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$CuInS_2/In_2S_3$ Cells using a Cost-effective Technique: Significance of Precursor Ratios on Cell Parameters

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Abstract

Thin film solar cells having structure $CuInS_2/In_2S_3$ were fabricated using chemical spray pyrolysis (CSP) technique over ITO coated glass. Top electrode was silver film (area 0.05 cm^2). Cu/In ratio and S/Cu in the precursor solution for $CuInS_2$ were fixed as 1.2 and 5 respectively. In/S ratio in the precursor solution for In_2S_3 was fixed as 1.2/8. An efficiency of 0.6% (fill factor -37.6%) was obtained. Cu diffusion to the In_2S_3 layer, which deteriorates junction properties, is inevitable in $CuInS_2/In_2S_3$ cell. So to decrease this effect and to ensure a Cu-free In_2S_3 layer at the top of the cell, Cu/In ratio was reduced to 1. Then a remarkable increase in short circuit current density was occurred from 3 mA/cm^2 to 14.8 mA/cm^2 and an efficiency of 2.13% was achieved. Also when In/S ratio was altered to 1.2/12, the short circuit current density increased to 17.8 mA/cm^2 with an improved fill factor of 32% and efficiency remaining as 2%. Thus Cu/In and In/S ratios in the precursor solutions play a crucial role in determining the cell parameters.

Keywords: Semiconductors; thin films; $CuInS_2$; In_2S_3; solar cells; chemical spray pyrolysis

1. Introduction

An important research goal in developing photovoltaic devices is the replacement of costly materials and toxic heavy metals with more benign and cheap elements. Thin film technologies aim to use less material to obtain a considerable efficiency. Chalcopyrite semiconductors have been successfully applied as absorber layers for polycrystalline thin-film solar cells. Among them the ternary compound $CuInS_2$ has the potential to reach high conversion efficiencies due to its exceptional material properties. In the last decade, significant development was made in this type of cell [1, 2]. $CuInS_2$ based devices show excellent stability and reproducibility than its selenide counterpart as its band gap [~1.5 eV] matched well with the solar spectrum. The best reported efficiency for a pure $CuInS_2$-based solar cell was 12.5% for a Mo/

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$CuInS_2/CdS/ZnO$ cell [3] and 13% was achieved when Goto *et al*. incorporated $CuGaS_2$ in the structure [4]. The highest active-area efficiency of a Cd-free and Se-free thin film solar cell obtained so far was 11.4 % using $In_x(OH,S)_y$ buffer layer [5]. A suitable buffer layer that substitutes toxic CdS layer is In_2S_3 film, which is a wide-bandgap material with high photoconductivity and luminescent properties [6-8].

Cost effective techniques are necessary to meet world's major energy needs and it can be accomplished using chemical deposition methods. Among these chemical spray pyrolysis (CSP) is an attractive cost-effective technique for large area deposition of absorber and buffer layers. Cell structure 'ITO/$CuInS_2$/In_2S_3/Ag' capable of giving 9.5% efficiency was fabricated using CSP technique [9]. Here we have also employed the same structure with spray pyrolysed $CuInS_2$ and In_2S_3 layers. Precursor ratios of absorber layer and buffer layer play an important role in determining the cell characteristics. Cu rich $CuInS_2$ thin films were found to be more conducting than Cu poor samples [10]. While using this Cu rich $CuInS_2$ thin film for $CuInS_2/In_2S_3$ cell, Cu may diffuse in to the In_2S_3 layer so as to disturb the proper junction formation. Also when In/S ratio was varied in solution, β-In_2S_3 film properties were also varied. In this paper, we investigated the significance of Cu/In ratio in the $CuInS_2$ layer and In/S ratio in the In_2S_3 layer on determining the performance parameters of the cell.

2. Experimental details

2.1. Preparation of $CuInS_2$ thin films

As an absorber layer, $CuInS_2$ layer was coated first onto the glass substrates and on the ITO surface using CSP technique. $CuInS_2$ film was deposited by spraying aqueous solutions of copper chloride ($CuCl_2 \cdot 2H_2O$), indium chloride ($InCl_3$), and thiourea ($CS(NH_2)_2$) keeping the substrate at 300 ± 5 ºC with a spray rate of 20 ml/min. Total volume of solution sprayed was 375 ml. Cu/In & S/Cu ratios in the films were controlled by varying the molar concentrations of respective solutions. Here at first, Cu/In and S/Cu ratios were kept at 1.2 and 5 respectively in solution. The samples were kept at the same temperature for half an hour after each spray and then the temperature was reduced to room temperature. This $CuInS_2$ sample on glass is named as C1. Then Cu/In ratio was varied to 1 by increasing the In concentration in the solution and the sample is named as C2. The thickness of the films, C1 & C2 was 0.4 and 0.5 μm respectively.

2.2. Preparation of In_2S_3 thin films

In_2S_3 layer was coated over $CuInS_2$ layer and also onto the glass substrates. For preparing In_2S_3 layer, indium chloride ($InCl_3$) and thiourea ($CS(NH_2)_2$) were used as precursor solutions. In/S ratio was kept at 1.2/8 in the solution as it was showing maximum photosensitivity. For this, molarities of $InCl_3$ and $CS(NH_2)_2$ were kept at 0.015 M and 0.1 M respectively. Two layers of In_2S_3 were given in two steps; the cell was allowed to cool after spraying 200 ml of In_2S_3 solution and then it was reheated to 300 ºC to spray another 200 ml. Thickness of In_2S_3 was 0.5 μm. The In_2S_3 sample on glass substrate having In/S = 1.2/8 is named as I1. Then In/S ratio was varied to 1.2/12 by decreasing the Indium concentration in the solution and the sample is named as I2, having a thickness of ~0.45 μm.

2.3. Fabrication of $CuInS_2/In_2S_3$ cell

To fabricate a solar cell, In_2S_3 buffer layer in which In/S ratio was kept at 1.2/8 in the solution was deposited onto two $CuInS_2$ films, with Cu/In ratios; 1.2 & 1 on ITO coated glass substrates. Also In_2S_3 layer with In/S ratio, 1.2/12 was also tried on those $CuInS_2$ films. Then the effect of precursor ratios of both layers on the cell parameters was analysed. Top electrode was Ag of thickness 45 nm over an area of $5mm^2$, which was deposited using vacuum evaporation.

2.4. Characterisation techniques

Structural analysis was done using X-ray diffraction (XRD) (Rigaku-D. Max. C-X-ray diffractometer having, Cu-K_α radiation of wavelength, 1.5405 Å). Optical absorption studies were carried out with UV-Vis-NIR spectrophotometer (Hitachi U-3410 Model). Depth profile and atomic ratio of the cell samples were obtained using X-ray photoelectron spectroscopy (XPS) ULVAC-PHI unit; (Model-ESCA 5600 CIM) employing argon ion sputtering. Here the cells were sputtered layer-by-layer using Ar ion and XPS measurements were taken after every 1 minute of sputtering. Atomic concentration was studied with the help of Energy Dispersive X-ray Spectroscopy (EDX), (Oxford Model 7060). Thickness measurements were carried out using a Dektak surface profilometer (Dektak 6 M). Dark and illuminated *J-V* characteristics of the cell were measured with the help of Keithley source measure unit (SMU, K 236) and Metric's interactive characterisation software (ICS). The cell was illuminated using a tungsten halogen lamp, having an intensity 100 mW/cm^2 on the substrate surface.

3. Results and discussions

3.1. Effect of variation of Cu/In ratio in the $CuInS_2$ layer

3.1.1. On the structural and compositional analysis of $CuInS_2$ thin films

Crystalline structure of the films was analysed by X-ray diffraction. Figures 1(a) and 1(b) show the XRD patterns of CIS samples C1 and C2. Characteristic peaks at 2θ values of 28.05 and 46.5 º corresponding to the $CuInS_2$ planes (112) and (220) with preferential orientation along (112) plane indicated the formation of $CuInS_2$ phase. The d values coincided with that of $CuInS_2$ in standard JCPDS data card (JCPDS-270159).

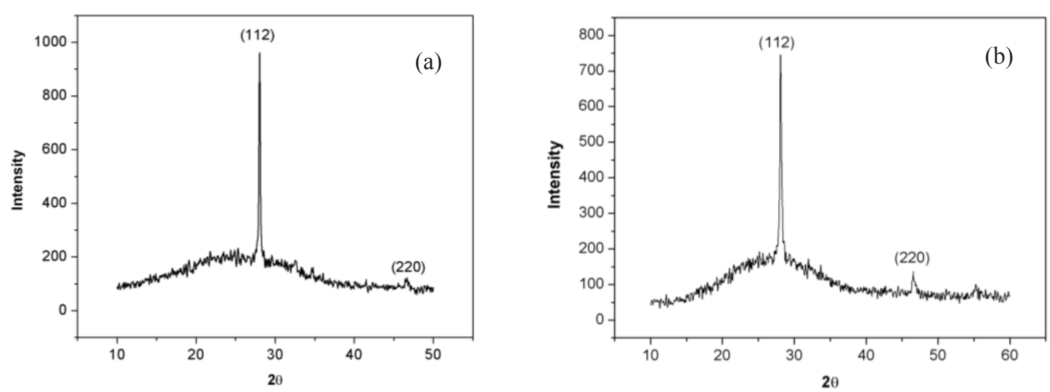


Fig. 1. XRD patterns of (a) C1; (b) C2

Better crystallinity was observed for sample C1 prepared using In-poor solution, which can be attributed to the higher copper mobility in the sample. It is reported that Cu-rich films were more crystalline than Cu-poor samples [11]. Composition of the films C1 and C2 can be compared by EDX analysis. Atomic concentrations of Cu, In, S and Cl of samples C1 and C2 are represented in Table 1.

From EDX analysis, Cu/In ratio in the film also was found to be less for C2 compared to that of C1. Indium concentration was evidently higher for C2, which was prepared using In rich solutions.

Table 1. Atomic percentage of the elements in C1 and C2 from EDX measurements

	Cu	In	S	Cl	Cu/In
C1	27.22	23.95	47.13	1.69	1.13
C2	32.53	30.79	32.35	4.32	1.05

3.1.2. On the optical and electrical properties of $CuInS_2$ thin films

Band gaps of $CuInS_2$ films were determined from $(\alpha h\nu)^2$ vs. hν plots. For the film having Cu/In ratio = 1.2, the band gap was 1.43 and for the film having Cu/In ratio = 1, it was 1.53 eV. Higher band gaps were reported for samples with low Cu/In ratio [11]. The band gap value depends on the crystallite size of the sample [12, 13]. Higher the crystallinity of the sample, the lesser will be the band gap. Electrical studies proved that all the samples were p-type. Resistivity of the sample C1 was 3.93 Ωcm and that of C2 was 937.5 Ωcm. The electrical properties of $CuInS_2$ films largely depend on their atomic composition [14, 15]. The lower resistivity of C1 may be due to the higher Cu/In ratio in the film [11].

3.1.3. On the J-V characteristics of $CuInS_2$ /In_2S_3 cell

The cell parameters obtained for the cell prepared using C1 and I1 were V_{oc} = 539 mV, J_{sc} = 3 mA/cm^2, FF = 37.5%, η = 0.6%. A considerable improvement in short-circuit current density and efficiency was observed for the cell prepared using C2 and I1. The cell parameters were V_{oc} = 466 mV, J_{sc} = 14.8 mA/cm^2, FF = 31%, η = 2.13%. Figures 2(a) and 2(b) depict I-V curves of the cells. The cell having improved J_{sc} has low series resistance, which may be due to the better carrier generation in the cell.

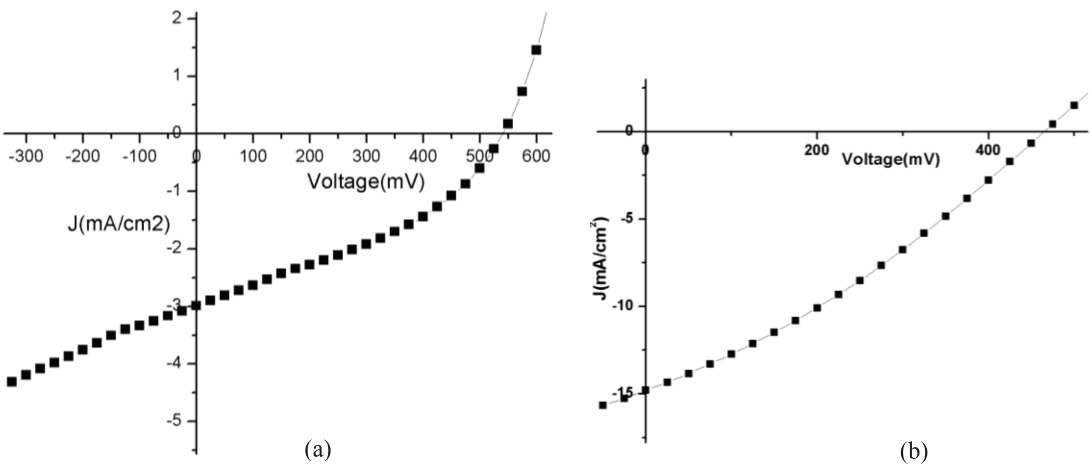


Fig. 2. I-V characteristics of the cells prepared using (a) C1 and (b) C2 with I1 as the buffer layer

When indium concentration in the solution was increased for C2, low copper concentration can be maintained in the solution so that the copper diffusion in to the surface of the cell can be reduced. Thus a layer of In_2S_3 [free of Cu] at the top could be ensured. Hence a higher short circuit current density was obtained for cell fabricated using C2.

From the XPS data of the cells prepared using C1 and C2 (Figs. 3 and 4), we can infer that a Cu-free In_2S_3 layer can be clearly observed on the surface of the cell (using C2) in which Cu/In = 1 for $CuInS_2$ layer (Fig. 4). For the cell prepared using C1, sulphide formation was less and so In_2S_3 layer formation on the surface was seemed to be only partial.

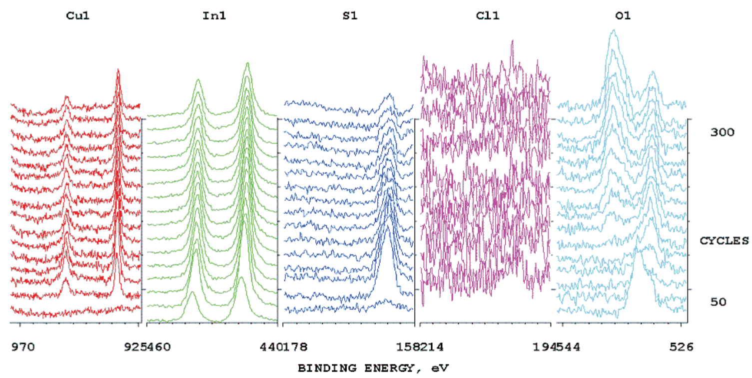


Fig.3. XPS depth profile of cell prepared using C1

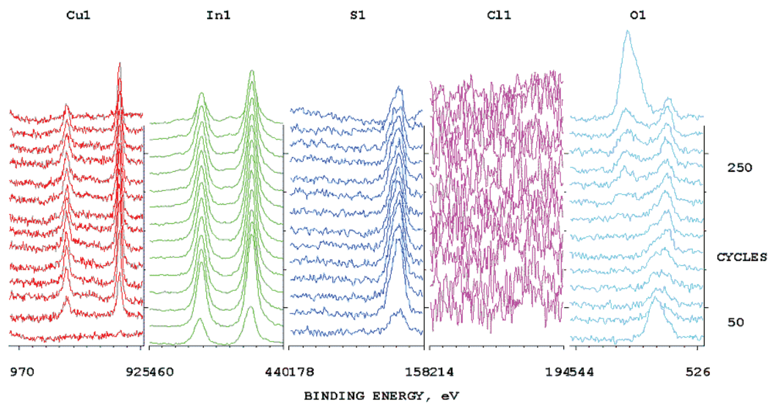


Fig.4. XPS depth profile of cell prepared using C2

3.2. Effect of variation in In/S ratio of the In_2S_3 layer

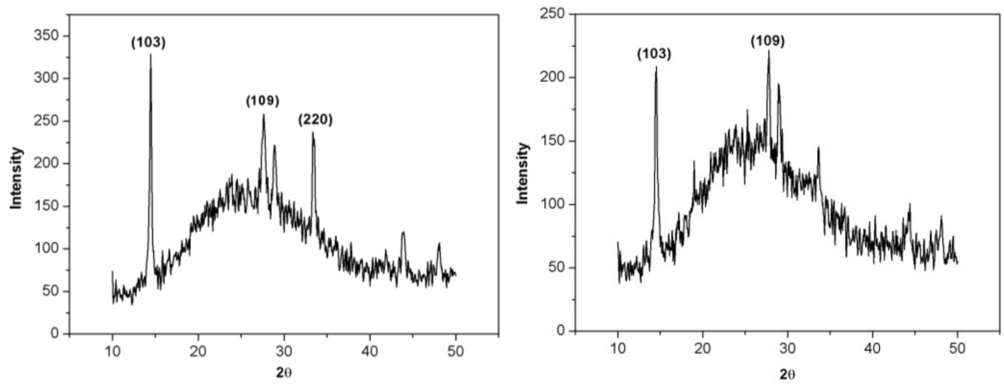
3.2.1. On the structural and compositional analysis of In_2S_3 thin films

The crystallinity of In_2S_3 films was analysed using X-ray diffraction. Figures 5(a) and 5(b) show the XRD patterns of In_2S_3 samples I1 and I2. The samples showed β-In_2S_3 phase with an orientation along the (103) plane at $2\theta = 14.3^o$ (JCPDS-25-390). The grain size was calculated using Debye-Scherrer formula. I1 has 30.9 nm grain size and I2 26.7 nm. Hence sample I1, prepared using In-rich solution, was slightly more crystalline than I2.

Composition of the films I1 and I2 can be compared by EDX analysis. Atomic concentrations of In, S and Cl of samples I1 and I2 are shown in Table 2. From EDX analysis also, In/S ratio in the film also was less for sample I2 compared to I1. Also a sulphur-rich atmosphere was being created in the sample I2.

Table 2. Atomic percentage of the elements in I1 and I2 from EDX measurements

	In	S	Cl	In/S
I1	29.49	61.84	8.67	0.48
I2	25.95	66.86	7.19	0.39



(a) (b)

Fig. 5. XRD patterns of (a) I1 and (b) I2

3.2.2. On the optical and electrical properties of In_2S_3 thin films

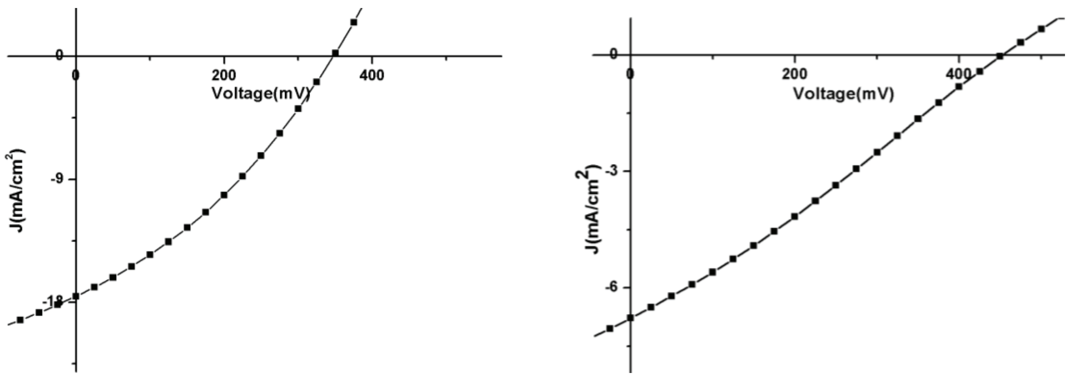
Optical absorption spectra of the samples were analysed and the band gaps of $CuInS_2$ thin films were determined from the plot of $(\alpha h\nu)^2$ vs hν. For the film having In/S ratio = 1.2/8, the band gap value was 2.85 and for the film having In/S ratio = 1.2/12, the band gap was 2.95. Both the In_2S_3 samples were n-type. Sample I2 was more conductive than I1, which was prepared using In-rich solution. The electrical resistivity of I1 was 4730 Ωcm and that of I2 was 268 Ωcm.

3.2.3. On the J-V characteristics of $CuInS_2/In_2S_3$ cell

When sample I2 was used as the buffer layer, the short-circuit current increased. In the cell prepared using C1 and I2, the cell parameters were V_{oc} = 461 mV, J_{sc} = 6.7 mA/cm^2, FF = 27.5%, η = 0.85%, see Table 3. In the cell prepared using C2 and I2, the parameters were V_{oc} = 347 mV, J_{sc} = 17.85 mA/cm^2, FF = 32%, η = 2%. In both cases the J_{sc} improved when the In/S ratio in In_2S_3 layer was 1.2/12 and a 2% efficiency was achieved when Cu/In = 1 in $CuInS_2$ sample. The higher conductivity of I2 than I1 helped in better carrier collection in the cell and hence improved J_{sc} value. Figures 6(a) and 6(b) depict the cell characteristics of the cells prepared using C1 and C2 samples, when I2 is used as the buffer layer.

Table 3. Cell parameters of cells prepared using C1 and C2 & I1 and I2

Cells using	**V_{oc} (mV)**	**J_{sc} (mA/cm^2)**	**FF %**	**Eff %**	**R_s Ω**	**R_{sh} Ω**
		Cells	using	I1		
C1	539	3	37.6	0.6	57	278
C2	466	14.8	30	2.13	23	54
		Cells	using	I2		
C1	461	6.7	27.5	0.85	67.6	91.2
C2	347	17.85	32	2	11.4	39.1



(a) (b)

Fig. 6. I-V characteristics of the cells prepared using (a) C1 and (b) C2 with I2 as the buffer layer

4. Conclusions

Significant increase in short circuit current density has been achieved, when Cu/In ratio in the $CuInS_2$ film was reduced to1 and also when In/S ratio in the In_2S_3 layer was changed to 1.2/12. So to fabricate an efficient $CuInS_2/In_2S_3$ cell, less Cu/In ratio helps to prevent the diffusion of Cu towards the In_2S_3 layer, thereby providing a Cu free active buffer layer. Also the In_2S_3 layer with In/S ratio 1.2/12, having more conductivity with higher band gap acts as an efficient buffer and window layer in the $CInS_2/In_2S_3$ cell. Hence Cu/In ratio and In/S ratio plays a momentous role in determining the IV parameters of the cell.

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