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All sprayed ITO-free $CuInS_2/In_2S_3$ solar cells

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Abstract

$CuInS_2$, In_2S_3 and fluorine doped tin oxide (FTO) thin films were prepared by simple, cost effective Chemical Spray Pyrolysis (CSP) method and effect of [Cu]/[In] ratio on the structural, optical, electrical and morphological properties of $CuInS_2$ thin films were investigated. X-ray diffraction analysis shows that grain size of $CuInS_2$ samples increases with increase in [Cu]/[In] ratio in the spray solution. It could be figured out that Cu_xS binary phases are absent in the films. Optical studies reveals that the band gap of the films decreases on increasing the [Cu]/[In] ratio. Type of conductivity and resistivity of $CuInS_2$ films were estimated from Hall measurement system. On increasing [Cu]/[In] ratio resistivity decreases. Surface morphology of the films deposited at different spray rates were analyzed using Atomic Force Microscopy (AFM) and results shows that there should be an optimum spray rate for device fabrication and was fixed at 4 ml/min. Surface structure and uniformity were confirmed by employing Scanning Electron Microscopy (SEM). Composition and p-type conductivity of $CuInS_2$ samples were analyzed through Energy Dispersive X-ray analysis (EDX). Finally the optimized $CuInS_2$ films were used for device fabrication. The best device in this study has open circuit voltage of 457 mV and short circuit current density of 5.45 mA/cm^2. Efficiency and fill factor were 0.94% and 38% respectively.

Keywords: Chemical Spray Pyrolysis; Solar cells; $CuInS_2$; In_2S_3

1. Introduction

Copper indium sulphide ($CuInS_2$) is one of the I-III-VI_2 compound semiconductors which have theoretically the highest conversion efficiency among the chalcopyrite based solar cells (Parameshwari et al., 2012; Klaer et al., 1998). Direct band gap of 1.55 eV, high absorption coefficient ($\sim 10^5$ cm^{-1}) and non-toxicity of the constituents are the important attributes of $CuInS_2$ films to be used as an absorber layer in thin film solar cells (Qiu et al., 2006). Indium sulphide (In_2S_3) has been observed to be an efficient alternative to toxic CdS buffer layer for $CuInS_2$ based solar cells (Trigo et al., 2008; Kilani et al., 2011). Fluorine doped tin oxide (FTO) films are promising candidate as transparent conducting oxides (TCO) for thin film solar cells due the high transparency and conductivity among easily available TCOs (Elangovan and Ramamurthi, 2005). For the simplicity and versatile implementation of thin film solar cells, the entire layers essential for their fabrication i.e., absorber layer, buffer layer and transparent conducting oxides must be prepared by the same deposition technique. More over the deposition technique should also be cost effective to ensure low economic payback time affordable to common people. In the present work, we fabricated $CuInS_2$ absorber layer, In_2S_3 buffer layer and fluorine doped tin oxide TCO layers essential for the fabrication of FTO/$CuInS_2$/In_2S_3 solar cell by simple, cost effective

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Chemical Spray Pyrolysis (CSP) method. Solar cells having efficiencies up to 9.5% has been reported using sprayed $CuInS_2/In_2S_3$ heterojunction (John et al., 2005), but in most cases the back contact materials used was either tin doped indium oxide (ITO) or molybdenum (Mo) prepared by sputtering or vacuum evaporation (Klenk et al., 2005; Braunger et al., 1996). This work used sprayed FTO samples for device fabrication. Prior to the fabrication of the device we optimized sprayed $CuInS_2$ thin films structurally, electrically and morphologically to implement as an absorber layer in FTO/$CuInS_2/In_2S_3$ solar cells. Finally the optimized $CuInS_2$ absorber layer was used for the fabrication of all sprayed solar cells.

2. Experimental details

FTO thin films (sheet resistance of 25 Ω per square) were deposited on ultrasonically cleaned soda lime glass substrates kept at 425 °C by automated Chemical Spray Pyrolysis machine. The precursor solution used was stannic chloride ($SnCl_4$). Ammonium fluoride (NH_4F) was added in the spray solution for doping with fluorine (Elangovan and Ramamurthi, 2005; Shewale et al., 2010). $CuInS_2$ thin films were deposited on FTO coated glass substrate also by CSP machine (John et al., 2005). Aqueous solutions of $CuCl_2$, $InCl_3$ and thiourea were used as the precursors for Cu, In and S (Cherian et al., 2012). It was observed that the deposition rates of $CuInS_2$ over FTO films are very low. Therefore it will take a long time to deposit the necessary thickness of $CuInS_2$ absorber layer over FTO films. For a particular volume, thickness of spray deposited $CuInS_2$ layer can be increased by increasing the [Cu]/[In] ratio in the precursor solution (Hussain et al., 2012). For that [Cu]/[In] ratio in the precursor solution was varied as 0.8, 1, 1.2 and 1.4. Above [Cu]/[In] ratio 1.4 the solution gets precipitated. [S]/[In] ratios in all these films were maintained as 5. Deposition temperature and spray volume for $CuInS_2$ thin films were fixed at 350 °C and 80 ml (Sebastian et al., 2009). Spray rate was optimized at 4 ml/min as explained in Section 3.5. Trials shows that as [Cu]/[In] ratio increases, the deposition rate over the FTO layer increases. In order to characterize these films structurally, optically and electrically, ultrasonically cleaned soda lime glass plates were also placed along with FTO in each spray and the deposited films were named as Cu-0.8, Cu-1, Cu-1.2 and Cu-1.4. Finally In_2S_3 buffer layer was deposited by spraying 35 ml of aqueous solution containing indium and sulfur precursors in the ratio 1.2:12 (Santhosh et al., 2011; Mathew et al., 2010). For electrical contact at the top, silver electrode (thickness ~50 nm) was vacuum evaporated at a pressure of 2×10^{-5} mBar.

$CuInS_2$, In_2S_3 and FTO samples were structurally characterized using Rigaku (D. Max. C) X-ray diffractometer employing Cu Kα line and Ni filter operated at 30 kV and 20 mA. Thicknesses of the films were measured using the Stylus profilometer (Dektak-6 M). Optical absorbance of the samples at normal incidence was studied employing UV–VIS–NIR spectrophotometer (JASCO V-570 model). Using Van der pauw four probe technique, Hall effect measurement system (HMS 5300, Ecopia) was employed to characterize the electrical transport properties of the $CuInS_2$ thin films at room temperature. 'Nanosurf easyScan 2' AFM System was used for the morphological analysis of the films. Surface features of $CuInS_2$ thin films were explored using Scanning Electron Microscopy (SEM) (JEOL, JSM-840, operated at 20 kV). Composition analysis of the deposited films was done using Energy Dispersive X-ray (EDAX) analysis which is attached with SEM. Photovoltaic response of the heterojunction was studied using class AAA solar simulator (PET, model SS50AAA).

3. Results and discussion

3.1. Structural characterization

XRD profiles of each layer of the fabricated device are shown in Fig. 1.

From Fig. 1(a) it is clear that FTO films were crystalline in nature with preferential orientation along (200) plane. XRD analysis of samples Cu-0.8, Cu-1, Cu-1.2, Cu-1.4 prove the tetragonal structure of $CuInS_2$ (JCPDS data card 270159) with preferential orientation along (112) plane (Fig. 1(b)). One of the main challenges regarding $CuInS_2$ based solar cells is the formation of binary phases such as Cu_xS, which affects the performance of the device. From XRD analysis, the films deposited during CSP do not show any peak corresponding to binary phases even though [Cu]/[In] ratio was varied from 0.8 to 1.4 (John et al., 2005). Hence KCN etching (which is a difficult process due to toxicity of KCN) and optimized 3-stage growth process usually employed to remove these secondary phases can be avoided (Ogawa et al., 1996; Calderon et al., 2010). Grain sizes of the deposited films were calculated using Scherer's formula. As [Cu]/[In] ratio increases grain size also improves and for [Cu]/[In] ratio 1.4 the films possess a grain size of 32 nm. Thickness and grain size for samples Cu-0.8, Cu-1, Cu-1.2 and Cu-1.4 are tabulated in Table 1. It is very important to mention that this increase in grain size is appreciable for a good quality absorber layer as it improves electrical transport properties in thin film solar cells (Bergmann, 1999). Variation of grain size with [Cu]/[In] ratio is shown in Fig. 2. In_2S_3 film showed (Fig. 1(c)) preferential orientation of (220) plane which is the characteristics of β-In_2S_3 thin films.

3.2. Optical properties

Optical absorption spectra of the $CuInS_2$ samples with different [Cu]/[In] ratios are depicted in Fig. 3(a). Absorption coefficient (α) is related to the energy gap (E_g) according to the equation