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Preparation and characterization of Cu_2FeSnS_4 quaternary semiconductor thin films via the spray pyrolysis technique for photovoltaic applications

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ABSTRACT

The Cu_2FeSnS_4 (CFTS) nanostructured thin films have been spray deposited onto glass substrates without any post-sulfurization in toxic atmosphere such as H_2S or 'S' vapor. The influence of substrate temperatures on the structural, morphological, compositional, optical, electrical and photoconductivity properties of the CFTS thin films have been studied. These properties are found to be strongly dependent on the substrate temperature. XRD spectra analysis revealed that all CFTS thin films showing pure stannite structure. The improved crystallinity of the CFTS with a (112) orientation was observed with increasing the substrate temperature. The spray synthesized CFTS films exhibit a smooth, uniform and dense topography. EDS study reveals that the deposited thin films are nearly stoichiometric. The direct band gap energy for the CFTS thin films is found to be about 1.50 eV, which is close to the ideal band gap for the highest theoretical conversion efficiency of solar cell. Electrical conductivity and hole mobility of the CFTS films increases with increasing substrate temperatures. The films were p-type and shows photoconductivity. Electrical measurements (I–V curves) were registered in dark and under light exposure and were correlated with the films composition and structure, as obtained from the EDS analysis and XRD patterns.

1. Introduction

Currently, researches on low-cost thin film solar cells are increasing significantly. Various types of well-known solar cell materials such as CdTe and $CuIn(Ga)Se_2$ (CIGS) have been extensively investigated [1–5]. These materials have the toxicity of cadmium, expensive and scarce elements like indium and gallium, respectively, which affects large-scale production. To achieve the goal of cost-effective photovoltaic technology, it is necessary to explore new materials contains less toxic material S instead of Se and more abundant elements, Fe, Sn, than In, like Cu_2FeSnS_4 (CFTS) and other quaternaries of these chalcopyrite-like semiconductors. CFTS is reported to have a band gap between 1.2 and 1.5 eV (ideal for a single junction solar cell) [6–12] and a band edge absorption coefficient above 10^4 cm^{-1}. A thorough understanding of material properties is very much essential for the successful utilization of this compound in solar cells.

Recently, several techniques including physical and chemical methods have been employed for preparing CFTS thin films namely: sputtering [11] and successive ionic layer absorption and reaction [12]. Generally these techniques are multi steps processes, they are based on sequential or co-deposition of precursor metallic stacked layers followed by a subsequent sulfurization. Also, other techniques such as hot injection and the ultrasound-assisted microwave irradiation for the deposition of CFTS layer were utilized [7,8]. However, the above methods for synthesizing CFTS are usually complex and time-consuming. Considering these problems, for a large scale solar cell production a single step and facile deposition process is more economic and well suitable.

Chemical spray pyrolysis (CSP) technique is low-cost, non-vacuum and eco-friendly, and can be used for cost-effective large-area deposition, with no need of any sophisticated instrumentation. However, to the best of our knowledge, spray deposition of CFTS thin films has rarely been reported. Prabhakar et al. [10] reported deposition of CFTS thin films by spray pyrolysis followed by sulfurization at different temperatures of 400, 500 and 600 °C. The effect of sulfurization temperature on the properties of CFTS thin films was studied.

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In this study, we report a simple method to prepare CFTS thin films by spray pyrolysis technique on the glass substrate without sulfurization in toxic atmosphere such as H_2S or 'S' vapor. Different substrate temperature conditions (250–370 °C) were used to study the effect of substrate temperature on the structural, compositional, morphological, optical, electrical and photoconductivity properties of CFTS thin films.

2. Experimental

2.1. Synthesis of CFTS thin films

Cu_2FeSnS_4 (CFTS) thin films were deposited by spray pyrolysis method on glass substrate. The CFTS precursor solution was prepared by mixing $CuCl_2$. $2H_2O$ (0.1 M), $FeCl_3$. $6H_2O$ (0.05 M) and $SnCl_4{\cdot}5H_2O$ (0.05 M) in 50 ml double-distilled water. Tin (IV) chloride react with water to produce tin (IV) hydroxide and hydrogen chloride (hydrolysis of $SnCl_4$) as follows:

$$SnCl_4 + 4H_2O \rightleftarrows Sn(OH)_4 + 4HCl \quad (1)$$

Therefore, In order to enhance the solubility of tin chloride, a few drops of hydrochloric acid (typically of the same or greater molarity as the stannic chloride) was also added to the solution to maintain the equilibrium towards the left-hand side.

Then 0.4 M of thiourea ($CS(NH_2)_2$) was dissolved into the mixture. The excess quantity of thiourea was added to prevent any deficiency of sulfur in the prepared films because sulfur is a very volatile element, especially at elevated temperatures. Since the thiourea can be decomposed in air upon heating to generate H_2S, the our spraying system and furnace was kept inside an airtight metallic chamber of size 60 × 60 × 60 cm^3 and the outlet of the box was fitted with an exhaust fan to remove the toxic gases produced during the decomposition of the spray solution. However, because of the acute health hazard associated with H_2S vapor that could be accidentally released from a spray pyrolysis unit, operator is also needed to protect his health. Some safety precautions when working with system are: do not breathe mist/vapors/spray, and also do not eat, drink or smoke when working with system. The final solution was stirred for 30 min. CFTS thin films were deposited at different substrate temperatures from 250 °C to 370 °C at the step of 40 °C with an accuracy of ±5 °C using a digital temperature controller to investigate substrate temperature effect. Other deposition parameters such as spray deposition rate, the distance between nozzle and substrate and hot plate rotation speed were set at: 10 ml/min, 30 cm and 50 rpm, respectively. The samples are denoted as 'CFTS250′, 'CFTS290′, 'CFTS330′, and 'CFTS370′.

2.2. Characterization techniques

The structure confirmation of films were performed by using X-ray Diffractometer (D8 Advance Bruker system) with Cu−Kα radiation (λ = 1.5406 Å) operated in the 2θ range from 10 to 70°. The elemental composition was determined using an energy-dispersive spectrometer (EDS) system attached to VEGA2 SEM. Field emission scanning electron microscope (FE-SEM, S-8000, Hitachi), and Atomic Force Microscope (AFM, 95-50-E, DME) are used to study the surface morphology of the CFTS film. Optical characterization was done using Shimadzu-UV1800 spectrophotometer.

The film thickness was measured using a Taly step profilometer (roughness detector with a stylus-Taylor Hobson model). Taly profile (a dedicated software package designed for use with laboratory instruments) has complete laboratory analysis functions such as: roughness parameters and Step height measurement etc.; and the information can be displayed graphically and numerically. By step height measurement between coated glass and uncoated part of glass we could determine the thickness of the studied samples with a precision of about 10 nm.

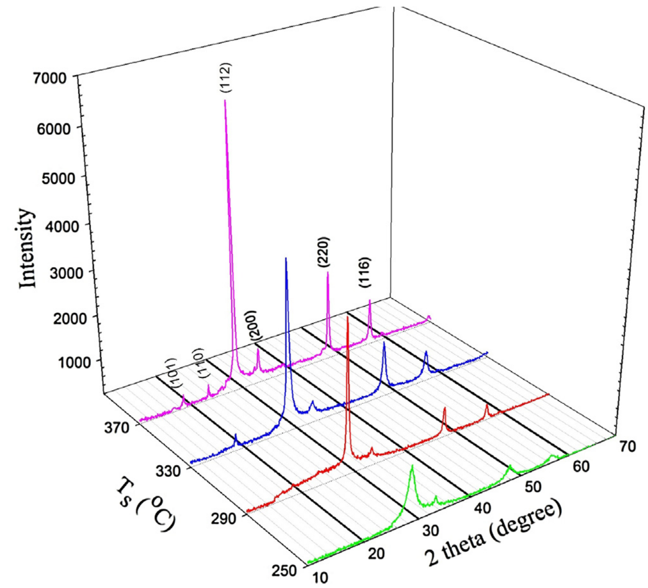

Fig. 1. XRD patterns of CFTS thin films deposited at various substrate temperature.

Electrical resistivity and Hall effect data (magnetic field strength = 240 mT) of the samples were measured in the Van der Pauw configuration [13]. To study the photoconductive properties of prepared films, samples were exposed to light radiation with fixed intensity (3500 lx) at a fixed distance (20 cm). Then, the resistance of films were recorded under lighting at specified time intervals at room temperature. The electrical measurements (I–V curves) of the films were investigated by using the two-point-probe method. To this purpose, two ends of samples were coated with aluminum by thermal evaporation in vacuum using Edwards E-306 coating system. The distance between two electrode and instrument was set at 25 cm.

3. Results and discussion

3.1. Structural characterization

Fig. 1 presents the X-ray diffraction patterns of CFTS films deposited at different substrate temperatures (250, 290, 330 and 370 °C). All thin films are polycrystalline irrespective of substrate temperature. The data analysis show the single stannite structure of Cu_2FeSnS_4 (JCPDS No. 44-1476) in the tetragonal space group *I-42m*, with the major diffraction peaks (112), (200), (220), and (116) in all the studied samples [10–12]. Also, with increasing the substrate temperature, the presence of other orientations along (101) and (110) which belong to Cu_2FeSnS_4 tetragonal phase was also detected. Except for these peaks, no characteristic peaks were detected for other phases/impurities such as FeS, CuS or Cu_2S, which indicates that the as-prepared films might have a complete synthesization without post-annealed. It can be seen that (112)-oriented texture is dominant for all CFTS thin films, and the intensity and full width at half maximum (FWHM) of (112) peak become strong and narrow with increasing the substrate temperature, which indicates that the films have good crystallinity.

The crystallite size of the films, calculated using Scherrer's formula:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$