

Investigation of of Selenization Temperature on High Efficient CZTSe-Based Solar Cells by Sputter Technique

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Abstract

We report the electrical and optical properties of a series of sputtered-Cu₂ZnSnSe₄ (CZTSe) solar cells with different first-step selenization temperature, which was varied from 100 to 300 °C and second-step temperature of 480 °C. The highest power conversion efficiency had exceeded 6 % with short circuit current density of 32.3 mA/cm², the open voltage of 0.365 V and a fill factor of 51.3 %.

1. Introduction

Cu₂ZnSnSe₄ (CZTSe), as being a promising material to replace Cu(In,Ga)Se₂, has many superior properties for photovoltaic devices such as suitable bandgap (~ 1 eV), ability in cost down fabrication and high absorption coefficient over the whole solar spectrum [1]. However, as the best of we know, the highest efficiency for this kind of solar cells have only 8.9 % [2], which is far below the highest efficiency of CIGS solar cell (~ 20.3 %) [3]. Such barrier between the two kinds of material can be mainly attributed to the obstacle of phase controlling during deposition.

In this article, a series of CZTSe absorbers were fabricated by sputtering of Cu, Zn and Sn on Mo-coated soda lime glass and then selenized in different first-step temperature (100~300 °C), and in the same second-step temperature (480 °C), follow by the cell fabrication using standard structure of CZTSe/CdS/ZnO/AZO and metal finger as contact. After the absorber deposition, the cross-sectional morphology, elemental ratio and crystal structure were investigated by transmittance electron microscope (TEM), energy dispersive X-ray spectroscopy (EDS) and the X-ray diffraction (XRD). The electrical properties were examined by current density-voltage (J-V) measurement under standard AM1.5G illumination and external quantum efficiency (EQE) as a function of incident wavelength from 300 to 1400 nm.

2. Result and Discussion

Table 1 shows the detail growth parameters and elemental ratio extracted from EDS measurement, as the first-step selenization temperature ($T_{s1st.}$) increased, the samples change from overly Cu-poor and Zn-rich to slight-

ly Cu-poor and Zn-rich. On the other word, as $T_{s1st.}$ increased, the CZTSe absorber performs a more stoichiometry condition. According to the previous research [4], CZTSe-based solar cells usually have the better performance under the condition of $Cu/(Zn+Sn) \sim 0.9$ and $Zn/Sn \sim 1.3$. The variation of elemental ratio can be explained as that: when sample was selenized, the copper, zinc and tin first reacted with selenium to form Cu₂Se, ZnSe and SnSe₂ at $T_{s1st.}$ and then and then formed the CZTSe at $T_{s2nd.}$. However, SnSe₂ has a rather large vapor pressure [5], hence the $Cu/(Zn+Sn)$ increased with $T_{s1st.}$ due to the evaporation of SnSe₂. On the other hand, the increasing of $T_{s1st.}$ result in the decreasing of Zn/Sn and increasing of Se/metals, which were due to the starting of evaporation of zinc at higher $T_{s1st.}$ and the increasing of selenium incorporation into the precursor films, respectively.

Table 1 detail growth parameters and the elemental ratio of absorbers, $T_{s1st.}$ is the first-step substrate temperature during selenization and $T_{s2nd.}$ stands for the second-step temperature.

Sample	$T_{s1st.}$ (°C)	$T_{s2nd.}$ (°C)	$Cu/(Zn+Sn)$	Zn/Sn	Se/metals
A	100	480	0.71	1.8	1.67
B	200	480	0.91	1.63	1.93
C	300	480	0.97	1.32	1.93

Figure 1 reveals the XRD result, all samples contain CZTSe phase. However, significant secondary and ternary phases signal show up in sample B and C, which was assigned to SnSe₂, SnSe and ZnSe in sample B, and SnSe, Cu₂SnSe₃ in sample C. Such result was due to that, at the lowest $T_{s1st.}$, most elements didn't receive enough energy to form secondary and ternary compounds but diffuse isotropically. As $T_{s1st.}$ was high enough (eg. Sample B), the SnSe₂ was formed, and part of it start to decompose into SnSe and pure selenium [5], hence these two phases both can be observed in sample B. furthermore, ZnSe secondary phase was also appeared in sample B due to zinc also acquired enough energy to form ZnSe with selenium, which was a common secondary phase in CZTSe. For sample C, SnSe₂ secondary phase had totally decomposed into SnSe. Except for the SnSe, a Cu₂SnSe₃ ternary phase appeared,

which can be attributed to the over evaporation of zinc. Figure 2 (a)-(c) shows the cross-sectional TEM image, there were two significant differences between samples: 1) the grain size decreased as $T_{s1st.}$ increased, 2) the area of air voids between CZTSe and Mo-coated SLG substrate increased with $T_{s1st.}$. Such result might be due to that, as the $T_{s1st.}$ increasing, the amount of secondary and ternary phases increased. Hence, even the selenization temperature was raised from $T_{s1st.}$ to $T_{s2nd.}$ still cannot totally transform the non-CZTSe compound into pure CZTSe phase. On the other hand, due to the temperature raising rate was fixed for all samples, the different thermal expansion coefficient between CZTSe and Mo-coated substrate could cause a more serious influence with higher $T_{s1st.}$, hence lead to a crack of films and large air void area.

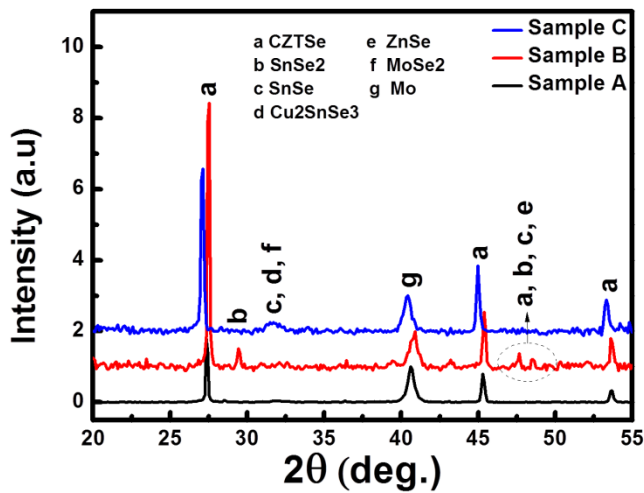


Figure 1 XRD θ - 2θ pattern of samples from 20 to 55 degree, the alphabets inside the figure represent different crystal structure.

After investigation of crystal structure and sample morphology, the as-grown films were fabricated into cells with 0.141 cm^2 active area, the cell structures use standard CdS/ZnO/AZO and metal grid. The J-V characteristic under standard AM 1.5 G illumination was shown in figure 2 (d), the detail cell parameter was listed in table 2. Sample A shows a conversion efficiency over 6 %. However, sample B exhibits a better performance in fill factor, series resistance and shunt resistance, the reason was still un-clear. The short circuit current density decreased linearly with increased $T_{s1st.}$, which was consistent with the change of area of air voids. The open voltage falls between $0.3 \sim 0.37 \text{ V}$, such value was far below the experiment band gap value of CZTSe ($\sim 1 \text{ eV}$), which indicates the strong influence of interface and bulk recombination.

Table 2 detail cell electrical properties

Sample	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	R_s (Ω -cm)	R_{sh} (Ω -cm)	η (%)
A	32.3	0.365	51.31	0.035	6.6	6.1
B	30.85	0.303	53.85	0.031	9.38	5.4
C	28.88	0.344	45.68	0.047	4.2	4.4

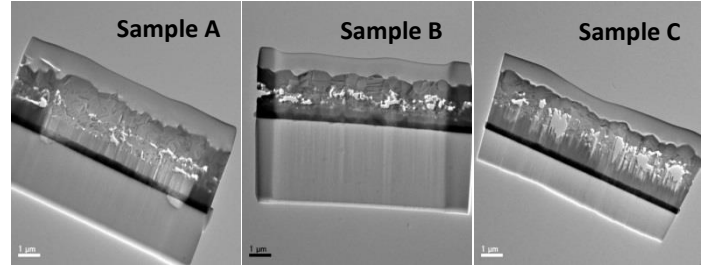


Figure 2 TEM cross-sectional images of (a) sample A, (b) sample B and (c) sample C.

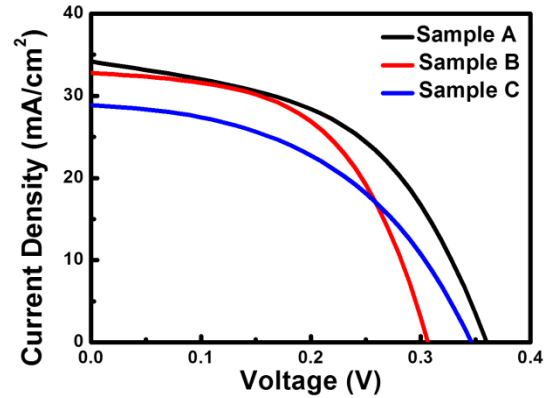


Figure 3 J-V property of three different samples, the electrical property was extracted under standard AM 1.5 G illumination.

3. Conclusions

In summary, we investigated the influence of two-step selenization process on electrical and optical properties of sputtered-CZTSe thin films. Our champion cell with $\text{Cu}/(\text{Zn}+\text{Sn}) \sim 0.71$ and $\text{Zn}/\text{Sn} \sim 1.8$ shows power conversion efficiency over 6 %, which was comparable with other high quality CZTSe-based solar cells. Although the other two cells show rather low power conversion efficiency, the elemental ratios were much closer to the ideal value. In order to further improve the cell performance, to optimize the temperature raising rate and precursors would be an important in the future.

Acknowledgements

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