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Modification of the optoelectronic properties of sprayed In_2S_3 thin films by indium diffusion for application as buffer layer in CZTS based solar cell

V.G. Rajeshmon, N. Poornima, C. Sudha Kartha, K.P. Vijayakumar *

Department of Physics, Cochin University of Science and Technology, Cochin 682 022, India

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ABSTRACT

In this report the authors discuss the effect of diffusion of metallic indium on the optoelectronic properties of chemical spray deposited indium sulfide (In_2S_3) thin films which are prospective candidates for buffer layer application in thin film solar cells. Thin layers of metallic indium having different thicknesses were diffused into the films by evaporating different quantities of indium using vacuum evaporation technique followed by annealing. 'In' diffusion was done with an aim to reduce resistivity and improve the crystallinity to ensure better carrier collection. X-ray diffraction, X-ray photoelectron spectroscopy, optical absorption, photoluminescence and electrical studies were performed on the films. Analysis indicated that crystallinity attained a maximum for an optimum 'In' diffusion and then showed a retracing nature. Resistivity was found to decrease drastically from $2.3\times 10^5\ \Omega$ cm [pristine] to 4.7 Ω cm [for the optimum indium diffused samples]. Using the optimized In_2S_3 layer and copper zinc tin sulfide (CZTS) deposited using chemical spray pyrolysis, a heterojunction device was successfully fabricated with a conversion efficiency of 1.85% and fill factor of 52%. The optimum quantity of indium to be diffused depends on the thickness of the In_2S_3 thin film.

1. Introduction

Recently, there has been an increasing interest in III–VI materials, which find applications in optoelectronic, photovoltaic devices [1]. Among these materials, In_2S_3 thin films appear to be promising candidates for many technological applications due to their stability and photoconductive behavior [2]. It can be used as an effective nontoxic substitute for cadmium sulfide (CdS) in thin film chalcogenide based solar cells. Even though CdS is capable of forming efficient heterojunction, there is great interest in replacing CdS by a cadmium-free buffer due to environmental reasons. We have already reported that In_2S_3 buffer layer is quite efficient in yielding good results for ITO/$CuInS_2$/In_2S_3/Ag thin film solar cell [3]. Cu(In,Ga)Se_2 based solar cell with In_2S_3 buffer layer deposited by ALCVD could reach efficiencies (16.4%) near to those obtained by devices made with a standard CdS buffer layer [4]. Using sprayed In_xS_y buffer layer CIGS based solar cell could attain an efficiency of 8.9% [5].

Deposition of thin layer indium sulfide has been carried out by different methods such as MOCVD, spray pyrolysis, and chemical bath deposition (CBD) [6–8] by several groups. β-In_2S_3, the stable phase of In_2S_3 at room temperature, crystallizes in a defect spinel lattice, with a high degree of vacancies, ordering at tetrahedral cationic sites [9]. The characteristics of the film obtained depend highly on the fabrication method and can be changed by introducing dopants such as silver, tin, cobalt, aluminium etc. [10–14]. The primary purpose of our work was to decrease the resistance of In_2S_3 layer, so that when it is used as buffer layer the reduced series resistance of the device will yield an increased short circuit current, and its verification on CZTS based solar cell.

The most efficient thin film solar cells currently use chalcogenides, such as Cu(In,Ga)$(Se,S)_2$ and CdTe as absorber layers giving laboratory efficiencies up to 20.3% [15] and 16.7% [16] respectively. Despite the promise, both technologies rely on elements that are scarce in the earth's crust. Currently immense research is going onto explore new alternative materials like $AgInSe_2$ [17,18] $Cu_2ZnSn(S,Se)_4$ etc. Among them Cu_2ZnSnS_4 is a promising absorber layer material with an absorption coefficient of $10^4\ cm^{-1}$ and band gap energy in the range 1.4–1.6 eV [19–21]. Another key advantage is that CZTS can be synthesized by several economical techniques [22–25]. The highest conversion efficiency reported so far is 10.1% in a mixed sulfoselenide [$Cu_2ZnSn(S,Se)_4$] device [26] and 8.4% for the pure sulfide Cu_2ZnSnS_4 device [27]. In the present work authors discusses the modification in the optoelectronic properties of In_2S_3 buffer layer on indium diffusion and also the

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* Corresponding author. Tel.: +91 484 2577404; fax: +91 484 2577595.
E-mail addresses: rajeshvgopinath@gmail.com (V.G. Rajeshmon), kpv@cusat.ac.in (K.P. Vijayakumar).

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improvement in the performance parameters of a cell with this ‘In’ diffused In_2S_3 as buffer layer and CZTS as absorber layer.

2. Experimental details

In_2S_3 thin films were deposited on soda lime glass (SLG) substrates using indigenously fabricated automated Chemical Spray Pyrolysis unit [20,28]. Aqueous solution containing indium chloride (0.03 M) and thiourea (0.3 M) is sprayed at a rate of 6 ml/min onto the substrate kept at 603 K using compressed air (pressure-1.5 bar) as the carrier gas. At the substrate surface, the spray droplets vaporize leaving a dry precipitate which instantly decomposes to form a thin layer of In_2S_3. Following deposition, films were annealed for 30 min at the substrate temperature. Concentration of thiourea was larger than the stoichiometric requirement to compensate for the loss of sulfur during pyrolysis. Out of the five films deposited (each having a thickness of 500 nm) four were taken and four different quantities of indium were evaporated. The thicknesses of the evaporated layers were 4, 6, 8, 10 nm (monitored using quartz-crystal thickness monitor attached to the vacuum evaporation unit) respectively. The films were then annealed at 100 °C for 1 h. Finally the samples were named as P:4In, P:6In, P:8In and P:10In respectively. The In_2S_3 film devoid of indium evaporation was named as P. The crystal structure of the films was investigated using Rigaku (D. Max. C) X-ray diffractometer (employing Cu-K_α line (λ = 1.5405 Å) and Ni filter) operated at 30 kV and 20 mA. The observed XRD patterns were interpreted by comparing with the appropriate JCPDS cards. The depth wise variation of atomic concentration in the films was obtained using an X-ray photoelectron spectroscopy (XPS) ULVAC-PHI unit (Model-ESCA 5600 CIM) employing argon ion sputtering. Optical properties were studied using UV–vis-NIR spectrophotometer (Jasco V-570 Model). For Photoluminescence studies the samples were excited using the 325 nm output from a He–Cd laser and the emission was collected using CCD coupled spectrophotometer interfaced to the computer via custom made software OOIBase32. Electrical studies were conducted using Keithley 236 Source Measure Unit (SMU).

Glass plates coated with ITO (thickness 200 nm, optical transmission 82% and electrical resistivity $2.25 \times 10^{-4}\,\Omega$ cm) were used as the substrate for junction fabrication. For depositing CZTS films, aqueous solution containing cuprous chloride (0.025 M), zinc acetate (0.01 M), stannic chloride (0.007 M) and thiourea (0.12 M) is sprayed at a rate of 6 ml/min onto the substrate kept at 623 K using compressed air (pressure $\sim$ 1.5 bar) as the carrier gas. Concentration of thiourea was three times the stoichiometric requirement (0.04 M) to compensate for the loss of sulfur during pyrolysis. Thickness of CZTS layer was about 550 nm. In_2S_3 layer of thickness 500 nm was deposited on top of CZTS layer. Five junctions were prepared using pristine as well as ‘In’ diffused In_2S_3 layers and were named as D-P, D-P:4In, D-P:6In, D-P:8In and D-P:10In respectively. The *J–V* characteristics of the devices were measured using the Keithley SMU K236 and Metric’s Interactive Characterization Software (ICS). The devices were illuminated using a tungsten halogen lamp with an intensity of 100 mW/cm^2, on the substrate surface. An infrared filter along with a water jacket was used to ensure that there was no heating of the device during measurement.

3. Results and discussion

3.1. X-ray diffraction studies

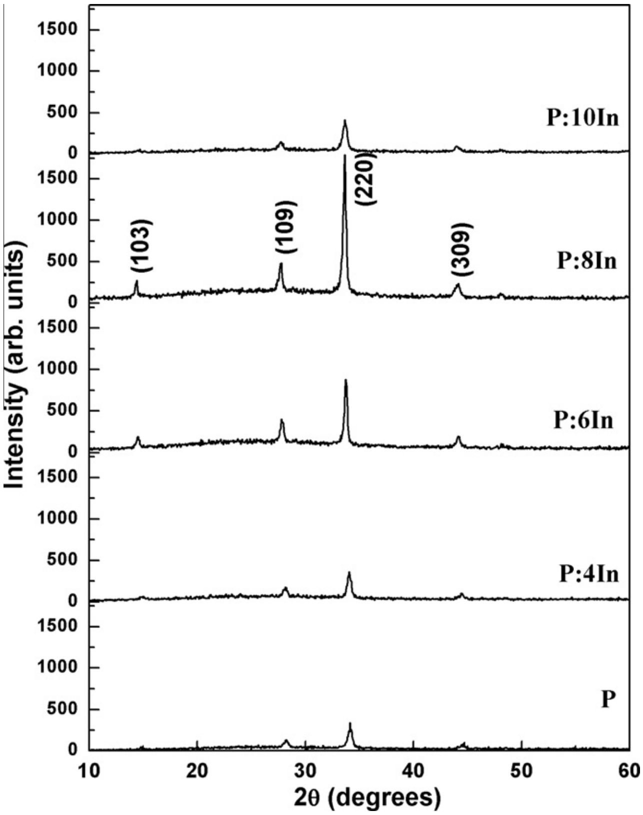

Fig. 1. X-ray diffraction patterns of pristine as well as ‘In’ diffused In_2S_3 thin films prepared on SLG substrates.

Table 1
XRD data for pristine as well as ‘In’ diffused In_2S_3 thin films.

Sample	*d* (A^0)	Preferential orientation	FWHM (degrees)	Grain size (nm)
P	2.67	[2 2 0]	0.36	23.0
P:4In	2.67	[2 2 0]	0.35	23.7
P:6In	2.69	[2 2 0]	0.25	33.2
P:8In	2.70	[2 2 0]	0.24	34.5
P:10In	2.70	[2 2 0]	0.38	21.8
Standard JCPDS (25–390)	2.69	[2 2 0]	...	...

Fig. 1 shows the XRD pattern from 10° to 60° of pristine as well as indium diffused In_2S_3 thin films. Well defined peaks corresponding to the (1 0 3), (1 0 9), (2 2 0) and (3 0 9) planes of β-In_2S_3 could be clearly observed. The ‘*d*’ values coincided with that of β-In_2S_3 in standard JCPDS data card (25–390). The intensity of peak corresponding to (2 2 0) plane was observed to be much greater than that of the other peaks present, indicating a strong preferential orientation in the (2 2 0) plane. For indium diffused samples, the Bragg peaks in the XRD pattern are more intense and the full width at half maximum (FWHM) of the diffraction peak is very small, indicating a clear improvement in crystallinity. However, it is also evident that there exists an optimum for the thickness of indium to be diffused, up to which the crystallinity increases and beyond which a retracing phenomenon is observed. For the 500 nm thick In_2S_3 film studied here, the optimum thickness of indium to be diffused was 8 nm. The grain size was calculated (Table 1) from Debye–Scherrer formula, $D = \frac{0.9\lambda}{\beta \cos\theta}$, where D is the grain size, λ is the wavelength of Cu-K_α line and β is the FWHM. Also no metallic phase was observed in the film in the detection limits of XRD analysis even for 10 nm ‘In’ diffused sample (P:10In). To investigate the effect of film thickness on the optimum quantity of indium to be diffused we prepared In_2S_3 films with thickness 600 nm. It was seen that the optimum thickness of indium diffused up to which crystallinity was enhanced increased from 8 to 9 nm with increase in thickness of In_2S_3 film.

3.2. XPS studies

In order to confirm the formation of In_2S_3 and to understand the variation of In/S ratio from surface to depth of the film on indium diffusion, XPS measurements were done. Fig. 2 shows the XPS depth profile of samples P and P:8In which indicates that indium and sulfur were uniformly distributed throughout the depth of the samples. Binding energies of indium and sulfur indicated the formation of In_2S_3 (162.5 eV for S2p, 444.9 and 452.9 eV for In $3d_{5/2}$ and In $3d_{3/2}$ respectively) and were in agreement with the reported values [29]. Carbon was present as a surface contaminant (285 eV). Oxygen at the surface, which is found for all spray deposited samples, is due to surface contamination in the form of sulfite or sulfate. Oxygen content in the bulk of the sample is very low, but as we approach the substrate, it can be observed that oxygen