SOLUTION-PROCESSING OF CHALCOGENIDE MATERIALS FOR DEVICE APPLICATIONS

YUNLAI ZHA

A DISSERTATION
PRESENTED TO THE FACULTY OF PRINCETON UNIVERSITY IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

RECOMMENDED FOR ACCEPTANCE BY THE DEPARTMENT OF ELECTRICAL ENGINEERING

ADVISOR: CRAIG B. ARNOLD

JUNE 2014
© Copyright by YUNLAI ZHA, 2014.

All Rights Reserved
Abstract

Chalcogenide glasses are well-known for their desirable optical properties, which have enabled many infrared applications in the fields of photonics, medicine, environmental sensing and security. Conventional deposition methods such as thermal evaporation, chemical vapor deposition, sputtering or pulse laser deposition are efficient for fabricating structures on flat surfaces. However, they have limitations in deposition on curved surfaces, deposition of thick layers and component integration. In these cases, solution-based methods, which involve the dissolution of chalcogenide glasses and processing as a liquid, become a better choice for their flexibility. After proper treatment, the associated structures can have similar optical, chemical and physical properties to the bulk.

This thesis presents an in-depth study of solution-processing chalcogenide glasses, starting from the 'solution state' to the 'film state' and the 'structure state'. Firstly, chalcogenide dissolution is studied to reveal the mechanisms at molecular level and build a foundation for material processing. Dissolution processes for various chalcogenide-solvent pairs are reviewed and compared. Secondly, thermal processing, in the context of high temperature annealing, is explained along with the chemical and physical properties of the annealed films. Another focus is on nanopore formation in propylamine-processed arsenic sulfide films. Pore density changes with respect to annealing temperatures and durations are characterized. Base on a proposed vacancy coalescence theory, we have identified new dissolution strategies and achieved the breakthrough of pore-free film deposition. Thirdly, several solution methods developed along with the associated photonic structures are demonstrated. The first example is "spin-coating and lamination", which produces thick (over 10 µm) chalcogenide structures. Both homogeneous thick chalcogenide structures and heterogeneous layers of different chalcogenide glasses or metals can be fabricated. Second, "micro-molding in capillaries" (MIMIC) and "micro-transfer molding" (µTM) methods are introduced for fabri-
cating waveguides on flat and curved surfaces. The flexibility of the solution process allows waveguides to be patterned, for the first time, on a curved surface. Third, 'micro channel filling' is demonstrated to produce the lowest loss among solution-processed chalcogenide waveguides. These results contribute to the advancement of chalcogenide processing technologies and help move closer towards the ultimate goal of fabricating reliable IR sensors.
Acknowledgements

I am grateful to many individuals who have helped me in one way or another while performing my research at Princeton University, so my thanks goes to:

My advisor, Craig Arnold, for his continuous encouragement, support and guidance. I am fortunate to be your student.

The readers of my thesis Gerard Wysocki and Nao Yao, for their helpful thoughts and comments.

My research collaborators, Maike Waldmann and Pao-Tai Lin (MIT), as well as all Arnold group members, especially Romain Fardel, Marti Duocastella, Yu-Cheng Tsai, Shanshan Song, Candice Tsay, Chao Lu, Juliana Mara Pinto de Almeida, Frederik Brasz, John Cannarella and Joshua Spechler.

Professor Claire Gmachl and Anna Michel, for their generosity regarding lab space and equipment.

The PRISM micro-fabrication lab and imaging and analysis staff, including Pat Watson, Nan Yao, Joe Palmer, Conrad Silvestre, Yong Sun and Jerry Poirier, for providing the expert support and enabling quality research.

Dr. Edeline Fotheringham from Daylight Solutions for valuable discussions.

The MIRTHE center staff for their involvement and support, as well as the big MIRTHE family for years of quality interaction and collaboration.

My family in China for care and comfort at all times. I love you, always.
# Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>iii</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>v</td>
</tr>
<tr>
<td>List of Tables</td>
<td>ix</td>
</tr>
<tr>
<td>List of Figures</td>
<td>x</td>
</tr>
<tr>
<td>List of Papers</td>
<td>xiii</td>
</tr>
</tbody>
</table>

## 1 Introduction

1.1 Motivation                                                          | 1    |
1.2 Chalcogenide glass and their properties                             | 5    |
1.3 Solution-processing of chalcogenide glasses                         | 10   |
1.3.1 Spin-coated waveguide over-cladding for low-temperature rough-    | 12   |

1.3.2 Inkjet printing of microlenses                                    | 13   |
1.3.3 Chalcogenide layers in fibers                                    | 14   |
1.3.4 Inverse opal photonic crystal                                    | 15   |
1.4 Processing challenges                                               | 15   |
1.5 Thesis overview                                                     | 20   |

## 2 Background of chalcogenide dissolution and chalcogenide solutions  | 23   |

2.1 Introduction                                                        | 23   |
2.2 Dissolution mechanisms of arsenic sulfide                           | 24   |
2.3 Dissolution study of other chalcogenides ............................ 28
2.4 Summary .............................................................. 30

3 Solution-processed chalcogenide films .................................... 31
  3.1 Introduction .......................................................... 31
  3.2 Spin-coating and thermal processing ................................. 32
  3.3 Chemical structures and light exposure ............................ 34
  3.4 Physical structures .................................................... 35
    3.4.1 Introduction ...................................................... 35
    3.4.2 Experimental method ........................................... 36
    3.4.3 Pore formation and trend ..................................... 37
    3.4.4 Vacancy coalescence mechanism ............................. 42
    3.4.5 Pore removal .................................................... 43
    3.4.6 Summary ........................................................ 48

4 Solution-processed thick chalcogenide structures ...................... 49
  4.1 Introduction .......................................................... 49
  4.2 Experimental method ................................................. 51
  4.3 Homogeneous thick structures ...................................... 54
  4.4 Heterogeneous thick structures .................................... 58
  4.5 Summary .............................................................. 65

5 Solution-processed photonic chalcogenide structures .................. 67
  5.1 Introduction .......................................................... 67
  5.2 Waveguides and losses .............................................. 68
    5.2.1 Optical waveguides .......................................... 68
    5.2.2 Losses in optical waveguides ............................... 71
  5.3 Loss improvement: from MIMIC and µTM to micro-channel filling . 75
    5.3.1 Waveguides by MIMIC and µTM ............................. 75
5.3.2 Low loss waveguides by micro-channel filling ............... 79
5.4 Other structures by MIMIC, μTM or micro-channel filling ......... 88
  5.4.1 Waveguides on curved surfaces ................................ 88
  5.4.2 Rings and microlenses by MIMIC or μTM ..................... 91
  5.4.3 Gratings by micro-channel filling ............................... 93
5.5 Summary and discussion ............................................. 99

6 Conclusion ..................................................................... 101
List of Tables

3.1 Solvents used for pore formation tests .......................... 47

5.1 Comparison of µm and micro-channel filling methods ........... 87
List of Figures

1.1 Absorption of CO$_2$ for 1 cm pathlength under atmospheric conditions 3
1.2 Schematic of a gas sensor design . . . . . . . . . . . . . . . . 4
1.3 Chalcogens from the periodic table . . . . . . . . . . . . . . . . 6
1.4 Refractive index for arsenic sulfide . . . . . . . . . . . . . . . . 7
1.5 Refractive index for solution-processed arsenic sulfide . . . . . . 7
1.6 Infrared transmission for several bulk glass samples . . . . . . . . 8
1.7 Arsenic sulfide structure and lone pair electrons . . . . . . . . . . 9
1.8 Ge-Sb-S waveguides and claddings . . . . . . . . . . . . . . . . 13
1.9 Photonic crystal fiber deposited with As$_2$S$_3$ layers . . . . . . . 14
1.10 Inverse opal As-S structure . . . . . . . . . . . . . . . . . . . . . 15
1.11 Photonic crystal fiber deposited with As$_2$S$_3$ layers . . . . . . . 18
1.12 Cut-back measurement of arsenic sulfide waveguides . . . . . . . . 19
2.1 Arsenic sulfide dissolution in propylamine . . . . . . . . . . . . . . 25
2.2 Arsenic sulfide dissolution in EDA . . . . . . . . . . . . . . . . 26
3.1 Disappearance of the nitrogen peak after annealing at 180°C for 24 hours . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 33
3.2 Comparison of samples annealed at different conditions under the effect of water . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 34
3.3 Pore distribution at different temperatures . . . . . . . . . . . . . . . 38
3.4 Pore area percentage at different temperatures .................................. 39
3.5 Cross-sectional SEM showing pore formation at various temperatures 40
3.6 Pore distribution with various annealing duration ................................. 41
3.7 Percentage of pore area with various annealing duration ....................... 41
3.8 Pore removal by adding EDA ................................................................. 45
3.9 Pore distribution of samples mixed with EDA ....................................... 46
3.10 Percentage of pore area of samples mixed with EDA ........................... 47

4.1 Spin-coating and lamination steps ....................................................... 52
4.2 $\text{As}_2\text{S}_3$ films floating on water after substrates dissolution ............... 53
4.3 Photo-illumination and Ag diffusion in spin-coated chalcogenide films .... 54
4.4 Step measurement of a four-layer structure ........................................ 55
4.5 A 24 $\mu m$ layer of $\text{As}_2\text{S}_3$ uniformly deposited on a substrate by spin-
coating and annealing ........................................................................... 55
4.6 FTIR spectra of multilayer films ........................................................... 57
4.7 The annealing effect on multilayer structures ...................................... 58
4.8 Heterogeneous chalcogenide multilayer structure ................................. 59
4.9 Heterogeneous silver-chalcogenide multilayer structure ...................... 60
4.10 Silver dissolution into chalcogenide films under different conditions ... 61
4.11 UV-vis transmission curves for exposed and unexposed silver-coved
arsenic sulfide films .............................................................................. 62
4.12 Silver dissolution into laminated layers .............................................. 63
4.13 Setup for demonstrating grating fabrication ..................................... 64
4.14 Alternative lines observed after Ag dissolution .................................. 65

5.1 Types of channel waveguides .............................................................. 69
5.2 Modes in a 3 layer planar waveguide .................................................. 70
5.3 Loss per bubble for varying bubble radii .............................................. 73
List of Papers

The graduate research performed in the support of this dissertation has resulted in several journal articles. These publications are listed below, sorted by the corresponding chapter of this thesis.


Chapter 1

Introduction

1.1 Motivation

Infrared technology has been experiencing rapid growth recently for its capability to supply many important societal needs. Its applications range across industries such as health, security, information technology and environmental sensing [8–17]. For instance, IR sensors have been deployed to study and monitor the green house gas emission, contributing to the climate change research [18]. In the medical field, such sensors can be used to analyze patients’ breathe, giving indication to kidney or liver disorders [19]. In terms of security screening, IR sensors are used for hazardous material detection to make our transportation terminals safer [20]. Additionally, infrared systems have already been utilized in many other areas such as night vision [21–24], industrial heat tracking [25–27], pollution monitoring [28–30], veterinary diagnosis [31] and data transfer [32–34]. Many of these problem are not only critical, but also difficult to tackle with other existing technologies. Therefore, infrared technology will continue to grow and supply this burgeoning demand.

The common IR technology used for sensing is IR spectroscopy, which uniquely identifies molecules based on its absorption spectrum and have many clear advan-
tages. Spanning the range from 750nm to 1mm, the infrared wavelength covers the "fingerprint" region of many molecules including carbon dioxide, sulfur dioxide, sulfur trioxide, nitrogen monoxide, water, glucose, TNT and sarin. It is called "fingerprint" because each molecule has its unique absorption peaks which are closely related to its vibration modes [35–37]. Since IR spectroscopy is based on strong resonance lines, it can have great sensitivity, sometimes down to single-molecule or ppt (parts-per-trillion). For example, ammonia (NH$_3$) can be detected far more readily in the mid-infrared than using light from other parts of the spectrum [38]. Strong absorption bands of CO$_2$ and CO reside at 4.3 and 4.6 microns, respectively, (Fig.1.1), allowing for easier detection with mid-infrared sensing without multiple pass optical cells or external optics. In addition to gas sensing, waveguide-based IR sensors can be readily used in aqueous environment, because water is optically transparent in near-IR. Such detection targets include biological macromolecules (e.g. proteins) and metal ions [39–41]. Moreover, the nature of optical measurements makes the procedure fast and neither invasive nor destructive, allowing many possibilities such as remote sensing or non-invasive medical diagnosis [42].

One of the critical building block of the IR technology is chalcogenide materials [44–46]. As a part of the MIRTHE (Mid-InfraRed Technology for Health and Environment) research center at Princeton University, we have dedicated our research to provide such basic materials for higher level applications. Therefore, the theme of our research is processing chalcogenide materials and fabricating photonic components for IR sensor systems. At the application level, an IR sensor system can be realized by combining our mid-infrared photonic structures/microoptics with low power quantum cascade lasers, low power laser control electronics and wireless communications. Such a complete picture of a conceptual design is illustrated in Fig.1.2. In a situation of CO$_2$ and CO detection with such device, quantum cascade lasers at 4.3 and 4.6 microns are mounted on the board with waveguides processed by our
group integrated on each facets. On the right side, the laser light passes through 2 cm of ambient air before being combined into a common waveguide and sent to a detector; whereas on the left, it passes through a 2 cm cuvette filled with a reference standard of CO$_2$/CO instead. In this fashion, signals through standards and ambient air can be compared to give direct absorbance spectroscopy, without external optics, optical cells, or alignment procedures. To this end, we choose chalcogenide glasses as our research material based on their unique properties. I not only develop deposition methods for different applications, but also study how to optimize the optical performance of our fabricated components while taking convenience, cost, reliability...
and compatibility into consideration.

Figure 1.2: Schematic of a gas sensor design (top) and comparison in size to a typical PDA (bottom). The sensor is based upon novel advances in mid-infrared technologies. Figure adapted from [43]
1.2 Chalcogenide glass and their properties

Chalcogenides are compounds comprise of at least one chalcogen anion and one electro-positive element. Chalcogen refers to elements from group 16 of the periodic table except that oxides are not considered as chalcogenides (Fig. 1.3). The chalcogenide material network formed can be both crystalline and amorphous. For example, crystalline arsenic sulfide has ruffled sheet structure and Van der Waals forces exist between the layers. Whereas amorphous arsenic sulfide has continuous and random structures, with no long-range order but is more cross-linked. This thesis is mostly concerned with amorphous type chalcogenides. More examples of chalcogenide glasses include binary chalcogenides As-Se, Ge-S, ternary chalcogenides As-S-Se, Ge-Sb-S and chalcogenides with four or more elements. The ratio of each element within a compound is not fixed. For instance, As:S ratio in the As-S system can vary between 1.5 and 9. As a result, physical properties including refractive index, absorption coefficient, nonlinear optical susceptibility, resistance, crystal structure and morphology can be modified from the original glass accordingly [47, 48].

The bonding arrangements of the chalcogenide molecules are a combination of covalent and Van der Waals-like attraction. Such bonds are relatively weak compared to the ionic bonding in other glasses, giving the material physical flexibilities [49]. For instance, arsenic sulfide has a glass transition temperature T_g of 185 °C, a low Young’s modulus of 16 GPa and a high coefficient of thermal expansion (CTE) of 21.4 (10^{-6} C^{-1}) [50].
The refractive indices of chalcogenide glasses are usually greater than 2 \[52\], making them appropriate to be used as the core material of waveguides (Fig. 1.4). In the case of solution process, the refractive index has a dependence on the thermal processing conditions (temperature and duration). In general, prolonged annealing at elevated temperatures removes more solvents and results in a refractive index closer to the bulk (Fig. 1.5) \[53\].
Figure 1.4: Refractive index for arsenic sulfide. Figure modified from [49]

Figure 1.5: (a) The refractive index dispersion for the films spin-coated from n-propylamine solutions and treated with different annealing conditions; (b) refractive indices at 900 nm wavelength as a function of annealing temperature and time. Figure adapted from [53]
A number of amorphous chalcogenide materials, including As$_2$S$_3$, have excellent infrared transmission. The transparency windows is defined by the absorption edge at $E_g$, and a long wavelength cut-off defined by phonon absorption. As shown in Fig.1.6, the transparency windows of chalcogenide glasses extend into the mid-IR as compared to the oxide glasses. This is due to the heavy atomic masses of the chalcogens relative to oxygen, which result in lower vibrational energies of the bonds (i.e. longer wavelengths). The trend shows that telluride glasses have the longest cut-off wavelengths, followed by selenides, then sulfides. Meanwhile, transmittance increases from telluride < selenide < sulfide as refractive indices decrease [49, 54].

![Figure 1.6: Infrared transmission for several bulk glass samples. Figure adapted from 49](image)

Chalcogenide glasses are also well known for their versatile photo-induced phenomena [55–58]. Upon exposure or current injection, photo-electric reactions such as photocrysallization, photopolymerization, photodissolution and electromigration can take place [59–62]. Moreover, the relatively weak bonds and bonding arrange-
ments of the chalcogenide glass network can cause the lone pair non-bonding electrons (Fig. 1.7) altering bond numbers and significant photo-induced structural changes \[63, 64\]. With illumination above the bandgap (2.2-2.3 eV for As$_2$S$_3$) \[53\], refractive index and density changes can be achieved inside the material. Such phenomenon has been exploited to locally modify the patterned areas on photonic chips and create chalcogenide Bragg gratings \[65\] or waveguides \[66\].

Figure 1.7: Arsenic sulfide structure and a lone pair of electrons shown around the arsenic center. Figure modified from http://en.wikipedia.org/wiki/File:Orpiment-unit-cell-3D.png
1.3 Solution-processing of chalcogenide glasses

Solution-based processing of chalcogenide glasses for optical applications was first explored by Chern et al. in the early 1980s. Their goal was to fabricate thin photosensitive chalcogenide glass films to be used as photoresists in lithography in a similar fashion as standard polymeric materials [67–75]. Such an approach was met with moderate success however it did not find widespread adoption due to the difficulties in material handling. Moving beyond photoresists, other researchers were motivated by the simplicity and low cost of solution-based methods [76] and the resulting chemically homogeneous films as compared to traditional approaches [77, 78].

For most chalcogenide-based solution-processes, finely grounded amorphous or crystalline [78] arsenic sulfide is readily dissolved in different amine solvents, such as n-propylamine, n-butylamine and EDA. Typically they are mixed together and stirred for a few days, preferably in the absence of moisture and air. Solutions can be very highly concentrated: solutions up to 0.4 g/ml in n-propylamine [79] and 1.5 g/ml in EDA [78] have been fabricated. A different route was taken by Santiago et al. who also dissolved chalcogenide glasses in n-butylamine, but then dried the resultant solutions to obtain the butyl ammonium salt as a powder which they subsequently dissolved in N,N-dimethylacetamide. The amide solution is less hygroscopic and can be used to spin-coat multiple layers [80].

The concentration and viscosity affect the flow properties of the solutions during processing. Spin-coating of denser solutions leads to thicker films, and homogenous films in a wide thickness ranging between tens of nanometers and tens of microns can be fabricated [80]. Taking it further, thicker films over tens of microns was recently demonstrated and detailed in Chapter 4.

The color of chalcogenide solutions ranges between pale yellow and dark amber in arsenic sulfide and selenide solutions, depending on concentration and type of solute [78]. The solution viscosity of arsenic sulfide in EDA as well as n-propylamine shows
Newtonian behavior and increases with concentration \[78, 79\]. The solution properties of arsenic sulfide do not depend on whether crystalline or amorphous material is used \[78\], and the solutions can be stored for months under inert gas atmosphere. Occasionally, slowly-formed precipitation may occur due to oxidation and can be filtered out prior to processing.

Apart from the solution process, researchers have invented a variety of methods to deposit chalcogenide materials. The conventional processes include vacuum coating (thermal evaporation, chemical vapor deposition or sputtering) and pulse laser deposition \[46, 81–89\]. Each method has a different pathway to achieve successful deposition, but has its own limitation. First, thermal evaporation involves vaporizing the material under high temperature before condensing on a cool substrate to give a thin film. Second, chemical vapor deposition uses gaseous precursors to react on the substrate and form films. However, stoichiometry fidelity can be affected in these two processes. Third, in a chalcogenide sputtering process, atoms are knocked off from the source material with high energy particles and condense on the substrates. Its limitation lies in producing high density films and achieving the variety of chalcogenide composition. Fourth, pulse laser deposition uses a laser to vaporize the material instead of heating. It is good for depositing small amount of material, but can hardly handle area deposition.

Comparing these conventional methods as a whole with the solution method, there are both advantages and disadvantages. Conventional methods do not deal with solvents, so the chance of contamination is smaller. When combined with etching or other photolithography steps, these approaches are efficient for fabricating 2D structures on flat surfaces. However, their functions become limited in more practical situations. Such case arises when chalcogenide deposition needs to be done on IR lens surfaces to manipulate light output, or thick chalcogenide layer deposition is required to create volumetric optical components, or integration among different optical
devices needs to be achieved. In these situations, solution-based methods, in which chalcogenides are dissolved by solvents and processed as a liquid, become a better choice. After proper treatment, the produced structures can have similar optical, chemical and physical properties to the bulk [53]. Nevertheless, it should be noted that all deposition methods will cause changes in material properties. As-deposited films will not have the exact same properties as the bulk material. Apart from this common drawback, other advantages for using the solution process include lower cost, energy saving, small surface roughness, low temperature controllability and large area processing.

The advantages of the solution process can be more directly appreciated from the following 4 results published by other groups. In the first case, the solution process smooths out the surface roughness of evaporated chalcogenide waveguides by an order of magnitude. Second, micro-lenses with curved surfaces can only be produced by the solution process. Third, the fluidic property of chalcogenide solutions is capitalized to deposit layers inside fibers, where unreachable by other methods. Fourth, photonic crystals with special shapes are fabricated with the solution process.

1.3.1 Spin-coated waveguide over-cladding for low-temperature roughness reduction

Annealing is a common fabrication step to smooth out the surface roughness of chalcogenide structures, and it can be the key to reduce optical loss. However, some chalcogenides such as Ge-Sb-S are thermally less stable and prone to surface crystallization, which make them unsuitable for high-temperature annealing. To overcome this problem, the solution process can be used to deposit an arsenic sulfide over-cladding structure and achieve roughness reduction at sub-$T_g$ annealing.

Carlie et al. demonstrated such surface roughness reduction in evaporated Ge-Sb-S structures while achieving optimization in refractive index, density and optical
losses. Rib waveguides are first fabricated with Ge-Sb-S, onto which a 25mg/ml As-S solution is spin-coated and act as a waveguide over-cladding structure (Fig. 1.8). After heat treatment, the surface roughness is reduced from 50nm to 5nm and the sidewall roughness is reduced from 19nm to 1.4nm. The optical loss measured at 1550nm also becomes smaller after spin-coating [90].

Figure 1.8: Cross-sectional SEM pictures of Ge-Sb-S waveguides (a) before and (b) after solution cladding. Figure adapted from [90]

1.3.2 Inkjet printing of microlenses

Another interesting application of solution-processing comes from the direct printing of microlenses. This technique enabled by inkjet-printing chalcogenide solutions can directly write patterns or precisely deposit individual microscopic infrared lenses. This method can find its application in places where the deposition surface is non-flat and becomes challenging for traditional methods. Inkjet printing overcomes the problem and allows deposition on any user-defined surfaces. Potentially, it also enables efficient lens fabrication in a large scale.

By controlling the solution concentration and pulse setting, spherical lenses of approximately 10-300 µm in diameter are fabricated [91]. Lens focal length ranges from 10 to 700 µm. The nature of the deposition technique allows post-deposition modification of the lens. Additionally, thermal treatment can lead to an increase of
the lens radius and refractive index, enabling precise adjustment of the F-number.

1.3.3 Chalcogenide layers in fibers

Depositing chalcogenide materials inside photonic crystal fibers is needed for super-continuum generation and other non-linear applications. However, the hollow cores in such fibers are only a few microns in radius and would be difficult to achieve homogeneous deposition with the evaporation method. In such situation, solution process stands out for its deposition flexibility.

Marcos et al. chose butylamine and EDA solutions to pattern thin and thick As$_2$S$_3$ layers on the channel surfaces inside a photonic crystal fiber (Fig. 1.9). The solution fills the micron size channels under capillary force and the process may take hours depending on the solution and channel size. The optical transmission measurements reveals strong photonic bandgaps from visible to near-infrared wavelengths. From the transmittance spectra measured in the wavelength range 500-1750 nm, the lowest loss is found to be 3dB/cm [92].

![Figure 1.9](image)

Figure 1.9: (a) Cross-section of the core of a photonic crystal fiber deposited with As$_2$S$_3$ layers (b) Single hole with As$_2$S$_3$ layer. Figure adapted from [92]
1.3.4 Inverse opal photonic crystal

Lastly, inverse opal photonic crystal structures have been studied for their intriguing optical phenomena, as well as important applications in optical sensing, electronic paper and flexible laser devices. Given the 3d nature and complexity of this structure, it is desirable to choose the solution route over evaporation. Low-cost and low-temperature processing are the added advantages of this process.

Kohoutek et al. spin-coated arsenic sulfide solutions on highly-ordered silica colloidal crystal templates, filling in the interstitial spaces with solution. The template was subsequently rinsed in HF to remove the silica backbone and produce an inverse opal As-S photonic crystal (Fig. 1.10). Such structure demonstrated an enhanced reflectivity and wider photonic bandgap compared with the template film, opening the door to flexible colloidal crystal laser devices, photonic waveguide and novel chemical sensors [93].

![Figure 1.10: (A) Optical microscope image of the inverse opal As-S structure (orange stripe) obtained on the edge of silica/As-S opal film by removing silica beads in HF solution (B) SEM image shows the cleaved silica/As-S opal film (C) The inverse opal As-S structure obtained by rinsing the samples edge in HF acid solution. Figure adapted from [93]](image)

1.4 Processing challenges

The solution process has clear advantages, but several issues need to be addressed in order to produce high quality structures. One of the prime concerns is material
homogeneity, which is especially challenging for the solution processes due to residual solvents. Optimizing heat treatment is essential to remove solvents in deposited films, which otherwise can degrade the optical properties of produced films [53, 94]. In addition, solvent also causes the formation of porous structures (Fig. 1.11) which have been observed in many cases of solution-processed chalcogenides [90, 95, 96]. The presence of pores introduces defects to the structure, disrupts material homogeneity and degenerates film properties such as refractive index, bandgap and roughness. Since most device applications require uniform and homogeneous material deposition, such defects will inevitably cause poor performances. Therefore, from the fabrication point of view, it is imperative to ensure consistent solvent removal to achieve a homogeneous density.

The second challenge is to lower the loss of solution-processed structures. Waveguide is the most basic structure in many applications and the key indication of the optical performance is its propagation loss. Waveguide losses usually arise from scattering, absorption or structure design and will result in signal attenuation, as well as poor sensor performance. Published research on chalcogenide waveguides patterned with the solution method has reported losses as large as 4-9 dB/cm (Fig. 1.12) [4, 98], which in fact is much bigger than those by thermal methods. Therefore, to make the solution process a viable choice for producing reliable photonic structures, the fabrication method must be improved to lower the loss.

The third challenge is applying the solution method to problems unresolved by the conventional methods. Previously published "integrating waveguide with lasers by the solution process" [4] is one example that has demonstrated the flexibility of solution processes. Many other similar applications, however, are still waiting to be addressed, especially in aspects that can differentiate the solution method from conventional methods. These areas can be unconventional or difficult to implement deposition, such as fabricating thick structures, deposition on non-flat surfaces and
etc.

These challenges and concerns are the roadblocks, but also the driving forces of our research. Much of research work discussed in this thesis is built upon these problems. Going beyond just solving the practical issues, study of the fundamental science to explain mechanisms and develop commonly applicable methods has also been performed.
Figure 1.11: (a) Spin-coated Ge$_{23}$Sb$_7$S$_{70}$ thin films with nanoporous. (b) AFM images of the topography of the surface of a solution-derived Ge$_{23}$Sb$_7$S$_{70}$ thin film after heat treatment at 198°C. (c) Pores from a 5 µm x 5 µm area of a cleaved waveguide cross-section (inset). Voids appear as dark spots in the SEM image. Figure adapted from [95]–[97].
Figure 1.12: Cut-back measurement. Losses of rib waveguides of varying width, with height = 4.5 µm, on a LiNbO$_3$ substrate. The waveguides are aligned to and end-fired coupled to a QCL emitting at $\lambda = 4.8$ µm. Each point represents averaged data from at least 5 different waveguides. Propagation loss of the 2.5 µm wide waveguide is given. Figure adapted from [1].
1.5 Thesis overview

This thesis is about the processing a special group of IR-transparent materials and fabricating photonic components. To achieve this goal, we must first understand the underlying science in the solution dissolution and thermal processing. Second, at the level of film processing, material and structure optimization should be studied to improve the device performances. Lastly, various photonic components fabricated by our method can be demonstrated.

My work is built upon two previous students’ theses by Candice Tsay [97] and Shanshan Song [79]. Candice led the effort in using micro-transfer molding (µTM) to fabricate waveguides on lithium niobate substrates, as well as developing micro-molding in capillaries (MIMIC) to integrate quantum cascade lasers with waveguides. Shanshan studied the dissolution, spin-coating, annealing and photo-exposure of chalcogenide materials. Their work has always been inspiring to my research, giving me the opportunity to address new problems and provide innovative solutions in this thesis, such as:

- Why do nanopores form in solution-processed arsenic sulfide films? How to remove them?

- Spin-coating usually deposit films of 1 µm, but what if thicker films are needed? How to achieve that using solution methods?

- The propagation loss of chalcogenide waveguides reported is 4.5dB/cm [4]. How can it be lowered? What are the losses like at other mid-IR wavelength regions?

- How to improve the waveguide design to confine mode better? How to improve the measurement system to accurately determine the loss?

- All previous waveguides are deposited on flat surfaces. How can I utilize the flexibility of the solution method and fabricate waveguide on non-flat surfaces?
• Other than waveguides, what other optical components can I demonstrate with the solution method?

To answer these questions and following an order from understanding basic materials to developing new devices, the rest of the thesis will contain these chapters:

In Chapter 2, I study the established theories of chalcogenide dissolution mechanisms to compare the similarities and differences among several chalcogenide-solvent combinations. In addition, the physical properties of chalcogenide solutions are discussed.

In Chapter 3, the theme is on solution-processed chalcogenide films. I start with introducing the spin-coating process and thermal treatment, followed by a discussion of the chemical and physical structures of the films. For the chemical structure part, light exposure and its effects are included. For the physical structure part, the emphasis is on the nanopores in solution-processed films, including its formation, characterization and removal method, discussed in the context of the dissolution and annealing mechanism.

In Chapter 4, I discuss thick chalcogenide deposition. Chalcogenide films of arbitrary thicknesses can be achieved via lamination of solution-processed individual chalcogenide layers. Fabrication of homogeneous multilayers and heterogeneous multilayers composed of different chalcogenides or metal-chalcogenide hybrids are demonstrated. Ag dissolution in spin-coated and laminated chalcogenide films is shown to verify the photo-response of such structures.

In Chapter 5, I present a number of photonic components that are fabricated by our solution methods. Examples include waveguides on flat and curved surfaces, low-loss trench waveguides, rings and gratings. Both previously developed MIMIC/µTM and more recent micro-channel filling methods are used. In addition to showing the optical characterization of these components, a comparison among the methods is given to highlight their advantages and disadvantages. The reasons for significant
waveguide loss improvement is also highlighted.

In Chapter 6, I conclude the thesis, discuss the impact of the research and comment on the future development of the solution process in the realm of chalcogenide fabrication technology.
Chapter 2

Background of chalcogenide dissolution and chalcogenide solutions

2.1 Introduction

Understanding the chalcogenide dissolution mechanism is the key to reveal the underlying science of the solution process and has multiple important implications. First, the study of glass dissolution is essential for explaining properties of the solution and the corresponding solution-processed films. Second, such understanding in fundamental science sheds light on improving existing fabrication techniques and expanding its range of materials.

In this chapter, I review the principles and equations governing the chalcogenide solution chemistry. In addition, I also discuss the properties of chalcogenide solutions. As we will see later, different solvents have distinct pathways to dissolve the chalcogenide solutes, forming corresponding particles in the solutions. Of all the chalcogenides, arsenic sulfide is the most common material and has been studies against
many different solvents. Nevertheless, the dissolution study of other chalcogenide materials also provide valuable insights in terms of similarities or differences.

2.2 Dissolution mechanisms of arsenic sulfide

Chern et al., the pioneers in this field, investigated the dissolution of arsenic sulfide in n-propylamine and n-butylamine [67-72]. They treated the starting material, amorphous arsenic sulfide, as having a layer-like structure and suggested that the solvent breaks up the bulk into small flat clusters starting at defect sites between the layers. This occurs by nucleophilic substitution of a sulfide atom by the alkyl amine group of the solvent. The resulting arsenic alkyl ammonium group splits off its excess hydrogen to form $\text{RNH}_3^+$ group, which then bonds to the negatively charged sulfur dangling bond. The arsenic atom in the alkyl ammonium group now exhibits a lower electron density than prior to the substitution, with the highly electronegative nitrogen pulling away electron density from the arsenic. This makes the arsenic vulnerable to a second and third nucleophilic attack, resulting in an alkyl amino arsenic compound and three hydrogen terminated sulfide groups. The hydrogen sulfide groups in combination with additional solvent molecules are in chemical equilibrium with the alkyl ammonium sulfide salt. Breaking up the arsenic sulfide layers leads to the formation of amorphous, arsenic-deficient arsenic sulfide fragments that are terminated by excess sulfide dangling bonds and charge compensating alkyl ammonium ions (Fig. 2.1), as well as an insoluble alkyl amino arsenic compound which precipitates. The size (as well as the shape) of the arsenic sulfide fragments determines the extent of the sulfur excess, and it is in the order of 2-10 nm. Indeed, 25 years later, Kohoutek et al. found a correlation between solution concentration and cluster size of arsenic sulfide dissolved in n-butylamine [99]. The polar alkyl ammonium sulfide shell around the arsenic sulfide fragments makes the material more soluble in the chosen solvent as
well as in a wide range of other polar solvents. As for the precipitating alkyl amino arsenic compound the exact composition or even the chemical formula could not be determined, since it is likely to be a mix of different reaction products, including oxide-species from a competing nucleophilic attack by trace amounts of water in the solvent. However, the thermodynamic (ideally, in chemical equilibrium) dissolution products of arsenic sulfide in n-propylamine would be as follows [68 74]:

\[
\text{As}_2\text{S}_3 + 6\text{C}_3\text{H}_7\text{NH}_2 \rightarrow (\text{C}_3\text{H}_7\text{NH}_3)_3\text{AsS}_3 + (\text{C}_3\text{H}_7\text{NH})_3\text{As}
\]  

(2.1)

Figure 2.1: Chemical equations and cluster image. (Left) Electrophilic substitution reaction proposed for the arsenic sulfide dissolution process. (Right) Proposed schematic structure of \( \text{As}_2\text{S}_3 + \text{n-propylamine} \). Figure adapted from [68].

In the late 1980s, Guiton and Pantano investigated the dissolution of arsenic sulfide in a different kind of amine solvent, ethylenediamine (EDA) [77 78], for a low-temperature route to optical chalcogenide glass films. They ruled out the formation of alkyl ammonium salts or hydrogen sulfide in this system, but claimed the existence of polymer-like chains of \( \text{As}_4\text{S}_4 \) rings interlinked by bridging sulfur atoms, each ring chelated by two solvent molecules. This completely different mechanism is only possible due to the chelating nature of a diamine solvent. During drying of the
solution the material loses solvent and condenses in analogy to the sol-gel process of silicate gels (Fig. 2.2). Guiton et al. argued that a proton source (other than the amino group) was needed in order to create alkyl ammonium species which was the reason that they were unable to detect any in their water free solutions. However, it should be noted that Chern et al. detected alkyl ammonium salts even though their suggested dissolution mechanism involves no water molecules [68].

![Figure 2.2: Proposed As$_2$S$_3$/EDA solution species and gel-to-glass transition.](image)

A third group of researchers including Mamedov and Michailov investigated the dissolution mechanism and kinetics of arsenic sulfide glass in alkaline water solutions and amine based solvents starting in the early 1990s [73, 74, 100, 101]. They found that the dissolution mechanism in alkaline water solutions as well as some alkyl amine solvents including n-butylamine consists of two steps, first the adsorption of
nucleophiles (hydroxyl anions or amine groups) at the glass surface and then the nucleophilic substitution of a sulfur atom by the nucleophile [100]:

\[ OH^- + AsS_{3/2} \rightleftharpoons OH^- \cdots AsS_{3/2} \text{ (fast)} \]  \hspace{1cm} (2.2)

\[ OH^- \cdots AsS_{3/2} \rightarrow OHAsS_{2/2} + S^-_{1/2} \text{ (slow)} \]  \hspace{1cm} (2.3)

Thus breaking up the glass network into fragments and creating a sulfide dangling bond whose charge is compensated by either the metal cation from the inorganic base, or alkyl ammonium, as well as an arsenic hydroxide or alkyl amino arsenic species [74, 100]. This second step, the nucleophilic attack of the arsenic in the covalent glass network is consistent with the dissolution mechanism introduced by Chern et al. [69].

While the dissolution mechanism described here is valid for stoichiometric and chemically ordered arsenic sulfide such as bulk arsenic sulfide glass or annealed evaporated films, the dissolution rate decreases when homopolar bonds as in as-evaporated films are present, because these defects decrease the electrophilicity of the glass network [74]. If many homopolar bonds are present, the use of amine reactants in an aprotic solvent, which allows sulfur to dissolve, offers a different dissolution mechanism that enables higher dissolution rates allowing amines to act as catalysts in forming free sulfur radicals as suggested in [74] with diethylamine as the solvent:

\[ (C_2H_5)_2NH + S_n \rightarrow (C_2H_5)_2NH^+ S^-_n \]  \hspace{1cm} (2.4)

\[ (C_2H_5)_2NH^+ S^-_n + As_{2S_{1/2}} + (C_2H_5)_2NH \rightarrow (C_2H_5)_2NH^+ S^- AsS_{2/2} + S_{n-1} + (C_2H_5)_2NAsS_{2/2} \]  \hspace{1cm} (2.5)

In addition, Mikhailov et al. suggested the effect of material stoichiometry on dissolution rate. In particular, the dissolution rate of the film in the dipentylamine solution is found to depend on the film composition, excess sulfur concentration in the
solution and the spatial orientation of the sample. This could be due to the different reactivities of sulfur, as the intermediate product of the dissolution process [101].

Summarizing the three dissolution mechanisms, I can conclude a common pattern and some differences. The similarity is that the solvent molecules tend to be electron-rich and therefore can initiate dissolution with nucleophilic attacks. This can become a general rule in search for appropriate solvents to dissolve other chalcogenides. One important difference I have noticed is that propylamine tends to break the chalcogenide glass into small clusters, while EDA tends to break the chalcogenide glass into polymer-like chains. This difference in fact can be used to explain a couple of problems I discuss in later chapters. For practical applications and our research project, I choose propylamine and EDA as our solvent choices for better dissolution rates and chalcogenide solubilities.

2.3 Dissolution study of other chalcogenides

The detailed study of As$_2$S$_3$ has inspired more research on other chalcogenides, and one of the them is As$_2$Se$_3$, which shares a similar As-chalcogen trigonal pyramidal structure. Although arsenic selenide dissolved poorly in propylamine and butylamine, Zou et al. found that up to 0.6g/mL As$_2$Se$_3$ could be dissolved in EDA with no clear phase separation. Raman study shows peaks corresponding to As$_4$Se$_4$ unit, Se-Se chain, Se-Se ring and AsSe$_3$ pyramidal unit. Similar to As$_2$S$_3$ dissolution in EDA, the first three units become present in the dissolution process as As-Se heteropolar bonds breaks to form Se-Se homopolar bonds [98].

More complicated ternary chalcogenides have also been explored with solution process. In a study of As$_{33}$S$_{67-x}$Se$_x$ (x = 0, 17, 33.5, 50 and 67 at.%) processed with butylamine, similarities were found with respect to previously-studied As-S and As-Se chalcogenides. Raman spectrum showed peaks of AsSe$_3$ pyramids, Se-Se chains,
AsS₃ pyramids, As₄S₄ units, weak S₈-rings and S-Se bonds in spin-coated and pre-baked films. It is observed that these bonds approach bulk values along with solvent removal, except for the fragmentation and disappearance of S and Se ring structures [102].

Additionally, Waldmann et al. studied the dissolution chemistry of a Ge-based chalcogenide glass with the composition Ge₂₃Sb₇S₇₀. The Ge building blocks of this glass, GeS⁴ tetrahedra, rearrange during dissolution in n-propylamine to form adamantane-like Ge₄S₁₀⁻ clusters [95]. This molecular structure is retained during spin-coating, leading to thin chalcogenide films which are more similar to the solution than the bulk glass. Raman spectrum measurement shows the disappearance of solvent peaks and band shifts indicating the formation of a tighter structure. In another comparative, it was found that Ge₂₃Sb₇S₇₀ glass dissolves with a similar rate as As₂S₃ when immersed in KOH, but had a higher rate when immersed in NH₄OH and a lower rate in propylamine or butylamine. One of the causes for the higher rate could be the difference in material structures and dissolution routes. Another factor could be the less covalent nature of Ge-S bonds than As-S bonds, and therefore Ge₂₃Sb₇S₇₀ should dissolve faster in more polar solvents such as OH-based solutions and slower in organic solvents such as amines [79].

Furthermore, Orava and Kohoutek investigated the dissolution of As-S, As-Se-S and As-Se thin films in inorganic aqueous bases as well as amines. They confirmed the existence of different dissolution mechanisms, resulting in varying etching rates and chemical selectivity [75, 99, 103, 104]. The same group also demonstrated solution-processing of ternary and quaternary chalcogenides by first introducing Ag to the As-S, As-Se-S and As-Sb-S system through melting [104, 107]. The rate of dissolution was found to depend on film composition film, choice of etchant and its concentration, with the highest resolution on the scale of nanometers.

By now, I have introduced big picture of the research landscape on chalcogenide
dissolutions. The understanding of various mechanisms is essential for us to identify the best choice of solvent, which determines our processing strategies during fabrication. Since arsenic sulfide in propylamine or EDA is most researched and best understood, they naturally become our choice for experiments.

2.4 Summary

In this chapter, I have discussed different chalcogenide dissolution mechanisms in the context of several solute-solvent pairs, as well as their associated properties. There exist similarities and differences among various routes, but the distinction between structurally-close chalcogenide materials is not huge in terms of dissolution. So, a similar dissolution process is expected for other chalcogenide materials with appropriate solvents. More importantly, the dissolution mechanism affects the dissolution rate and the solution’s viscosity (discussed in Chapter 1). These parameters will have an impact on developing fabrication methods, since the thickness of the spin-coated films, as well as the filling length inside capillaries are limited by the solution viscosity. We will rely on the knowledge here to shape our fabrication strategies for chalcogenide films and optical components.
Chapter 3

Solution-processed chalcogenide films

3.1 Introduction

Solution casting and thermal processing are usually applied together to chalcogenide solutions to produce desired structures. As mentioned in Chapter 1, pore formation can become a serious problem for solution processes. It is, therefore, the first and most challenging roadblock that prevents researchers from producing high quality chalcogenide components.

This chapter expands on fabricating high-standard chalcogenide films from the solution process. It starts with a review of the thermal treatment steps and chemical structures of solution-processed films. With this background, the other half emphasizes on the characterization of pore formation in deposited films and our method to counter this problem. In essence, this chapter answers our research question about the origin of the pore formation and finding an appropriate removal method.
3.2 Spin-coating and thermal processing

Spin-coating dissolved chalcogenide glasses is usually done in the dry, oxygen-free atmosphere of a glovebox to prevent reaction with moisture or oxygen from the air. A few drops of the solution are deposited onto a substrate which is then spun at different speeds to produce films of different thicknesses. Since there are no sudden temperature changes involved in solution-based spin-coating, different thermal expansion properties of substrate and film material, which have to be considered for conventional deposition techniques, are usually not an issue.

Spin-coated films are usually treated thermally in two steps, a soft-bake at lower temperatures that removes most of the solvent, and a hard-bake closer to the glass transition temperature of the bulk glass to remove residual solvent and reaction products, and to densify the glass. For instance As$_2$S$_3$ films made from amine solutions start to lose molecular amine at 70 – 80°C when the alkyl ammonium salts decompose, leaving behind HS-terminated clusters. At 130 – 150°C, these clusters start to interlink, releasing H$_2$S and leaving behind a material similar to the bulk according to the reaction,

\[ 2S_{2/2}As - SH \rightarrow S_{2/2}As - S - As - S_{2/2} + H_2S \tag{3.1} \]

Prolonged baking at 180°C ensures the further removal of organic residues [53, 69]. A direct observation is from Fig.3.1 where the presence of solvent, represented by the nitrogen peak, is significantly suppressed after annealing at 180°C for 24 hours. Alternatively, the presence of solvent can be tested against some water or acid solutions. Fig.3.2 demonstrates the difference between samples annealed at 120°C for 2 hrs (Left) and at 180°C for 24 hrs (Right). Samples insufficiently annealed disintegrate very quickly under the effect of water due to the substantial amount of solvent presents, whereas the other type stays intact because of its better solvent
removal. In light of this result, I have adopted high temperature annealing for my waveguide processing, but a shorter duration (6 hrs) is sufficient for our purposes. For the resultant film, the stoichiometry of the material is maintained because the S evolved with H₂S is compensated by the As precipitation explained in Chapter 2. Measurements also show that the resulting film stoichiometry approaches that of bulk with an increasing annealing temperature [70].

Figure 3.1: Residual solvents represented by the nitrogen peak is present with annealing at low temperature for short durations (above), but disappears after annealing at a higher temperature for longer hours (below).
Due to the different nature of the deposition techniques, vacuum deposition vs. solution methods, the deposited materials show differences in structure, and thus they respond differently to thermal treatment [68, 108]. Arsenic sulfide which has been evaporated at high temperatures and under vacuum is known to form $\text{As}_4\text{S}_4$ clusters and sulfur chains which can be found in the deposited films. The homopolar bonds ($\text{As-As}$ in $\text{As}_4\text{S}_4$ and $\text{S-S}$ in $\text{S}_n$) are susceptible to light and easily break under thermal treatment, leading to a material closer to arsenic sulfide bulk glass. On the other hand, arsenic sulfide dissolved in alkyl amines, as explained in Chapter 2, can be described as a nanocolloidal solution consisting of flat clusters, that internally retain the structure of the layer-like starting material, but capped by ionic pairs of sulfide dangling bonds and alkyl ammonium molecules. These nanoclusters agglomerate in spin-coating forming larger clusters [99]. During baking the material first loses non-bonded solvent molecules before the alkyl ammonium sulfide groups split off alkyl amine molecules under the formation of hydrogenated arsenic sulfide at around $80\,^\circ\text{C}$. Above $130\,^\circ\text{C}$, the hydrogenated sulfide groups evaporate as $\text{H}_2\text{S}$ [68], leaving behind the stoichiometric arsenic sulfide $\text{As}_2\text{S}_3$ with a structure close to the bulk material.
as described above. This can be confirmed by the converging refractive index and infrared absorption spectrum with the annealing duration. Comparing 1 hr baking at 60°C with higher temperatures up to 180°C, the optical bandgap of resulting thin films decreases to 2.23, refractive index increases to 2.4 at 900nm, density increases to 3.8 g/cm³ and the solvent absorption peak decreases significantly giving transmission over 80% [79].

In terms of photo-induced phenomena, there is some qualitative agreement between spin-coated and evaporated films, but they can be quantitatively different. For instance, similar to evaporated films, the response of solution-deposited arsenic sulfide to light shows signs of approaching the bulk material, in terms of an increase of the refractive index as well as densification [79]. In other studies, researchers found photodarkening and photo-induced Ag diffusion in spin-coated As-S, As-Se and Sb-S films which were consistent with evaporated materials [3, 79, 109–111]. On the other hand, photo-induced linear dichroism was shown in spin-coated arsenic selenide films, with a value even larger than evaporated films, which could be associated with the larger 'free volume’ in spin-coated films [109].

3.4 Physical structures

3.4.1 Introduction

The surface morphology of spin-coated films is influenced by solvent evaporation during fabrication, therefore is affected by solvent properties and preparation condition. In a study of spin-coating As$_{33}$S$_{67}$ with butylamine solutions, surface structures of about 25 and 50nm diameter were found on films produced by a dilute solution and such pattern smooths out after thermal treatment. The author concluded that this structure was from the agglomeration of 1 to 4.2 nm radii clusters during solvent evaporation [99]. In another example, the film properties of spin-coated Ge$_{23}$Sb$_7$S$_{70}$
films are investigated against spinning parameters such as spin-speed and wait time between applying the solution to the substrate and spin start. Increased spin speed leads to thinner films with lower surface roughness. Another important result from this study is that in order to obtain a smooth and uniform film, it is crucial to start spinning immediately after applying the volatile solution to the substrate. Otherwise, the solution on the substrates will have higher viscosity and spread out less uniformly [94].

Although the surface roughness can be treated with annealing, nanopores observed inside propylamine-processed arsenic sulfide films are persistent to the high-temperature annealing [90, 95]. Such formation could degrade the quality of fabricated films by disrupting material homogeneity and introducing perturbation in refractive index, bandgap and roughness. The following subsections describes the experimentally observed pore formation trends and explain with an As and S vacancy coalescence mechanism in the context of the dissolution chemistry.

### 3.4.2 Experimental method

Arsenic sulfide stock solutions are prepared by dissolving 2g of amorphous As$_2$S$_3$ (metal basis) pieces into 10 mL n-propylamine solvent. The dissolution is carried out inside a sealed glass container to prevent solvent evaporation and a magnetic stirrer can be used to expedite the process. Most procedures are done inside a nitrogen-filled glove box to minimize the exposure to atmospheric moisture and oxygen, since the former can lead to precipitation and the latter results in oxidation [109]. Additional miscible solvents including ethanol, n-butanol, butylamine, pentyamine and EDA are mixed with the solution at a concentration up to 20%, which is then passed through 0.1µm filters before being transferred onto Si substrates. The substrate is spun at 1500-2500 rpm for 10 seconds. The resulting films are soft-baked under vacuum at 60°C for 1 hour to remove most of the solvent, followed by heat treatment at
100 – 200°C to further densify the glass. Vacuum pressure is set around 50 torr. For the pore size study, a series of samples are hard-baked at temperatures of 140°C, 160°C, 180°C and 200°C each for 1, 2, 4, 8, and 12 hours. In our study, scanning electron microscope (SEM) images are taken with a Quanta 200 FEG environmental SEM at 15 keV in high vacuum mode. The SEM is equipped with an energy-dispersive X-ray spectroscopy (EDX) system for compositional analysis.

Imaging software Fiji is used to analyze the pore size and distribution. The algorithm sets a threshold to distinguish pore and non-pore areas. SEM pictures of film cross-sections are cropped and rotated to a vertical position. Pixels in each column are scanned from left (film bottom) to right (film surface). The percentage of pore pixels is plotted for each step position from bottom to top, representing the pore area percentage at each depth. Since the position is also normalized from 0 to 1, the total area under the curve represents the percentage of pore area. For propylamine-only solutions, 10 SEM pictures (with about 30-80 pores per picture) are analyzed for each data point (Fig.3.3 and Fig.3.6). For films mixed with EDA, 6 SEM pictures are analyzed. Standard deviations are calculated statistically.

3.4.3 Pore formation and trend

The first trend we have found is that the amount of pores increases with baking temperature. Fig.3.3 shows the average distribution of pores across the film from bottom (position 0: film-substrate interface) to top (position 1: film-air interface). All these samples are pre-baked at 60°C for 1 hour and annealed at four different temperatures for 12 hours. The pore distribution figure reveals the relative pore density at different film depths.

The porous film has 3 distinct areas in terms of micro-structures. The top part (0.8-1) of the film is mostly pore-free and resembles a depletion region, which extends about 20% of the total thickness. Underneath (0.1-0.8) is the bulk part of the film
when pores are seen. The diameter of pores ranges from a few nm to approximately 200 nm. Close to the bottom Si substrate, there is another thinner depletion region (0-0.1), with occasional occurrence of pores stuck to the substrate. The spin-coated films in this research have measured thicknesses ranging from 1.5 µm to 2.5 µm. It is noted that when the thickness is smaller than 300 nm, no pores are observed.

![Image showing pore distribution](image.png)

**Figure 3.3:** Pore distribution of samples baked at 140 – 200°C for 12 hours. Inset: a cross-sectional SEM of a sample indicating the relative positions

The integrated area under the curve represents the percentage of total pore area and is plotted in Fig. 3.4 showing an increase in pore density with baking temperature. Although the exact relationship is not deterministic, we can use a line to guide the eye and extrapolate these data points to find the x-axis intercept, which lies close to 120°C. The plot suggests that the onset temperature for pore formation is around 120°C. This is in fact experimentally observed by examining SEM pictures and identifying pores. Examples of these samples are taken with SEM and shown in Fig. 3.5. The films are processed with propylamine and baked for three consecutive stages at 100°C, 120°C and 140°C for 2 hours each. At the end of every stage, cross-sectional SEM is performed. With baking up to 100°C, no pores are observed. Only from
Figure 3.4: Percentage of pore area of samples baked at various temperatures, a straight line is plotted to guide the eye and identify the approximate onset temperature for pore formation.

120°C, pores start to appear in a small amount. This observation corresponds well with our deduction of the onset temperature from the Fig.3.4 plot. As the temperature goes up to 140°C, pores increase both in number and size. At even higher temperatures, there are more pores of large sizes, but still with a substantial amount of small pores.
Figure 3.5: Cross-sectional view of 3 SEM pictures cropped and rotated such that the right side is the top of the film. Films are processed with propylamine only and baked up to 100°C, 120°C and 140°C. Some pores in the middle picture are pointed with arrows for better viewing.

Secondly, the baking duration also influences the formation of pores. For a series of 5 samples annealed at 200°C for 1, 2, 4, 8 and 12 hours, average pore distribution is plotted in Fig. 3.6. The same three regions are clearly seen, with an almost constant depletion region close to the substrate and the top depletion region shrinks with baking time. Overall, the total pore area percentage also increases with baking duration as shown in Fig. 3.7.
Figure 3.6: Pore distribution of samples baked at 200°C for 1 to 12 hours

Figure 3.7: Percentage of pore area of samples baked at 200°C for various durations
3.4.4 Vacancy coalescence mechanism

We believe that the phenomenon observed in our experiment can be understood in the context of a vacancy coalescence mechanism, in which voids form from the combination and nucleation of Schottky defect pairs. Previously, researchers have reported similar pore formation in several cases involving aqueous preparation procedures, such as zinc oxide [112] and barium titanate [113]. In these two examples where water is used, hydroxide ions are incorporated to the oxygen sites and cation vacancies are generated to compensate for the charge discrepancy. Thermal treatment brings water out of the film, leaving behind oxygen vacancies, which then combine with cation vacancies and vacancy pairs nucleate to form void space in the structure. Meanwhile, oxygen vacancies are continuously generated with water removal.

Our solution method shares a similar chemical process. Upon dissolution in propylamine, arsenic sulfide pieces are broken into small clusters by incorporating solvent molecules to the S sites. Chern suggests that the reaction is initiated by an electrophilic substitution in eqn 3.2 as the lone pair of electron in N attacks As center and cleaves the As-S bond [68]. The overall dissolution process is described by eqn 3.3 [69], in which the second by-product precipitates out, causing As vacancies. The remaining product decomposes under low-temperature baking to give a hydrogenated arsenic sulfide intermediate, as shown in eqn 3.4 [69]. Chern also proposes that the evolution of H$_2$S gas starts from high temperature anneal at 130°C, when the hydrogenated arsenic sulfide reacts with neighboring HS entities to form sulfur bridge networks, as shown in eqn 3.5 [69]. This result is close to our observation of pore formation only above 120°C. As such, S vacancies are generated from the evolution of H$_2$S and can then combine with the As vacancies to form void pairs. The trend in Fig. 3.7 shows that the increase in pore area percentage has a decreasing rate with respect to time. Looking more closely, the data up to 4 hrs of annealing seem to follow a diffusion relationship (pore area percentage scales proportionally with the square
root of time). However, the pore area percentages with longer annealing are smaller than predicted values by the diffusion model. One possible explanation could be that the vacancy combination/pore nucleation process eventually reaches completion with sufficient annealing. Top and bottom depletion regions are expected because vacancies near the interfaces can simply diffuse towards them rather than nucleating pores underneath. As a result, the majority of pores are observed in bulk of the film. The relatively sharp boundary between top depletion region and pores is probably due to the limitation of vacancy mobilities.

\[
(3 + x)\text{As}_2\text{S}_3 + 12x\text{RNH}_2 \rightarrow 3\text{As}_2\text{S}_{3+x}(\text{RNH}_3^+)_2x + 2x\text{As}(\text{RNH})_3 \downarrow \quad (3.3)
\]

\[
\text{As}_2\text{S}_{3+x}\text{H}_{2x}(\text{RNH}_3^+)_2x \xrightarrow{\leq 80-90^\circ C} \text{As}_2\text{S}_{3+x}\text{H}_{2x} + 2x\text{RNH}_2 \uparrow \quad (3.4)
\]

\[
\text{As}_2\text{S}_{3+x}\text{H}_{2x} \xrightarrow{\geq 130^\circ C} \text{As}_2\text{S}_3 + x\text{H}_2\text{S} \uparrow \quad (3.5)
\]

3.4.5 Pore removal

The presence of pores is undesirable in most optical applications. Such defects can cause scattering and power loss if the structure prepared by solution methods is used to transmit light (detailed discussion can be found in Chapter 5 section 2). Since chalcogenide materials are usually used for transmitting IR beams, a lower degree of homogeneity can degrade the transmission efficiency by orders of magnitude. Combating this pore issue is critical to fabricating high quality devices.

In order to suppress the formation of pores, we have to disrupt the vacancy reaction mechanism by preventing H\(_2\)S evolution. Previous work reveals that dissolving arsenic
sulfide with EDA does not involve S-H bond formation or H$_2$S evolution\cite{78}. Recently, similar studies of As$_2$Se$_3$ further support the different dissolution mechanism in EDA solvents\cite{98}. However, the fact that EDA does not wet most substrates limits its usability in fabrication. We hypothesize that adding a small but sufficient amount of EDA to our propylamine solutions may reduce the formation of nanopores while retaining the wettability.

In fact, we find that when the EDA concentration reaches approximately 10%, most pores can be removed with very few stuck against the substrate. SEM pictures of films processed with different amounts of EDA and under the same annealing conditions are shown in Fig.3.8. As long as the EDA concentration does not exceed 12%, the mixed solution can still wet Si substrates uniformly. EDX on the cross-section has shown a homogeneous material composition free of solvents.
Figure 3.8: Cross-sectional view of 3 SEM pictures positioned vertically. Films are processed with propylamine mixed with different amounts of EDA and baked at 180°C for 6 hours.
Fig. 3.9 displays the average pore distribution from the analysis of multiple SEM pictures. We notice the statistical fluctuations, but on average the amount of pores decreases as a function of EDA percentage. The one exception is the region near the substrate (x=0) where in all cases we see the presence of pores, which is not observed in previous figures with propylamine solvent alone. We attribute this effect to the non-wettability of EDA on the substrate which can lead to gaps at the interface. The total pore percentage decreases with the addition of EDA as shown in Fig. 3.10. The absolute values of pore percentage are much smaller than those from Fig. 3.4 and 3.7, indicating a dramatic effect of adding EDA.

![Figure 3.9: Pore distribution of samples mixed with EDA](image)

Upon getting the EDA results, one concern we had was that the relatively high boiling point of EDA might have affected our results. Therefore, in order to further probe the cause of pore removal and isolate the effects of boiling points (b.p.), we use a number of different solvents (Table 3.1) of the same amount in place of EDA to spin-coat films. As expected, both amine solvents still result in pores. Alcohols which do not change the chemistry but have higher boiling points are added, and we
find that in all cases pores remain. Thus, we can rule out the effect of higher boiling points on pore removal.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ethanol</th>
<th>n-Butanol</th>
<th>n-Butylamine</th>
<th>Pentylamine</th>
<th>EDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.p./°C</td>
<td>78</td>
<td>118</td>
<td>77</td>
<td>94-110</td>
<td>117</td>
</tr>
<tr>
<td>Pore</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 3.1: Additional 10% solvents used and the results for the pore formation tests

From the experiment and literature, it is more reasonable to attribute the pore-removing phenomenon to the diamine group and EDA dissolution mechanism. In contrary to propylamine which breaks down arsenic sulfide into small cluster 16, EDA-dissolved solution and gel are molecular in nature, with the formation of polymeric amorphous network upon annealing [78, 98]. Therefore, in solutions with EDA, the molecular nature of the intermediate implies that no complete charge transfer or ammonium salt formation occurs. As a result, pores are not observed in EDA-processed arsenic sulfide films even after high temperature annealing. In our case
here, 10% EDA is enough to behave as the dominant solvent.

3.4.6 Summary

Our result has shown that there exists a threshold temperature around $120 - 130^\circ C$, above which arsenic vacancies from precipitation and sulfur vacancies from gas evolution recombine resulting in pore formation. One way to combat this problem while retaining wettability on common substrates is to add no more than 10% of EDA to the propylamine solution. EDA-dissolved solution/gel is molecular in nature and forms polymeric amorphous networks upon annealing, without ammonium salt precipitation or gas evolution. Therefore, in such EDA-processed films, homogeneous structures are obtained. As for practical applications, in addition to having pore-free films, a more thorough plan of solvent removal is necessary to produce high quality products.
Chapter 4

Solution-processed thick chalcogenide structures

4.1 Introduction

In many applications, well-controlled thicknesses of chalcogenide layers over large distances are critical to device performances. In fact, thick layers are desired for a number of uses. In fabricating Bragg gratings for holographic data storage, the diffraction efficiency increases with the reflector thickness \[114\]. In the case of 3D optical data storage with femtosecond lasers, where layers of data are stacked upon one another and separated by 5-100 \(\mu\)m, a larger film thickness essentially increases storage capacity per disc \[115\]. Similar to the ‘deep-depletion’ technology \[116\], a thick chalcogenide layer may also be applied on CCD arrays to effectively increase the absorption path length, thereby improving the detector sensitivity.

One approach that has been used successfully to create arbitrarily thick layers and multilayers of organic (or composite) materials is spin-coating and laminating multiple layers \[117\, 118\]. In the realm of chalcogenide materials, spin-coating has been widely used by researchers to produce functional structures such as waveguides
or tunable claddings \[58,90,98\]. Compared to conventional methods such as vacuum coating (thermal evaporation or sputtering) \[84\] or pulsed laser deposition \[85\], solution methods can generally achieve a larger range of thicknesses \[67,119\] over large areas in a time and cost effective manner. Furthermore, there is the potential to reduce or eliminate intrinsic and/or thermal mismatch stresses that occur during growth and annealing of these traditionally deposited films leading to film delamination \[119,122\].

Combining spin-coating with lamination to create thick films has a number of benefits over monolithic or multilevel spin approaches. Repeatedly spin-coating multiple layers to achieve a thick film is impractical due to the redissolution that occurs as one attempts to spin-coat with the same solution. Furthermore, the lamination technique allows for the fabrication of heterogeneous multilayer structures, which have significant importance to many applications. One example is phase-change memory devices based on the principle of photo-induced or electro-induced metal dissolution. Switching between amorphous and crystalline states has been reported in multilayer structures of two different chalcogenide materials \[123,124\] or chalcogenide-Ag \[125–127\].

In this chapter, I present a low-cost fabrication process that can deposit chalcogenide films of arbitrary thicknesses via lamination of solution-processed thin chalcogenide films. Homogeneous multilayers, heterogeneous multilayers composed of different chalcogenide materials or metal-chalcogenide hybrids can be achieved. Ag dissolution in spin-coated and laminated chalcogenide films is demonstrated in order to verify the photo-response of such structures with a positive refractive index increase above 0.2 found. Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) are also used to characterize the cross-section and transmission spectra in visible and infrared wavelength are analyzed. In short, this chapter answers our research question about developing solution methods which can consistently
deposit chalcogenide films thicker than 1 µm.

4.2 Experimental method

Amorphous As$_2$S$_3$ (metal basis) pieces are dissolved into propylamine and As$_2$Se$_3$ pieces are dissolved in ethylenediamine (EDA) solvent, both at a concentration of 0.8mol/L to obtain the stock solutions. The dissolution process usually takes a day with a magnetic stirrer to expedite this process. Throughout the process, the solution is kept inside a sealed glass container to minimize solvent evaporation. With the help of a glove box, exposure of the solution to oxygen and moisture is kept to a minimum throughout the preparation procedure since water can lead to precipitate formation [109]. The solution is passed through 0.1µm size filters before being spin-coated on a substrate. To minimize pore formation during subsequent processing, 10% EDA can be added to the solution [2].

Following dissolution, films are spin-coated and laminated following the steps outlined in Fig.4.1. The substrate is spun at 1000 rpm for 10 seconds. For substrate choices, I use silicon wafers for ellipsometry measurement and SEM study, lithium niobate for infrared spectroscopy measurement, glass microscope slides for optical spectroscopy, or polished NaCl disc substrates for multilayer lamination experiments. Films prepared under these conditions typically have thicknesses around 2µm. By varying the solution concentration and spin conditions, I can spin films of thicknesses up to about 6µm. The resulting films are soft-baked under vacuum at 60 °C for 1 hour to remove most of the solvent and then hard-baked at 120 – 180 °C for up to 6 hours to remove excess solvent and further densify the glass [53 94]. After heating, samples are cooled down to room temperature by turning off the heating element and allowing the oven to reach ambient temperature. When making heterogeneous structure, metal layer evaporation is carried out in a clean room facility with a Denton/DV-502A
E-Beam Evaporator.

Figure 4.1: Spin-coating and lamination steps for fabricating chalcogenide multilayer structures (a) Spin-coat solution-dissolved chalcogenide onto a piece of NaCl substrate (b) Soft and hard baking to remove solvents (c) [optional] Evaporate a metal layer onto the solidified chalcogenide film (d) Dissolve the NaCl substrate in water to detach films (e) Stack films on top of each other to obtain multilayer structures (f) Post-bake or anneal at a high temperature

To create multilayer structures without brittle fracture associated with free standing thin chalcogenide films, I begin with a spin coated film on a non-dissolvable substrate (e.g. Si wafer, LiNbO$_3$, glass slide) on which I place a spin-coated film supported on the NaCl. This substrate assembly is transferred to a beaker of purified DI water to dissolve the salt substrate. Resulting free-standing films floating on water are shown in Fig. 4.2. The remaining multilayer can be compressed to remove residual air or water pockets between the layers. Additional layers are then incrementally added in this fashion until the desired number of layers is achieved. Finally, multilayered samples undergo either post-baking at 50°C for 1 hour or annealing at 200°C for 1
hour to study the effects of temperature difference on the interface. The samples are cooled to room temperature in the same manner as described above. SEM images are taken with a Quanta 200 FEG environmental SEM at 15 keV high vacuum mode. Compositional analysis and elemental mapping is done with an EDX system. Film thickness is measured with an Olympus Laser Confocal Microscope, LEXT OLS4000. Refractive index is measured with a Gaertner L3W16 ellipsometer. Infrared transmission spectra of the films are measured with a Nicolet Fourier transform infrared (FTIR) spectrometer using a cooled mercury cadmium telluride detector with a resolution of $4\text{cm}^{-1}$. The UV-VIS transmission spectra are measured with an Ocean Optics HR4000 high-resolution spectrometer.

Figure 4.2: Examples of As$_2$S$_3$ films floating on water after the NaCl substrates are entirely dissolved

Experimental steps for the silver dissolution experiment is outlined in Fig. 4.3. The deposition steps are similar to those shown before. Photo-induced Ag dissolution into chalcogenide layer is performed with a broadband light source (150 W, IR filter) and a laser ($<0.5$ mW) inside a glove box maintained with minimum oxygen and moisture content. The exposure time for the refractive index measurement is 0.5 hours.
4.3 Homogeneous thick structures

Multilayer lamination enables one to arbitrarily increase layer thickness or introduce new material layers. For instance, Fig. 4.4 shows the thickness measurement of a four-layer structure before annealing. A total thickness of about 16 µm is measured with each layer approximately 4 µm. Another thick film sample (24 µm) is captured by a 3D confocal microscope and shown in Fig. 4.5. The RMS surface roughness of our spin-coated films was measured to be 0.75 nm [4]. After annealing, films adhere strongly to all the substrates and survive repeated ‘scotch tape’ adhesion tests.
Figure 4.4: Thickness steps measured of a four-layer As$_2$S$_3$ structure before annealing

Figure 4.5: A 24 µm layer of As$_2$S$_3$ uniformly deposited on a substrate by spin-coating and annealing
Multilayer lamination also alleviates problems associated with removing residual solvent from the films. As spin-coated layers increase in thickness, it becomes progressively harder to remove all solvent. Through the multilayer lamination method for thick films, individual layers can be more thoroughly baked before lamination and the structure as a whole retains less solvent. Such a comparison is demonstrated Fig.4.6(a) for monolithic and multilayered films with layer thickness of 4µm. Each data point is taken from the lowest transmission portion of the corresponding FTIR spectrum such as those shown in Fig.4.6(b). The absorption at 2950cm⁻¹ (3.38 µm) is associated with the aliphatic C-H stretch in residual propylamine solvent. Under the same baking condition and total thickness, multilayer structures demonstrate greater transmission and thus less residual solvent in the films. The solid line in Fig.4.6(a) corresponds to an exponential fit of the data with an absorption coefficient of 7x10⁻² µm⁻¹. The quality of the fit to the multilayer data suggests a minimal contribution of interfaces to the overall absorption loss. Conversely, the single layer films exhibit linear behavior (dashed line) indicating an increasingly greater absorption due to residual solvent as the film thickness increases.

As shown in the complete FTIR spectra Fig.4.6(b), optical transmission windows below 2.9 µm and above 3.6 µm exhibit transparency greater than 95%. Thus these thick films are viable for IR applications within these windows. Within the solvent absorption band, it is possible to significantly increase the transmission by increasing the annealing temperature to the glass transition temperature as shown in the prior literature.
Figure 4.6: FTIR spectra of multilayer films and extracted transmission valleys. Films are annealed at 150°C for 13 hrs. (a) Lowest transmission of single and multilayer structures plotted against total film thicknesses. Dashed line is a linear fit and solid line is an exponential fit. (b) Full FTIR spectra of multilayer structures
Further verification of the film quality in the spin-coated/laminated thick films can be found in the SEM. I observe that interfaces between the layers are removed by the annealing step. Fig. 4.7 shows the cross section of a laminated film on top of a spin-coated film with (right) and without (left) being annealed above $T_g$. This sample was produced by cleaving the film and substrate. I find that the films can be cleaved at room temperature without any delamination which enables the direct coupling of light into and out of these thick films. As densification takes place, the total thickness decreases from 3.60 $\mu$m to 3.41 $\mu$m, while the material composition remains almost unchanged. EDX analysis on the films indicates a uniform distribution of both As and S throughout the cross section and a ratio that is consistent with the stoichiometry.

![Figure 4.7](image-url)

Figure 4.7: Left: Films with no annealing shows an interface in the middle; Right: Interface removed with annealing at 200°C

### 4.4 Heterogeneous thick structures

When the newly laminated layer is different from the host material, a heterogeneous multilayer structure, with modulation in refractive index, absorption and other properties, can be achieved. Lamination is critical in this process because direct spin-coating will only redissolve the previously-spun layers, making thick multilayer structures impossible.
Fig. 4.8 (left) shows a double-layer structure of arsenic sulfide and arsenic selenide by the lamination technique. EDX analysis in Fig. 4.8 (right) characterizes the interface. Beyond 1µm from the interface, material composition is shown to be pure arsenic sulfide and arsenic selenide as expected. Although near the interface it appears that there could be a diffusion region extending for approximately 1 µm to either side, I note that the EDX analysis method used for this data averages over a similar length scale and therefore it is not possible to conclude the presence of significant diffusion. Given that the sample is only annealed at 120°C for 2 hours this result is reasonable as one would expect little solid-state diffusion to occur under this temperature/time combination.

Figure 4.8: Left: An As$_2$S$_3$ and As$_2$Se$_3$ double-layer; Right: Normalized EDX analysis of material composition across the interface

Another technologically important multilayer structure is one containing alternate thin metal layers within the chalcogenide. These structures find importance in plasmonics or high contrast photodarkening and photodoping used in applications ranging from electrochemical systems to optoelectronics and data storage [128]. In particular, Ag doped chalcogenide is one of the most widely studied systems. Multilayer lamination and photo-diffusion can effectively enhance the control and depth of Ag diffusion as well as index modulation at any depth in a thick structure. In Fig. 4.9 such fabricated structure is shown, demonstrating a uniform contact between the chalcogenide
and Ag layer.

Figure 4.9: Cross-sectional SEM of 200 nm thick Ag (thin white layers in the middle) and As$_2$S$_3$

In order to test the effect of photo-dissolution in spin-coated arsenic sulfide films, I start with testing single layers of Ag and the chalcogenide. As shown in Fig. 4.10, the effect of silver dissolution under different exposure conditions is directly observable to naked eyes. In the experiment, I use silicon or lithium niobate substrates and illuminate the sample with a green laser pointer or a broadband source. In all cases, the exposed area shows a visible mark, which is clearest when using transparent substrates. Before the exposure, the sample is opaque, but turns transparent to ambient light after the Ag-dissolution takes place. Ag-dissolved chalcogenide layers look almost no different from spin-coated chalcogenide-only layers. It is confirmed by either
ellipsometry (for Si substrates) or UV-vis spectroscopy/FTIR (for glass/lithium niobate substrates) that Ag diffuses into the chalcogenide layer in these regions. Fig. 4.11 illustrates the rapid UV-vis transmission increase after exposing the Ag layer. From the measurement I can tell that the exposed film almost matches the reference arsenic sulfide films in terms of UV-vis transmission. In addition, I find out that the positional order of Ag or chalcogenide layer is unimportant in terms of Ag dissolution. Exposure both from the top of the sample or from bottom through transparent substrates can excite Ag dissolution. In all experiments, our results are tested against chalcogenide-only films, which show little change under the same exposure conditions.

Figure 4.10: Silver dissolution into chalcogenide films under green laser and broadband exposure. Visible mark can be observed by naked eyes. Dark circles on the top 2 samples and the transparent circle on the third sample are regions exposed to light.
In case of multilayer structures, I test the photo-response of a 20 nm thick silver layer laminated between two layers of As$_2$S$_3$. Broadband illumination for 10 minutes causes complete silver dissolution into the surrounding material. The time resolved spectrum Fig. 4.12 (left) with the transmission level at 700 nm is plotted against exposure time in Fig. 4.12 (right). Transmission rapidly increases for the first 3 minutes before tapering down as the amount of silver fully dissolves. This trend is in general agreement with other published work on thin films [128, 129].

The increase in transmission over illumination time indicates a change in refractive index, which is verified by directly measuring the index of refraction of a single Ag layer on top of a chalcogenide layer. I note that both broadband and green laser
produce a net change in the index, whereas a red laser does not. This result is consistent with the need for above band gap illumination to initiate the bond-breaking and doping process \cite{130}. For our high temperature annealed samples, the optical band gap is determined to be 2.23 eV \cite{53} and green light (2.3-2.6 eV) is just above the band gap. The refractive index (at 632.8 nm) of the illuminated area is measured to be 2.41±0.04 with broadband illumination and 2.37±0.01 with green laser illumination, as compared to a measured index of 2.16±0.07 for non-illuminated spin-coated films. This increase with Ag photodoping is comparable and consistent with other published work using traditional film preparation methods \cite{67, 127}.

This refractive index change can be useful in gratings fabrication. Photonic gratings are commonly used in optical devices to manipulate light. Illumination modifies the refractive index of exposed region and photonic gratings are essentially made of materials of alternative indices.

To prove the concept of principle, I put in a mask between the light source and film to create such grating structures (Fig. 4.13). The sample is exposed to a green laser pointer (<5 mW) for 5 minutes with a Cr photo mask with line pattern width of 75 µm. Laser light has to pass through the glass substrate and chalcogenide film.
(3.3 μm) to reach the Ag layer (20 nm). The resultant film is shown in Fig. 4.14, with the white strips representing exposed areas and dark regions are unexposed. As such, alternative refractive index is achieved in a pre-designed fashion in a chalcogenide film, demonstrating the concept of potentially creating IR gratings with our method.

However, due to the limited penetration depth and the instability of unexposed regions, such gratings are not reliable enough for practical usages. An improved method for grating fabrication will be introduced in the next chapter.

Figure 4.13: Setup for demonstrating grating fabrication: the green laser has a power less than 5 mW and the Cr photo mask pattern is written by a standard laser writer.
4.5 Summary

I have demonstrated the feasibility of fabricating thick metal-chalcogenide and chalcogenide-chalcogenide multilayer structures via the spin-coating and lamination method. I have shown that these films exhibit regions of high transmission in the IR and annealing above the glass transition temperature can effectively remove the interface. The photo-response of our multilayer structures is verified through photo-induced Ag dissolution in laminated films, which shows a refractive index increase of more than 0.2. This new fabrication method proves its value as a low-cost and efficient way
to produce large area thick chalcogenide structures. Such structures are particularly useful in areas such as 3D optical memory device, IR beam combiner, IR detectors and waveguides.
Chapter 5

Solution-processed photonic chalcogenide structures

5.1 Introduction

Our ultimate goal of research solution methods is to fabricate applicable optical components. Depending on the specific condition and requirement, there can be a variety of solution methods that suit their purposes in fabrication. From these attempts, techniques become refined and better products are made. This chapter aims at providing an answer to our original research questions on lowering the loss of solution-processed waveguides, improving mode confinement and measurement system, as well as depositing structures on unconventional surfaces.

In this chapter, I first review the optical waveguide fundamentals and different causes for the waveguide losses. Then, two variations of the solution methods are demonstrated. The chalcogenide-based photonic structures developed by each method are characterized and compared, with an emphasis on loss improvement. At the end, the chapter is concluded with a future outlook.
5.2 Waveguides and losses

5.2.1 Optical waveguides

Optical waveguides are the basic elements to confine and transmit light, whether for a few microns inside integrated photonics or several kilometers in optical fibers. Optical waveguides also form the key components in semiconductor lasers and passive/active communication devices.

The basic structure of a dielectric waveguide consists of core and cladding. The former is usually a high-index optical medium, while the latter has a lower index. A guided optical wave propagates along the core direction inside the waveguide. Based on the geometry of the waveguides and their substrates, they can be grouped into planar waveguides and nonplanar waveguides. Nonplanar waveguide with the core surrounded by claddings in all transverse directions is the most commonly used in device applications. Nonplanar waveguides can be further divided into channel or circular waveguides. The waveguides I fabricate are rib/ridge type under the channel waveguide category (Fig. 5.1).

In order for the light to be guided by the waveguide, the repeatedly reflected wave has to fulfill the constructive interference condition. Under such transverse resonance condition, a guided waveguide mode can exist. A waveguide mode characterizes the transverse field pattern whose amplitude and polarization profile remain constant along the longitudinal direction. The guided mode with \( m = 0 \) is called the fundamental mode and those with \( m = 1, 2, \ldots \) are called high-order modes. Depending on the polarization, the modes can be classified into transverse electric and magnetic mode (TEM), transverse electric mode (TE), transverse magnetic mode (TM) and hybrid mode. These modes are essentially solutions to the Maxwell’s equations describing...
Figure 5.1: Types of channel waveguides. Figure adapted from [131]

the electromagnetic field of the traveling wave:

\[
\nabla^2 E(r, t) = \left[ \frac{n^2(r)}{c^2} \right] \frac{\partial^2 E(r, t)}{\partial t^2}
\]  

(5.1)

where \( E \) is the electric field vector, \( r \) is the radius vector, \( n(r) \) is the index of refraction, and \( c \) is the speed of light.

And the solution assumes the form:

\[
E(r, t) = E(r) e^{i\omega t}
\]  

(5.2)

where \( \omega \) is the radian frequency.

With some substitution and assuming infinite boundaries in y direction, the above
equations can be reduced to:

\[
\frac{\partial^2 E(x,y)}{\partial x^2} + (k^2 n^2 - \beta^2)E(x,y) = 0
\]  

(5.3)

where \( k = \omega/c \), \( \beta \) is a propagation constant, \( n \) is the region-dependent refractive index \[132\].

Solving the equation in different regions yield the mode distribution. The solutions are either sinusoidal or exponential functions of \( x \) and three modes are shown in Fig. 5.2 as an example.

![Figure 5.2: Modes in a 3 layer planar waveguide. Figure adapted from [132]](image)

In real waveguides, the number of supported modes depends on the index differences between materials, the dimensions of the waveguide and the wavelength of the source light. Generally speaking, the dimensions of the waveguide should be near (or less than) the target wavelength for single mode propagation. Single mode operation is desirable for sensing when well defined polarization and sensitivity are required. High sensitivity is achieved by constructing interferometers to measure small phase
changes between the light passing the measuring region and the reference light from
the source via a protected path.

Going back to the simples 3 layer case where the waveguide index \( n_f \) is larger
than substrate index \( n_s \) and much larger than the cladding index, the total number
of modes is:

\[
\Delta n = n_f - n_s > \frac{(2m + 1)^2 \lambda_0^2}{16(n_f + n_s)T^2}, \quad m = 0, 1, 2, 3... \quad (5.4)
\]

where \( T \) is the slab thickness, and \( m \) is the mode index [132].

For more complicated structures, the exact solutions to the wave equations cannot
be solved analytically. However, I can take advantage of software such as Beam-
PROP to simulate mode profiles using the finite difference and the Beam Propagating
method.

### 5.2.2 Losses in optical waveguides

Optical loss is an important measurement of the waveguide quality, which also defines
the key performance parameter of many waveguide-based devices. Modern silica
fiber operating at 1550 nm usually has a loss less than 0.2 dB/km, thanks to the
availability of ultra-pure silicon that makes absorption and scattering losses extremely
low. Reported losses for arsenic sulfide based optical fibers are in the range of 100
dB/km (at 4.3 \( \mu \)m). In comparison, the loss of arsenic sulfide planar waveguides
is larger, usually caused by imperfect surface conditions during fabrication and the
exposure to air. Waveguides fabricated by the solution method also have the solvent
evaporation issue discussed earlier, which makes the loss improvement even harder.
This section discusses the main sources for losses in solution-processed waveguides,
which are our targets to minimize in our fabrication process.

In general, photons can be scattered, absorbed or radiated while passing through
the waveguide, thus reducing the total transmitted power. When photons are absorbed, they are annihilated by passing their energy to the atoms or subatomic particles of the absorbing material. In contrast, when photons are scattered, they only alter their direction of travel or energy. Nevertheless, scattered photons are removed from the optical beam, thus constituting a loss for the waveguide.

Thus, for our waveguides, the losses could come from 1) scattering, 2) absorption or 3) radiation \[132\]. For scattering losses, extrinsic surface and volume scattering are usually the main contributors, and intrinsic Rayleigh scattering can be ignored if assuming perfect bulk material quality. For our samples, while surface roughness can be optimized by high temperature annealing \[4\], volume scattering caused by void/pore/bubble formation is persistent regardless of the annealing condition. Researchers have used Mie scattering theory to estimate the amount of scattering from such void/bubbles \[133\]. Fig.\[5.3\] shows the calculated loss per void/bubbles \(n = 1\) of varying size in As\(_4\)S\(_4\) (\(n_{\text{bulk}} = 2.41\)). The scattering behavior shifts from Rayleigh \((\lambda^{-4})\) to Rayleigh-Gans \((\lambda^{-2})\) to wavelength-independent with an increasing bubble size-wavelength ratio. Using parameters from Chapter 3, I can estimate the loss caused by the bubbles. Under our annealing condition without pore treatment, approximately 5% of the cross section is the pore area. For a waveguide of a 5 \(\mu\)m by 5 \(\mu\)m cross-section, a rough estimate gives about 40 bubbles of 0.1 \(\mu\)m radius, assuming them of the same size. So for a 2 cm waveguide, there are about \(6.4 \times 10^6\) pores. Loss per bubble is \(10^{-7}\) dB at 4.8 \(\mu\)m. Hence, total loss by bubbles is estimated to be 0.6 dB. This number shows that the bubble loss is almost at the same level of magnitude as the total loss, can be a significant component of the total loss. The aggregated loss will be more substantial in a waveguide with larger size bubbles and is measured at a shorter wavelength (close to 1 \(\mu\)m).
Figure 5.3: Loss per bubble for varying bubble size. The bubbles in our waveguide volume have a diameter up to 200 nm. Figure adapted from [133].
Second, residual solvent is the major contributor to absorption losses. In this case, intrinsic absorption from material or free carrier can be ignored if assuming perfect material. Usually, FTIR measurement can give a good indication of the solvent presence. For propylamine, the absorption peak will center around 2.38 µm. A 80% transmission can translate to about 1 dB loss. So while trying to avoid using the wavelength bands in the absorption range, I try to evaporate as much solvent as possible. Although it is extremely hard to remove the solvent entirely, it can be shown that prolonged annealing at elevated temperatures can significantly reduce the residual solvent.

Third, radiation loss is not usually encountered in typical good-quality waveguides; however, for curved channel waveguides, it can be significant. In real life, waveguide irregularities or inhomogeneities can cause mode conversion from lower-order modes to the higher-order modes, coupled with energy loss even though the particular mode may be well confined [134]. Such radiation loss becomes significant when the light passes through bend structures. Using the velocity approach developed by Marcatili and Miller, the loss can be expressed as:

\[ \alpha = C_1 e^{-C_2 R} \]  

(5.5)

where \( C_1 \) and \( C_2 \) are constants that depend on the dimensions of the waveguide and on the shape of the optical mode [132]. Since the radiation loss coefficient depends exponentially on the radius of curvature, it can become a limiting factor to produce functional waveguides on curved surfaces.

In light of these potential problems and limitations, I start processing our waveguides with the goal to optimize the output mode and minimize the optical losses. Initially, I worked with Candice Tsay to pattern conventional straight waveguides on flat surfaces and integrate them with QCL lasers to minimize coupling losses. In this project, I begin to process waveguides with an addition of EDA, to prevent pore
formation. Annealing is set to a higher temperature and for a longer period to efficiently remove solvents. Structure design is also taken into consideration to minimize the loss. From these experiences, a number of fabrication methods are developed for different applications. The structures I developed either extended the waveguide functions or performed better in terms of optical properties.

5.3 Loss improvement: from MIMIC and µTM to micro-channel filling

5.3.1 Waveguides by MIMIC and µTM

Solution-based processing enables new techniques for waveguide integration that are unattainable by evaporation methods. Using the flow properties of liquids, micromolding in capillaries (MIMIC) [135, 136] and micro transfer molding (µTM) [4, 135] can directly integrate chalcogenide glass waveguides with existing optical devices without extra etching steps. The advantages of these techniques are multifold. The methods are simple and require no high-vacuum equipment. Moreover, complex geometries such as bend waveguides, y-splitters or interferometers can easily be realized using corresponding molds [4]. The dimensions of the waveguides can be in the order of tens of microns in width and height, which makes them suitable for integration with mid-infrared devices such as quantum cascade lasers (QCLs). In comparison, these large dimensions are difficult to obtain by evaporation methods. Furthermore, the process requires only moderate temperatures, although the surface roughness and waveguide loss can be further reduced by a subsequent annealing step at higher temperatures such as 120°C for arsenic sulfide [4].

The MIMIC method uses a soft and flexible polydimethylsiloxane (PDMS) mold which has a reverse pattern from photolithography-made reusable master mold [136].
After the PDMS mold is laid onto a substrate, a small amount of the chalcogenide solution is deposited at the channel entrance and fills up the channel by capillary action (Fig. 5.4). After baking, the PDMS mold can be easily removed to obtain the final structure. In such fashion, a successful demonstration of an arsenic sulfide waveguide directly integrated with a QCL (Fig. 5.5) was presented before [135]. However, for structures with a small cross section (< 5 µm in dimension), the MIMIC method is limited by the capillary forces to shorter filling lengths.

Figure 5.4: 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 pipette to inlets. Channels fill by capillary action. Sample is baked in vacuum oven to solidify structures. PDMS mold is removed.
Figure 5.5: SEM image of integrated $\text{As}_2\text{S}_3$ waveguide and QCL. The waveguide is aligned to the right-most laser ridge. The waveguide bend has $r = 1$ mm, and a total length of 7 mm.

The µTM method uses similar PDMS molds and complements the MIMIC method, because it is not limited by capillary forces or the mold geometrics. In this method, the solution is spin-coated to form a thin film directly on the patterned PDMS mold. Immediately after spinning, a substrate is put on top of the film, and the whole assembly is transferred to a vacuum oven where a weight is added on top of the stack to increase the adhesion between film and substrate. The sample is baked
at temperatures up to 100°C before the PDMS mold is removed, leaving behind a patterned glass film on a substrate, see Fig. 5.6 [4].

![Figure 5.6: Waveguides by µTM. (a) A PDMS mold with relief-pattern is attached to a microscope cover slip, which serves as a rigid backing. (b) As$_2$S$_3$ solution is spun-coat onto the mold surface. (c) A LiNbO$_3$ substrate, 0.5 mm thick, is pressed down onto the As$_2$S$_3$ film. It adheres by capillary forces. The sample is baked to solidify the As$_2$S$_3$ structures. (d) The PDMS mold is removed. The As$_2$S$_3$ film stays adhered to the LiNbO$_3$ substrate.](image)

In our previous collaborative effort published in [4], the propagation loss of the µTM-generated waveguides were determined to be 4.52 ± 0.07 dB/cm at 4.8 µm. From a starting length of 16 mm, waveguides of width 2.5, 5, 7.5, and 10 µm, and height 4.5 µm, and surrounding slab height of 1 µm, are measured. Propagation loss of the 2.5 µm x 4.5 µm waveguides (Fig. 5.7 Left) as measured by cut-back is 4.52 ± 0.07 dB/cm on the LiNbO$_3$ substrate. Surface and edge roughness is characterized to determine scattering effects. Characterization of the film roughness is conducted by AFM. The RMS roughness of the As$_2$S$_3$ film is found to be 0.75 nm. This surface roughness value compares favorably to other examples of chalcogenide glass waveguides, thermally evaporated and dry etched which show a 1.5 nm roughness [137], and thermally evaporated and patterned by lift-off reporting a roughness of 1.6 nm [138]. The cause for the loss could come from the bubbles and solvent inside the waveguides, since the solvent mix and annealing conditions are not optimized. This will be discussed in more detail in the next section.
Figure 5.7: Waveguides by µTM published by Candice. (Left) SEM image of 2.5 µm wide by 4.5 µm high waveguide. A thin As$_2$S$_3$ slab film surrounding the waveguide is visible. An area of a slight delamination of this film from the substrate is visible to the right of the waveguide. (Right) SEM image (top view) of waveguides configured as a y-splitter. Width of branches is 5 µm.

5.3.2 Low loss waveguides by micro-channel filling

This section introduce a new method called "micro-channel filling", in which chalcogenide waveguides with lower losses are fabricated without using plastic molds. The main distinction in fabrication from the previous section is the addition of EDA in the solvent mix for pore removal and improved annealing conditions to reduce residual solvents.

For fabrication, metal basis arsenic sulfide pieces (As$_2$S$_3$ Alfa Aesar) are dissolved with propylamine solution at a concentration of 2g/10mL. The dissolution takes a few days in a sealed glass bottle and a magnetic stirrer can be used to expedite the process. The stock solution is passed through 0.1 µm filters and 10% ethylenediamine is added to minimize pore formation. The silicon dioxide layer is prepared by plasma-enhanced chemical vapor deposition (PECVD) and reactive ion etching. The precursor gases used were N$_2$O and SiH$_4$ and the deposition rate is 450 nm/min.
The channel structures are transferred from photoresist into the SiO$_2$ layer through an optimized inductively coupled plasma reactive ion etching (ICP-RIE) process in Ar/H$_2$/CHF$_3$/CF$_4$ with flow rates of 6/30/50/2 sccm respectively. The channel cross section has an inverted isosceles trapezoid shape of 8 µm height, 8 µm top and 5 µm bottom. The prepared solution is then drop-casted onto a substrate and spun at 1500-2500 rpm for 10 seconds. Alternatively, one could use doctor blade, drop casting and etc. to backfill the trench with solution. The resulting film is soft-baked under vacuum at 60°C for 1 hour to remove most of the solvent, followed by heat treatment at 180°C for 6 hours to further densify the glass. Vacuum pressure is set around 50 Torr. All preparation and fabrication steps are performed in a glove box connected to a vacuum oven, so that the material is exposed to minimum levels of oxygen and moisture. More importantly, a glove box environment protects researchers from directly contacting the material. In our study, FTIR spectra are taken with a Nicolet 8700 by subtracting the substrate spectra from the sample spectra. The data is processed by including a correction due to the Fresnel reflections. Given the arsenic sulfide refractive index of 2.4 and the lithium niobate substrate refractive index of 2.15, the normal reflectance from the chalcogenide surface, the chalcogenide-substrate surface and the substrate-only front surface is calculated to be 17.0%, 0.3% and 13.3% respectively. Hence, the correction is determined by adding the reflectance of the chalcogenide and chalcogenide-substrate surfaces and subtracting the substrate-only surface, yielding a total of 4.0%. Scanning electron microscope (SEM) images are taken with a Quanta 200 FEG environmental SEM at 15keV in high vacuum mode. The SEM is equipped with an EDX system for compositional analysis. Film thickness is measured with an Olympus Laser Confocal Microscope, LEXT OLS4000, by scanning the step height of a scratched film.

The experimental setup for evaluating the waveguide performance involves a mid-IR test platform as illustrated in Fig.5.8. The light source is a pulsed optical para-
metric oscillator laser with 150 mW average power and the laser wavelength is tunable from $\lambda = 2.4 \, \mu m$ to $\lambda = 3.7 \, \mu m$. Using a parabolic mirror, the light is first focused into a 9 $\mu m$ core and 125 $\mu m$ cladding single-polarization fluoride fiber, and then butt coupled into the waveguide. The core of the mid-IR fiber is lined up with the smooth cleaved front facet of the waveguide. Alignment between the optical fiber and the waveguide is achieved using high-precision positioning stages and the fine adjustment is monitored by an upper microscope equipped with a long working distance objective. The mid-IR signals from the waveguides are focused by a calcium fluoride biconvex lens and then imaged by an InSb camera.

![Figure 5.8: Measurement setup and mode observation at different alignment configurations for efficient coupling. Left: fundamental mode observed when fiber is aligned with the waveguide. Right: mode disappears when misaligned](image)

To accurately characterize the samples, I have thoroughly studied the material and optical properties of both as-deposited films and fabricated waveguides. Since residual solvent is a prevalent problem in most solution processed structures, I use 6 hrs of annealing at 180°C to ensure optimal removal of solvent [53]. Fourier trans-
form infrared spectroscopy (FTIR) in Fig. 5.9 shows that the spin-coated films have transmission above 80% from 2.5-5 \( \mu \)m and over 98% from 2.5-2.8 \( \mu \)m, which is our wavelength regime of interest. Our transmission loss values are comparable with or better than other published data \[3, 53, 98\]. The solvent band which is still visible between 2.9-3.6 \( \mu \)m as a dip in transmission, is mainly due to the aliphatic C-H stretch, but is kept to a minimum. The rest of the band shows excellent transmission and can be safely utilized for device applications. In another test, I dip the processed film into 3% acid solutions for at least 3 minutes and the films come out intact. This result indicates that although there still exists trace solvent in the film, its amount is not significant to cause reactions.

Figure 5.9: FTIR of 2 \( \mu \)m thick spin-coated films showing high transmission across the spectrum.

Inverted-rib waveguides are fabricated by spin-coating and annealing solution-dissolved chalcogenide in pre-etched channels, as described in the experimental section. Energy-dispersive X-ray spectroscopy (EDX) mapping is used to verify the material composition. Looking at the cross-sections in Fig. 5.10, oxygen is found in the
substrate structure, whereas the waveguide region only contains arsenic and sulfur. The results show uniform material distribution throughout the waveguide structure and no solvent-specific composition is detected, reaffirming the material integrity of our samples.

![SEM of a waveguide cross-section showing a concave top with the main waveguide region underneath. EDX mapping showing mid-IR lightwave homogeneity of the waveguide.](image)

In order to characterize the optical properties of our waveguides, I couple a tunable laser from 2.4 to 2.8 µm to the structure. Within the entire wavelength range, a sharp fundamental mode can be clearly resolved. A typical intensity profile of the
mode image at $\lambda = 2.6 \, \mu\text{m}$ is shown in Fig. 5.11. No major scattering or distortion is observed, which implies that the mid-IR light is well confined inside the waveguides. Furthermore, the fundamental mode remains the dominant one within the wide spectral range, indicating that the waveguides can efficiently transmit mid-IR light at least in the measurement range we performed.

![Figure 5.11: Typical mode output profile measured from infrared images and an infrared camera capture at 2.6 $\mu$m. Both show sharp contrast to the background.](image)

Furthermore, I measure the attenuation in optical power through waveguides of differing lengths to determine transmission loss. For this, paper clip structures are used such that a single cleave yields a common facet used for every waveguide, minimizing variations in coupling loss. By fitting the length-dependent optical powers...
from the waveguide outputs (Fig 5.12 Right), an optical loss as low as 1.87 dB/cm is obtained at $\lambda = 2.6 \, \mu m$ and the same order result is found from 2.4 to 2.8 $\mu m$.

Solution-processed arsenic selenide waveguides with a similar configuration had a loss of 9 dB/cm at 1.55 $\mu m$ [98]. Our previous solution-processed waveguides showed 4.52 dB/cm loss on LiNbO$_3$ substrate at 4.8 $\mu m$ [4]. Such a loss improvement can significantly enhance the usability of these waveguides.

![Figure 5.12: 'Paper-clip' waveguide configuration and loss measurement from such waveguides. Left: waveguides of different 'paper-clip' sizes have different path lengths, Right: 1.87 dB/cm loss extrapolated from the power attenuation data](image)

Part of the loss improvement can be attributed to better processing and design. Previously, the waveguides were only heated up to 100 $^\circ$C and would have a refractive index of 2.15, close to that of the substrate used (lithium niobate). This time, our samples are annealed at 180 $^\circ$C and have a refractive index of 2.4, much closer to the bulk. Such processing reduces residual solvent and enhances transmission. Moreover, the slab mode is suppressed with our design and material absorption is reduced. Since our waveguide structure is engineered upside-down, the slab part is exposed during annealing. Solvent evaporates during the annealing step causing volume contraction, which results in shrinkage at the main waveguide. This leads to the slab directly above the waveguide bending downwards in a concave fashion as shown in Fig 5.10.
The effect of such a structural difference is modeled in BeamPROP simulation software to predict mode output, using the optical properties \( n=2.4, k=8\times10^{-8} \) of the materials and approximate shapes of the waveguides [53, 97]. The calculated field profiles are displayed in Fig5.13 demonstrating the fundamental modes expected from waveguides of such dimensions. A wavelength range from 2.4 to 3.7 µm corresponding to the laser source is simulated for the left structure and shows similar mode profiles in agreement with our experimental observations. The approximate mode area (intensity above 0.1 from the diagram) is 28 µm² for the left structure and 47 µm² for the right structure. The direct benefit from the mode area contraction is reduced total material absorption integrated over the entire waveguide. However, it is noted that such structure supports high-order modes. A pure single mode structure would require further dimension reduction. I also notice that it is possible to remove the slab mechanically or chemically by polishing or etching, leaving just the waveguide in the trench. Such a process adds complexity to the overall fabrication process, without significant improvement in the confinement. Our models show that this ideal waveguide, without a slab, has a mode area of about 26 µm², which is very close to our existing structure.
Figure 5.13: Better mode confinement in our concave-top structure from simulated fundamental mode profiles at $\lambda = 2.6 \, \mu m$. Rectangular cross-section is assumed for the waveguides. Left: inverted-rib with a concave top, Right: inverted-rib with a flat top.

Overall, I can obtain mid-IR solution-processed chalcogenide waveguides reproducibly, without apparent size limitation. Our main improvement and achievement are summarized in Table 5.1. This work has demonstrated a low-cost, reliable and highly efficient method to achieve mid-infrared on-chip photonic structures, offering hybrid integration compatibility and flexibility with lower loss compared to other solution-processed waveguides.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Solvent</th>
<th>Annealing Temperature/ °C</th>
<th>Annealing Duration/hr</th>
<th>Wavelength/ µm</th>
<th>Loss/ dB/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>µTM</td>
<td>propylamine</td>
<td>100</td>
<td>1</td>
<td>4.8</td>
<td>4.52</td>
</tr>
<tr>
<td>Micro-channel filling</td>
<td>propylamine + EDA</td>
<td>180</td>
<td>6</td>
<td>2.6</td>
<td>1.87</td>
</tr>
</tbody>
</table>

Table 5.1: Comparison of µTM and micro-channel filling methods
5.4 Other structures by MIMIC, µTM or micro-channel filling

5.4.1 Waveguides on curved surfaces

The flexibility of solution has also given the possibility of depositing waveguides on curved surfaces. In many application, the substrates or components are non-flat and optical fibers cannot be used, such as 3D circuits in optical chips or depositing photonic structures on lens surfaces. Therefore, it is interesting to take advantage of our method and explore the possibility of unconventional deposition.

This sections describes how I use MIMIC to pattern waveguides on curved surfaces. For the fabrication steps, metal basis arsenic sulfide pieces (As$_2$S$_3$ Alfa Aesar) are dissolved with propylamine solution at a concentration of 2g/10mL. The dissolution takes a few days in a sealed glass bottle and a magnetic stirrer can be used to expedite the process. The stock solution is passed through 0.1 µm filters and 10% ethylenediamine is added to minimize pore formation. Pre-designed channel patterns are first etched on Si substrates with standard photolithography procedures. PDMS is then poured onto the master mold and cured to have the reverse pattern transferred to itself.

For channel filling, the PDMS must be held tight against the substrate wall (curved glass). A small amount of the chalcogenide solution is deposited at the channel entrance and fills up the channel by capillary action. To ensure the PDMS conforms to the substrate and the micro channel stay air-tight, the PDMS layer has to be thin (less than 0.5mm) to give it more flexibility in bending radius. Moreover, tapes should be used to secure the PDMS layer in place while annealing. After these extra steps, the resulting films are soft-baked under vacuum at 60°C for 1 hour to remove most of the solvent, followed by heat treatment at 180°C for 6 hours to further densify the glass. Vacuum pressure is set around 50 Torr. All preparation and fabrication steps
are performed in a glove box connected to a vacuum oven, so that the material is exposed to minimum levels of oxygen and moisture. More importantly, a glove box environment protects researchers from directly contacting the material.

To experimentally evaluate the performance of the fabricated chalcogenide waveguides, we set up a mid-IR test platform based on fiber coupling (Fig. 5.14). The light source is a pulsed optical parametric oscillator laser with 150 mW average power and the laser wavelength is tunable from $\lambda = 2.4 \, \mu\text{m}$ to $\lambda = 3.7 \, \mu\text{m}$. Using a parabolic mirror, the probe light is first focused into a 9 \, \mu\text{m} core and 125 \, \mu\text{m} cladding fluoride fiber, and then butt coupled into the waveguide. The core of the mid-IR fiber is lined up with the front facet of the waveguide. Alignment between the optical fiber and the waveguide is achieved using high-precision positioning stages and the fine adjustment is monitored by an upper microscope equipped with a long working distance objective. The mid-IR signals from the waveguides are focused by a calcium fluoride biconvex lens and then imaged by an InSb camera.
Patterned waveguides are shown in Fig. 5.15 (Left), with 160µm width and 40µm height. Output from the waveguide is captured by an IR camera Fig. 5.15 (Right). The lower bright spot is the output mode and is observed to dim when shifting the fiber facet slightly off-center. This output light is detected throughout our wavelength measuring range (λ = 2.4 µm to λ = 3.7 µm). The figure shown here is taken at 3.3 µm. The other spot on top could be stray light that is guided by glass, because it stays constant in brightness when the fiber is shifted side-wise. Here, for the first time, I have demonstrated the deposition of well-defined mid-IR waveguides on a non-planar surface, overcoming the fabrication barrier faced by traditional methods. It can be inspirational to patterning of photonic structure on lens surfaces to modify the optical properties. Such 3D flexibility has great potential for applications such as sensing and data storage or simply IR light manipulation, where complicated chalcogenide
structures are needed. More quantitative data such as propagation loss is to be collected to quantify our results. However, it is very difficult to acquire substrates that are curved, cleavable, inexpensive and transparent in IR. So far, I have not found any appropriate substrate to further this part of the study.

Figure 5.15: Left: waveguides patterned on a curved surface by MIMIC; Right: output from the curved waveguide captured by an IR camera

5.4.2 Rings and microlenses by MIMIC or µTM

Our solution methods have few restrictions in terms of fabrication geometry. In addition to waveguides and Y-splitters, more complicated circular structures such as ring resonators and micro lenses can also be created by the µTM method. Fig. 5.16 and Fig. 5.17 demonstrate the fabricated structures. Rings of a range of diameters are produced and in general, larger rings of 10s of µm radius have a much higher yield than smaller rings. From our study, the top roughness is 0.75 nm.

However, in this process, one main limitation arises from the lithography method
Figure 5.16: Waveguides by µTM. Top: Top view of arsenic sulfide ring resonators by µTM; Bottom: Image of the top right ring resonators taken by a 3D confocal microscope.

Figure 5.17: Chalcogenide microlenses made by µTM on a flat substrate. The smallest lenses are 2 µm in diameter and indicated in the figure by the circles.
used to create the PDMS molds. The smoothness of the ring curvature and separation between the rings depend on the quality of the plastic molds, which also depends on the availability of equipment. For instance, when the rings are placed too close (in the order of a few microns), laser mask and UV lithography will fail to perfectly develop the separation region because of the diffraction limit. In such situation, e-beam will be required to create appropriate master molds.

5.4.3 Gratings by micro-channel filling

Beyond micron size devices that I have fabricated so far, sub-wavelength photonics has generated no less interest for its superior ability to manipulate light. In optical circuits where many components are of sub-wavelength scale, sub-wavelength photonic devices are more ready to be integrated with [139, 140]. In addition, sub-wavelength photonics are necessary for ultra-high speed data processing and low energy operation [141, 142]. In the realm of mid-IR, however, there are not as many published examples due to the material constraint. Spin-coating chalcogenide on a pre-etched structure seems to be a reliable approach for fabrication, such as the inverse opal photonic crystal [93] shown in Chapter 1 and optical tuning of QCLs (Fig. 5.18) [58]. Moving beyond, it is very interesting to explore the reflection band in chalcogenide gratings, as well as its possibility of application in communications. As such, this section demonstrates our preliminary results of fabricating chalcogenide gratings.
Depending on the degrees of freedom, sub-wavelength photonic devices can be classified in one, two or three dimensions. Figure 5.19 illustrate 1-D, 2-D, and 3-D photonic crystals. For instance, Bragg grating is a one dimensional photonic structure, whereas the photonic crystal waveguide is a two dimensional photonic structure. Their photonic lattices are composed of two different materials have distinct refractive indices.
Figure 5.19: Structures of 1-D, 2-D, and 3-D photonic crystals. A and B indicate different dielectric materials, and $a$ is the photonic lattice constant. Figure adapted from [144]
The interaction between the light and the optical materials in nano scale cannot simply be described by ray optics. This is because when the features are close to or below the light wavelength, the electromagnetic resonance must be considered. This is similar to the effect of the periodic atomic structure on the electron wave propagation in solids. In the case of sub-wavelength photonics, "photonic crystals" structures with nano- or sub-micro cavities composed of photonic crystal lattices have been explored by researchers. The electromagnetic wave can be manipulated by building artificial photonic crystal structures. The photonic crystal band structure can be achieved by arranging dielectric or metallic arrays periodically [145, 146]. An electromagnetic wave with a frequency within the photonic crystal band gap will be reflected. Otherwise, it passes through. Our experiment was set up to verify this "photonic crystal band gap" or "reflection wavelength band" by scanning through certain wavelength range.

For our experiment, our grating can be approximated to an uniform fiber Bragg grating. The expected behavior under Fresnel reflection is shown in Fig5.20. For its spectral response, the incident broadband signal splits into transmitted and reflected components, about the Bragg wavelength.

The Bragg wavelength is defined to be:

\[ \lambda_B = 2n_e \Lambda \] (5.6)

where \( n_e \) is the effective refractive index of the grating and \( \Lambda \) is the period of our structure. In our case, the index for arsenic sulfide is 2.4 and the index for the oxide is 1.5. I can estimate the effective index to be around 2 by assuming 50:50 duty cycle. Since I would like to scan through and find the reflection peak in \( \lambda_B \) in \( \lambda = 2.4 \ \mu m \) to \( \lambda = 3.7 \ \mu m \) range, the period should be around 0.8 \( \mu m \).

For the fabrication steps, metal basis arsenic sulfide pieces (\( \text{As}_2\text{S}_3 \) Alfa Aesar) are
dissolved with propylamine solution at a concentration of 2g/10mL. The dissolution takes a few days in a sealed glass bottle and a magnetic stirrer can be used to expedite the process. The stock solution is passed through 0.1 µm filters and 10% ethylenediamine is added to minimize pore formation. The silicon dioxide layer is prepared by plasma-enhanced chemical vapor deposition (PECVD) and reactive ion etching. The precursor gases used were N₂O and SiH₄ and the deposition rate is 450 nm/min. The grating structures are transferred from photoresist into the SiO₂ layer through an optimized inductively coupled plasma reactive ion etching (ICP-RIE) process in Ar/H₂/CHF₃/CF₄ with flow rates of 6/30/50/2 sccm respectively. Fabricated grating structures have several different period lengths. Selected gratings with longer
periods are shown in Fig. 5.21.

![Figure 5.21: Grating structures before spin-coating](image)

The prepared solution is then drop-casted onto a substrate and spun at 1500-2500 rpm for 10 seconds. Alternatively, one could use doctor blade, drop casting and etc. to backfill the trench with solution. The resulting film is soft-baked under vacuum at 60°C for 1 hour to remove most of the solvent, followed by heat treatment at 180°C for 6 hours to further densify the glass. Vacuum pressure is set around 50 Torr. All preparation and fabrication steps are performed in a glove box connected to a vacuum oven, so that the material is exposed to minimum levels of oxygen and moisture. More importantly, a glove box environment protects researchers from directly contacting the material.

The experimental setup for evaluating the waveguide performance involves a mid-IR test platform similar to the last section. The light source is a pulsed optical parametric oscillator laser with 150 mW average power and the laser wavelength is tunable from $\lambda = 2.4 \, \mu m$ to $\lambda = 3.7 \, \mu m$. Using a parabolic mirror, the light is first focused into a 9 \(\mu\)m core and 125 \(\mu\)m cladding single-polarization fluoride fiber, and then butt coupled into the waveguide. The core of the mid-IR fiber is lined up with the smooth cleaved front facet of the waveguide. Alignment between the optical fiber and the waveguide is achieved using high-precision positioning stages and the
fine adjustment is monitored by an upper microscope equipped with a long working
distance objective. The mid-IR signals from the waveguides are focused by a calcium
fluoride biconvex lens and then imaged by an InSb camera.

The IR grating structure is successfully fabricated with our method. Since the
structure is covered under the arsenic sulfide layer, microscopy is not able to charac-
terize the gratings. For the experimental measurement, I have not been able to detect
the reflection peak. One possible explanation could be the inaccuracy in grating pe-
riods, since a small change in the period can significantly affect the optical output.
The lithography fabrication and quality control need to be improved in order to verify
our predicted results. Nevertheless, I have demonstrated an efficient process that can
readily fabricate grating type structures.

5.5 Summary and discussion

In this chapter, I have demonstrated two types of solution-based methods for fabri-
cating chalcogenide photonic components: MIMIC/µTM and micro channel filling.
These methods complement each other in fulfilling the needs for device fabrication.
MIMIC is very advantageous over other traditional methods in special applications
such as component integration and deposition on curved surfaces. However, due to
the viscous nature of the solution, the waveguide dimension has to be 10s of microns
and above and the channel filling lengths are limited to less than 10s of millimeters.
To overcome such limitation, µTM and micro channel filling have been developed to
fabricate longer and narrower structures. The difference between them is that the
waveguide is defined by the PDMS mold in the former and by substrate lithography
in the latter. When provided with appropriate substrates (Si wafer with at least 3 µm
of oxide layer on top), micro channel filling becomes a more reliable, more accurate
and simpler method than µTM.
Another great improvement I have shown in this chapter is the small propagation loss in trench waveguides. The improvement to 1.87 dB/cm loss is significant in terms of enhancing the waveguide performance. Our results are achieved based on the understanding of loss mechanisms and combating such problems with proper strategies. Although it is hard to compare waveguides loss by micro channel filling directly with that MIMIC for the difference in measurement wavelengths, I can definitely point out some changes made that have contributed to the leap forward. First is the use of EDA to remove pore structures, which can reduce scattering losses from nanopore regions. Second is the improved thermal processing. Previously samples were annealed at 100°C and have a refractive index of 2.15, whereas now the samples are annealed at 180°C and have a refractive index of 2.4, much closer to the bulk value. Third is switching substrate from high index lithium niobate to lower index silicon dioxides, which reduces the possibility of having slab mode. Moreover, the makeover of the measurement system and waveguide configuration now allows us to find the losses more accurately. Earlier on the waveguides were straight and light coupling is achieved by aligning QCL closely to the waveguide end. Now I use fiber to couple the light from the laser to the waveguide and have adapted the paper-clip configuration, so that out-coupled light can be easily differentiated from any stray light coming directly from the fiber end. In future, industrial standard equipment will be helpful to further improve the quality and reduce waveguide losses.
Chapter 6

Conclusion

This thesis has studied several important problems in the solution processing of chalcogenide materials and has demonstrated a number of photonic components by solution methods. Previously, our group developed plastic molding methods to deposit chalcogenide waveguide on flat substrates, but suffered from large losses. In this work, several aspects of the solution process from the dissolution chemistry to post processing are studied and new methods are demonstrated to produce better structures.

In Chapter 3, I characterized the nanopore formation within propylamine processed arsenic sulfide films. Pore density is shown to increase with both annealing temperatures and durations. Such mechanism is explained with the vacancy coalescence theory and I have developed a method to remove such pores. Homogeneous films are obtained with addition of EDA solvents. This result has great implications for improving the quality of optical chalcogenide components processed with solution methods. It also reinforces the pore formation mechanism that has been relevant to many solution-processed materials.

In Chapter 4, I presented a new technique for fabricating thick (>10 µm) chalcogenide multilayer structures. Films of arbitrary thicknesses are readily achieved
through spin-coating, lamination and baking. For homogeneous systems, layer interfaces can be effectively removed by annealing above \( T_g \). Alternatively, heterogeneous multilayer films can be realized by introducing layers of different chalcogenide materials or metals. In particular, photo-induced Ag dissolution is verified in a laminated multilayer film, with a refractive index increase greater than 0.2. This result has promising potentials for chalcogenide deposition in applications such as data storage, IR detection and IR beam combining.

In Chapter 5, I demonstrated two groups of fabrication methods and fabricated photonic components including waveguides on flat surfaces, waveguide on curved surfaces, rings and gratings. The fabrication and characterization of solution-processed chalcogenide waveguides by \( \mu \)TM and micro-trench filling method are compared. Micro-trench filling now produces waveguide of the lowest loss of 1.87 dB/cm among solution-processed waveguides. In this process, channels are etched on substrates and back-filled with solution-dissolved arsenic sulfide before being annealed. The waveguides are homogeneous in elemental composition and have good mode confinement. Both simulation and experimental measurements confirm a dominant fundamental mode covering 2.5-2.8 \( \mu \)m.

Overall, I have completed a thorough study of the solution process of chalcogenides and built a system to test the performance of fabricated structures. Our results have a significant impact on the research and industry community. First, I have thoroughly characterized the pore formation phenomenon and proposed a theory for the process. In addition, we are the only group that has proposed an efficient solution to solve this persistent pore problem. Second, we are the first to demonstrate thick chalcogenide deposition by a lamination method, creating a convenient pathway to achieve volumetric optical components. Third, we are the first to demonstrate a reliable method for depositing chalcogenide waveguides on curved surfaces. Last but not least, our waveguides by micro-channel filling are measured to have the lowest loss
among solution-processed chalcogenide waveguides. It significantly improves quality of such solution-processed structures and the credibility of the solution process as a whole.

Future research can build upon our existing platform and expand on the variety of chalcogenide structures, to realize the full potential of the solution process. In order to achieve this, creative measuring strategies need to be developed in order to characterize unconventional structures. In addition, the material system used can expand to include more types of chalcogenides and metals. Apart from the arsenic sulfide and Ag-arsenic sulfide systems, there are many more chalcogenide materials and their associated optical-material interactions that can be studied. The impact of solution-processing chalcogenide materials will continue to grow with increasing research efforts.


of Applied Physics, 103(6), 2008.


2002.


1994.


in design, fabrication, and characterization, 2004.


