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Thin film solar cells with extremely thin absorber layer having multiple absorption bands: A novel attempt

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Abstract

Chemical Spray Pyrolysis (CSP) technique was utilized for depositing 'Extremely Thin Absorber (ETA)' layer solar cells having phases of both $CuInS_2$ and Cu_2S in the absorber, so as to have multiple band gaps of 1.45 eV and 1.80 eV respectively. Cell fabricated using this absorber is almost equivalent to a tandem cell capable of absorbing photons of two energies. This was achieved simply by lowering concentration of indium in conventional $CuInS_2$. Presence of both $CuInS_2$ and Cu_2S phases were confirmed through X-ray diffraction and Raman studies. Multiple absorptions in the film were evident from the absorption spectra. Also the '$CuInS_2$:Cu_2S' absorber was used for the fabrication of ETA solar cell with structure ITO/($CuInS_2$:Cu_2S)/In_2S_3/Ag. Comparing with performance of ITO/$CuInS_2$/In_2S_3/Ag solar cells, they exhibits 17%, 15% and 47% increases in short circuit current, fill factor and efficiency respectively. The best device realized in this study has open circuit voltage of 518 mV and short circuit current density of 14.25 mA/cm^2. Efficiency and fill factor were 3.82% and 52% respectively.

Keywords: Chemical spray pyrolysis; $CuInS_2$; Cu_2S; Parasitic resistances

1. Introduction

Copper based chalcogenide compounds such as $CuInS_2$ and Cu_2S thin films draw attention among thin film absorber materials because of their high absorption coefficient ($\sim 10^5$ cm^{-1}), easiness in preparation and environmentally benign nature (Santhosh et al., 2014a; Scheer et al., 1993; Hall et al., 1981; Isac et al., 2007). Cu_2S is a well-established absorber material for photovoltaic (PV) application, especially in the old Cu_2S/CdS solar cells, which gained paramount importance in commercial viability for terrestrial application due to its low cost and simple production possibility (Hall et al., 1981; Isac et al., 2007; Hadley and Tseng, 1977; Gill and Bube, 1970). However, toxic nature of Cd and Cu diffusion from Cu_2S layer to CdS were the major issues for these solar cells. Another copper based compound viz., $CuInS_2$ exhibits direct band gap of $\sim$1.5 eV, which is well matched with the solar spectrum for PV performance (Braunger et al., 1996; Siemer et al., 2001). Theoretically, the maximum efficiency for $CuInS_2$ based single junction cells is 28.5%, which is the highest value when compared with other chalcopyrites (Siebentritt, 2002). Present work deals with deposition of thin films having mixed phase of $CuInS_2$ and Cu_2S ($CuInS_2$:Cu_2S). $CuInS_2$ and Cu_2S possess band gaps of 1.45 eV and 1.80 eV respectively. By introducing these two absorber phases in a single film, more efficient light

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absorption is achieved as this material can absorb photons having these two energies. This new absorber material is a suitable candidate for ETA solar cells, using 'earth-abundant' and 'eco-friendly' materials. Major difficulty of low diffusion length of charge carriers (causing heavy loss in charge collection), especially observed in thin film solar cells, can be rectified by using ETA concept (Tena-Zaera et al., 2008; Kaiser et al., 2001). $CuInS_2$ and Cu_2S already proved their capability in ETA solar cell structures (Kaiser et al., 2001; Konenkamp et al., 2002). Usually micro or nano-structured electron conducting layer such as ZnO or TiO_2 has an inevitable role in ETA solar cell structure (Krunks et al., 2008; O'Hayre et al., 2007). However for the present study, these layers are avoided for simplicity. The cell structure followed in this study was ITO/($CuInS_2$:Cu_2S)/In_2S_3/Ag (Santhosh et al., 2014a). In_2S_3 was preferred here as the buffer layer because, on comparing with CdS buffer layer, it is non-toxic and has better light transmission in the blue wave length region (Cherian et al., 2012; John et al., 2005). Moreover, the thermal diffusion of copper (from absorber layer) into the In_2S_3 layer (buffer layer) causes only the conversion of In_2S_3 into $CuInS_2$ which results in the increase in thickness of absorber layer and this improves cell parameters. Indeed this was the major reason for the failure of CdS/Cu_2S solar cell. Furthermore, this is a well-studied material in our lab (Santhosh et al., 2014a; John et al., 2005). Among different chemical routes for the fabrication of thin films, Chemical Spray Pyrolysis (CSP) offers significant advantage over other methods as CSP is simple, versatile and cost effective. Also CSP already proved its capability for large area deposition (Sebastian et al., 2009; Santhosh et al., 2014b) which depicts its suitability for the production-line approach in industries. Hence both absorber and buffer layer, for the present study, were deposited using CSP technique.

In order to deposit absorber layer with mixed phases of $CuInS_2$ and Cu_2S, we purposefully reduced indium concentration in the precursor solution used for depositing $CuInS_2$ thin films. Among different binary phases of Cu and S, only Cu_2S is better absorber (Pathan et al., 2002). Interestingly, binary phases other than Cu_2S were not observed in the films. Structural, morphological, optical and electrical properties of the $CuInS_2$:Cu_2S absorber material were studied and compared with well-established $CuInS_2$ absorber.

2. Experimental details

An indigenously developed automated spray pyrolysis unit was employed for cell fabrication (Santhosh et al., 2014a,b). For film deposition, ultrasonically cleaned soda lime glass substrates were placed over heater which can maintain stable and uniform temperature over an area of $\sim$50 cm^2. Aqueous based precursor solution was sprayed over the glass plates using air blast type atomizer. The precursors used for absorber layer deposition are $CuCl_2$:$2H_2O$, $InCl_3$ and thiourea [$CS(NH_2)_2$]. $CuInS_2$ absorber layer (without Cu_2S phase) was deposited by taking Cu:In:S ratio in the precursor solution as 1.4:1:5 (Santhosh et al., 2014a) and the films were named as C-1. In order to deposit the mixed phases of $CuInS_2$ and Cu_2S, indium concentration in the precursor was reduced such that Cu:In:S ratio in the precursor solution was 1.4:0.2:5. These samples were named as C-0.2. Substrate temperature (350 °C) and spray rate (4 ml/min) were fixed for all samples (Santhosh et al., 2014a).

For device fabrication, precursor solution of absorber layer was sprayed over ITO coated glass substrates (Thickness $\sim$220 nm; Sheet resistance $\sim$12 Ω/□; Geomatec, Japan). Over this, In_2S_3 (buffer layer) was spray deposited using $InCl_3$ and thiourea [$CS(NH_2)_2$] as precursors (John et al., 2005). Here also substrate temperature and spray rate were the same. For top contact from the device, silver was vacuum evaporated (2×10^{-5} Torr) over the cell structure (Santhosh et al., 2014a).

Structural characterizations of the samples were carried out using Rigaku (D. Max. C) X-ray diffractometer employing Cu Kα line and Ni filter operated at 30 kV and 20 mA. For the exact identification of different crystalline phases in the deposited films, Raman analysis was also done (Horiba Jobin Yvon LabRam HR system). Optical absorbance spectra of the samples at normal incidence were recorded using UV–VIS–NIR spectrophotometer (JASCO V-570 model). Electrical properties of the absorber layer at room temperature were studied using Hall Effect measurement system (HMS 5300, Ecopia). In order to explore variation in surface features of $CuInS_2$ thin films (on reducing indium concentration), Scanning Electron Microscopy (SEM: JEOL, JSM-840, operated at 20 kV) was utilized. Energy Dispersive X-ray (EDAX) analysis set up attached with SEM was used for composition analysis of the deposited films. *J–V* characteristics of the heterojunctions were recorded using source measure unit (NI PXI-1033). 'Class AAA' solar simulator (PET, model SS50AAA) was used to illuminate solar cells.

3. Results and discussion

From XRD analysis of samples (Fig. 1), C-1 shows only (1 1 2) and (2 2 0) planes which represent tetragonal phase of $CuInS_2$ (Santhosh et al., 2014a). However, sample C-0.2 shows (1 0 3) plane corresponding to tetragonal Cu_2S phase also (JCPDS file no 72-1071) (Isac et al., 2007). Preferential orientations of both samples are along (1 1 2) plane even though Cu/In ratio was varied from 1.4:1 to 1.4:0.2. In the present study, In_2S_3 was the buffer layer, which is also tetragonal in nature (Mathew et al., 2010).

In order to obtain clear picture of any other binary phases (if present) in the samples, Raman analysis was carried out (Fig. 2). Raman peak at 300 cm^{-1} for C-1 sample corresponds to A_1 mode of $CuInS_2$ (Chung et al., 2012). For C-0.2 sample, in addition to A_1 mode, another peak is observed at 472 cm^{-1} and this confirms presence of Cu_2S phase (Wang et al., 2003). Indeed for C-0.2 samples,