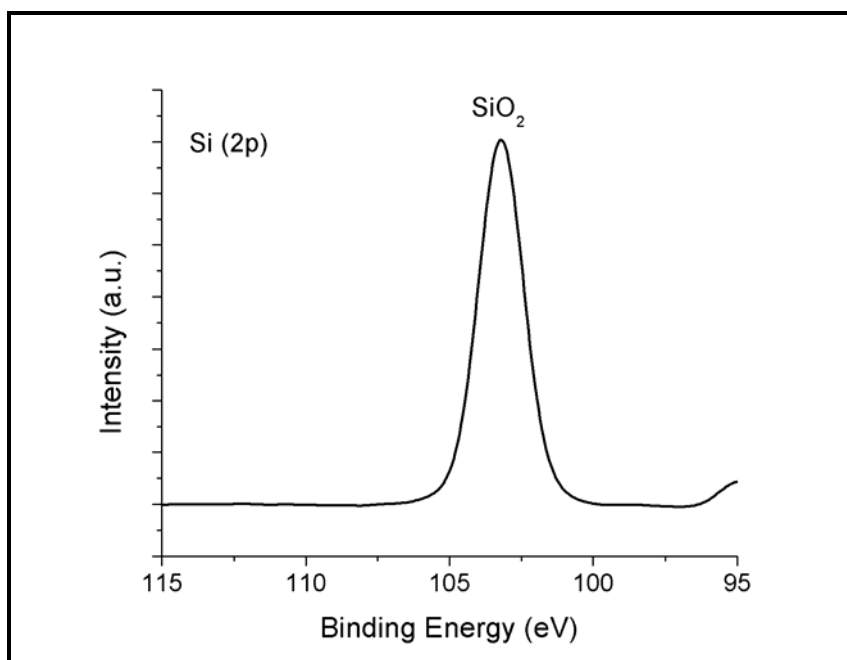
The surface chemistry of the silica-titania hybrid was studied using the XPS utilizing PHI ESCA spectrometer (model 5400, Perkin-Elmer, Minnesota, having energy resolution of  $\pm 0.1$  eV, at a base pressure of  $5 \times 10^{-9}$  Torr using Mg K $\alpha$  radiation (1253.6 eV). The X-ray power during the analysis was 300 W. Both the survey and the high-resolution narrow-scan spectra were recorded at the pass energies of 44.75 and 35.75 eV, respectively, to achieve the maximum spectral resolution. The binding energy (B.E.) of the Au 4f<sub>7/2</sub> at 84.0 $\pm$ 0.1 eV was used to calibrate the B.E. scale of the spectrometer. Any charging shifts produced by the samples were carefully corrected using the C (1s) B.E. level of 284.6 eV in the adventitious carbon<sup>21</sup>.

A Fourier Transform Infrared (FTIR - Spectrum One system, having wavelength range 7,800-350 cm<sup>-1</sup> with KBr beamsplitter) was utilized for measurement of the transmission spectra over the desired wavelength of 1.5 to 5 micrometer. The resolution of the system is 0.5 cm<sup>-1</sup> with a wave number accuracy of 0.1 cm<sup>-1</sup> at 1,600 cm<sup>-1</sup>. The FTIR was used to measure the transmission of the bare and coated chalcogenide glass samples. The alignment of the sample was guaranteed through an alignment board and complimentary screw inserted sample holder. All measurements were reproduced multiple times to verify results obtained.

### ***Surface Chemistry of the Hybrid Coating***

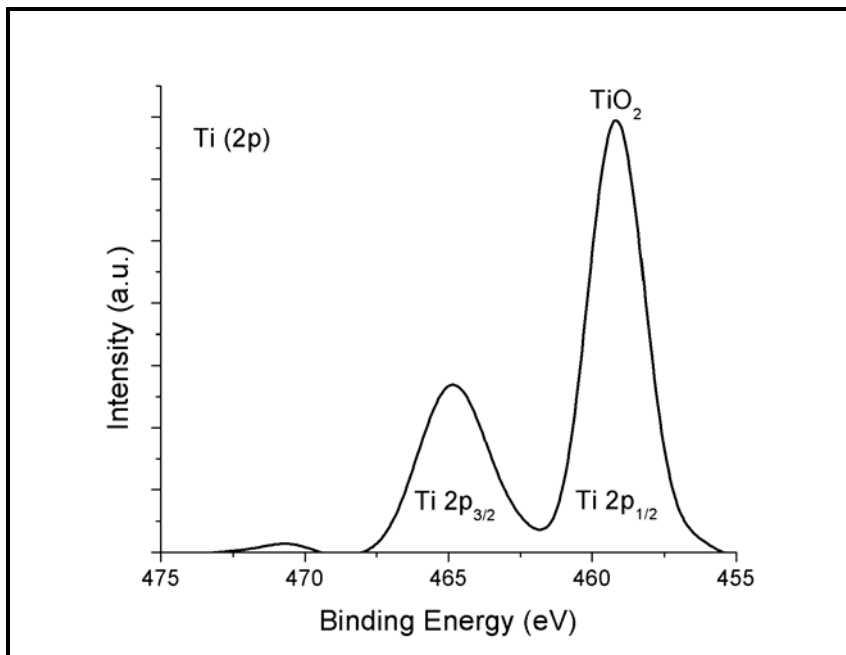
XPS broad scan spectrum for the hybrid sol-gel showed the presence of O, Si, and Ti as expected. Upon further analysis using narrow high resolution XPS scans obtained for Si (2p) and Ti (2p), within the B.E. ranges of 95-115 eV, Figure 11, and 444-474 eV, Figure 12. After analysis of the Si (2p), a peak at 103.2 is identified as the gel form of SiO<sub>2</sub>. The presence of SiO<sub>2</sub> and TiO<sub>2</sub> is confirmed with the O (1s) peak, Figure 13. Heat treatments commonly used

increase porosity and lower RI<sup>22</sup>. This was not necessary as the coating performed well without such treatments. Similar heat treatments are usually performed on the titania sol-gel coatings, mainly used to create a crystalline structure<sup>22</sup>. The basic drying procedure involves a heating at 100°C in order to dry the coatings and then using increased heat, between 400°C and 1000°C, to achieve the desired crystallinity<sup>1</sup>. However, in our coating system, the use of heat beyond 100°C is not possible leaving the TiO<sub>2</sub> in the non-crystalline or amorphous phase. The Ti (2p) peak shows the amorphous nature of TiO<sub>2</sub> with a peak at 459.2 eV.

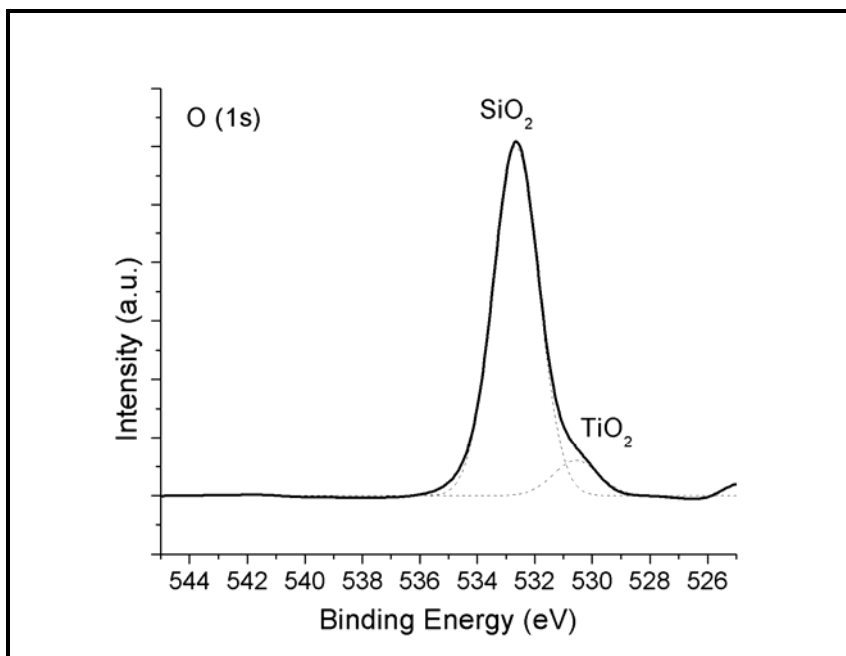


**Figure 11: XPS Si (2p) spectrum showing the SiO<sub>2</sub> formation. The peak is centered at 103.2 eV indicating the presence of SiO<sub>2</sub>.**





**Figure 12: XPS Ti (2p) showing formation of TiO<sub>2</sub>. The peak is centered at a binding energy of 459.16 eV signifying the presence of TiO<sub>2</sub>.**



**Figure 13: XPS O (1s) showing formation of SiO<sub>2</sub> and TiO<sub>2</sub>. The SiO<sub>2</sub> peak is centered at a binding energy of 532.7 eV. The second peak, TiO<sub>2</sub>, is located at 530.4 eV.**

The increasing porosity with an increase of temperature of thermal treatment of the silica portion of the coating would typically be a useful method of lowering the RI and thereby increasing the

anti-reflective quality of the silica coating. The titania in the coating is used solely for its refractive index value upon the combination of the two. The hybrid coating used in the present research uses the particular refractive index of silica which is 1.25 and any decrease in refractive index due to thermal treatment above 100°C would be to the detriment of the coating, rather than advantage. Also, the titania portion of the coating is more porous in its non-crystalline form than after it has been thermally treated shown in literature during heat treatments whereby the titania is crystallized<sup>1</sup>. This increased porosity lowers the RI to a value of 1.91. With the combination of the two sol-gels, as previously discussed, the RI of the hybrid can be set near 1.64. The analysis of the XPS narrow scan spectra confirmed of the formation of silica and titania chemical compounds in the hybrid sol-gel coating.

### ***Transmission***

In the present research, the original transmission in the range of 1000-5000nm wavelengths is 61.9%, Figure 2. As shown in Figure 14, the coating enhances the transmission at the first key wavelength of 1500-1600nm to 78%. The middle area at 3 micrometer there is a dip in transmission due to absorption. The band's range 3100-3600 cm<sup>-1</sup> corresponds to the stretching vibration of O-H in hydroxyl groups. The absorption can be blamed on residual alcohol solvent used in sol-gel preparation and H<sub>2</sub>O which is used in the preparation and adsorbed from atmospheric moisture. The absorption can be decreased through heat treatments, but no heat treatments are used in the present research. The convenient location of the peak, not at a key wavelength of interest, allows for the continuation of research without solving this problem. The substrate/film matching is not flawless, but still yields an increase in transmission. At the next wavelength of interest, 3500-5000nm, the increase is very significant. The matching of the

substrate and the film is much better here, increasing transmission 22.6%, yielding 84.5% total transmission. In comparison, a typical fused silica glass system with a base transmission of ~90% is increased to a coating with a final transmission of 99.5% at one particular wavelength and an average that seems closer to 94%<sup>16</sup>. The increase in the fused silica glass system even at its highest point was only 9%, giving perspective to the incredible 22.6% increase shown in the chalcogenide system. Due to the higher strength requirements of a single coating, prepared presently, the transmission will be sacrificed slightly.

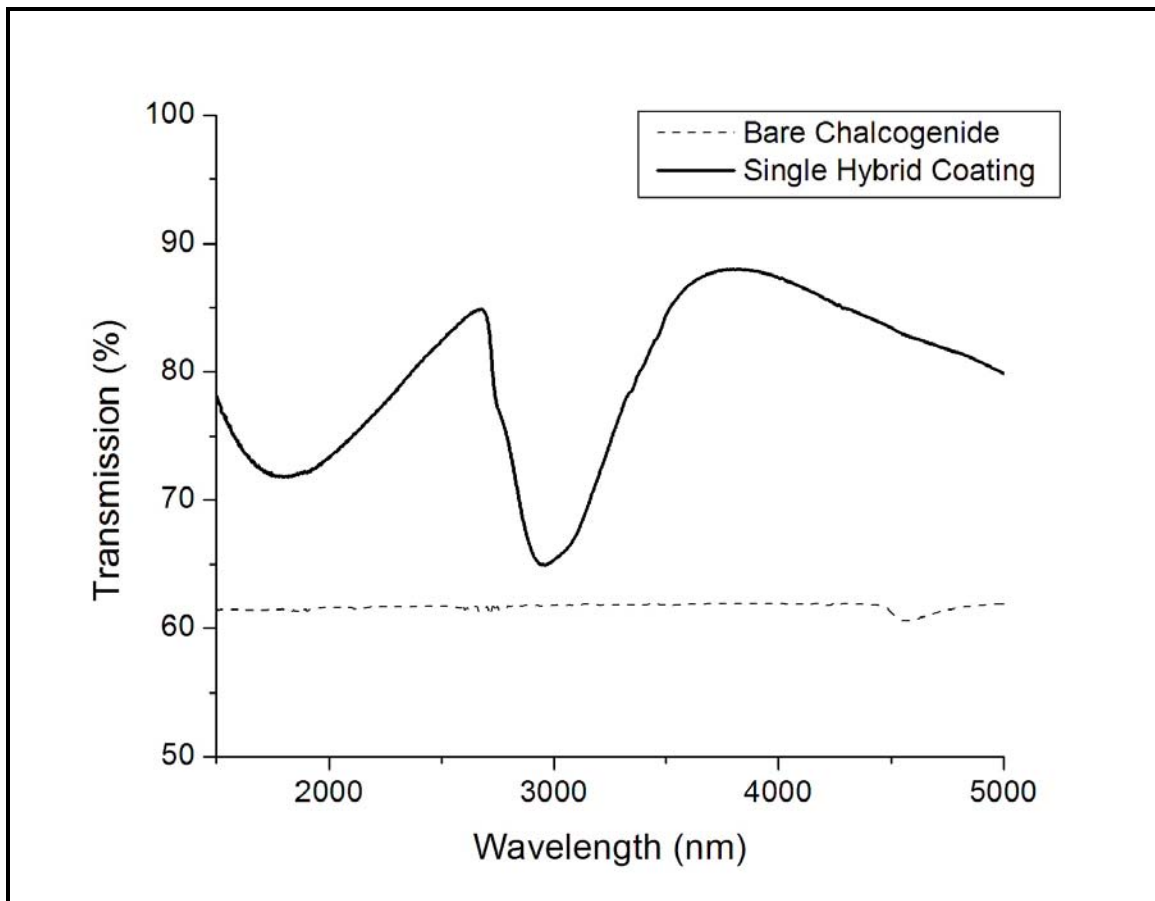


Figure 14: Anti-reflective coating on chalcogenide glass

The ability of a coating to perform within one week of its original creation is an important step in the development of a successful coating. However, it is more relevant to view

the functioning of a coating several weeks after its initial application and testing. It is the intrinsic nature of a sol-gel to relax over time, slowly releasing moisture and solidifying the network bonding further. The first step towards aging is denoted as polymerization and represented by the condensation reaction  $\equiv\text{Si}-\text{OH} + \text{HO}-\text{Si}\equiv \rightarrow \equiv\text{Si}-\text{O}-\text{Si}\equiv + \text{H}_2\text{O}$  which link up the initial network<sup>23</sup>. Following polymerization, hydrolysis occurs which further strengthens the network. Hydrolysis is shown here by the reaction  $\equiv\text{Si}-\text{OR} + \text{H}_2\text{O} \rightarrow \equiv\text{Si}-\text{OH} + \text{ROH}$ <sup>24</sup>. The coating shown in Figure 14 was allowed to age unobstructed in ambient storage for two weeks and then tested. The relaxation of the film with aging presumably involves densification and thinning of the film<sup>25</sup>. The densification process is mediated by bond cleavage due to the movement of electrons from the valence band to the conduction<sup>23</sup>. The movement leads to the rearrangement of the gel network through the condensation reaction which causes densification. This densification changes the phase cancellation properties of the reflected waves affected each of the wavelengths differently.

Other experimental results yielded excellent transmission in one of the two regions of interest, but not both. These coatings were 2 and 3 layer versions of the same hybrid coating on chalcogenide substrate. The double coating of the hybrid was done using three different aging times for the sol-gel solution to produce thin, medium, and thick layer thicknesses. The 3 layer was done at only one thickness as the limit to the defect free coating was being tested with this thick of a coating. Shown in Figure 15, the transmission is approaching 95% at the first wavelength of interest for all of the double layer coatings. Each of these was offset slightly from the last due to the increased

thickness. The three layer coating approaches 98% transmission, but is away from a wavelength of interest. Also displayed in Figure 15 is the comparison to the single layer coating. The optimization of the coating thickness would be an important next step to the design.

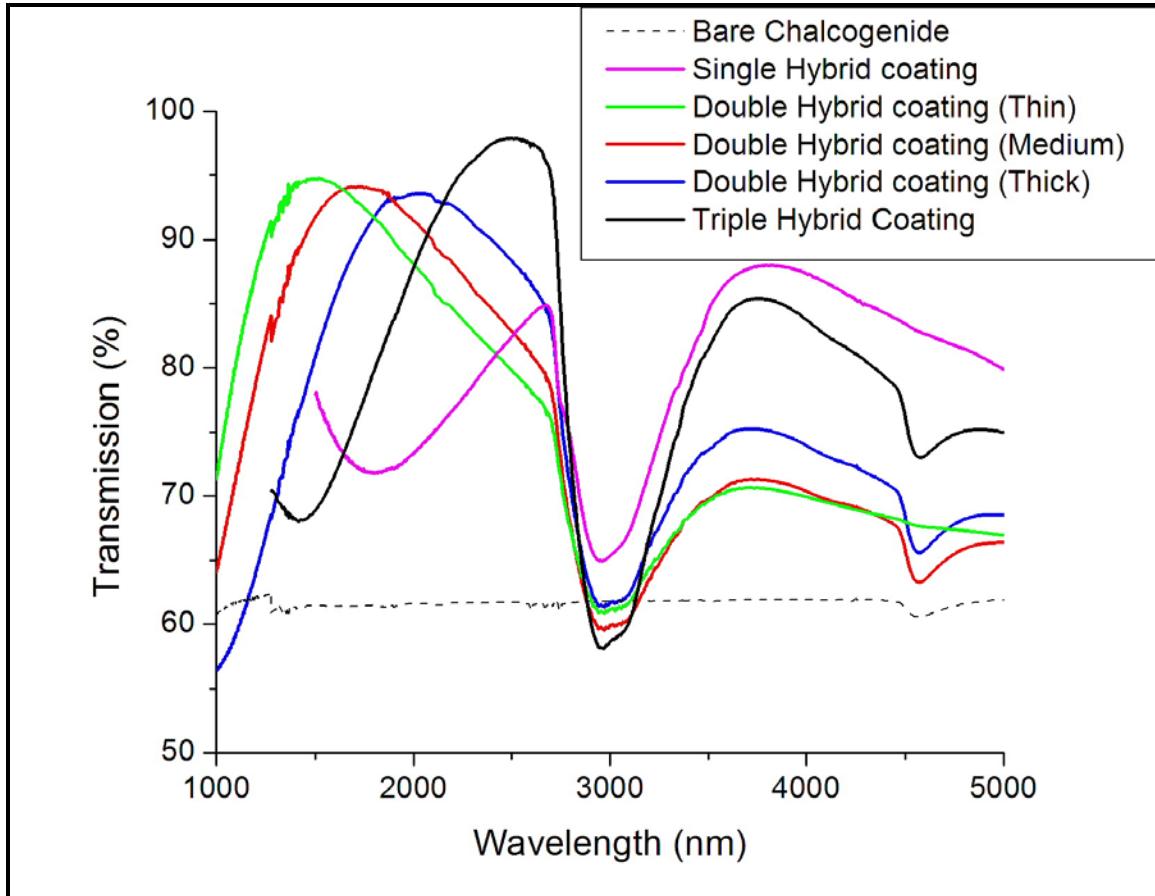


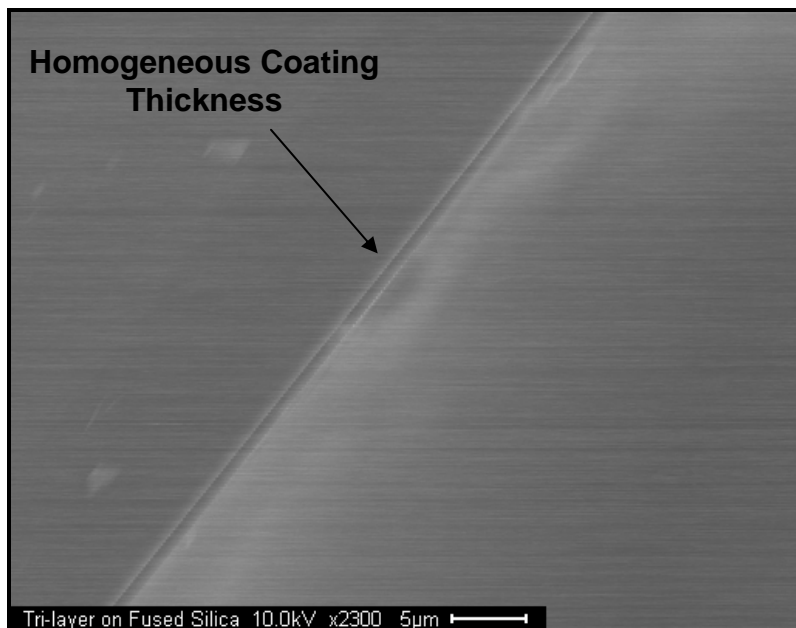
Figure 15: One, two, and three layer coatings on chalcogenide

## MULTI-LAYER AND GRADED INDEX

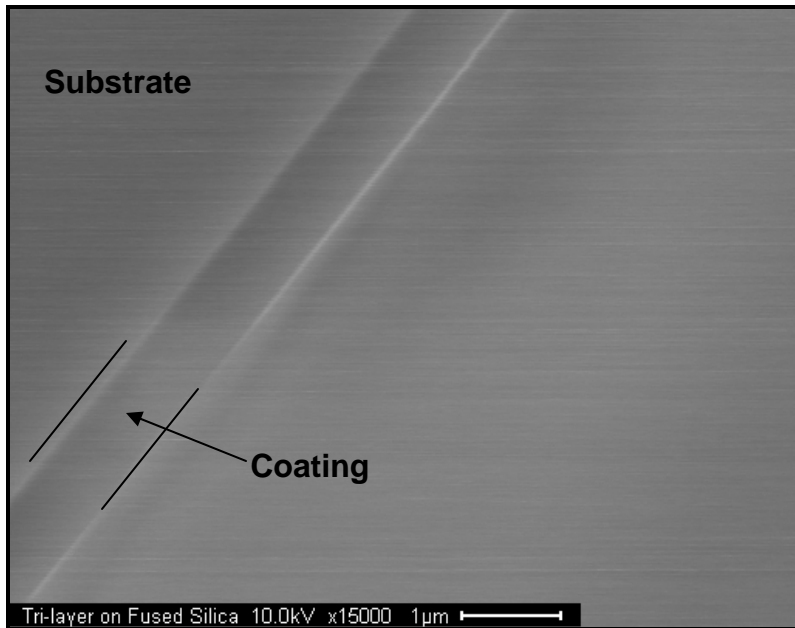
The concept of square wave transmission spectra through the use of multi-layers of different materials is very enticing. Multi-layer anti-reflective coating consists of an alternating combination of materials of low refractive index and high refractive index. Specifically, the layer closest to the substrate would be the expected  $\frac{1}{4}$  wavelength incident light thickness and square root of the refractive index of the coating. The next layer, however, is a very high refractive index of  $\frac{1}{2}$  wave incident light thickness or more. In doing this, the layer becomes transparent acts as a pseudo substrate. The next layer would consist of a coating that would match the thick layer previous in  $\frac{1}{4}$  wavelength and square root refractive index. This would continue for any number of layers until the range of anti-reflection was expanded sufficiently. The final layer of the coating would always be the lowest refractive index possible, completing the design. The theory of multi-layer anti-reflective coatings is well known and explained in greater detail elsewhere, but it's the extension of this theory that is of most application to the findings of this research.

A typical multi-layer coating consists of the steps described above, but through the addition of a series of coatings that grade, or step, the refractive index upward from the first layer to the layer of high refractive index, an extremely broadband coating can be applied. In addition, this type of coating performs well with light at angles of incidence not normal to the surface. In simulations, graded index coatings are created with many layers, sometimes as many as 50. This is not feasible for either cost or time and even a 20 layer coating can be many micrometers thick, far beyond the capability of sol-gel. The concept of graded index does, however, have great

possibility using sol-gel methods and during the course of research this was stumbled upon. In Figure 16, a Scanning Electron Micrograph of a cross-section of a 3 layer coating is shown. Figure 17 is a further magnified view of this multi-layer coating. The first noticeable feature is the interface between the substrate and the coating. The next is the lack of interfaces between the layers of the coating. Being 750nm thick, the coating should show 3 separate layers at 250nm and 500nm positions. The lack of interfaces allows the assumption that there is an intermixing between the layers even if allowed to relax between applications of each. This intermixing is not significant, but the absence of interfaces makes the possibility of a graded index a reality.



**Figure 16: Showing a 2300x micrograph of the 3 layer sol-gel coating on fused silica**



**Figure 17: Showing a 15000x micrograph of the 3 layer sol-gel coating on fused silica**

Due to the limitations of minimum layer thickness that can be applied using sol-gel solutions, there is a maximum number of layers that can be applied without defects arising or mechanical stability degrading. This number can be as high as 20 when using heat treatments and their densification. Using a more reasonable number of 10 layers, the graded index coating can be theoretically developed. The application of a starting layer using the square root refractive index theory and  $\frac{1}{4}$  wavelength optical thickness theory is followed by 6 layers of graded index from the refractive index of the first layer to that of the highest layer will bring the total to 7 layers. The layer of high refractive index would make a total of 8 layers. The final two layers would be 1.4 and 1.2, respectively for a total of 10 layers. This discussion was carried out in full illustrate that the feasibility of applying a 10 layer coating exists and through its creation the extreme broadband nature of graded index can be realized within the sol-gel methods.



## CONCLUSION

The nano-porous nature is tunable to certain refractive index values by changing the sol-gel chemistry and aging times. The nano-particles can be created in different sizes so that they act like sub-wavelength structures making the coatings broadband. There are even possibilities of graded index coatings for better anti-reflection at higher angles of incidence. Each of these reasons supports the need for further study into sol-gel coatings for anti-reflective properties.

The results shown with the fused silica substrate are an excellent example of a very close realization of the theory for a particular coating system. The chalcogenide system showed great results with over 20% increase in transmission at some points. The success of this research has helped us understand the feasibility of better anti-reflective coatings in the near infrared region of light and the progress we have already made.

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