Chemically grown Zinc Bismuth Sulfide ($ZnBi_2S_3$) thin films for optoelectronic applications

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Zinc Bismuth Sulfide ($ZnBi_2S_3$) thin films are successfully deposited on a glass substrate by chemical bath deposition technique at different bath temperatures (60°C, 70°C, 80°C). The basic chemical bath contains bismuth nitrate, zinc nitrate and sodium thiosulphate as chemical reagents. The deposited films are characterized by XRD, FESEM, EDAX, UV Spectroscopy and PL for structural, morphological and optical properties. The formation of $ZnBi_2S_3$ is evidenced by the peaks in X-ray diffraction pattern. FESEM observation indicates the spherical grain shape of films at different temperatures. EDAX confirms the composition of $ZnBi_2S_3$. The bandgap energy obtained for deposited films is in the order of 2.31eV and depends on the film thickness. The PL spectrum reveals the green emission in the visible region.The Present work indicates the feasibility of $ZnBi_2S_3$ as a solar material.

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Keywords:Thinfilms, Chemical bath deposition, Ternary compounds, Semiconductors, Bandgap, Solar energy material

1. Introduction

In the present scenario, ternary compounds draw much attention for its photoelectric properties. [1]. Bi_2S_3 is used for the development of ternary compounds such as $CuBiS_2$, $PbBiS_2$that to be used as an alternative absorber layer in thin film solar cells [2]–[4]. Bismuth sulfide is group V-VI semiconductor with a band gap of 1.7eV [5]–[7], promising candidate for the fabrication of photovoltaic devices, photo conductors, etc. [8], [9]. On the other hand,ZnS as a typical II-VI semiconductor with bandgap of 3.8eV [10], [11] has attracted considerable attention. ZnS has been used for the electro optic modulators and window layer of solar cells due to its wide band gap [12]–[14]. The $ZnBi_2S_3$ ternary compounds are of current interest because of its solar cell and photovoltaic applications.

The Synthesis of ternary thinfilms has been reported by several techniques like spray pyrolysis [15]–[17], thermal deposition [18],[19] and chemical bath deposition (CBD) [20]–[22]. Among these, CBD has several advantages in comparison with other preparation techniques as its inexpensive and convenient method for large area deposition of film at low temperatures. In the Present study, first time $ZnBi_2S_3$thin film are successfully deposited by chemical bath deposition over the glass substrate with different bath temperatures (60°C, 70°C, 80°C). The deposited thin films are characterized in order to obtain the morphological, structural and optical properties.

2. Experimental details

Initially, the glass slides (75mm × 25mm × 1.45mm) were washed with chromic acid for 10 to 15 min followed by washing in double distilled water. Finally, allthe substrates were ultrasonically cleaned and dried using isopropyl alcohol.

For the preparation of $ZnBi_2S_3$ thin films, AR grade of 25ml of 0.3 M zinc nitrate, 25ml of 1.7M bismuth nitrate and 50ml of 2M sodium thiosulphateare mixed together and continuously stirred for 45min. The light yellow solution transforms to blackish brown color while stirring. Ethylene diamine tetra acetic acid disodium salt (EDTA) was used as complexing agent for uniformity of thin films [18]. After required bath temperature was reached, the substrates are vertically immersed in the solution. Substrate fixing setup wasnovelly designed for deposition (Fig. 1).

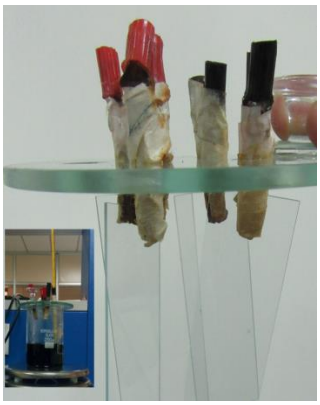

Fig. 1. Substrate fixing setup used for the deposition

After deposition for 2h in bath temperatures (60°C, 70°C, 80°C) the solutions are kept at room temperature for 6 h.$ZnBi_2S_3$ films were formed after the 8hof deposition.

The films are prepared at three different bath temperatures (60°C, 70°C, 80°C).

The reaction mechanism in chemical bath deposition:

(i) Formation of metal complexes

Aqueous solution of $Bi(NO_3)_3.5H_2O$with EDTA results were the formation of complexed species. Exhortation of bismuth ions in the presence of EDTA

$$Bi(NO_3)_3{\cdot}5H_2O + EDTA^{-4} \rightarrow [Bi(EDTA)]^{-1} + 5H_2O \quad (1)$$

Similarly, zinc ions with EDTA as,

$$Zn(NO_3)_2{\cdot}6H_2O + EDTA^{-4} \rightarrow [Zn(EDTA)]^{-2} + 6H_2O \quad (2)$$

(ii) Dissociation of sodium thiosulphate

$$Na_2S_2O_3 \rightarrow 2Na^+ + S_2O_3^{2-} \quad (3)$$

In acidic medium

$$4.5S_2O_3^{2-} + 9H^+ \rightarrow 6HSO_4^- + 3S^{2-} \quad (4)$$

(ii) The net reaction for $Zn_xBi_{2-x}S_3$ formation(x = 0.3 M)

$$[Bi(EDTA)]^{-1} + [Zn(EDTA)]^{-2} + 8H^+ + 3S^{2-} \rightarrow Zn_{0.3}Bi_{1.7}S_3 + 2EDTA \quad (5)$$

The ternary films deposited under these conditions are analyzedfor the crystalline nature by X-ray diffraction technique (Shimadzu XRD 6000), the surface morphology by field emission scanning electron microscope (FE-SEM) (ZEISS ultraplus), stoichiometry by energy dispersive analysis of X-ray (EDAX), the band gap energy by UV-Vis spectroscopy (Agilent - Cary 100) and photo optic properties by photoluminescence (PL) spectroscopy (Cary Eclipse-EL08083851).

3. Results and discussion

3.1. Crystalline analysis

Fig. 2 shows XRD patterns of the stacked films prepared under different bath temperatures annealed at 300°C. The standard diffraction pattern of Bi_2S_3 (PDF 65-2435) is as shown in figure. The major peaks appearing at 2θ of 25.04° (130), 22.47° (220) and 40.08° (141) corresponds to the bismuth sulfide (orthorhombic). Several peaks are observed for bismuth sulfide. On increasing the bath temperatures, compositional changes occur, resulting in XRD pattern. While increase in bath temperature ZnSpeaks were located at 2θ of 30.04°, 47.43°(PDF 89-7386) which has been indexed as (107), (110) respectively at 70°Cand 80°C. Whereas the peaks corresponding to the ZnS phase are of relatively lower intensities due to the ternary nature [24]–[29]. Some of the bismuth sulfide peaks are shifted due to the ZnS phase. Moreover the 2θ of 30.04° corresponding to the ZnS phase merged with bismuth sulfide of 28.72°. It is difficult to distinguish the Bi_2S_3 peaks and ZnS peaks on increasing the bath temperatures. At 70°C the prominent peaks are observed for both Bi_2S_3 and ZnS which seems to be the stable phase formation of $ZnBi_2S_3$. Beyond 80°C intensity of the peaks were suppressed.

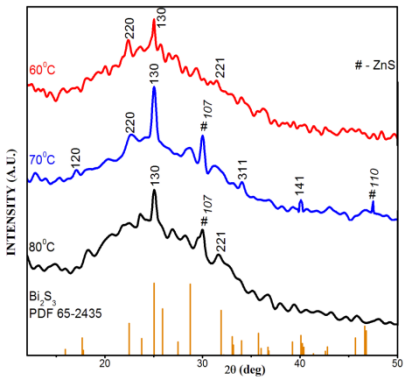

Fig. 2. XRD pattern of $ZnBi_2S_3$ films deposited at different temperatures (60 °C, 70 °C, 80 °C)

3.2. Thickness of the films

The thickness of $ZnBi_2S_3$ films are measuredthroughprofilometery technique. Thickness of the films at 60°C, 70°C, 80°C is 182 nm, 215 nm and 209 nm respectively (Table 1). Atthe bath temperature of 60°C to 70°Cthickness of the films are increaseddue to increase in grain size.

3.3. Surface morphology and EDAX

The FESEM image of the $ZnBi_2S_3$films is as shown in figure. The micrograph indicates surface morphology of the films. Apparently, increase in bath temperature from 60°C to 80°C (Fig. 3),growth of grain size is observed. When the bath temperature is above 60°C surfaces are ofspherical shaped, randomly distributed and well covered (Fig. 3b, 3c). But at 60°C (Fig. 3a) it is seem to be rough and non uniform. FESEM pictures clearly reveal the distribution of particles, interfused together with the neat boundary between neighboring particles.

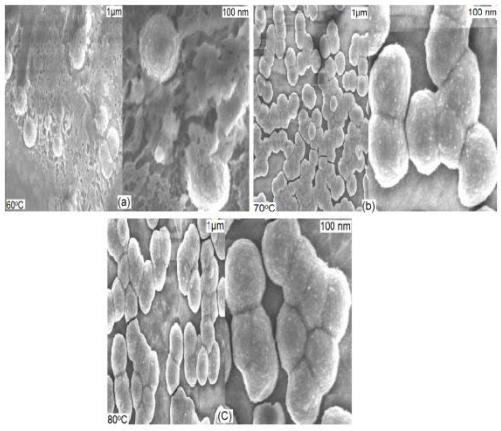

Fig. 3. FESEM micrographs of the $ZnBi_2S_3$ films deposited at different temperatures 60 °C (a), 70 °C (b), 80 °C (c)

The quantitative and compositional analysis of the deposited films is carried out by EDAX technique. The EDAX spectra of the film at 70°C indicate the presence of bismuth, zinc and sulphur elements is as shown in Fig. 4. The extra peaks observed in EDAX pattern corresponds to the glass substrate. The composition is found to be stoichiometric and homogeneous. This confirms the formation of $ZnBi_2S_3$ thin films.

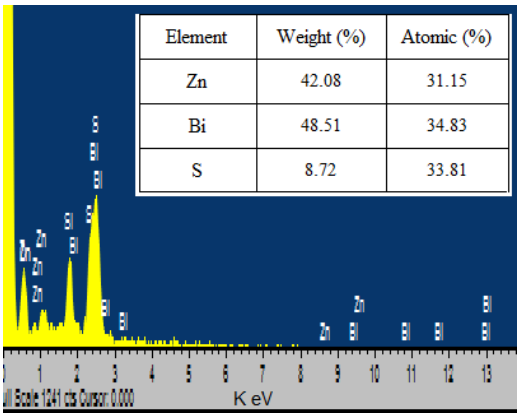

Fig. 4. EDAX spectra for the $ZnBi_2S_3$ film deposited at 70 °C

3.4. Optical properties

UV-Visible studies

Fig. 5a shows the absorbance spectra of the films. It showsan absorption edge about 400nm, proving that these films are perfectly suitable for solar cell applications.

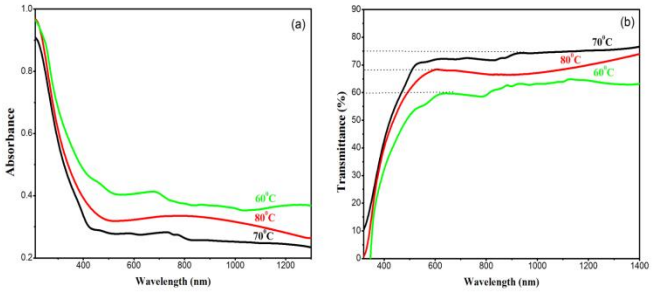

Fig. 5a. Absorbance spectra for the $ZnBi_2S_3$ films deposited at (60 °C, 70 °C, 80 °C) b. Transmittance spectra of the $ZnBi_2S_3$ films deposited at (60 °C, 70 °C, 80 °C)

Fig. 5b shows the transmission spectra of $ZnBi_2S_3$ films. The result illustrates the optical transmittance of 60% to 75% in the visible region. The maximum transmittance is observed in the film deposited at bath temperature of 70°C. The bandgap energies of these films are calculated with the use of absorption spectra corresponds to the excited electrons from the valence band to conduction band. Bandgap energy E_g value can be estimated from the relation[30]

$$(\alpha\ h\upsilon)^2 = A\ (h\upsilon - E_g)$$

Where α is the optical absorption coefficient, hυ is the energy (eV), h is the planks constant. Fig. 6 illustrates the $(\alpha\ h\upsilon)^2$ versus energy plot. The estimated bandgap energy E_g for 60°C, 70°C, 80°C is 2.65 eV, 2.31 eV and 2.48 eV respectively (Table 1) [31]–[33]. It is found that the deposited $ZnBi_2S_3$thin films have $E_g$value increases from 2.31 eV to 2.65 eV with decrease in film thickness and its variation is nearly linear. It is due to the growing process of impurity levels in conduction band of high thickness and rearrangement of clusters at different elevated temperatures. In the case of large thickness, films allowed states are merged with conduction band which reduces the band gap [34]–[36].

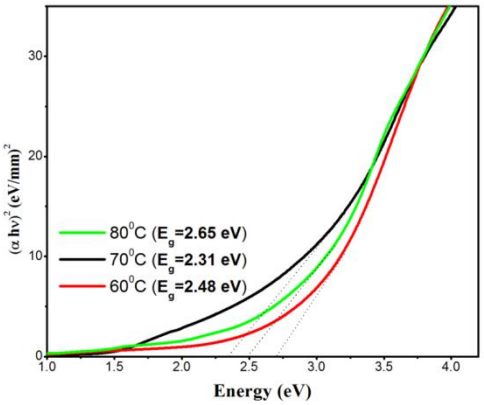

Fig. 6. $(\alpha h\upsilon)^2$ versus hυ of $ZnBi_2S_3$ thin films of different bath temperatures (60 °C, 70 °C, 80 °C)

Table 1. Thickness and bandgap energy (eV) of $ZnBi_2S_3$ film for different deposition temperatures

Deposition temperatures (°C)	Thickness (nm)	Bandgap energy (eV)
60	182	2.48
70	215	2.31
80	209	2.65

Photoluminescence studies

Fig. 7 shows the photoluminescence (PL) spectra for deposited films at different bath temperatures. In our present samples, a broad emission spectrum is observed at 545 nm (2.28eV). The results posses green photoluminescence properties under the excitation of 400 nm. The wide green emission at 545nm is very strong and is similar to the results reported for ZnS doped with Al and Cu [36]–[38]. At 60°C emission significantly decreases, which implies the recombination of photo generated carriers are suppressed due to the composite effect of ternary semiconductor [39]–[43]. The curve shows relatively strong green emission in the visible region at 70°C and 80°C. The green emission arises due to the self activated centers of Zn, interstitial states associated with the nano structures of Bi and it depends on the preparation techniques [39],[44]-[45].

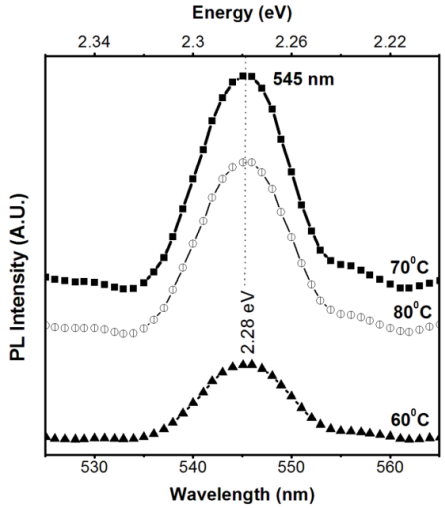

Fig. 7. Photoluminescence spectra of $ZnBi_2S_3$ films of different bath temperatures (60 °C, 70 °C, 80 °C) excited at 400 nm

4. Conclusion

In the present study reportes first time that $ZnBi_2S_3$ have been deposited successfully on the glass substrates by chemical bath deposition technique. XRD spectra illustrate the predominant peaks for deposited films at 70°C. FESEM imagesare indicatingthe surface uniformity of the films at different bath temperatures (60°C, 70°C, 80°C). The composition of the deposited film is found to be homogeneous and stoichiometric by EDAX. Using absorption spectra the band gap is estimated which depends on thickness of films. The PL reveals the strong emission at 545nm corresponding to Zn vacancies and interstitials of Bi. This work demonstrates $ZnBi_2S_3$ as a candidate for potential applications in solar and optoelectronic devices.

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