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FABRICATION AND CHARACTERIZATION OF SLG/Mo/CZTS/CdS/i-ZnO/Al:ZnO/Al THIN FILM SOLAR CELL DEVICE

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A cost effective p-type Copper zinc tin selenide $Cu_2ZnSnSe_4$ (CZTSe) thin film was fabricated on molybdenum (Mo) coated soda lime glass substrate by sputtering method followed by rapid thermal processed (RTP) selenization. The n-type CdS layer with 50 nm were fabricated by chemical bath deposition, a resistive zinc oxide (i-ZnO) and a conducting transparent Al doped ZnO (Al:ZnO) were fabricated by sputtering consecutively. The structural, surface morphology and optical properties were investigated by X-ray diffraction, scanning electron microscopy (SEM),and Raman spectroscopy. The preliminary solar cell device of SLG/Mo/CZTS/CdS/i-ZnO/Al:ZnO/Al structure were precisely fabricated and the obtained results were presented.

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1. Introduction

CZTS is a compound semiconductor of $(I)_2(II)(IV)(VI)_4$ with a high absorption coefficient (greater than 104 cm^{-1}) and Wadia et al. calculated the minimum cost of raw materials for the existing PV technologies and the emerging PV technologies [1-2]. Theoretical calculations have shown that photo-conversion efficiency as high as 32% was possible for CZTS TFSCs with a CZTS layer of several micrometers.

CZTS is one of the important low cost and earth abundant solar cell absorber material and many research groups involved to increase the real time photo-conversion efficiency. Band gap of the CZTS thin film can modified from 0.94 to 1.6 eV by changing the zinc and tin composition and replacing the selenium (Se) by sulfur (S).CZTS belongs to the Kesterites structure and composed of Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe) and CZTSSe are the competitors to the CIGS and CdTe based thin film solar cells. Also the Cost effective manufacturing needs the earth abundant and also non-toxic materials such as zinc, copper, tin, selenium and sulfur. The suitable opto-electronic characteristics of kesteritebased CZTS solar cells and its fine tuningwas widely reported and the further improvement also ongoing. The recent recorded efficiency of 11.1%, 9.15% and 9.3% were reported from $Cu_2ZnSn(S,Se)_4$ (CZTSSe) absorber fabricated by chemical as well as physical routes [3-7].More recently the solution based CZTS fabrication process also becoming superior [8-10]. In case of solution based process only the scale up and uniformity is a notable huddle.

Especially by the hybrid sputtering method Tanaka et al prepared CZTS thin films [11] in 2005. In that the hybrid sputtering system consists of the fabrication chamber with two effusion cells for zinc and sulfur and two separate sputtering source targets for Cu and Sn. Further the

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CZTS thin films were fabricatedby sequential deposition of Sn, Zn, and Cu followed by rapid thermal annealing in well controlled S vapor atmosphere and the substrate temperature was tuned between 300-500 °C.

Recently Hironori Katagiri et alfabricated the CZTS-based thin film solar cell with 5.74% in conversion efficiency using an inlinetypevacuum based process.Usually in the commercial process, the CZTS absorber layer wasformed on the Mo coated soda-lime glass (SLG) substrate.Then an-type CdS buffer layer was deposited by a well established chemicalbath deposition (CBD) method. For the successful carrier transport, the Al-doped ZnO(ZnO:Al) transparent conducting window layer was formed on top of the n-type CdS buffer layerby sputter-deposition of deposition at high vacuum condition. However, η = 5.74% is still lowcompared to conversion efficiencies exceeding over 18% of CIGS based solar cells in spite of the moresuitable optical properties of CZTS [12-15] thin film absorber layer. The further improvement on the CZTS fabrication process and ultra fine tuning of the optical band gap, composition, grain boundary and surface quality controlling are needed to exceed the CIGS solar cell efficiency.

2. Experimental

Soda lime glass (SLG) substrate of 2 mm was purchased and utilized for the fabrication of Mo back metal contact. The Mo metal layer of 1.2 µm was deposited by a pre optimized load lock sputtering condition and the fabricated Mo showed a good electrical conductivity and continuity throughout the large area of 5 cm^2.The suitable small area was cleave out and utilized for the CZTS thin film absorber layer fabrication.

CZTS fabrication process:

[1] Zn + Sn deposition,[2] Cu layer deposition, [3] Selenization done in the selenium atmosphere, [4] Substrate temperature of 500 °C was kept throughout the selenization process, [5] Finally cooled down to room temperature and kept in vacuum, [6] 3 min soaked in DI water to prevent the device pin hole.

n-type CdS layer was fabricated on well grown CZTS layer by using chemical bath deposition method and then the sample dried in air atmosphere using hot plate at 100-120 °C. A thick resistive zinc oxide layer of 100 nm was fabricated on top of the n-type CdS layer and an Al doped zinc oxide of thickness 500 nm TCO layer also fabricated to cover the final device. Al metal grid of 1 µm thick layer was evaporated by electron beam evaporation under low Al growth rate. Finally the device were isolated with the each small device are of 0.45 cm^2 from the large area device.

3. Results and discussion

3.1 Structural analysis

The X-ray diffraction analysis of the fabricated CZTSe thin film absorber layer were investigated to find the possible structural disorders and residual peak related to the impurity incorporation during the RTP selenization without any carrier gas.

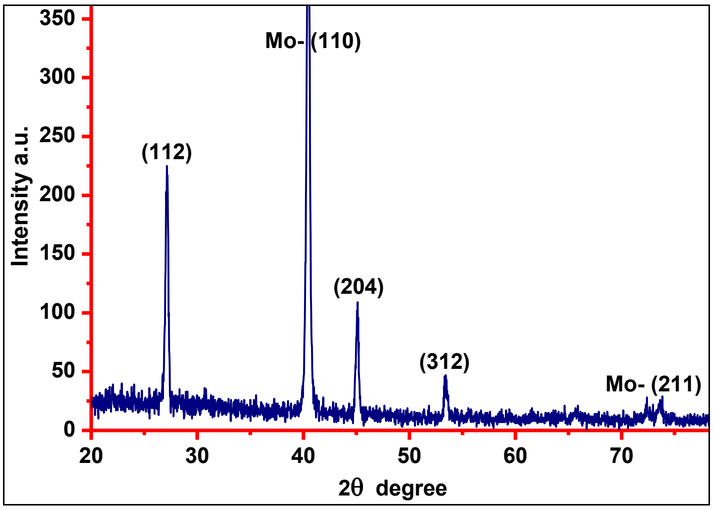

Fig. 1 X-ray diffraction of CZTS/Mo/SLG thin film layers

Figure 1 shows the XRD pattern of the fabricated CZTSe thin film absorber at the scan rate of 0.02 ° per min measured at room temperature. The obtained XRD pattern of the fabricated CZTSe layer showed a dominant growth direction of (112) plane at the 2θ value of 27.12 ° and other two minor diffraction peaks at 2θ value of 45.13 ° and 53.4 ° which originate from the growth direction of (204) and (312) planes. The Mo back metal substrate major and minor diffraction peak position at 2θ values of (110) and (211) plane respectively. The observed CZTSe major and minor growth direction was in good agreement with the previously reported literatures [16-19].

3.2 Surface morphology

Surface micro morphology of the fabricated CZTSe absorber (Figure 2) showed a porous morphology with many pinholes and the SEM cross-section of the fabricated CZTSe absorber showed the total thickness of around 1.5 to 1.8 μm and the cross-view SEM of the total CZTSe device (Al:ZnO/i-ZnO/CdS/CZTSe/Mo/SLG) displayed in the Figure 3.

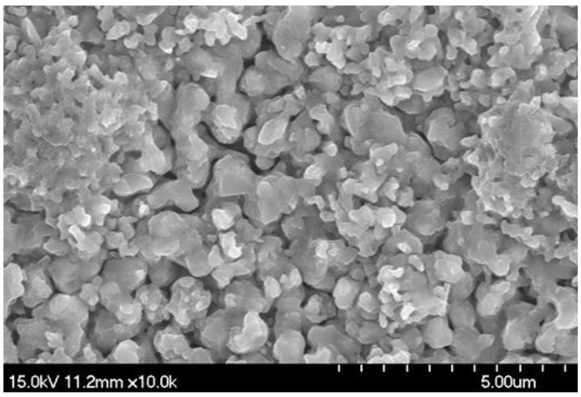

Fig.2 SEM top surface morphology of the fabricated CZTSe thin film absorber layer

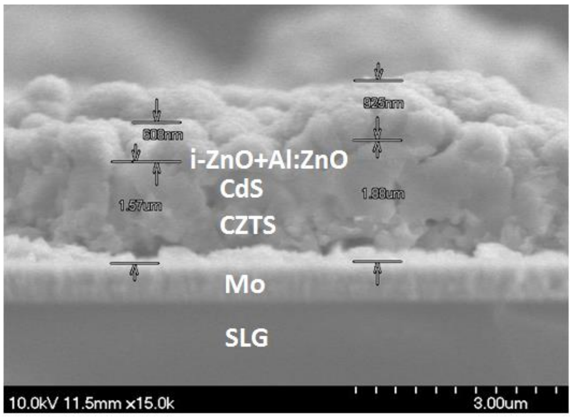

Fig. 3 SEM cross section of ourAl:ZnO/i-ZnO/ZnCdS/CZTSe/Mo/SLG device structure

3.3 Raman spectroscopy

A Raman spectrum was recorded at the wave number from 100 to 500 cm^{-1} at ambient temperature(Figure 4).

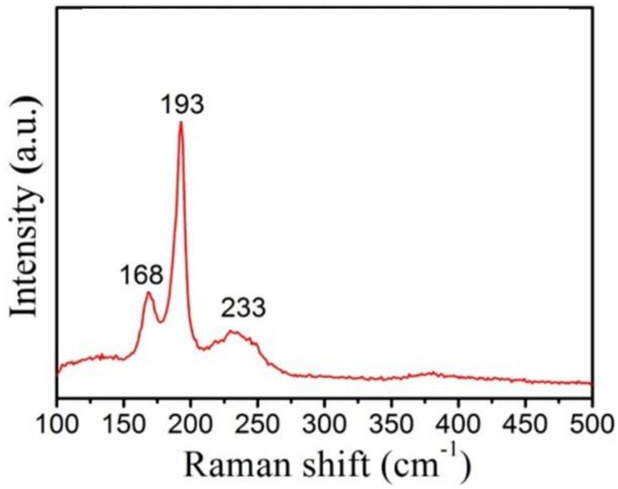

Fig. 4 Raman spectrum of the fabricated CZTS absorber layer

The observed Raman spectra showed a major shift peak positioned at 193 cm^{-1} and two residual shift peaks existence at the Raman shift of 168 and 233 cm^{-1} also originated from the other phases of CZTS. So the fabricated CZTS thin film absorber layer showed less defects which is more important to develop the active solar cell devices.

3.4 CZTS solar cell performance

The complete SLG/Mo/CZTS/CdS/i-ZnO/Al:ZnO/Al solar cell structure was fabricated and the photo conversion efficiency was recorded at one Sun radiation condition at room temperature. The fabricated solar cell showed an efficiency of 1.2% (Figure 4) and there is no anti reflection coating was employed in the present device fabrication process.

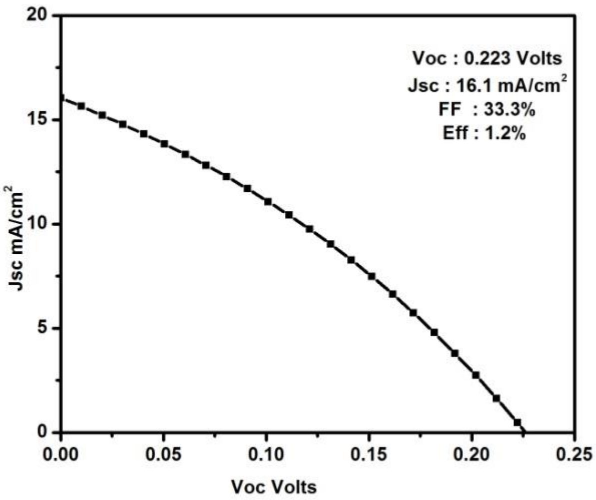

Fig. 5 Solar cell photo conversion efficiency

The obtained solar cell device performance such as open circuit voltage (Voc): 0.223 V, current density (Jsc): 16.1 mA/cm^2, fill factor (FF): 33.3% and the final obtained photo conversion efficiency is 1.2% and further improvement is also ongoing to increase the efficiency of the CZTS solar cell.

4. Conclusion

The X-ray diffraction analysis showed the fabricated CZTS thin film having good crystalline quality. SEM analysis on the top surface of CZTS absorber layer showed less pin holes and having smooth surface morphology. The SEM cross-section view of CZTS solar cell device showed a well defined boundary between each layer and well matched each other. The photo-conversion efficiency of the present fabricated cost effective CZTS solar cell showed an efficiency of 1.2%. This positive efficiency result motivated us for further research and development based on the CZTS based solar cells.

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