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Original research article

Effect of Al doping on structural, morphological, optical, and electrical properties of Cu_2ZnSnS_4 thin films prepared by sol-gel spin coating

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ABSTRACT

Preparation of aluminum (Al) -free and Al- doped copper zinc tin sulfide (CZTS) thin films have been reported using low-cost, low-temperature (280 °C) sol-gel spin coating method without sulfurization. Effect of Al doping on structural, morphological, optical and electrical properties of the films have been presented. It has been found that both Al-free CZTS thin film sample (S0) and Al-doped CZTS thin film samples with 1% (S1), 3% (S2) and 4% (S3) show kestrite, polycrystalline tetragonal structure using X-ray diffraction and confirmed with Raman spectroscopy measurements. Scanning electron microscope (SEM) images show that the undoped sample has 3D architecture structure with porous flake-like surface, while the doped samples are smooth and with less porous structure. Energy dispersive spectroscopy results have been presented for reporting chemical composition of the constituting elements. Effect of annealing at two different temperatures of 350 °C and 400 °C for further enhancement of film crystallinity has also been presented. Interference fringes have been observed in the reflectance spectra, which indicate the good optical quality of the films. Optical properties of undoped and Al- doped samples have been reported. It has been found that decrease in the optical bandgap energy from 1.89 eV (undoped sample) to 1.73 eV at 1% Al doping, 1.69 eV at 3% Al doping, and 1.68 eV at 4% Al doping occurs, which is desirable for solar cell applications. At 350 °C, the resistivity of 3% Al doped film (S2) has the lowest value, 9×10^{-2} Ω cm, compared to the other samples. On the other hand, at 280 °C, the resistivity of the film increases from 1.14×10^{-1} Ω cm for the undoped film, to 1.45 Ω cm for 1% Al doping, 0.877 for 2% Al doping, 0.29 Ω cm for 3% Al, and 2 Ω cm for 4% Al doped sample.

1. Introduction

There is need for obtaining solar cell absorbing materials that are earth abundant, low cost, benign, and simple in preparation. In the first generation of solar cells, silicon was used as the absorbing material with the advantage of achieving high conversion efficiency. However, silicon is indirect bandgap semiconductor, thus the absorption coefficient of silicon is low and hence, much quantity of it are used. Since silicon is not earth-abundant, there had been need for alternative absorbing material(s). Copper indium gallium sulfide (or selenide) thin films have been used in the second generation, with an efficiency of 20.3%. However, there are some problems for utilizing these materials, since indium and gallium are not earth abundant,

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Table 1
Molar and weight ratio of the precursors.

	$CuCl2{\cdot}2H_2O$	$Zn(ac)2{\cdot}2H_2O$	$SnCl_2{\cdot}2H_2O$	CH_4N_2S
Molar ratio	1.5	0.75	0.75	4.5
Weight ratio	1.278	0.823	0.958	1.712

and selenium is not benign. Zinc and tin are cheaper and earth abundant elements compared to indium and gallium, thus there is much interest in copper zinc tin sulfide thin films.

Reports of synthesis, characterizations, and applications of ZTS thin films have been reported in several work. These include: preparation of kestrite CZTS thin films using sol-gel method on glass substrate by Park et al. [1] (this led to the conclusion that with 540 °C heat treatment, a large crystallite size can be obtained which is suitable for solar cell applications); preparation of CZTS thin film using non-vacuum liquid method. D. Tang et al. prepared CZTS thin film through non vacuum liquid method by preparation of Cu-Zn-Sn composite oxide and sulfur was incorporated during sulfurization [2]. However, the conversion efficiency was 1.22%. X. Yu et al. prepared CZTS thin films using sol-gel spin coating without sulfurization process [3]. According to their work, the sheet resistance of the film was 4.08 kΩ/□ and a resistivity of 0.4896 Ω cm. Y. B. K. Kumar studied the effect of copper and thiourea on the formation of CZTS thin film by spray pyrolysis on soda lime glass substrate at 373 °C [4]. M. Jiang et al. prepared CZTS thin films by sol-gel spin coating and achieved a solar cell conversion efficiency of 0.63% [5]. G. L. Agwana et al. studied the effect of annealing atmosphere such as N_2, sulfur powder and H_2S on the properties of sol-gel CZTS thin films deposited on molybdenum substrate [6]. They achieved power conversion efficiency of 0.77%. T.K. Chaudhuri et al. prepared CZTS thin films at a temperature of 200 °C using sol-gel dip coating [7]. The electrical resistivity of the film was 2 Ω cm. S. Islam prepared and characterized sol-gel spin coating of CZTS at a temperature of 280 °C [8]. Y. Sun et al. prepared CZTS films using ethylene glycol as solvent by dip coating [9]. S. Kumar and Swami achieved low resistive (0.014 Ω cm) kestrite CZTS thin films using sol-gel spin coating method [10]. J. Wang et al. used CZTS thin films for photo electrochemical reaction for H_2 production [11]. They concluded that the film was stable and efficient for H_2 production. However, little work has been done in investigating the effect of doping on the properties of CZTS thin films.

In this work, Al-doped Cu_2ZnSnS_4 nanocrystalline thin films have been synthesized using sol-gel spin coating. The effect of Al doping on structural, morphological, optical, and electrical properties have been presented. It has been found that Al dping (at certain concentrations) increases the crystallite size and changes the surface morphology of the films. Effect of annealing at temperatures of 350 °C and 400 °C enhance the crystallinity. However at ambient atmosphere with these annealing temperatures, sulfur volatilization problem arises. Raman and Fourier transform infra-red spectra have been presented and confirms the presence of kestrite CZTS phase. EDS for undoped and Al doped films have been presented.

2. Experimental details

The chemicals used for the film synthesis are as follows: zinc acetate dehydrate, $(CH_3COO)_2$ $Zn{\cdot}2H_2O$ (ZAD), which acts as zinc precursor, copper chloride dehydrate $Cucl_2{\cdot}2H_2O$, used as source for copper precursor, aluminum nitrate $Al(NO_3)_3{\cdot}9H_2O$, as precursor for aluminum, thiourea CH4N2S, and stannic chloride dehydrate $SnCl_2{\cdot}2H_2O$ as source for tin. All chemicals have been utilized without further purification. Thin films have been spun on microscope glass substrates using a spin coater; model Spin-1200D, MIDAS system.

Table 1 shows the weight and molecular ratio of materials used for preparation of the films. A mixture of water to ethanol with ratio of 3.5 mL: 1.5 mL has been used to dissolve the materials under 60 °C for 25 min. Then it spun on cleaned glass substrate with spin speed of 3000 rpm for 1 min. The films are preheated at temperature of 280 °C for half an hour. The procedures of spin coating and heat treatment are repeated another two times. The undoped sample is called S0 and the doped sample with amount of 1%, 3%, 4% by weight of $Al(NO_3)_3{\cdot}9H_2O$ is called S1, S2, and S3, respectively.

The films were characterized by XRD for the structural properties using P Analytical X'pert pro X-ray diffraction unit. The surface morphology of the ZnO thin films were measured by scanning electron microscope, model Quanta 250 FEG. Raman spectra have been done using dispersive Raman microscope, Bruker, Sentrea, operating at 532 nm laser wavelength. Fourier transform Infra-Red spectra have been done using Jasco FTIR 4100. Optical transmittance and reflectance spectra have been recorded by Jasco V-670 double-beam recording spectrophotometer in the range from 350 nm to 2000 nm. The optical bandgap energy was estimated using an extrapolation of the linear portion of $(\alpha h\nu)^2$ versus $h\nu$ where α is the absorption coefficient and $h\nu$ is the photon energy.

Electrical resistivity has been measured using Keithley 2400. All measurements have been carried out at room temperature.

3. Results and discussion

3.1. Surface morphology

Fig. 1 shows micrograph images obtained using field emission scanning electron microscope for the undoped and doped samples. The undoped film S0 (Fig. 1(a) with low magnification and (b) with high magnification) has 3D architecture structure