Multilayer thin film coatings for reduced infrared loss in hollow glass waveguides

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ABSTRACT

Hollow glass waveguides (HGWs) are an attractive alternative to traditional solid-core and 2D photonic crystal, infrared transmissive fibers. Applications for HGWs at wavelengths longer than 2 microns include use of the guides for the delivery of laser power and for use as chemical and thermal sensors. To date, the most common HGW is one with an inner coating of Ag followed by a single-dielectric layer of AgI. These single-layer dielectric coated HGWs have losses for a 700-micron bore guide as low as 0.2 dB/m at 10.6 microns. However, if a multilayer stack of alternating high/low index thin films is deposited instead of a single dielectric layer then the loss can be reduced substantially. In the present study, multilayer dielectric thin films have been deposited inside silica tubing using a liquid-phase deposition method. High index coating materials used include metal sulfides such as PbS while the low index materials include polystyrene (PS) and some sulfides. To date it has been possible to deposit two-layer coatings using, for example, CdS and PS but a lower loss is possible if the coating stack is composed of three dielectric layers. In past work CdS/PbS/CdS coatings were deposited and found to have a measured a loss at $\lambda = 10.6$ microns that is approximately two times lower than that for a single dielectric layer. In this paper the theory of multilayer coatings will be presented along with the optical loss measurements from $\lambda = 2$ to 12 microns for the multilayer dielectric coatings.

Keywords: Infrared fiber optics, hollow waveguides, dielectric thin films, multilayer thin films.

1. INTRODUCTION

Hollow glass waveguides (HGWs) are an attractive alternative to conventional solid-core IR fibers for applications ranging from laser power delivery to broadband chemical sensing and thermal imaging. The principle behind HGWs is the enhanced reflectivity of an electro-less deposited silver coating through the incorporation of dielectric thin films. As a result, HGWs can be easily optimized for maximum transmission at a variety of desired wavelengths from 2 to 15 μm through careful control of the fabrication parameters which determine the thickness of each of the dielectric thin films used. Furthermore, the incorporation of dielectric thin films for producing low-loss IR HGWs allows for broadband transmission at wavelengths determined by the individual thickness of the dielectric layer or layers. HGWs also enjoy the typical advantages of hollow waveguides including high laser power thresholds, low insertion loss, no end reflection, ruggedness, and small beam divergence as compared to solid core fibers. HGWs of different bore sizes can be fabricated to meet desired specifications, with a loss varying as $1/a^3$ where a is the radius of the HGW bore. Additionally, there is a bending dependency on loss in HGWs varying as $1/R$ where R is the radius of curvature. [1]

Traditionally, HGWs have consisted of a single dielectric layer of a highly transparent IR material such as silver iodide (AgI), cadmium sulfide (CdS), or lead sulfide (PbS) which enhances the reflectivity of the underlying silver coating through thin film interference effects. Novel HGW designs look for the incorporation of multilayer dielectric thin film designs to further enhance reflectivity, thus lowering the optical attenuation. Multilayer dielectric thin film designs consist of alternating layers of dielectric materials with different refractive indices with alternating thin films with high (n_H) and low (n_L) refractive indices resulting in enhanced reflectivity due to the refractive index mismatch, thus substantially reducing the waveguide loss. The structures of both single and multilayer HGWs are shown in Figure 1.

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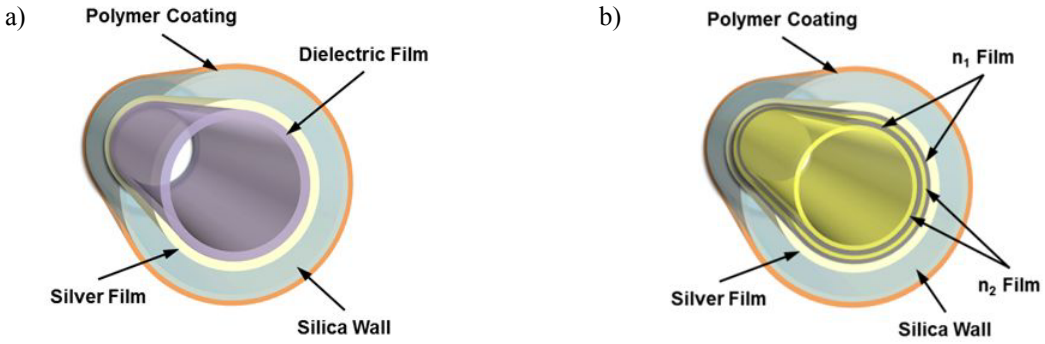

Figure 1 – a) Single layer HGW structure cross section, b) multilayer HGW structure cross section ($n_1 \neq n_2$)

The direct effect of incorporating functional dielectric films in silver coated HGWs has been theoretically studied by Miyagi and Kawakami [2], particularly for TE_{0m}, TM_{0m}, and hybrid HE_{1m} modes of propagation. The theoretical loss reduction in loss due to dielectric layers compared to silver-only coated HGWs is dependent on the refractive index of the individual dielectric layer(s) incorporated, the number of dielectric layers used, and the thickness of the individual layer(s). Theoretically, very low losses can be achieved through the incorporation of a greater number of films, with the greatest loss reduction achieved for any particular number of films when the refractive index contrast between the two adjacent film materials is greatest. [2] Multilayer designs in HGWs have been primarily studied utilizing the material with lower refractive index as the dielectric layer closest to the metal film followed by the material with higher refractive index and so forth. Despite this, multilayer thin film designs utilizing the material with higher refractive index closest to the silver film followed by the material with the lower refractive index are also of great importance due to the loss reduction obtained as determined in this study. Utilizing either silver iodide (AgI), cadmium sulfide (CdS), or lead sulfide (PbS) as high refractive index materials and polystyrene (PS) as a low refractive index material, dual-layer dielectric designs in HGWs have been produced and optimized for maximal transmission at the CO_2 laser emission wavelength of $\lambda = 10.6$ µm. The refractive indices of commonly incorporated dielectric thin film materials in HGWs, as well as the refractive index contrast between different dielectric layer materials proposed for multilayer dielectric film stacks in HGWs are given in Table 1. [3]

Table 1 – Refractive Index Contrasts of Dielectric Thin Films Deposited in HGWs

First Dielectric Layer	Second Dielectric Layer	Refractive Index Contrast
AgI (n = 2.10 λ = 10.6 µm)	PS (n = 1.58 @ λ = 1.064 µm)	0.52
CdS (n = 2.25 λ = 10.6 µm)	PS (n =1.58 @ λ = 1.064 µm)	0.67
PbS (n = 4.00 λ = 10.6 µm)	PS (n = 1.58 @ λ = 1.064 µm)	2.42

For the proposed multilayer dielectric design for use in HGWs outlined above, the expected loss reduction of incorporating a second dielectric thin film material of low refractive index is expected to be greatest for the PbS/PS dielectric layer pair due to the higher refractive index contrast.

2. FABRICATION OF LOW-LOSS HGWS

2.1 General Fabrication of HGWs

The basic structure of HGWs consists of high purity silica single-bore capillary tubing with a protective outer UV acrylate or polyimide coating to prevent atmospheric degradation of the silica tubing, thus preserving its mechanical strength. The capillary silica tubing is obtained from Polymicro Technologies and can range in bore size and wall thickness. Utilizing dynamic liquid phase deposition (DLPD) techniques, optically functional thin films are then deposited along the entire length of the inner surface of the capillary tubing from precursor solution(s) via both chemical

and mechanical deposition routes. The DLPD process used in the fabrication of HGWs involves continuous pumping of precursor solution(s) through the waveguide for the desired amount of time using a rotating peristaltic pump. While the DLPD process is modified slightly for the specific thin film material being deposited, the three main DLPD configurations used in the fabrication of HGWs are shown in Figure 2.

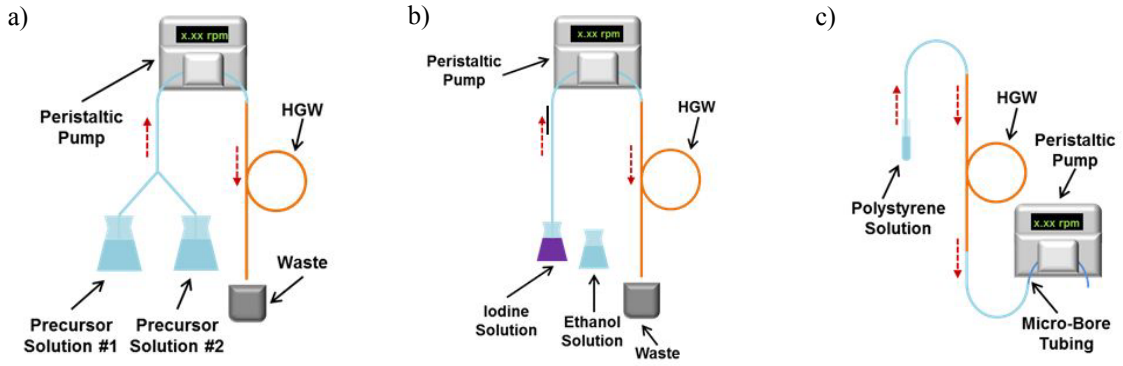

Figure 2 – a) Ag and metal sulfide thin films, b) AgI thin films, c) PS thin films

The first step in the fabrication of HGWs via DLPD technology involves sensitization of the inner silica tubing surface with an acidic stannous chloride solution. This serves to decrease the necessary deposition time of the succeeding electroless silver plating step as well as also reducing the surface roughness of the silver layer. After the sensitization step, a highly reflective silver film is deposited on the inner silica capillary surface through the reduction of a diamminesilver complex cation containing solution by an aldehyde containing solution. The silver deposition time ranges from 25 – 45 minutes depending on the desired silver film thickness as determined by the choice of the dielectric thin film used. The actual silver thin film must be of adequate thickness to prevent any transmission of incident light through the silver film while at the same time being sufficiently thick to be both mechanically stable and provide an appropriate substrate for deposition of any subsequent dielectric layer(s). To date, AgI, CdS, PbS, and polystyrene (PS) have been successfully and consistently deposited as infrared transparent dielectric thin films in HGWs. Ongoing research focuses on the deposition of other IR transparent II – VI compounds such as zinc sulfide (ZnS) and zinc selenide (ZnSe). The deposition mechanisms for the dielectric thin films vary depending on the actual material deposited and can be either chemical or physical in nature. The deposition type, active chemical precursors, and deposition mechanisms for the different dielectric thin film materials deposited in HGWs via DLPD processes are tabulated in Table 2.

Table 2 – Critical parameters involved in the DLPD processes of various dielectric thin film materials

Thin Film Material	Deposition Type	Active Precursors	Deposition Mechanism
Silver iodide (AgI)	Chemical subtractive	Elemental Aqueous Iodine Pre-Deposited Silver Substrate	Subtractive Conversion of Silver to Silver Iodide
Cadmium sulfide (CdS)	Chemical additive	Tetrammine Cadmium Complex Organosulfur Solution	Alkali Decomposition and Sulfide Synthesis
Lead sulfide (PbS)	Chemical additive	Plumbate Ion Complexes Organosulfur Solution	Alkali Decomposition and Sulfide Synthesis
Polystyrene (PS)	Mechanical additive	Polystyrene Solution	Evaporation of Volatile Organic Solvent
Zinc sulfide (ZnS)	Chemical additive	Tetrammine Zinc Complex Organosulfur Solution	Alkali Decomposition and Sulfide Synthesis

As previously discussed, one of the great advantages of HGWs is their ability to be optimized for maximum transmission at a desired wavelength or range of wavelengths through alteration of the dielectric thin film thickness. The dielectric film thickness depends heavily on a number of coating parameters for the particular material, generally solution

concentration and volumetric flow rate. The thickness of dielectric films deposited via chemical reactions can most easily be optimized by controlling the deposition time, with thicker films resulting from longer deposition times. Furthermore, the deposition of metal sulfide films is greatly dependent on pH and choice of complexing ligand. [4] The thicknesses of dielectric films of deposited via mechanical deposition mechanisms are largely independent of deposition time and are largely dependent on the viscosity of the solution and the evaporation rate of the solvent. Utilizing this methodology, optical dielectric thin films of good uniformity can be deposited in HGWs to enhance their transmission at desired target wavelengths.

2.2 Fabrication of Multilayered HGWs

The fabrication of HGWs incorporating multi dielectric thin film stacks via DLPD processes requires knowledge of the dielectric material properties as well as of the deposition mechanisms for the individual dielectric materials, most notably the deposition kinetics of dielectric thin films in the case of chemical driven deposition processes and the evaporation rates of solvents used in the case of physical driven deposition processes. Since it is essential to optimize the layer thickness of each thin film accordingly to obtain minimal optical attenuation at the target wavelength(s), the first step in incorporating multilayered designs in HGWs is an understanding of the parameters governing the thicknesses of the individual films so as to properly control each of the film thicknesses to create a successful multilayered stack system. Furthermore, the degree of compatibility between the different films in the system must be taken into consideration, not just from the optical response perspective, but also in terms of mechanical strength and adherence as well as in ease and reliability of fabrication. To date, multilayered film stacks in HGWs via DLPD processing have been limited primarily to CdS / PbS systems due to their high refractive index contrast, high mechanical stability, and processing compatibility. Recently novel dual-layer designs have been successfully fabricated incorporating systems involving either AgI, CdS, or PbS with PS. This involves the deposition of the first dielectric layer, either AgI, CdS, or PbS, having the desired thickness through careful control of the deposition time, followed by deposition of a second PS dielectric layer via physical evaporation of the organic solvent. Due to the high chemical inertness of AgI, CdS, and PbS to the organic solvent used in the PS deposition process, the integrity of the first dielectric film remains intact, allowing for the successful deposition of a secondary dielectric PS film upon evaporation of the organic solvent.

3. OPTICAL RESPONSE – DEPOSITION KINETICS

3.1 Experimental Methodology

To determine the deposition kinetics of AgI, CdS, and PbS dielectric thin films in 700 μm bore HGWs, twenty 14 cm long waveguide samples were prepared using the aforementioned sensitization procedure and standard silver film deposition scheme for a deposition time of 30 minutes to allow for a silver film of appropriate thickness. While not critical, the thickness of the silver film should be thicker than the skin depth of silver at the target wavelength as well as thick enough to support subsequent film depositions while at the same time having good uniformity and minimal surface roughness to prevent loss due to scattering. The determination of the kinetics for the deposition of AgI films involved the use of five 14 cm long segments which were then iodized for deposition times ranging from 15 – 90 seconds in increments of 15 seconds using a 39.4 mM elemental iodine solution and a volumetric flow rate of 10.0 mL/min. The determination of the kinetics for the deposition of CdS films involved the use of five 14 cm long segments through which a 12.8 mM ammonia-complexed cadmium (II) nitrate tetrahydrate solution and a 83.3 mM thiourea solution were simultaneously pumped at a volumetric flow rate of 21.0 mL/min for deposition times ranging from 300 – 420 minutes in increments of 30 minutes. The PbS deposition kinetics were then studied by simultaneously pumping a 6.0 mM hydroxide-complexed lead (II) nitrate solution and a 39.4 mM thiourea containing solution at a constant volumetric flow rate of 14.4 mL/min through five 14 cm long segments, each at a different deposition time ranging from 40 – 80 minutes in increments of 10 minutes. Additionally, PS dielectric thin films were deposited on five 14 cm long silver coated samples for direct study of the PS only thin films at PS solution concentrations of 2, 3, 4, 5, and 6 weight percent PS in toluene.

3.2 Optical Determination of Film Deposition Kinetics

The dielectric coated HGW segments were allowed to dry and each sample was characterized by Fourier-Transform Infrared (FTIR) spectroscopic analysis utilizing a Thermo Nicolet Protégé 460 FTIR spectrometer in conjunction with Teledyne-Judson InSb and MCT/A cryogenic IR detectors. In this manner, the IR optical spectrum of each Ag/AgI,

Ag/CdS, and Ag/PbS sample was obtained in the 2 – 15 μm wavelength range and the spectrum of each Ag/PS sample was obtained in the 1 – 4 μm range. The resulting IR spectra for select samples coated with a given dielectric film at a different variable critical deposition parameter is given in Figure 3.

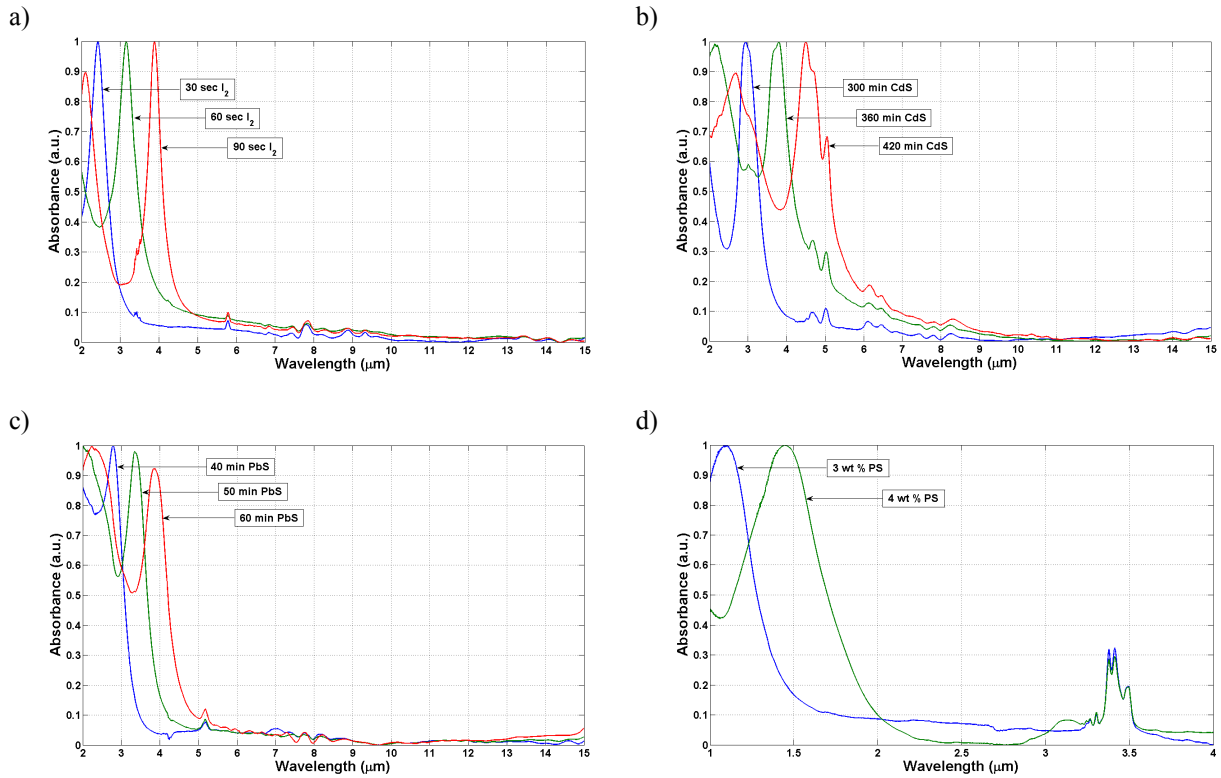

Figure 3 – Spectra of a) Ag/AgI, b) Ag/CdS, c) Ag/PbS, and d) Ag/PS HGWs at different deposition parameters

As expected, the position of the absorption peaks shifted to longer wavelengths with increasing deposition time, and thus increasing film thickness, for the AgI, CdS, and PbS dielectric coatings due their chemical deposition route. For the PS thin films, the film thickness increased with increasing solution concentration, thus shifting the position of absorbance peaks to longer wavelengths. Furthermore, all deposited films exhibited superb uniformity as suggested by the narrow interference peaks. For the single dielectric film case, the film thickness can be determined from the wavelength of the interference (absorption) peak position using Equation 1 where n_f is the refractive index of the dielectric film, m is the integer defining the mth order absorbance peak with m = 1 for the absorbance peak observed at the longest wavelength, and λ_p is the wavelength of the mth absorption peak. [5]

$$d_p = \frac{m \cdot {\lambda_p}^m}{4\sqrt{{n_f}^2 - 1}} \tag{1}$$

Using this methodology, the dielectric layer thickness for each sample was calculated after locating the central wavelength of the first absorption peak. For the case of the AgI, CdS, and PbS chemically deposited coatings, the calculated film thickness was plotted as a function of deposition time to experimentally determine the dielectric thin film deposition reaction kinetics and the results are shown in Figure 4.

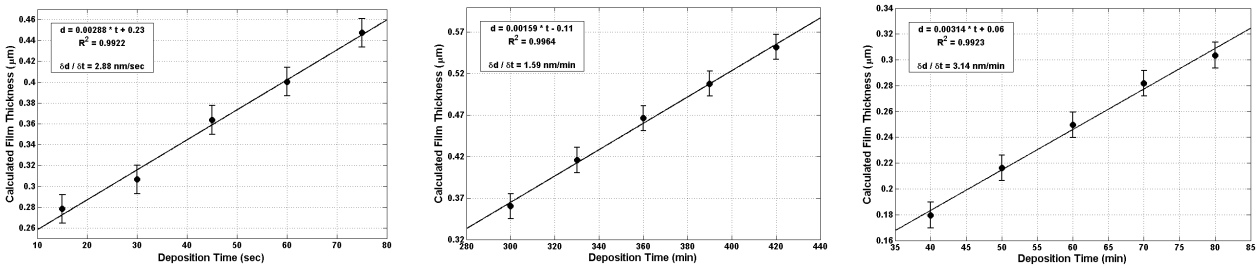

Figure 4 – Thickness as a function of deposition time for a) AgI, b) CdS, and c) PbS films in HGWs

The growth kinetics of all three different types of dielectric films were highly linear in nature, as would be expected as a result of the DLPD fabrication methodology in which unreacted precursor solutions are continuously pumped through the samples, preventing the depletion of available precursors as experienced in traditional chemical bath deposition (CBD) processes. The high linearity of the dielectric film growth kinetics allows for simplified optimization of the dielectric film thickness as desired by varying the deposition time. Therefore, it is possible to optimize the dielectric coated HGW for maximum transmission at a given target wavelength or range of wavelengths by sole variation of the deposition time for the given film material. The film growth kinetics in the linear growth rate region for the AgI, CdS, and PbS dielectric thin films in 700 μm bore HGWs is determined to be 2.88 nm/sec, 1.59 nm/min, and 3.14 nm/min respectively. The differences in growth rates are indicative of the chemical processes behind the deposition procedures for the various thin film materials. From the experimentally obtained growth rate and linear intercept coefficient, the necessary deposition times for AgI, CdS, and PbS so as to fabricate films of appropriate thickness for optimal transmission at a desired target wavelength or range of wavelengths can be determined and is of great use for optimization of dielectric coated HGWs incorporating both single and multilayer designs.

4. DUAL-LAYER POLYSTYRENE HGW DESIGNS

4.1 Experimental Methodology

To determine the effect on the optical response of depositing secondary dielectric PS thin films in HGWs, three 1.5 m long 700 μm bore sample were prepared and silvered using the previously described silver deposition methodology. Each of the guides was then coated with AgI, CdS, and PbS thin films respectively so as to obtain a layer thickness that would allow for maximum transmission in the 8.5 – 11.0 μm range. The necessary deposition times that would allow for such film thicknesses were determined from the deposition kinetics analysis above. The optimal deposition times were determined to be 50 second, 210 minutes, and 55 minutes for the AgI, CdS, and PbS films, respectively. After fabrication of the samples, attenuation measurements were taken using a 40 Watt CW Laser Engineering CO_2 laser emitting at 10.6 μm in addition to FTIR spectroscopic analysis of each sample for post-PS deposition comparison. A secondary PS thin film was then deposited in the remaining 1.2 m long samples through vacuum pulling of a 3% by weight solution of PS in toluene for 30 minutes. A 3% by weight solution was chosen due to its proven ability to deposit PS films of adequate thicknesses as well as for its low viscosity allowing for increased workability given the sample dimensions. The prepared samples where then allowed to dry for a period of 24 hours at room temperature. The finished dual-layer PS film containing samples were then analyzed using FTIR spectroscopy and loss measurements were taken on the final 1.1 m long samples.

4.2 Infrared Spectroscopy Measurements

The IR spectrum of each of the three dual-layer HGW samples was obtained using FTIR spectroscopy both before and after the deposition of the secondary PS thin film for comparison. The wavelengths of interest spanned from 2 – 15 μm, with the IR spectrum of each sample prior to and after the PS film deposition given in Figure 5.

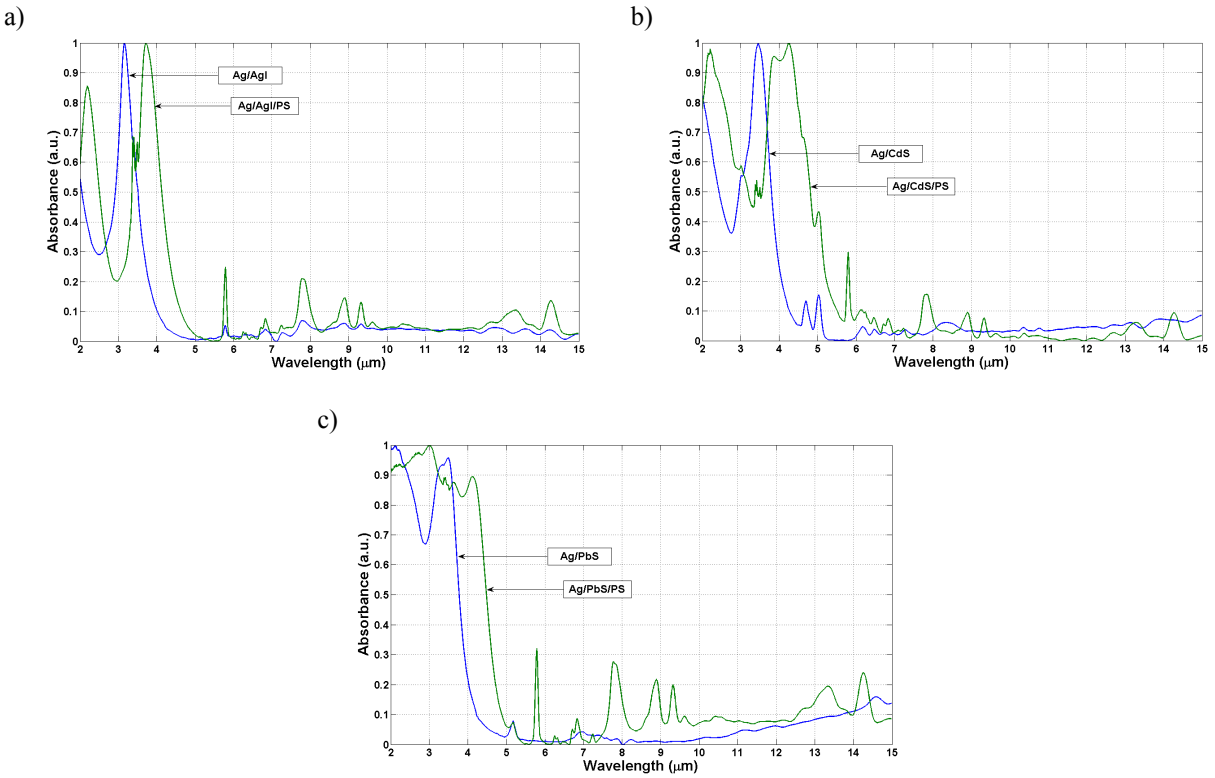

Figure 5 – IR spectra of a) Ag/AgI, b) Ag/CdS, and c) Ag/PbS samples before and after PS film deposition

All samples showed a clear shifting of the entire optical response to longer wavelengths, as would be expected as a result of thicker dielectric thin films, thus signifying the successful deposition of a secondary PS thin film which contributed to the overall optical response of the entire dielectric film system. Furthermore, the sharp organic bond absorbance peaks seen in the IR spectra all due to the successful deposition of secondary PS thin films. The thickness of the secondary PS thin film can be calculated by finding the shift in wavelength of the position of the 1st interference peak due to the underlying primary dielectric layer. Using this wavelength shift in absorbance peak position as λ_p in Equation 1 as well as $n_f = 1.58$ for the refractive index of PS, the thickness of the PS film in the dual-layer dielectric stack can be estimated. In the case of the Ag/AgI/PS sample, a shift in the first absorption peak position of 0.556 μm was seen, corresponding to a calculated PS film thickness of 0.11 μm, while in the cases of the Ag/CdS/PS and Ag/PbS/PS samples, the shifts were 0.784 and 0.633 μm, corresponding to PS film thicknesses of 0.16 μm and 0.13 μm, respectively. These differences in PS film thicknesses, as well as the broadening of the absorption peaks seen in the IR spectra of each sample are indicative of reduced film uniformity of the PS films. Further study of the deposition of PS thin films involves increased control of the PS film deposition parameters.

4.3 Attenuation Measurements

Optical attenuation measurements at a wavelength of 10.6 μm were taken of each sample both prior to and after the addition of the secondary PS layer for comparison. The experimentally obtained straight losses for all the samples are given in Table 3.

Table 3 – Straight losses for single and dual dielectric layer 700 μm ID HGWs at λ = 10.6 μm

First Dielectric	Measured Loss without PS Film (dB/m)	Measured Loss with PS Film (dB/m)	Loss Reduction Factor
AgI	0.183	0.097	1.88
CdS	0.259	0.131	1.97
PbS	0.409	0.194	2.11

The experimental error in measuring the power output was determined to be ± 2.0 mW due to minimal instability of the output with time. The measured straight losses for the single deposited dielectric layers were found to be higher than theoretical values, but in accordance with previous experimental values for the individual dielectric layers. The addition of a secondary PS dielectric thin film was experimentally determined to substantially reduce the measured straight loss of the waveguide samples. The loss reduction factor for all samples was approximately two, with higher loss reduction factors seen for dual-layer designs with higher refractive index contrasts as would be expected by theory. While substantially reducing the loss, the addition of a secondary PS thin film resulted in lower laser power handling capability as damage to the PS layer was seen at input powers of approximately 2.5 Watts. The loss is further expected to decrease when using additional dielectric layers.

5. SUMMARY AND CONCLUSIONS

HGWs are capable of low-loss broadband transmission of IR radiation from λ = 2 to 15 μm, with a specific optimal transmission range being determined by the specific thickness of the dielectric layer deposited. While HGWs have traditionally incorporated single dielectric layers to enhance transmission, it has been theoretically and experimentally determined that the incorporation of multilayer dielectric stacks with alternating low and high refractive index materials can further reduce their loss, depending on the number of films incorporated as well as in the refractive index contrast of the two materials chosen. In this study, the deposition kinetics of AgI, CdS, and PbS single thin films in 700 μm bore HGWs has been thoroughly studied with the eventual purpose of optimizing dielectric layer thicknesses for incorporation in multilayer stack structures in HGWs for reduced loss. Utilizing these thin films as high refractive index materials, it has been possible to deposit secondary low index polystyrene thin films for successful loss reduction at the CO_2 laser wavelength of λ = 10.6 μm. The incorporation of dual-layer designs in HGWs involving PS thin films has been shown to reduce the actual loss by a factor of approximately two when compared to losses measured without the secondary PS film. Furthermore, FTIR spectroscopy supports the claim of successful PS thin film dielectric deposition via DLPD techniques as evident by a definitive shifting of the optical spectra after the deposition of the secondary PS. Further study of multilayer designs in HGWs will include the full optimization of presently deposited dual-layer PS containing thin film systems for use in IR radiation transmission, as well as incorporation of multi-dielectric stacks involving a greater number of dielectric layers.

6. ACKNOWLEDGEMENTS

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REFERENCES

[1] Harrington, J. A., *Infrared Fiber Optics and Their Applications*, (SPIE Press, Bellingham, WA, 2004).
[2] Miyagi, M. and Kawakami, S. "Design theory of dielectric-coated circular metallic waveguides for infrared transmission," IEEE Journal of Lightwave Technology. LT-**2**, 116-126 (1984).
[3] Palik, E. D. and Ghosh, G., Handbook of optical constants of solids, (Academic, London, 1998).
[4] Chaparro, A. M., "Thermodynamic analysis of the deposition of zinc oxide and chalcogenides from aqueous solutions," Chem. Mater., **17** (16), 4118-4124 (2005)

[5] Rabii, C. D., Gibson, D. J., and Harrington, J. A., “Processing and characterization of silver films used to fabricate hollow glass waveguides,” Appl. Opt. **38**, 4486-4493 (1999).