

Deposition and characterization of metal sulfide dielectric coatings for hollow glass waveguides

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Abstract: Metal sulfide dielectric thin films have been deposited using dynamic wet chemistry processing on silver coated hollow glass waveguides (HGWs). The sulfides used were cadmium sulfide (CdS) and lead sulfide (PbS); both films have excellent infrared transparency and high refractive index contrast. The thickness of these thin films can be tailored to minimize the attenuation of the HGW over specific infrared wavelengths. We have made both single and multiple dielectric (2 and 3 layer) metal coated HGWs using CdS and PbS deposited over an inner Ag layer. The straight lowest loss measured at 1.55 μm for a 1,000- μm bore Ag/CdS/PbS/CdS HGW was 0.06 dB/m. This loss is three times less than that measured for a single layer Ag/CdS coated HGW at 1.55 μm .

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OCIS codes: (060.2390) Fiber optics, infrared; (310.1860) Deposition and fabrication; (310.6860) Thin films, optical properties

References and links

1. E.D. Palik and G. Ghosh, *Handbook of optical constants of solids*, (Academic, London, 1998).
 2. Sopra database for n and k, <http://www.sopra-sa.com> (2003).
 3. Y. Fink, J. N. Winn, S. Fan, C. Chen, J. Michel, J. Joannopoulos, and E. Thomas, "A dielectric omnidirectional reflector," *Science*, **282**, 1679-1682 (1998).
 4. R. S. Mane and C. D. Lokhande, "Chemical deposition method for metal chalcogenide thin films," *Mat. Chem. Phys.* **65**, 1-31 (2000).
 5. P. K. Nair, M. T. S. Nair, V. M. Garcia, O. L. Arenas, Y. Pena, A. Castillo, I. T. Ayala, O. Gomezdaza, A. Sanchez, J. Compos, H. Hu, R. Suarez, and M. E. Rincon, "Semiconductor thin films by chemical bath deposition for solar energy related applications," *Solar Energy Materials and Solar Cells* **52**, 313-344 (1998).
 6. P. C. Rieke and S.B. Bentjen, "Deposition of cadmium sulfide films by decomposition of thiourea in basic solution," *Chem. Mat.* **5**, 43-53 (1993).
 7. V. Gopal, and J. A. Harrington, "Dielectric coatings for Ag/dielectric hollow glass waveguides," in *Optical Fibers and Sensors for Medical Applications II*, Proc. SPIE **4616**, 143-151 (2002).
 8. V. Gopal, and J.A. Harrington, "Metal sulfide coatings for hollow glass waveguides," in *Optical Fibers and Sensors for Medical Applications III*, Proc. SPIE **4957**, 97-103 (2003).
 9. M. Miyagi and S. Kawakami, "Design theory of dielectric-coated circular metallic waveguides for infrared transmission," *J. Lightwave Technol.* **LT-2**, 116-126 (1984).
 10. M. Mohebbi, R. Fedosejevs, V. Gopal, and J. A. Harrington, "Silver-coated hollow-glass waveguide for applications at 800 nm," *Appl. Opt.* **41**, 7031-7035 (2002).
 11. K. Matsuura, Y. Matsuura, and J. A. Harrington, "Evaluation of gold, silver, and dielectric-coated hollow glass waveguides," *Opt. Eng.* **35**, 3418-3421 (1996).
 12. C. D. Rabbii, D. J. Gibson, and J. A. Harrington, "Processing and characterization of silver films used to fabricate hollow glass waveguides," *Appl. Opt.* **38**, 4486-4493 (1999).
 13. T. Abel, J. Hirsch, and J. A. Harrington, "Hollow glass waveguides for broadband infrared transmission," *Opt. Lett.* **19**, 1034-1036 (1994).
 14. R. Dahan, J. Dror, and N. Croitoru, "Characterization of chemically formed silver iodide layers for hollow infrared guides," *Mater. Res. Bull.* **27**, 761-766 (1992).
 15. C. D. Rabbii and J. A. Harrington, "Measurement and control of thin film uniformity in hollow glass waveguides," *Opt. Eng.* **38**, 2009-2015 (1999).
 16. M. Ohring, *The materials science of thin films*, (Academic Press, Boston, 1992).
 17. Y. Matsuura, T. Abel, and J.A. Harrington, "Optical properties of small-bore hollow glass waveguides," *Appl. Opt.* **34**, 6842-6847 (1995).
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1. Introduction

Many metal sulfide compounds have excellent optical properties in the visible and IR region of the spectrum. A particularly attractive feature of these materials is the wide range of their refractive indices which vary from as low as 1.6 to as high as 5 [1,2]. This high contrast in refractive indices makes these materials an excellent choice for the fabrication of multilayer, dielectric-coated hollow waveguides. Specifically, they may be deposited in alternating layers of low/high index films inside a tubular structure to form a 1D photonic bandgap hollow waveguide [3]. Such a hollow waveguide should not only have a very low loss but also be omnidirectional in nature. In this paper we describe the first use of two metal sulfide films, CdS and PbS, to make multilayer HGWs. These films were deposited inside silica glass tubing over a metallic film of silver. In the original work on omnidirectional waveguides by Fink, et al. [3] they described an all-dielectric structure of alternating low/high index films. Our use of a metallic film in conjunction with a multilayer dielectric stack means that we will need fewer dielectric layers to achieve the same loss as an all dielectric omnidirectional structure.

CdS and PbS films are transparent in the 2 to 12 μm region. The refractive indices of CdS and PbS are 2.25 and 4.27 at 1.55 μm and 2.25 and 4.0 at 10.6 μm , respectively. This gives an index contrast of $4.27/2.25 = 1.9$ at 1.55 μm and 1.78 at 10.6 μm . These two dielectric materials and other sulfides such as ZnS and ZnSe may be deposited in thin film form using straightforward solution chemistry methods [4-6]. Furthermore these two materials are compatible and the wet chemistry methods used to deposit both films are similar [7,8].

Dielectric-coated metallic HGWs that we have studied are designed to minimize the attenuation of the HGW over a particular IR wavelength region by optimizing the thickness of each dielectric layer. We used the well-established theory of Miyagi and Kawakami [9] to calculate the expected losses for multilayers of CdS and PbS coatings. Using their theory and the n and k values for CdS and PbS, we calculated the losses for single and multilayer films at both 1.55 and 10.6 μm . Our calculations at 10.6 μm show that a 1,000- μm bore HGW with a 3-layer stack of CdS/PbS/CdS films deposited over Ag will have a straight loss of 0.016 dB/m compared to a straight loss of 0.07 dB/m for a single layer CdS film deposited over Ag. That is, the calculated attenuation coefficients are approximately four times less for the three layer design compared to a single dielectric layer at 10.6 μm .

2. Experimental procedure

HGWs are prepared in a two step process in which an Ag film is first deposited on the inner surface of the silica tubing and then a dielectric layer of CdS or PbS is deposited on top of the metallic layer. For multilayer dielectric structures, sequential deposition of alternating low/high films leads to the structures, Ag/CdS, Ag/CdS/PbS, and Ag/CdS/PbS/CdS. The Ag film is deposited on the inner surface of the silica tubing using a liquid-phase reduction reaction typical of that used in our earlier work on Ag/AgI HGWs [10-12]. The thickness of the Ag film is chosen to be sufficiently thick to prevent any transmission through the film but thin enough so that the surface roughness is as low as possible. Specifically, the thickness of the Ag film is chosen to be at least ten times the skin depth at 10.6 μm . The skin depth of an Ag film at 10.6 μm is 12 nm. In all our experiments CdS and PbS have been deposited on Ag films that vary in thickness from 150 to 200 nm. At this thickness the Ag films are quite smooth (< 12 nm rms roughness) and, therefore, they provide a good surface for the deposition of the dielectric layers. A very important feature of the CdS and PbS coatings is that they are additive and, thus, independent of the Ag film. This is in strong contrast to the HGWs made using AgI coatings [11, 13, 14]. AgI is deposited in a subtractive process in which AgI is formed by the diffusion of iodine ions into the underlying silver film. Therefore, to produce a thick dielectric layer of AgI will require a thick starting layer of Ag. Rabbii and Harrington [15] have shown that the surface roughness of both the Ag and the AgI film increases with increasing thickness of the Ag layer.

CdS and PbS thin films were deposited using a wet chemistry deposition technique [4]. Cadmium nitrate and cadmium acetate are used as the source of Cd ions; lead nitrate the source of Pb ions; and thiourea, (SC(NH₂)₂), the source of S ions. It is important to accurately control pH of these solutions since the CdS and PbS precipitates are stable only in the pH range 10 to 13. pH control and chelating is achieved using an ammonia solution for CdS and sodium hydroxide for PbS. Specifically, the pH for aqueous Cd(NO₃)₂ is maintained between 11 and 12. Since the reaction rate also changes with the pH, it is necessary to calibrate the process for a given pH range. The thickness of both CdS and PbS increases with increasing concentration of Cd, Pb and S ions in solution and with increasing deposition time. From a study of the growth kinetics for both CdS and PbS thin films, we have established optimal concentration and flow rate conditions for uniform film deposition for tubing with lengths greater than 1.5 m. The best coatings were made using > 0.01 M solutions and pumping rates of 30 ml/min.

The multilayer dielectric structures of Ag/CdS/PbS and Ag/CdS/PbS/CdS, were prepared in a manner similar to the single-layer dielectric metallic waveguides. The different layers were coated in a sequential manner with an intermediate drying step after coating each layer. An Ag-only tube was coated with a single layer of either CdS or PbS when the 2- and 3-layer structures were being coated as an independent check on the thickness for each layer.

3. Optical characterization of Ag/sulfide film HGWs

The spectral characteristics of the Ag/CdS and Ag/PbS HGWs were evaluated using a Perkin Elmer UV-VIS spectrometer and Nicolet Protégé FTIR. A typical spectral response shows interference peaks which depend on the thickness of the dielectric thin films. The thickness of a single layer dielectric, d , was calculated from the peak position of the longest-wavelength interference band, $\lambda_p^{(m)}$, using the relation [12],

$$d = \frac{m \cdot \lambda_p^{(m)}}{4 \cdot \sqrt{n_1^2 - 1}}, \quad (1)$$

where m is the order of the interference maxima ($m = 1$ for the longest-wavelength band); λ_p is the wavelength of the m^{th} absorption peak; and n_1 is the refractive index of the dielectric film. From Eq. (1) we see that the peak position shifts to longer wavelengths as the thickness of the film increases. Spectral data has been used to determine the thickness of films prepared using different growth kinetics. The film thickness obtained from the optical measurements has then been correlated with direct thickness measurements using a field-emission scanning electron microscope (FESEM). In this way we obtain the growth kinetic curves for CdS and PbS deposited on Ag, shown in Fig. 1.

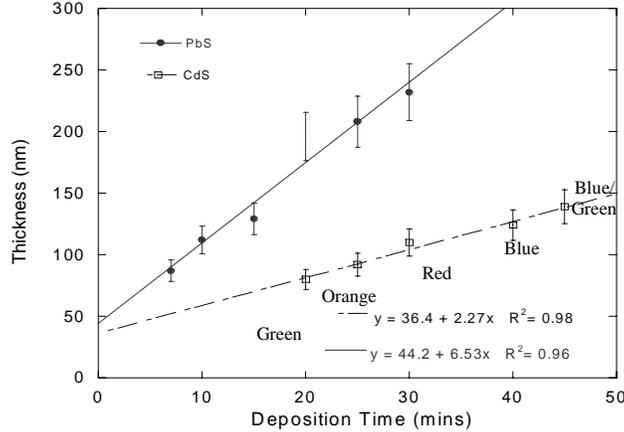


Fig. 1 The growth kinetic curves of the CdS and PbS thin films deposited in a Ag coated, 1,000 μm bore HGWs. The color indicated is the color that one would see looking through the waveguides with an optical microscope.

All films were prepared using 0.01 M solutions and a flow rate of 30 ml/min. The growth kinetics curves in Fig. 1 indicate that CdS (open symbols) has a slower growth rate on Ag compared to PbS (solid symbols) under similar conditions. The reason for the slower growth rate for CdS compared to PbS is that the CdS complexes with the ammonia used in the deposition and this decreases the rate of deposition. The data also show that the thickness of both dielectrics increases linearly with time, with growth rates of ~ 2.3 and 6.9 nm/min for CdS and PbS, respectively. The mechanism for linear growth is based on the Stransi-Krastanov model of island-like growth [16]. This mechanism involves nucleation and growth and we are in the linear growth region. This information is important as we need to carefully control film thickness for single and multilayer structures. The UV-VIS spectra for the Ag/CdS is given in Fig. 2 and the FTIR spectra for the Ag/PbS in Fig. 3. The spectral data clearly show that the position of the interference peaks shifts to longer wavelengths as the thickness of the film increases as predicted by Eq. (1). We also note from the insert photos in Fig. 2 that the HGWs show a color variation. This is due to selective filtering of the input white light by the thin film coating (interference effect). This color variation is seen with the CdS coatings but not the PbS films as these films do not transmit well at visible wavelengths.

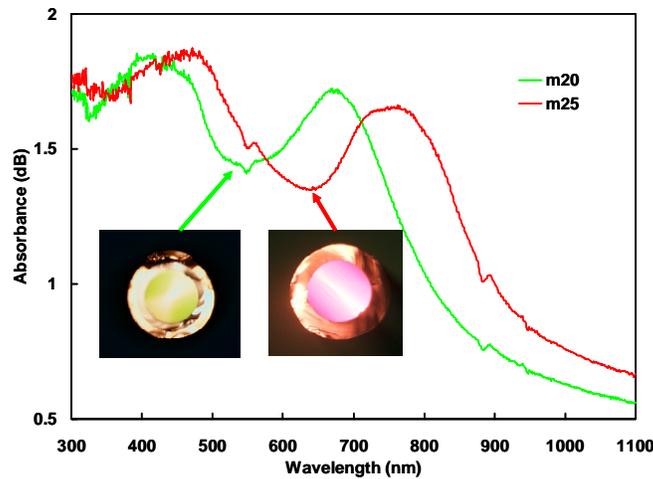


Fig. 2 UV-VIS spectra of 1,000- μ m bore Ag/CdS HGWs for different deposition times in m minutes. The insert shows the color of the transmitted light as filtered by the coating.

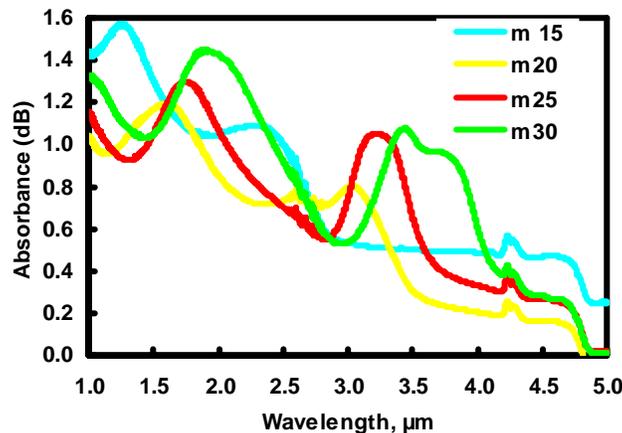


Fig. 3 FTIR spectra of 1,000- μ m bore Ag/PbS HGWs for different deposition times in m minutes.

The thickness of the thin films was obtained by direct measurements using a FESEM. A photomicrograph taken with the FESEM for a typical cross-section of the thin film combination Ag/CdS/PbS is shown in Fig. 4. The CdS film appears darker than the PbS film because the in-lens detector produces a negative image of the secondary electron image. The thicknesses of the films shown in Fig. 4 are; Ag 154 nm, CdS 169 ± 16 nm, PbS 82 ± 6 nm. We do not see any degradation of the underlying film when the new film is deposited over it. That is, CdS and PbS do not react with each other during the deposition of successive layers. The film thickness measured from the FESEM micrographs of both single and multilayer dielectric film are summarized in Table 1. These results agree very well with the optical thickness measurement.

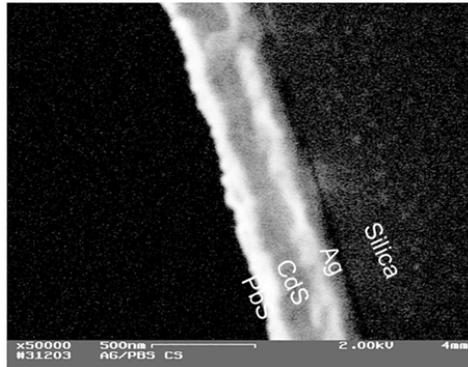


Fig. 4 Cross sectional FESEM image of a 1,000- μ m bore Ag/CdS /PbS HGW. The CdS and PbS thin films are deposited sequentially inside the Ag coated HGW.

Table 1 Thickness values for CdS and PbS thin films on Ag determined from FESEM images

HGWs	Thickness of Ag nm	Thickness of CdS nm	Thickness of PbS nm
Ag/CdS	156 ± 16	172 ± 16	—
Ag/PbS	158 ± 20	—	96 ± 16
Ag/CdS/PbS	154	169	82 ± 6

A series of 1,000- μ m-bore HGWs with 1, 2, and 3 dielectric layers deposited over Ag were fabricated using wet chemistry methods [8, 11]. The spectral losses for these straight waveguides are shown in Fig. 5. From Fig. 5, it may be seen that the addition of each dielectric layer shifts the interference peaks to longer wavelengths. This is a result of the increase in thickness with each additional layer.

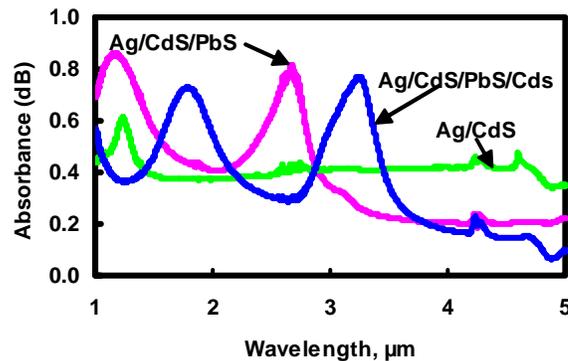


Fig. 5 FTIR Spectra of a 1,000- μ m bore of 1, 2, and 3-layer dielectric coatings on Ag coated HGWs. The spectra beyond 4 to 12 μ m region are essentially flat and featureless.

The thickness of each dielectric layer was determined from a witness sample composed of each dielectric layer deposited separately on Ag. These witness samples were deposited along with the multilayer waveguide. From the witness samples we determined the thickness of the individual layers using the position of the long wavelength interference peak and Eq. (1). The thicknesses obtained were; Ag 200 nm, CdS (adjacent to Ag) 156 nm, PbS 87 nm, and CdS (next to air) 97 nm. The thickness values of CdS and PbS layers measured optically agree very well with FESEM measurements and are within experimental errors as shown in Table 1. From Fig. 5 we see that this waveguide is best suited for operation beyond 5 μm .

Losses measurements were made at 1.55 μm using a diode laser rather than a CO₂ laser at 10.6 μm where the HGWs would ultimately be most useful. The reason for using a 1.55 μm laser was that we were interested in developing a new waveguide for secure communication systems at 1.55 μm . Clearly, solid-core silica fibers are a better choice for most applications at 1.55 μm . The output of the diode laser was via a pigtailed single mode fiber terminated with a Selfoc lens. The spectral response of the HGWs chosen for loss measurements was similar to that shown in Fig. 5. In general, coating thicknesses were not optimized for lowest loss at 1.55 μm ; however, as may be seen from the cut-back loss data given in Table 2, the losses were still quite low. The measured losses in Table 2 may be compared to the theoretical losses calculated at both 1.55 and 10.6 μm using the n and k values of the dielectric films and the theory of Miyagi and Kawakami [9]. The losses at 1.55 μm are high when PbS is used because k is rather large at this wavelength ($k=0.39$). At 10.6 μm k for PbS is 0.008 and the calculated loss for Ag/CdS/PbS/CdS is over four times less than for Ag/CdS. The bending losses for the waveguides were not measured. It is well known that there is an additional loss on bending for non-omnidirectional waveguides which varies as $1/R$, where R is the radius of the bend [17]. Since our waveguides have no more than 3 dielectric layers it is expected that we would not observe omnidirectional behavior rather there would be an added loss on bending.

Table 2 Loss values for 1,000- μm bore HGWs with 1, 2, and 3-layer dielectric coatings.

Multilayer structure	Measured loss at 1.55 μm , dB/m	Theoretical loss at 1.55 μm , dB/m	Theoretical loss at 10.6 μm , dB/m
Ag/CdS	0.2 ± 0.04	2.7×10^{-3}	7.0×10^{-2}
Ag/PbS	0.26 ± 0.04	2.5×10^{-2}	7.3×10^{-2}
Ag/CdS/PbS	0.1 ± 0.04	8.6×10^{-3}	3.3×10^{-2}
Ag/CdS/PbS/CdS	0.06 ± 0.04	6.7×10^{-3}	1.6×10^{-2}

4. Conclusions and summary

We have demonstrated that liquid-phase chemistry methods can be used to deposit good optical quality CdS and PbS thin films to form both single and multiple dielectric/metallic HGWs. The spectral response for waveguides with these films deposited over Ag show well defined interference bands indicating good film thickness uniformity over the entire length of the guide. The position of the interference peaks is controlled by varying the deposition time. Furthermore, we have found that CdS and PbS are compatible and the deposition of each material does not affect the underlying film. In this way the thickness of each layer in the multilayer stack can be tailored for use over a wide wavelength range. The final 3-layer stack showed that it is possible to make a multilayer coating but we have yet to reduce the attenuation to the level predicted by theory. Moreover, the measured losses for the single-layer CdS or PbS films at 1.55 μm are in general agreement with the well studied Ag/AgI HGWs at 10.6 μm [17]. In reality, the greatest potential for these waveguides is likely to be at 10.6 μm for applications involving CO₂ laser power delivery and IR fiber sensors.

Acknowledgement

This work was supported by a grant from NSF.