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Synthesis and characterization of ternary Cu_4SnS_4 Nanocrystalline semiconductor thin films: A review

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Abstract

Recently, a significant number of researches have been carried out regarding the synthesis of Cu_4SnS_4 thin films. This review will try to cover preparation of Cu_4SnS_4 films by using various deposition methods. The obtained films were investigated using various tools such as scanning electron microscopy, energy dispersive X-ray analysis, X-ray diffraction and UV-visible spectrophotometer.

Keywords: Thin films, Semiconductor, Nanocrystalline, Solar cells

1. Introduction

Binary [1-14] and quaternary [15-19] thin films have attracted much attention in recent years. These films have been developed and characterized by many researchers. Ternary Cu_4SnS_4 thin films are well known for applications in a wide range of thermoelectric and solar cell devices. Some unique properties such as high thermoelectric, low thermal conductivity and tunable electronic properties make them applicable for the mentioned uses. Cu_4SnS_4 films have a direct band gap of 1.2 eV, resulting in a high absorption coefficient. Appropriate band gap, high natural abundance [20], non-toxic and low cost [21] of starting materials are the objectives in photovoltaic research and applications. The need for economical energy source has increased interest in the development of solar applications.

This paper reports the preparation of Cu_4SnS_4 thin films by using various deposition techniques. The experimental conditions limiting the behavior of the obtained films were discussed. Studies are focused on structure, surface morphology, optical absorption and composition of these Nano crystalline films.

2. Literature survey

Many deposition techniques have been developed for depositing Cu_4SnS_4 nano crystalline thin films. Generally, these techniques could be divided into two major groups, namely physical or chemical deposition method based on the nature of deposition process. Among them, deposition from aqueous solutions using chemical deposition technique is the most important method due to simple, cheap and easy to scale up.

Thermal co-evaporation was used to prepare Cu_4SnS_4 thin films on glass substrate at a constant substrate temperature of 400°C as reported by Vani and co-workers [22]. The main objective of their works was to investigate the effects of source-substrate distance (10-25 cm) on the chemical and physical properties of films. The energy dispersive X-ray analysis (EDAX) analysis of the deposited films showed that the films are stoichiometric at a source-substrate distance of 20 cm. The strong peaks related to the presence of copper, Sulphur and tin and no other impurity peaks were found in the spectrum within the EDAX detection limit. The scanning electron microscopy (SEM) studies showed needle like grains were distributed on the substrate surface. Further, they observed that as source-substrate distance increases, the grain size decreases. X-ray diffraction (XRD) investigations revealed that the deposited films were Nano crystalline in nature and displayed (311) peak as preferred orientation, indicating orthorhombic structure. Energy band gap of the Cu_4SnS_4 films was calculated from the observed transmittance data, indicating that varied in the range, 1.25-1.34 eV with the change of source-substrate distance.

Simple mechanochemical ball milling process will be employed in order to synthesis Cu_4SnS_4 (CTS) as described by

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Chen and co-workers [23]. They fabricate solar cell structure of Mo/CTS/In_2S_3/TiO_2/fluorine-doped tin oxide glass for the first time in order to study the photovoltaic properties of films. J-V photoelectric characteristics analysis was carried out for the thin films annealed at different temperatures. Conversion efficiency of CTS absorber layer increases as the annealing temperature increase from 350 to 375 °C under the standard AM 1.5 condition. However, it significantly reduces as the temperature is further increased to 500 °C.

Cu_4SnS_4 thin films were deposited on substrates using electrodeposition method under various deposition parameters such as deposition potential, deposition time, bath temperature, pH and concentrations. Based on the overall results, the optimum deposition conditions for the preparation of Cu_4SnS_4 thin films were using lower concentration of 0.01 M of electrolytes [24] at 25 °C [25] for 45 minutes [26] in acidic medium at pH 1.5 [27] and at deposition potentials of -600 mV versus Ag/AgCl [28]. The XRD patterns showed that the films obtained were polycrystalline in nature. Based on the XRD data, the highest number of Cu_4SnS_4 peaks could be observed and the sample obtained was pure without existence of any impurity. Orientation along (221) plane was found to be most prominent. The films exhibited highest absorption characteristics and better photo activity. The atomic force microscopy images indicated that the grain size, film thickness, surface roughness and grain shape were dependent on the deposition parameters. The band gap energy was found to be 1.55 eV with direct transition according to optical absorption technique for the films prepared at the best experimental conditions.

Solvo thermal synthesis of Cu_4SnS_4 thin films in the presence of $SnCl_2$, thio urea and $CuCl_2$ was described by Mahesh kumar et al [29]. The structure (orthorhombic) of these materials were confirmed by XRD. There are some diffraction peaks such as (102), (620) and (040) could be seen in XRD pattern. The scanning electron microscopy images show irregular pattern with wide range of particle size. The atomic ratio of Cu:Sn:S about 46:9:45 for the composition of the prepared sample as shown in EDAX analysis. The band gap value is 1.2 eV as calculated from the plot of $(\alpha hv)^2$ versus E_g.

The Cu_4SnS_4 thin films were prepared using cheaper and simple chemical bath deposition technique. Disodium salt of ethylenediamine tetra acetic acid was used as a complexing agent during deposition process. The presence of complexing agent was found to improve the lifetime of the deposition bath and improved the quality of thin films. The best deposition parameters such as bath temperature of 50 °C [30], deposition time at 120 minutes [31], electrolyte concentration of 0.05 M [32], pH=1.5 [33] in the presence of complexing agent [34] were described by researcher in order to obtain good quality of films. According to XRD patterns, the films obtained were polycrystalline in nature. The X-ray data exhibited the most intense peak occurred at $2\theta = 30.2°$ which belonged to (221) plane of Cu_4SnS_4. No obvious peaks resulting from any other secondary phases were detected, indicating good purity of the product. Atomic force microscopy image revealed that grains were uniformly distributed over the surface of substrate. The films prepared under optimized conditions showed the highest photo response activity and better absorption values. The optical absorption in the visible region indicated that these materials could be used in photo-electrochemical cells. The band gap was found to be 1.6 eV with direct transition under these conditions. On the other hand, Cu_4SnS_4 films formed by heating SnS-CuS layers (300-340 °C in nitrogen atmosphere) deposited from chemical bath as reported by Nair et al [35]. The obtained films are photosensitive and the electrical conductivity in the dark is about 1 $\Omega^{-1}cm^{-1}$.

Physical properties of Cu_4SnS_4 films were investigated by depositing a CuS films of 200 nm thickness on tin sulfide films (180 nm thick) by sequential chemical deposition as reported by David and co-workers [36]. The layers were heated at different temperatures (350 and 400 °C) under nitrogen atmosphere. The obtained films are *p*-type semiconductor, having a band gap of 1.2 eV with electrical conductivities of 0.5-10 $\Omega^{-1}cm^{-1}$.

Thermoelectric properties of the Cu_4SnS_4 thin films produced were studied by Suzumura et al [37]. They explain that these properties change around 230 K along with a phase transition between a high temperature phase and a low temperature phase. In their works, the crystal structures of obtained films were analyzed using synchrotron radiation. They highlighted some points such as high temperature phase was determined to be orthorhombic structure with the space group P_{nma}, lower thermal conductivity in high temperature phase results from an additional phonon scattering resonated with an anharmonic Cu vibration in the double well potential. First principles calculations of electronic structure of Cu_4SnS_4 (orthorhombic and monoclinic) were carried out by Goto and co-workers [38]. They point out that first order phase transition at 232 K according to the generalized gradient approximation of the density functional theory. They also conclude that orthorhombic phase has larger activation energy than monoclinic phase. Temperature distribution of thermoelectric device consisted of Cu_4SnS_4 films was reported by Kondo and co-workers [39]. They observed that the temperature distribution is strongly dependent on the length of thermoelectric device (especially when the length is very thin).

3. Conclusion

In this work, chemical bath deposition, electro deposition and thermal evaporation have been used to prepare Cu_4SnS_4 thin films. Researchers find that these films with direct band gap in a range of 1.2-1.6 eV are very suitable for applications in thin-film based photovoltaic cells. The formation of the orthorhombic and monoclinic structure was revealed by XRD pattern.

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