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Synthesis and characterization of chemical spray pyrolysed CZTS thin films for solar cell applications

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Abstract

In present work, thin films of CZTS have been prepared by chemical spray pyrolysis (CSP) by spraying precursor solution directly onto the soda lime glass (SLG) substrates by varying sulphur molar concentration. Copper chloride [$CuCl_2.2H_2O$], zinc chloride [$ZnCl_2.2H_2O$], tin chloride [$SnCl_4.5H_2O$] and thiourea [$(NH_2)_2CS$] were used as precursor materials to deposit CZTS thin films by using home-built chemical spray pyrolysis system. Influence of sulphur variation on structural, optical, morphology and electrical properties of CZTS films have been investigated by using variety techniques such as low angle x-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FE-SEM), UV-Visible spectroscopy, four probe method, etc. The formation of CZTS has been confirmed by low angle XRD and Raman spectroscopy. The structural analysis reveals formation of kesterite tetragonal phase with preferential orientation along (112) direction. The band gap values of CZTS thin films have been calculated and found in the range 2 - 2.25 eV over the entire range of sulphur variation studied. The change in band gap may be due to quantum confinement effects at nanoscale. The morphological studies show formation of islands of nanoscale particulate clusters which constitute the films in most of the samples. The films exhibit higher resistivity values (in KΩ) which may be due to presence of the strain in the films.

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1. Introduction

Thin films solar cells based on copper indium gallium selenide (CIGS) and cadmium telluride (CdTe) absorbers have been proven to be an alternative to Si based solar cells technology owing to their lower processing cost. Among them, thin-film CIGS solar cells have demonstrated a record efficiency of more than 20 % owing to their gleaming photovoltaic properties and great efforts have been devoted to the research of CIGS thin film solar cells in recent years due to these achievements [1]. However, the wide range commercial applications, CIGS solar cells has received the set back by the shortage of In and Ga leading to their expensiveness. On the other hand, CdTe solar cells technology has also not lagged behind in terms of solar cells performance. They have exhibited efficiencies to the tune of 14 % to 17 % regularly [2-4]. However, CdTe based solar cell technology suffers from the use of potentially hazardous substance in both absorber layer (CdTe) and window material (CdS), thus posing the problems of safe disposal of non-function, outdated CdTe solar cells.

Recently, considerable work has been done on the quaternary compound semiconductor, Cu_2ZnSnS_4 (CZTS) to make it a good absorber layer for thin film solar cells [5, 6] and thermoelectric power generators [7]. CZTS has excellent physical properties, such as the direct band gap (~1.5 eV), high optical absorption coefficient (> 10^4 cm^{-1}), low thermal conductivity etc. It is derived from the CIGS structure by the isoelectronic substitution of two In (or one In and one Ga) atoms by one Zn and one Sn atom. As a consequence, CZTS has some similar properties as CIGS. The availability of Cu, Zn, Sn and S in the earth's crust are ~ 50, 75, 2.2 and 260 ppm respectively and the availability of In is only ~ 0.049 ppm [8], so that all the constituents of CZTS are abundant in the earth's crust. Intrinsic point defects in CZTS make its conductivity p-type. Crystal structure of CZTS can allow some deviation from stoichiometry [9] making its deposition process easier. Moreover, grain boundaries in CZTS thin films are favorable to enhance the minority carrier collection [10]. Theoretical calculations have shown that conversion efficiency as high as 32.2 % [11] is possible for CZTS thin film solar cells with a CZTS layer of few micrometers. *Wadia et al.* [12] calculated the minimum cost of raw materials for the existing PV technologies and the emerging PV technologies and found that the cost of raw material for CZTS PV technology is much lower than that of the existing thin film PV technologies.

Various methods have been applied for CZTS thin film fabrication which includes solution methods [13-15], sol-gel [16, 17], electroplating [18-20], co-evaporation [21], pulsed laser deposition [22, 23], evaporation [21, 24] etc. These techniques have several problems such as high energy consumption, not suitable for large-area fabrication, and require high temperature anneal and/or sulfurization processes. Chemical spray pyrolysis (CSP) is an important preparation method for CZTS thin films because of its simplicity, moderate temperature processing and ability to prepare highly crystalline, large area thin films. In CSP method stoichiometry of CZTS is very sensitive to the concentrations of precursors in the spraying solutions. There are several reports on fabrication of CZTS thin films using CSP method; however studies of influence of change in sulphur concentration on CZTS properties are few. With this motivation an attempt has been made to synthesize CZTS thin films by CSP method. In present paper we report influence of sulphur (S) concentration on structural, optical, morphology and electrical properties of CZTS thin films prepared by chemical spray pyrolysis method.

2. Experimental

In present work, copper chloride ($CuCl_2$), zinc chloride ($ZnCl_2$), tin chloride ($SnCl_4$) and thiourea [$(NH_2)_2CS$] were used as precursor materials to deposit CZTS films by using home-built chemical spray pyrolysis unit onto soda lime glass (SLG) and fluorine doped tin oxide (FTO) substrates. All the chemicals used were of analytical grade as obtained from Sigma Aldrich (99.99 % purity) and were used as received. The molar concentration of $CuCl_2.2H_2O$, $ZnCl_2.2H_2O$ and $SnCl_4.5H_2O$ were kept constant at 0.04 M, 0.02 M and 0.02 M respectively whereas the concentration of $(NH_2)_2CS$ was varied from 0.12 M to 0.18 M. The substrate temperature was kept constant at 325 ^0C using in-built thermocouple and temperature controller. The air flow rate and nozzle-to-substrate distance were kept fixed at 22 LPM and 26 cm, respectively. The deposition was carried out for desired period of time and samples were allowed to cool to room temperature and then taken out for the characterization.