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# A REVIEW ON THE LINEAR/NONLINEAR OPTRICAL PROPERTIES OF PROTON IRRADIATED CHALCOGENIDE THINFILMS AND THEIR APPLICATIONS

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## ABSTRACT

The distinctive linear and nonlinear optical characteristics of chalcogenide thin films, particularly containing selenium (Se), have aroused considerable attention in photonics research. We examine how proton irradiation changes the optical characteristics of thin films made of chalcogenides. from a theoretical and experimental perspective in this work. Researchers have found that proton irradiation can change the physical and optical properties of these films, which in turn changes how well they work in a number of photonic uses. We look at how proton treatment changes the nonlinear optical behavior by looking at changes in transmission, absorption, and the refractive index. The potential applications in fields like optoelectronics and photonics are examined.

**Keywords**: Chalcogenide Thin Films, Proton Irradiation, Linear optical Properties, Nonlinear Optical Properties, Photonic Applications

## i. INTRODUCTION

Elemental chalcogenide glassy alloys, such as those composed of tellurium, selenium, and sulfur, are attracting considerable attention due to their distinctive applications. These materials are great for photonic and optoelectronic devices. They have high refractive indices (2.0–3.7), allow infrared light to pass through, and respond strongly to changes in light. Their disorganized atomic structure makes remarkable changes possible when subjected to light—darkening, lightening, and changes in the way light bends upon impact by light or intense radiation [1–5].

Phase-change memory applications and infrared detectors call for alloys high in tellurium while imaging and biological sensing both benefit from selenium compounds. These materials become more stable when doped, their capacity to form glass is enhanced, and their performance in nonlinear optics is raised by adding germanium (Ge) and arsenic (As). They are mostly synthesized with either physical or chemical vapor deposition techniques [6-12].

Numerous investigations on effects of proton irradiation on chalcogenide thin films have revealed that the degree of radiation they receive determines the structural alterations and optical characteristics they have. Sahoo et al. [13] found that when the $As_{40}Se_{50}Sb_{10}$ films were exposed to proton irradiation, the bandgap changed in a way that was not straightforward. They connected this shift to the mobility of the material's flaws. Priyadarshini and colleagues observed an increase in optical conductivity and nonlinear susceptibility after exposing low-energy protons to $Bi_5In_{30}Se_{65}$ films. Experimental evidence suggests that proton irradiation alters optical properties. The different results, such as whether the bandgap increases or decreases with higher exposure, indicate that we need to closely look at what causes these changes [14].

Although earlier studies have carefully investigated the optical properties of chalcogenide thin films, nothing is known about the exact effect of proton irradiation as a modifiable method for changing these properties. Unlike conventional techniques such as elemental doping or thermal annealing, which cause slow compositional or structural changes, proton irradiation provides an exact atomic method for defect engineering. Without additional material production processes, this method allows exact changes of both linear and nonlinear optical properties. Moreover, proton irradiation offers advantages over other techniques by allowing depth-dependent property modulation, necessary for photonic uses including optical switching and nonlinear signal processing [13,17]. This work systematically examines recent findings on proton-irradiated chalcogenide thin films, resolving differences in experimental results and analyzing potential processes behind the observed changes in characteristics. By means of a thorough framework for improving proton-irradiated chalcogenide films for next-generation photonics, this work aims to compare several irradiation conditions and their effects.

## ii. PREVIOUS PROTON IRRADIATION IMPACT STUDIES

Recent investigations show that proton irradiation changes bandgap, optical conductivity, dielectric constants, and nonlinear susceptibility fluence-dependently. Irradiation causes defect development, structural reorganization, and morphological changes, depending on material composition, energy, and fluence. New findings from recent studies demand more discussion even if our knowledge of how proton irradiation affects chalcogenide thin films has developed greatly. The main subjects of several studies done before 2020 were structure and bandgap changes. In recent years, researchers have looked into defect dynamics, real-time in-situ characterization methods, and fluence-dependent nonlinear optical enhancements. Recent research has shown that proton irradiation can change the refractive index and third-order nonlinear susceptibility selectively. This opens up interesting possibilities for photonic applications. Variances in irradiation settings, initial material disorder, and deposition techniques, however, are most likely responsible for the seen bandgap variances. Table 1 contrasts experimental and theoretical data with an eye on important patterns, unresolved questions, and future research goals.

When $As_{40}Se_{50}Sb_{10}$ films were exposed to 30 keV radiation, the bandgap first decreased but later recovered at higher levels of exposure because of the movement of defects and changes in structure [13]. Thin films of $Bi_5In_{30}Se_{65}$ showed increased dielectric constants and nonlinear refractive indices with irradiation fluence, indicating potential for photonic switching devices [14]. These alterations vary per material system. Studies on $Se_{70}Te_{20}In_{10}$ and Ag-Ge-Se systems indicate that irradiation-induced alterations rely on parameters such defect formation energy, ion penetration depth, and starting film disorder, emphasizing the need for material-specific research [15–16].

Matabana et al. found fluence-dependent behavior in $Se_{70}Te_{20}Sn_{10}$ thin films after 3 MeV proton irradiation. At intermediate fluences, bandgap ($E_g$) reduced from 1.84 eV to 1.61 eV. This pattern was verified by dielectric constant tests, which indicated a peak augmentation at $5 \times 10^{13}$ ions/cm² before recovering at $5 \times 10^{16}$ ions/cm². Surface roughness and optical property alterations were correlated using atomic force microscopy (AFM), indicating the material's potential for radiation-resistant photonic applications [17].

Despite these advances, proton irradiation effects vary between investigations. Different deposition processes, film disorder, and irradiation circumstances might result in different optical conductivity and third-order susceptibility ($\chi^3$) results. Recent research has used improved in-situ spectroscopy and atomic-scale characterization to resolve these differences. These methods help construct predictive models for improving chalcogenide films by revealing defect dynamics and their influence in optical property evolution. The complicated interaction between irradiation parameters, material composition, and defect dynamics requires systematic investigations to fully understand and harness these effects. Such efforts are essential for advancing chalcogenide films in next-generation photonic devices.

## iii. SYNTHESIS OF THIN FILMS

Thin films can be created using physical vapor deposition (PVD) processes. The target material is vaporized and then condenses onto the substrate, forming a thin film layer. On the other hand, chemical vapor deposition (CVD) techniques use a heat source to vaporize the material of interest and break it down into its component atoms and molecules. The development of thin films happens when the vapor reacts with nearby gases and liquids, which are close to the substrate. Though expensive, photovoltaic deposition (PVD) technologies yield thin films with higher power conversion efficiencies and can be used at lower temperatures than more cost-effective chemical processes, which often require higher temperatures [18]. The chemical and physical properties of thin films are affected by the deposition method that is chosen [19]. Therefore, when dealing with thermoelectric materials, it is essential to choose the right method. A thin film is deposited by following the steps shown in Figure1.

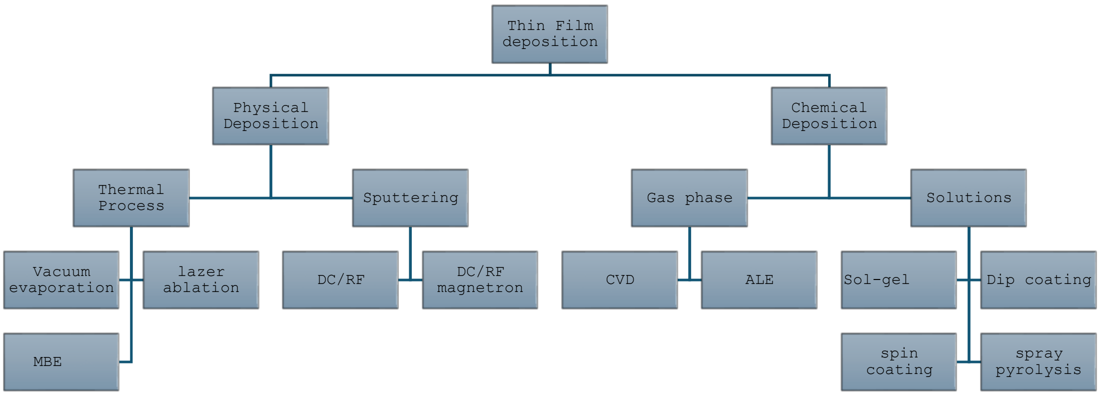

**Figure 1. Deposition technique of thin films illustration**

## iv. MECHANISM OF PROTON IRRADIATION

As noted by Matabana et al. [15], the Tandem accelerator is the predominant method for irradiation. At iThemba LABS in Gauteng, samples underwent proton irradiation utilizing the 6 MV Tandem Accelerator, which operates at 3 MV. The samples were positioned on hexagonal carousel holders and placed inside vacuum-operated atomic microprobe chambers. The proton beam passed through collimators onto illuminated objects, producing a concentrated sample with a spot size of 20-30 µm via magnetic quadrupole triplets. The beam was scanned in both the x and y directions following a raster pattern, creating a uniformly illuminated area of approximately 1.8 mm × 1.8 mm. Shining a wide beam on the sample without moving it created a Gaussian light pattern that wasn't good for checking for damage. At the beginning and end of each irradiation cycle, we recorded the beam current in seconds. [20-22]. Proton irradiation causes structural and electrical changes in chalcogenide thin films that then affect their optical properties. High-energy protons contacting the material generates electron pairs, holes, and defects. These changes affect conductivity, light absorption, and optical bandgap as well as other aspects. Ion bombardment alters the refractive index and nonlinear optical characteristics by small structural changes in the material. Over time, defects may relax or combine to produce nonlinear optical properties. Understanding these mechanisms is crucial to customize the light characteristics of proton-irradiated films to specific applications.

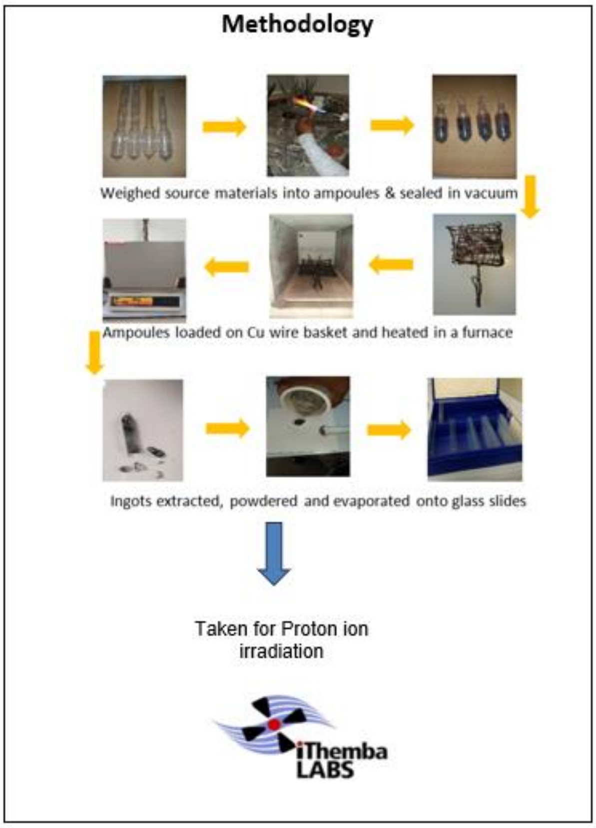

**Figure 2: Step-by-step methodology for the preparation of chalcogenide thin films before proton irradiation.**

As shown in Figure 2, there were several crucial phases involved in the creation of chalcogenide thin films. To stop oxidation, high-purity source materials were precisely weighed and vacuum-sealed in quartz ampoules. The constituent elements were then uniformly melted and homogenized by heating these ampoules in a controlled furnace setting. Following cooling, a thermal evaporation process was used to extract, finely grind, and deposit the resultant ingots onto glass substrates. In order to produce high-quality thin films with consistent thickness and composition that were appropriate for further proton irradiation research, this methodical preparation procedure was necessary. This is well described in our work when studying irradiated thin films in [15,17]

## v. LINEAR AND NONLINEAR CHARACTERISTICS

Nowadays, thin films are absolutely necessary for photonic and photovoltaic systems. Research on thin films has gained a lot of attention due to their technical value, particularly in terms of elucidating their optical features. The linear and nonlinear optical aspects of chalcogenides define their features and uses [24]. From the perspective of materials, a thorough knowledge of these features is absolutely vital. Modern photonic and photovoltaic systems depend on thin films absolutely. Thin dielectric plates and coatings are included into manufactured solar cells, including the most basic models. Because of their technical relevance—especially in terms of clarifying their optical characteristics—research on thin films has attracted a lot of interest. The linear and nonlinear optical aspects of chalcogenides define their features and uses [24]. From the perspective of materials, a thorough knowledge of these features is absolutely vital.

## vi. LINEAR OPTICAL PROPERTIES

Proton irradiation creates defects and changes bond configurations, which affects the optical bandgap, or the lowest energy required for electron transport. This causes the bandgap to narrow due to radiation, whereas severe exposure causes the defects to alter shape, which increases the bandgap. Proton discharge also has an impact on the complex dielectric function, which in turn influences light travel, refractive index, and attenuation coefficient. These factors are essential for photonic waveguides and nonlinear optics.

### a. Transmittance and Optical Parameters

Usually starting with reflectance and transmittance measurements with a spectrophotometer, including FTIR and UV-VIS spectrometers, optical investigations for photonic device applications, material optical transmittance denotes its ability to let electromagnetic radiation pass [25]. Constants including film thickness, extinction coefficient, refractive index, and others are found using optical transmission measurements. Many times, these aspects are evaluated using both experimental and theoretical methods. One powerful and highly used method [26] is ellipsometry. Ellipsometric data need interpretation in line with a proper theoretical model for correctness [27].

### b. The energy bandgap in optics and Absorption Coefficient

The minimum energy required to raise an electron from the surface of a material is marked by the optical band's gap. The absorption coefficient α is important since it helps to define the extent of light intensity reduction throughout the material. Usually, Tauc's relation is used in areas of $\alpha > 10^4$ cm$^{-1}$ to clarify the relationship between the optical bandgap and the absorption coefficient. The formula for computing α is given in equation below [28–31].

$$\alpha = \frac{1}{t} ln\left(\frac{(1-R)^2}{T}\right) \qquad 1$$

The variable R is reflectance, T is transmittance, and t is thickness of film

### c. Extinction Coefficient

Reflecting the degree of material absorption of electromagnetic radiation at a given wavelength, The extinction rate shows how much less light is passing through because of scattering and absorption. Proton irradiation-induced structural modifications can influence the complex dielectric function, resulting in alterations to both the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) components of permittivity. This affects light propagation, refractive index (n), and extinction coefficient (k), influencing applications in photonic waveguides and nonlinear optics. [32].

### d. Dielectric Constant and Optical Conductivity

A material's reaction to an applied electric field is defined by its dielectric constant. This complicated variable, which has both real and imaginary parts, explains why the speed of light decreases and why absorption losses caused by polarization occur during propagation [30–31]. dielectric constant complex $\varepsilon = (n + ik)^2$. The dielectric's ability to refract radiation is represented by the real part of the complex dielectric constant, $\varepsilon_r = n^2 - k^2$,. As a result of dipole alignment, the imaginary part $\varepsilon_i$=2nk shows how the dielectric material absorbs energy that hits it.

## vii. NONLINEAR OPTICAL CHARACTERISTICS

### (a) Categories of Nonlinear Materials

Resonant and non-resonant materials are the two primary types of nonlinear materials. Resonant nonlinear materials exhibit high nonlinearity at the electronic absorption edge, but their reaction times are protracted due to carrier relaxation. In contrast, non-resonant nonlinear materials can react at light wavelengths outside their absorption edge, allowing them to react very rapidly [32]. For all-optical switching, silica glasses are perfect because of their low-loss characteristics. On the other hand, their restricted nonlinearity renders them inappropriate in certain scenarios.

### (b) Mechanisms of Nonlinearity

Exposure to intense light causes materials to undergo significant property changes due to optical nonlinearity [33-34]. This is because chalcogen-rich materials are suitable for nonlinear applications since their lone-pair electrons are polarized. A power series expansion is seen in the induced polarization vector as P.

$$\boldsymbol{P} = \epsilon_0 ( \chi^{(\mathbf{1})} . \boldsymbol{E} + \chi^{(\mathbf{2})} . \boldsymbol{E}^{(\mathbf{2})} + \chi^{(3)} . \boldsymbol{E}^{(\mathbf{3})} + \cdots ) \tag{2}$$

Where $\chi^n$ represents the nth-order susceptibility vector and $E^n$ stands for the nth-order electric field vector. In materials lacking inversion symmetry, the second-order susceptibility ($\chi^2$) is present, while $\chi^1$ represents the linear polarization component. The third-order susceptibility ($\chi^3$) is associated with certain nonlinear phenomena in disordered materials [35-36]. This is the way third-order susceptibility is linked to linear susceptibility ($\chi^1$) according to Miller's generalized rule:

$$\boldsymbol{A} \left( \chi^{(\mathbf{1})} \right)^{\mathbf{4}} = \chi^{(3)} \tag{3}$$

Where A = 1.7 × $10^{-10}$ esu, and:

$$\frac{(n^2-1)}{4\pi} = \chi^{(1)} \tag{4}$$

Considering the energy of photons as they approach 0:

$$\left( \frac{(n_o^2-1)}{4\pi} \right)^{\mathbf{4}} \boldsymbol{A} = \left( \left(\frac{1}{\mathbf{4}\pi}\right) \left(\frac{E_d}{E_{\boldsymbol{o}}}\right) \right)^{\mathbf{4}} \boldsymbol{A} = \left(\frac{E_d}{4\pi E_{\boldsymbol{o}}}\right)^{4} A = \chi^{(3)} \tag{5}$$

Amorphous materials' nonlinear refractive index ($n_2$) is represented by the relationship between third-order susceptibility ($\chi^{-3}$) and the material itself.

$$n_2 = \frac{12\pi}{n_0} \chi^{(3)} \tag{6}$$

### (a) Third-Harmonic Generation and Four-wave mixing

Third harmonic generation (THG) is an optical phenomenon whereby three photons with the same frequency (ω) produce a photon with a frequency of 3ω. Third harmonic generation differs from second harmonic production in that it needs to be done in two stages: first, generating second harmonics follows the contact with an extra photon at frequency ω. When photons of two or three different frequencies interact to generate new photons with one or two different frequency components when they pass a nonlinear medium [37–40], four-wave nonlinear effects result.

**Table 1: Recent Studie Analysis**

| **Material composition** | **Energy of irradiation** | **Urbatch energy (eV)** | $\boldsymbol{\omega_p^2}$ | **$E_o$ (eV)** | **$E_d$ (eV)** | **$N_0$** | **$M_{-1}$** | **$M_{-3}$** | **Author** |
|---|---|---|---|---|---|---|---|---|---|
| $Se_{70}Te_{20}In_{10}$ | 3Mev | 0.24-0.36 | 2.3-6.7 | 2.3-3.1 | 1.33-9.7 | 1.26-2.03 | 0.579-3.131 | 0.102-0.323 | [15] |
| $Ag_{45}Se_{40}Te_{15}$ | 0.03 Mev | 0.3-0.5 | 4.4-5.470 | 1.6-1.8 | 0.20-0.26 | 1.060-1.07 | 0.120 - 0.140 | 0.040-0.050 | [67] |
| $As_{40}Se_{50}Sb_{10}$ | 0.03 Mev | 0.2432 - 0.2494 | 2.722 - 5.108 | 5.17-6.56 | 26.61 - 29.87 | 2.481-2.535 | 5.148 - 5.424 | 0.119 - 0.195 | [13] |
| $Bi_5In_{30}Se_{65}$ | 0.03 Mev | - | 1.0 – 1.30 | - | - | 3.3 -3.6 | - | - | [14] |
| Ag-Ge-Se | 3Mev | 1.8 – 1.850 | - | 3.60-3.71 | 18.9-20.8 | 2.50-2.63 | - | - | [16] |

The table shows that the optical and structural properties of chalcogenide thin films are affected by the irradiation energy, with lower values suggesting less disorder. For optoelectronics, photonics, and memory storage optimization of chalcogenide thin films, understanding these alterations is critical.

**Discussion and Critical Analysis**

Although much research has been done on the effects of proton irradiation on chalcogenide thin films, documented trends point to underlying complexity still unsolved. Although some studies show a monotonic drop in the optical bandgap with increasing fluence [12], others show non-monotonic behavior whereby the bandgap first decreases then increases at higher fluences [14]. Though comprehensive studies are rare, such variances may result from differences in starting film compositions, deposition processes, or defect-generating mechanisms. Likewise, defect-induced band structure changes [15, 14] are usually blamed for nonlinear optical improvements in irradiation chalcogenide films. Still, other processes, including defect clustering, nanoscale phase separation, and ion-induced strain fields, could be rather important. The degree to which these effects support the observed optical responses is yet unknown and calls for sophisticated characterization methods like in-situ electron microscopy and ultrafast pump-probe spectroscopy. Further exposing gaps in the literature is a comparison of irradiation energy-dependent effects.

For instance, whereas high-energy (3 MeV) irradiation of $Se_{70}Te_{20}In_{10}$ causes notable changes in the dielectric function and refractive index [15], low-energy (30 keV) proton irradiation of $Bi_5In_{30}Se_{65}$ results in improved optical conductivity and nonlinear sensitivity [14]. A prediction model for customizing chalcogenide thin films for particular photonic uses might be established by a methodical investigation of irradiation-induced changes throughout several fluence levels, energies, and compositions. Real-time monitoring of optical property change during irradiation should also be investigated in the next work. This could offer a closer understanding of the transient defect dynamics controlling structural and electrical transformations. Moreover, by means of defect generation and migration paths in proton-irradiated chalcogenides, theoretical methods such as density functional theory (DFT) computations and molecular dynamics simulations could augment experimental results. Future studies could offer a more complete framework for maximizing chalcogenide thin films in uses including nonlinear optics, optical switching, and memory storage by filling in these voids.

Through additional irradiation methods, such as electron irradiation, one can obtain a more exact understanding of the effects of proton irradiation on chalcogenide thin films. Unlike protons, which have a specific penetration depth and mostly cause defects through nuclear collisions, electrons mostly participate in inelastic scattering and so provide different processes for defect generation [68-70]. Studies on electron-irradiated chalcogenides show less structural disorder relative to proton irradiation at equivalent energy levels and slower changes in bandgap. Protons' higher mass and momentum transfer cause this disparity, which produces deeper defect states and more notable structural rearrangements. Furthermore, whereas electron irradiation usually results in surface changes with no bulk restructuring, proton irradiation has been shown to increase nonlinear optical properties by induction of localized structural changes. By means of a comprehensive comparison of several approaches, one can acquire improved knowledge for tailoring irradiation-induced changes for specific photonic uses. The combined effect of both irradiation methods should be investigated in further studies to improve material properties for nonlinear optical devices.

## ii. APPLICATIONS

### (a) Chalcogenides as PCM (phase change materials)

The worldwide market demands highly efficient non-volatile memory (NVM) devices that can store data for extended periods of time without power in order to meet the storage demands of today [40]. Many people are interested in using phase change memory (PCM) devices to improve memory storage systems. Ge-Sb-Te (GST) compounds have been extensively studied for their beneficial phase change features, making them one of the most studied chalcogenide phase change materials [41]. A wide variety of photonic devices and systems make use of these materials, including optical switches, non-volatile displays, all-optical computers, and photonic memory. However, GST materials do have limitations, such as a lack of stability in the amorphous phase, poor heat conductivity, and an inadequate ability to form glasses. Their unsuitability for large production is due to these problems, which prevent them from being re-amorphized. Additionally, they are only useful in extremely thin film configurations for optical devices due to their low figure-of-merit [42–53].

### (b) Chalcogenides in Optical Sensing Platforms

In both fiber and flat forms, chalcogenides find widespread application in optical sensing devices. In a fiber-based system, the evanescent wave interacts with the medium (liquid or vapor) by exposing a section of the fiber core to it, and then the system monitors any changes in the transmission of the fiber as a result. Due to their availability in fiber format and strong mid-infrared transparency, chalcogenides are particularly attractive for this technique, which is called fiber evanescent wave spectroscopy [54-55]. Chalcogenide glasses are more sensitive because they are hydrophobic and because surface functionalization is easy [57-59].

In recent years, planar waveguides have attracted considerable interest as a potential chemical sensing technique. The utilization of Raman or evanescent wave spectroscopy using these waveguides allows for improved reproducibility compared to fiber devices, smaller dimensions, and the ability to integrate with sources/emitters, detectors, and microfluidic analyte delivery systems all in one seamless package. It has been shown that planar optical resonators can be connected with waveguides. providing reduced-footprint sensitivity comparable to commercially available surface-plasmon devices [60-65].

### (c) Optical Switching Applications

This requires controlling the propagation of an optical field through a device, which allows for the transition between multiple optical states. When it comes to optical time-division multiplexing, ultrafast all-optical switching is king. Ultrafast temporal responsiveness (broadband) and other criteria are necessary to achieve this functionality [66]. When working with materials that exhibit substantial nonlinearity, it is feasible to achieve low switching energy. Particularly well-suited for use in all-optical switching applications are their non-resonant characteristics, which include low absorption and fast temporal responses. Materials exhibiting substantial non-resonant optical nonlinearity can meet these requirements.

### (d) Real-World Application Challenges and Limitations

Proton irradiation produces intriguing optical enhancements, but there are a number of obstacles that prevent commercial photonic devices from widely using proton-irradiated chalcogenide thin films. Problems with integration, material stability, and processing are the root causes of these restrictions in current optical platforms.

#### The Effects of Radiation on the Stability of Defects and Aging

Proton irradiation can enhance nonlinear optical properties, but it can also harm optical properties because of issues like the recombination, movement, or formation of defects caused by the irradiation. This makes one wonder how practical proton-modified films will hold up in the long run. Main concerns encompass unstable temperature and environmental friendliness. When the device is operating at high temperatures, it might cause the annihilation of defects, which reduces the positive optical changes. Chalcogenide films are sensitive to environmental conditions, so they need strong protective coverings to avoid damage from moisture and oxidation.

#### Scalability of Fabrication and Financial Limitations

The specialized characteristics of proton irradiation render it predominantly suitable for large-scale manufacturing applications, which often have access to limited accelerator facilities. Stringent fluence regulation is essential for modifying the material during the generation and manipulation of proton beams utilizing tandem accelerators. The method's architecture limits its throughput to small numbers of gadgets or materials. Overall, it's not feasible for industrial device fabrication; thus, it's better for research or specialized usage.

#### Compatibility with Photonic and CMOS-Based Systems

To enable enhanced functions, proton-irradiated chalcogenides must seamlessly merge with silicon photonics and integrated optical circuits. Several major obstacles prevent compatibility. Proton irradiation can stress or delaminate film-substrate adhesion, compromising device mechanical integrity and long-term stability. Chalcogenides and typical photonic substrates have an optical mode mismatch.

## iii. Conclusion

Chalcogenide thin films are fundamental in modern photonics and optoelectronics because of their remarkable linear and nonlinear optical properties. Chalcogenide thin films excel in memory storage, optical sensing, and switching due to their transparency in the mid-infrared band, high refractive indices, and evident nonlinear optical properties. Proton irradiation is a great way to fine-tune these properties for photonic uses because it lets you change the bandgap in a controlled way and improves the third-order nonlinear susceptibility. Because it generates more significant structural changes than traditional modification techniques like heat annealing or UV exposure, proton irradiation permits better control of optical responses. Even with these encouraging developments, material stability, mass production, and flawless integration into commercial devices remain difficult issues, though. Future research should focus on using Raman spectroscopy, transmission electron microscopy (TEM), and other advanced methods to learn about how irradiation changes the structure of things at the atomic level. Combining proton irradiation with other processing techniques and enhancing multi-energy irradiation schemes would help to further improve nonlinear optical characteristics for quantum communication systems and advanced photonic circuits.

## iv. REFERENCES

1. B. J. Eggleton, Chalcogenide photonics: Fabrication, devices and applications. Introduction, Opt. Express, vol. 18, no. 25, p. 26632, 2010.
2. I. Pethes, R. Chahal, V. Nazabal, C. Prestipino, A. Trapananti, S. Michalik, Chemical short-range order in selenide and telluride glasses, J. Phys. Chem. B, vol. 120, p. 9204, 2016.
3. S. Mishra, P. K. Singh, P. Lohia, D. K. Dwivedi, Thin Film Preparation and Optical Properties of Se–Te Based Chalcogenide Glasses for Optoelectronic Applications, Glass Physics and Chemistry, vol. 46, no. 4, pp. 341–349, 2020, https://doi.org/10.1134/S1087659620040094.
4. D. M. Habashy, H. E. Atyia, H. I. Lebda, Exploring conduction mechanisms in chalcogenide thin films: an experimental and soft computing approach with ANN and GP techniques, Eur. Phys. J. Plus, vol. 138, article 798, 2023, https://doi.org/10.1140/epjp/s13360-023-04382-7.
5. Z. Ghorbanishiadeh, A. Bhuyan, B. Zhou, M. Sheibani Karkhaneh, M. G. Kuzyk, Mechanisms of the photomechanical response in thin-film dye-doped glassy polymers, Polymers, vol. 17, article 254, 2025, https://doi.org/10.3390/polym17020254.
6. V. Sharma, A. Thakur, Effect of visible light on a-SeTe thin film, Optoelectron. Adv. Mater. Rapid Commun., vol. 3, no. 10, pp. 1046–1049, 2009.

7. S. Gautam, A. Thakur, D. K. Shukla, H. J. Shin, K. H. Chae, K. P. Singh, N. Goyal, Effect of proton irradiation on electrical properties of a-$As_2S_3$, J. Non-Cryst. Solids, vol. 357, no. 11–13, pp. 2340–2343, 2011, https://doi.org/10.1016/j.jnoncrysol.2010.11.076.

8. L. Xu, S. Guo, V. Ralchenko, et al., Progress in infrared transparencies under opto-electro-thermo and mechanical environments, Surf. Sci. Tech., vol. 1, article 2, 2023, https://doi.org/10.1007/s44251-023-00002-9.

9. A. Arsh, M. Klebanov, V. Lyubin, L. Shapiro, A. Feigel, M. Veinger, B. Sfez, Glassy $mAs_2S_3 \cdot nAs_2Se_3$ photoresist films for interference laser lithography, Opt. Mater., vol. 26, no. 3, pp. 301–304, 2004.

10. V. Lyubin, M. Klebanov, A. Feigel, B. Sfez, Films of chalcogenide glassy semiconductors: New phenomena and new applications, Thin Solid Films, vol. 459, no. 1-2, pp. 183–186, 2004.

11. M. Mitkova, M. N. Kozicki, H. C. Kim, T. L. Alford, Local structure resulting from photo and thermal diffusion of Ag in Ge–Se thin films, J. Non-Cryst. Solids, vol. 338, pp. 552-556, 2004.

12. S. K. Tripathi, A. Thakur, G. Singh, J. Sharma, V. Sharma, K. P. Singh, N. Goyal, Proton-induced changes on the optical parameters of a-$(Ge_{20}Se_{80})_{0.96}Ag_{0.04}$ thin films, 2005.

13. D. Sahoo, S. Sahoo, D. Alagarasan, R. Ganesan, S. Varadharajaperumal, R. Naik, Proton Ion Irradiation on $As_{40}Se_{50}Sb_{10}$ Thin Films: Fluence-Dependent Tuning of Linear-Nonlinear Optical Properties for Photonic Applications, ACS Appl. Electron. Mater., vol. 4, no. 2, pp. 856–868, Feb. 2022, doi: 10.1021/acsaelm.1c01223

14. P. Priyadarshini et al., The impact of fluence dependent proton ion irradiation on the structural and optical properties of $Bi_5In_{30}Se_{65}$ thin films for nonlinear optical devices, RSC Adv., vol. 12, no. 8, pp. 5012–5026, Feb. 2022, doi: 10.1039/d2ra00097k.

15. T. K. Matabana, C. B. Tabi, M. Madhuku, D. P. Sebuso, C. M. Muiva, The impact of proton ion irradiation on $Se_{70}Te_{20}In_{10}$ thin films: Linear and non-linear optical properties for photonic applications, Physica B: Condensed Matter, vol. 696, p. 416663, 2025, ISSN 0921-4526, https://doi.org/10.1016/j.physb.2024.416663.

16. S. K. Tripathi, A. Thakur, G. Singh, J. Sharma, V. Sharma, K. P. Singh, G. S. S. Saini, N. Goyal, Irradiation effects on the optical properties of a-Ge-Se-Ag thin films, J. Optoelectron. Adv. Mater. 7, 2095–2101 (2005).

17. T. K. Matabana, C. Muiva, L. K. Benjamin, M. Madhuku, T. Mosimanegape, C. B. Tabi, Effect of 3 MeV proton ion irradiation on optical properties of $Se_{70}Te_{20}Sn_{10}$ thin films for photonic applications, Physica B: Condensed Matter, vol. 2025, article 416930, ISSN 0921-4526, https://doi.org/10.1016/j.physb.2025.416930.

18. K. Wasa, M. Kitabatake, H. Adachi, Thin Film Materials Technology: Sputtering of Control Compound Materials, Springer Science & Business Media, 2004.

19. S. L. Dhere, S. S. Latthe, C. Kappenstein, S. K. Mukherjee, V. A. Rao, Comparative studies on p-type CuI grown on glass and copper substrate by SILAR method, Appl. Surf. Sci., vol. 256, pp. 3967-3971, 2010.

20. H. Jivan, et al., Radiation hardness of plastic scintillators for the Tile Calorimeter of the ATLAS detector, in Proceedings of SAIP2014, University of Johannesburg, 2015, pp. 199–205, ISBN: 978-0-620-65391-6.

21. H. Jivan et al., Radiation hardness of plastic scintillators for the Tile Calorimeter of the ATLAS detector, J. Phys. Conf. Ser., vol. 623, p. 012016, 2015.

22. H. Jivan, J. E. Mdhluli, E. Sideras-Haddad, B. Mellado, R. Erasmus, M. Madhuku, Radiation damage effects on the optical properties of plastic scintillators, Nucl. Instrum. Methods Phys. Res., Sect. B, vol. 409, pp. 224–228, 2017,https://doi.org/10.1016/j.nimb.2017.05.061.19.M. Buffiere, D. S. Dhawale, F. El-Mellouhi, Chalcogenide materials and derivatives for photovoltaic applications, Energy Technol., vol.7, p. 1900819, 2019.

23. M. Buffiere, D. S. Dhawale, F. El-Mellouhi, Chalcogenide materials and derivatives for photovoltaic applications, Energy Technol., vol. 7, p. 1900819, 2019.

24. L. K. Benjamin, P. Dube, C. B. Tabi, C. M. Muiva, Physical, linear and nonlinear optical properties of amorphous $Se_{90-x}Te_{10}M_x$ (M = Zn, In, Pb, x = 0, 5) chalcogenide thin films by electron-beam deposition, J. Non-Cryst. Solids, vol. 557, p. 120646, 2021.

25. A. S. Hassanien, R. Neffati, K. A. Aly, Impact of Cd-addition upon optical properties and dispersion parameters of thermally evaporated $Cd_xZn_{1-x}Se$ films: discussions on bandgap engineering, conduction and valence band positions, Optik, vol. 212, p. 164681, 2020.

26. G. G. Politano, C. Versace, Spectroscopic ellipsometry: advancements, applications and future prospects in optical characterization, Spectrosc. J., vol. 1, pp. 163–181, 2023, https://doi.org/10.3390/spectroscj1030014.

27. T. Das, K. Bhattacharya, Topometry of metal surfaces using reflection of polarized light, Optik 243 (2021), 167448 (Stuttgart).

28. P.K. Singh, D.K. Dwivedi, Chalcogenide glass: Fabrication techniques, properties and applications, Ferroelectrics 520 (2017) 256.

29. I. Uddin, H. Howari, G.A. Ansari, Laser irradiation effect on the optical properties of a-$Se_{88}Te_{12-x}Al_x$ thin films, Chalcogenide Lett. 13 (2016) 117.

30. C. Muiva, E. Muchuweni, D. P. Sebuso, T. K. Matabana, M. Thobega, H. Vasco, Microstructural analysis and optical linearity and nonlinearity of nanostructured Al─doped ZnO/SnO2 thin films, Crystal Research and Technology, 2025, https://doi.org/10.1002/crat.202400118.

31. J. Orava, A.L. Greer, B. Gholipour, D.W. Hewak, C.E. Smith, Characterization of supercooled liquid $Ge_2Sb_2Te_5$ and its crystallization by ultrafast-heating calorimetry, Nat. Mater. 11 (2012) 279.

32. S.P. Singh, N. Singh, Nonlinear effects in optical fibers: origin, management and applications, 2007. https://doi.org/10.2528/PIER07040201.

33. E. Romanova, Yu. Kuzyutkina, Vl. Shiryaev, N. Abdel-Moneim, D. Furniss, T. Benson, A. Seddon, St. Guizard, Measurement of non-linear optical coefficients of chalcogenide glasses near the fundamental absorption band edge, J. Non-Cryst. Solids 480 (2018) 13.

34. S. Mishra, P.K. Singh, R.K. Yadav, A. Umar, P. Lohia, D.K. Dwivedi, Investigation of glass forming ability, linear and non-linear optical properties of Ge-Se-Te-Sb thin films, Chem. Phys. 541 (2021). https://doi.org/10.1016/j.chemphys.2020.111021.

35. C. Muiva, E. Muchuweni, D. P. Sebuso, T. K. Matabana, M. Thobega, H. Vasco, Microstructural analysis and optical linearity and nonlinearity of nanostructured Al─doped ZnO/SnO2 thin films, Crystal Research and Technology, 2025, https://doi.org/10.1002/crat.202400118.

36. S.P. Singh, N. Singh, Nonlinear effects in optical fibers: origin, management and applications, 2007. https://doi.org/10.2528/PIER07040201.

37. P.B. Chapple, J. Staromlynska, J.A. Hermann, T.J. McKay, R.G. McDuff, Single-beam Z-scan: measurement techniques and analysis, J. Non-Cryst. Solids 6 (2012) 251–293.

38. M.P. Fok, P.R. Prucnal, Switching based on optical nonlinear effects, Opt. Switch. Mater. Des. (2010) 181–205.

39. D. Shen, J. Cao, W. Wan, Wavefront shaping with nonlinear four-wave mixing, Sci. Rep., vol. 13, article 1, 2023, https://doi.org/10.1038/s41598-023-29621-w.

40. J. Cao, Y. Zheng, Y. Feng, X. Chen, W. Wan, Metal-free flat lens using negative refraction by nonlinear four-wave mixing, Phys. Rev. Lett., vol. 113, no. 21, article 217401, 2014.

41. D. Sahoo, R. Naik, GSST phase change materials and its utilization in optoelectronic devices: a review, Mater. Res. Bull. 148 (2022), 111679.

42. J. Feldmann, M. Stegmaier, N. Gruhler, C. Ríos, H. Bhaskaran, C.D. Wright, W.H.P. Pernice, Calculating with light using a chip-scale all-optical abacus, Nat. Commun. 81 (8) (2017) 1–8.

43. C.D. Wright, C. Rios, H. Bhaskaran, M. Stegmaier, N. Youngblood, W.H.P. Pernice, Z. Cheng, Controlled switching of phase-change materials by evanescent-field coupling in integrated photonics, Opt. Mater. Express 8 (2018) 2455–2470.

44] K. Du, Q. Li, Y. Lyu, J. Ding, Y. Lu, Z. Cheng, M. Qiu, Control over emissivity of zero-static-power thermal emitters based on phase-changing material GST, Light Sci. Appl. 6 (2017) e16194.

45. A. Tittl, A.-K.U. Michel, M. Schäferling, X. Yin, B. Gholipour, L. Cui, M. Wuttig, T. Taubner, F. Neubrech, H.A. Giessen, A switchable mid-infrared plasmonic perfect absorber with multispectral thermal imaging capability, Adv. Mater. 27 (2015) 4597–4603.

46. P. Hosseini, C.D. Wright, H. Bhaskaran, An optoelectronic framework enabled by low-dimensional phase-change films, Nature 511 (2014) 206–211.

47. F. Duport, B. Schneider, A. Smerieri, M. Haelterman, S. Massar, K. Vandoorne, W. Dierckx, B. Schrauwen, D. Verstraeten, R. Baets, P. Bienstman, J. Van Campenhout, All-optical reservoir computing, Opt. Express 20 (2012) 22783–22795.

48. J. Hu, J. Li, Q. Zhang, R. Soref, T. Gu, Y. Zhang, Broadband nonvolatile photonic switching based on optical phase change materials: beyond the classical figure-of-merit, Opt. Lett. 43 (2018) 94–97.

49. P. Xu, J. Zheng, J.K. Doylend, A. Majumdar, Low-loss and broadband nonvolatile phase-change directional coupler switches, ACS Photonics 6 (2019) 553–557.

50. A. Hosseinkhani, M. Tavoosi, A. Ghasemi, The optical, structural and thermal optimizations of Ge-As-Se-S-Te glasses, Infrared Phys. Technol. 85 (2017) 421–430.

51. H.K. Lyeo, D.G. Cahill, B.S. Lee, J.R. Abelson, M.H. Kwon, K.B. Kim, S.G. Bishop, B.K. Cheong, Thermal conductivity of phase-change material Ge2Sb2Te5, Appl. Phys. Lett. 89 (2006), 151904.

52. Z. Gong, F. Yang, L. Wang, R. Chen, J. Wu, C.P. Grigoropoulos, J. Yao, Phase change materials in photonic devices, J. Appl. Phys. 129 (2021), 030902.

53. J. Lee, E. Bozorg-Grayeli, S. Kim, M. Asheghi, H.S. Philip Wong, K.E. Goodson, Phonon and electron transport through $Ge_2Sb_2Te_5$ films and interfaces bounded by metals, Appl. Phys. Lett. 102 (2013), 191911.

54. P. Lucas, M.R. Riley, C. Boussard-Pledel, B. Bureau, Advances in chalcogenide fiber evanescent wave biochemical sensing, Anal. Biochem. 351, 1–10 (2006).

55. Y. Yang, K. Ge, P. Tao, S. Dai, X. Wang, W. Zhang, T. Xu, Y. Wang, T.-J. Lin, P. Zhang, Mid-infrared evanescent wave sensor based on side-polished chalcogenide fiber, Ceram. Int., vol. 49, no. 1, pp. 1291–1297, 2023, https://doi.org/10.1016/j.ceramint.2022.09.108.

56. M. L. Anne et al., Chalcogenide glass optical waveguides for infrared biosensing, Sensors 9, 7398–7411 (2009).

57. B. Mizaikoff et al., Infrared fiber-optical chemical sensors with reactive surface coatings, Sens. Actuat. B 29, 58–63 (1995).

58. D. Le Coq et al., Chalcogenide double index fibers: Fabrication, design, and application as a chemical sensor, Mat. Res. Bull. 38, 1745–1754 (2003).

59. S. Hocde et al., Recent developments in chemical sensing using infrared glass fibers, J. Non-Cryst. Sol. 274, 17–22 (2000).

60. A. Ganjoo et al., Planar chalcogenide waveguides for IR evanescent wave sensor, J. Non-Cryst. Sol. 352, 584–588 (2006).

61. A. Pope et al., Chalcogenide waveguide structures as substrates and guiding layers for evanescent wave Raman spectroscopy of Bacteriorhodospin, Vib. Spectrosc. 42, 249–253 (2006).

62. J. Hu et al., Demonstration of chalcogenide glass racetrack microresonators, Opt. Lett. 33, 761–763 (2008).

63. J. Hu et al., Planar waveguide-coupled, high-index-contrast, high-Q resonators in chalcogenide glass for sensing, Opt. Lett. 33, 2500–2502 (2008).

64. J. Hu et al., Fabrication and testing of planar chalcogenide waveguide integrated microfluidic sensor, Opt. Express 15, 2307–2314 (2007).

65. W. C. Tan et al., Optical characterization of a-As2S3 thin films prepared by magnetron sputtering, J. Appl. Phys. 107, 033524 (2010).

66. G. I. Papadimitriou, C. Papazoglou, A. S. Pomportsis, Optical switching: switch fabrics, techniques, and architectures, J. Light. Technol. 21, 384–405 (2003).

67. S. Das, S. Senapati, D. Alagarasan, R. Ganesan, S. Varadharajaperumal, R. Naik, Modifications in the structural, morphological, optical properties of Ag45Se40Te15 thin films by proton ion irradiation for optoelectronics and non-linear applications, *Ceram. Int.*, vol. 49, no. 7, pp. 10319–10331, 2023, https://doi.org/10.1016/j.ceramint.2022.11.212.

68. F. S. M. de Oliveira, M. J. Nogueira, Z. E. Fabrim, P. F. P. Fichtner, Electron irradiation effects in Au thin films, Journal of Materials Science: Materials in Electronics, vol. 32, no. 10, pp. 13291–13304, May 2021, doi: 10.1007/s10854-021-05907-5.

69. B. S. An, Electron beam irradiation induced crystallization behavior of amorphous Ge2Sb2Te5 chalcogenide material, Appl. Microsc., vol. 49, no. 1, Dec. 2019, doi: 10.1186/s42649-019-0021-5.

70. A. V. Krasheninnikov, K. Nordlund, Ion and electron irradiation-induced effects in nanostructured materials, 2010, doi: 10.1063/1.3318261.