Solvothermal Synthesis of $CuSbS_2$ Nanoparticles for Photovoltaic Application

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Abstract

Copper-based chalcogenide nanomaterials with orthorhombic crystal were synthesized using solvothermal method. The obtained $CuSbS_2$ nanoparticles were characterized for their structural, morphological, optical and electrical properties by means of suitable analytical techniques. The X-ray diffraction (XRD) results showed that the obtained sample showed orthorhombic crystallinity with (310), (111), (410), (301), (620) and (521) planes of the $CuSbS_2$ nanoparticles with average crystallite size of 7.16 nm. The morphological investigation results given by the field emission scanning electron microscope (FESEM) showed $CuSbS_2$ nanoparticles are uniform sphere like structure. UV-Vis-NIR results revealed that there was broad absorption in the entire visible region and estimated direct band gap was found to be 1.35 eV. The atomic force microscopy (AFM) images of the deposited film gave spherical surface with the thickness of 816 nm and the hall measurements showed p-type conductivity with carrier concentration in the range of 10^{17} cm^{-3}. These results indicate that $CuSbS_2$ nanomaterials are a promising absorber material for photovoltaic application.

Keywords

$CuSbS_2$ nanoparticles, solvothermal method, absorber material, photovoltaics

Introduction

The main focus in the future development of thin film solar cells is to obtain a device with low production cost, high efficiency, earth abundant materials and comparatively less toxic elements. Recently lots of research is being carried out for II–VI, IV–VI, I–III–VI_2, I–II–III–VI_2 group compound semiconductors in the field of energy conversion from the renewable energy source [1-2]. One among them is copper antimony sulfide an emerging material, useful for the fabrication of thin film solar cells. By tuning the chemical composition, size and morphology of the material, it is possible to achieve improved optoelectronic properties suitable for photovoltaic applications. Copper antimony sulfide has four major phases with p-type conductivity, namely – $Cu_{12}Sb_4S_{13}$ (Tetrahedrite, having the band gap of 1.6 eV), Cu_3SbS_3 (Skinnerite, band gap of 1.4 eV), Cu_3SbS_4 (Fematinite, band gap of 1.2 eV) and $CuSbS_2$ [3]. $CuSbS_2$ is a direct band gap material with the band gap of 1.4-1.6 eV and having the high absorption

coefficient over 10^5 cm^{-1} [4]. Power conversion efficiency of 3.22% have achieved in the configuration of Al:ZnO/CdS/CuSbS2/Mo/glass solar cell devices [5].

However, the preparation routes of $CuSbS_2$ thin films have been reported, such as spray pyrolysis, Sputtering, thermal evaporation, chemical bath deposition, and electro-chemical deposition [6-10]. In all these methods, the relative complex devices such as vacuum system or an electro deposition apparatus are required. Nevertheless, the non-vacuum based solvothermal methods are used to acquire nanostructures with controllable dimensions and well-defined morphologies. In this process, the reaction temperature and autogenous pressure plays a major role to enhance the chemical reactivity. The synthesized $CuSbS_2$ nanoparticles could be converted as ink that were coated on a substrate inorder to prepare large uniform area film with non-toxic and low-cost materials which acts as a promising p-type candidate for photovoltaic applications.

In the present work, phase pure $CuSbS_2$ nanoparticles are synthesized using the solvothermal method, using ethylenediamine as solvent and PVP as a surfactant and size reducing agent. Once the solvothermal reaction was over, the structural, morphological, optical and electrical properties of the obtained nanoparticles and deposited thin films are carried out.

Experimental Procedure

Synthesis of $CuSbS_2$ nanoparticles were carried out utilizing solvothermal method. In a typical reaction, 2.5 mM copper (II) acetate monohydrate, 2.5 mM antimony (III) chloride and 7.5 mM thiourea were dissolved in ethylenediamine under constant stirring for 30 min. Later 0.5 g Polyvinylpyrrolidone (PVP) was added to the above mixture inorder to stabilize the growth and allow the formation of well defined structure. When the chemicals were completely dissolved, the precursor solution was transferred into a Teflon lined stainless steel autoclave, placed it in a hot air oven and maintained at 180 °C for 24 h. Once the reaction was over the oven was cooled down to reach the ambient temperature. The nanoparticles were collected using centrifuge at 3000 rpm for 10 min. Centrifugation process was carried out several times using deionized water and ethanol inorder to obtain final product. The obtained product was gray in color and kept for drying overnight. Finally using the nanoparticle ink $CuSbS_2$ thin films were deposited onto soda lime glass substrate.

The synthesized $CuSbS_2$ nanoparticles were characterized by powder X-ray diffraction (XRD, Rigaku) equipped with Cu-K β (λ = 1.39220 Å, 40 kV, 30 mA and step width 0.02 degree). The particle size and morphology of the sample were determined by field emission scanning electron microscope (FE-SEM, ZEISS at accelerating voltage 5 KV). The optical absorption spectrum was obtained using a UV-3600 Shimadzu spectrophotometer. Thickness of the obtained film was measured using Bruker AFM (atomic force microscopy) and the electrical properties were done using an Agilent B1500A semiconductor device analyzer.

Results and Discussion

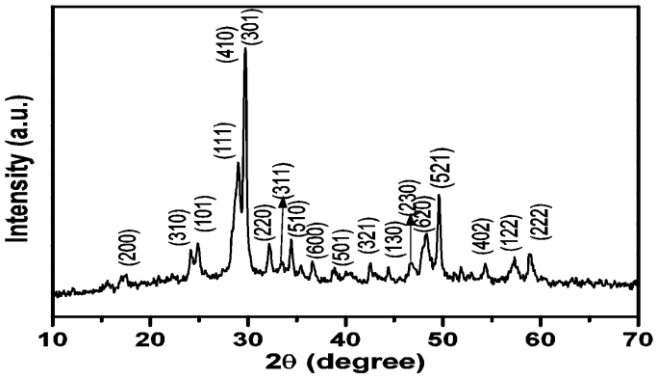

Fig. 1: XRD pattern of the synthesized $CuSbS_2$ nanoparticles

Fig.1 shows the XRD pattern, of which the major peaks are 2θ =23.58°, 28.44°, 28.72°, 29.91°, 48.23° and 49.78°, that are attributed to the planes (310), (111), (410), (301), (620) and (521) perfectly indexed as $CuSbS_2$ nanoparticles with unit cell as orthorhombic (JCPDS, Card No. 44-1417) [11]. The cell parameters are determined to be a = 14.559081Å, b = 6.009334Å and c = 3.807885Å, which are comparable with the values shown in JCPDS, card no. The average crystallite size of $CuSbS_2$ nanoparticles is determined from full width at half maximum of these peaks using the Debye-Scherrer equation is found to be 7.16 nm.

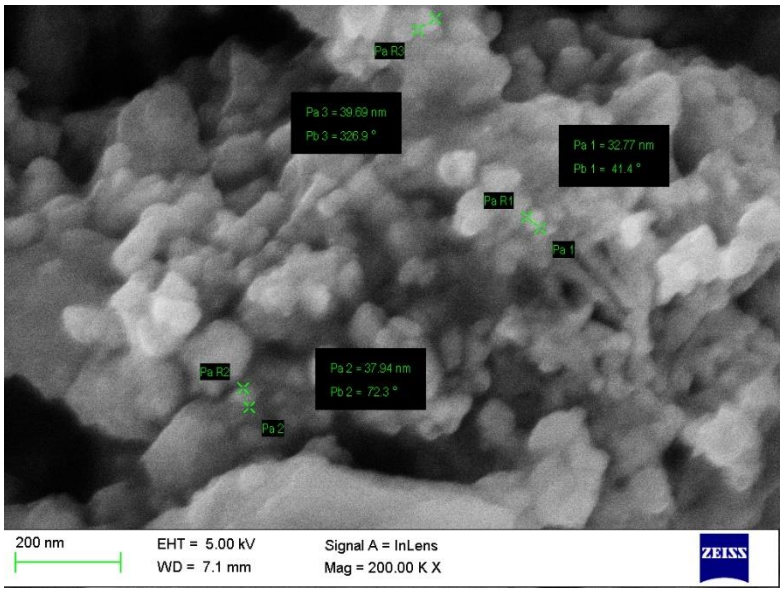

Fig. 2: High magnification FESEM images of the synthesized $CuSbS_2$ nanoparticles

The particle size and surface morphology of the synthesized $CuSbS_2$ nanoparticles analyzed using the FE-SEM images are shown in Fig. 2. From the images it is clear that the added amount of PVP influences the final morphology and the obtained $CuSbS_2$ nanoparticles are composed of a large number of uniform spheres like particles with average size of 30-40 nm.

Figure 3(a) and (b) are the UV-Vis-NIR absorption spectrum and the resultant direct band gap $CuSbS_2$ nanoparticles that are determined using Tauc's plot. The absorption spectrum depict a broad absorption in the entire visible region with a band gap of 1.35 eV and are having optical absorption coefficient of 10^4 cm^{-1}, which are consistent with the literature value [11].

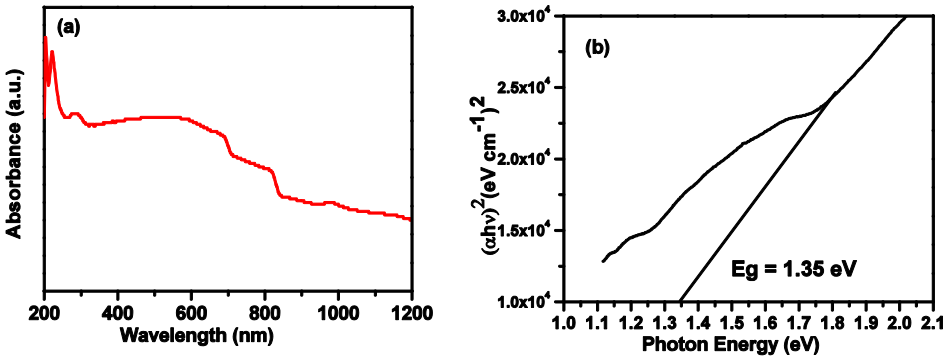

Fig. 3: (a) UV-Vis-NIR absorption spectrum of $CuSbS_2$ nanoparticles and (b) Tauc's plot extrapolated to estimate a direct band gap of 1.35 eV

Atomic force microscopy (AFM) images of two and three-dimensional micrographs of the deposited $CuSbS_2$ thin film samples are given in Fig. 4(a & b). The micrographs evidently showed that thin film surface is covered with the formation of densely packed sphere like particles and the height or the thickness of the film is about 816 nm.

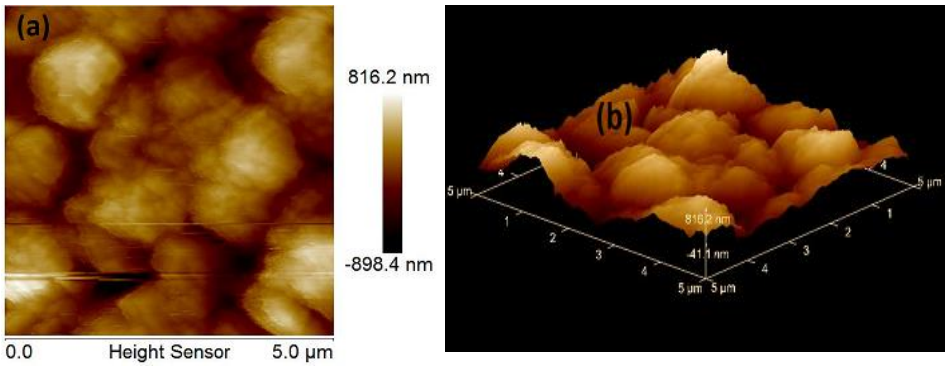

Fig. 4: AFM (a) 2D and (b) 3D images of the deposited $CuSbS_2$ thin films

The electrical properties such as electrical conductivity (σ), mobility (μ) and carrier concentration (n_p) are measured using the Van der Pauw Hall measurement technique. The deposited $CuSbS_2$ film reveals p-type conductivity with electrical conductivity of 1.65 S cm^{-1}, high electrical mobility of 27.69 $cm^2V^{-1}s^{-1}$, and having the carrier concentration of 3.74×10^{17} cm^{-3} [12].

Conclusions

Synthesis of $CuSbS_2$ nanoparticles were carried out by facile solvothermal method. Here ethylenediamine and PVP played major role for the production of $CuSbS_2$ nanoparticle without agglomeration and forming a well-defined sphere like particles. The average crystallite size of the obtained $CuSbS_2$ nanoparticle was found to be 7.16 nm. The structure and composition of the as-synthesized nano powder was confirmed by XRD. From FESEM analysis it was clear that $CuSbS_2$ nanopowder obtained sphere like particles with average particle size of 30-40 nm and the AFM images gave the thickness of 816 nm. Optical absorption spectral analysis showed maximum absorption in the visible region and having the direct band gap energy of 1.35 eV. Electrical studies revealed that the material was having the carrier concentration of 3.74×10^{17} cm^{-3}. The above-mentioned results highlight $CuSbS_2$ nanoparticle are promising p-type absorber material for photovoltaic applications.

Acknowledgements

One of the authors Ms. Bincy John thanks the University Grants Commission of India, for providing research fellowship (Maulana Azad National Fellowship, Grant No: F1-17.1/2016-17/MANF-2015-17-KER-53161). This research was performed using facilities at CeNSE, Indian Institute of Science, Bengaluru, funded by the Department of Electronics and Information Technology (Deit Y), Government of India.

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