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Solar Energy a green solution: Cu₂ZnSnS₄ Thin Film Solar Cells Using Non-Vacuum Method

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Abstract - A suitable solution based approach is used to fabricate a thin film hetero junction solar cell with spray deposited Cu₂ZnSnS₄ (CZTS) as absorber layer and chemical bath deposited CdS as window layer. The cell exhibited as open circuit voltage of 150 mV and short circuit current density of 1.0 mA /cm² with a conversion efficiency of 0.2 % in this maiden effort. The reason for the observed low performance is explained and the steps needed to improve the efficiency are mentioned.

Key words- Solar cell, Thin film, CZTS, Spray.

I. INTRODUCTION

Cu₂ZnSnS₄ (CZTS), is emerging as an alternative solar cell absorber layer to CuInGaSe₂, which exhibited a record efficiency of 20.1%. This is mainly due to relative abundance of Zn and Sn relative to In and Ga as well as less toxic nature of sulphur compared to selenium. CZTS films exhibit direct band gap of 1.5 eV and having high optical absorption coefficient $(> 10^4 \text{ cm}^{-1})$. The films exhibit p-type electrical conductivity. Ito and Nakazawa first time fabricated CZTS thin film cell and they achieved 165 mV [1]. Past five years, many groups were working on this material by various techniques. Katagiri et al. reported CZTS based thin film solar cell

with an efficiency 6.7% using co-sputtered CZTS absorber layer [2]. Recently Shin et al. fabricated CZTS thin film solar cells with an efficiency of 8.4% by thermal evaporation method [3]. In view of its potential as solar cell absorber layer, an attempt is made in the present investigation by to fabricate a typical CZTS thin film hetero junction solar cell using a totally solution based approach. This paper reports the details of preparation of CZTS films for the fabrication of device.

II. EXPERIMENTAL

CZTS thin films were deposited by spray pyrolysis technique with aqueous solution containing cupric chloride (0.009 M), zinc acetate (0.0045 M), stannic chloride (0.005 M) and thiourea (0.05 M). The solution was sprayed onto glass substrates held at substrate temperature (T_s) of 643 K, experimental details have been described in our previous paper [4]. The thickness of the film was around 2.0 µm.

The CZTS based thin film solar cell fabricated in substrate configuration, a CZTS/CdS/Al structures were fabricated on Mo-coated glass substrates. CdS film chosen as the buffer layer and these films were deposited by chemical bath deposition (CBD). An aqueous solution containing CdCl₂ (0.1 M), thiourea (0.1 M) was used in the bath and deposition was carried out at 333 K. CZTS films coated



on Mo-coated glass substrates was dipper in this bath and deposited was carried out for 20 min. Finally, a metal (Al) grid was deposited onto CdS layer to form the top contact. Individual cells of about 0.1 cm² were made by mechanical scribing.

III. RESULTS AND DISCUSSION *A. Structure analysis*

Figure 1 shows the XRD pattern of as deposited CZTS films. XRD studies revels that the films are likely to be single phase, polycrystalline nature with kesterite structure. The lattice parameter were found to be a = 0.543 nm and c = 1.085 nm [5]. The average crystallite size determined using Scherrer's formula was 25 nm.

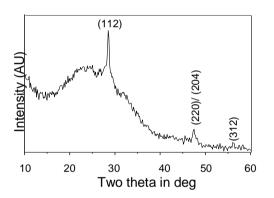


Fig. 1 XRD pattern of as deposited CZTS film.

Figure 2 shows the SEM images of CZTS films. From the image it is clear that film consists of well defined grains, size of the grains was about 2.5µm. The elemental composition of CZTS films determined using energy dispersive spectrometer and was found to be 24.0, 14.2, 15.6 and 46.2 atomic percentages respectively. The composition data revels that films were near-stoichiometric without any sulphurization, but annealing studies improves the quality of crystal.

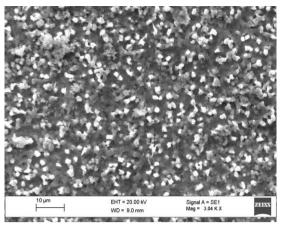


Fig. 2 SEM image of CZTS film

B. Optical analysis

Figure 3 shows the spectral transmittance of CZTS films. The direct optical band gap of the film determined by extrapolating the linear region of the plot $(\alpha hv)^2$ versus hv and taking the intercept on hv-axis. The band gap of the CZTS films was found to be 1.43 eV [1] and the optical absorption coefficient was found to be >10⁴ cm⁻¹.

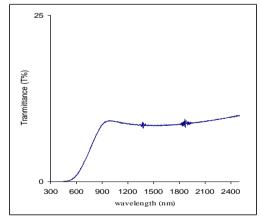


Fig. 3 Spectral transmittance of CZTS films

C. Electrical properties

The room temperature electrical resistivity of CZTS films was determined using van der Pauw technique and it is found to be 2.5 Ω -cm. The films were found to be p-type nature by hot probe method. The CdS films were found to be

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n-type conducting and resistivity found to be $10^4 \Omega$ -cm.

D. Device properties

Figure 4 shows the CZTS thin film solar cell. The cell was characterized with illumination from a tungsten halogen lamp and adjusted with 100 mW/cm² intensity. The current was measured by measuring the voltage drop across a standard resistance of 0.1 Ω . The CZTS cell showed the open circuit voltage of 150 mV and the short circuit current density of 1.0 mA $/cm^2$. The conversion efficiency was found to be 0.2 %, however efficiency was very low. The fill- factor was found to be 0.33 and much depends on a series resistance of a solar cell. The poor device performance might be due to compositional deviations, poor crystallinity and low mobility of absorber layer. In addition to this, the resistivity of CdS layer is too high, it reduces the series resistance of the solar cell. Hence interface recombination losses and collection losses takes place in the device. But these results are in no way comparable to the device parameters reported data.

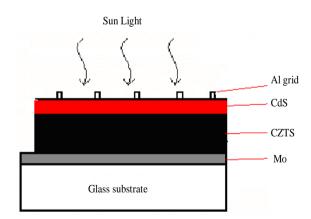


Fig 4. CZTS thin film solar cell

IV. CONCLUSION

The near-stoichiometric **CZTS** films could be prepared successfully by spray pyrolysis technique. The films exhibit kesterite structure with lattice parameters a = 0.543 nm and c = 1.085nm. The direct optical band gap of CZTS films is found to be 1.43 eV. The films are found to be p-type. The fabricated CZTS solar cell exhibits very low photovoltage and photocurrent. In order to obtain reasonable conversion efficiency and fill factor, optimization of thickness and properties of the individual layers is very much essential. In this study we showed the possibility of CZTS cell with non vacuum technique.

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