Mid-infrared characterization of solution-processed $\text{As}_2\text{S}_3$ chalcogenide glass waveguides

Candice Tsay,¹ Elvis Mujagić,¹,² Christi K. Madsen,³ Claire F. Gmachl,¹ and Craig B. Arnold¹,4,*

¹Department of Electrical Engineering, Princeton University, Princeton, NJ 08544 USA
²Department of Electrical and Computer Engineering, Texas A&M University, College Station, TX 77843 USA
³Institute for Solid State Electronics, Vienna University of Technology, 1040 Vienna, Austria
⁴Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544 USA

*cbarnold@princeton.edu

Abstract: An etch-free and cost-effective deposition and patterning method to fabricate mid-infrared chalcogenide glass waveguides for chemical sensing applications is introduced. $\text{As}_2\text{S}_3$ raised strip optical waveguides are produced by casting a liquid solution of $\text{As}_2\text{S}_3$ glass in capillary channel molds formed by soft lithography. Mid-IR transmission is characterized by coupling the output of a quantum cascade (QC) laser ($\lambda = 4.8 \mu m$) into the 40 $\mu m$ wide by 10 $\mu m$ thick multi-mode waveguides. Loss as low as 4.5 dB/cm is achieved using suitable substrate materials and post-processing. Optical absorption and surface roughness measurements indicate that the solution-processed films are of sufficient quality for optical devices and are promising for further development of waveguide-based mid-IR elements.

©2010 Optical Society of America

OCIS codes: (130.2755) Glass waveguides; (130.3060) Infrared; (310.1860) Deposition and fabrication.

References and links


1. Introduction

Mid-infrared ($\lambda = 3-25$ $\mu$m) optical technologies for small-footprint chemical sensors have the potential to bring about low-cost, widely-accessible health and environmental monitoring, but require miniaturization and integration of photonic components to be practical [1–3]. While the emergence of compact quantum cascade (QC) lasers [4] along with innovations in detector design are important steps toward size reduction, the technology to link these devices using low-loss planar waveguides is lacking. Waveguides based on Si have been proposed [5], however this technology is hampered by complicated processing of suspended structures. On the other hand, chalcogenide glasses such as As$_2$S$_3$ possess desirable optical properties in the near- and mid-IR such as a wide transmission window (long wavelength cut-off at 9.4 $\mu$m), high refractive index ($n = 2.4$ at $\lambda = 4.8$ $\mu$m) [6], high nonlinearity [7,8], and photorefractive behavior [9–11]. These attributes make chalcogenide glasses a good match for integrated near- and mid-IR applications.

Previously, chalcogenide glass ridge or embedded channel waveguides have been fabricated by depositing thin films of As$_2$S$_3$ or closely related chalcogenides by thermal evaporation, RF sputtering, or pulsed laser deposition, followed by a patterning process consisting of photolithography and dry etching [12,13] or wet etching [11], lift-off [14], embossing [15,16] or laser writing [11,17,18]. However, many of these methods are not optimal for fabrication of thick films for the mid-IR wavelengths due to growth rate limitations and residual stress present in deposited layers [19]. In addition, As$_2$S$_3$ is attacked by NH$_4$OH-based photoresist developers, leading to film delamination and pinhole formation [11]. Extra steps to process protective layers are therefore needed, adding complexity to the
overall process [20,21]. Utilizing the photo-modifiability of chalcogenide glasses to laser-write waveguides is an alternative, but good refractive index contrast for high-density devices is difficult to achieve and the long-term stability of the modified material is unclear. Embossing drawn chalcogenide fiber to make rib waveguides has also been demonstrated [22], but again film thicknesses can be process-limited.

The solution-casting and molding approach we employ to fabricate As$_2$S$_3$ waveguides (Fig. 1) is a low-cost, low temperature, and etch-free process [23]. Unlike conventional thin film processing techniques, solution-molding readily produces structure heights exceeding a few microns. This enables waveguides with dimensions that are comparable to the ridge widths and heights of an edge-emitting (Fabry-Pérot) QC laser, and to the wavelengths of interest. Thus alignment to QC lasers for cut-back measurement of the waveguide propagation loss at the mid-IR is straightforwardly accomplished. Here we demonstrate the formation of multi-mode waveguide structures and examine how the optical properties of the substrate and post-process annealing steps affect the propagation loss.

![Fig. 1. Solution casting and molding method. (a) Generating the PDMS mold. (L-R) Master mold patterned by photolithography using SU-8 photoresist. PDMS precursor cast on master mold. Cured PDMS mold peeled away. (b) Forming As$_2$S$_3$ structures by capillarity. (L-R) PDMS mold placed on substrate, forming channels. Droplets of As$_2$S$_3$ solution pipetted to inlets. Channels fill by capillary action. Sample is baked in vacuum oven to solidify structures. PDMS mold is removed.](image)

2. Experimental

The process to create a solution of As$_2$S$_3$ by dissolving As$_2$S$_3$ in propylamine or butylamine solvent was first described by Chern et al. with the aim of using spin-coated films as high resolution photo-patternable material [24]. We find that by using various methods to deposit solutions, these types of materials can successfully be carried over to photonic applications [9,25]. Bulk As$_2$S$_3$ (Cerac Specialty Inorganics) is crushed into a powder and dissolved in anhydrous propylamine solvent (>99.0%, Fluka) at a concentration of 0.2 g ml$^{-1}$. After complete dissolution, the stability of the solution is such that, with minimal exposure to ambient humidity or light, the solution remains precipitate-free over several weeks. When baked, the excess solvent evaporates, leaving solid structures that retain compositions close to bulk [25–27]. To ensure high film quality, processing is done in a N$_2$ environment.

In order to fabricate As$_2$S$_3$ structures we employ a micromolding technique, in which an elastomeric poly-dimethylsiloxane (PDMS) mold is filled with a fluid precursor by capillarity and post-processed [23]. In the past, such a technique has shown itself to be versatile, in the variety of materials patterned, including polymers [28] and ceramics from sol-gel precursors [29], and in the variety of shapes and dimensions generated, from serpentinaes to stars. To generate the PDMS mold (Fig. 1(a)), first a thick-film photoresist (SU-8 2025, MicroChem) is
patterned by photolithography into a relief pattern on a Si substrate. PDMS (Sylgard 184, Dow Corning) is then cast over the master mold and cured for 6 hours at 65° C, forming a soft mold with rectangular channels that defines the shape of the waveguides. The SU-8 master molds can be conveniently reused for rapid fabrication of samples.

The PDMS mold is placed on the waveguide substrate, making conformal contact and forming enclosed channels with open ends through which the As$_2$S$_3$ solution flows (Fig. 1(b)). As droplets of As$_2$S$_3$ solution are pipetted to an open end of the channels, capillary forces draw the liquid in, filling the channels. Oven-baking for 1 hr at 60° C and 2 hrs at 80° C forms solid waveguide structures, after which, the compliant PDMS mold is peeled away from the substrate. The resulting waveguides preferentially adhere to the substrate rather than the mold due to the comparatively low surface energy of PDMS.

Since the solution fills the mold purely by capillary forces, the channel incursion length depends on the channel dimensions, surface energies of the mold and substrate, and viscosity of the liquid [28]. The As$_2$S$_3$ in propylamine solution does not fill the channels adequately due to the high volatility of the propylamine. Therefore the solution is diluted with ethanol, a solvent with higher vapor pressure, which also decreases the solution’s viscosity. As a result, using a 40 µm wide by 20 µm high PDMS mold on a glass substrate, a solution diluted to a ratio of 1 part ethanol to 3 parts As$_2$S$_3$-propylamine solution has a filling length of over 2 cm, compared to 0.2 cm with the unmodified solution. As a route to longer, single mode waveguides, the PDMS mold may be interfaced with microfluidic pumps. It has been shown that such vacuum-assisted molding yields increased filling lengths [30].

In mid-IR waveguide design, the absorbance of the substrate material is an important criterion for low loss. Waveguides are fabricated on three different substrate materials: SiO$_2$, LiNbO$_3$, and NaCl. For the SiO$_2$ samples, As$_2$S$_3$ waveguides are fabricated on a 2 µm thick SiO$_2$ cladding layer deposited by plasma-enhanced chemical vapor deposition on highly doped (n +) GaAs wafers. For the other samples, the waveguides are fabricated directly on x-cut LiNbO$_3$ wafers (0.5 mm thick, Thorlabs) or polished NaCl crystals (4 mm thick, International Crystal Laboratories). The waveguides adhere well to all of the substrate types, allowing for sample cleavage without delamination from the substrate.

Mid-IR propagation measurements at $\lambda = 4.8$ µm are carried out on the waveguides, which are aligned and butt-coupled to an edge-emitting buried heterostructure QC laser [31] under pulsed operation at room temperature (Fig. 2). The waveguide output is collected by 2” diameter ZnSe lenses and focused onto a liquid-nitrogen cooled HgCdTe (MCT) detector. The detector signal is read out on a lock-in amplifier used to discriminate the actual signal from ambient background. The cut-back method is employed to determine the propagation loss. For each sample length, waveguide faces are prepared by cleaving the wafer, but are not polished.

![Fig. 2. Schematic of mid-IR propagation loss measurement setup. Inset photo: Top view of an As$_2$S$_3$ waveguide aligned and butt-coupled to a QC laser. Laser biased at 50V, pulsed at 0.8% duty cycle, at room temperature (with exception of measurement on SiO$_2$ sample: laser biased at 72V, pulsed at 2% duty cycle).](image)

3. Propagation loss due to substrate absorbance

Straight waveguides 40µm wide by 10 µm high on the three different substrate materials are characterized (Fig. 3). At these dimensions, the waveguides support multiple transverse
modes. The large refractive index differences at the air gap between the waveguide and laser facets result in coupling loss from reflectance. Additional coupling loss stems from modal mismatch, discussed in the next section, and facet roughness. The cut-back measurement results show that the propagation loss of the As$_2$S$_3$ waveguides depends heavily on the transmittance of the underlying substrate. There is a 3.2 dB/cm reduction in waveguide attenuation going from SiO$_2$ to NaCl substrates.

![Image](image.png)

**Fig. 3.** Cut-back measurement showing waveguide attenuation for waveguides on different substrate materials, $\lambda = 4.8$ µm. Un-annealed waveguide samples are successively cleaved in 1 mm increments. Each data point represents measurements from four distinct waveguides.

Table 1 shows the optical properties of the substrate materials as well as As$_2$S$_3$, including literature values of the extinction coefficient, $k$, where $k$ is related to the absorption coefficient, $\alpha$, by $k = \lambda \alpha/4\pi$. Of the considered substrate materials, SiO$_2$ is highly absorbing at the 5 µm wavelength, LiNbO$_3$ is transmissive, but near its long-wavelength transmission cutoff, and NaCl is most transmissive deep into the mid-IR.

<table>
<thead>
<tr>
<th>Material</th>
<th>$n$</th>
<th>$k$</th>
<th>$\lambda$ cut-off</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>1.3</td>
<td>4.0x10$^{-3}$</td>
<td>3.7 µm</td>
</tr>
<tr>
<td>LiNbO$_3$</td>
<td>2.0</td>
<td>4x10$^{-5}$[b]</td>
<td>5.2 µm</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.5</td>
<td>1.7x10$^{-9}$</td>
<td>15.4 µm</td>
</tr>
<tr>
<td>As$_2$S$_3$</td>
<td>2.4</td>
<td>8x10$^{-11}$[c]</td>
<td>9.4 µm</td>
</tr>
</tbody>
</table>

Table 1. Material properties at $\lambda = 5$ µm$^{[a]}$


### 4. Loss reduction through post-process annealing

It has been shown that post-deposition annealing can have a significant effect on the loss parameters of vapor deposited waveguide structures [20,32] and we find similar results for molded structures albeit through different mechanisms. The loss reduction we see for these structures primarily stems from densification of the material due to solvent removal and an accompanying change in the overall shape of the waveguide, all occurring at temperatures below the 185°C glass transition temperature [25].

In a parallel study conducted on spin-coated As$_2$S$_3$ films, we observe improved optical quality of the solution-processed As$_2$S$_3$ films with additional heat treatment [25]. Annealing the films in vacuum at temperatures between 120°C to 150°C is found to result in complete solvent removal through evaporation, as well as material densification (manifested as an increase in refractive index) that brings the solution-processed glass structure closer to the amorphous network structure of bulk As$_2$S$_3$. In FTIR transmission spectra, absorption peaks associated with solvent residue lie between 2200 and 3200 cm$^{-1}$, well away from the experimental wavelength, 4.8 µm (2083 cm$^{-1}$). Figure 4 shows that on the solution-processed, ethanol-diluted As$_2$S$_3$ films, there is high transmittance at 2083 cm$^{-1}$ and that solvent absorption does not significantly affect waveguide loss at this particular wavelength region.
However, we still benefit largely from improved optical propagation stemming from the stabilization of bonds and densification of the amorphous glass network.

An additional effect of post-process annealing is a change in the waveguide shape. A micrograph of a typical cleaved, un-annealed waveguide, shown in Fig. 5(a), displays inwardly curved sidewalls and a slight depression in the top caused by shrinkage and debonding of the structure from the mold as the solvent evaporates [29]. With the mold still attached to the substrate, annealing the waveguides above 100° C results in a smoothed out morphology as the As$_2$S$_3$ densifies and surface tension dominates the shape, as Fig. 5(b) illustrates. This shape change occurs under conditions well below fiber-drawing temperatures, but happens over a relatively long time scale of hours rather than seconds. Moreover, this change, from a concave structure into a convex structure, translates into reduced modal mismatch loss. Figure 5(c) shows field intensity profiles of the fundamental mode of each of the observed waveguide morphologies, calculated using BeamPROP modeling software. In un-annealed waveguides the profile of the lowest order mode is deformed due to the dip at the center of the structure.

Annealing parameters are optimized to a baking temperature of 135°C, under vacuum, for a duration of 6 hours. Figure 6 shows cut-back measurement results of waveguides annealed under these conditions. The best result, 4.5 dB/cm, comes from annealed waveguides on a NaCl substrate. The annealing step improves the propagation loss by 1.7 dB/cm. Moreover,
we see a reduction in overall insertion loss. Coupling efficiency increases because of the more favorable rounded waveguide shape, reducing loss through modal mismatch.

![Fig. 6. Cut-back measurement of annealed As$_2$S$_3$ waveguides. Loss of un-annealed waveguides on NaCl plotted for comparison. Each data point represents measurements from four distinct waveguides.](image)

Attenuation due to surface scattering also decreases with annealing. The top surfaces of the waveguides are examined by atomic force microscopy (AFM) to determine surface roughness. RMS surface roughness values decrease from 2.0 nm for un-annealed waveguides to 0.45 nm for annealed waveguides. Moreover, since we do not perform an etching step, we are able to avoid etching-induced roughness that occurs in dry-etched waveguides [12].

Edge roughness may be a significant source of loss, however. Waviness of the line edges on the order of the mid-IR wavelength is present in the measured samples. Since the waveguides support multiple modes, and higher order modes are more greatly affected by surface scattering, waveguide loss due edge roughness is amplified. This edge roughness can be reduced with better control of the surface properties of the substrate, for example by careful cleaning or surface treatment of the substrates prior to molding, to ensure that the solution wets all surfaces evenly. Another measure to improve performance includes adding a top cladding to reduce evanescent loss. The implementation of such design improvements are underway.

5. Conclusion

We demonstrate that solution-casting and molding provides a unique and viable pathway to fabricating mid-IR chalcogenide glass waveguides. 4.5 dB/cm propagation loss over more than 1 cm length is measured in cut-back measurements at the mid-IR using a $\lambda = 4.8$ $\mu$m QC laser source. Selecting NaCl substrates over highly absorbing SiO$_2$ substrates leads to improved guiding. Annealing has a significant and positive effect on the solution-processed As$_2$S$_3$ optical and structural properties, waveguide shape, and surface roughness, all contributing to reduced insertion loss. Characterization of the waveguide material and morphology shows that the measured loss is primarily due to sidewall scattering, not material absorption. Further improvement in processing should lead to improved edge roughness and reduction in loss.

The ability to do rapid and straightforward fabrication of chalcogenide glass waveguides is the first step toward establishing cost-effective and miniaturized mid-IR photonic circuits for the next generation of sensing devices. This fabrication method is purely additive and etch-free, opening the door to direct integration of chalcogenide waveguides with mid-IR sources, such as QC lasers.
Acknowledgments

This work was supported by NSF grant EEC-0540832 through the Mid-Infrared Technologies for the Health and Environment (MIRTHE) Center. The authors thank X. Xia and P. F. Murphy for assisting the measurements and S. Song for discussions on As$_2$S$_3$ solution-processing. We acknowledge the usage of PRISM Imaging and Analysis Center, which is supported in part by the Princeton Center for Complex Materials (NSF grant DMR-0819860).