

A Review of Photo-Induced Inter-Diffusion in Nano-Layered Chalcogenide Films

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Abstract | A growing interest in the research of chalcogenide glasses can be currently witnessed, which to a large extent is caused by newly opened fields of applications for these materials. Applications in the field of micro- and opto-electronics, xerography and lithography, acousto-optic and memory switching devices and detectors for medical imaging seem to be most remarkable. Accordingly, photo induced phenomena in chalcogenide glasses are attracting much interest. These phenomena can be found both in uniform thin films as well as multilayered films. Among amorphous multilayers, chalcogenide multilayers are attractive because of the potential it has for tailoring the optical properties. I will be presenting some basic idea of photoinduced effects followed by the diffusion mechanisms of Se, Sb and Bi in to As_2S_3 films.

1. Introduction

Chalcogenide glasses are known to manifest a variety of photoinduced phenomena.¹⁻⁴ The photoinduced anisotropy phenomenon, which was demonstrated in chalcogenide, is one of them. One of its manifestations is an optical birefringence under the irradiation of amorphous chalcogenide by linearly polarized light. To explain the results of experimental investigations, various models were proposed, in particular, those considering the native U-charged defects,⁵ the orientations of normal bonding orbitals,⁶ or certain structural formations.⁷ The appearance of the well-known photoinduced optical anisotropy, which disappears after thermal annealing is also possible. The formation of the optical anisotropy of fresh specimens is explained by the formation of a microstructure units of As_4S_4 and S.⁸

The availability of amorphous semiconductors in the form of high quality multi-layers provides

potential applications in the field of micro- and optoelectronics.^{9,10} Among amorphous multi-layers, chalcogenide multi-layers are attractive because of the prominent photoinduced effect.¹¹⁻¹³ These amorphous nanolayered chalcogenide structures (ANCs) are similar to crystalline super lattices, yet distinct from the ideal crystalline super lattices produced by molecular beam epitaxy. The ANCs can be thought of as well-correlated layers with good periodicity and smooth interfaces. A surface geometry analysis made with an atomic force microscope (AFM) showed that the surface roughness of these ANCs is 0.5 to 1 nm.¹⁴ These ANCs exhibit prominent photoinduced effects which are similar to those exhibited by uniform thin films. For example, photoinduced interdiffusion in short period multilayer systems is important because of its potential applications in the holographic recording and fabrication of phase gratings.^{10,12} In spite of its practical usefulness,

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Chalcogenide glass: is a glass containing one or more chalcogenide elements (sulfides, selenides, and tellurides)

the mechanism of photoinduced interdiffusion is not properly understood. Since most structural transformations are related to atomic diffusion, an understanding of the structural transformation must be based on the diffusion process.

2. Optical Properties

Most chalcogenide glasses have their band gap lying between 1-3 eV of the electromagnetic spectrum. A typical energy-dependent optical absorption spectrum for a chalcogenide glass is divided into three regions¹⁵ as shown in Figure 1. Region I is believed to arise directly from transitions involving defect-states as the absorption in this region has been found to depend strongly upon the material preparation and thermal history.¹⁶ On the other hand, for nearly all chalcogenide glasses, region II is characterized by exponential behavior, termed the 'Urbach edge'.¹⁷ In most of the chalcogenide systems investigated, absorption in region III deviates from exponential behavior and occurs in the final states beyond the band-tails. Region III is where the value of absorption coefficient (α), $\alpha \geq 10^4 \text{ cm}^{-1}$ is termed as the Tauc Region and can be written as $\alpha h\nu = B(h\nu - E_g)^s$ where $s = p + q + 1$ and p and q are equal to $1/2$ in special cases, where both valence and conduction band edges have a parabolic shape.

At the energy levels where the Tauc model is used (for photon energies corresponding to $\alpha > 10^4$), the joint density of states does not include tail states.¹⁸ The information at the band

tails was obtained from Urbach energy. The absorption coefficient in this region is governed by the equation¹⁷

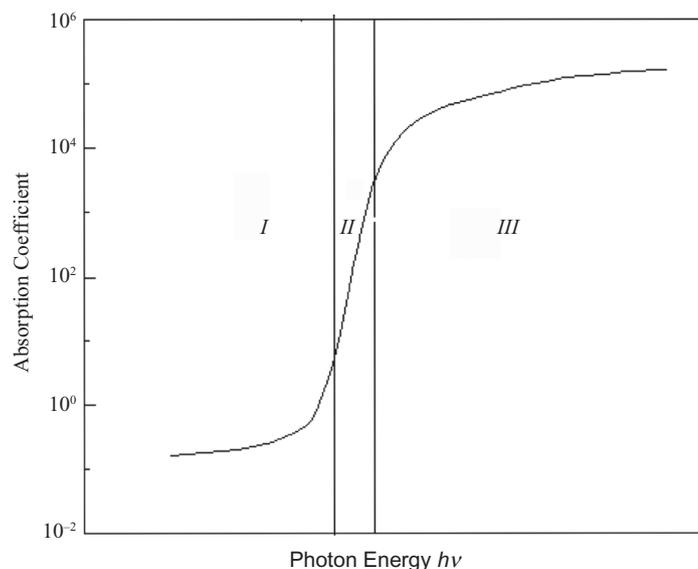
$$\alpha = \alpha_0 \exp\left(-\frac{E_0 - h\nu}{E_e}\right)$$

where E_0 , α_0 , and E_e are optical bandgap, absorption coefficient at E_0 and Urbach energy respectively. The origin of the Urbach edge is still unclear, but two general mechanisms may be responsible: either the exponential dependence of α arises from the exponential energy dependence of valence and conduction band densities at the band edges (ignoring matrix element effects) or a universal absorption mechanism exists, which gives rise to the exponential behavior of α , e.g., the field broadened exciton model of Dow and Redfield, Abel and Yoyozawa and Soukoulis et al.¹⁹⁻²¹ Theoretically it has been shown that exponential band tails can result from potential fluctuations associated with structural disorder.²¹ Although there is experimental evidence in the case of *a*-Si:H that the magnitude of E_e is determined by the degree of disorder, that of chalcogenide is not very clear.

3. Photoinduced Effects

The irradiation of semiconductors and insulators with bandgap light produces hole-electron pairs. Such optically excited carriers can subsequently separate, thereby contributing to the electrical response of the material (e.g. photoconductivity) or recombine either radiatively (e.g. photoluminescence) or non-radiatively. The non-radiative recombination of these excited hole-electron pairs can leave the material in a state which is different from the initial state (e.g. defects creation). In crystals, because of the constraints imposed by lattice periodicity on the positions of atoms, the number of pathways available to the hole-electron pairs is rather limited. Amorphous semiconductors and insulators can exhibit a number of photoinduced phenomena because of the following two reasons. The first is the flexibility and freedom associated with the atomic structure from the relaxation of crystallographic constraints in the amorphous state. The second is the presence of structural disorder which leads to the localization of electron hole pairs at the band edges near the bandgap. Such disorder-induced localization of the charge carriers results in photostructural changes. Photostructural changes are favoured in chalcogenide glasses because of their structural flexibility (low coordination of chalcogens) and the lone pair p states in the valence band.²² Shimakawa broadly classified photo-induced effects into defect-related photo-induced effects and

Figure 1: Schematic representation of absorption spectrum in chalcogenide glass.



structure-related photoinduced effects.³ Defect-related photoinduced effects are photoluminescence fatigue, electron spin resonance, midgap absorption, decay of photoconductivity and ac conductivity and structure-related photoinduced effects are photodarkening, photocrystallization (or amorphization), photopolymerization, photo contraction or expansion, photo dissolution or diffusion and photoinduced fluidity.

3.1. Photoluminescence Fatigue

Irradiation with above bandgap light reduces the intensity of Photoluminescence (PL) in amorphous chalcogenides and is termed PL fatigue.²³ The rate of PL fatigue depends on irradiation intensity and excitation energy. PL fatigue is stable at low temperatures but is recovered by heating or IR irradiation.^{3,24} PL fatigue with short-time irradiation was recovered by annealing at 150 K, while PL fatigue with long-time irradiation was recovered only after annealing at room temperature.²⁵ The most plausible interpretation of the fatigue of PL for short-time irradiation is due to the increase of non-radiative recombination channels associated with the D^0 state, resulting from the occupation of an electron or a hole in preexisting charged defects. Moreover, the D^0 state is responsible for light-induced electron spin resonance and midgap absorption. PL fatigue due to prolonged illumination is mainly because of the formation of new metastable self-trapped excitons (mSTE), which destroys radiative, self-trapped excitons. The results show that the mSTEs act as non-radiative recombination centers with a thermal stability greater than the D^0 non-radiative centers.

The enhancement of PL intensities by photo-induced interdiffusion in nano-layered a -Se/ As_2S_3 were reported by Adarsh et al.²⁶ PL studies on nonirradiated and irradiated multilayered samples of a -Se/ As_2S_3 (sublayer thickness of a -Se is 4–5 nm for one set of samples and 1–2 nm for the other set. However As_2S_3 sublayer thickness is 11–12 nm for both sets of samples) showed an increase of PL by several orders of magnitude when the Se well layer (lower band gap) thickness was reduced. This was further increased by irradiating the samples with appropriate wavelengths in the range of the absorption edge. The broadening of luminescence bands takes place either with a decrease in Se layer thickness or with irradiation. The former is due to the change in interface roughness and defects because of the increased structural disorder, while the latter is due to photo-induced interdiffusion. The photo-induced interdiffusion creates defects at the interface between Se and As_2S_3 by forming an As–Se–S solid solution. From the deconvoluted

PL spectrum, it is shown that the peak PL intensity, full width half maximum, and the PL quantum efficiency of particular defects giving rise to PL, can be tuned by changing the sublayer thickness or by interdiffusion. It is also shown that the optical parameters can be changed with a change in the Se sublayer thickness.

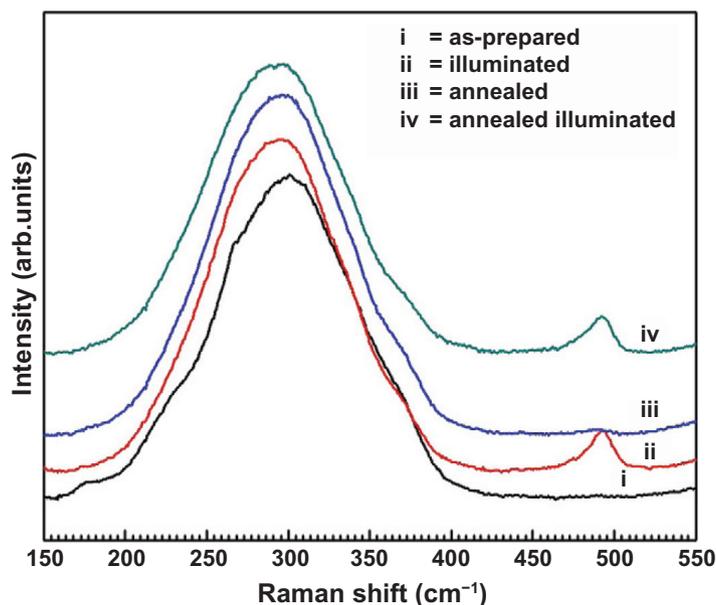
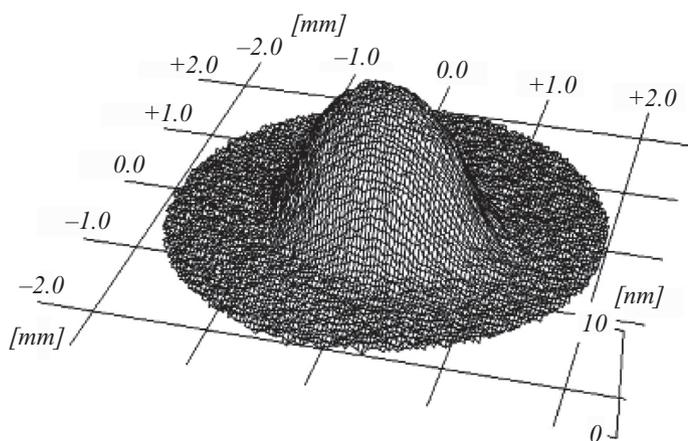
3.2. Midgap Absorption

Irradiation at low temperatures induces a midgap absorption in amorphous chalcogenides, which disappears with low temperature annealing.^{27,28} The precise shape of the midgap absorption depends on the intensity and wavelength of the inducing light.²⁵ The midgap absorption bands have been ascribed to electron or hole transitions to the conduction band or valence band respectively from the optically induced defect D^0 centers. Midgap absorption is always annealed out above 200 K since the defects are not stable above this temperature.

3.3. Photoinduced Fluidity

Hisakuni and Tanaka observed that the glass transition can be induced by light in a number of chalcogenide glasses.^{29,30} They demonstrated that photo-induced fluidity is caused not by heating but by photo-electronic excitations. The most provocative feature of photo-induced fluidity is its anomalous temperature dependence i.e. photo-induced fluidity is more efficient at low temperatures than at high temperatures.³¹ Photo-induced fluidity is caused by the cumulative effect of recombination-induced atomic motions and bond changes during irradiation. These photo-structural changes are favored in chalcogenides because of the rapid localization of photo-excited carriers, the low energy of VAPs and the freedom of low-coordination atoms to change their positions and bond configurations.³²

Direct evidence of structural changes in $(As_2S_3)_{0.85}Sb_{0.15}$ thin films caused by annealing and illumination has been obtained from the Raman Spectra.³³ According to the molecular model,³⁴ each Sb atom in the As–Sb–S ternary glasses is covalently bonded to three S atoms in a pyramidal unit ($Sb-S_3$), and As atoms are covalently bonded to three S atoms in a pyramidal unit ($As-S_3$). The basic structural units AsS_3 and SbS_3 are interconnected through bridging S atoms. The coupling between the basic structural groups via S atoms is assumed to be weak, and the vibrational modes are separated into AsS_3 and SbS_3 like modes. The $(As_2S_3)_{0.85}Sb_{0.15}$ films have an over stoichiometry of metal atoms (As, Sb), and some As–As, Sb–Sb bonds should be present in the films, too. The SbS_3 pyramidal vibrational band is positioned at 302 cm^{-1} in the

Figure 2: Raman spectra of $(As_2S_3)_{0.85}Sb_{0.15}$ thin film.Figure 3: Surface height map for an As_2Se_3 film.

neighborhood of the dominant vibrational band of AsS_3 in the Raman spectra (Figure 2). In the spectrum shown in Figure 2, it is clear that the main band at 302 cm^{-1} is due to the $Sb-S$ vibration in $Sb-S_3$, $(S_2) Sb-Sb (S_2)$ and the AsS_3 mode is superimposed on that band. The peak at 491 cm^{-1} corresponds to disulfide bonds $S-S$ (or two membered S_2 chains) in $S_2As-S-S-AsS_3$ vibration. The illumination of the as-prepared film causes an increase in homopolar bond density due to which the $S-S$ peak at 491 cm^{-1} appears to be more prominent than the as-prepared film due to the

formation of a greater number of $S-S$ homopolar bonds. But in case of annealed film, the $S-S$ bonds are destroyed which can be seen clearly in the Raman Spectra. This clearly shows the photo induced structural changes in these glasses.

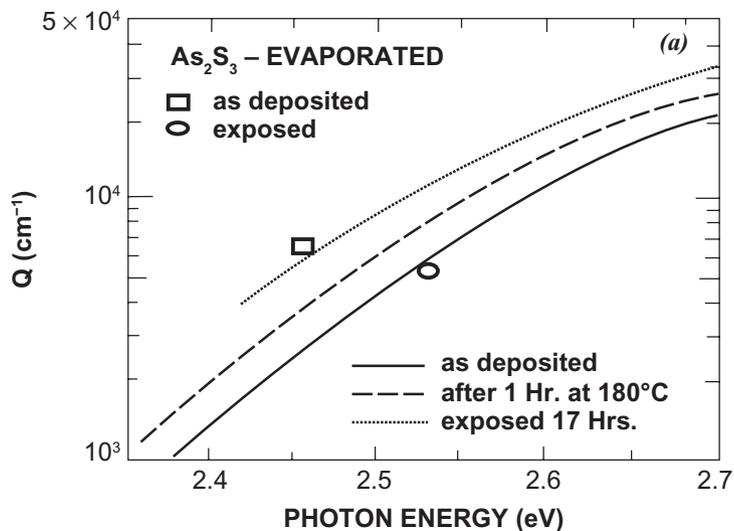
3.4. Photoexpansion

The irradiation of amorphous chalcogenide films with bandgap light produces an increase in thickness and is termed photoexpansion.^{35,36} It has been demonstrated that amorphous As_2S_3 film will expand by about 0.5% when irradiated with bandgap light, and by 4% (giant Photoexpansion) when irradiated with sub bandgap light.³⁷ Both the photoexpansion and the giant photoexpansion disappeared after annealing the samples near the glass transition temperature. Similarly when the material is irradiated with super bandgap light, photodepression was observed and is ascribed to photovaporization.³⁸ New exciting possibilities of optical micro fabrication were opened up by this discovery, since the response of the medium is local.³⁹ Figure 3 shows an example of the surface height map of As_2Se_3 film measured during photoexpansion by a Twyman-Green interferometer.⁴⁰ Photoexpansion was explained based on the charging model.⁴¹ According to this model, photo-excited electrons remain in the irradiated region, and photo-excited holes diffuse away from the irradiated region, owing to the higher diffusion coefficient of holes in the amorphous chalcogenides. Thus the irradiated region becomes negatively charged, causing the layer to expand and minimize the coulombic repulsion.

3.5. Photodarkening

The irradiation of chalcogenides with bandgap or near bandgap light can lead either to an increase or decrease in bandgap, depending on the material and preparation conditions.³ The shift of the optical absorption edge to lower energies is called photodarkening and the reverse is termed as photobleaching. Photodarkening⁴²⁻⁴⁵ is commonly observed in As based chalcogenides. Annealing the photodarkened samples, near the glass transition temperature leads to the recovery of the initial parameters but the recovery is not complete and is shown in Figure 4. If the annealed film is again irradiated, the optical absorption shifts to a lower energy. On subsequent annealing of the film, the bandgap recovers to the initial parameters of the previously annealed film.^{42,43} This completely reversible behavior during illumination-annealing cycle is called reversible photodarkening. It is believed that the reversible part of photodarkening is due to the change in

Figure 4: Influence of irradiation and annealing on the optical absorption of As_2S_3 film.



chalcogen lone-pair interactions, which induce the broadening of the valence band. This broadening of the valence band reduces the optical bandgap and the result is photodarkening. A variety of models have been proposed in support of the above mechanism, but none of them were successful in explaining these phenomena in a complete sense.⁴⁰ The existing models can be classified into the following categories: 1) change in atomic positions⁴⁶ 2) bond breaking⁴⁷ and 3) electronic charging of the illuminated regions.⁴¹ Recent experimental results are in favor of the electronic charging model.⁴⁰ According to the electronic charging model, photo-excited electrons remain in the irradiated region, and photo-excited holes diffuses away from the irradiated region, owing to the higher diffusion coefficient of holes in the amorphous chalcogenides. Due to coulomb interaction, neighboring atoms slip away from a position of equilibrium and the change in the mutual positions of the atoms results in a change in interaction between the lone-pair electrons. This causes a change in the forbidden gap and results in photodarkening.⁴¹ The irreversible part, which never recovers after annealing near the glass transition temperature, is termed as the irreversible photo-darkening. The irreversible part of photo-darkening is believed to be caused by the thermal polymerization of the as evaporated film, which is formed from numerous vapor species present during the evaporation procedure.³ In Ge based chalcogenides, the photobleaching observed is mainly due to the bond-breaking mechanism.

During irradiation, the heteropolar bonds replace homopolar bonds.⁴⁸ This mechanism result in a change in band structure and produces the photobleaching effect.

3.6. Photoinduced Diffusion

A very important photoinduced effect in amorphous chalcogenides is the photoinduced diffusion of elements. The effect was first observed by Kostyshin et al.⁴⁹ They observed a large dissolution of certain metals in chalcogenides under light irradiation. The photoinduced diffusion is exhibited by Ag, Zn, Bi, and Se and the mechanism of photoinduced diffusion for different elements may be different.^{11,49-58} The most notable among photoinduced diffusion is the behaviour of Se observed with illumination of above band gap light in nanolayered $\text{Se}/\text{As}_2\text{S}_3$ films.¹¹ The experimental data of $B^{1/2}$ and E_e for as-prepared samples do not show the clear correlation implied by the Mott-Davis model. The increase found in $B^{1/2}$ after photodiffusion was coherent with a corresponding decrease of Urbach energy. This fact was discussed in terms of the structural changes induced by the photoinduced interdiffusion, i.e., the creation of new bonds between components, which modified the conduction and valence bands. XPS analysis showed that, during photodiffusion, homopolar bonds were replaced by heteropolar bonds, i.e., the irradiated samples were more chemically ordered than the corresponding as-prepared samples. Mott-Davis had proposed a model to describe the photodiffusion, which suggests that diffusion takes place through the wrong bonds. They had also shown that the optical parameters can be changed with a change in the Se sublayer thickness. Variations of these optical parameters as a function of the modulation period and photoinduced interdiffusion were discussed in terms of the quantum confinement effect and changes in the valence and conduction bands.

The kinetics of photoinduced effects in nanolayered $\text{Se}/\text{As}_2\text{S}_3$ film by *in situ* optical absorption measurements reveal that photodarkening in these films is followed by photoinduced diffusion.⁵⁷ An increase in disorder during photodarkening and its subsequent decrease during photoinduced diffusion were also observed. The photodarkening of Se at room temperature when confined between As_2S_3 layers suggests that the glass transition temperature of Se shifts to a higher energy. The analysis shows that the atoms which take part in photodarkening play a vital role in photoinduced diffusion. X-ray photoelectron spectroscopy measurements show atomic movements during photoinduced diffusion.

They also show that some of the As–S bonds are converted into As–Se bonds. Since it is energetically difficult to break an As–S bond to form an As–Se bond, we assume that the new bond formations are taking place by a bond rearrangement mechanism.

The role of compositional modulation at nano-scale dimensions (–2–10 nm) in the enhancement of optical recording parameters in nanomultilayers, which contain Sb as active, optical absorbing and diffusing layers and As_2S_3 as barrier (matrix) layers was investigated.^{58–61} A comparison was made with single homogeneous layers made of ternary $(\text{As}_2\text{S}_3)_x\text{Sb}_{1-x}$ glasses and co-deposited from Sb and As_2S_3 . It was shown that an essential increase of the recording efficiency, sensitivity of the bleaching process and broadening of its spectral range occurs due to the stimulated interdiffusion of adjacent components in Sb/ As_2S_3 nanomultilayers with optimized Sb layer thickness.

4. Photoinduced Effects in Other Amorphous Systems and Polymers

There is marked similarity in the photoinduced response of chalcogenides and a-Si:H (silicon hydrides). a-Si:H shows photoinduced effects such as photoluminescence fatigue, decrease in photoconductivity after prolonged illumination, change in ac conductivity, midgap absorption and photoinduced diffusion of hydrogen.^{3,62–65} a-Si:H exhibits ESR under dark conditions at low temperatures, and this is increased by light irradiation.⁶⁵ a-Ge:H also exhibits similar kinds of photoinduced effects.³ Photodarkening was not observed in these materials since the structural flexibility is very less compared to the chalcogenide glasses.

The atomic structure of oxide glasses is considered more stable against exposure to light due to the large bandgap. Ultraviolet radiation, however, induces photoinduced effects such as photo densification, photorefractive and also photoinduced anisotropy.^{54,66–68}

Polysilanes are another group of compounds which exhibit photoinduced ESR, change in photoconductivity and ac conductivity. Since the structural flexibility in these materials is higher than in chalcogenides, they exhibit photobleaching which is in sharp contrast to the photodarkening in chalcogenides.^{3,69,70}

Polymers are usually soft materials and exhibit photoinduced effects. Due to the poor stability of polymers, photoinduced effects not only lead to a change in physical structure but also to a change in chemical structure and composition. Leading examples of polymers include those based on azobenzene, spiropyran, fuldigenes and

diarylethenes. Among them, azo-polymers have been investigated most extensively.^{54,71–74}

5. Current Status

Chalcogenide materials are of interest for a variety of reasons: they can be prepared in amorphous form either as vapor deposited thin films or as met quenched glasses, their physical properties vary continually. They exhibit behavior which is often unique and finally they have a number of potential technological applications. For example, a-Se is a classic material for Xerographic applications⁷⁵ and has recently been highlighted as a promising photoconductive material for digital X-ray radiography.⁷⁶ Certain chalcogenides can be reversibly interchanged from the amorphous to crystalline state by suitable light exposure; a property which has been applied to high density read and write memory storage devices.⁷⁷ Some chalcogenides ($\text{As}_{12}\text{Ge}_{33}\text{Se}_{55}$) are promising host media for rare-earth photonic devices.^{78,79} The recently observed linear magneto resistance in silver doped chalcogenides makes it an attractive candidate for high field magnetic sensors.⁸⁰ Also, the non-linear optical properties of chalcogenide glasses have become the focus of growing scientific and technological interest.^{22,81–83} These glasses are optically highly non-linear and could therefore be useful for all-optical switching.⁵⁶

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Research Interest

Role of defects in chalcogenide glasses.
 p to n conduction changes in glasses.
 Light induced anisotropies in glasses.
 Optical properties of amorphous thin films.
 Fluoride glasses.