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Preparation of Copper Antimony Sulfide Thin Film Solar Cells by Chemical Synthesis

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Abstract

Copper Antimony Sulfide ($CuSbS_2$) is a promising ternary semiconductor for use as an absorber layer in third-generation thin film heterojunction solar cells. This newly developed optoelectronic material offers a viable alternative to cadmium telluride (CdTe) and copper indium gallium di-selenide ($Cu(In,Ga)Se_2$) due to its composition of inexpensive, readily available, and non-toxic elements. These films were successfully produced at an optimal substrate temperature of 533 K using the conventional spray technique. X-ray diffraction and Raman studies confirm that the films exhibit a chalcostibite structure. Characterization studies reveal that the films possess lattice parameters of a = 0.60 nm, b = 0.38 nm, and c = 1.45 nm, with an absorption coefficient of 10^5 cm^{-1} and a band gap of 1.50 eV. Notably, the films exhibit p-type conductivity. All of these studies confirm that $CuSbS_2$ is an excellent choice for the absorber layer in solar cell applications. An attempt was made in this study to improve the crystallinity of the $CuSbS_2$ films by different experimental conditions. (i) $CuSbS_2$ films have been fabricated using two different carrier gases (air and nitrogen) via chemical spray pyrolytic technique. (ii) To enhance the crystallinity of these films, spray pyrolytic films have been kept on the hot plate at optimal substrate temperature for about 15 minutes. Subsequently, a $CuSbS_2$ solar cell is developed entirely through the non-vacuum method. The absorber layer is fabricated by using the spray pyrolytic method. A n-CdS buffer layer is successfully deposited via the chemical bath technique. The cell's efficiency increased from 0.488% to 0.54% when the absorber layer in the solar cell was left on hot substrates for about 15 minutes following the pyrolytic reaction. The study discusses how these techniques contribute to improving the efficiency of the solar cell parameters.

Keywords

$CuSbS_2$, thin films, absorber layers, solar cells, spray

Introduction

Energy is essential for running our societies, driving economic growth, and improving lives globally. At present, every nation primarily depends on conventional energy. Conventional energy sources like coal, oil, and natural gas contribute to climate change and environmental degradation [1]. Renewable energy is essential for reducing dependence on fossil fuels and mitigating climate change through sustainable energy sources. Solar energy is the best renewable energy source and offers a sustainable alternative to fossil fuels. Solar energy includes photovoltaic systems for producing electricity as well as solar thermal systems for generating heat. First-generation solar cells are silicon-based, efficient but rigid. The second generation introduced thin film technology for flexibility and lower cost.

Solar cells made up of silicon are expensive to manufacture. Cadmium telluride and Copper indium gallium selenide solar cells face challenges related to abundance and toxicity. Copper-antimony-sulfide ($CuSbS_2$) thin film solar cells have emerged as an alternative to the above due to their potential as a low-cost, earth-abundant material with promising light absorption properties. These absorber layers have silent features like high optical absorption coefficient, direct band gap (~1.5 eV), and p-type conductivity, aligning closely with ideal characteristics for photovoltaic applications [2]. Banu et al. [3] achieved a record efficiency of 3.22% by depositing ternary films with hybrid inks. Septina et al. [4] attained 3.13% efficiency through electrodeposition. Zhang et al. [5] achieved 2.55% via co-sputtering, and Lijuan et al. [6] reached 2.48% using spray pyrolysis. Chalapathi et al. [7] attained a maximum efficiency of 2.2% through sulfurization in stacks, and Wan et al. [8] obtained 1.9% efficiency using the co-evaporation method. $CuSbS_2$ thin films have been synthesized using various physical and chemical methods [2, 3, 4, 5, 6, 7, 8, 9, 10].

In the current investigation, these thin films were synthesized using the chemical spray pyrolytic method. This is a very simple and cost-effective method suitable for large-scale production [9,10]. This study investigates the effects of pure air as well as the effect of nitrogen (N_2) as a carrier gas on the fabrication of $CuSbS_2$ thin films. Additionally, efforts were made to enhance the crystallinity of the films using a simple technique. In the spray pyrolysis method, after completing the chemical pyrolysis, the films were removed from the heated plate. To improve their crystallinity, the deposited films were maintained on the heated substrate for 15 minutes to enhance solidification and adhesion. This effect is thoroughly discussed in the study. Finally, $CuSbS_2$ thin film solar cells were grown using a non-vacuum method, and their properties are discussed.

Experimental Details

Deposition of $CuSbS_2$ Thin Films

$CuSbS_2$ thin films were fabricated via a simple spray pyrolysis method using a salt solution containing cupric chloride (10 x 10^{-3} M), antimony trichloride (10 x 10^{-3} M), and thiourea (80 x 10^{-3} M) salts [11,12]. To avoid sulfur loss during the spray pyrolytic process, the thiourea concentration in the precursor solution was maintained above the stoichiometric level. The viscosity of liquid plays a vital role in the pyrolytic method. The low-viscosity liquid is favourable for quality films since low-viscosity liquid produces tinny and more uniform droplets while depositing the films. $CuSbS_2$ films were deposited at an optimized substrate temperature of about 533 K on the well-cleaned SLG glass substrate [11]. The salt solution was sprayed onto the well-cleaned and dried glass substrates at a rate of 10 ml per minute [13]. Two sets of films were deposited using two different carrier gases. In the first set, the $CuSbS_2$ films were fabricated by using pure air as the carrier gas. In the second set, $CuSbS_2$ films were fabricated by using N_2 as carrier gas. In both cases, all other parameters were maintained constantly. The detailed spray unit description was discussed in our previous literature [11, 12, 13]. Once the chemical spray pyrolytic process was finished, some of the deposited films were taken off the hot substrate, while others remained on the hot plate for about 15 minutes.

Characterization Techniques

The structural characterization of the films was employed by two analytical techniques. X-ray diffraction (XRD) patterns were done using a Bruker X-ray diffractometer with Cu-Kα radiation. Raman spectra were obtained using a conventional green laser source. Morphological images were captured using an SEM and the elemental studies were performed using an EDAX. The optical properties of the films were measured using a dual-beam spectrophotometer.

Results and Discussions

Structural Analysis

All the deposited films were extremely adherent and homogeneous. The thickness of the deposited films was identified using the density of the film. The thickness (t) of the films was found to be 5000 to 6000 Å.

Fig. 1 illustrates the XRD spectrum of $CuSbS_2$ films deposited by using pure air as the carrier gas. The intense peak obtained at 2θ = 28.48°, 47.99°, and 56.91° indicates the characteristic peaks of chalcostibite structure. This structure belongs to the orthorhombic system. These peaks are well coinciding with the Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 65–2416 and the reported data [7,8]. The XRD data confirms that the films consist of $Cu_{2-x}S$ as an impurity phase along with the $CuSbS_2$ films [14]. The XRD analysis of the films left on the hot surface for 15 minutes confirmed the improvement in the impurity phases.

FIGURE 1 XRD spectrum of the $CuSbS_2$ thin films deposited by using pure air as the carrier gas

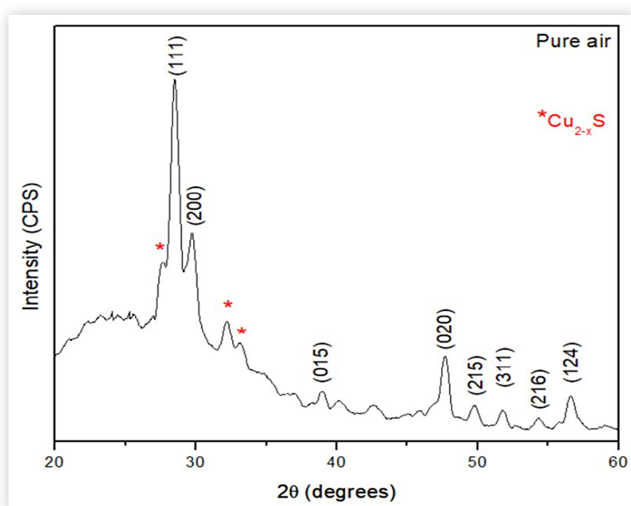
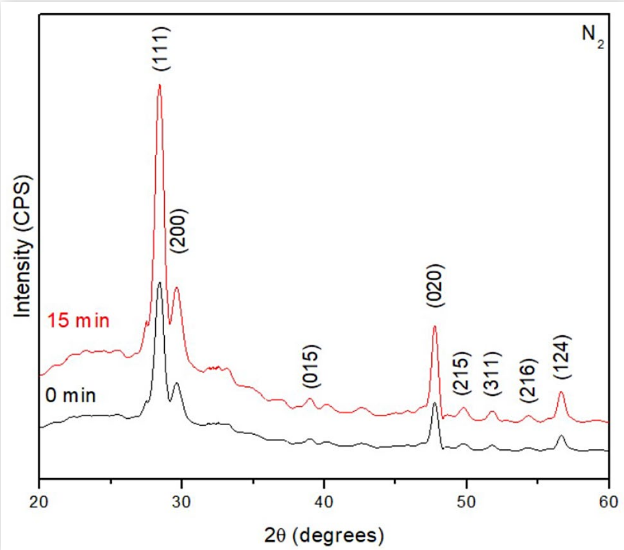


FIGURE 2 XRD spectrum of the $CuSbS_2$ thin films deposited by using N_2 as the carrier gas and films were taken off in 0,15 min



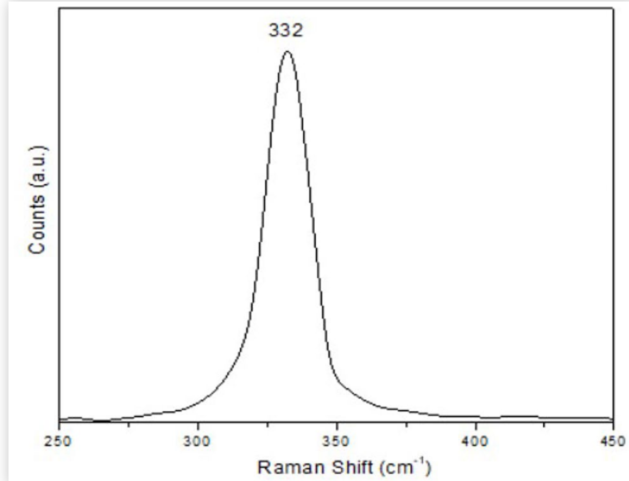
[Fig. 2] illustrates the XRD spectra of $CuSbS_2$ films deposited by using N_2 as the carrier gas. The characteristic peak corresponding to the 2θ values well coincides with the JCPDS Card data (65–2416) as well as the reported data. The intense peaks obtained at different 2θ values confirm the orthorhombic system with a chalcostibite structure. The XRD data confirms that the $CuSbS_2$ films deposited by using N_2 as the carrier gas vanishes the $Cu_{2-x}S$ impurity phase. This might be due to nitrogen gas having a lack of moisture content which could minimize the impurity phase in the films. XRD analysis of the films that were left on the hot surface for 15 min, the intensity ratio value of $I_{(111)}/I_{(020)}$ was improved this indicates the enhancement in the crystallinity of these films [15].

Comparing the XRD spectra with the two carrier gases, the ratio values of the weight of N_2 gas/the salt solution were lower when compared to the weight of pure air/the salt solution, this might be also one reason for enhancement in the crystallinity of the films [16]. The lattice parameters of the $CuSbS_2$ films deposited by using N2 as the carrier gas were calculated using a simple formula [12].

$$\frac{1}{d} = \sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}$$

The lattice parameters were identified as a = 0.60, b = 0.38, and c = 1.45 nm respectively, and were good coincides with the reported values [7,8]. The microstrain of the films was calculated using the equation $\frac{\beta \cos\theta}{4}$ [10]. It was found that the microstrain declined in the films from 1.311 to 1.128 when films were left on the hot surface for 15 minutes. Enhanced crystallinity in the films typically suggests a lower microstrain and this is a favorable condition for efficient thin-film solar cells [17].

FIGURE 3 Raman spectra of the $CuSbS_2$ thin films taken off from the hot plate in 15 min after pyrolysis



The typical Raman spectra of $CuSbS_2$ films were left on the hot surface for 15 minutes as shown in [Fig. 3]. The Raman modes obtained at 332 /cm confirm the presence of $CuSbS_2$ films exhibit chalcostibite structure [18].

Elemental Analysis

[Table 1] represents the elemental analysis of $CuSbS_2$ films that were deposited by using N_2 as carrier gas. 1st row in the table represents the elemental studies of $CuSbS_2$ films that were collected immediately after deposition and 2nd row indicates the elemental analysis of the films that were collected from the hot surface after 15 minutes of the pyrolysis completed. This analysis confirms that there is significant variation in the copper and sulfur composition in the films. The reduction in the sulfur composition confirms the sulfur volatile nature at high temperatures [19].

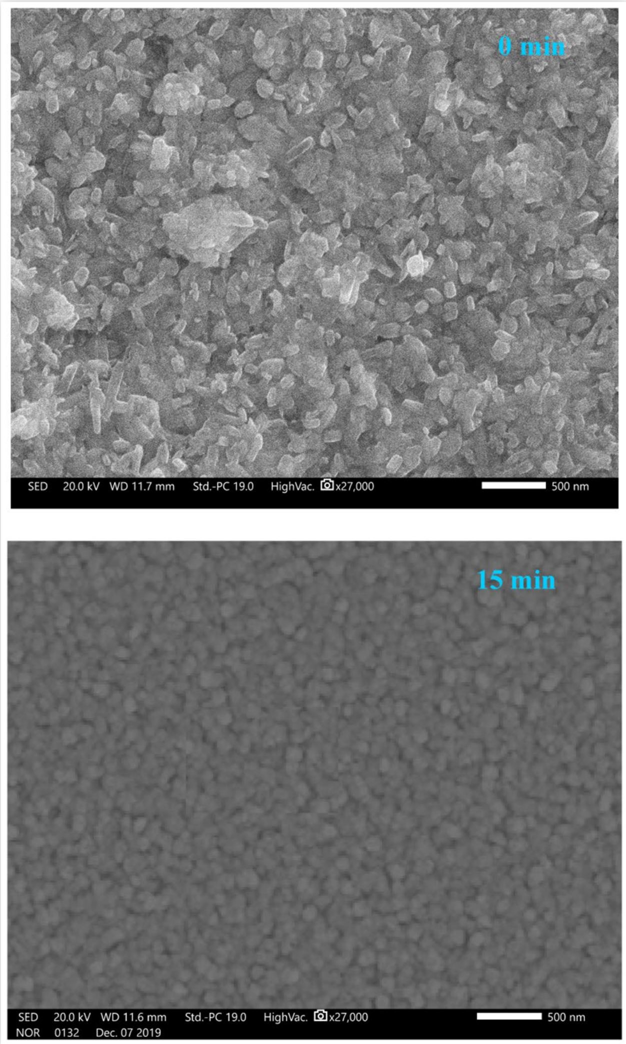
Morphological Analysis

[Fig. 4] shows the SEM images of $CuSbS_2$ thin films fabricated using N_2 as carrier gas. SEM images of $CuSbS_2$ films collected immediately after deposition were shown on top and the films removed from the hot surface 15 minutes after pyrolysis are displayed at the bottom. There was an improvement in the grain morphology of the films when the films were kept for 15 minutes on the hot plate. Compact surface morphology is crucial for an absorber

TABLE 1 Elemental analysis of $CuSbS_2$ films obtained using N_2 as carrier gas

Collection Time (min.)	Elemental composition (at %)			$\frac{Cu}{Sb}$	$\frac{S}{Cu+Sb}$
	Cu	Sb	S		
0	26.9	23.4	49.7	1.149	0.988
15	27.3	23.5	49.2	1.161	0.968

FIGURE 4 SEM images of the $CuSbS_2$ thin films deposited by using N_2 as the carrier gas and films were taken off in 0,15 min



layer of the solar cell [20]. It was observed that cracks began appearing on their surface after the films were kept for more than 15 minutes [17].

Optical Studies

Optical properties of $CuSbS_2$ thin films were analyzed with the transmittance spectra. The optical absorption coefficient (α) and the nature of the energy gap of the deposited films were assessed by using simple mathematical expressions $\alpha = \ln\left(\frac{1}{T}\right)\cdot\frac{1}{\tau}$ and $(\alpha h\nu) = A(h\nu - E_g)^n$ where T, t, h denotes the percentage of transmittance of film, the thickness of the film, and Planck's constant. In the above expression satisfied when the power value of $n = ½$, this confirms the films exhibit direct optical transitions [1,12]. The absorption coefficient of $CuSbS_2$ thin film is shown in Fig. 5 and was found to be greater than 10^5 cm^{-1}. This value also confirms that $CuSbS_2$ thin film exhibits as a good absorber layer in heterojunction thin film solar cells. The band gap of these films was estimated using the $h\nu$ versus $(\alpha h\nu)^2$ plot from Fig. 6 and was found to be around 1.5 eV, which is an eminent property of a good absorber layer in solar cells [1,10].

Electrical analysis of the films was found using the van der Pauw technique and the Hall effect. These two experimental studies were carried out at room

FIGURE 5 Optical absorption coefficient of $CuSbS_2$ thin films

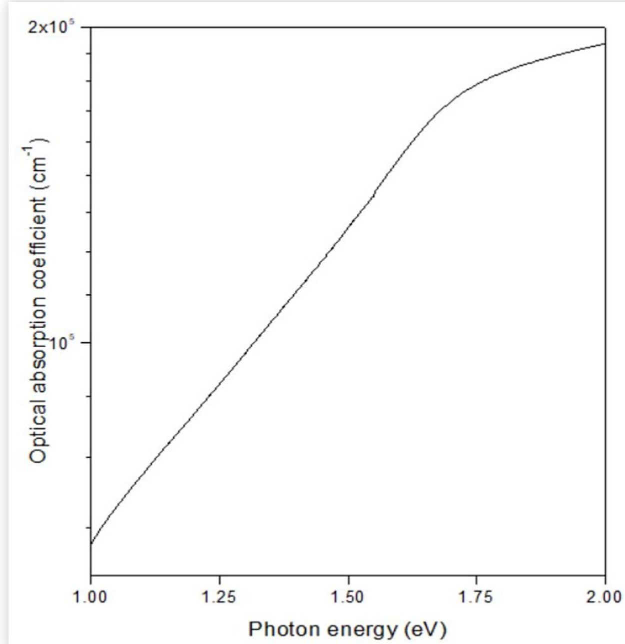
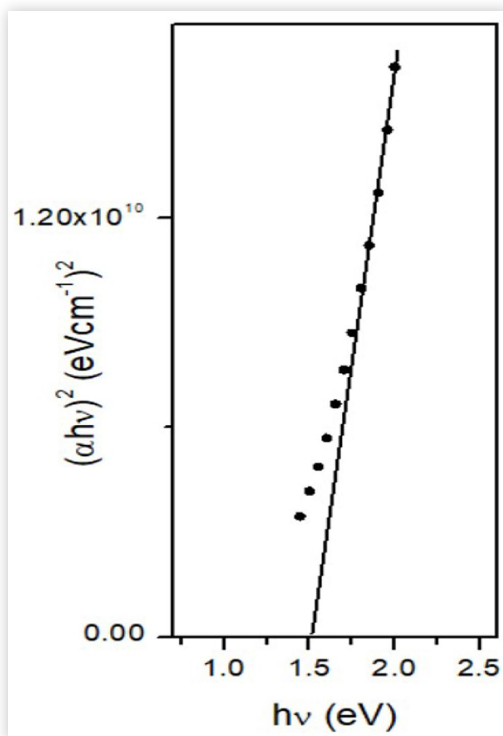


FIGURE 6 Tauc plot of $CuSbS_2$ thin film



temperature. The room temperature electrical resistivity was about 12 Ω cm. The Hall mobility and carrier concentration of the films were found to be 1.2 $cm^2(Vs)^{-1}$ and 5.9 × 10^{17} cm^{-3} respectively. The hot probe method confirms the films show a p-type nature.

Device Studies

Fig. 7, shows the sequence of $CuSbS_2$ thin film solar cell. The p-type absorber layer ($CuSbS_2$ film) was fabricated by the spray pyrolytic method and the n-type buffer layer (CdS film) was fabricated by chemical bath deposition [21,22]. The current density-voltage (J-V) characteristics of the developed solar cells are shown in Fig. 8. These thin film solar cells were analyzed under 100 m. watts per sq. cm and the cell parameters are tabulated in Table 2. The efficiency of the cell has been improved from 0.488% to 0.54% when the absorber films were held on the hot substrates for 15 min after the completion of the pyrolytic reaction. The increase in cell efficiency confirms that the crystallinity of the films improved when they were kept on hot substrates for 15 minutes. However, the poor performance of these cells may be attributed to the non-optimization of the thickness of both the absorber and buffer layer, as well as issues with the metallurgical interface between these layers. Low carrier mobility also declines the efficiency of the cell.

FIGURE 7 Order of layers in heterojunction solar cell

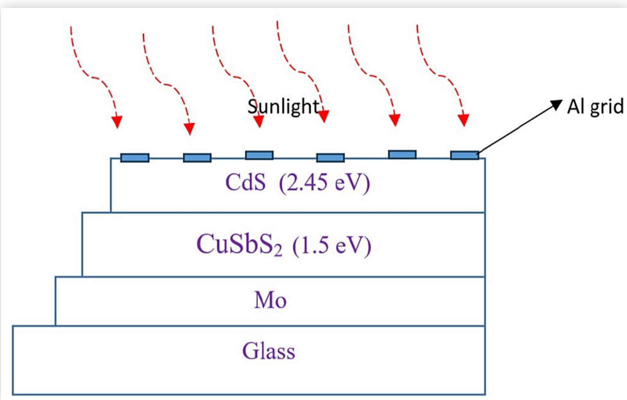


FIGURE 8 J-V studies of $CuSbS_2$ heterojunction solar cell

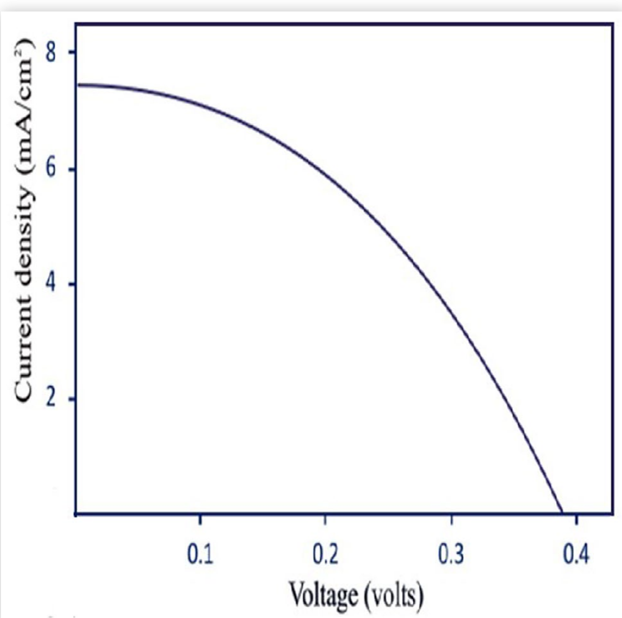


TABLE 2 J-V studies of $CuSbS_2$ heterojunction solar cell

S. No.	Carrier gas	V_{OC} (V)	J_{SC} (mA/cm^2)	Efficiency (%)
1	Pure air	0.14	1.62	--
2	Nitrogen (0 min)	0.37	7.40	0.488
3	Nitrogen (15 min)	0.39	7.49	0.540

Conclusions

$CuSbS_2$ thin films have been deposited using the traditional chemical spray pyrolytic method. Pure air and N_2 are used as the carrier gas in this study. For improving the crystallinity of these films, the deposited $CuSbS_2$ thin films were kept on the hot surface for 15 minutes. The structural characterization confirms the $CuSbS_2$ films exhibited a chalcostibite structure with lattice parameters a = 0.60 nm, b = 0.38 nm, and c = 1.45 nm. The optical studies confirm the optical absorption coefficient and band gap values as 10^5 cm^{-1} and 1.50 eV. After improving the crystallinity of the $CuSbS_2$ films efficiency of the cell has been improved from 0.488% to 0.54%.

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