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Interdependence of Deposition Time, Doping Concentration, and annealing on the Optical Behavior of Mg-Doped antimony sulphide (Sb_2S_3) Thin Films.

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ABSTRACT

Mg-doped antimony sulphide (Sb_2S_3*) thin films were deposited on glass substrates via chemical bath deposition at room temperature, with deposition times of 60 and 120 minutes. Post-deposition, films were annealed at 100°C, 200°C, and 300°C for 60 minutes. Optical properties, assessed using a UV-Vis spectrophotometer (200-1000 nm range), reveal significant influences of deposition time, Mg concentration, and annealing temperature on absorbance, refractive index, and bandgap energy. Films deposited for 120 minutes show higher refractive indices and initial bandgap energies, decreasing more upon annealing than 60-minute films. Increased Mg concentration and higher annealing temperatures enhance refractive indices and cause a red shift, reducing the bandgap energy. Bandgaps range from 3.61 to 3.91 eV, indicating potential for high-power electronics applications. This study underscores the importance of deposition time, doping concentration, and annealing temperature in tailoring Mg-doped* Sb_2S_3 *thin films for optical devices.*

1. Introduction

The development of high-performance optoelectronic devices, such as solar cells, photodetectors, and light-emitting diodes etc., hinges critically on the materials' optical and electronic properties. Antimony sulphide (Sb_2S_3) has emerged a promising candidate for such applications due to its excellent optical properties, including a high absorption coefficient and a suitable bandgap for visible light absorption [1].

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However, to fully harness these properties, precise control over the material's deposition, doping, and post-deposition treatment processes is essential.

Doping is a well-established technique to modify the electronic and optical properties of semiconductors [2-3]. By introducing dopant atoms into the Sb_2S_3 lattice, we can tailor its band structure, carrier concentration, and defect states, thereby influencing its overall performance in devices. Magnesium (Mg) is being studied as an effective dopant for Sb_2S_3, capable of enhancing its optical absorption and modifying its band gap. However, the concentration of Mg doping must be carefully controlled to avoid detrimental effects on the film's properties. In addition to doping, the method and duration of thin film deposition which affects the film thickness, crystallinity, and homogeneity play a crucial role in determining the material's quality and characteristics. Thin film deposition techniques are categorized into chemical and physical methods [4], with some techniques incorporating both. Chemical deposition includes chemical vapor deposition (CVD), spray pyrolysis, screen printing, exchange reactions, electro deposition, anodization, and electrophoresis and solution growth techniques (SGT), while Physical deposition includes physical vapor deposition (PVD), sputtering, and plasma techniques. These methods can also be divided into solution deposition (chemical and electrochemical methods) and vapor deposition (chemical and physical vapor methods), each with distinct mechanisms. Chemical vapor transport techniques are used for thin and thick coatings [5]. In chemical deposition, a fluid precursor chemically changes at a substrate, forming a conformal solid layer. Chemical Bath Deposition (CBD), utilized in this study, is popular for its simplicity, reproducibility, convenience, and cost-effectiveness, allowing controlled fabrication of thin films [6-7].

Many workers have obtained Sb_2S_3 compound by these techniques, and have studied the effect of deposition conditions on the physical properties [8]. In 2001, [9] used chemical bath deposition to prepare antimony trisulfide (Sb_2S_3) thin films with varying particle sizes and distinct band gaps on glass substrates. Structural investigations revealed that the as-deposited films were amorphous and optical absorption edge shifted from the bulk energy gap of 2.2 eV to 3.8 eV with decreasing particle size, a phenomenon attributed to the quantum size effect of electrons and holes in Sb_2S_3 nanoparticles. They used the Swanepoel method, based on interference maxima and minima in the wavelength range of 400-2500 nm to determine the optical constants of the Sb_2S_3 thick films (589 nm). In 2020 [1], conducted a study on Antimony sulphide (Sb_2S_3), focusing on its structural, electronic, and optical properties when doped with nickel (Ni). The findings reveal that Ni doping reduces the band gap energy of Sb_2S_3 compared to its pure form. The results also show that Ni-doped Sb_2S_3 exhibits a higher optical absorption coefficient in the visible region than pure Sb_2S_3, making it promising for optoelectronic applications. In 2011, [8] investigated the electronic and optical properties of Sb_2S_3 using the full potential linearized augmented plane wave (FP-LAPW) method, as implemented in Wien2k. They comprehensively analyzed the optical properties, including the dielectric function, absorption spectrum, refractive index, extinction coefficient, reflectivity, and energy-loss spectrum. The contributions of various bands were examined through total and partial density of states curves. Their calculated band structure reveals a direct band gap.

The simplicity and scalability of CBD make it particularly attractive for large-scale production of Sb_2S_3 thin films [7]. For optimizing thin film properties, post-deposition treatments are often required. These treatments enhance the structural and optical characteristics of the films. One such effective method is annealing, which involves heating the films to elevated temperatures in a controlled environment. In this study, the films were annealed at temperatures of 100°C, 200°C, and 300°C, and the effects of these treatments on the optical and structural properties of the films were examined. This process helps in improving film quality by altering its microstructure and reducing defects, leading to enhanced performance [10]. Annealing has been demonstrated as an effective method for inducing structural transformations, improving crystallinity, and optimizing electrical properties in thin films [11]

Despite the individual understanding of deposition, doping, and annealing processes, their interdependent effects on the optical properties of Mg-doped Sb_2S_3 thin films remain Untapped. Specifically, the combined influence of deposition time, Mg doping concentration, and annealing conditions on the optical absorption, band gap energy, and refractive index of Sb_2S_3 thin films needs thorough investigation. The understanding of these interdependencies is essential for optimizing the fabrication process to achieve desired optical properties. In this study we examined the effects of deposition time, doping concentration, and annealing on the Optical behavior of Mg-doped antimony sulphide (Sb_2S_3) Thin Films deposited via the Chemical Bath Deposition (CBD) technique. The objectives were to analyze the optical properties of films deposited for 60 and 120 minutes after annealing at 100°C, 200°C, and 300°C, evaluate the impact of annealing on the films' optical properties and band energy, determine the optimal annealing temperature for enhanced performance, and compare the optical properties of the films before and after annealing to assess improvements in quality and functionality.

2. Materials and Methods

In this experiment, glass substrates measuring 75 mm×25 mm×1 mm each were prepared by soaking in hydrochloric acid, acetone, and distilled water sequentially for 10 minutes each to remove contaminants and ensure uniform deposition. 5.7g of $SbCl_3$ was first dissolved in 17 ml of C_3H_6O to which 15.5 ml of 1M $Na_2S_2O_3$ and 100 ml 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 250 ml 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 250 ml beakers. The set up was allowed for 1 hour 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. The process was repeated for another deposition time of 2 hours with different set of substrates. To improve the structural 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 of 60 minutes. The optical properties of the films were measured using a UV-Vis spectrophotometer in the wavelength range of 200-1000 nm, which were then used to infer the electronic properties. The effect of deposition time, doping concentration, and annealing temperature on the optical properties of Mg-doped Sb_2S_3 thin films was systematically analyzed to determine the optimal conditions for enhanced optical performance of the films. Comparisons were made between films deposited for different durations, with varying doping concentrations, and annealed at different temperatures.

3. Results and Discussion

Figures 1 to 16 present the absorbance curves, refractive index curves, and band energy plots of the films studied. The plot of absorbance against wavelength for 0.1M, 0.2M, and 0.3M concentrations of Mg-doped antimony sulphide (Sb_2S_3) thin films, deposited for 60 and 120 minutes and annealed at 100°C, 200°C, and 300°C, respectively, reveals important trends related to deposition time, annealing temperature, and magnesium concentration. All the Mg-doped Sb_2S_3 thin films exhibit absorbance in the visible spectrum, with maximum absorption wavelengths between 300 nm and 400 nm. This is similar to that obtained by other researchers like [1, 13]. This is attributed to electronic transitions within the Sb_2S_3 structure [9]. The absorbance of all thin films decreases with increasing wavelength and stabilizes between 500 nm and 1000 nm. When annealed at 100°C in Fig. 2; Films deposited for 60 Minutes shows a slight decrease in absorbance with increasing wavelength up to the near-infrared region.

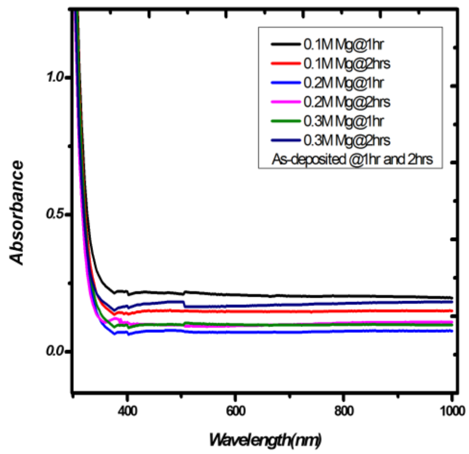

Fig 1: Absorbance curve for as-deposited films at 1and 2hrs

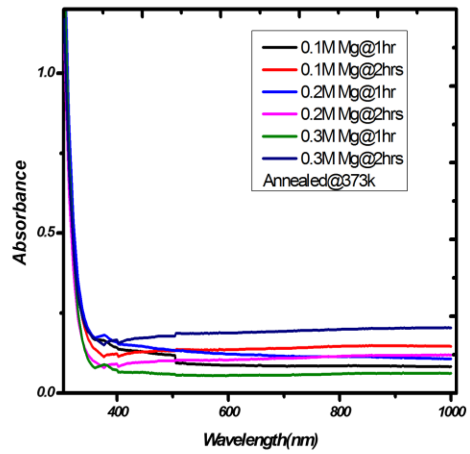

Fig 2: Abs curve for films deposited at 1and 2hrs and annealed at 100°C.

The 0.3M Mg-doped film shows the lowest absorbance. Films Deposited for 120 Minutes show an increase in absorbance with increasing wavelength from 400 nm to 1000 nm. The highest absorbance is observed for the 0.3M Mg-doped film, followed by the 0.1M, and then the 0.2M Mg-doped film. At Annealing temperature of 200°C in Fig.3, all films exhibit a decrease in absorbance with increasing wavelength. The absorbance of the films doped with 0.3M and 0.2M Mg deposited for 1 hour overlap. When annealed at 300°C in Fig. 4; all films exhibit a decrease in absorbance with increasing wavelength.

Generally, Films deposited for 120 minutes generally show higher absorbance across the wavelength range compared to those deposited for 60 minutes. At 0.3M concentration, films exhibit the highest absorbance when deposited for 120 minutes and annealed at 100°C. The 0.1M Mg-doped film deposited for 120 minutes shows a significant increase in absorbance compared to the 0.2M Mg-doped film, indicating a possible interaction between concentration and deposition time that influences absorbance properties. Higher annealing temperatures (200°C and 300°C) generally enhance the absorbance for films with 0.2M and 0.3M concentrations. For films with a 0.1M concentration, increasing the deposition temperature decreases absorbance, suggesting a possible degradation or alteration in film structure.

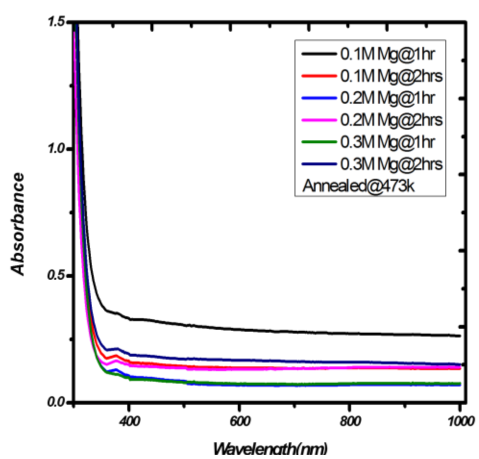

Fig 3: Abs curve for films deposited at 1and 2hrs and annealed at 200°C.

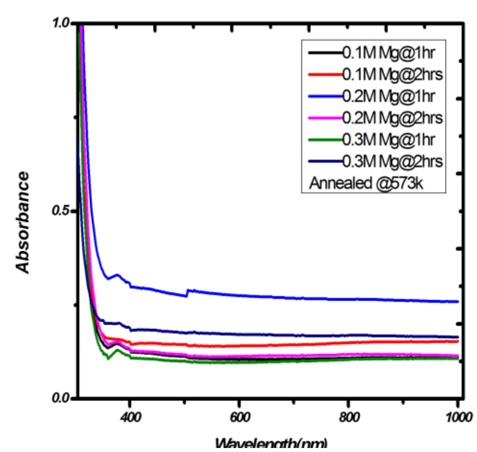

Fig 4: Abs curve for films deposited at 1and 2hrs and annealed at 300°C.

The refractive index of a material measures how light behaves as it passes through, which is crucial for optical communication, device design, and spectral dispersion. A higher refractive index indicates that the material significantly slows down and bends light [1, 7].
Figures 5 to 8 show the plots of refractive index against wavelength for films with varying deposition times, magnesium molar concentrations, and annealing temperatures.

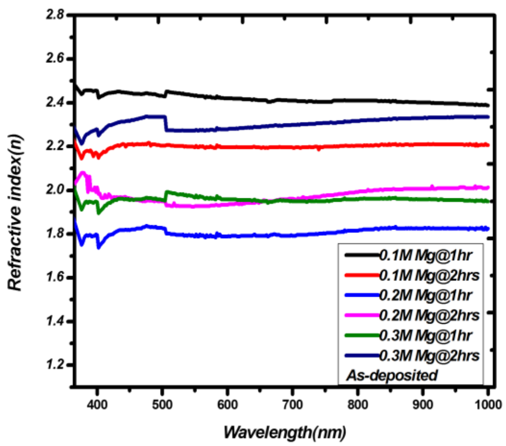

Fig 5: Refractive index curve for as-deposited films at 1and 2hrs unannealed.

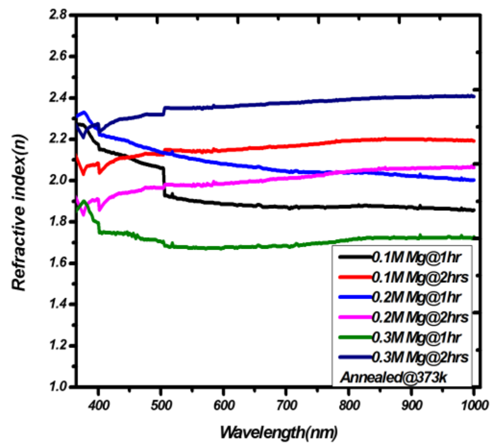

Fig 6: Refractive index curve for films deposited at 1and 2hrs and annealed at 100ºC.

When annealed at 100ºC as displayed in fig 6, while Films deposited for 60 minutes decreased in refractive index with increasing wavelength (400 nm to 1000 nm), Films deposited for 2 hours increased in refractive index with increasing wavelength. When annealed **at 200°C as displayed in fig 7**, all deposited films showed a decrease in refractive index with increasing wavelength. When annealed at 300ºC as displayed in fig 8, it was also noticed that All deposited films showed a decrease in refractive index with increasing wavelength.

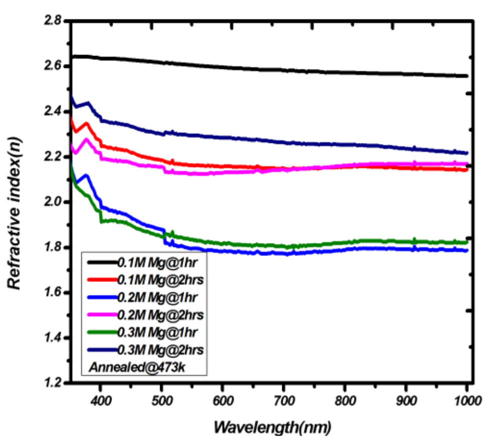

Fig 7: Refractive index curve for films deposited at 1and 2hrs and annealed at 200ºC.

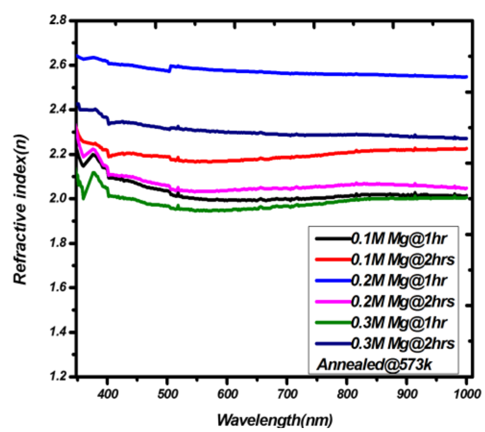

Fig 8: Refractive index curve for films deposited @at1and 2hrs and annealed at 300ºC.

A holistic look at the films indicates that the refractive index of the films is influenced by deposition time, molar concentration of magnesium, and annealing temperature. Generally, films deposited for longer times (2 hours) tend to have higher refractive indices compared to those deposited for shorter times (1 hour). The refractive index decreases for all concentrations at higher wavelengths, except for films deposited for 120 minutes and annealed at 100°C, as shown in Figure 6. This observation is consistent with the findings of other authors [12]. The molar concentration of magnesium also plays a significant role, with higher concentrations generally leading to higher refractive indices. Annealing at higher temperatures (200°C and 300°C) tends to increase the refractive index across the board, although the specific values and trends can vary depending on the exact combination of deposition time and concentration.

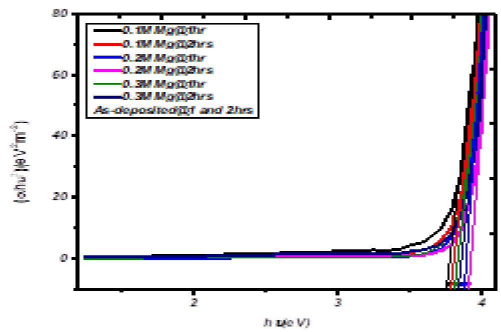

Fig 9: Band Energy curve for as-deposited films at 1and 2hrs unannealed

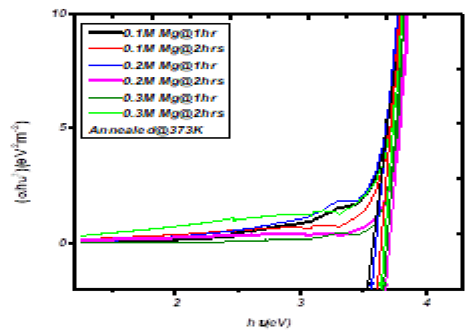

Fig 10: Band Energy curve for films deposited at 1and 2hrs and annealed at 100°C.

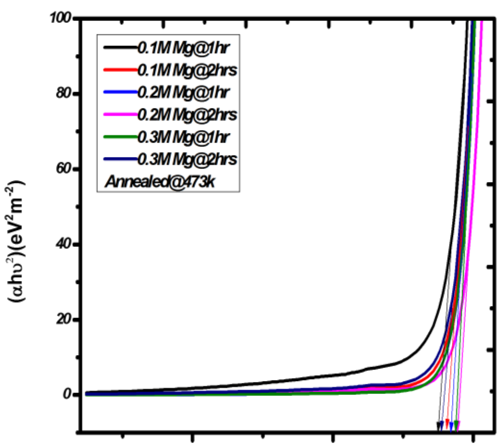

Fig 11: Band Energy curve for films deposited at 1and 2hrs and annealed at 200°C.

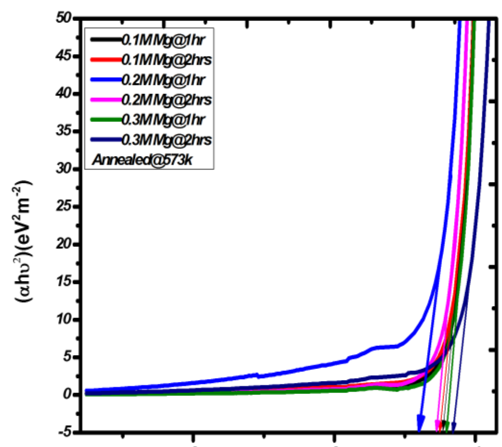

Fig 12: Band Energy curve for films deposited at 1and 2hrs and annealed at 300°C.

The plots for determining the band gap energy (Eg) of the deposited films, both at 60 and 120 minutes, are presented in Figures 9 through 12. The band gap energy was determined by extrapolating the linear portion of the graphs to the hv axis. The results indicate that the band gap of the deposited films ranged from 3.61 eV to 3.91 eV. A detailed examination of the plots reveals a noticeable red shift in the band gap of all the films upon annealing, regardless of magnesium doping concentration and deposition temperature. The red shift which is the decrease in the energy gap between the valence band and the conduction band, results in the material absorbing light at longer wavelengths (lower energy) than it previously did. Similar shifts in band gap have been reported by other researchers, such as [13] using chemical deposition methods. Additionally, the plots demonstrate that changes in deposition temperature led to a decrease in the band gap, which is consistent with the behavior observed in the absorbance curves. This correlation underscores the influence of annealing and deposition conditions on the optical properties of Mg-doped antimony sulphide (Sb_2S_3) thin films.
Unannealed Films (Fig. 9) has Band gap Range between 3.76 - 3.91 eV, when Annealed at 100°C (Fig. 10), the range is between 3.63 - 3.74 eV, when Annealed at 200°C (Fig.11), the Band gap Range

is between 3.75 - 3.90 eV, an increase of Annealing temperature to 300°C (Fig.12) gives the range 3.61 - 3.85 eV. Generally, films deposited for 60 minutes show lower band gap energies compared to those deposited for 120 minutes across all annealing temperatures. As annealing temperature increases, the band gap energy tends to decrease for these films. Films deposited for 120 minutes generally show higher band gap energies in the unannealed and lower temperature annealed states, but a notable decrease in band gap with increased annealing temperature. These films exhibit a clear red shift, indicating a reduction in band gap energy with increased annealing temperature. This behavior could be attributed to modifications in the valence and conduction band edges introduced by magnesium impurities. Additionally, the differences in lattice constants between the dopants and host atoms may be responsible for the observed phenomena. The results for the energy band gap align with findings from other studies [14-15, 16].

Considering Magnesium Concentration Influence, 0.1M Mg-doped Unannealed films have the lowest band gap energy at 3.76 eV (60 minutes) and 3.78 eV (120 minutes). Annealing decreases the band gap energy further, reaching the lowest value of 3.63 eV at 100°C for 60 minutes deposition. For 0.2M Mg-doped, Unannealed films show the highest band gap energies, 3.88 eV (60 minutes) and 3.91 eV (120 minutes). Annealing decreases the band gap to as low as 3.61 eV at 300°C for 60 minutes deposition. In the case of 0.3M Mg-doped, these films exhibit intermediate band gap energies in the unannealed state. Annealing at higher temperatures shows a similar trend of decreasing band gap energy, with the lowest is being 3.72 eV at 100°C for 120 minutes deposition. This wide band gap observed made Mg-doped antimony sulphide (Sb_2S_3) a key material for use in **High-Power Electronics** for applications like electric vehicles, renewable energy systems, and industrial motors [17].

4. Conclusion

In this study, various concentrations of Mg-Doped antimony sulphide (Sb_2S_3) Thin Films fabricated at different deposition times via solution growth have been examined. The absorbance characteristics, refractive index and band gap energy of the thin films were significantly influenced by deposition time, molar concentration of Mg, and annealing temperature. Films deposited for longer times (2 hours) tend to have higher refractive indices compared to those deposited for shorter times (1 hour). The increase in molar concentration of magnesium leads to higher refractive indices. Annealing at higher temperatures (200°C and 300°C) tends to increase the refractive index across the board, although the specific values and trends can vary depending on the exact combination of deposition time and concentration. Higher annealing temperatures result in a red shift, reducing the band gap energy. Films deposited for 120 minutes show higher initial band gap energies that decrease more significantly with annealing compared to those deposited for 60 minutes. The concentration of magnesium doping also plays a crucial role, with 0.2M doping showing the highest initial band gap energies and the most significant decrease upon annealing. These factors collectively determine the film's optical properties, which are crucial for their potential applications in optical devices.

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