Design and fabrication of multilayer thin film coated hollow waveguides for enhanced infrared radiation delivery

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ABSTRACT

Metal coated Hollow Glass Waveguides (HGWs) incorporating single dielectric thin films have been widely used for the low-loss transmission of infrared radiation in applications ranging from surgery to spectroscopy. While the incorporation of single dielectric film designs have traditionally been used in metal/dielectric coated HGWs, recent research has focused on the development of alternating low/high refractive index multilayer dielectric thin film stacks for further transmission loss reduction. Continuing advances in the deposition of optically functional cadmium sulfide and lead sulfide thin films in HGWs have allowed for the simultaneous increase in film quality and greater film thickness control necessary for the implication of such multilayer stack designs for enhanced reflectivity at infrared wavelengths. This study focuses on the theoretical and practical considerations in the development of such multilayer stack coated waveguides and presents novel results including film growth kinetics of multilayer stack thin film materials, IR spectroscopic analysis, and IR laser attenuation measurements. The effects of incorporating progressive alternating cadmium sulfide and lead sulfide dielectric thin films on the optical properties of next generation dielectric thin film stack coated HGWs in the near and mid infrared regions are thoroughly presented. The implications of incorporating such dielectric multilayer stack coatings based on metal sulfide thin films on the future of IR transmitting hollow waveguides for use in applications ranging from spectroscopy, to high laser power delivery are briefly discussed.

Keywords: Infrared fiber optics, hollow waveguides, multilayer dielectric thin film designs, optical materials

1. INTRODUCTION

Hollow glass waveguides (HGWs) have experienced widespread success in the low-loss, broadband delivery of infrared radiation across the $\lambda = 2 - 12$ μm region and have thus been used in a variety of applications ranging from photothermal imaging to infrared spectroscopy.[1] Traditionally, the functional structure of HGWs has relied on light propagation within a hollow fused silica capillary of predetermined, constant dimensionality whose inner surface is coated with a silver film followed by a single dielectric thin film of adequate thickness to enhance reflectivity of the inner HGW surface, thus allowing for low-loss propagation of infrared radiation along the waveguide length. In HGWs, the loss achieved depends on a number of factors, most importantly the waveguide bore size, the surface quality of the deposited metal and dielectric films, the transparency of the dielectric thin film material, the film thickness of the dielectric thin film, and the degree of bending that the waveguide is subjected to. Theoretically and experimentally, the propagation loss in HGWs has been shown to increase as $1/a^3$ where a is the bore radius and upon bending as $1/R$ where R is the radius of curvature.[1,2] While current Ag/AgI HGWs are capable of achieving acceptable transmission losses for most applications, as is the case in any transmissive system, it is desirable to further decrease propagation losses of passive components, in this case the waveguide. In order to decrease the waveguide loss, one must first look at the waveguide components which influence the attenuation. Eq. 1 is the geometrical optics equation for the power attenuation coefficient of meridional rays propagating in a straight, constant bore HGW.[3]

$$2\alpha(\theta) = \frac{1 - R(\theta)}{2a\,cot(\theta)} \tag{1}$$

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where a is the bore radius, θ is the angle of propagation of the light ray, and $R(θ)$ is the reflectance of the inner HGW surface, which of course depends on the angle of propagation, the film structure, and the polarization of light. While either the bore size can be increased, or the propagation angle may be decreased to lower the loss, in practice it is often not desirable to do so for various reasons (ie. to achieve a desired propagating mode or to enable the waveguide to have flexibility). Therefore, the loss must be decreased in another manner, namely in increasing the surface reflectivity.[1-3]

In considering the possibilities, perhaps the most practical manner to modify the HGW surface structure so as to increase reflectivity is through the incorporation of multilayer dielectric thin film stacks with layers composed of alternating low and high refractive index materials in place of the traditional single dielectric layer, as shown in Fig. 1.
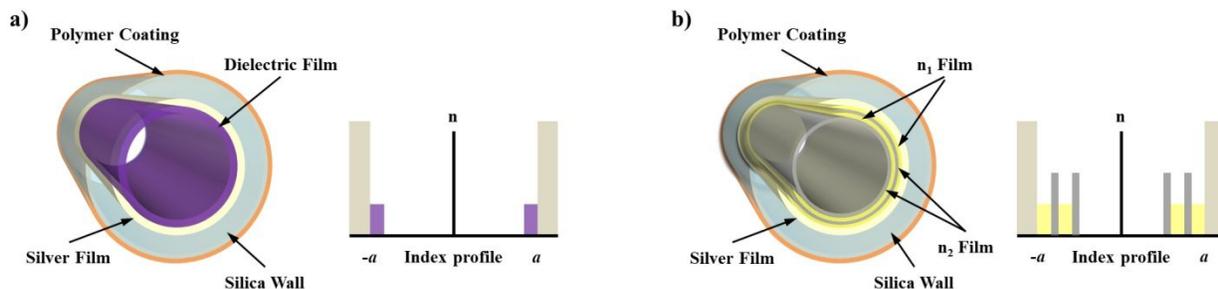

Figure 1 – Representative cross-sections of a) single dielectric layer and b) multilayer dielectric stack HGWs

By optimizing the thin film thickness of each of the dielectric layers depending on the desired wavelength range of operation, it is theoretically possible to increase the reflectivity, and thus lower the transmission loss, to a level beyond that attainable through the use of any single dielectric layer. To increase the reflectivity of such a multilayer structure, one can either increase the number of total layers or increase the refractive index mismatch between the two dielectric materials for a given number of layers. The dielectric materials must thus be carefully selected and must be transparent at the wavelength(s) of operation. To date, our laboratory has had considerable success in the deposition of metal sulfide, particularly CdS and PbS thin films, in HGWs using fabrication methods similar to those used for the fabrication of Ag/AgI HGWs.[4-6] The combined IR transparency, mechanical and chemical compatibility, and considerable index mismatch ($n_{CdS} \approx 2.28$ / $n_{PbS} \approx 4.00$) between CdS and PbS make these two materials ideal for use in the fabrication of enhanced reflectivity next generation multilayer dielectric stack HGWs.[1,7,8]

2. THEORETICAL CONSIDERATIONS

2.1 Theory and Design of Multilayer Film Structures

Multilayer dielectric stacks consisting of a periodic arrangement of alternating low and high refractive index materials are capable of producing high reflectivity while simultaneously exhibiting minimal absorption. Such designs have been widely used in a number of applications ranging from selective filters to high efficiency dielectric mirrors to 1-D photonic bandgap devices.[8,9] A representative diagram of such a multilayer dielectric stack is given in Figure 2.
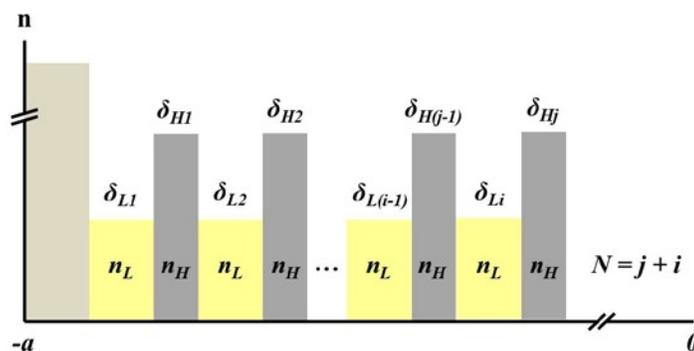

Figure 2 – Representative diagram of periodic multilayer dielectric stack

In order to achieve the desired reflectivity, the physical dimensions of each individual dielectric layer, δ_L / δ_H, must be such that its optical thickness is a quarter-wavelength thick depending on the target wavelength and angle of incidence (compliment of propagation angle). By controlling the individual film thicknesses and obtaining the desired layer dimensions, coherent scattering from each subsequent interface results in constructive interference of reflected light and thus an enhancement in reflectance. As previously mentioned, the reflectance may be increased in any of several different manners including increasing the total number of layers, N, and/or selecting dielectric materials with a larger refractive index mismatch. When optimizing the individual layer thicknesses for $\lambda = 1.0$ μm, a CdS film thickness of 122 nm ($n_{CdS} = 2.28$ at $\lambda = 1.0$ μm) and a PbS film thickness of 58 nm ($n_{PbS} = 4.43$ at $\lambda = 1.0$ μm) are necessary.[1,2,8,9]

2.2 Multilayer Stack Calculations

Calculation of the reflectance achieved by a stack of dielectric thin films can be calculated in several methods. For this particular study, reflectance was calculated using the ray transfer matrix method due to its versatility in accounting for varying influential parameters including the polarization of light, the angle of incidence, the total number of layers, the optical properties of each of the materials, and the thickness of each individual layer. The ray transfer matrix method is a numerical method for determining the optical response of such a system and its fundamental function lies with Eq. 2.

$$\begin{bmatrix} E_z \\ H_z \end{bmatrix} = \prod_{i=1}^{N} \begin{bmatrix} A_i & B_i \\ C_i & D_i \end{bmatrix} \begin{bmatrix} E_0 \\ H_0 \end{bmatrix} \tag{2}$$

where E is the amplitude of the electric field, H is the amplitude of the magnetic field, A, B, C, D are the characteristic matrix coefficients, and N is the total number of layers.[9] Using this method, the electric and magnetic field amplitudes at any point z along the axis of propagation (normal to interface) may be calculated and compared to the initial amplitudes to determine the reflection and transmission of the system. Calculations carried out in this manner yielded the optical responses presented in Figure 3 for the particular multilayer stack system under investigation with increasing number of total layers in the stack.
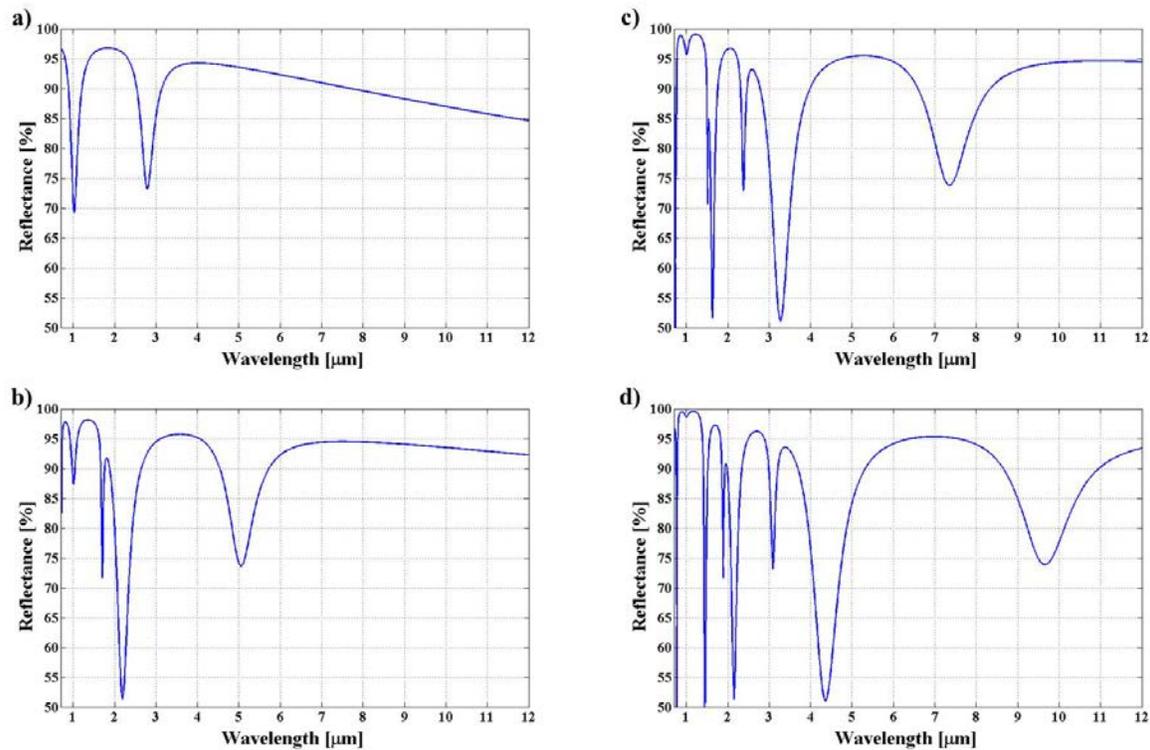

Figure 3 – IR reflectance as a function of total number of layers optimized for $\lambda = 1.0$ μm with a) N = 2, b) N = 4, c) N = 6, d) N = 8

From Figure 3, it can be seen that the reflectance does indeed increase at the target wavelength ($\lambda = 1.0 \, \mu m$), as the total number of CdS/PbS alternating layers increases. For this calculation, the ideal case was assumed with no surface roughness related scattering losses and; $n_L = 2.28$, $n_H = 4.43$, $\delta_L = 122$ nm, $\delta_H = 58$ nm, and $\theta_i = 87.5°$ ($\theta_p = 2.5°$).[7] If surface roughness can be neglected and the number of layers continues to maintain its ideal periodicity, the structure will eventually lead to the emergence of a photonic bandgap at the design wavelength as the number of layers is increased.[8]

3. FABRICATION METHODOLOGY

The fabrication of metal / dielectric HGWs involves the controlled deposition of the desired material on the inner fused silica capillary surface from precursor containing aqueous solutions via dynamic liquid phase deposition (DLPD). DLPD is a versatile technique similar in nature to chemical bath deposition (CBD) in which synthesis of a desired material on the substrate surface is achieved via electroless chemical reaction between precursor containing aqueous solutions. However, unlike CBD, DLPD has the advantages of a higher degree of control over the thickness of the deposited thin film and, given that the precursor solutions are continuously being simultaneously pumped through the fused capillary, film growth is not limited by depletion of reactive species in solution. The DLPD process involves simultaneous pumping of precursor containing solutions at equal rates through the silica capillary using a peristaltic pump. The quality and thickness of the films depends on several parameters including solution concentrations, solution temperature, reactivity of precursor species, total procedure time, and fluid flow velocity. In practice, it is desirable to minimize variables during the fabrication process and thus the solution concentration and temperature, as well as the fluid flow speed are kept constant regardless of the dimensions of the silica capillary or type of procedure being carried out. Experimentally, optimal quality thin films have been deposited through the entire waveguide length at fluid flow speeds around 70 cm/s and thus the pump rate is programmed to allow for the corresponding volumetric flow rate to be achieved for any HGW bore size and length. In this particular study all experimental samples had a bore size of 700 μm and were initially approximately 220 cm long, corresponding to an optimal volumetric flow rate of 16.2 mL/min. Using this standard volumetric pump rate, the silver film was deposited, followed by either a cadmiums sulfide (CdS) or lead sulfide (PbS) dielectric thin film and so on.

3.1 Deposition of Silver Films

As previously mentioned, the reflective Ag film is deposited on the inner fused silica capillary via DLPD as a result of an electroless red-ox reaction between a complexed silver ion and a reducing solution. Prior to depositing the Ag layer, samples undergo a simple sensitization procedure which involves flowing an acidic tin (II) chloride solution having a concentration of 0.35 g/L [Sn(II)Cl$_2 \cdot$ 2H$_2$O] for a total of five minutes. This allows replacement of surface hydroxyl species and adsorption of active tin (II) ion species on the silica surface, thus improving the film quality of the subsequently deposited Ag film and drastically reducing the procedure time necessary for obtaining a silver film greater than 200 nm thick. After the sensitization procedure, reducing dextrose and ammonia-complexed silver ion solutions are simultaneously pumped through the silica capillary, depositing a silver film on the silica surface substrate. The concentrations of the precursor solutions involve 0.56 g/L of dextrose for the reducing solution and 2.44 g/L of silver (I) nitrate along with approximately 15 mL/L of NH$_4$OH and 44 mL/L of NaOH for the active silver ion solution. The procedure is continued for as long as necessary, keeping in mind that too thin of a silver film will lead to light penetration through the film while an excessively thick film will result in unnecessary and unwanted increase in surface roughness and related scattering losses. In practice, the silver film deposition procedure is carried out at 20 °C, resulting in a necessary deposition time of 15 min to achieve silver films thicker than 200 nm while simultaneously minimizing surface roughness and thus its detrimental effects.

3.2 Deposition of Metal Sulfide Dielectric Films

After deposition of the Ag film, the reflectivity enhancing dielectric film, or as in the case of this study films, is/are deposited via DLPD methods. As for the silver deposition procedure, the metal ion precursor solution must be complexed in solution so as to achieve a high degree of control over the rate of film growth.[10,11] In the case of CdS deposition this involves preparation of an ammonia-complexed cadmium (II) ion solution at a standard concentration of 4.55 g/L of Cd(NO$_3$)$_2 \cdot$4H$_2$O along with 150 mL/L of NH$_4$OH. In the case of PbS deposition this then involves preparation of a hydroxide-complexed lead (II) ion solution at a standard concentration of 1.80 g/L of Pb (NO$_3$)$_2$ along with 9 g/L of NaOH. The reducing solution for both procedures involves a thiourea solution at concentrations of 11.418 g/L and 4.141 g/L, when depositing CdS and PbS, respectively. All solutions are heated to 30 °C and kept at this

temperature (± 1 °C) in a water bath throughout the entire deposition procedure. Holding all other fabrication parameters constant, the dielectric thin film thickness is controlled by modulating the total deposition procedure time, with thicker films being deposited as deposition time increases. Thus, in order to achieve a high degree of control over the deposited thin film thickness, the film deposition kinetics (in particular the film growth rate), must be known. Depending on the overall film structure desired and the wavelength of operation, the metal sulfide deposition procedure is repeated as many times as desired, with each metal sulfide (CdS or PbS) being deposited every other deposition procedure in order to achieve the alternating low / high refractive index profile. In practice, it should be noted that the fabrication of a larger number of layers leads to decreased film quality and performance as a result of increasing surface roughness and its exponentially detrimental effect on light propagation. The same is true of very thick single CdS or PbS films, thus limiting their practical use to SWIR and MWIR wavelengths. In this study, prior to fabrication of multilayered CdS / PbS HGWs, the deposition kinetics for each procedure was experimentally studied in order to achieve the desirable CdS and PbS film thicknesses and will be presented in the proceeding section.

4. MEASUREMENTS AND OPTIMIZATION

4.1 Determination of Thin Film Growth Kinetics

Initial analysis involved experimental determination of the thin film growth kinetics of the different procedures involved in the proposed fabrication of CdS / PbS multilayer thin film stacks. As such, four 220 cm long Ag coated HGWs were prepared and either CdS, PbS, or both were deposited using the standard solution concentrations and temperatures given in the preceding section. The first of these guides was coated with CdS for a total of 210 min with 12 cm segments being cut and collected from the output end of the waveguide at 15 min intervals in order to investigate the deposition kinetics of CdS on an Ag coated HGW (Ag substrate). The second of these guides was coated with PbS for a total of 70 min with 12 cm segments being cut and collected from the output end of the waveguide at 5 min intervals in order to investigate the deposition kinetics of PbS on an Ag coated HGW (Ag substrate). The third sample was then coated with PbS for 25 min in its entirety after which CdS was deposited for a total of 150 min with 12 cm segments being cut and collected from the output end of the waveguide at 15 min intervals in order to investigate the deposition kinetics of CdS on an Ag/PbS coated HGW (PbS substrate). The final sample was then coated with CdS for 155 min in its entirety after which PbS was deposited for a total of 37 min with 12 cm segments being cut and collected from the output end of the waveguide at 4 min intervals in order to investigate the deposition kinetics of PbS on an Ag/CdS coated HGW (CdS substrate). All fabricated samples where then analyzed using a Bruker Tensor 37 FTIR in conjunction with a cryogenic Teledyne / Judson MCT detector in order to obtain the spectral response from $\lambda = 2.0 – 15.0$ μm. As expected, the spectral response shifted to longer wavelengths with increasing total deposition time (film thickness). In order to obtain the film growth kinetics, the dielectric film thickness of each sample was calculated using Eq.3.

$$\delta_F = \frac{\lambda_p}{4\sqrt{n_F{}^2 - 1}} \tag{3}$$

where λ_p is the centroid wavelength of the first interference peak and n_F is the refractive index of the dielectric material at $\lambda = \lambda_p$. Through this methodology, the deposited film thickness as a function of deposition time for each of the four procedures was calculated and the resulting measurements, along with the linear fit in each case is given in Figure 4.
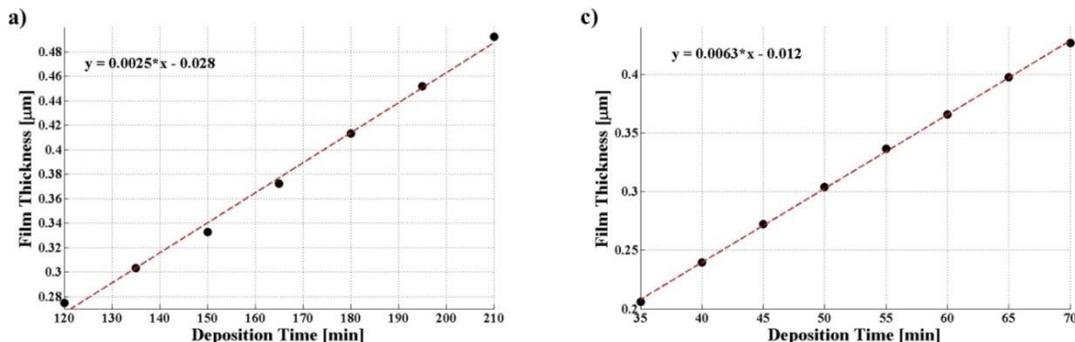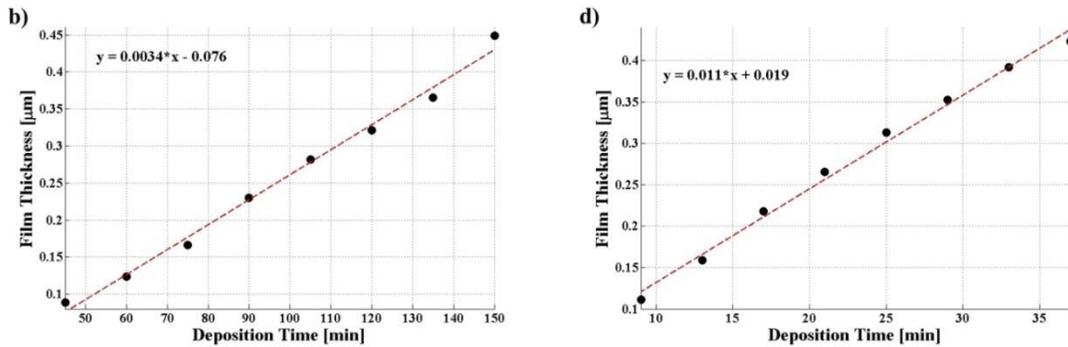
Figure 4 – Film Thickness as a function of time for a) CdS on Ag, b) CdS on PbS, c) PbS on Ag, and d) PbS on CdS

From the film growth data presented in Figure 4 several things can be noted. First, it is interesting to note that there is considerable difference (particularly for PbS) in the film growth rates depending on the substrate with a difference of 0.9 nm/min and 4.7 nm/min for CdS and PbS, respectively. Furthermore, it can be seem that a higher degree of variability in film thickness occurs when the substrate is the alternate metal sulfide, rather than silver. It can be seen that the fastest film growth occurs for the case of PbS on CdS at 11.0 nm/min, while the slowest film growth occurs for the case of CdS on Ag at 2.5 nm/min. The considerably higher deposition times necessary for depositing CdS arises from the two step reaction process of converting deposited cadmium hydroxide to CdS rather than the direct deposition of PbS from aqueous solutions.[10,11] Consequently, optimization of CdS thin films for longer wavelengths requires thicker films, longer deposition times, and a greater probability of low film quality and increased surface roughness. Thus, in practice, the overall film structure, and thus the wavelength of optimization, is restriction by the limitations of CdS films. After analyzing the deposition kinetics data, it was decided that the film structure for this particular study would be optimized for λ = 1.0 μm, requiring individual film thicknesses of 122 nm and 58 nm for CdS and PbS, respectively. These desired film thicknesses are predicted to require deposition times of 60 min for CdS on Ag, 100 min for CdS on PbS, 12 min for PbS on Ag, and 8 min for PbS on CdS.

4.2 Spectroscopic Analysis

The metal sulfide multilayer dielectric stack coated HGWs analyzed in this study consisted of individual CdS and PbS film thicknesses optimized for λ = 1.0 μm, requiring a CdS film thickness of 122 nm and a PbS film thickness of 58 nm. The 220 cm multilayer sample fabricated in this study was first coated with a silver layer using the aforementioned standard silver film deposition procedure. The CdS / PbS multilayer stack was then fabricated one additional film at a time, alternating between CdS and PbS and having have had started with CdS for the first film. After each subsequent deposition procedure, the straight loss at λ = 10.6 μm was tested and a 12 cm segment was taken off the end of the waveguide for spectroscopic analysis. The next coating procedure was then carried out on the longer remaining segment and this methodology was continued for as long as possible until a final waveguide length of less than 80 cm. The spectral response from λ = 2.0 – 15.0 was taken with an FTIR spectrometer to track changes in the optical response as a function of additional layers as well as to determine the actual film thickness of the last film deposited. Using this methodology, a total of 10 (N = 10) alternating CdS/PbS layers were deposited before the optical response in this region became too low for qualitative and quantitative analysis. The spectral response for select total number of layers is presented in Figure 5.
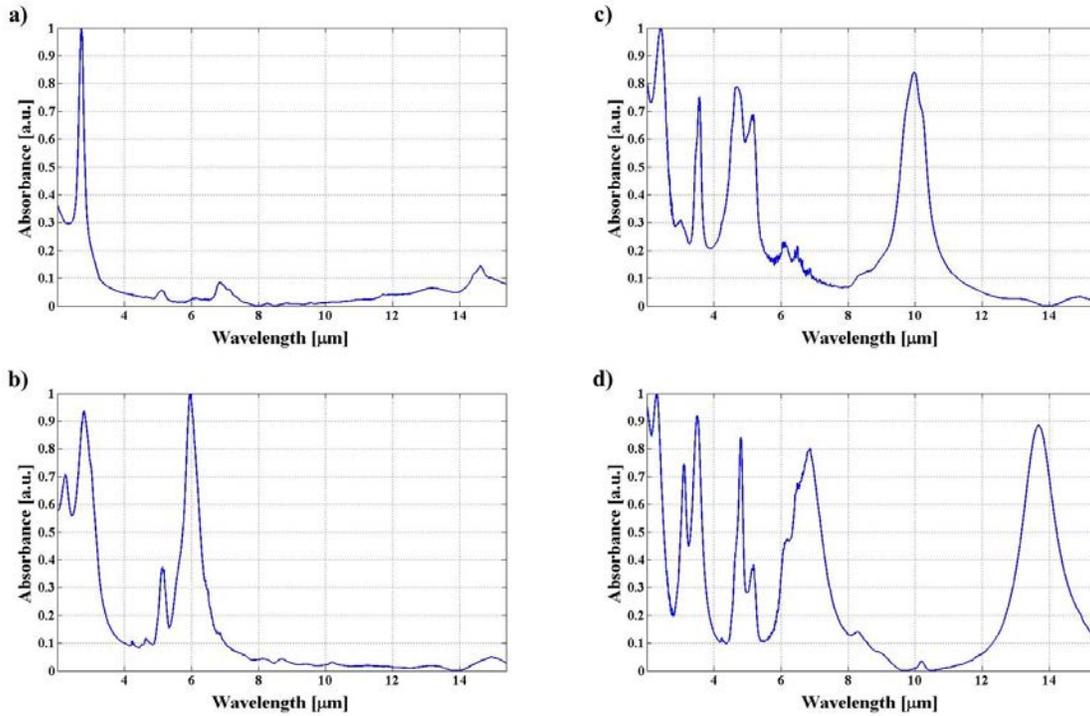
Figure 5 – IR optical response as a function of deposited layers for a) N = 2, b) N = 4, c) N = 6, and d) N = 8

From the spectral response of these CdS/PbS multilayer stack HGWs it can be seen that high quality, optically functional dielectric film stacks have been successfully deposited. The ability to deposit up to 10 layers while maintaining a high degree of film quality denotes a great deal of improvement over previous attempts, which have been successfully in depositing up to 5 to 6 films before film quality degraded to the point of failing to obtain a clear spectral response. This achievement shows that through the proposed methodology, a greater degree of control over the film thickness can be achieved while maintaining high quality films for up to a total of 10 layers.

4.3 Attenuation Measurements

As mentioned earlier, in addition to obtaining the spectral response of the sample after each subsequent metal sulfide deposition, the straight waveguide loss was also measured at $\lambda = 10.6$ μm using a Synrad I-series 15 W max output CW CO_2 laser. Obtaining the attenuation in this manner allowed for straight transmission loss as a function of total layers deposited to be obtained at this important IR wavelength. The resulting attenuation measured for up to a total of 10 layers is given in Figure 6.a for analysis.
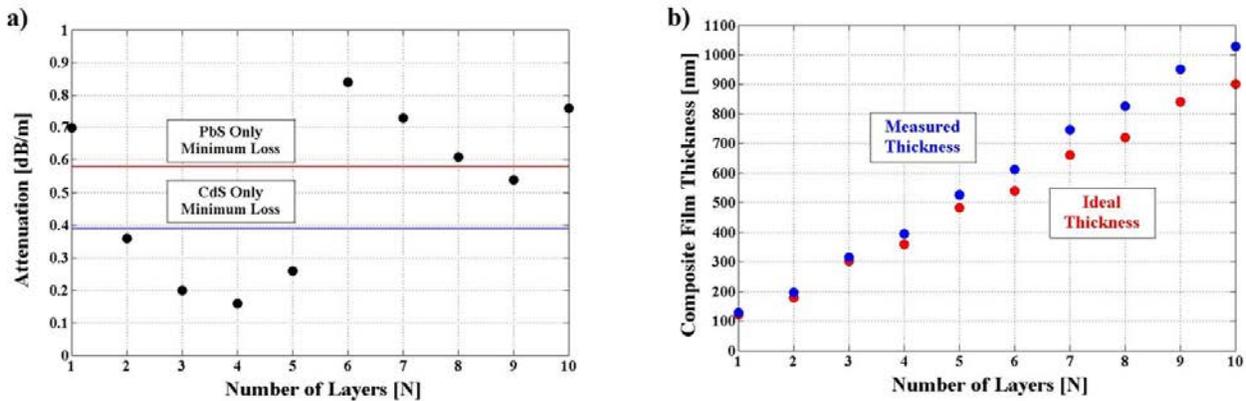

Figure 6 – a) Attenuation and b) composite film thickness as a function of total number of layers

As given in Figure 6.a, it is seen that the attenuation does indeed decrease with an increase in total number of layers as would be expected for the case of an ideal multilayer dielectric stack. The loss is the lowest at a total of N = 4 alternating CdS/PbS layers but then rises once more, jumping considerably at N = 6. It is then seen to decrease at a rather steady rate until N = 9 before going back up at N = 10. From the spectral response, the substantial increase in attenuation around N = 6 can be attributed to the first absorbance peak, which pushes the loss up as it shifts in the vicinity of λ = 10.6 μm. The increased loss for a larger number of total layers N > 6 could be attributed to a decrease in film quality resulting from an increase in surface roughness and related scattering losses. It is important however to note that for N = 2 – 5, the measured loss drops significantly and is lower than that obtained with any single dielectric film for this particular bore size. As such, increasing the number of layers can be seen to successfully decrease transmission losses by a considerable amount (nearly by a factor of 2 at N = 4).

At the same time, we can see from Figure 6.b that the measured composite film thickness deviates from the optimized composite film thickness as the measured thickness is consistently higher than ideal and as would be logical, continues to deviate from the ideal as the number of total layers increases. The difference between measured and ideal film thicknesses is seen to be small up to N = 4 after which point it continues deviating further, resulting in a considerable difference for a larger number of layers. This deviation from the ideal composite film thickness can be expected to further contribute to higher losses with a larger number of films as the structure begins to deviate from having the desired periodicity. As such, a greater degree of control over the individual film thicknesses must be obtained in order to truly optimize the thin film structures for any given wavelength. Furthermore, while unable to do so in this particular study, losses should be measured at the target wavelength (λ = 1.0 μm) rather than at a different wavelength. Albeit this variation, it is noteworthy to see that through the use of CdS/PbS multilayer stack HGWs the loss at λ = 10.6 μm can in fact be decreased relative to using a single dielectric layer, whether it be CdS, PbS, or AgI.

5. SUMMARY AND CONCLUSIONS

This study was successfully in further investigating the theoretical and experimental results of CdS/PbS multilayer dielectric stacks in HGWs at infrared wavelengths. Specifically, the argument for incorporating multilayer dielectric stacks in HGWs in place of single dielectric films for enhanced performance next generation HGWs was made, and the proposed structure was analyzed through numerical methods through use of the transfer matrix method. Calculations based on theory confirmed that the loss could indeed be expected to decrease as reflectance was enhanced with less than a dozen layers. Experimental work focused on the initial determination of an empirical film growth kinetics relationship for the deposition of CdS and PbS films on Ag and the alternate metal sulfide as substrate. The film growth rate was seen to be nearly linear for the deposition times selected and was determined to be highly dependent on the species being deposited as well as the substrate species. Following empirical derivation of the metal sulfide film growth kinetics, deposition of CdS/PbS multilayer stack designs in HGWs were attempted using the appropriate deposition times suggested by the empirical film growth relationships. The deposition of metal sulfide multilayer stacks in HGWs was shown to be successful as supported by the high quality of the spectral response obtained (up to N = 10), and the acceptable losses measured. Furthermore, the multilayer design presented in this study achieved losses lower than previously recorder for any single dielectric layer HGW for certain number of total films (N = 3 – 4). This study has set the foundation for more in depth study and optimization of next generation CdS/PbS multilayer stack HGW designs. Further study of these novel designs in HGWs will involve further control of the deposition procedure in order to more closely approach the ideal individual film thicknesses as well as focusing measurements at the target wavelength.

6. ACKNOWLEDGEMENTS

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