Properties modification of chalcogenides by various external stimuli and the applications

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Abstract

Chalcogenides are fascinating materials with striking properties. Since the emergence in the 1960s, chalcogenides have been extensively studied for their low processing temperature, wide transparency window in mid-infrared, a wide range of photo-induced phenomena, as well as high linear and nonlinear refractive indices. They have been used in various applications such as phase-change memories, solar cells, sensors, holographic information storage, micro lenses, all-optical switching, and laser written waveguides, etc. Moreover, the chalcogenides also provide a platform for fundamental investigations of light-matter interactions in nanophotonics structures, such as photonic crystal and even metamaterial structures.

Taking into account the essential task of enlarging the class of materials for modern science and technology as well as pursuing a deeper understanding of the properties of chalcogenides, the main theme of this dissertation is to explore the possible methods to achieve controllable and optimized modifications of the fundamental properties of chalcogenides.

The first kind is about the structural modifications through light exposure. The shape changes of the thin film are created when exposed to light pattern. We then investigate the mechanisms of photo-induced surface relief formation. We derive a generalized model to explain the spatial and temporal evolution of photoinduced surface structure in photosensitive amorphous thin films. The model describes these films as an incompressible viscous fluid driven by a photoinduced pressure originating from dipole rearrangement. This derivation requires only the polarizability, viscosity and surface tension of the system. Using values of these physical parameters, the validity of the model is checked by fitting to experimental data of As$_2$S$_3$ and demonstrating good agreement.

Another way of modifications is achieved by the doping of silver nanoparticles. We also achieve the in-situ and uniform generation of Ag nanoparticles in chalco-
genide solution using laser ablation. Ag-doped chalcogenide films are fabricated by spin-coating the resulting solution. The prepared solution and films are analyzed using transmission electron microscopy, dynamic light scattering and UV-vis spectroscopy to investigate particle shape and size distributions. Uniform doping has been achieved. The kinetics of Ag-photodissolution into As-S glass films are investigated using ellipsometry. Increased refractive indices of the films upon near bandgap light irradiation have been measured.

Besides the uniform doping of nanoparticles, we are able to incorporate a variety of ions into chalcogenide glassy matrices using in-situ wet chemistry processing. Various chlorides are incorporated into chalcogenide matrices, leading to multifarious property changes, such as absorption and refractive indices of the chalcogenides.

In addition, we also explore modifications through photonic crystals. We use complementary metal-oxide-semiconductor (CMOS) processed silicon photonic crystals with angstrom surface roughness to spatially confine the solution processed arsenic sulfide and achieve controllable modulations of chalcogenides emission. A planar emitter array of chalcogenides is fabricated based on this novel periodic hetero-structures of semiconductor.
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6.6 Optical properties of arsenic sulfide: absorption (black) and photoluminescence (red). The absorption curve measured through UV-vis of an arsenic sulfide film on glass substrate (2µm thick), shows a bandgap around 2.4 eV and a low absorption coefficient above 550nm. Under 532nm laser excitation, chalcogenide’s photoluminescence spectrum of bulk As₂S₃ gives a major peak at 691 nm (1.80 eV) central wavelength and 104 nm bandwidth.

6.7 Optical properties of the material. Raman spectrum of the chalcogenide-silicon photonic crystals. Inset: Intensity mapping of the As-S-As bond at 330 cm⁻¹, where chalcogenide is only found in the photonic crystal region. Scale bar: 5µm.

6.8 Chalcogenide photonic crystal emitters. (a) Photoluminescence spectrum of the photonic crystal emitter array with lattice constant of 415nm and hole radius of 110 nm, inset shows correspondent SEM of the chalcogenide array in silicon host anti-dots array, (b) 120nm (c) 130nm (d) 140nm.
6.9 Photoluminescence spectra of the photonic crystal emitter arrays with lattice constant of 415nm and a variety of hole radius, from 90 to 140 nm, with a step size of 10nm. Spectra are summarized together for a comparison, where shapes and resonances of the spectra are distinctive, denoting an energy redistribution resulting from the confinement from photonic crystals.

6.10 Enhanced modes for photonic crystal emitters with different holes. For photonic crystal emitter array with hole radius of 90 nm, modes of 677.5 nm and 820.1 nm are enhanced, while the resonance modes are \{647.6nm, 790.1nm\} for 100nm-, \{636.2, 741.1\} for 110nm-, \{643.3, 676, 719.8, 746.9\} for 120nm-, \{668.8, 691.5, 711.7\} for 130nm-, \{670, 699.5, 744\} for 140nm-, respectively.
Chapter 1

Introduction

1.1 Motivation

Chalcogenides are fascinating materials with striking properties. Namely they are the amorphous compounds containing a major constituent the group VI elements of the periodic table (sulfur, selenium, and tellurium, but excluding oxygen), covalently bonded to other elements such as As, Ge, Sb, Ga, Si, or P. On one hand, they are classified to be a sub-class of inorganic glasses that exhibit numerous unusual properties not found in common oxide glasses. On the other hand, as a promising semiconductor material candidate for integrated photonics in infrared wavelengths, researches on chalcogenides serve as significant part of the main stream in the rapid development of solid state electronics, which started with the invention of the transistor in 1947, aiming at saving weight and size while improving the speed of functions of the devices. An example of chalcogenides is shown in FIG. 1.1, the arsenic sulfide glass rod displays a reddish color in visible light while the oxide glasses (fused silica, SiO$_2$) are transparent. For comparison, photos of orpiment, quartz (crystalline SiO$_2$) are also included.
Since their emergence in the 1960s [2], chalcogenides have been extensively studied for their low processing temperature, wide transparency window in mid-infrared, a wide range of photo-induced phenomena, as well as high linear and nonlinear refractive indices. Besides the significance to fundamental solid state physics as a typical disordered and amorphous material, they are ideal material candidates for electronics industry, imaging and in infrared photonics. They have been used in various applications such as phase-change memories, solar cells, sensors, holographic information storage [3,4], micro lenses [5], all-optical switching [6], and laser written waveguides [7], etc. In addition, the photosensitive properties of chalcogenide glasses enable optical tuning of photonic structures, such as tuning for solid-state lasers and photonic crystal waveguides. Moreover, the chalcogenide also provide a platform for
fundamental investigations of light-matter interactions in nanophotonics structures, such as photonic crystal and even metamaterial structures [8].

Although researchers have devoted much efforts investigating chalcogenide glassy materials for over six decades, the structures and mechanisms for many unusual properties remain under debate, due to the diversity and complication of the various effects present in these materials. Taking into account the essential task of enlarging the class of materials for modern science and technology as well as pursuing a deeper understanding of the properties of chalcogenides, our group as a part of the MIRTHE (Mid-InfraRed Technology for Health and Environment) research center at Princeton University, have dedicated the research to the underlying physics of the fundamental properties of the chalcogenides, the processing and fabrication for devices, as well as investigating new chalcogenide materials with new properties for higher level applications. Following previous systematic studies [9] in the solution processing techniques and the device fabrication, we set the main theme of this dissertation to be exploring the possible methods to achieve controllable and optimized modifications of the fundamental properties of chalcogenides.

1.2 General aspects of chalcogenides

As typical covalently bonded glassy materials, chalcogenides possess unique features such as: presence of lone pair electrons; similar electronegativity of constituent atoms; relatively well-defined medium range order (no long range order) [10]; presence of (various kinds of) electronic defects. Their semiconducting features enable the applications in photocopying machines, digital x-ray imaging while the rich photo-induced phenomena power their availability in photolithography, optical waveguide [11]. In this section, we review the general aspects of chalcogenides, including the properties, structure and applications.
It is well-known that solid has a variety of atomic bonds including ionic, covalent, metallic and also weaker van der Waals types. In terms of the nature of the atomic bonding, chalcogenide glasses, which consist of predominantly covalent bonds because of the similar electronegativity of the constituent atoms, is intrinsically distinct from other glasses, whereas fluoride and halide glasses are made of ionic bonds while oxide glasses possess mixed (ionic & covalent) bonds. Due to the fundamental differences between chalcogenide glasses and their oxide, fluoride, as well as halide counterparts, the optical, thermal behavior and response of these glass families is markedly different in many important ways. The fact that chalcogenides are comprised of covalently bonded heavy elements is one of the major origins of their unique properties for infrared, nonlinear and waveguide optics.

Because their inter-atomic bonds are weak relative to those in oxides, the bandgap of chalcogenides is redshifted to the visible or near-infrared region of the spectrum. The vibrational energies of the bonds are low because the constituent atoms are particularly heavy. This leads to one remarkable properties of chalcogenides: their transparency in infrared. As the critical solids for infrared applications, most chalcogenide glasses transmit well from visible up to infrared. In general, classical oxides covered a transparency region from 3 \( \mu m \) to 5 \( \mu m \) with the heavy oxide materials helping to extend that region to up to 8 \( \mu m \), while chalcogenide glasses show wide infrared transmittance window over the wavelength region from \( \sim 400 \text{nm} \) through \( \sim 20\mu m \), depending on their composition. Typically, the transparency is in the range of 0.5 \( \sim 11\mu m \) for sulphide glasses, 0.8 \( \sim 15\mu m \) for selenides and 1.2 \( \sim 20\mu m \) for tellurides \[12\][13]. The transmittance of several commonly used chalcogenides as well as conventional optical materials is summarized in FIG. 1.2 for a comparison.

The bonding energies of chalcogenides glasses are much lower than oxides. Typical values are 260 kJ/mol for As-S and 230 kJ/mol for As-Se bonds, while for the oxide glasses, they are 500 kJ/mol for Si-O and 374 kJ/mol for B-O \[15\]. The low
bond energy results in low glass transition temperature ($T_g$). The common transition temperatures for chalcogenides like As$_2$S$_3$ are 200°C, while the $T_g$ is about 1500°C. Because of the low bonding energy and open network structure, chalcogenide glasses often have higher ionic conductivity than oxide glasses, which is useful for the applications [15]. In addition, the low $T_g$ of chalcogenide glasses provides the advantage of relatively low processing temperature, for example, extrusion, precision glass moulding becomes a viable approach for fabricating low-cost optical components for applications like thermal imaging and fiber optic drawing.

The heavy elements forming chalcogenides result in a relatively high glass densities compared to oxide glasses. When combined with strong polarizability, this leads to a high refractive index ($n \approx 2 \sim 3+$), providing the advantage of strong optical field confinement [15]. It allows small waveguide bend radii and thus compact circuit designs. For example, the refractive index for As$_2$S$_3$ glass reads 2.35 and it is 2.70 for As$_2$Se$_3$ glass [13]. A high linear refractive index implies, according to the empirical Miller’s rule $\chi^{(3)} = (\chi^{(1)})^4 \times 10^{-10}$, high refractive index results in high $\chi^{(3)}$ optical

Figure 1.2: Transmittance and long-wavelength absorption edge of commonly used IR materials. Materials groups are denoted by colours, i.e., red (chalcogenide) glasses, black (different glassy systems) and blue (crystalline IR materials). Thicknesses are 1-3 mm [14].
susceptibility (equivalent to a high nonlinear refractive index, \(n_2\)) in chalcogenide glasses as well, which are about 1000 times larger than silica glass, with the possibility of a fast response time. The extremely large optical nonlinearities are due to the highly electronically polarizable nature of chalcogen atoms present. When chalcogenide glasses are exposed to short laser pulses, large Kerr-type nonlinearities are induced. This opens up possibilities for their use as the active element in all-optical switching (AOS) devices, which are considered as one of the key technologies for high-speed optical communication networks. Photo-induced stable second-harmonic generation has also been reported in chalcogenide glasses.

Many of the physical properties of chalcogenide glasses can be readily modified by electromagnetic irradiation, which has important applications in lithography, direct laser writing, and microfabrication. The photoinduced phenomena are very broad and complicated, and their mechanisms are not understood completely. The photosensitivity of chalcogenide glasses is generally associated with the low bond energy, structural flexibility and relaxation, homopolar bonds, lone pair electrons of chalcogens, and charged defects. It will be discussed in detail in Chapter 2.

The composition of chalcogenides could be unitary which consists of only chalcogen itself, binary, ternary or even more complex, with the ratio of the constituent elements to be either stoichiometric or non-stoichiometric. One of the most important binary alloy, Arsenic sulfide (As\(_2\)S\(_3\)) has been extensively studied. This stoichiometric glass is fairly covalent and stable, with an optical gaps of \(\approx 2.4\) eV and the glass transition temperature measured to be \(\approx 200^\circ C\). The average atomic coordination number is 2.4, which is a signature of stable glasses. Besides the widely used As-S chalcogenide alloys, ternary chalcogenide Ge-Sb-S films have drawn attention for their high nonlinear optical properties and compositional dependencies of various properties either within the Ge-Sb-S film system, or within the quaternary Ge-Sb-S-Se system by progressively replacing sulfur by selenium. For example, with the substitution of S for Se
in the Ge-Sb-S-Se system, the glass transition temperature decreases while the density increases, making optimization of the glass composition for specific applications possible.

The unique properties of chalcogenides are explained by structural disorder, thermodynamic non-equilibrium and metastability. The designation metastable state is reserved for states whose lifetimes are relatively long. Metastability is a general scientific concept that describes states of delicate equilibrium. A system is in a metastable state when it is in equilibrium but is susceptible to fall into lower-energy state with only slight interaction. This may be bandgap illumination or annealing [11].

The fabrication methods include melt-quench (for bulk material processing); wet processing (solution, sol-gel processing); PVD such as thermal evaporation (thermal and e-beam), sputtering, pulse laser deposition (PLD) [16].

Flexible structures lead to various unique properties of chalcogenides, opening the door for a number of applications in many areas modern science and technology as summarized in table [1.1] including numerous passive applications, such as IR transmission, waveguide IR transmitting window, lenses, photo-induced optical waveguides, Ag-photodissolved waveguides, photoetched waveguides Bragg diffraction gratings, polarization gratings, holographic recordings, photonic crystals (3D Bragg gratings) etc. Examples of typical active applications include undoped or doped

<table>
<thead>
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<tr>
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<td>Lithography, selective dissolution</td>
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<tr>
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<td>Integrated optics, micro-optics</td>
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<tr>
<td>Amorphization/devitrification</td>
<td>CD-RW, DVD-RW</td>
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<tr>
<td>Viscosity</td>
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<td>Electrical properties</td>
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Table 1.1: Summary of the typical properties and applications of chalcogenide glassy semiconducting materials.
optical amplifiers and lasers, all-optical ultrafast nonresonant-type optical switches, photoresists for photolithography, and so on.

1.3 Outline of this dissertation

Based on the introduction above, to accomplish the main objective of this dissertation, i.e. to explore the possible methods to achieve controllable and optimized modifications of the fundamental properties of chalcogenides, the tasks are incorporated into the following six chapters.

Chapter 2 reviews the theoretical and experimental backgrounds of the techniques utilized for this study, including the various photo-induced effects of chalcogenides and the underlying mechanisms; the solution processing techniques which are heavily used to fabricate devices for our study; and different techniques for the characterization of chalcogenides.

Chapter 3 studies the mechanisms of photo-induced surface relief formation. With our generalized model combining the photo-induced pressure and navier stokes for viscous flow, we identify the physical origin and quantify the kinetics of this process.

In chapter 4, we achieve the uniform doping of silver nanoparticles into chalcogenide glassy materials using pulse laser ablation and solution processing. The aggregation of the nanoparticles which is usually inevitable using other doping technique is successfully avoided.

Chapter 5 is about the study on modifying and control the properties of chalcogenides using in-situ wet chemistry processing. Various chlorides are incorporated into chalcogenide matrices, leading to multifarious property changes, such as absorption and refractive indices of the chalcogenides.

In chapter 6 we use CMOS processed silicon photonic crystals with Amstrome-
achieve controllable modulations of chalcogenides emission. A planar emitter array of chalcogenides is fabricated based on this novel periodic hetero-structures of semiconductor.

Finally chapter 7 summarized the work in this thesis and provides thoughts, suggestions and directions for future work.
Chapter 2

Theoretical and experimental backgrounds

In this chapter, we review the theoretical and experimental backgrounds of the techniques involved in this study, including the various photo-induced effects of chalcogenides and the underlying mechanisms and the solution processing techniques which are intensively utilized to fabricate devices for our study.

2.1 Various photo-induced phenomena and the mechanisms

Photo-induced structural and property changes are one of the exciting phenomena in amorphous chalcogenides [1]. Due to the metastable physicochemical nature of these materials, a wide range of effects associated with these photostructural changes have been reported since the beginning of the 1970s, including photoexpansion [17–20], photocontraction [21], photodarkening and bleaching [22], photoanisotropy, including dichroism and birefringence [23], photofluidity and mass transport [24], as well as the photo-chemical reaction like photo-doping [25], etc [26,27]. These photo-induced
Figure 2.1: Examples of various photo-induced effects, such as photo-induced refractive index changes, surface relief grating formation as well as the photodoping where silver reacts with As$_2$S$_3$ within the region illuminated by laser beam.

Changes are observed for a variety of complexities of compositions, from the chalcogen itself to binary, ternary and more complex compounds [28].

Because of their unique properties, chalcogenides have found applications in low-cost and rapid fabrication of optical components such as microlenses and waveguides using direct write methods [29]. In addition, periodic structures such as surface relief gratings have been produced using holographic beam interference patterns [30] and their mechanism of formation as well as their stability and aging have been investigated [31]. It was also shown that the self-enhancement phenomenon of holographic recording in amorphous chalcogenide films by light or thermal treatment can be used to increase the diffraction efficiency of the holograms [9]. While surface gratings are normally produced on thin films, it was also shown that periodic index patterns could be created in bulk glass using a self-developing interference pattern induced by a single beam reflected between parallel faces of a polished glass disc [32].
According to their reversibility, these effects could be classified to be transitory, reversible or irreversible. The irreversible is a kind of photoinduced stabilization processes, such as photopolymerization, which appear in as-prepared films. The reversible is assumed to be disordered processes, which can be completely removed by annealing near the glass transition temperature $T_g$. And the transitory changes appear only when the sample is being exposed to electromagnetic field but disappear after the field is off. An example of reversible changes of volume and bandgap is shown in FIG. 2.3. In addition, some of these effects are scalar (isotropic), i.e. independent of light polarization, while others are vector (anisotropic) upon excitation of polarized laser filed. A diagram illustrating the classifications is shown in FIG. 2.2.

**Figure 2.2:** Classification of photo-induced effects. (a) By the ability to recover, these effects are classified as irreversible (also denoted as permanent, can’t be recovered without remaking the glass), metastable (recovered on heating to $\sim T_g$), transitory (recovered on removing the light). (b) According to the response to light polarization, those effects are divided into two categories: scalar changes (isotropic) and vector effects (anisotropic, depend upon the polarization of the light).

**Photodarkening**

Chalcogenide glasses exhibit reversible photodarkening, as shown in FIG. 2.4, which is a scalar effect and characterized by a shift of absorption edge to the low-energy side (hence the material gets darker at a given wavelength). The photodarkening
Figure 2.3: The principal results for the reversible photoinduced changes of volume, also thickness $d$ and bandgap $E_g$ of a-As$_2$Se$_3$. A decrease in the optical bandgap, $\Delta E_g/E_g \sim -2\%$ and a volume expansion (VE), $\Delta V/V \sim 0.5\%$ are observed. Measurement conditions are as follows: A, as deposited; B, after pre-illumination annealing; C, after illumination; D, after post-illumination annealing [34].

is observed after prolonged illumination with bandgap light, whilst subsequent thermal annealing to the glass-transition temperature, $T_g$, erases the effect. While in photobleaching the optical absorption edge of the material shifts to higher energies, on illumination with bandgap light. The phenomenon is simple and inherent to bulk amorphous phases, and in addition, the reversibility is attractive with respect to applications such as erasable holographic memories. Arsenic-based materials with higher sulfur contents and germanium sulfide materials seem to favor photobleaching, for reasons that are not clear at present. Reversible photodarkening is observed in bulk glasses, well-annealed thin films, as well as liquid state [33], while irreversible shifts of the optical absorption edge occur in initial (as-evaporated) thin films of amorphous chalcogenides containing structurally unstable molecular fragments from the vapor phase [36] that are particularly vulnerable to photoinduced (or thermal) change. It has been pointed out that the photodarkening arise from photoinduced enhancement
Figure 2.4: Reversible photodarkening effect is a red shift of the optical absorption edge by band gap illumination and annealing near the glass transition temperature \(^{35}\).

of randomness in amorphous structures, while the entity of atomic change is still speculative. It is related to the non-local structural changes, which differ from local structural changes such as the creation of defects. In addition, the excitation of lone-pair electrons plays a crucial role in the occurrence of photodarkening \(^{33}\). A double well potential model has also been proposed to explain the mechanism of this effect \(^{35,36}\).

Defective models have been presented, which assumed that the conversion of normal bonds to \(D^+\) and \(D^-\) is the origin of photodarkening. The relatively high bond energy and delocalization of the valence and conduction band wavefunctions mean that these defects can exist as pairs with opposite electrical charge, one atom being over-coordinated and the other under-coordinated, these charged defects are 'frozen in' during glass production and are physically separated throughout the glass \(^{12}\). It
is suggested by street \[37\] and Fritzsche et. al. \[24,38,39\] a model considering electron-phonon coupling to account for the reversible photostructural changes in chalcogenide glasses. It is postulated that As$_2$Se$_3$ or As$_2$S$_3$ contains $10^{18} - 10^{19}$cm$^{-3}$ dangling bonds. And the localized gap states are at dangling bonds, and lattice-distortion effects are also sufficiently strong that these states exhibit an effective negative electron-electron correlation energy. These are point defects at which the normal coordination (2 for Se, 3 for As) cannot be satisfied because of the constraints of local topography; the neutral dangling bond therefore contains an unpaired electron. It is assumed that a dangling bond may be occupied by zero, one, or two electrons, and label these states D$^+$, D$^0$, and D$^-$, respectively, the superscripts denoting the total charge of the center, i.e. D$^+$ and D$^-$ are positively and negatively charged defects, respectively. Local lattice distortion occurs when the electron occupation of the dangling bond changes and that it is sufficiently strong for the reaction

$$2D^0 \rightarrow D^+ + D^-,$$

to be exothermic. All defect centers are therefore either positively or negatively charged and D$^0$ only occurs by excitation.

The self-trapped exciton model is supported by quantum chemistry calculation. Using clusters of atoms that model the local structure of amorphous As$_2$S$_3$, Uchino et. al. performed quantum-chemical calculations on the model clusters in which nonradiative recombination proceeds through the creation of these metastable charged defects \[40\], and have obtained their equilibrium configurations, charge distributions, molecular-orbital structures, and excitation energies. It is discovered by the first principle calculate that there exist at least two types of metastable structural defects. One has a fivefold-coordinated As unit, and the other comprises a fourfold-coordinated As atom and a nonbridging S atom. Each type of defect results from the breaking of an As-S bond and subsequent structural rearrangement.
**Photoinduced anisotropy**

A particularly interesting metastable vectoral photoinduced effect exhibited by chalcogenide glasses is photoinduced anisotropy (PA), wherein the initially isotropic amorphous chalcogenide glasses become optically anisotropic solids with the optical axis parallel to the direction of the inducing light beam after exposure to linearly polarized light \[41\]. It’s rather universal that isotropic disordered solids exhibit anisotropy when illuminated with linearly-polarized light \[42\]. The material is detected to be dichroic \[43\] when probing above-bandgap region and birefringent \[44\] while probing transmission region. In the case of well-annealed thin films and bulk glasses, the effect is completely reversible optically, i.e., the induced optical axis is fully rotated when the light-polarization vector is rotated, and the PA can be annealed out thermally or optically using unpolarized or circularly polarized light. PA can be quantitatively defined by the parameter \( P \),

\[
P = \frac{2(I_\perp - I_\parallel)}{(I_\perp + I_\parallel)}
\]  

where \( I_\perp \) and \( I_\parallel \) are the intensities of transmitted probe beam with polarization perpendicular and parallel to the polarization of pump beam, respectively. The absorption of probe light with polarization parallel to the pump usually becomes less than that of probe light with perpendicular polarization, leading to an optical axis of anisotropy which can be reoriented by changing the polarization of inducing light. FIG. 2.5 shows the PA effect in As\(_2\)S\(_3\) film. The magnitude and kinetics of PA and its decay remain unchanged during the course of photodarkening. PA can be erased by unpolarized or circularly polarized light, and it can be recovered again by the linearly polarized light. PA is also reported have a temperature dependence by Tanaka et. al, \[45\], who observed that the photoinduced birefringence in As\(_2\)S\(_3\) becomes maximal at certain temperature, which is higher for illumination with a lower photon energy.
Figure 2.5: The kinetics of relative transmission and photoinduced dichroism (anisotropy) in an As$_{50}$Se$_{50}$ film ($\lambda = 633$ nm) (a) at successive irradiation by the linearly polarized light and the unpolarized or circularly polarized light of He-Ne laser with an incident power of 350 mW/cm$^2$. (b) at successive irradiation by the linearly polarized light with the electric vector direction $E_\parallel$ and $E_\perp$ with an incident power of 50 mW/cm$^2$ [46].

Figure 2.6: Fritzsche’s anisotropic microvolume model for photoinduced optical anisotropy [15, 47]. The units size of medium order range could be simplified to be two dimension harmonic oscillator.

As a universal property of all chalcogenides, including those in which photodarkening is absent, optical anisotropy (PA) is believed to have mechanisms different from that of the photo-induced scalar effects such as photodarkening. The effects of PA are considered in terms of photon-assisted rearrangements of some intrinsic struc-
tural units. Reversibility of PA with respect to rotations of the polarisation axis of the inducing light proves that the optically active structural units must be stable with respect to photon excitations \[48\]. This notion is also supported by the fact that the saturation of the anisotropy is only weakly dependent on light intensity. Due to the lack of translational symmetry, the structural origin of metastable macroscopic PA in glasses is different from the anisotropy of crystals and is more similar to the structural anisotropy of liquid crystals. Traditionally, the effects of PA are suggested to be the result of a photoinduced change of the dielectric tensor. Should a sample be irradiated by linearly polarized, its dielectric tensor becomes an ellipsoid \[15\].

Fritzsche \[47\] suggested a phenomenological model that the macroscopically isotropic dielectric tensors characterizing annealed glasses become anisotropic with illumination, since structural elements having the tensor components parallel to the electric field of illumination are excited preferentially, which may be rotated to other directions when relaxed, as illustrated in FIG. 2.6. Therefore, consistent with experimental observations, the negative anisotropy is induced; that is, the birefringence $\Delta n = n_\parallel - n_\perp$ and the dichroism $\Delta \alpha = \alpha_\parallel - \alpha_\perp$ are negative, where $n$ is the refractive index at transparent wavelengths and $\alpha$ is the absorption coefficient at around optical absorption edges \[45\].

Tanaka et. al. proposed a crystalline model. It is suggested that the photoinduced anisotropy arises from orientation of quasicrystalline clusters. This model is mainly supported by the temperature and composition dependence of the photoinduced birefringence, i.e. the photoinduced birefringence becomes greater in the order of $\text{As}_2\text{S}_3$, $\text{As}_2\text{Se}_3$, and $\text{a-Se}$, which is the same with the order of the natural birefringence in the corresponding crystals \[45\].

An electronic model of photoinduced optical anisotropy is proposed by Emelianova et. al. The model assumes the occurrence of correlated pairs of localized states for electrons and holes and relates photoinduced anisotropy to generation of geminate
electron-hole pairs trapped by these localized states. Carrier trapping by energetically disordered localized states leads to typically dispersive time dependences of the PA kinetics. This attribution is possible in a disordered material with appropriately correlated traps, illuminated by polarized light that can generate aligned geminate pairs. Since creation of stable oriented geminate pairs occurs in the dispersive transport regime, the PA build-up can be fitted with a stretched-exponential time dependence. This notion is also supported by the fact that the saturation of the anisotropy is only weakly dependent on light intensity \cite{48}.

Lyubin et. al. studied the kinetics of appearance and reorientation of photinduced dichroism in chalcogenide glassy films by means of the polarization modulation technique \cite{49}. They identified two distinct processes, which include the creation of photoinduced defects and photo-stimulated orientation of defects, both native and photoinduced. Of these processes, the first one can be carried out by both unpolarized and polarized radiation and has much larger time constant than the second. The annealing temperatures of the two effects are also different.

![Figure 2.7: Shimakawa’s model for photodarkening and photo-expansion \cite{50}. Coulombic expansion E and slip motion S give rise to the volume expansion and the photodarkening.](image)
Finally Shimakawa et al. [50] postulated a microscopic mechanism for the origin of these changes in terms of the repulsive Coulomb force between layered clusters, as illustrated in FIG 2.7. During the illumination, the holes diffuse away while the electron stays for they are localized in the conduction-band and have much smaller mobility. So the clusters are negatively charged by electron accumulation in the conduction band tails. This gives rise to a repulsive Coulomb interaction between layers which produces a weakening of the van der Waals forces, increasing the interlayer separation, which is responsible for the volume expansion, and it also induces an in-plane slip motion which causes the reduction in the bandgap.

**Photoinduced deformation and fluidity**

Besides the changes of optical properties, it was discovered by Hamanaka et al. that bandgap illumination leads to volume deformation to chalcogenides [51]. They reported, after illumination at room temperature, a macroscopic expansion of $\sim0.4\%$ in $\text{As}_2\text{S}_3$ and contraction of $\sim0.2\%$ in $\text{Ge}_1\text{As}_4\text{Se}_5$, whereupon both of which can be recovered by annealing at the glass-transition temperatures. Similar volume changes have been unearthed in annealed films or bulk samples of chalcogenides [52], and even in a-Se films at room temperature [53]. Arsenic sulfide and a-Se show qualitatively the same behaviors in the mechanical effect and the deformation, which suggests that these photoinduced phenomena are inherent to the covalent chalcogenide glass. It was pointed out that this effect depends on photon energy, light intensity, and the temperature during illumination. Later on, Hisakuni and Tanaka demonstrated that, upon illumination of subbandgap light, chalcogenide glasses exhibit more dramatic expansion, which can be referred to as “giant photoexpansion”. For instance, arsenic sulfide exposed at room temperature to light emitted from a He-Ne laser exhibits volume expansions of 5%, as shown in the inset of FIG. 2.8 [54]. Since photoinduced
volume change is spatially localized within the illumination area, accurate fabrications of microlens have been achieved\textsuperscript{55}.

Figure 2.8: (a) Schematic illustrations of the giant photo-expansion. (a1) Illumination of light with a spot diameter $2r$ and a penetration length $L$ is initiated. (a2) The illuminated volume tends to expand with some mechanism, in which only the expansion toward the free surface (black arrow) may appear. (a3) However, if the stress toward unilluminated regions can be relaxed with the photoinduced fluidity, a giant photo-expansion $\Delta L$ appears on the surface. If a sample is thinner than $L$, an expansion also appears on a rear surface. (b) Temperature dependence of the expansion in an As$_2$S$_3$ flake ($\sim$400 $\mu$m thick) as a function of exposure times indicated. The horizontal axis shows the temperature at which the sample is illuminated. The expansion height $\Delta L$ (vertical axes) is measured at room temperature. The exposure is provided from a He-Ne laser of 20 mW, which is focused onto a spot with a diameter of $\sim$50 $\mu$m. (c) An expansion (0.12 $\mu$m high) with a central dip produced on a surface of an annealed As$_2$S$_3$ film (4 $\mu$m thick), which is deposited on a glass slide. The deformation, which manifests the expansion and the fluidity, has been produced as follows: First, an AFM cantilever is fixed at a position on the film. Then, the position is illuminated from the rear side through the substrate by focused 633 nm light for several minutes. After the illumination being switched off, the image is taken by scanning the cantilever. Figures adopted from\textsuperscript{19}
Figure 2.9: The photoexpansion $\Delta L$ and the photodarkening $\Delta E$ as a function of exposure times in arsenic sulfide for bandgap (a) and subbandgap (b) illumination. $\Delta L$ is evaluated at the height of expansion, and $\Delta E$ denotes the redshift of the optical-absorption edge. The samples in (a) and (b) are an arsenic sulfide film with a thickness of 3 mm and a bulk arsenic sulfide flake with a thickness of 50 mm. Light sources are (a) an Ar laser ($\hbar \omega = 2.4$ eV) and (b) a He-Ne laser ($\hbar \omega = 2.0$ eV). [18]

It is discovered by Krecmer et al. that reversible, controllable optical nanocontraction and dilatation in a chalcogenide glass film was induced by polarized light. They also observed a direct correlation of this optomechanical effect with the reversible optical-induced optical anisotropy (dichroism) also exhibited by the chalcogenide glass. The experimental set-up for photoinduced stress measurement consists of a-As$_{50}$Se$_{50}$ thin film of thickness 250 nm, deposited on a SiN cantilever with dimensions of 200 $\mu$m in length, 20 $\mu$m in width, 0.6 $\mu$m in thickness. The illumination source is a He-Ne laser with intensity of 17~963 mW/cm$^2$. The time-dependences of photoinduced mechanical stress and PA were measured independently as shown in FIG. 2.10. They also present a microscopic model of the photoinduced, wherein the reversible structural phenomenon responsible for the optomechanical behavior. This opto-mechanical effect forms the basis of a number of mechanical applications driven by polarized light.

Tanaka [56] discovered that illumination of linearly-polarized bandgap light produces visible-scale anisotropic deformations in a covalent chalcogenide glass As$_2$S$_3$. It is reported a fluidity of $10^{-12}$ P$^{-1}$ can be induced with photons of $\hbar \omega \sim 2.0$eV in
Figure 2.10: Stress ($\sigma_{film}$) and photoinduced optical-anisotropy (PA) in the As$_{50}$Se$_{50}$ film caused by different illuminations. The vertical and horizontal arrows denote linearly polarized light and the four-pointed arrow denotes effectively unpolarized light. The “zero” stress is arbitrary because the technique measures stress variations rather than absolute stress. (A) Unpolarized and polarized light (in two orthogonal directions) were alternated. (B) Orthogonal polarizations were alternated. Note that the difference of induced stress is twice that in (A). (C) Different growth kinetics of photoinduced stress from the stress-free state (light extinguished) caused by a superposition of scalar and vectoral effects. (D) Kinetics of the appearance of PA when switching between two orthogonal linear polarizations [44].

As$_2$S$_3$. They also conducted X-ray diffraction and Raman-scattering measurements for deforming As$_2$S$_3$ flakes detect no microscopic structural changes. It is suggested that the anisotropic deformation occurs through radiation force and photoinduced fluidity to from the measurements of optical torque in deforming flakes and comparative exposure experiments for crystalline As$_2$S$_3$ and amorphous Se.
As demonstrated in FIG. 2.12, Hisakuni et. al. found that chalcogenide glasses can be shaped by stressing the glass under light illumination because light illumination enhances the fluidity of the glass. A stressed arsenic sulfide flake, size of 0.2mm×2mm×50µm shows deformation at the illuminated region of a focused He-Ne laser, with intensity of 102 W/cm². The mechanism of photoinduced fluidity was found to be photoelectronic, and athermal. It is proposed that this process can be applied to microfabrication of optical fibers and glassy films with a typical dimension of 10 to 100 micrometers.

For the origins of the volume expansion effects, there are roughly two ideas. One is an atomic mechanism. Tanaka assumes that the disordering in intermolecular
 distances, which may be caused by the photoinduced bond twisting, is responsible for the expansion. If a glass structure is not dense, interchanges in atomic bonds may cause a volume contraction, as observed in Ge\textsubscript{1}As\textsubscript{4}Se\textsubscript{5}. On the other hand, Shimakawa et al. propose an electrical model. Coulombic repulsion forces produced by photogenerated electrons, which are immobile in the chalcogenide glass of interest, trigger the expansion. However, this idea has difficulty in explaining the contraction.

Fritzsche et al. suggested a configuration change model, as shown in FIG. 2.13. It is argued the cumulative effect of local configuration changes involving essentially all atoms produces the macroscopic changes, as the deformation observed shows. After extended light exposure the changes in physical properties approach saturation. This dynamic equilibrium is equivalent to a glass held near the glass transition temperature, where there is a constant change at the local level without a change in the macroscopic properties once a steady state is reached\cite{24}.

**Photo-dissolution**

Light can also cause or speed up “chemical” reactions of chalcogenide glasses with other elements like oxygen (photo-oxidation) or silver (photo-dissolution). For example, overlayers of certain metals (notably silver) diffuse into the undoped bulk glass on illumination. On the other hand, Ag-containing chalcogenide glasses, rich in Ag, ex-
Figure 2.13: The configuration change model proposed by Fritzsche et. al. (a) Normal bonding configuration, (b) photon-excited (transient) self-trapped exciton, (c) one of several new bonding configuration with motion of atom indicated by arrow. Top example is amorphous arsenic sulfide, while bottom example is vitreous Se.

hibit the opposite effect, namely photoinduced surface deposition, wherein the metal exsolves from the glassy matrix on illumination.

The photo-dissolution effect is observed in chalcogenide-metal double layer, which is usually fabricated by evaporating metal onto a chalcogenide film. By exposing light onto As$_2$S$_3$, silver ion can readily dissolve in the direction of illumination, resulting in a silver-doped chalcogenides layer. A refractive index change up to 0.5 has been reported. Of the various photoinduced phenomena exhibited by chalcogenide glasses, the photodoping effect is probably one of the most useful as far as fabricating diffractive IR elements is concerned because it produces the largest changes in the physical and chemical properties of the glass, especially the optical constants and etch resistance [58].

The metal photo-dissolution effect has many potential applications in areas requiring the fabrication of high resolution or high aspect ratio surface relief or embedded
structures, featuring desirable for image creation and storage. In view of the good transparency of these materials in the IR, the technique is particularly suited to producing components for operation at IR wavelengths, such as gratings, mirrors, lenses and beam combiners. For example, the microlens arrays have been fabricated by Wagner et. al., as the fabrication steps illustrated schematically and AFM measurements shown in FIG. 2.14 [58]. Moreover, on removal of the illumination at ambient temperatures, there is no further movement of the metal ions and hence no degra-
dation of the image. The embedded or surface relief structures achieved by metal photodoping are attractive for making components for infrared diffractive optics and also for small-scale integrated optics.

The silver photo-dissolution rate depends on temperature, as reported by Zekak et. al. [59]. Raising the temperature of an As$_{40}$S$_{60}$ film by $\sim 100$ °C during exposure increases the rate of Ag photodissolution by at least a factor of 10. The photodissolution process has an activation energy of $\sim 0.24$ eV and this was found to be independent of whether laser or white light was used to stimulate the effect. Lateral Ag migration was found to be negligible at about 110°C and a grating was successfully recorded by mask exposure at this temperature. Enhancement of the photodissolution rate by heating makes the fabrication of deep and efficient diffraction gratings a practical possibility.

The mechanism has been explained through the initial formation of AgS bond at silver and chalcogenides interface, followed by the generation of electron-hole pairs and by the mobility of holes toward the silver layer, while Ag$^+$ moves to the opposite direction [60–63]. As shown in FIG. 2.15, Sava et al. monitor the kinetics of silver photo-dissolution process in thin amorphous As$_2$S$_3$ film with a holographic setting. According to the measurements of optical transmission through the Ag-As$_2$S$_3$ bilayer, a mechanism is proposed based on a gradual filling of the structural voids existing in the network of the thin chalcogenide layer [63].

- An electric double layer builds up at the Ag/As$_2$S$_3$ interface, due to the contact potential of chemical origin.

- The electric double layer assisted by the laser light helps to detach and transfer Ag into the As$_2$S$_3$ matrix, most probably as Ag$^+$ ions.

- The Ag$^+$ ions feeling the driving force of the internal electric-field distribution in the a-Ch layer, will begin to roam around in the vicinity of the interface.
- New Ag\(^+\) ions being pumped out from the Ag film by the continuous laser illumination, a charge-distribution gradient will be produced. This charge-distribution gradient will be the cause, which will give a preferential drift direction to the roaming Ag\(^+\) ions, pushing them away from the interface, toward the inside of the a-Ch film.

Figure 2.15: (a) The curve of optical transmission through the Ag-As\(_2\)S\(_3\) bilayer. (b) Experimental setup to evidence the photodissolution of the silver in chalcogenides layer: 1. red laser diode; 2. green laser diode; 3. sample; 4. power meter [63].

Wagner et. al. [58] suggested a two-stage process for the photo-doping effects, with the second stage having a sublinear time dependence. They investigated the kinetics of the solid state chemical reaction of silver with amorphous As\(_{33}\)S\(_{67}\) films in a conventional sandwich structure was measured by optically monitoring the change in thickness of the undoped chalcogenide. They measured rate coefficients and activation
Figure 2.16: kinetics of the solid state chemical reaction of silver with amorphous As$_{33}$S$_{67}$ films in a conventional sandwich structure. Growth of intermediate Ag-As-S layer is monitored by the oscillations obtained from reflectance interferometry when the sample is heated to 162.5 °C. Solid line represents two separate diffusion coefficients square-root rate laws!

energies in the case of the photostimulated process as well as the composition and structure of the reaction products. The Ag concentration is determined to be 19.5 %.

For a detailed discussion please see Chapter 4

Photo-induced phase transition

Another metastable photoinduced structural change exhibited by chalcogenide materials is photoinduced crystallization and amorphization, as used in rewriteable “phase-change” CDs and DVDs. Essentially, these processes are transition the system made from non-equilibrium phase to equilibrium state to lower the overall energy, when excited by light exposure. The amorphization process there is believed to result from a photoinduced melting and subsequent very rapid quenching of the material to the glassy state. However, illumination of certain crystalline chalcogenide materials (e.g., As$_{50}$Se$_{50}$) can also cause athermal photo-amorphization. These photo-induced phase
transitions in chalcogenide glasses are the basis for optical mass memory applications. A focused laser writes information by inducing a localized phase transition, and data are read by utilizing the difference in reflectance between the amorphous and crystalline phases. Antimony-based chalcogenide glasses appear to be the most suitable materials for such applications [64]. GeSbTe is often used in rewritable DVDs.

Mechanisms of photoinduced effects

![Figure 2.17: The electron distributions of the sulfur atoms in solids (center), and energy levels in the isolated atoms and solids. Lone pair electrons (LP) persist inside the solids, which possess higher energies than the bonding (σ) electrons, thus play an important role in the properties of chalcogenides.](image)

![Figure 2.18: Schematic model and SEM image of arsenic sulfide, which has a two-dimensional distorted layer structure. In the schematic, As and S are shown by solid and open circles with three and twofold coordination.](image)

Photoinduced changes in the structure and properties generally occur in materials having structural flexibility or relatively large internal free volume. The mechanism
Figure 2.19: The mechanism of photo-induced phenomena, simply from point view of minimizing system energy. The amorphous solids are intrinsically metastable for their disordered structure as well as the lack of long range order. Thus the system is susceptible to external stimuli in order to lower the energy. Structural changes lead to properties changes, resulting in photo-induced phenomena.

Figure 2.20: The mechanism of photo-induced phenomena. The weak intralayer Van der waals force, the flexibility of the network, as well as the existence of lone pair electrons are the main factors leading to structural changes.
Figure 2.21: The bond twisting, breaking models. Upon illumination, different kinds of defect including wrong bonds, three-fold or singly coordinated sulfur are generated. The photo-induced bond twisting involving the two-fold-coordinated chalcogenide atoms could account for the photo-induced effects as well.

resulting in photo-induced phenomena. As shown in FIG. 2.20, the weak intralayer Van der waals force, the flexibility of the network, as well as the existence of lone pair electrons are the main factors leading to structural changes, from a detailed view. Another possible factor leading to photo-induced phenomena is strong localization of the photoexcited electron-hole pairs, which may change the valency and coordination number of the atoms involved in the charge localization. This localization can thus be envisaged as a charged defect state. These factors pertaining to photo-induced phenomena are characteristic of amorphous systems, and, therefore, photoinduced structural and chemical changes are observed in glassy materials [40].

Chalcogen elements are only two-fold coordinated while the chalcogen atoms possess a lone pair of electrons, which can undergo light-induced reactions to produce structural defects of three-fold or single-coordinated atoms. In addition, chalcogenide glasses exhibit no long-range order and are susceptible to photo-induced structural and bonds change due to their structural flexibility. Thus the atomic structural modification may arise from medium-range structures, as intermolecular disordering, or from defective structures. These photo-induced changes might be reversible or not,
depending on the composition and the experimental parameters used to induce the change. A photoinduced process proceeds from photo-electronic excitation to some atomic structural changes, which appear as modifications of macroscopic properties.

In summary, the photoinduced effects in chalcogenides are associated with the presence of a high degree of structural flexibility. Residing in a metastable state, the systems have tendency to lower the total energy when there are external stimuli. Various model have been proposed, including structure disordered, defect creation, bond exchange, structural orientation, as well as optical forces, etc.

2.2 Processing of chalcogenide bulk glasses and thin films

2.2.1 Bulk materials preparation

The bulk glass fabrication is usually done by weighing the respective elemental chemical compounds and placing them inside an ampoule, preferably high quality quartz. The different processing steps take place under vacuum in order to avoid releasing of the volatile and highly toxic constituents and to protect ingredients from oxide formation. The ampoules are rotated or shaken following sealing to promote the homogenization of the melt. Quenching can take place either in the furnace by letting the oven cool down after turning off the power, in air or in a cold liquid, usually water when more severe quenching is required. Due to the large thermal coefficients of expansion of these glasses, internal stress has to be dealt with by annealing below the glass transition temperature ($T_g$) followed by a slow cooling to room temperature. In this study, most of the As$_2$S$_3$ glass used is commercial glass with purity of 99.9% or 99.999%.
2.2.2 Spin-coating techniques

Spin-coating of chalcogenide glass films is a low-cost, scalable method that provides additional flexibility in adding these important materials to existing devices. Chern and Lauks first introduced the spin-coating deposition method of preparing chalcogenide films in 1982 [65]. They demonstrated that amorphous and microstructure free chalcogenide glasses can be deposited from their solutions and retain many of the properties of the solute. Thermal, optical and structural properties of spin-coated As$_2$S$_3$ films deposited from propylamine or butylamine were elaborated. The possibility of spin-coating other kind of binary chalcogenide glasses (e.g., As$_2$S$_2$, As$_2$Se$_3$, As$_2$Te$_3$, and GeSe) is also confirmed. Later, several groups followed up and studied spin-coated chalcogenide films of As$_2$S$_3$, As$_2$Se$_3$ and Sb$_2$S$_3$ systems and investigated some potential applications such as high resolution.

We take arsenic sulfide as a typical example to show the preparation of chalcogenide solution and thin films. As shown in FIG. 2.22 (a), arsenic sulfide (As$_2$S$_3$) solution was prepared by grinding bulk As$_2$S$_3$ pieces into a fine powder and dissolved into n-propylamine solvent at a concentration of 0.8 mol/L. Dissolution was carried out inside a sealed glass chamber to prevent solvent evaporation. The dissolving process usually took more than three days and a magnetic stirrer was used to expedite this process. Exposure of solution to atmospheric moisture was kept to a minimum throughout preparation procedure since water can lead to precipitate formation [66].

Thin films of arsenic sulfide were prepared from solutions using spin-coating technique, as shown in FIG. 2.22. Spinning was typically carried out at 2000 rpm for 20-30s. Glass or silicon substrates were prepared according to the further characterization utilized. A pre-cleaning procedure of those substrates was performed, which includes the spray of glass cleaner, 20 min of ultrasonic bath in acetone as well as 15 min of ultrasonic bath in ethanol followed by drying with N$_2$ flux. For solvent removal, the thin films were vacuum baked at 60 °C during 1 hour and then at 180
°C for two hours. After such annealing, no amine group from the solvent is expected to remain in the film structure, while pore formation is avoided [65,67].

Figure 2.22: Spin-coating of chalcogenide glass films. (a) Arsenic sulfide (As$_2$S$_3$) solution was prepared by grinding bulk As$_2$S$_3$ pieces into a fine powder and dissolved into n-propylamine solvent at a concentration of 0.8 mol/L. Dissolution which usually takes more than three days was carried out inside a sealed glass chamber to prevent solvent evaporation. Exposure of solution to atmospheric moisture was kept to a minimum throughout preparation procedure since water can lead to precipitate formation. (b) The spin-coating technique to prepare thin films from arsenic sulfide solution. Spinning was typically carried out at 2000 rpm for 20-30s. Pre-cleaned glass or silicon substrates were employed depending on the further characterization. For solvent removal, the thin films were vacuum baked at 60 °C during 1 hour and then at 180 °C for more than 2 hours.
Chapter 3

Photo-induced modifications of surface structures and the mechanisms

The capability to create surface structures like gratings is of importance in technologies such as solid state device fabrications. Due to the photo-induced mass transport effect, the operations are convenient to construct surface relief structures in chalcogenides thin films. In this phenomenon, thin films of chalcogenides such as arsenic sulfide/selenide respond to nonuniform (in either intensity or polarization) illumination by changing their surface morphology. For example, the sinusoidal intensity modulation of a typical interference pattern leads to sinusoidal ripples in the film's surface.

In this chapter, we present a generalized model to explain the spatial and temporal evolution of photoinduced surface structure in photosensitive amorphous thin films. The model is constructed by employing an incompressible viscous fluid model, driven by a photoinduced pressure originating from dipole rearrangement. This derivation requires only the polarizability, viscosity and surface tension of the system. Despite
the fact that both polarization and intensity modulation may lead to this effect, a
single expression for photo-induced pressure, is shown to be sufficient. We check the
validity of the model by fitting to experimental data of As$_2$S$_3$ and demonstrating good
agreement using two free fitting parameters. This approach is found to be extremely
effective in predicting many aspects of photo-induced surface relief formation includ-
ing observed surface profiles and relief amplitude growth rates, which are adequate
to meet the demands of future engineering and industrial applications.

3.1 Overview of the photo-induced surface struc-
ture formation

Photoinduced surface relief structures are generated in a variety of materials including
azobenzene-containing polymers, chalcogenide glasses (like As$_2$S$_3$, AsSe, GeAsSe) and
other amorphous materials [68–72]. Macroscopic surface structures can be inscribed
by illumination with a laser field having spatially-varying intensity or polarization [73].
This phenomenon is potentially useful for technologies such as rewritable optical data
storage, active optical devices, nanofabrication, and optical actuators [74]. However,
to date a complete description of the underlying mechanism has not been produced
[75].

Much experimental and theoretical work has been performed to clarify the mech-
anism of this phenomenon. Saliminia et al. report the observation of a photo-
refractive-like nonlinearity responsible for the formation of giant relief modulations
in amorphous semiconductor glasses. They proposed that photoinduced softening of
the matrix, formation of defects with enhanced polarizability, and their drift under
the optical field gradient force is the origin of the mass transport [70]. Responses
from films of arsenic sulfide to intensity modulation is summarized by Saliminia, as
shown in FIG. 3.1 (a). While FIG. 3.1 (b) and (c) demonstrate surface profile probed
Figure 3.1: (a) AFM image of an area exposed by a plane polarized light, power $\sim 10$ mW, exposition time $\sim 480$ sec, illumination spot size $\sim 40-50$ $\mu$m (vertical axis is in “nm” and the horizontal axis is in “$\mu$m”); (b) surface profile probed perpendicular to the polarization direction; (c) surface profile probed along the polarization direction; (d) A typical surface relief grating with a period of $\sim 15$ $\mu$m in a 2-$\mu$m-thick As$_2$S$_3$ thin film. The grating was recorded by two p polarized interfering beams with a dose of $\sim 40$ kJ/cm$^2$ with an intensity-modulation period of $\sim 13.5\mu$m. From [70].

perpendicular to the polarization direction and surface profile probed along the polarization direction, respectively. A typical surface relief grating with a period of $\sim 15$ $\mu$m in a 2-$\mu$m-thick As$_2$S$_3$ thin film is shown in FIG. 3.1 (d), an interference pattern is formed when a film is exposed to the intensity variations. The grating was recorded by two p-polarized interfering beams with a dose of $\sim 40$ kJ/cm$^2$ with an intensity-modulation period of $\sim 13.5\mu$m. In addition, relationship between grating amplitude (maximum minus minimum in FIG. 3.1 d) and total exposure energy to intensity-modulated light with a spatial period of 13.5$\mu$m, is summarized in FIG. 3.2. While FIG. 3.3 capture the dependence of amplitude growth rate on grating period,
by plotting the surface relief grating amplitude against grating (intensity modulation) period for doses of 34 kJ/cm² and 23 kJ/cm².

Later on Asatryan et al. observed giant relief modulation in amorphous chalcogenide As₂S₃ glass under polarization modulated near band gap light illumination. It is worth noticing that these periodic modulations are created as a result of the photoinduced mass transport despite the very low and uniform intensity light illumination, with only the electric field vector $\vec{E}$ of light modulated spatially, also know as vector holography, as the measurements shown in FIG. 3.4 and 3.5. It’s also reported all the formations of relief gratings is permanent and not be able to anneal out.

3.2 Fluid dynamics of surface relief formation

Levich \cite{77} derived the general equation of motion for the flow of a thin liquid film, wherein stipulating laminar flow of the glass and time-independent illumination that varies in one direction along the surface (the $x$ axis) but is uniform along the other
Figure 3.3: Surface relief grating amplitude plotted against grating (intensity modulation) period for doses of 34 kJ/cm$^2$ (open squares) and 23 kJ/cm$^2$ (filled diamonds). Lines are drawn solely for clarity. From [70].

Figure 3.4: Surface relief grating amplitude plotted against total exposure energy to polarization-modulated light with a spatial period of 30µm. Lines are drawn solely for clarity. From Asatryan [76].

surface axis (y) and with depth (z) brings surface relief formation in As$_2$S$_3$ within the scope of the treatment. In this section we follow Levich’s calculation while gradually
Figure 3.5: Surface relief grating amplitude plotted against grating (polarization modulation) period for a dose of 8 kJ/cm$^2$. Lines are drawn solely for clarity. From [76].

Figure 3.6: Schematic of the typical experimental setup used to generate surface structure. Two beams, W1 and W2, interfere on the surface of a thin film of amorphous, light-sensitive material, leading to the pictured definitions of the coordinate system and polarization directions. Figure is drawn by Ashley Prescott.

bring in the specific information about the illumination of As$_2$S$_3$ to bear on the problem we are trying to tackle [75].
The first step of Levich’s treatment is to simplify the Navier-Stokes equation into a two-dimensional boundary layer equation in \( x \) and \( z \):

\[
\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_z \frac{\partial v_x}{\partial z} = -\frac{1}{\rho} \frac{\partial P}{\partial x} + \nu \frac{\partial^2 v_x}{\partial z^2} + f,
\]

in which the \( v_i \)'s are components of the velocity vector, \( \rho \) is the mass density, \( P \) is the total pressure, \( f \) is the body force, and \( \nu \) is the kinematic viscosity.

Next, it is assumed that the film is thin, which results in several ramifications. First, it sanctions the replacement of \( P \) with its value at the surface since there is very little depth over which the pressure can change. At the surface, \( P \) comprises surface tension, \( S \), and the photoinduced pressure, \( P \). Surface tension is traditionally assumed to be proportional to surface curvature,

\[
S = \sigma \frac{d^2 h}{dx^2} \left[ 1 + \left( \frac{dh}{dx} \right)^2 \right]^{3/2} \approx \sigma \frac{d^2 h}{dx^2},
\]

where \( \sigma \) is a constant whose units are force per length, \( h \) is the thickness of the film which varies spatially, and the last step is justified by the thin film approximation since this condition implies \( dh/dx \ll 1 \). The photoinduced pressure is discussed at length section 3.3. For now it is enough to note that since the illumination is modulated only along the \( x \) axis, the photoinduced pressure can vary only with \( x \). The thin film approximation, and the fact there are no body force thus make it possible to perform a further simplification:

\[
p \approx P(x) - \sigma \frac{\partial^2 h}{\partial x^2}.
\]

Combining this information with equation 3.1 leads to

\[
\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_z \frac{\partial v_x}{\partial z} = -\frac{1}{\rho} \frac{\partial \left[ P(x) - \sigma \frac{\partial^2 h}{\partial x^2} \right]}{\partial x} + \nu \frac{\partial^2 v_x}{\partial z^2}.
\]
Again the thin film approximation results in

\[ v_x \frac{\partial v_x}{\partial x} \ll v_z \frac{\partial v_x}{\partial z} \]  

(3.5)

since \(v_x\) and \(v_z\) are of on the same order and the film is assumed to be much wider than its thickness. Following analysis suggested by Ledoyen et al. and Pimputkar et al., it is possible to drop all the terms on the right-hand side because they turn out to be small in practice \[78,80\], which yields

\[ \frac{\partial^2 v_x}{\partial z^2} \approx \frac{1}{\eta} \left[ \frac{\partial P(x)}{\partial x} - \sigma \frac{\partial^3 h}{\partial x^3} \right], \]  

(3.6)

where \(\eta = \rho \nu\) is the dynamic viscosity.

Equation 3.6 is thereby solvable. Hence, it is time to investigate constraints and boundary conditions. The first of these is the continuity equation

\[ \frac{\partial v_x}{\partial x} + \frac{\partial v_z}{\partial z} = 0, \]  

(3.7)

which is derived from incompressibility and conservation of mass. Next, assuming perfect adhesion to the substrate implies

\[ v_x = v_z = 0 \text{ at } z = 0, \]  

(3.8)

where \(z = 0\) is the film-substrate interface. At the free surface of the film, the shear stress along \(z\) goes to zero \[77,80\], which leads to,

\[ \frac{\partial v_x}{\partial z} = 0 \text{ at } z = h. \]  

(3.9)
Finally, the $z$ velocity at the free surface is the rate of change in the height. This can be represented formally as

$$v_z = \frac{\partial h}{\partial t} \text{ at } z = h.$$  (3.10)

As will be shown below, equations 3.7 through 3.10 are enough to specify the problem.

Since the right-hand side of equation 3.6 has no $z$ dependence, the whole equation can be integrated with respect to $z$.

$$\int \frac{\partial^2 v_x}{\partial z^2} \, dz \approx \int \frac{1}{\eta} \left[ \frac{\partial P(x)}{\partial x} - \sigma \frac{\partial^3 h}{\partial x^3} \right] \, dz$$  (3.11)

$$\frac{\partial v_x}{\partial z} \approx \frac{z}{\eta} \left[ \frac{\partial P(x)}{\partial x} - \sigma \frac{\partial^3 h}{\partial x^3} \right] + C_1,$$  (3.12)

where $C_1$ is an integration constant. Applying the shear stress boundary condition (equation 3.9) allows for the determination of $C_1$. Thus

$$\frac{\partial v_x}{\partial z} \approx \frac{(z - h)}{\eta} \left[ \frac{\partial P(x)}{\partial x} - \sigma \frac{\partial^3 h}{\partial x^3} \right].$$  (3.13)

Integrating with respect to $z$ again gives

$$v_x \approx \frac{(z^2/2 - h z)}{\eta} \left[ \frac{\partial P(x)}{\partial x} - \sigma \frac{\partial^3 h}{\partial x^3} \right] + C_2.$$  (3.14)

Application of the $x$ part of the substrate boundary condition (equation 3.8) clearly shows that $C_2$ is 0. Taking the derivative of both sides with respect to $x$ allows the use of continuity (equation 3.7).

$$\frac{\partial v_x}{\partial x} \approx \frac{\partial}{\partial x} \left( \frac{(z^2/2 - h z)}{\eta} \left[ \frac{\partial P(x)}{\partial x} - \sigma \frac{\partial^3 h}{\partial x^3} \right] \right)$$  (3.15)

$$-\frac{\partial v_z}{\partial z} \approx \frac{\partial}{\partial x} \left( \frac{(z^2/2 - h z)}{\eta} \left[ \frac{\partial P(x)}{\partial x} - \sigma \frac{\partial^3 h}{\partial x^3} \right] \right)$$  (3.16)
This too can be integrated with respect to $z$.

$$- v_z \approx \frac{\partial}{\partial x} \left( \frac{(z^3/6 - h z^2/2)}{\eta} \left[ \frac{\partial P(x)}{\partial x} - \frac{\sigma}{3} \frac{\partial^3 h}{\partial x^3} \right] \right) + C_3 \tag{3.17}$$

The $z$ part of the substrate boundary condition reveals $C_3$ to be 0 as well.

From the current data gained from the literature, there is no way to check the veracity of predictions about the internal motion of the film. Thus, it is completely reasonable to consider only the case $z = h$. Making this substitution in equation 3.17 yields

$$v_z \bigg|_{z=h} \approx \frac{\partial}{\partial x} \left( \frac{h^3}{3 \eta} \left[ \frac{\partial P(x)}{\partial x} - \frac{\sigma}{3} \frac{\partial^3 h}{\partial x^3} \right] \right) . \tag{3.18}$$

Finally, applying the last boundary condition (equation 3.10) gives

$$\frac{\partial h}{\partial t} \approx \frac{\partial}{\partial x} \left( \frac{h^3}{3 \eta} \left[ \frac{\partial P(x)}{\partial x} - \frac{\sigma}{3} \frac{\partial^3 h}{\partial x^3} \right] \right) . \tag{3.19}$$

The significance of equation 3.20 is that it is readily solvable by standard numerical methods like the FDTD method, as will be seen in Section 3.4. It is also interesting to note that, aside from the $P(x)$ term, equation 3.20 is a standard result of lubrication theory [81]. Turning to the literature of that discipline, one finds that Zeytounian has provided the framework for a three dimensional analogue that also accounts for gravity [82]. If the proposed model is successful, it can thus be expanded to cover the three dimensional case in a straightforward manner [75].

### 3.3 Construction of the model

As derived in section 3.2, we start the construction of our equation of motion from

$$\frac{\partial h}{\partial t} \approx \frac{\partial}{\partial x} \left( \frac{h^3}{3 \eta} \left[ \frac{\partial P(x)}{\partial x} - \frac{\sigma}{3} \frac{\partial^3 h}{\partial x^3} \right] \right) , \tag{3.20}$$
in which $h(x, t)$ is the film thickness, $\eta$ is the dynamic viscosity, $s$ is the curvature coefficient of the surface tension, and $P(x)$ is the optically-induced pressure, which is assumed to vary only in $x$ because that is the only dimension in which the illumination is modulated \[77\--\[80\]. The complete derivation can be found in the appendix. Given a model of the optically-induced pressure, Equation \[3.20\] is readily solvable by standard numerical methods.

\[\]

Figure 3.7: Schematic of photo-induced dipoles (on the scale of about 3 coordination spheres \[83\]) and their rearrangement leading to mass transport \[84\]. Dipoles can lower their energy by changing configurations in response to the optical electric field. In the case of linear polarization the dipoles will align with the optical electric field.

Our model of the optically-induced pressure is based on two assertions. First, the pressure arises from the electric field of the incident light. Second, the material responds through the motion of small (perhaps a few coordination spheres or less) electrically-induced dipoles. The strength of the dipoles can be calculated by the equation $\vec{P} = \int d^3r \rho(\vec{r})\vec{r}$, where the charge distribution $\rho(\vec{r})$ might be obtained from high-accuracy, first-principles calculations. An example of such calculation conducted by Uchino et. al. is show in FIG. \[3.8\]. Mass transport, and thus surface relief formation, occurs because the dipoles align and move under the influence of the applied electric field.

There is substantial support in the literature for photo-induced dipoles in As$_2$S$_3$ that arise from medium-range order and are capable of rearranging (i.e., mass transport). Most of this evidence was produced in the context of the much-studied photodarkening/photorefraction phenomenon in this material. One example of evidence of medium-range order in As$_2$S$_3$ is the Raman spectroscopy performed by Tanaka 47
et al on As\textsubscript{2}S\textsubscript{3} samples quenched at different rates \cite{84}. Lee et al. \cite{83} observed anisotropic photodarkening effects in As\textsubscript{2}S\textsubscript{3} and used X-ray absorption spectroscopy to ascribe those effects to light-induced distortions of an eleven-atom cluster. Such an anisotropic response to light implies the existence of a dipole in the material and Lee’s cluster explanation suggests that the dipole is on the scale of medium-range order and can undergo mass transport. Perhaps the most relevant evidence is the work by Tikhomirov and Elliott \cite{85}. They performed a novel kind of one-beam holography using a sample of As\textsubscript{2}S\textsubscript{3} and could explain the optical effects they observed only by invoking the rearrangement of photoinduced dipoles. Moreover, they estimate the
density of photo-induced dipoles to be $10^{18} \text{cm}^{-3}$. The model’s use of photo-induced dipoles that are on the scale of medium-range order and are capable of rearrangement is well supported by the literature.

Specifically, the photo-induced dipoles that were discussed above appear in the presence of illumination and persist while the illumination is present. Although clearly there is oscillation from the nature of the electric field of the light, this is not the same as the more traditional induced dipoles associated with spatial fluctuations of electron density in molecular systems. The photo-induced dipoles we are referring to disappear after the illumination ceases. If the illumination is polarized, the dipoles can lower their energy by changing configuration in response to the light.

To calculate the photo-induced pressure we start with the relation $\text{Pressure } \propto \frac{\partial \text{Energy}}{\partial V}$. Equations describing the total free energy density of a dipole interaction system in the presence of an electric field are given by Landau [86],

$$\text{Energy} = F_0 + \epsilon_{ik}\epsilon_0 E_i E_k, \quad (3.21)$$

where $E_i$ and $E_k$ are components of the electric field and $F_0$ is the free energy of the system in absence of an external field. In the dipole interaction model, $\epsilon_{ik}$, a component of the relative permittivity tensor, describes the polarizability of the dipoles when exposed to the optical electric field. Also we use Einstein notation throughout. Rigorous results for the pressure are obtained from equation 3.21 in terms of the stress tensor

$$\sigma_{ik} = \epsilon_0 E_i D_k. \quad (3.22)$$

Inserting $D_k = \Sigma(\epsilon_{km}E_m)$ into equation 3.22, yields

$$\sigma_{ik} = \epsilon_0 E_i(\epsilon_{kx}E_x + \epsilon_{ky}E_y + \epsilon_{kz}E_z). \quad (3.23)$$
Optical electric fields oscillate much faster than any timescale relevant to the flow and so we assume that the material must respond to the time-average of the electric field. Thus, taking the trace of the stress tensor and calculating its time average, we can write the pressure as

\[
P = \frac{1}{3} \langle \text{Trace}(\sigma) \rangle
= \frac{1}{3} \langle \sigma_{xx} + \sigma_{yy} + \sigma_{zz} \rangle
= \frac{\varepsilon_0}{3} \langle E_x (\varepsilon_{xx} E_x + \varepsilon_{xy} E_y) + E_y (\varepsilon_{yx} E_x + \varepsilon_{yy} E_y) \rangle
= \frac{\varepsilon_0}{3} \langle \varepsilon_{xx} E_x^2 + 2\varepsilon_{xy} E_x E_y + \varepsilon_{yy} E_y^2 \rangle .
\] (3.24)

Noting that the material can respond only to the real part of the electric field, we require that \( P(E_x, E_y) = P(\tilde{E}_x, \tilde{E}_y) \) where \( \tilde{E}_x = \Re \{ E_x \} \). In this case, equation 3.24 becomes

\[
P(E_x, E_y) = P(\tilde{E}_x, \tilde{E}_y)
= \frac{\varepsilon_0}{3} \langle \varepsilon_{xx} \tilde{E}_x^2 + 2\varepsilon_{xy} \tilde{E}_x \tilde{E}_y + \varepsilon_{yy} \tilde{E}_y^2 \rangle .
\] (3.25)

The coefficients in equation 3.25, which describe the polarizability of the material, could be measured experimentally. With these coefficients, the pressure is readily calculated. Equation 3.25 together with 3.20 completes our model. All the coefficients are determined by the properties of the material. This approach is general for materials that can be thought of as a collection of small, mobile, polarizable units. Furthermore, photoinduced surface relief formation is not observed in most materials because the polarizability of these units is small or because the viscosity and/or surface tension is large.
Table 3.1: Summary of the photoinduced pressure predicted by equation 3.29 for various polarization conditions. \(I, \psi,\) and \(\Delta \phi\) can easily be derived from the interference of plane waves. \(\delta = \frac{2\pi}{\lambda} x \sin \theta\) for \(\theta\) as in figure 4.7. A trigonometric identity was used to derive the second form of \(P(x)\) for LCP-RCP interference in order to show that for all cases considered \(P(x)\) can be expressed as twice the intensity of one of the initial beams times the sum of a constant and a sinusoidal oscillation.

### 3.4 FDTD simulation

To check the validity of the model, we calculate the solution to equation 3.20 on a typical holographic setup used to generate surface structure (see Figure 4.7). In the setup, everything about the two interfering beams is identical except for the direction of their wave vectors and possibly their polarization. The most generic electric field produced by such interference can then be written

\[
e^{i(kx - \omega t)} \left( \begin{array}{c} |E_x| e^{i\phi_x} \\ |E_y| e^{i\phi_y} \end{array} \right), \quad (3.26)
\]

where \(|E_x|, |E_y|, \phi_x,\) and \(\phi_y\) are arbitrary, real, and time (but not necessarily position) independent. Taking \(E_x\) and \(E_y\) from equation 3.26, inserting them into equation 3.25, and computing the time averages gives

\[
P = b_1 |E_x|^2 + b_2 |E_y|^2 + b_3 |E_x| |E_y| \cos \Delta \phi, \quad (3.27)
\]

where \(b_1 = \epsilon_0 \epsilon_{xx}/6, b_2 = \epsilon_0 \epsilon_{yy}/6\) and \(b_3 = \epsilon_0 \epsilon_{xy}/3.\) Defining a generalized polarization angle (applicable to elliptical polarizations) \(\psi = \arctan |E_y|/|E_x|,\) equation 3.27 can be rewritten as
\[
P = I \left[ b_1 \cos^2 \psi + b_2 \sin^2 \psi + b_3 \sin 2\psi \cos \Delta \phi \right] \quad (3.28)
\]

\[
= I(x) \left[ c_1 + c_2 \cos 2\psi(x) + c_3 \cos \Delta \phi(x) \sin 2\psi(x) \right], \quad (3.29)
\]

where, in going from equation 3.28 to equation 3.29, the \( x \) dependence is explicitly indicated and the coefficients redefined as: \( c_1 = \epsilon_0 \epsilon_{xx}/6 \), \( c_2 = \epsilon_0(\epsilon_{yy} - \epsilon_{xx})/6 \) and \( c_3 = \epsilon_0 \epsilon_{xy}/3 \). Equation 3.29 is intuitively reasonable since it depends on intensity, polarization, and \( \Delta \phi \), the three quantities whose modulation has been experimentally shown to cause surface relief formation \[70, 87\]. Taking the first spatial derivative of Equation 3.29 yields

\[
\frac{\partial P}{\partial x} = \frac{\partial I}{\partial x} \left[ c_1 + c_2 \cos 2\psi(x) + c_3 \cos \Delta \phi(x) \sin 2\psi(x) \right]
+ 2I(x) \frac{\partial \psi}{\partial x} \left[ -c_2 \sin 2\psi(x) + c_3 \cos \Delta \phi(x) \cos 2\psi(x) \right]
+ I(x) \frac{\partial \Delta \phi}{\partial x} \left[ -c_3 \sin \Delta \phi(x) \sin 2\psi(x) \right]. \quad (3.30)
\]

Equation 3.30 cleanly separates into three independent terms governing the pressure gradient induced by modulation of the intensity, polarization direction, and phase. Accordingly, this model is consistent with the idea suggested by previous experiments that the intensity and phase modulation effects can be saturated without saturating the polarization modulation effect \[70, 76, 88\].

Table 3.1 lists the pressure functions predicted by equation 3.29 for commonly used polarization conditions. Despite the widely varying initial conditions considered, the \( P(x) \)'s can all be represented by the same general form. Recalling that \( E_0^2 \) typically has a Gaussian profile, we reexpress the pressure as
\[ P(x) = p_1 e^{-2(x/p_2)^2} \left[ p_3 + \cos (p_4 x + p_5) \right], \quad (3.31) \]

where the \( p_i \)'s are parameters decided either by the experimental setup or the properties of the material. \( p_4 \) is fixed as the spatial modulation frequency and \( p_2 \) is the beam radius; both are the same across all polarization conditions. \( p_5 \) is included to account for the possibility that the Gaussian intensity profile is not centered on a peak of the modulation. \( p_1 \) and \( p_3 \) are parameters of the material, whose values are determined by fitting the model with the experimental data.

Figure 3.9 demonstrates the model's prediction of the dynamics of light-induced grating formation in different hypothetical materials defined by a set of parameters \( \{p_1, \sigma, \eta\} \). The values of \( p_1/\sigma \) and \( \sigma/\eta \) are listed in the figure, the constrained fitting parameter \( p_2 \) is taken to be 57 \( \mu m \), and the model is evaluated using the Runge-Kutta method with a time step of 1/200 of a second. As can be seen from the figure, surface tension sets the maximum grating amplitude while viscosity determines the speed at which the maximum amplitude is reached.

In order to test our model we compare it to experimental results for \( \text{As}_2\text{S}_3 \) in [70]. Setting \( c_2 = 3c_1 \) and \( c_3 = 2c_1 \) approximates that paper’s qualitative description of the observed size ordering for different polarization conditions [70]. This choice captures the well-known anisotropy of \( \text{As}_2\text{S}_3 \)'s response to an external optical field and suggests that \( \epsilon_{yy} = 4\epsilon_{xx} \) and \( \epsilon_{xy} = \epsilon_{xx} \).

Specifically, the model makes use of five material properties: surface tension \( \sigma \), dynamic viscosity \( \eta \), and three polarizabilities \( \epsilon_{xx}, \epsilon_{xy}, \epsilon_{yy} \). The polarizabilities become grouped into the parameter \( p_1 \) according to the polarization geometry as described in equations 9-11. We then combine the \( p_1, \eta, \sigma \) into two parameters, \( p_1/\sigma \) and \( \sigma/\eta \) and do a least square fit to get the optimal values for these two ratios.
Figure 3.9: Plots of maximum grating amplitude evolution versus irradiation fluence (time). The curve is produced by taking snapshots of the surface profile at different fluence (time) and recording the maximum grating amplitude for each. Each curve corresponds to a set of material parameters: \( \{ p_1, \sigma, \eta \} \). The upper curve, generated by \( \{ p_1/\sigma = 0.88 \mu m^{-1}, \sigma/\eta = 0.0019 \mu m/s \} \), simulates the response of As$_2$S$_3$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Comment</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters from experimental setup</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( h_0 )</td>
<td>Initial Thickness</td>
<td>2 ( \mu m )</td>
</tr>
<tr>
<td>( T )</td>
<td>Total Illumination Time</td>
<td>381 s</td>
</tr>
<tr>
<td>( p_2 )</td>
<td>Illumination Radius</td>
<td>57 ( \mu m )</td>
</tr>
<tr>
<td>( p_3 )</td>
<td>Non-Oscillatory Pressure</td>
<td>1</td>
</tr>
<tr>
<td>( p_4 )</td>
<td>Modulation Frequency</td>
<td>( 2\pi/13 \ \mu m^{-1} )</td>
</tr>
<tr>
<td>( p_5 )</td>
<td>Modulation Phase</td>
<td>( \pi/2 )</td>
</tr>
<tr>
<td>Fitting Parameters by model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( p_1/\sigma )</td>
<td>Relative Pressure Strength</td>
<td>0.30 ( m^{-1} )</td>
</tr>
<tr>
<td>( \sigma/\eta )</td>
<td>Characteristic Growth Rate</td>
<td>0.0114 ( \mu m/s )</td>
</tr>
<tr>
<td>Parameters from calculation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( p_1 )</td>
<td>Extracted from [89] (10$^{-2}$J/m$^3$)</td>
<td>0.45 $\sim$ 1.8</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Surface tension (J/m$^2$)</td>
<td>0.015 $\sim$ 0.060</td>
</tr>
<tr>
<td>( \eta )</td>
<td>Dynamic viscosity (10$^{11}$Pa $\cdot$ s)</td>
<td>0.052 $\sim$ 0.208</td>
</tr>
</tbody>
</table>

Table 3.2: Summary of the parameters used in constructing the fit depicted in figure 3.11.
To determine the reasonableness of these parameters, we can extract materials properties from the literature. For instance, in the work of Perrin et al, they find $\epsilon_{ij} = 5 \sim 20$ \cite{89} for As$_2$S$_3$.

Armed with a value for the polarizabilities, we can now determine a range of values for $p_1$ and further estimate $\sigma$ and $\eta$ from the fitting parameters. In the 'p-p' polarization configuration, we obtain:

$$p_1 = 2 E_0^2 (c_1 + c_2)$$

$$= 2 \frac{2I_0}{n c \epsilon_0} \epsilon_0 \left( \frac{\epsilon_{xx}}{6} + \frac{\epsilon_{yy} - \epsilon_{xx}}{6} \right) = \frac{2}{3} \frac{\epsilon_{yy} I_0}{n c}$$

(3.32)

where $E_0$ is electric field strength and $I_0 = 105 W/cm^2$ is the intensity of the laser beam, as reported in \cite{70}; $\epsilon_0$ is the vacuum permittivity; and $n = 2.6$ is the refractive index of Arsenic Sulfide \cite{90}. Plugging in the above values $\epsilon_{ij} = 5 \sim 20$ gives $p_1 = (0.45 \sim 1.8) \times 10^{-2} J/m^3$.

Based on this range of $p_1$, we can extract the surface tension $\sigma = 0.015 \sim 0.060 J/m^2$, and dynamic viscosity $\eta = (0.052 \sim 0.208) \times 10^{11} Pa s$, both of which agrees well with the measured value of $\sigma = 0.059 \sim 0.168 J/m^2$ \cite{91} and $\eta = 10^{11} \sim 10^{12} Pa s$ reported by Yannopoulos et al. \cite{92}. We note that the viscosity is on the low side compared to the literature, however the measured viscosity depends sensitively on the light intensity and the literature value does not provide sufficient data as to how the value was obtained nor what light intensity was used to infer these values.

Figures \ref{fig:3.10} and \ref{fig:3.11} shows the model’s fit to the time and space dependence of surface relief formation observed in \cite{70}. The model parameters are listed in table \ref{tab:3.2}. The strong correspondence over long times and large length-scales provides strong support for the model.
Figure 3.10: The model’s fit to a section of a surface relief profile data from [70]. Results generated by the model agree well with experimental measurements, both in amplitude and frequency.

Figure 3.11: Fluence (time) dependence of maximum surface relief amplitude for the fit in figure 3.10.
3.5 Summary

In this chapter, we model surface relief formation as arising from viscous flow driven by the opposition of surface tension and an optically-induced pressure which provides a driving force for mass transport that depends on both intensity and polarization. Accommodating both of these dependencies in a single model formulation is the main innovation of this work. Simulations using our model agree well with literature data on the temporal and spatial dependence of optically-induced surface relief in As$_2$S$_3$. 
Chapter 4

Modification through uniform doping of nanoparticles

In this chapter, we demonstrate on the in-situ generation of silver nanoparticles (Ag-NPs) in chalcogenide solutions using pulsed laser ablation and the uniform distribution of AgNP in the resulting spin coated films. The prepared solution and films were analyzed using UV-Vis spectroscopy, dynamic light scattering (DLS), energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM) to investigate the particle shape and size distribution. We identified an average size of 14nm and a redshift of the optical absorption edge associated with increasing Ag NP content in solution. By calculating the nearest neighbor index (NNI) and standard normal deviate of the nanoparticle locations inside the films, we verified that a uniformly dispersed distribution was achieved through this process.
4.1 Overview

4.1.1 The background and challenges

As discussed in Chapter 2, the photodoping effect has drawn much attention recently due to its potential application in various areas, such as mid-infrared communications, holographic data storage, diffractive elements and sensing devices [93,95]. However, in conventional photodoping procedures, which rely on thermal evaporation and sputtering to create a thin layer of metal on top of the chalcogenide film (shown in FIG. 4.1), the thickness of the doped layer is limited by the diffusion depth of the silver [96]. Also the uniformity of the doped layer is difficult to control, thereby setting limitations in fabricating application-favorable bulk structures.

![Figure 4.1: (a) Photo-dissolution of silver layer with spin-coated arsenic sulfide layer: illumination with broad band source creates a circle spot. (b) Diagram and AFM topography images of photo-dissolution between silver and arsenic sulfide prepared by thermal evaporation [60].](image)

One possible method to resolve these difficulties in fabricating chalcogenide films is to employ a solution-based process [66]. In particular, by incorporating nanoparticles into the deposited films, we can hope to achieve a uniform distribution of silver throughout the entire depth, rather than having silver concentrated only at the surface. In addition, this approach can readily realize large area or large thickness films, and the same solutions can also be adopted for other precision dispensing techniques.
such as mold casting, ink jet or laser direct write, allowing spatial control over the added material \[97\]. Nevertheless, uniform doping of silver nanoparticles (Ag NPs) into a chalcogenide glass matrix without agglomeration remains challenging, due to the tendency of Ag NPs to aggregate.

In previous chapter, we discussed the method and underlying mechanisms to modify the surface structure of the thin films by light exposure. In this chapter, we lay the focus on another way to modify the chemistry of the materials, which is achieved through the photo-doping effects. We present experimental results of fabricating uniformly dispersed nanoparticle-doped chalcogenide glass using laser ablation \[98,99\] and solution processing methods. In the fabrication process, we first focus a pulsed laser beam onto the surface of a bulk metallic sample and ablate the material, which is then ejected into the liquid solution, forming a suspension of Ag NPs \[100,101\]. Ag-doped chalcogenide films are then fabricated by spin-coating the resulting solution. The prepared solution and films are analyzed using UV-Vis spectroscopy, DLS, EDX and high resolution TEM to investigate the particle structure and distribution. The results demonstrate that by carrying out the nanoparticle generation step directly in the solution of interest instead of ideal solvents such as water or ethanol, the laser ablation method can effectively avoid the aggregation and additional processing steps associated with other nanoparticles generation techniques, such as wet chemical approaches \[102\].

We conduct our efforts to tackle this problem initially through several ways. One of the attempts is the “direct mix” method, as shown in FIG. 4.2, a batch of silver powder with average parameters of 70 nm are directly added into arsenic sulfide solution. Trying to avoid the aggregation we employ a magnetic bar to stir the mixture for 10 minutes, resulting a suspension of Ag NPs/As\(_2\)S\(_3\) immediately after the stirring. Nevertheless, silver particles eventually submerge to the bottom which prevents the formation of a uniform Ag/As\(_2\)S\(_3\) suspension. It’s not surprising that since the density
of silver nanoparticles is much high than the solution, so in a condition without any additional interaction like the couloumb interaction usually brought by the surfactant in other possible ways of doping, the Ag NPs are not able to suspend for long.

Figure 4.2: The “direct mix” method to incorporate silver nano-powders into chalcogenides. Silver nano-powers are directly added into arsenic sulfide solution, followed by stirring with magnetic bar for 10 minutes. Suspending for around 2 minutes, silver particles eventually submerge to the bottom, declining the formation of a uniform Ag/As$_2$S$_3$ suspension.

Another method called “solvent switching” is also tested. Following the well-known oxidation-reduction protocol from Lee and Meiselby [103] we synthesize silver nanoparticles with an average size of 20 nm using sodium citrate (Na$_3$C$_6$H$_5$O$_7$ · 2H$_2$O) and silver nitrate dissolved in water. Since chalcogenide solution are not in favor of water, we apply the “solvent switching” method to pick up the silver nanoparticles and get them dispersed inside arsenic sulfide solution. Basically, the solvent switching technique consists of three steps, listed as the following: (1) using centrifuge to separate the Ag NPs and water; (2) taking out the water and further rinsing with propylamine and arsenic sulfide solution; (3) repeating step 1 and 2 for a few times. As shown in FIG. 4.3, successfully applying solvent switching from water to propylamine leads to a silver nanoparticles suspension in propylamine whose color is a little more reddish, enabling a further step mixing with arsenic sulfide solution (in propylamine as well) to obtain Ag NPs / arsenic sulfide colloids with a dark green color. It is by this means that we move one step further than the “direct mix” procedure, for a long lasting colloid has been synthesized. However, after spin coating the resulting novel colloids onto silicon substrate, SEM measurements clear show the formation
of silver nanoparticle aggregation, which prevents a further advance of the “solvent switching” method.

Figure 4.3: The “solvent switching” method aiming to uniformly dope silver nanoparticles into chalcogenide matrices. Silver nanoparticles colloid is synthesized through chemical reaction between sodium citrate \( (\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}) \) and silver nitrate, where the size of silver nanoparticles suspended in water is around 20 nm. A solvent switching technique is followed consisting of three steps: (1) using centrifuge to separate the Ag NPs and water; (2) taking out the water and further rinsing with propylamine and arsenic sulfide solution; (3) repeating step 1 and 2 for a few times. Finally the resultant Ag NPs/Arsenic Sulfide solution is spin-coated onto silicon substrate. The SEM images of the Ag NPs/As₂S₃ films clearly show the existence of silver nanoparticles aggregation.

4.1.2 Overview of the pulse laser ablation technique

Finally we attempt to using the pulse laser ablation method to generate silver nanoparticles directly inside the arsenic sulfide solution. Laser ablation synthesis in solution, which removes material from a solid surface by irradiating it with a laser
beam, emerged as a reliable alternative to conventional chemical reduction methods (such as the one we used in our “solvent switching” method [103]) for obtaining metal nanoparticles. At high laser flux, the material is typically converted to a plasma. As a “green” technique, it does not need stabilizing molecules or other chemicals. Moreover, this technique possesses a rich parameter space including the species of metal target, solvent, solutes, as well as fluence, wavelength, duration, repetition frequency of the laser pulse, which enable a flexible and accurate control of particle shape and sizes. Various nanoparticles including Au, Ag, Cu, and Pt has been fabricated within different solutions like water, acetone with the radii ranging from several nm to tens of nm as list in FIG. 4.5.

![Figure 4.4](image)

Figure 4.4: (a) Various nanoparticles obtained by pulse laser ablation. (b)&(c) HRTEM images of AgNP and AuNP obtained by LASis in dimethylformamide and water, respectively [104]. (d) UV-vis spectra of AgNPs synthesized in DMF(1, black), acetonitrile (2, red), THF (3, blue), and DMSO (4, green) [105].

In our study, we use a Q-switched pico-second pulse Nd:YAG laser system (EK-SPLA PL-2210A) to perform our ablation experiment. To avoid the absorption from arsenic sulfide, the operation wavelength is taken as 1064 nm, at which the output energy per pulse is 1mJ, running at a typical 1000Hz reputation rate, with a pulse...
width around 30 ps. We measure the size of focal spot to be 20 µm after the beam passes through a lens with a focal length of 5 cm. We thereby calculate the power density using the equations shown in FIG. 4.5.

Figure 4.5: (a) Typical near field beam profile of PL2210A laser, from PL2210A manual. (b) Diagram showing the f number (f#) definition. (c) The power density calculation of the pico-second laser system.

4.2 Fabrication of uniformly dispersed nanoparticle-doped chalcogenide glass

Arsenic sulfide (As₂S₃) solution was prepared by grinding bulk As₂S₃ pieces into a fine powder and dissolved into n-propylamine solvent at a concentration of 0.8 mol/L. Dissolution was carried out inside a sealed glass chamber to prevent solvent evaporation. The dissolving process usually took more than three days and a magnetic stirrer was used to expedite this process. Exposure of solution to atmospheric mois-
titure was kept to a minimum throughout preparation procedure since water can lead
to precipitate formation [66].

To obtain the nanoparticles in $\text{As}_2\text{S}_3$ solution, we used the experimental setup
described in FIG. 4.7. A silver target (>99.99% purity, thickness 5.0mm) was placed at
the bottom of a Teflon cell, which was filled with $\text{As}_2\text{S}_3$ solution. The silver target
was covered by a layer of solution 4 millimeters deep. The cell was then transferred
into an air-tight vacuum chamber. All these operations were carried out inside a
nitrogen-filled glovebox, to avoid the influence of oxygen.

The chamber was then placed under the focus of a 30ps, 1000Hz, 1064nm Q-
Switched Nd:YAG laser beam, with maximum energy of 1mJ/pulse. The Gaussian
laser beam was focused, through the liquid layer, onto the target surface with a lens
with a focal length of 50mm. Since absorption by the arsenic sulfide solution was
very small at the operating wavelength, the ablation beam passed through without
significant loss. The position of the target relative to the laser beam was controlled
by an X-Y-Z stage to maintain proper focus and to avoid deep hole drilling in the tar-
get. Ablation was performed for 10, 25 and 40 minutes, and we denote the obtained solutions as 10-, 25-, and 40-minute solutions in this paper, respectively. Ablation was accompanied by the emission of plasma light from the surface, and bubbling was observed immediately upon irradiation, which indicates the occurrence of Coulomb explosion [101, 107]. The solution gradually turned brownish-yellow as the concentration of Ag NPs increased. Finally the chamber was moved back to the glovebox, where the solution was collected.

Immediately after the ablation experiment, UV-Vis absorption measurements of silver were conducted using an Ocean Optics HR4000 high-resolution spectrometer. Dynamic light scattering (Malvern Zeta Sizer) was used to determine size distribution of the nanoparticles in the solutions. In order to characterize the distribution of nanoparticles in thin films, TEM experiments were carried out on a Philips CM200
microscope operating at 200 KV. High resolution images were acquired using a Gatan Orius 200 camera. Samples for TEM characterization were prepared by pouring a droplet of the colloidal solution onto 400-mesh copper grids covered with a holey carbon film (from Ted Pella). The excess solvent was then allowed to evaporate.

The Ag-doped suspensions were then deposited onto silicon wafers for EDX analysis. Specifically, the solution was first pipetted onto a silicon substrate, and the substrate was immediately spun at 1000 rpm for 30 seconds. Resulting films were soft-baked under vacuum at 60°C for 1 hour to remove most of the solvent and then hard-baked at 180°C to remove excess solvent and to further densify the glass [90]. Films prepared under these conditions typically were approximately 1 µm thick and ready for subsequent analysis.

4.3 Optical and structural characterizations

As photos of the generated Ag NPs solution in FIG. 4.8 (inset) show, the color of these solutions gets noticeably darker due to the increasing Ag NPs concentration resulting from higher number of laser shots. Absorption of these solutions is measured by UV-Vis spectroscopy using arsenic sulfide solution as a control. In the results shown in FIG. 4.8 different curves denote spectra from solutions experiencing different ablation duration. The existence of Ag NPs introduces surface plasmon resonance bands, but due to the absorption of the As$_2$S$_3$ solution, only tails of these resonance bands are observable. Moreover, these measurements disclose a redshift behavior of the absorption edge associated with the increasing concentration of Ag NPs, which agrees well with the literature [108–110].

UV-Vis measurements indicate the existence of Ag NPs without revealing information about size of those Ag NPs. In order to determine the size distribution of the Ag NPs, DLS measurements are performed on the 40-minute solution. The sig-
nal from pure $\text{As}_2\text{S}_3$ solution is also acquired for comparison. As shown in FIG. 4.9, measurements from $\text{As}_2\text{S}_3$ peak around 8nm, which originate from the dissolved $\text{As}_2\text{S}_3$ units [90]. The peak from Ag NPs solutions is centered around 14nm, which reveals the average size of the majority of nanoparticles. The DLS measurements are also performed on 10- and 25-minute solutions, and the same distribution of Ag NPs are obtained, revealing the size is independent with ablation time. These values are in good agreement with the literature [112, 113], where nanoparticles average size of 5-25nm are generated in ideal solutions like water.

Measurements on the solution phase demonstrate that the size of the nanoparticles is independent of ablation time while the concentration of particles is clearly rising with increasing ablation time. However, the ultimate test of the particle distribution is the fabrication of a film with a uniform dispersion of nanoparticles. FIG. 5.9 shows EDX results from spin-coated films using the 40-minute solution. The relative
Figure 4.9: DLS study of the 40-minute solution, with areas of the curves normalized. Background signal from As$_2$S$_3$ solution is taken for comparison. In the figure, the measurement data are represented by the circles, while the trendlines are fitting curves using Gaussian models [111]. Scattering intensity shows background of As$_2$S$_3$ solution peaks around 8nm, while the average diameters of the silver particles are approximately 14nm.

The weight of silver is measured to be 1.3%. Armed with this value, the concentration of As$_2$S$_3$ solution (2g/10mL), and the average particle size from DLS measurements, the generation rate of Ag NPs is calculated to be $1.52 \times 10^8$ nanoparticles formed per pulse, which is equivalent to 7.8$mg$ per hour in terms of the particles weight, as shown in Table 4.1.

To determine the structure and distribution of the Ag NPs we use high-resolution TEM, shown in FIG.4.12. The TEM images (FIG.4.12a, b) demonstrate the existence of Ag NPs and indicate their uniform distribution. In the dark field image, only the diffraction signal from crystalline structures is collected. Since arsenic sulfide is in an amorphous state, the bright spots in FIG.4.12a are the silver nanoparticles. The diffraction pattern from the Ag NPs (FIG.4.12c, inset) exhibits hexagonal symmetry that can be attributed to the basal plane of the hexagonal phase. This agrees well
Figure 4.10: EDX study of the film spin-coated using the 40-minutes solution. A silicon wafer was used as the substrate, which leads to the Si peak. The relative weight of silver is 1.3%.

with the literature where it has been shown the hexagonal phase of silver stabilizes only in the nanocrystalline form for particles less than 30nm [114]. FIG. 4.12] shows a high resolution TEM image of silver nanoparticles which demonstrates a high degree of crystalline order. The spacing between the lattice fringes is measured to be 2.5 Å.

Finally using utilities provided by ImageJ [115], the TEM image from FIG. 4.12a is then processed into a high contrast image, as shown in FIG. 4.12b, which more clearly shows the spacing distribution of nanoparticles. We quantify uniformity and dispersion of the distribution using the nearest neighbor index (NNI), a standard method in spatial analysis that is used to determine the degree of spatial dispersion in a population [116]. In general, if the distribution of the points is clustered together, the average distance between nearest neighbors will be shorter than if the particles
<table>
<thead>
<tr>
<th><strong>Arsenic sulfide</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>2g/10ml</td>
</tr>
<tr>
<td>Solution volume</td>
<td>2ml</td>
</tr>
<tr>
<td>Total weight</td>
<td>0.4g</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Silver NPs</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total silver weight</td>
<td>$0.52 \times 10^{-2}$g</td>
</tr>
<tr>
<td>Diameter</td>
<td>14nm</td>
</tr>
<tr>
<td>Density</td>
<td>9.932g/cm³</td>
</tr>
<tr>
<td>Weight per particle</td>
<td>$1.43 \times 10^{-17}$g</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Ablation duration</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ablation time</td>
<td>$2.4 \times 10^4$s</td>
</tr>
<tr>
<td>Total number of ablation pulses</td>
<td>$2.4 \times 10^6$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Generation rate</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Particles formed per pulse</td>
<td>$1.52 \times 10^8$/pulse</td>
</tr>
<tr>
<td>Total particles mass per hour</td>
<td>7.8 mg/h</td>
</tr>
</tbody>
</table>

Table 4.1: Calculation of Ag NPs generation rate.

are scattered throughout the sample. The NNI is defined as the ratio of the average inter-point distance between nearest neighbors $\bar{d}$ to the expected value of the average inter-point distance if the sample were randomly dispersed $E(\bar{d})$ [117,118]. The value of the NNI can range between the theoretical extremes of 0 (where all points are at the same location) and 2.1419 (where points have a perfectly uniform distribution).

The equations for these parameters are given by

$$NNI = \frac{\bar{d}}{E(\bar{d})}$$

$$\bar{d} = \frac{1}{n} \sum_{i=1}^{n} d_i/n$$

$$E(\bar{d}) = 0.5\sqrt{A/n}.$$ 

For the data in FIG. 4.12b, $n = 236$ is the total number of particles, obtained using the ‘particles analysis’ utilities from Image J, and $A = 1848 \times 1848 \, nm^2$ is the area of the studied region. $d_i$ is the distance from $i_{th}$ particle to its nearest neighbor, determined by measuring all neighboring distances and taking the minimum. $\bar{d}$ is
calculated to be 60.64 nm using ImageJ. \( E(\bar{d}) \) is determined to be 60.15 nm. The NNI is then readily evaluated to be 1.01, which reveals a random dispersion.

Finally to test if the calculated NNI is statistically different from that of a random process it is necessary to calculate the standard normal deviate of the distribution \((Z)\) using

\[
Z = \frac{\bar{d} - E(\bar{d})}{\sigma_{\bar{d}}},
\]

where \( \sigma_{\bar{d}} = \sqrt{0.0683A/n^2} \) is the standard deviation of \( \bar{d} \). If the value of \( Z \) is within \([-1.96, 1.96]\) the distribution of points is considered to be random at the 95% confidence level \([118]\). Using equation 4.2 \( Z \) is calculated to be 0.243. The value of NNI and \( Z \) are evidence of a good spatial dispersion of the particles.

As shown in FIG. 4.13 the process of ablation and uniform distribution of silver nanoparticles consists of four stages. Stage 1-3 are typical Coulomb explosion process. Electronic excitation energy is coupled from intense electromagnetic fields into atomic motion. With their low mass, outer valence electrons responsible for chemical bonding are easily stripped from atoms, leaving the solids positively charged. Given a mutually repulsive state (strong Coulombic repulsion) between atoms whose chemical bonds are broken, the material explodes into a plasma of ionized atomic particles.

4.4 Summary

In conclusion, we demonstrate the direct generation of silver nanoparticles by laser ablation in \( \text{As}_2\text{S}_3/\text{propylamine} \) solutions. We are able to obtain uniform distribution of nanoparticles in both the solution and thin film phases, which is evidenced by the high resolution TEM measurement and the NNI analysis. The clustering or agglomeration that is typically associated with solution based methods in nanoparticles fabrication are successfully avoided. These materials have a great potential for applications in diffractive elements and sensing devices, particularly in cases where
thick films uniformly doped by Ag NPs are crucial. Furthermore, they have ability to be photo-responsive, and could be used for direct writing, as well as recording of optical information, such as holographic data storage.
Figure 4.11: Typical transmission electron micrograph image of Ag NPs generated by laser ablation of a silver target in As$_2$S$_3$/propylamine solution. (a) Dark field TEM image of silver nanoparticles uniformly distributed inside As$_2$S$_3$ film. Image is taken using a central beam stop in the back focal plane of the objective lens. Only crystals diffracting strongly into objective aperture give bright contrast in the image. (b) Processed high contract image corresponding to FIG.a, generated by ImageJ. Black dots are silver nanoparticles. (c) Electron diffraction patterns from a cluster of Ag NPs of the hexagonal phase with colored lines added for eye guiding. (d) A high resolution TEM image of silver nanoparticles which demonstrates a high degree of crystalline order. The spacing between the lattice fringes is measured to be 2.5 Å. (e) Table of diffraction intensity from different facets of crystalline silver. (f) Diffraction pattern of high resolution TEM images of silver nanoparticles, which shows a high degree of crystalline order.
Figure 4.12: Particle statistics performed on the ImageJ processed TEM dark filed image shown in FIG. 4.12. (a) The ImageJ processed TEM dark filed image with auxiliary lines equally dividing into 49 grids. (b) and (c) Number counting and plot for each row and column. (d) Histogram with respect to the radii of the particles.
Figure 4.13: The diagram showing the mechanism of uniform distribution resulted from pulse laser ablation, consisting of four stages: (1) Under the focus of pulse laser, strong electric field oscillates electron to be hot (different local equilibrium temperature from that of silver ions). (2) Electron following the oscillation of electric field continues getting hot until the ejection, leaving ions experiencing unbalanced coulomb force. (3) The coulomb force increases as more electron ejected resulting silver ions ejected eventually. (4) The 'hot' and positive charged attract propylamine which posses a lone pair electron to act as surfactant, preventing the aggregation from occurring.
Chapter 5

Modifications by wet chemistry processing

One aspect of the latest achievements in the development of chalcogenide glasses are also connected with the modification through doping by metal ions in order to create new IR sources of radiation, lasers and amplifiers [119]. Lasing in rare earth metal ion doped chalcogenide fibers, waveguides, micro-spheres, as well as high quantum efficiencies of photoluminescence has been reported [120–122], where researchers employed conventional melt-quench method to achieve the device fabrication. This approach involves complex procedure wherein the careful control of the heating rate is crucial and tricky, bring severe difficulties to the operations. Another critical issue is the ingrained problem of achieving isothermal conditions during the processing.

Holding the target to solve the problems deep-rooted in the conventional melt-quench techniques, we thereby in this chapter demonstrate a one-step in-situ synthesis of the metal-ions doped chalcogenide glassy materials through a general strategy that involves dissolution of chalcogenides and metal chlorides followed by solution processing. This technique provides a framework to incorporate various metal ions into chalcogenide glassy matrices, including platinum (Pt), palladium (Pd), nickel (Ni),
cobalt (Co), copper (Cu), and iron (Fe). We characterize these solutions by measuring the optical absorption and demonstrate these behaviors are tunable by further mixing different ion-doped chalcogenide solution. We fabricate these solutions into solid-state thin films using standard spin-coating procedures, and perform analysis using SEM, EDX, TEM and ellipsometry to investigate the physio-chemical properties such as morphology, composition and refractive indices. At last we show the fabrication of chalcogenide gels from these solutions by solvent removal through heat treatment under vacuum.

5.1 Chemical synthesis

Solution-processing of chalcogenides in amine solvents is known since 1982, and the dissolution mechanism involves an electrophilic substitution reaction, where As atoms are attacked by the lone pair electron associated to RNH$_2$. In the chemical synthesis employed by this study, arsenic sulfide (As$_2$S$_3$, Alfa Aesar 99.999%) solution was prepared by grinding bulk As$_2$S$_3$ pieces into a fine powder and dissolved into n-propylamine (C$_3$H$_9$N, Sigma-Aldrich 99.999%) solvent at a concentration of 0.8 mol/L. Dissolution was carried out inside a sealed glass chamber to prevent solvent evaporation. The dissolving process usually took more than three days and a magnetic stirrer was used to expedite this process. Exposure of solution to atmospheric moisture was kept to a minimum throughout preparation procedure since water can lead to precipitate formation \cite{66}. Solutions of other chalcogenides such as arsenic selenide (As$_2$Se$_3$, alfa aesar 99.999%) were prepared with the same fashion.

A variety of chlorometallate salts were purchased from Sigma Aldrich, and used as received without further purification. All chlorides were added into n-propylamine solvent at a concentration of 0.05 mol/L and kept inside a dry-box with the levels of H$_2$O and O$_2$ below 1 ppm to stabilize.
Figure 5.1: Chemical synthesis used for the preparation of metal ions doped chalcogenide solution. From left to right: pictures of $\text{As}_2\text{S}_3$ (0.8 mol/L), CoCl$_2$ (0.05 mol/L) and Co$^{2+}$ doped chalcogenide solutions, in which propylamine ($\text{C}_3\text{H}_9\text{N}$) is the solvent.

To obtain the metal ion doped chalcogenides, solutions of the propylamine dissolved salt at a volume of 250 $\mu$L were dipped into 1mL $\text{As}_2\text{S}_3$ or $\text{As}_2\text{Se}_3$ solutions. Upon adding, color change of the chalcogenides solution was immediately observed, indicating reactions have readily happened, as shown in FIG. 5.1. It is noticeable that no heating or complex instruments were employed during the synthesis process, featuring a facile, fast and low cost method.

Figure 5.2: Table chart of metal chlorides reacting with chalcogenides. Elements with a cross denotes there’s no reaction observed, while red circles designate reactivity. Among the various chalcogenides tested, arsenic sulfide and arsenic selenide react with the salts; while chlorides of platinum (Pt$^{2+}$), palladium (Pd$^{2+}$), nickel (Ni$^{2+}$), cobalt (Co$^{2+}$), copper (Cu$^+$), and iron (Fe$^{2+}$) are reacting.

From FIG. 5.1 it is noticeable that a chemical reaction occurs between $\text{As}_2\text{S}_3$ and CoCl$_2$ solutions through the color change observed from the resultant solution. It is of interest to investigate the reactivity between distinct chalcogenides and chlorides. We
then took one step forward applying the same approach with various metal chlorides into chalcogenides. The results are summarized into the periodic table shown in FIG. 5.2. In the table, elements marked with a red circles denotes that the reaction is observed while elements with a black cross denotes no reactivity. Among the chalcogenides tested, arsenic sulfide and arsenic selenide showed the reactivity with the chlorides, while reactions were observed in Sb$_2$S$_3$ and GeS for they do not dissolve in propylamine. Similar procedures were applied to a variety of chlorides, and the results are shown in the table as well. Chlorides of platinum (Pt$^{2+}$), palladium (Pd$^{2+}$), nickel (Ni$^{2+}$), cobalt (Co$^{2+}$), copper (Cu$^+$), and iron (Fe$^{2+}$) react and get incorporated into the glassy matrices of chalcogenides. Finally we fabricate chalco-gel out of these solutions by solvent removal after 10 hours heat treatment of 50°C under vacuum, as photos shown in FIG. 5.3.

Figure 5.3: Photos of chalco-gel fabricated from mixing arsenic sulfide solution (0.8 mol/L) and various chlorides (0.05 mol/L) with a volume ratio of 4:1, followed by heat treatment in 50°C under vacuum for 10 hours.
5.2 Optical and structural characterizations

Immediately after the synthesis of these solutions, UV-Vis absorption measurements of these solutions were conducted using an Ocean Optics HR4000 high-resolution spectrometer. In order to characterize the morphology of the materials in thin films, TEM experiments were carried out on a Philips CM200 microscope operating at 200 KV, while their crystalline/amorphous pattern was investigated through electron diffraction measurements in the same microscope. High resolution images were acquired using a Gatan Orius 200 camera. Samples for TEM characterization were prepared by pouring a droplet of the 60x diluted colloidal solution solution onto 400-mesh copper grids covered with a holey carbon film (from Ted Pella). The excess solvent was then allowed to evaporate.

The suspensions were then deposited onto silicon wafers for SEM and ellipsometry analysis. A cleaning step was first performed on the substrates, which consists of a first step involving 30 min of ultrasonic bath in acetone, then 15 min of ultrasonic bath is applied in ethanol followed by drying with N\textsubscript{2} flux. Specifically, the solution was pipetted onto a silicon substrate, and the substrate was immediately spun at 1000 rpm for 30 seconds. Resulting films were soft-baked under vacuum at 60°C for 1 hour to remove most of the solvent and then hard-baked at 180°C for 7 hours to remove excess solvent and to further densify the glass [90]. Films prepared under these conditions typically were approximately 1 \( \mu \text{m} \) thick and ready for subsequent analysis. Ellipsometric characterization of the samples was performed using a Woollam M2000 variable-angle spectroscopic ellipsometer in the wavelength range from 100 to 2000 nm to investigate the properties of these materials, including thicknesses and refractive indices etc.

Upon successfully synthesis of the ion-doped chalcogenide materials, measurements of the properties were carried out. As photos of the generated ion-doped solutions of arsenic sulfide in FIG. 5.4 (inset) show, the color of these solutions gets
noticeably changed due to the outcome resulting from reaction between chalcogenides and chlorides. Absorption of these solutions is measured by UV-Vis spectroscopy using arsenic sulfide solution as a control. In the results shown, different curves denote spectra from solutions generated form different chlorides. The doping of different chlorides introduces shift of surface plasmon resonance bands. Arsenic sulfide doped with Pd, Pt, and Cu exhibit similar behavior the with only modification of the optical absorption edge. (b) The other group, including arsenic sulfide doped with Ni, Co and Fe, exhibits essential differences in not only the absorption edge but also the shape of absorption curve, among which $\text{As}_2\text{S}_3\langle\text{Co}\rangle$ is dissimilar from others, denoting the elementary absorption units are different. In the case of doping chlorides into arsenic sulfide solution, an almost identical behavior is observed.

As shown in FIG. 5.6, we propose a mechanism accounting for the doping and the resultant structure modification. When dissolved in propylamine, chalcogenides like arsenic sulfide/selenide turn into separate units size of several nanometers (medium-order range, [123]). Upon doping with various chlorides, the metal ions act as connecting pivots which attracts the lone pair electrons from chalcogen atoms, thereby the size as well as structure of chalcogenides units are modified. So when the photons interact with the doped material, sizes of the oscillating dipole moments get modified, which eventually altered the absorption behaviors. Different metal ions possess distinctive capability for the attraction of chalcogenides units. The fact that arsenic sulfide doped with Pd, Pt, and Cu exhibit similar behavior the with only modification of the optical absorption edge, evidences those ions creates modified chalcogenides units of similar structure with variance in the dipole moments. While the other subgroup of ions generate units with distinctive structures.

Refractive indices measurements by ellipsometry are shown in FIG. 5.7, these curves are similar with peak positions shifted.
SEM and TEM measurements are shown in FIG. 5.8. In the TEM diffraction pattern displayed in FIG. 5.8 (b), there’s no clear diffraction rings observed, which verifies the material is still in amorphous phase. The compositions of these materials are measured through EDX, for example, FIG. 5.9 shows results from iron doped arsenic selenide, where the relative weight of iron is measured to be 1.1%.

5.3 Summary

In this chapter, we present a novel solution-based framework to incorporate various metal ions into the chalcogenide matrices, including platinum (Pt$^{2+}$), palladium (Pd$^{2+}$), nickel (Ni$^{2+}$), cobalt (Co$^{2+}$), copper (Cu$^{+}$), and iron (Fe$^{2+}$), opening the door to a completely new family of metal ion doped chalcogenides, which are thermally and chemically distinct from the samples generated by the melt-quench method. This solution-based approach can readily achieve uniform doping, large area or thick films, and the same solutions can also be adopted for other precision dispensing techniques such as mold casting, ink jet or laser direct write, allowing spatial control over the added material [97]. Moreover, such strategy involving only one-step in-situ wet-chemistry processing at room temperature, features the simplicity of operation, low cost, and scalability, make itself attractive for the development of infrared optical devices.

In conclusion, we presented a systematic investigation on doping various metal ions into chalcogenide networks by solution processing and chemical reaction. We have used wet chemistry to produce in situ metal ion doped chalcogenides, in solution, thin-film, and gel phases. The chemical synthesis consists of the dissolution of the chalcogenides and chlorides in propylamine, and the mixture of both solutions using the ratio chalcogenides/chlorides = 1:0.25. Such method results in a fast formation of novel chalcogenides based materials. Confirmed by UVVis and ellipsometry
analyzes the fundamental properties such as absorption and refractive indices of the resulting chalcogenides are modified successfully due to the introduction of metal ions which act as linking center to connect chalcogenide units. Such doping strategy features the simplicity of operation, low cost, and scalability, opening a door to tailor the fundamental properties of chalcogenides by solution processing, which could be further utilized for MID devices fabrication.
Figure 5.4: Photos (inset) and UV-Vis absorbance spectrum of arsenic sulfide ($\text{As}_2\text{S}_3$) solution generated with PdCl$_2$, PtCl$_2$, CuCl, NiCl$_2$, CoCl$_2$, FeCl$_2$. $\text{As}_2\text{S}_3$ solution is included as a reference. The color change of those solutions indicates the optical absorption behaviors are modified. Two types of behavior emerged. (a) Arsenic sulfide doped with Pd, Pt, and Cu exhibit similar behavior with only modification of the optical absorption edge. (b) The other subclass, including arsenic sulfide doped with Ni, Co and Fe, exhibits essential differences in not only the absorption edge but also the shape of absorption curve, among which $\text{As}_2\text{S}_3\langle\text{Co}\rangle$ is very dissimilar from others, denoting the elementary units are distinctive.
Figure 5.5: Photos (inset) and UV-Vis absorbance spectrum of arsenic selenide (As$_2$Se$_3$) solution generated with NiCl$_2$, CoCl$_2$, FeCl$_2$, PdCl$_2$, PtCl$_2$, CuCl. As$_2$Se$_3$ solution is put aside as a reference. The color change of those solutions indicates the optical absorption behaviors are altered, which shares the similarity with the case of chlorides doped arsenic sulfide.
Figure 5.6: The underlying mechanisms of forming these novel materials. The positively charged metal ions approaches the chalcogenide units dissolved in the solution, get attached onto these units and further act as pivots further connecting multiple chalcogenides units through interaction with lone pair electrons possessed by chalcogen atoms.
Figure 5.7: Ellipsometry measurements on refractive index profiles of thin films fabricated out of arsenic selenide (As$_2$Se$_3$) and arsenic sulfide (As$_2$S$_3$) solution generated with different metal salts solutions. The curves share the similar shape with only peaks position modified.
Figure 5.8: (a) SEM measurements of cobalt doped arsenic sulfide. (b) Electron diffraction patterns from a cluster of the material, no clear diffraction rings are observed, indicating the synthesized material remain in amorphous phase.

Figure 5.9: EDX study of the TEM sample prepared using the As$_2$Se$_3$(Fe) solution. A 400-mesh copper grids covered with a holey carbon film was used as the substrate, which leads to the Cu peak. The relative weight of iron is 1.1%.
Chapter 6

Modifications through periodic optical nanostructures

In recent years, one of important advances in optics is the photonic crystals, fabricated by the state-of-the-art semiconductor nano-fabrication process, which realized various novel optical properties, such as: ultra strong light confinement in a wavelength-cubic volume; the extreme reduction in the speed of light frequency, resulting from frequency dispersion manipulation; as well as the unusual negative refraction as a result of their unique spatial dispersion.

Meanwhile it have been discovered the solution processed chalcogenides exhibits various striking physico-chemical properties, as discussed in the previous chapters. Researchers also have fabricated multi-mode arsenic sulfide waveguides using a method called micro-molding in capillaries methods [124], which lights up a possible way to combine the two powerful components in photonics – chalcogenides and photonic crystals, if we think of the air holes of silicon photonic crystal as capillaries.

In this chapter, we demonstrate the fabrication the two dimensional arsenide sulfide excitonic light emitter array utilizing a microtrench molding method. The air holes of silicon silicon photonic crystal are filled with chalcogenides. When excited by
CW lasers, the bulk emission of chalcogenides is altered by the confinement brought in by photonic crystal nano-structures. While from the opposite direction of view, by filling the holes with various chalcogenides, the essential properties such as refractive index contrasts and the resulting bandgap are readily modified in a controlled manner, activating a new freedom of photonic crystals. Moreover, since the novel photonic crystals utilize dispersive materials to achieve the holes filling and the refractive index contrasts, instead of the non-dispersive air, novel response to electro-magnetic excitation in frequency domain is anticipated.

6.1 Overview

6.1.1 Photonic crystals

As shown in FIG. 6.1, photonic crystals are composed of periodic structures with repeated high and low dielectric constant. The composition materials could be dielectric, metallo-dielectric or even superconductor microstructures or nano-structures. Similar to the way a semiconductor crystal affects the way that electron distributes, photonic crystals also define allowed and forbidden modes of photons, which also behaves as waves. It is the wavelength of the photons decides whether they are rejected or could propagate through the photonic crystals. Wavelengths that are allowed to travel are known as modes; groups of allowed modes form bands. Forbidden bands of wavelengths are known as photonic band gaps. It is worth noticing that light inside the band gap is forbidden to propagate in any direction. This unique features of photonic crystals lead to various optical phenomena and allow the manipulation of light in new and amazing ways due to their ability to control the propagation of light. Applications include the fabrication of lossless dielectric mirrors and resonant cavities for optical light, inhibition of spontaneous emission, high-reflecting omni-directional mirrors and low-loss-waveguiding. There are one-, two-, and three-dimensional pho-
tonic crystals. The fabrication methods include photo-lithography, or drilling holes drilling under different angles, stacking multiple layers on top of each other, direct laser writing, self-assembly of spheres in a matrix and dissolving the spheres etc.

Figure 6.1: Simple examples of one-, two-, and three-dimensional photonic crystals. The different colors represent materials with different dielectric constants. The defining feature of a photonic crystal is the periodicity of dielectric material along one or more axes [125].

Figure 6.2: A complete photonic band gap of a 1D photonic crystal [125].
Photonic crystals have numerous applications due to their ability to control and manipulate the flow of light, as well as distinct and engineerable optical properties \[125\]. For example, one dimensional photonic crystals can be used in thin-film optics with applications ranging from low and high reflection coatings on lenses, as well as omni-directional reflectors and low-loss optical filters. 2D photonic crystals can find their applications in photonic-crystal fibers and waveguides, logic devices such as optical switches. Compared to the situation that the two dimensional photonic crystals are beginning to find commercial applications, the development of 3D photonic crystal is still far from mature due to the difficulty with fabrication, and may have great potential in areas such as optical computation etc. Among various applications, it’s also worth noticing that photonic crystal is demonstrated to manipulate vertical light emission of material placed upon \[126,127\], lower \[128\] and within the photonic crystal plane \[129\].

### 6.2 Chalcogenide photonic crystal light emitters

We fabricate two dimensional arsenide sulfide photonic crystal excitonic light emitter by a microtrench filling method. The interference between subwavelength periodic light emitter leads to strong enhancement of far field intensity within the bandwidth of the substrate forbidden modes. Complementary metal-oxide-semiconductor (CMOS) processed silicon photonic crystals with angstrom surface roughness are used to spatially confine the solution processed materials and form periodic structure. Arsenic sulfide is one of the binary chalcogenides whose atomic network is van der Waals bonded two dimensional layers. The weak bonding force between layered structure leads to easy peel off with the drop-casting condensation in periodic silicon porous structure, leaving isolated arsenic sulfide disks to form self-assembling of two dimensional array in silicon module. Under visible CW light excitation, the planar emitter
array, surrounded by higher refractive index material silicon, enhances vertical extraction of light within the spectral bandwidth where the guiding modes are prohibited in the photonic crystal plane, and effectively modify the emission/absorption spectrum [126, 128, 130]. The indirect bandgap material silicon offers a robust platform for smooth geometric confinement of solution processed materials, compared to direct lithographic patterning. We experimentally demonstrated that the 2-D photonic crystal enhanced vertical emission magnitude of $\approx 2$ within the bandgap frequencies, for high efficient light-emitting diode [131]. Integration of solution processed chalcogenide with silicon devices is an easy and low cost solution for on-chip broadband light source in silicon photonics.

### 6.2.1 Fabrication

The nano-patterns were fabricated on a 250 nm thick silicon-on-insulator device layer via optimized 248 nm deep ultraviolet lithography and etching for reduced disorder scattering. It is worth noticing that the nano-imprint technique is available to speed up the fabrication process [132]. The lattice constant of the photonic crystal is 415 nm with hole radius varying from 90nm to 140nm in step of 10 nm. The sacrificial release of supporting silicon oxide buffer layer is performed by wet etch. Then the arsenic sulfide solution was prepared following the standard procedure: bulk $\text{As}_2\text{S}_3$ pieces were grinded into a fine powder and dissolved into n-propylamine solvent at a concentration of 0.8 mol/L. Dissolution was carried out inside a sealed glass chamber to prevent solvent evaporation. The dissolving process took more than three days and a magnetic stirrer was used to expedite this process. Exposure of solution to atmospheric moisture was kept to a minimum throughout preparation procedure since water can lead to precipitate formation. Droplets of the colloidal solution were then poured onto the silicon device to get the holes of the silicon pattern filled. The excess solvent was then allowed to evaporate and dry off. As we discussed in previous
Figure 6.3: Flow chart of the device fabrication. (a) Diagram and SEM image of 2D photonic crystal hexagonal nano-patterns fabricated on 250 nm thick silicon membrane by deep UV lithography. The lattice constant of the photonic crystal is 415 nm with hole radius varying from 90nm to 140nm in step of 10 nm. (b) The sacrificial substrate is removed through wet chemistry etch. (c) The silicon membrane of photonic crystal is drop cast with arsenic sulfide solution. (d) The weak van der Waals bonding force between layered structure leads to easy peel off with the drop-casting condensation in periodic silicon structure, leaving isolated arsenic sulfide disks to form self-assembling of two dimensional array in silicon module.

chapters, the atomic network of arsenic sulfide is van der Waals bonded two dimensional layers. The weak bonding force between layered structure leads to easy peel off with the drop-casting condensation in periodic silicon porous structure, leaving isolated arsenic sulfide disks to form self-assembling of two dimensional array in silicon module.
Figure 6.4: Geometric structures. (a) SEM of the chalcogenide array in silicon supporting structure. (b) EDX mapping showing the periodic nano-structures of silicon. (c) EDX mapping demonstrating the periodic chalcogenide distribution resulting from the hole filling. (d) Side view of the chalcogenide-silicon photonic crystal array. (e) EDX spectrum with electronic beam concentrated on the chalcogenide part.

6.2.2 Characterizations

As shown in FIG. 6.5, the geometric structure of chalcogenide and silicon is given by a Quanta 200 FEG environmental SEM at 5keV in high vacuum mode. Energy-dispersive X-ray spectroscopy (EDX) mapping equipped with SEM is used to verify the nano pattern of chalcogenide 250 nm thick silicon membrane in the supporting
anti-dot region and the hole region contains arsenic. The results show the formation of uniform arsenic sulfide array without solvent-specific composition. With limited residual from solvent, the surface roughness of silicon is measured to be 1 nm by atomic force microscope.

We then characterize the hetero nano-structure by Raman spectroscopy and photoluminescence. Identification of the Raman peak of As$_2$S$_3$ is found at 323.5 cm$^{-1}$ and the silicon substrate at 521.4 cm$^{-1}$, with 532nm continuous wave laser excitation and spectral resolution of 0.67 cm$^{-1}$, as shown in FIG. 6.7. Anti-stokes Raman peak at 530 cm$^{-1}$ is also observed with as-prepared samples. Anti-symmetric As-S-As stretching vibration in As$_2$S$_3$ pyramidal unit leads to the broad band Raman signal. The mapping of chalcogenide Raman peak intensity shows a typical profile of effective media of chalcogenide confinement in the porous silicon region, defined in a 20 micrometer wide strip of the hybrid structure (Inset of FIG. 6.7). Outside the photonic crystal region, the Raman signal of As-S-As is minimized to zero (white part in the
Figure 6.6: Optical properties of arsenic sulfide: absorption (black) and photoluminescence (red). The absorption curve measured through UV-vis of an arsenic sulfide film on glass substrate (2\(\mu\)m thick), shows a bandgap around 2.4 eV and a low absorption coefficient above 550nm. Under 532nm laser excitation, chalcogenide’s photoluminescence spectrum of bulk As\(_2\)S\(_3\) gives a major peak at 691 nm (1.80 eV) central wavelength and 104 nm bandwidth.

Figure 6.7: Optical properties of the material. Raman spectrum of the chalcogenide-silicon photonic crystals. Inset: Intensity mapping of the As-S-As bond at 330 cm\(^{-1}\), where chalcogenide is only found in the photonic crystal region. Scale bar: 5\(\mu\)m
inset of FIG. 6.7. Under 532nm laser excitation, chalcogenide’s photoluminescence spectrum gives a major peak at 691 nm (1.80 eV) central wavelength and 104 nm bandwidth.

Photo-luminescence spectrum is collected by coupling the light emitted from the sample to an Invia Raman spectrometer through a ×50 objective (Renishaw) as results shown in FIG. 6.8. Under subwavelength patterning, the emission spectrum is enhanced/suppressed by coupling to substrate forbidden/guiding modes. In FIG. 6.10 we list the enhanced modes for photonic crystals with different hole radii, for example, the two enhanced peaks from the photonic crystal with 90 nm holes are located at 677.5 nm and 820.1 nm. Similar to the mechanism of 1-D standing wave, the variation of the hole radii of the photonic crystal structure leads to distinctive periodic structure, which thereby results in different the energy redistribution. Moreover there are substrate conductive modes where vertical emission is suppressed. The behavior how the photonic crystal structure modifies the bulk emission of chalcogenides could be readily calculated by solving Maxwell equation with boundary conditions.

### 6.3 Summary

In conclusion, we use CMOS processed silicon photonic crystals with Angstrom surface roughness to spatially confine the solution processed arsenic sulfide. A dimensional amorphous chalcogenide photonic crystal light emitter array is fabricated based on this novel periodic hetero-structures of semiconductor. We use SEM, EDX, AFM to measure the structure, composition, as well as surface morphology of the device, whose optical responses are disclosed by Raman and photo-luminescence excited by a CW 532nm laser. Combining chalcogenides and photonic crystals, two powerful components in photonic, this nano-structure exhibits novel properties and great potential. The confinement from photonic crystals introduces immediate manipulation to the
chalcogenides bulk emitters. At the meantime, the self-peel-off behavior due to the layered structure from chalcogenides enables a uniform filling in photonic crystal fabrication, which is not as easily achieved by other means. Upon excitation from a CW 523 laser, under confinement from subwavelength patterning, the emission spectrum is enhanced/suppressed by coupling to substrate forbidden/guiding modes.

Based on the results showed above, novel devices could be fabricated in IR range, including filter, emitters where the modifications of the spectra are necessary. Also by combining the photonic crystals with different chalcogenides such as arsenic selenide as well as the ion-doped chalcogenides, various emitter arrays could be readily manufactured. Meanwhile, by filling the holes with various chalcogenides, the essential
Figure 6.9: Photoluminescence spectra of the photonic crystal emitter arrays with lattice constant of 415nm and a variety of hole radius, from 90 to 140 nm, with a step size of 10nm. Spectra are summarized together for a comparison, where shapes and resonances of the spectra are distinctive, denoting an energy redistribution resulting from the confinement from photonic crystals.

properties such as refractive index contrasts and the resulting bandgap are readily modified in a controlled manner, activating a new freedom of photonic crystals. It’s foreseen that new progresses could be made in the various applications photonic crystal structures have enabled, such as the confining and slowing of light. Moreover, since the novel photonic crystals utilize dispersive materials to achieve the holes filling and the refractive indice contrasts, instead of the non-dispersive air, novel response to electro-magnetic excitation in frequency domain is anticipated. At last, it would be of interest to deposit a thin layer of silver on top of the chalcogenides photonic crystal, and a laser beam could be introduced afterwards to enable a selective photo-doping.
Figure 6.10: Enhanced modes for photonic crystal emitters with different holes. For photonic crystal emitter array with hole radius of 90 nm, modes of 677.5 nm and 820.1 nm are enhanced, while the resonance modes are \{647.6 nm, 790.1 nm\} for 100 nm-, \{636.2, 741.1\} for 110 nm-, \{643.3, 676, 719.8, 746.9\} for 120 nm-, \{668.8, 691.5, 711.7\} for 130 nm-, \{670, 699.5, 744\} for 140 nm-, respectively.
Chapter 7

Conclusion and perspectives

7.1 Conclusions

The main aim of this dissertation is to explore possible means to modify the properties of chalcogenide glasses. And the major results and progresses in this dissertation can be summarized as follows.

The first kind is about the structural modifications through light exposure. The shape changes of the thin film are created when exposed to light pattern. We then investigate the mechanisms of photo-induced surface relief formation. With our generalized model combining the photo-induced pressure and navier stokes for viscous flow, we identify the physical origin and quantify the kinetics of this process.

Another way is to modify the chemistry of the materials, which is achieved through the photo-doping effects, where silver is deposited close to the thin films, and finally gets incorporated into the chalcogenide system upon illumination by light. It has been demonstrated by depositing a thin layer of silver on top of chalcogenides, while we show a method to incorporate silver nanoparticles uniformly throughout the material, using pulse laser ablation and solution processing. The aggregation of the
nanoparticles which is usually inevitable using other doping technique is successfully avoided.

Besides the uniform doping of nanoparticles, we are able to incorporate a variety of ions into chalcogenide glassy matrices using in-situ wet chemistry processing. Various chlorides are incorporated into chalcogenide matrices, leading to multifarious property changes, such as absorption and refractive indices of the chalcogenides.

Moreover, we also explore modifications through photonic crystals. We use CMOS processed silicon photonic crystals with angstrom surface roughness to spatially confine the solution processed arsenic sulfide and achieve controllable modulations of chalcogenides emission. A planar emitter array of chalcogenides is fabricated based on this novel periodic hetero-structures of semiconductor.

7.2 Future direction

We have demonstrated a generalized mechanisms of photo-induced surface relief formation, which has been proven to be accurate and sufficient. It’s noticeable the microscopic and macroscopic understanding as well as the equation of motion we present inherently consist of the vectoral electric fields, thereby setting a solid step toward unifying all the photo-induced vectoral effects, such as photo-induced surface relief formation, photo-induced anisotropy (both including dichroism and birefringence), which is critical in completely understanding the physics of amorphous glassy materials, as an important part of the modern solid state physics.

Moreover, uniform doping of silver nanoparticles into chalcogenide glassy materials has been achieved, which opens the door for devices fabrication utilized the photodoping effects and thick chalcogenides films, such as beam combiner and holographic storage systems in mid-IR. The next step utilizing the same technique to dope different metals as well as semiconductors nanoparticles like Ge, GaAs to make
a hetero semiconductor systems could be of importance in a number of areas such as uniform doped quantum dots array.

In addition, we have synthesized a new class of chalcogenides using in-situ wet chemistry processing, which exhibit novel optical properties such as new absorption and refractive indices of the chalcogenides. A further investigation of all the active and passive properties, such as nonlinear optical responses, photo-luminescence is helpful to achieve a deeper understanding of this new family of chalcogenides. We also foresee potentials of a further strategy of enlarge this family of chalcogenides by mixing current species to achieve refractive indice and absorption tuning. In addition, these materials could be used for device fabrications such as IR waveguides, photonic crystal devices.

Finally, based on our results on chalcogenides emitter utilizing the silicon photonic crystals, novel devices could be fabricated in IR range, including filter, emitters where the modifications of the spectra are necessary. Also by combining the photonic crystals with different chalcogenides such as arsenic selenide as well as the ion-doped chalcogenides, various emitter arrays could be readily manufactured. Meanwhile, by filling the holes with various chalcogenides, the essential properties such as refractive index contrasts and the resulting bandgap are readily modified in a controlled manner, activating a new freedom of photonic crystals. It’s foreseen that new progresses could be made in the various applications photonic crystal structures have enabled, such as the confining and slowing of light. Moreover, since the novel photonic crystals utilize dispersive materials to achieve the holes filling and the refractive indice contrasts, instead of the non-dispersive air, novel response to electro-magnetic excitation in frequency domain is anticipated. At last, it would be of interest to deposit a thin layer of silver on top of the chalcogenides photonic crystal, and a laser beam could be introduced afterwards to enable a selective photo-doping.
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