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Influence of Magnesium Doping Concentrations and annealing on the Transmittance and Energy Band-gap of Sb_2S_3 Thin Films Deposited via Chemical Bath Deposition Technique

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ABSTRACT
The incorporation of thin film materials into a wide range of technological applications has attracted considerable interest owing to their distinct properties and versatile functionalities. In this study, Magnesium alloyed and Antimony sulphide (Sb_2S_3) thin films were successfully deposited on glass substrates by chemical bath deposition technique. The films were grown at room temperature of constant *p*H. The concentrations of magnesium varied between 0.1M and 0.3M. The films were annealed at annealing temperature between 100˚C and 300˚C at a fixed annealing time of 1 hour. The films were characterized using UV-spectrophotometer to investigate the variation of optical and solid state properties with wavelength in the UV-VIS-NIR region. The result showed that the presence of the alloying agent and annealing treatments modified the optical and solid state properties of the films significantly. The transmittance of the films was high. Annealing led to reduced transmittance due to increased crystallite size, notably in films doped with 0.1M Mg2+ ions and annealed at 200˚C, suggesting enhanced photon absorption. The energy band gaps were found to be direct and in the range of 1.25 eV to 1.72 eV for the as grown films and 1.15eV to 1.3eV for the films annealed at annealing temperatures≤ 300˚C. The study identifies a direct correlation between magnesium doping concentration, annealing conditions, and shifts in the energy band-gap of the films. The values of the energy band gaps are all within the range suitable for use of the layers as absorbers in hetero-junction solar cell devices for sustainable energy applications.

Keywords:
Magnesium,
Antimony sulphide,
Thin films,
Burstein-Moss shift,
Annealing.

INTRODUCTION

The global demand for stable and cost-effective energy sources has led to increased interest in thin film technology for the production of solar cells. Thin film materials have gained considerable attention in various technological applications due to their unique properties and diverse functionalities. Among these materials, antimony sulfide (Sb_2S_3) has emerged a promising candidate for optoelectronic devices such as solar cells, photodetectors, and sensors, owing to its favorable optical and electrical characteristics (Han *et al.*, 2022). The tunability of Sb_2S_3 properties through doping offers intriguing possibilities for enhancing its performance in such devices (Islam and Thakur, 2023). However, challenges such as high resistivity and low optical transmission have hindered its widespread application (Shuah *et al.*, 2021, Kondrotas *et al.*, 2018).

To address these challenges, researchers have explored methods to modify the properties of Sb_2S_3 thin films, including doping with impurities. Magnesium (Mg) doping has emerged a viable strategy to enhance the performance of Sb_2S_3 thin films (Li *et al.*, 2022). Understanding the influence of magnesium doping concentration on the solid-state and optical properties of Sb_2S_3 thin films is crucial for optimizing their functionality in optoelectronic devices.

Diliegros-Godines *et al.*, (2018) investigated the impact of silver (Ag) doping on the structural, optical, and electrical properties of Sb_2S_3 films produced via citrate-mediated chemical bath deposition. The analysis of the optical properties of the films revealed a noticeable shift towards longer wavelengths, indicating a red shift in band gap values from 1.75 to 1.66 eV upon the incorporation of Ag into the Sb2S3 films. Additionally, the inclusion of silver resulted in a significant decrease in the dark resistivity of the Sb_2S_3 films, lowering it by one order. Ismail *et al*., (2015) successfully deposited high-quality tin (Sn)-doped antimony sulfide (Sb_2S_3) thin films using the chemical bath deposition (CBD) technique on glass substrates, followed by annealing at 250°C. The films exhibited remarkable characteristics, including a high absorption coefficient of approximately 104 cm−1, indicating strong light-absorbing properties. Furthermore, they demonstrated direct band gaps ranging from 1.45 to 1.80 eV, suggesting the potential for efficient light absorption. The films also exhibited high refractive indices ranging from 3.38 to 6.39, indicating their ability to efficiently refract light. Additionally, the electrical conductivity values fell within the range of 0.82 to 1.65 (Ω cm) −1, suggesting the potential for effective charge transport within the films. The results suggest that the Sn-doped Sb_2S_3 thin films are promising materials for solar cell applications due to their high absorbance, direct band gaps, and good electrical conductivity, highlighting their potential for use in photovoltaic devices.

Cárdenas et al., (2009) modified through the thermal diffusion of carbon the electrical properties of chemical-bath-deposited antimony sulphide (Sb_2S_3) thin films. The introduction of carbon led to a substantial reduction in the resistivity of the Sb_2S_3 thin films, decreasing from 10^8 Ω cm for undoped conditions to 10^2 Ω cm for doped thin films. It was observed that by varying the carbon content (wt %), the electrical resistivity of Sb_2S_3 could be controlled, thus making it suitable for various opto-electronic applications. In this study we, fabricated magnesium-doped Sb_2S_3 thin films with precise control over doping concentrations using Chemical bath deposition (CBD) technique which is a versatile and cost-effective technique for depositing thin films especially Sb_2S_3. Optical characterization techniques, including UV-Vis spectroscopy, was employed to examine the optical properties of the magnesium-doped Sb_2S_3 thin films. To improve the structural, electrical, and optical properties of the deposited films and activate dopants, the films were annealed. The analyzed absorption spectra and optical bandgap were used to provide insights into the effects of magnesium doping concentration on light absorption capabilities of the films.

MATERIALS AND METHODS

In this experiment, transparent glass slides measuring $75\,mm \times 25\,mm \times 1\,mm$ each were prepared by soaking in hydrochloric acid, acetone, and distilled water to remove contaminants and ensure uniform deposition. 5.7g of $SbCl_3$ was first dissolved in 17ml of C_3H_6O to which 15.5ml of 1M $Na_2S_2O_3$ and 100ml of distilled water were added sequentially and stirred vigorously for 5 minutes by a means of magnetic stirrer. The solution which changed from white to a clear transparent color was poured into different 250ml beakers labeled **A** (As-deposited, serving as a control experiment), **B (**0.1M $MgSO_4$,**)**, **C (**0.2M $MgSO_4$,**)** and **D(**0.3M $MgSO_4$,**).** Four of the prepared glass substrates were vertically and partially immersed by means of synthetic foams onto each of the four 250ml beakers. The set up was allowed for 2 hours deposition time after which the substrates were removed from the reacting baths, rinsed with distilled water, hung with clips in open air to dry and labeled accordingly for easy identification. To improve the structural, electrical, and optical properties of the deposited films and activate dopants, the deposited films were annealed at different annealing temperatures, 100˚C, 200˚C and 300˚C at constant annealing time.

RESULTS AND DISCUSSION

Figures 1 – 4 is the Plots of percentage transmittance versus wavelength for as-deposited and annealed films at different temperatures.

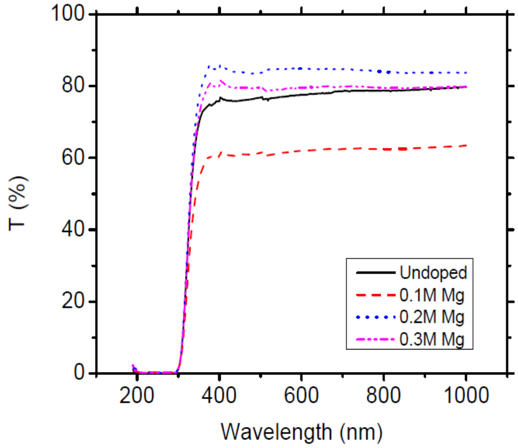

Figure 1: a Plot of transmittance Vs wavelength for as-deposited films

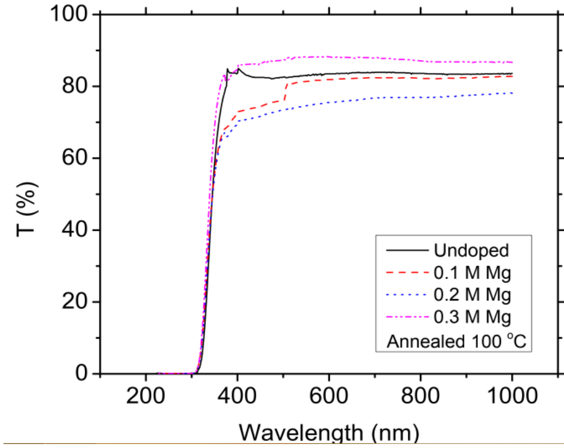

Figure 2: Plot of transmittance Vs wavelength for films annealed at 100˚C

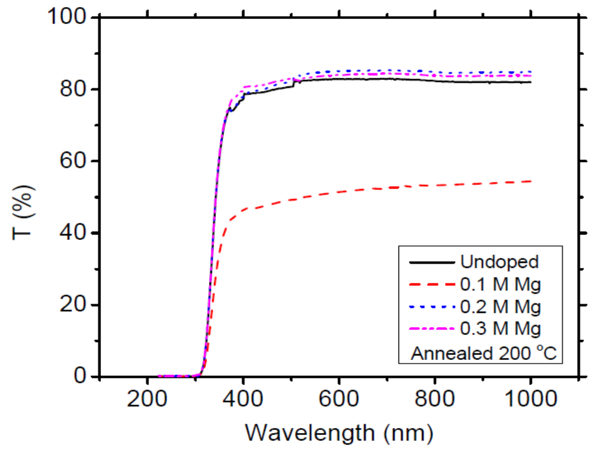

Figure 3: Plot of transmittance Vs wavelength for films annealed at 100˚C

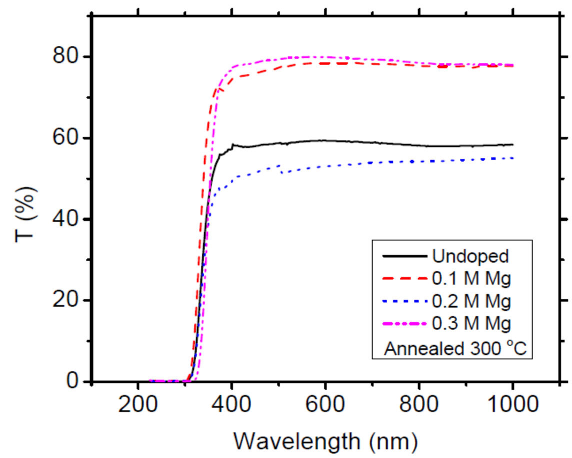

Figure 4: Plot of transmittance Vs wavelength for films annealed at 100˚C

Figs. 5 - 8 are the Plots of $(\alpha h\nu)^2$ versus $h\nu$ for the as-deposited and annealed films at different temperatures.

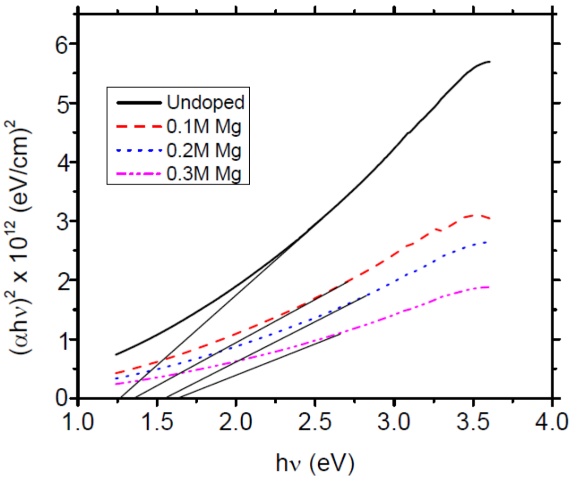

Figure 5: Plot of $(\alpha h\nu)^2$ against $h\nu$ for as-deposited films

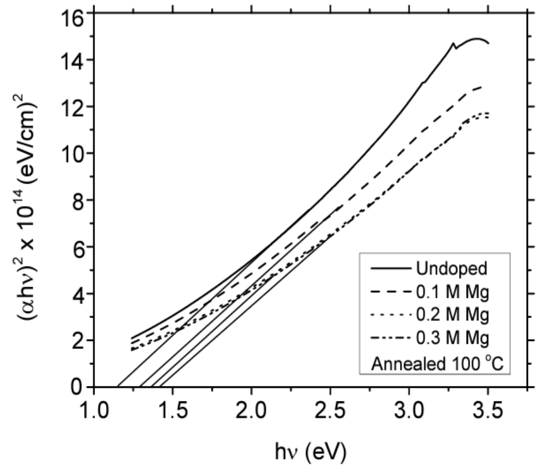

Figure 6: Plot of $(\alpha h\nu)^2$ against $h\nu$ for films annealed at 100˚C

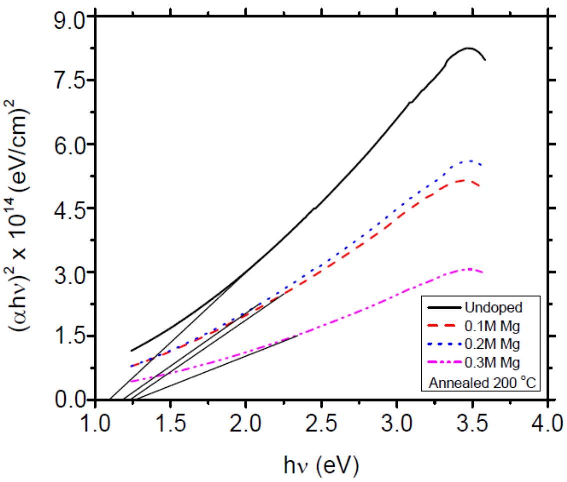

Figure 7: Plot of $(\alpha h\nu)^2$ against $h\nu$ for films annealed at 200˚C

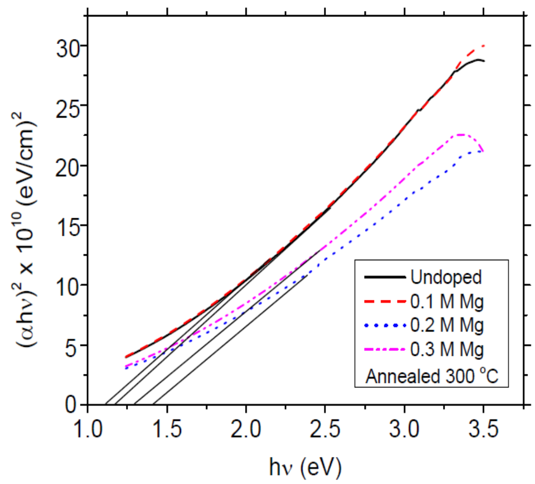

Figure 8: Plot of $(\alpha h\nu)^2$ against $h\nu$ for films annealed at 300˚C

The transmittance of the films remained consistently above 40% in the UV-VIS region regardless of doping and annealing treatments, with transmittance increasing as wavelength increased. Doping induced some changes in transmittance, as evidenced in Figs. 1-4. Notably, the 0.1M Mg2+ doping treatment exhibited unique behavior in both doped and annealed films. The addition of dopant affected the percentage transmittance of the films, consistent with findings reported by (Aousgi and Kanzari, 2011). Annealing treatments decreased transmittance, primarily attributed to increased crystallite size, aligning with (Tigau *et al.*, 2004) report. The most significant reduction occurred in films doped with 0.1M Mg2+ ions and annealed at 200˚C, due to higher photon absorption. Similar behavior has been observed in other thin films by research groups such as (Lakhdar *et al.*, 2014). The high transmittance displayed by the films above the UV region makes them suitable for constructing poultry walls and roofs. This property facilitates optimal temperature conditions for young chicks, potentially reducing energy costs associated with warming poultry houses using other energy sources.

The determination of the energy band gap involved extrapolating the intercept on the hν-axis from the plot of $(\propto h\nu)^2$ versus hν. In both the as-grown and heat-treated layers, the energy band gap was identified as direct and ranged from 1.25eV to 1.72eV. Dopants induced a Burstein-Moss shift (the phenomenon where the energy band gap of a semiconductor material increases due to the introduction of doping, particularly when doping introduces additional charge carriers into the material) in the energy band gap of the as-grown films within a specific range of dopant concentrations, as illustrated in Fig. 5. In the annealed films, as depicted in figs. 6-8, the band-gap energy ranged from 1.15eV to 1.35eV. Annealing treatments caused a shift in the energy band gap towards lower photon energies (longer wavelengths) for dopant concentrations of 0.1M and 0.2M respectively, while showing a different trend for higher concentrations of Mg2+ ions, as observed in Fig.8. The decrease in band gap energy could be attributed to the increase in grain size induced by annealing treatment. This reduction in band gap energy aligns with findings reported by (Agbo and Nnabuchi, 2011) regarding TiO2/ZnO thin films at various annealing temperatures, as well as (Augustine and Nnabuchi, 2017) in similar studies. The obtained values of the energy band gap are consistent with those reported by other researchers in the literature, such as (Vinayakumar *et al.*, 2017, Birkett et al., 2018, Nair *et al.*, 2018 and Wu *et al.*, 2018). These values fall within a suitable range for utilizing the films as absorbers in hetero-junction solar cell devices, contributing to sustainable energy applications.

CONCLUSION

In conclusion, this study investigated the effects of magnesium doping concentration and annealing treatments on the transmittance and bandgap characteristics of Sb_2S_3 films deposited via chemical deposition technique. Increasing magnesium concentration was found to increase the energy bandgap of the films, while annealing temperature decreased it. Magnesium doping induced changes in transmittance, particularly notable with 0.1M and 0.2M, Mg2+ concentrations highlighting the influence of dopant concentration on the optical properties. Annealing led to reduced transmittance due to increased crystallite size, notably in films doped with 0.1M Mg2+ ions and annealed at 200˚C, suggesting enhanced photon absorption. The energy band gap, determined as direct, ranged from 1.25eV to 1.72eV in both as-grown and heat-treated layers. Doping with magnesium induced a Burstein-Moss shift within a specific concentration range, while annealing caused a shift towards lower photon energies for certain dopant concentrations. The obtained bandgap values fall within a suitable range for the films' utilization in hetero-junction solar cell devices, thereby contributing to sustainable energy applications.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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