Investigation of metal sulfide optical thin film growth in low-loss IR hollow glass waveguides

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Abstract: In this study, the film growth kinetics for near and mid-IR reflection enhancing CdS and PbS dielectric thin films in HGWs is experimentally established. Crucial fabrication parameters including solution concentrations, pH, and fluid velocity are optimized. The film thickness of these films in HGWs is studied as a function of deposition time and temperature. Through IR spectral response analysis, the dielectric thin film thicknesses were determined and found to have a strong linear time dependence. Accurate metal sulfide film growth models in HGWs were developed, allowing for direct determination of necessary deposition times to yield metal sulfide HGW thin film coatings having a desired response.

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OCIS codes: (310.0310) Thin films; (310.1860) Deposition and fabrication; (310.6860) Thin films, optical properties; (060.2390) Fiber optic devices, infrared; (350.4600) Optical engineering.

References and links
1. Introduction

Metal / dielectric coated hollow glass waveguides (HGWs) have been successfully employed in a variety of applications ranging from high-powered medical laser delivery to highly sensitive gas sensing requiring the low-loss transmission of infrared radiation. As opposed to solid core fibers, photonic crystal fibers, and specialty infrared fibers such as fluoride glass fibers, HGWs are capable of broadband low-loss transmission, making them ideal for applications such as IR spectroscopy, while not suffering from limitations such as narrow band transmission windows, end reflection losses, relatively low power laser damage thresholds, and inherent material absorption losses [1]. As interest in the broadband transmission of mid-IR radiation continues to grow, fueled by the continuing development of new tunable mid-IR sources such as quantum cascade lasers (QCLs), the need has increased for fibers with a broadband, tunable optical response. Unlike solid core optical fibers, HGWs do not operate on the principle of total internal reflectance (TIR), rather they rely on the reflection of light from the inner HGW walls as it propagates along the waveguide. As such, the loss of HGWs depends strongly on the reflectivity of the inner surface material structure. Therefore, the deposition of a thin film over the Ag film enhances the reflectivity of this HGW dramatically and thereby reduces the waveguide loss.

As shown in Fig. 1(a), the structure of highly reflective metal / dielectric HGWs has traditionally involved deposition of a thin film of a highly reflective metal, such as silver (Ag), on the inner surface of a flexible glass capillary, followed by the deposition of a thin dielectric film of an IR transparent material.

![Cross-sectional representation of a) single and b) multiple dielectric layer film coated hollow glass waveguides (HGWs).](image)

Fig. 1. Cross-sectional representation of a) single and b) multiple dielectric layer film coated hollow glass waveguides (HGWs).

to enhance the reflectivity of the surface via thin film interference effects. To date, a number of IR transparent dielectric materials have been successfully deposited in HGWs for reflection enhancement, including silver iodide (AgI), cadmium sulfide (CdS), lead sulfide (PbS), and several polymers such as polystyrene (PS) and cyclic-olefin polymer (COP) [1–3]. Recently, CdS and PbS thin films have generated additional interest due to their possible use in a multilayer stack configuration to potentially yield an even lower loss 1-D photonic bandgap structure as shown in Fig. 1(b). These metal sulfide materials are of particular interest in the development of such a high reflectivity multilayer thin film structure due to their high IR transparency, refractive index contrast in the IR region (n$_{CdS}$ =2.28, n$_{PbS}$ =4.00), chemical and structural compatibility, and relatively consistent and controlled deposition methods [4]. However, as for any reflectivity enhancing thin film, it is essential to carefully control the deposition procedure to obtain an optimal thin film thickness which ensures constructive interference of reflected light depending on the wavelength region of interest. The optimal individual thin film thickness for a wavelength is given by Eq. (1) for a single dielectric film HGW structure and Eq. (2) for a multilayer dielectric thin film stack composed of individual films [1,5]:

#192580 - $15.00 USD Received 19 Jun 2013; revised 29 Jul 2013; accepted 8 Aug 2013; published 15 Aug 2013
(C) 2013 OSA 1 September 2013 | Vol. 3, No. 9 | DOI:10.1364/OME.3.001397 | OPTICAL MATERIALS EXPRESS 1398
\[
d_o = \frac{\lambda_d}{2\pi\sqrt{n_F^2-1}} \tan^{-1}\left(\frac{n_F}{(n_F^2-1)^{1/2}}\right)
\]
(1)

\[
d_o = \frac{\lambda_d}{4\sqrt{n_F^2-1}}
\]
(2)

where \(\lambda_d\) is the desired wavelength, \(n_F\) is the refractive index of the dielectric material. It is therefore crucial to gain an in-depth understanding of the deposition methods and the ensuing thin film growth kinetics so that thin films with optimal thicknesses may be deposited, thus ensuring that the lowest possible loss waveguide thin film structure is achieved for the desired wavelength(s) of operation. It is particularly valuable to have an experimentally verified model which allows for the accurate prediction of the process parameters necessary to consistently yield a dielectric thin film thickness for a particular wavelength(s) for the intended application. In this manner, one need simply modify the process parameters to precisely tune the optical response of the dielectric thin film(s) in HGWs.

The present study focuses on the growth of CdS and PbS optical thin films in HGWs via the dynamic liquid phase deposition (DLPD) method commonly employed for the deposition of high quality optical thin films in HGWs up to five meters in length. In particular, focus is placed on understanding the effects and optimizing the deposition process parameters, which include solution concentrations, solution temperatures, solution pH, fluid flow velocity, deposition procedure time, and deposition substrate on the film growth kinetics of optical CdS and PbS thin films in HGWs. Exclusively, this investigation looks at film growth of these films for mid-IR applications and for incorporation in multilayer CdS/PbS systems for use within this spectral range. In particular, this study expands on previous metal sulfide thin film deposition studies by optimizing the deposition procedures to improve film quality, film thickness variation and consistency, and achieving adequate film thicknesses for low-loss mid-IR transmission while focusing in detail on the effects of deposition time, precursor solution temperatures, and waveguide length on metal sulfide thin film growth [2,3,6,7].

2. Fabrication method

Fabrication of Ag / dielectric coated HGWs is carried out using a fused silica capillary of desired inner diameter, wall thickness, and total length depending on the application and required optical properties as the structural substrate. All silica capillary substrates used in this study were provided by Polymicro, Inc. and had a constant inner diameter of ID = 700 µm, a waveguide bore range suitable for the majority of mid-IR applications. Using the silica capillary as the fundamental waveguide structure, optical quality thin films of highly reflective materials such as Ag and subsequently reflection enhancing dielectric materials such as CdS and PbS are deposited on the inner surface of the capillary tubing to form the Ag / dielectric coated HGW. All samples were initially 200 cm in length and were coated with an Ag film approximately 200 µm in thickness according to the methods briefly discussed below. For the investigation of the growth of CdS and PbS films on an Ag coated HGW substrate, an Ag film was first deposited in each sample followed by the desired metal sulfide material, according to the experimental parameters for that particular trial. On the other hand, investigation of CdS and PbS growth using the alternative metal sulfide material as substrate, (thus CdS growth on an Ag/PbS coated HGW and PbS growth on an Ag/CdS coated HGW) required the deposition of the metal sulfide material serving as the substrate on the Ag coated HGW. All metal sulfide substrate material procedures were carried out at T = 30 °C holding all other experimental parameters at standard values as will be further discussed. The resulting Ag / metal sulfide coated HGWs were then used to investigate CdS and PbS film growth on
PbS and CdS, respectively, as a function of deposition time and deposition solution temperature.

Each metal sulfide deposition procedure was carried out as a function of deposition time, holding all other fabrication parameters constant at experimentally optimized standard values in terms of precursor solution concentrations and pH, along with precursor solution temperatures held constant with ± 1 °C variability using a temperature controlling water bath. The fluid flow speed of precursor solutions was also held constant for all procedures at approximately 70 cm/s (volumetric flow rate of ~16 mL/min). During each experimental deposition procedure, the final 14 cm of the remaining HGW sample length were cut and immediately rinsed with deionized water prior to drying with low velocity forced air at predetermined, evenly spaced time intervals for spectral analysis. Due to thin film interference effects, each sample yielded a rich spectral response which can be directly analyzed to determine deposited dielectric thin film thickness. In this manner, several segments for each experimental deposition procedure were obtained, each at a subsequently greater deposition time in order to determine film growth as a function of elapsed deposition procedure time. For complete analysis, each of the four deposition procedures (CdS on Ag, PbS on Ag, CdS on PbS, and PbS on CdS), was repeated at three different temperatures of T = 20, 25, and 30 °C.

2.1 Deposition of silver thin films

Initial fabrication of Ag / metal sulfide HGWs involves the deposition of highly reflective, low surface roughness Ag films on the inner silica capillary surface via DLPD method. DLPD is similar to chemical bath deposition (CBD) in that it results in the deposition of an insoluble compound from precursor containing aqueous solutions. However, unlike CBD, DLPD has the dual advantage in that it is a dynamic process in which the precursor containing solutions are simultaneously and continuously pumped by a peristaltic pump through the waveguide at a constant rate, thus preventing concentration depletion and depositing a highly uniform film along the entire waveguide length. Prior to depositing the Ag film, the inner capillary surface is pre-treated by flowing a 1.55 mM acidic stannous chloride dihydrate (SnCl$_2$·2H$_2$O) solution for 5 minutes through the waveguide followed by a rinse with deionized water for 30 seconds. This pretreatment allows for the rapid, subsequent deposition of Ag through modification of the silica surface, specifically by the deposition of a very thin layer of reducing tin (II) ion species. After the tin (II) ion sensitization pre-treatment, a basic diammoniessilver (I) precursor solution prepared using a 14.36 mM silver (I) nitrate (AgNO$_3$) solution and a reducing 3.11 mM dextrose (C$_6$H$_{12}$O$_6$) solution are simultaneously pumped at equal rates through the waveguide at the predetermined fluid flow speed of approximately 70 cm/s (volumetric flow rate of ~16 mL/min). This procedure is carried out at T = 20 °C for a total time of 20 minutes, depositing an Ag film approximately 200 nm in thickness [8]. The Ag coated waveguide is then rinsed with deionized water before being dried using low pressure dry air prior to performing subsequent depositions.

2.2 Deposition of metal sulfide thin films

Deposition of cadmium sulfide (CdS) and lead sulfide (PbS) thin films is also performed using the DLPD method involving the simultaneous pumping of two separate precursor ion containing solutions through the waveguide for the desired amount of time, as schematically shown in Fig. 2 [2,3,6,7].
CdS deposition procedure involves a basic ammonia-complexed 14.75 mM cadmium (II) nitrate tetrahydrate (Cd(NO$_3$)$_2$·4H$_2$O) solution using 150 mL/L of 18 M ammonium hydroxide (NH$_4$OH) and a reducing 150 mM thiourea (CH$_4$N$_2$S) solution (pH = ~10.1). These solution concentrations have been experimentally seen to yield high quality CdS films while reducing the necessary deposition times for IR enhancing film thicknesses relative to lower concentration [7]. On the other hand, higher solution concentrations have been shown to result in lower quality films despite further reducing deposition times, possibly due to an increase in undesirable cluster-by-cluster homogeneous film growth and resulting increased surface roughness related scattering mechanisms. The heterogeneous deposition of CdS films using this method has been explored in the literature and the mechanism has been suggested to occur via adsorption of a cadmium hydroxide species on the substrate which is then reduced to CdS as in Eq. (3) [9–15].

\[
Cd(NH_4)_2^{2+} + 2OH^-\rightarrow Cd(OH)_{2[ads]} + 4NH_3[\text{aq}] \quad (3a)
\]

\[
Cd(OH)_{2[ads]} + SC(NH_2)_{2[\text{aq}]} \rightarrow CdS_{[s]} + H_2NCN[\text{aq}] + 2H_2O[\text{l}] \quad (3b)
\]

In this particular study, CdS film growth as a function of total deposition time holding all other experimental parameters constant was investigated. Sample segments 14 cm in length were collected at deposition times ranging from 55 to 195 minutes in 15 minute intervals when using Ag as the deposition substrate and from 20 to 90 minutes in 10 minute intervals when using PbS as the deposition substrate. Each experiment was repeated at three different solution temperatures of $T = 20, 25, \text{and } 30 \degree C$ to investigate the effects of temperature on film growth. It should be noted that film growth deposition experiments at temperatures higher than $T = 30 \degree C$ were not carried out due to the relatively low boiling point of ammonium hydroxide.

The PbS deposition procedure involves a basic hydroxide-complexed 5.53 mM lead (II) nitrate (Pb(NO$_3$)$_2$) solution using 250 mL/L of 22.5 M sodium hydroxide (NaOH) and a reducing 54.4 mM thiourea (CH$_4$N$_2$S) solution (pH = ~12.0). These solution concentrations have been observed to yield high quality PbS films [16]. These concentrations are somewhat higher than used in the past yet the film quality remains high. However, higher solution concentrations are impractical because the highly basic nature of the lead (II) ion containing solution has a detrimental effect on the underlying Ag film. The heterogeneous deposition of PbS films using this method has been studied and the deposition mechanism has been suggested to be direct ion-by-ion deposition of lead sulfide on the substrate as in Eq. (4) [9,10,12,16]:
\[
Pb(OH)_{4+}^{\text{aq}} + SC(NH_2)_2^{\text{aq}} \rightarrow PbS^{\text{aq}} + H_2NCN^{\text{aq}} + 4OH^{-}^{\text{aq}} + 2H_2O^{\text{aq}} \quad (4)
\]

In this particular study, PbS film growth as a function of total deposition time holding all other experimental parameters constant was investigated. Sample segments 14 cm in length were collected at deposition times ranging from 30 to 65 minutes in 5 minute intervals using Ag as the deposition substrate and from 20 to 50 minutes in 5 minute intervals using CdS as the deposition substrate.

3. Spectroscopic analysis

Analysis of our samples involved a measurement of the spectral response of the thin-film coated samples using IR spectroscopy from 2 to 12 \( \mu m \). To obtain the spectral response of the fabricated samples, a Bruker Tensor 37 FTIR spectrometer was used along with an IR detector (InSb for near-IR and MCT-A for mid-IR). The thin film interference effect produces a rich absorption spectrum characterized by absorption peaks and transmission windows. The location of the interference peaks depends on the film thickness of the metal sulfide. Figure 3 gives representative IR spectral responses for select CdS and PbS thin film HGW samples deposited over Ag at T = 30 °C. From the data in Fig. 3, the broadband transmissive nature of metal / dielectric HGWs can be seen. Absorption inherent to the impurities present in the deposited films can also be seen, such as possible hydroxide species peaks in the \( \lambda = 4.5 - 5.0 \mu m \) for the CdS coated HGWs (Fig. 3(a)). Most importantly to the present analysis however, we see the large interference peaks due to thin film effects at the shorter wavelengths. The narrow and well defined interference peaks are indicative of high quality deposited thin films capable of low-loss propagation of IR radiation. Furthermore, we see that the entire spectral response shifts to longer wavelengths as the deposition time, and thus the film thickness, increases. The physical film thickness can be calculated from the spectral shift between the centroid wavelength corresponding to the first interference peak and the centroid wavelength corresponding to the first interference peak of any underlying dielectric thin film of a different material as given by [1,5].

\[
d_F = \frac{\lambda_n - \lambda_{n-1}}{4\sqrt{n_F^2 - 1}} \quad (5)
\]

where \( \lambda_n \) is the centroid wavelength of the first interference peak of the \( n^{th} \) dielectric thin film layer, \( \lambda_{n-1} \) is the centroid wavelength of the first interference peak of the \( n^{th}-1 \) dielectric thin film layer, and \( n_F \) is the refractive index of the \( n^{th} \) film material at \( \lambda_n \). In the case of a single dielectric thin film material, \( \lambda_{n-1} = 0 \) and the numerator in Eq. (5) reduces to \( \lambda_n \). It should be noted that Eq. (5) assumes light traveling at grazing incidence on the waveguide surface, as is the case for propagating low-loss rays in HGWs [1].

Fig. 3. Mid-IR spectral response of a) Ag/CdS and b) Ag/PbS coated HGWs at increasing thin film deposition times.
4. Thin film growth analysis

Determination of the thickness of the thin film from the optical response requires knowing the first interference peak position and the refractive index of the dielectric thin film material at that wavelength along with the position of the first interference peak corresponding to any underlying thin film(s) of a different dielectric material. To accurately determine the physical film thickness of the deposited CdS and PbS films, the dispersion of these materials in the near and mid-IR regions must be known. We have taken into account dispersion and used this information to determine the film thickness for each experimental procedure as a function of deposition time.

4.1 Cadmium sulfide thin films

To investigate the growth of CdS thin films on an Ag coated HGW, segments with CdS coating times ranging from 55 to 195 minutes in 15 minute intervals were collected and the first interference peak positions obtained from their spectral response. The corresponding calculated film thickness as a function of deposition times for the different trials carried out at T = 20, 25, and 30 °C is presented in Fig. 4(a). As seen in Fig. 4(a), the CdS film thickness is observed to be highly linear with increasing deposition time for all temperatures, with calculated film growth rates of 0.8, 1.2, and 2.4 nm/min as determined from the slope of the linear best fit for T = 20, 25, and 30 °C, respectively. The film growth rate is seen to increase less dramatically from T = 20 – 25 °C compared to T = 25 – 30 °C, suggesting that film growth rate increases nonlinearly at a faster rate at higher temperatures. Determination of CdS film growth on an Ag/PbS coated HGW was carried out similarly, involving segments with CdS coating times ranging from 20 to 90 minutes in 10 minute intervals. The corresponding calculated film thickness as a function of elapsed deposition times for the different trials carried out at T = 20, 25, and 30 °C is given in Fig. 4(b). As seen in Fig. 4(b), the CdS film thickness is highly linear for all temperatures, with calculated film growth rates of 0.7, 0.9, and 2.2 nm/min as determined from the slope of the linear best fit for T = 20, 25, and 30 °C, respectively. The film growth rate dependence on temperature is similar to the CdS deposition on Ag. It should also be noted that the CdS film growth rate was considerably faster at all temperatures for the deposition over Ag compared to the PbS substrate. The linear best fit slope and intercept coefficients for CdS film growth on both Ag and PbS substrates obtained from the experimental data are summarized in Table 1.

Fig. 4. Film thickness as a function of CdS deposition time on a) Ag and b) Ag/PbS coated HGWs at different deposition temperatures.
Table 1. Linear coefficients for CdS film growth

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<thead>
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<th>Ag Substrate</th>
<th>PbS Substrate</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Slope</td>
<td>Intercept</td>
</tr>
<tr>
<td>T = 20°C</td>
<td>0.841</td>
<td>7.746</td>
</tr>
<tr>
<td>T = 25°C</td>
<td>1.197</td>
<td>4.298</td>
</tr>
<tr>
<td>T = 30°C</td>
<td>2.359</td>
<td>−10.618</td>
</tr>
</tbody>
</table>

4.2 Lead sulfide thin films

To investigate the growth of PbS thin films on an Ag coated HGW, segments with PbS coating times ranging from 30 to 65 minutes in 5 minute intervals were collected and the first interference peak position obtained from the spectral response. The corresponding calculated film thickness as a function of deposition time for the different trials carried out at T = 20, 25, and 30 °C is presented in Fig. 5(a). As seen in Fig. 5(a), the PbS film thickness is highly linear with increasing deposition time for all temperatures, with calculated film growth rates of 2.6, 5.2, and 6.3 nm/min as determined from the slope of the linear best fit for T = 20 – 25 °C than for T = 25 – 30 °C, suggesting that film growth rate increases nonlinearly at a slower rate at higher temperatures. Determination of PbS film growth on an Ag/CdS coated HGW was carried out similarly, involving segments with PbS coating times ranging from 20 to 50 minutes in 5 minute intervals. The corresponding calculated film thickness as a function of deposition time for the different trials carried out at T = 20, 25, and 30 °C is presented in Fig. 5(b). As seen in Fig. 5(b), the PbS film thickness is seen to also be highly linear with increasing deposition time for all temperatures, with calculated film growth rates of 7.2, 9.5, and 12.4 nm/min as determined from the slope of the linear best fit for T = 20, 25, and 30 °C, respectively. The same film growth rate dependence on temperature as seen for PbS deposition on Ag is suggested by the data. It should also be noted that PbS film growth rate was considerably faster at all temperatures when using CdS rather than a Ag substrate. The linear best fit slope and intercept coefficients for PbS film growth on both Ag and CdS substrates obtained from the experimental data are summarized in Table 2.

Fig. 5. Film thickness as a function of PbS deposition time on a) Ag and b) Ag/CdS coated HGWs at different deposition temperatures.
Table 2. Linear coefficients for PbS film growth

<table>
<thead>
<tr>
<th></th>
<th>Ag Substrate</th>
<th></th>
<th>CdS Substrate</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Slope</td>
<td>Intercept</td>
<td>Slope</td>
<td>Intercept</td>
</tr>
<tr>
<td>T = 20°C</td>
<td>2.581</td>
<td>22.024</td>
<td>7.245</td>
<td>3.655</td>
</tr>
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</table>

4.3 Film variation as a function of hgw position

We have studied the thin film thickness variation as a function of waveguide position to determine if the films will vary in thickness over the waveguide length. To explore this possibility, 200 cm long Ag coated HGWs were coated with either CdS or PbS at T = 30 °C to produce film thicknesses of approximately 190 and 350 nm for CdS and PbS, respectively. These samples were then divided into 15 cm long segments to study film variation as a function of waveguide position. The spectral response of each of the segments was used to calculate the film thickness of each segment. In Fig. 6, we show the film thickness variation for position along the waveguide. A strong linearly decreasing relationship for both film materials is observed. We calculate a film thickness variation of approximately −9.3% and −6.3% per meter for CdS and PbS, respectively. This variation in film thickness can be most logically explained to the combined effects of differing fluid flow dynamics and to a lesser extent the depleting concentration of active precursor species in solution as a function of waveguide position. Such magnitudes of thin film variation can be considered negligible for the vast majority of HGW applications, except for those requiring a very high degree of spectral response accuracy and/or those requiring very long HGW lengths (L > 200 cm). For example, the majority of HGW applications require the broadband transmission of IR radiation at predetermined wavelength regions, such as \( \lambda = 4 – 10 \) μm in the case of mid-IR noxious gas spectroscopy. In such cases, the average film thickness can be optimized for the mid-range wavelength, with the position dependent thickness variation having no detrimental effect throughout this spectral range, as the interference absorption peak will remain at wavelengths lower than the minimum limit wavelength, even with the corresponding peak position variation being taken into account. Thus, for the broad majority of HGW applications, except those requiring large broadband spectral transmission or those requiring simultaneous transmission at considerably differing wavelength regions, such degree of film thickness variation is acceptable. If a higher uniformity is required it might be
possible to coat the waveguide for half the time in one direction and then reverse the direction of flow for next half of the procedure.

5. Conclusion

In this study, the film growth kinetics for near and mid-IR CdS and PbS dielectric thin films in HGWs has been studied. All metal sulfide thin films deposited in this study were deposited via electroless deposition methods from precursor containing ion aqueous solutions via DLPD. The optimization of key fabrication parameters including solution concentrations, pH, and fluid flow velocity was achieved in this study. Using these determined optimized deposition parameters, the film thickness of metal sulfide films in HGWs was measured as a function of deposition time at three different temperatures on different substrates. The thickness of the films was determined from their spectral response in the mid-IR region of the spectrum. In all cases, a strong linear dependence of film thickness on deposition time was seen, with film growth rates of 0.8, 1.2, and 2.4 nm/min for CdS on Ag, 0.7, 0.9, and 2.2 nm/min for CdS on PbS, 2.6, 5.2, and 6.3 nm/min for PbS on Ag, and 7.2, 9.5, and 12.4 for PbS on CdS at temperatures of T = 20, 25, and 30 °C, respectively. Furthermore, the dependence of film growth rate on temperature was seen to differ for CdS and PbS thin film deposition, increasing nonlinearly but at a slower rate at higher temperatures for PbS as opposed to a faster rate at higher temperatures for CdS. The deposition substrate was also seen to have a strong influence on the film growth rate, with CdS films having a faster growth rate on an Ag substrate than on a PbS substrate but PbS films having a slower growth rate on an Ag substrate than on a CdS substrate. Counter intuitively, it was seen that film growth rates for both materials were highly dependent on deposition substrate, regardless of total deposited film thicknesses. The deposition times studied yielded high quality metal sulfide thin films. These sulfide films may be used either as single films or in multilayer stacks to enhance the reflectivity of the HGWs. It should be noted that while all samples in this study consisted of constant 700 μm ID HGWs, the same metal sulfide film growth kinetics may be extended to waveguides of differing bore size so long as the volumetric flow rate is adjusted to achieve the same fluid flow speed of approximately 70 cm/s. CdS and PbS thin films deposited using the methods presented in this study have been measured to considerably improve straight HGW propagation losses relative to Ag only coated 700 μm ID HGWs at mid-IR wavelengths from approximately 2.5 – 3.0 dB/m to 0.30 – 0.45 dB/m and 0.45 – 0.60 dB/m for Ag/CdS and Ag/PbS coated HGWs, respectively. Furthermore, it should be noted that while surface roughness related scattering propagation losses have been found to increase with total deposited film thicknesses, the effect of surface roughness on propagation losses for the overall film thicknesses discussed in this study are small and can be largely neglected, thus this phenomenon was not probed in detail in this study.

A linear film growth enables direct determination of the deposition time required to achieve a film thickness optimized for the desired application wavelength(s). The growth rates of the two metal sulfide materials reflect the growth mechanisms suggested in the literature, with CdS film growth being considerably slower due to the intermediate adsorption of cadmium hydroxide species on the substrate prior to CdS formation as opposed to the faster growth rate of PbS, indicative of direct heterogeneous growth on the surface. Consequently, greater deviation from a strictly linear growth profile is seen for PbS compared to CdS films. Additional work focusing on testing the consistency of the linear film growth kinetics show a high degree of accuracy of the models derived in this study. Such accuracy is essential for the successful optimization of low-loss metal / metal sulfide coated HGWs for use at near and mid-IR wavelengths as well as in the development of next-generation CdS/PbS multilayer dielectric stack HGWs and eventually in the fabrication of a 1-D photonic bandgap metal sulfide multilayer structure for ultra-low-loss HGWs. Film thickness variation due to either the experimental variability of the DLPD procedure or the length of the HGW can be neglected for all applications except those requiring the most stringent degree of film
thickness accuracy and/or very long HGWs. In addition to the experimental development of accurate metal sulfide thin film growth models in HGWs, this study extended previous CdS and PbS thin film deposition methods in HGWs in optimizing the fabrication parameters to produce films of higher quality while essentially eliminating previously encountered difficulties and inconsistencies [2,3,6,7]. In particular, optimization of precursor solution concentrations for the deposition of PbS films performed as part of this analysis allowed for reduction of deposition solution pH while achieving high quality, uniform PbS films at high film growth rates. Such reduction in solution pH was proven to be crucial in ensuring prevention of previously encountered damage to the underlying Ag film, rendering the HGW useless, resulting from excessively basic solutions used during the deposition of PbS films. Furthermore, the considerable decrease in CdS deposition times relative to previous deposition procedures has opened up the possibility of depositing CdS films of adequate thicknesses for mid-IR optimization. Previously, the excessively long deposition times necessary to achieve such thicknesses (t > ~10 hours) limited the use of CdS films to NIR wavelengths, as such lengthy deposition times resulted in considerably lower quality CdS films with an undesirable degree of film thickness variation. In summary, the present study was shown to successfully improve and optimize CdS and PbS DLPD film growth procedures while simultaneously experimentally investigating in depth the dependence of CdS and PbS film growth in HGWs as a function of elapsed deposition procedure time, precursor solution temperatures, waveguide surface substrate material, and waveguide length, allowing for the successful and consistent deposition of these metal sulfide films for optimal low-loss transmission at mid-IR wavelengths.