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Preparing the high efficiency with non-vacuum and non-sulfurized CZTS (Cu_2ZnSnS_4) Solar Cell by improved annealing method

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Abstract

The CZTS solar cell was deposited the SnS, CuS, ZnS multi-layer films by a chemical bath stack deposition method and subjected to an improved annealing method with an optimum annealing temperature 500 degrees. The chemical device deposited the CZTS solar cell by part of the bottom side device's parameters with the record efficiencies 1.58%. Finally, the record efficiency for the CZTS solar achieves 1.58% in part of the bottom CZTS Cell device's Cu/(Zn+Sn):(Zn+Sn) ratio of 0.8: 1.15.

1. Introduction

In recent years, CZTS or CZTSSe films had developed by vacuum and non-vacuum methods such as sputtering[1], thermal co-evaporation[2], a chemical bath deposition (CBD) [3], photochemical deposition, the sol-gel method and electroplating [4].

In this study, we proposed that a method without sulfurization treatment and non-toxic process fabricate the low-cost CZTS solar cell.

2. Experimental

Initially, a CZTS absorber layer was deposited onto Mo-coated soda-lime glass (SLG) substrates (area: 6.25 cm^2) using a 3-steps of non-vacuum chemical bath deposition. Figure 1 is to show the experimental facilities.

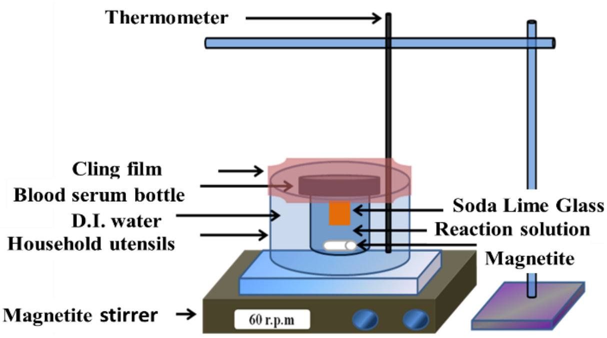

Fig. 1. The schematic diagrams of the chemical bath deposition.

The film of material was grown by chemical bath deposition method, and then the sample was purged by a nitrogen gun and was dried by hot plate a temperature of 120℃. Finally, the sample was baked at a temperature of 200 ° C to remove the moisture of the chemical bath deposition's film surface.

However, in the CZTS absorption layer annealing experimental step, we proposed two methods to improve this annealing experiment, First is to change the annealing method, which is to reduce the loss of elements by using the method of stacking and covering the test piece, as shown in Figure. 2; The second is used different annealing temperatures to make the structure between the contact of elements better. It will be desirable to adjust the part of the CZTS absorption layer to the optimum ratio be controlled.

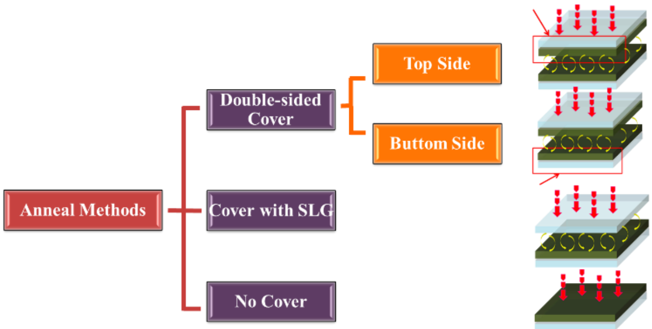

Fig. 2 Schematic diagram of annealing improvement method

The CZTS is a quaternary compound semiconductor. Therefore, Its elements composition ratio has a certain proportion. According to the ratio of chemical bonds, the ratio of Cu: Zn: Sn: S of each element should be closed to 2: 1: 1: 4.

In addition, the Cu:Zn:Sn:S ratio should be close to 2:1:1:4, also refer to Hiroki Sugimoto, Noriyuki Sakai and Homare Hiroi et al. in May 2012 on the CZTS block for Cu / (The ratio of Zn+Sn) to Zn/Sn is analyzed and reported in detail, and the CZTS patent is applied for in the "CZTS Thin Film Solar Cell and Manufacturing Method Thereof" at the

European Patent Office and the US Patent and Trademark Office until 2014. It was officially released in April, and the patent text mentioned that the ratio of Cu/(Zn+Sn) to Zn/Sn should be between 0.78 and 0.9 and between 1.18 and 1.32, respectively. The conversion efficiency produced by a region is higher [5].

3. Results and discussions

In this study, the first method was used to explore different annealing methods. As shown in the EDS element analysis in Table I, the element coverage of the uncovered test piece (No Cover) compared with the other elements of Sn is compared with other elements. In terms of methods, our improvement method is obviously effective.

Table I EDS analysis of annealing in different stacking methods

Element	Ideal At.(%)	Top	Bottom	Cover	No Cover
Cu	25.00	29.17	22.69	23.00	37.88
Zn	12.50	13.42	15.08	13.83	39.51
Sn	12.50	12.09	13.13	12.92	5.71
S	50.00	45.32	49.10	50.24	39.90

The ratio of Cu/(Zn+Sn) to Zn/Sn ratio between the European Patent Office and the US Patent and Trademark Office in Cu/(Zn+Sn) and Zn/Sn ratios, as shown in Table II, from the table Proportional analysis shows that the proportion of un-coated test pieces is extremely low compared to other meth-ods. In the improvement method, it can be known that the Buttom side test piece has a relatively high probability of achieving a high conversion efficiency of the CZTS solar cell.

Table II Cu/(Zn+Sn) and Zn/Sn ratios in different stacking methods

Ratio	Ideal Ratio	Top	Bottom	Cover	No Cover
Cu/(Zn+Sn)	0.8	1.14	0.8	0.86	1.67
Zn/Sn	1.2	1.11	1.15	1.78	2.96

After that, we compare the different annealing temperatures to EDS. It can be seen from Table III that the ratio of the ele-ments close to 480 °C and 500 °C is close to a reasonable value to obtain a higher efficiency, and the CZTS is also high. Under the temperature, it is not easy to produce a solar cell with high conversion efficiency.

Table III Cu/(Zn+Sn) and Zn/Sn ratios in different temperature

Ratio	Ideal Ratio	450 ℃	475 ℃	500 ℃	550 ℃	575 ℃	600 ℃
Cu/(Zn+Sn)	0.8	1.14	0.86	0.8	0.52	0.3	0.98
Zn/Sn	1.2	1.11	1.78	1.15	2.2	1.26	0.94

The part of the bottom side device's parameters with a single junction CZTS solar cell was under AM 1.5G are as follows: open circuit voltage of 0.22 V, short-circuit current of 17.72 mA/cm^2, fill factor of 40.89%, and a power conversion Efficiency of 1.58 %.

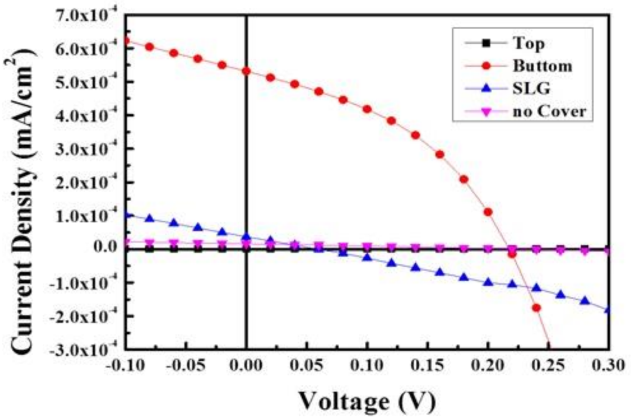

Fig. 3 The J-V characteristic of part of the bottom CZTS solar cell, showing efficiencies of 1.58%

4. Conclusion

The CZTS solar cell was deposited the SnS, CuS, ZnS multi-layer films by a chemical bath stack deposition method and subjected to an improved annealing method and a non-vulcanization heat treatment at an optimum annealing temperature of 500°C.

The chemical device deposited CZTS solar cell by part of the bottom side device's parameters with the record efficiencies 1.58%. This work demonstrates that a low cost, non-vacuum and non-sulfurized method using chemical bath deposition and annealing is a viable approach for the fabrication of CZTS solar cells.

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