

Synthesis and Characterization of CuMS_2 (M= Bi, Sb) Thin Films Prepared by CBD Method*

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Abstract: CuMS_2 (M= Bi, Sb) thin films (0.1 M) were deposited by chemical bath deposition (CBD) method and characterized by X-ray diffraction (XRD) and UV-Visible (UV) analyses. The XRD pattern confirms the formation of orthorhombic structured CuBiS_2 with Cu_2S phases as an impurity and orthorhombic structured CuSbS_2 . UV studies show higher optical absorption in the visible region, which indicates that the resulting material can be used as an absorbing material in solar cells.

Keywords: CuBiS_2 , CuSbS_2 , CBD, XRD, Orthorhombic, Absorbing materials.

Introduction

Metal-based ternary chalcogenide semi-conductors ABX_2 (A= Cu, Ag; B= Bi, Sb, In; X= S, Se, Te) have considerable applications for a wide variety of IR detectors, p-n junction solar cells and thermoelectric materials [1]. CuSbS_2 and CuBiS_2 are semi-conducting materials having the capability of covering maximum part of the visible region and infra-red region in the electromagnetic spectrum ($E_g = 1.5$ to 2.2 eV), higher optical absorption coefficient ($>10^4 \text{ cm}^{-1}$) [2] and can be easily obtained in the form of thin films. The advantages of these materials are: 1) earth abundance 2) low cost when compared to Ag, In and Te and 3) lower toxicity. Hence, the present study aims to deposit CuMS_2 (M= Bi, Sb) thin films by simple CBD method and to study their structural and optical properties.

Experimental Details

AR grade chemicals were used in this study. CuMS_2 (M = Bi, Sb) thin films have been prepared by CBD technique. For the preparation of CuBiS_2 thin films, 0.1M of $\text{Cu}(\text{NO}_3)_2$ and 0.1M of $\text{Na}_2\text{S}_2\text{O}_3$ were dissolved in double

distilled water and added into ethylene glycol dissolved 0.1M of $\text{Bi}(\text{NO}_3)_3$ solution at room temperature under vigorous stirring. Then, ultrasonically cleaned substrates were immersed in the prepared solution at rest for 24 h. The preparation of CuSbS_2 thin film process was similar to that of CuBiS_2 ; here, 0.1 M of acetone dissolved SbCl_3 was used instead of $\text{Bi}(\text{NO}_3)_3$. After dipping for 24h, the substrates were taken out of the bath, rinsed with double distilled water and dried in room temperature. The prepared films were annealed at 200°C in air atmosphere for 1h and characterized by X-ray diffraction (XRD) and UV-Visible (UV) analyses.

Results and Discussion

Film thickness was calculated by using Swanepoel method [3] and found to be 1191 nm for CuBiS_2 and 303 nm for CuSbS_2 thin films. Fig. 1 shows the XRD patterns of CuBiS_2 and CuSbS_2 thin films. The CuBiS_2 film shows the prominent peaks at $2\theta = 30.09^\circ$ and 54.05° corresponding to the reflection of (013) and (216) planes, respectively, for orthorhombic

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CuBiS₂ [JCPDS Card No. 65-1300 and 89-2670]. An additional peak is observed at $2\theta=37.88^\circ$ belonging to (102) plane of hexagonal structured Cu₂S [JCPDS Card No. 89-2670]. In the case of CuSbS₂, the peaks at $2\theta =28.78^\circ$ and 25.33° correspond to the planes of (111) and (011), which confirms the formation of

orthorhombic CuSbS₂. The low intensity of the peaks indicates that the films consist of coarsely fine grains/or are nanocrystalline in nature. Crystalline size was calculated using Scherrer formula and found to be 68 nm and 20 nm for CuBiS₂ and CuSbS₂, respectively.

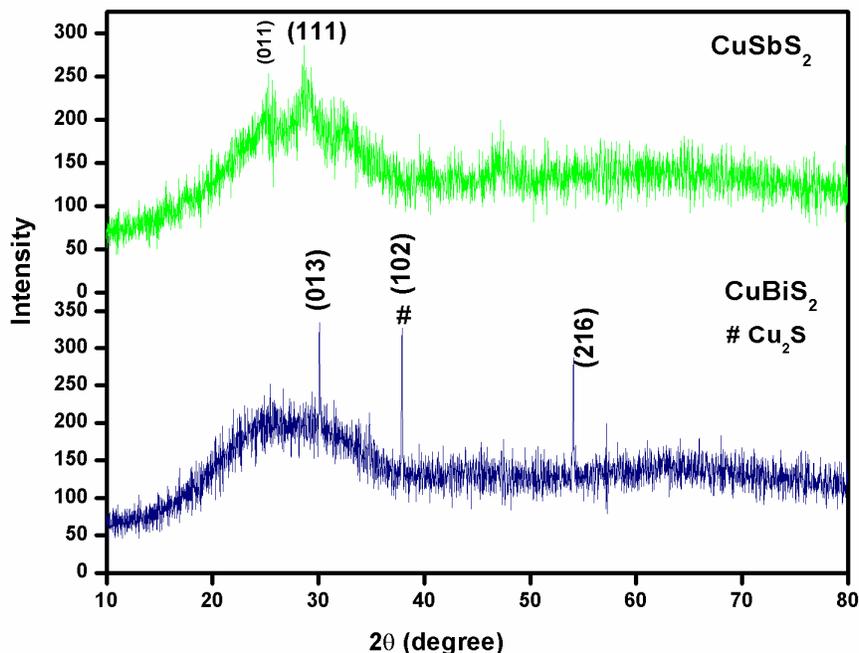


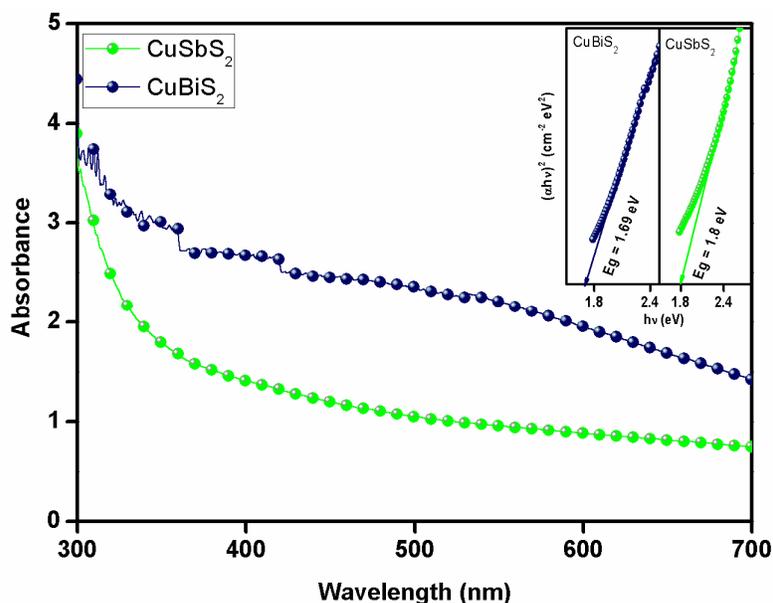
FIG. 1. XRD patterns of CuBiS₂ and CuSbS₂ thin films.

Fig. 2 shows the optical absorption spectra of CuBiS₂ and CuSbS₂ thin films. It can be seen from the spectra that the CuBiS₂ film showed better absorption in the visible region (300 -700 nm) compared to CuSbS₂ film. Optical absorption coefficient (α) was calculated and found in the range of 10^5 cm^{-1} . This higher α value confirms that the deposited films are potential candidates for solar cell applications. Eg plot (Fig. 2 inset) was drawn using Tauc's plot [1] and found to be 1.69 eV and 1.8 eV for CuBiS₂ and CuSbS₂ thin films, respectively, which is comparable to earlier literature (1.5 - 1.9 eV) [1,2]. ON the other hand, the thin films are having direct bandgap energy [4-7]. In the case of CuBiS₂, the band gap is comparatively lower than in the case of CuSbS₂ because of Bi³⁺ having higher anisotropic electronic behaviour,

low conduction band effective mass and high electron mobility [8]. The Eg values lie closer to optimum value for solar cells.

Conclusion

In this work, CuMS₂ (M= Bi, Sb) thin films (0.1 M) were deposited by chemical bath deposition method. The XRD pattern confirms the polycrystalline nature of orthorhombic structured CuBiS₂ and CuSbS₂. UV studies show higher optical absorption coefficient ($\alpha >10^4 \text{ cm}^{-1}$). Band gap energy was found to be 1.69 and 1.8 eV for CuBiS₂ and CuSbS₂ thin films, respectively, which indicates that the materials have potential applications in the field of solar cells.


 FIG. 2. UV-visible spectra of CuBiS_2 & CuSbS_2 thin films; inset: E_g plotplot.

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