# Fabrication of Cu<sub>2</sub>ZnSnSe<sub>4</sub> film solar cell by sputtering-selenization

Shou-Yi Kuo<sup>1</sup>, Jui-Fu Yang<sup>1,2</sup>, Fang-I Lai<sup>2</sup>, Chun-Jung Lin<sup>3</sup>

<sup>1</sup> Department of Electronic Engineering, Chang Gung University, 259 Wen-Hwa 1st Road, Kwei-Shan Tao-Yuan, Taiwan, 333,

R.O.C

Phone: +886-3-211-8800#3351 E-mail: sykuo@mail.cgu.edu.tw

<sup>2</sup> Department of Photonics Engineering, Yuan-Ze University, Chung-Li, 32003, Taiwan

<sup>3</sup> Solar Applied Materials Technology Corp., Tainan, 30347, Taiwan

## 1. Introduction

The high efficiency of  $CuIn_{1-x}Ga_xSe_2$  (CIGS) solar cell has been performed a world-record efficiency cell of 20.3% However, the cost of indium and gallium is [1]. high-priced in mass production for terrestrial solar cells. Thus, alternative materials based on Cu-II-IV-VI<sub>4</sub> solar absorbers have been developed, for example, copper-zinc-tin-selenum (CZTSe). This paper is accented CZTSe absorption layer composed of materials. The CZTSe is considered as a promising material or a leading candidate for an absorber of thin film solar cells, due to its suitable electro-optical properties, cheap, abundant and nontoxic materials, such as Zn and Sn are more abundant and less expensive than In and Ga. CZTSe has a high absorption coefficient  $(>10^4 \text{ cm}^{-1})$  [2] and the band gap is around 1.0 eV that matches the preferred range of solar irradiation. In this work, the precursors were deposition at substrate temperature at room temperature. Typically, the metallic precursors are deposited by sputtering, electron beam, or electro plating methods with various combinations such as stacked or co-sputtered Cu/Zn/Sn layers. However, the efficiency of CZTSe thin-films fabricated by a vacuum process is 3.2% [3]. In this paper, we study the optical properties and structure of Cu<sub>2</sub>ZnSnSe<sub>4</sub> using photoluminescence spectroscopy (PL), Raman spectroscopy, and X-ray diffraction (XRD) in order to increase the efficiency of the CZTSe solar film. The efficiency of CZTSe thin-films fabricated by a vacuum process selenization is 4.4 %.

# 2. Experimental

CZTSe precursors were deposition by radio-frequency (RF) magnetron sputtering at room temperature on Mo. The total thickness of the precursor was 750 nm. Precursors were converted into the CZTSe film by annealing in Se vapor. The selenization procedure was carried out in a vapor of elemental selenium in a vacuum chamber. The highest selenization temperature is approximately 550°C. After KCN etching for 30 minutes, buffer layer CdS was deposited onto a CZTSe absorber layer by CBD. The phases, structures and compositions of the CZTSe film were identified by PL, Raman spectroscopy, EDS, FESEM, and XRD. The composition of the films was determined using EDS. According to the EDS results, the ratios of Cu/ (Zn+Sn), Zn/Sn, and Se/metal are 0.9, 1.27, and 0.9,

respectively, in the CZTSe absorber layer.

#### 3. Results and discussion

In Fig.1, it is presented the XRD pattern of the CZTSe absorber layer. According to the JCPDS database, there are several distinct CZTSe peaks, a Mo peak, and two low intensity MoSe<sub>2</sub> peaks from the XRD measurement. No second phases, such as SnSe, ZnSe, and Cu<sub>2</sub>SnSe<sub>3</sub>, assessed by XRD. In which the full width at half maximum (FWHM) was 900 arcsec. The MoSe<sub>2</sub> imply that the selenisation reaction has continued through the precursor layer reaching the molybdenum substrate [4]. However, the Cu<sub>2</sub>Se, ZnSe, and Cu<sub>2</sub>SnSe<sub>3</sub> are close to the same as CZTSe (the peaks of 27.13°,45.06°, and 53.40° are (112), (204), and (312), respectively from JCPDS 52-0868). In our CZTSe thin film is not the same (the peaks of  $27.22^{\circ}$ ,  $45.2^{\circ}$ , and 53.4°), maybe the strain, and the ratios is not idea to effect the XRD data. It is arduous to identify the existence of single crystal CZTSe by the XRD pattern. Illustration is shown the thickness of CZTSe is 1.3 um.



Figure 1 XRD pattern was deposited on Mo.

In order to support the XRD result, We measured the Raman spectrum on the above sample. Raman modes of CZTSe were obtained using "A1" mode at room temperature. In Fig. 2, Raman spectrum of the CZTSe absorber was show existence during the room temperature. It measure of this film confirmed the XRD results by showing the no any presence of binary compounds, i.e., SnSe (132 cm<sup>-1</sup>, 151 cm<sup>-1</sup>) [5], ZnSe (250 cm<sup>-1</sup>), Cu<sub>x</sub>Se<sub>y</sub> (261 cm<sup>-1</sup>), and Cu<sub>2</sub>SnSe<sub>3</sub> (180 cm<sup>-1</sup>) [6], besides the main peaks of CZTSe [7]. There are two peaks that could be attributed to MoSe<sub>2</sub> – at 239 cm<sup>-1</sup> and glass at 125 cm<sup>-1</sup>.



Figure 2 Raman spectrum of CZTSe thin film deposited on Mo.

Fig. 3 shows the photoluminescence spectrum measured at 300 K by using 635nm laser diode. The peak of 0.93 eV that the majority corroborates by several authors is CZTSe [8,9]. The CZTSe structure/phase can be confirmed to form in the absorber layer is based on the results of XRD, Raman, and PL measured.



Figure 3 PL spectrum of CZTSe thin film deposited on Mo

From the dark- and light- current-voltage (I-V) curves, showed in Fig. 4, the electrical characteristics of the CZTSe solar cell were determined. The dark and light I-V curves for a representative cell with area of 0.33 cm<sup>2</sup>. The cell achieved without any anti-reflecting coating. The maximum power ( $P_{max}$ ), maximum current density at  $P_{max}$ , and maximum voltage at  $P_{max}$  of the CZTSe solar cell are 4.4 mW, 20.79 mA/cm<sup>2</sup>, and 0.21V, respectively.



Figure 4 Dark and light I–V curves of CZTSe cell measured at room temperature.

# 4. Conclusion

In this study, the formation of CZTSe structure was determined by Raman spectroscopy, XRD, and PL measurement. The CZTSe absorber has an optical band gap value of 0.93 eV at room temperature, and the thickness is almost 1.3 um. In Raman spectroscopy, the CZTSe thin films don't have any other phases. It has been shown that good quality CZTSe with the published data from others [8]. The CZTSe solar cell showed conversion efficiency of 4.4 % for 0.33 cm<sup>2</sup> under standard AM1.5 conditions. It shows the good quality CZTSe material in our sputtering and selenisation process. The CZTSe material can be produced for solar cell. In further work, we will increase the V<sub>oc</sub>, and get high efficiency CZTSe thin film solar cells.

## Acknowledgements

This work was supported by the Green Technology Research Center of Chang Gung University and the National Science Council (NSC) of Taiwan under contract nos. NSC97-2112-M-182-004-MY3 and NSC-100-2112-M-182 -004.

## References

- [1] Adrian Chiril<sup>\*</sup>a et al., NATURE MATERIALS. 10, 2011, 857.
- [2] Liang Shi, Congjian Pei, Yeming Xu, and Quan Li, Journal of the American Chemical Society. 133, 2011, 10328.
- [3] G. Zoppi, I. Forbes, R. W. Miles, P. J. Dale, J. J. Scragg and L. M. Peter, Prog. Photovolt: Res. Appl. 17, 2009, 315
- [4] F. Luckert et al., APPLIED PHYSICS LETTERS. 99, 2011, 062104.
- [5] H. R. Chandrasekhar, R. G. Humphreys, U. Zwick, and M. Cardona, Phys. Rev. B. 15, 1973, 2177.
- [6] M. Altosaar et al., Physica Status Solidi A, 205, 2008, 167.
- [7] Kyoo-Ho Kim and Ikhlasul Amal, Electronic Materials Letters. 7, No. 3, 2011, 225.
- [8] M. Grossberg, J. Krustok, J. Raudoja, K. Timmo, M. Altosaar, T. Raadik., Thin Solid Films ,519, 2011, 7403.