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Band-gap-graded Cu₂ZnSn(S,Se)₄ drives high efficient solar cells

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 Table S1 Comparison of results from selected relevant publications about heterojunction annealing of CZTS

 solar cells. (Annealing containing CZTS/CdS layers is collectively referred to heterojunction annealing) N/A:

 not available.

Туре	Absorber materials	Temperatur e [°C]	Duratio n [min]	PCE _{ma} × [%]	Absolute improvement [%]	Diffused elements	Referenc e
High- temperatur	CZTSSe	300	1	12.7	~3	In ³⁺ , Cu ⁺ , Sn ⁴⁺ , and Se ²⁻	31
	CZTSSe	270	3	8.0	~3.6	Cu ⁺ and Zn ²⁺	32
	CZTS:Cd	300	8	12.6	5.9	Cu ⁺ , Zn ²⁺ , In ³⁺ , Sn ⁴⁺ and Cd ²⁺	33
e	CZTS	270	10	11.0	3.1	Cd ²⁺ , Zn ²⁺ and Na ⁺	34
	CZTS	300	15	7.9	~4	N/A	35
	CZTS	300	15	6.6	~5	Cu ⁺ , Zn ²⁺ and Cd ²⁺	36
	CZTSe:Ge	250	15	11.8	N/A	N/A	37
Low- temperatur e	CZTSe	200	35	8.3	~5	Cu ⁺ and Zn ²⁺	38



Fig. S1 (a,c) Top-view and (b,d) cross-sectional SEM images of the CZTS precursor film and selenized CZTSSe film, respectively.



Fig. S2 X-ray diffraction patterns of the CZTS precursor film and selenized CZTSSe film.



Fig. S3 Raman spectra of the CZTS precursor film and selenized CZTSSe film.



Fig. S4 The statistic photovoltaic performances (V_{OC} , J_{SC} , FF and PCE) of the devices prepared at different deposition temperatures.

The CZTSSe/CdS heterojunction region for sample RT and HT was subjected to FFT as shown in Fig. 2. For the convenience of calculation, we give the simulation results of the FFT in Fig. S5. Firstly, as shown in Fig. S5a, three feature points 1, 2 and 3 were taken to measure their crystallographic spacing of 2.9 Å, 0.18 Å and 0.18 Å respectively. Feature points 1 and 2 can correspond to the {200} and {312} crystal planes of PDF#52-0868. The theoretical angle is 72.5° and the measured angle is 72.2°, which satisfies the self-consistency condition within the error range. The structure can be identified as CZTSSE with tetragonal phase and the calculated crystal band axis is $[0^{23}]$. Similarly, all the calculated results are listed in Table S2. Notably, the three feature points in Fig. S5d were measured at the plane spacing of 0.19 Å, 0.19 Å, and 0.19 Å. The angle between the three crystallographic planes was 60°. Combined with the mapping results, it can be determined that this region corresponds to the cubic Cu₂S structure (PDF#12-0175), and the three feature points correspond to the {220} crystal plane family of this cubic structure.



Fig. S5 Simulation of the crystal plane after fast Fourier transform (FFT) of the CZTSSe/CdS interface. FFT of CZTSSe region(a) and CdS region(b) for device RT. FFT of CZTSSe:Cd region (c) and Cu₂S region(d) for device HT.

	1	2	3	Angle	PDF Card	Phase
Fig. S5a	2.9 Å/(200)	1.8 Å/(312)	1.8 Å/(312)	<1,2> 74.7°	#52-0868	Tetragonal-CZTSSe
Fig. S5b	2.9 Å/(200)	1.8 Å/(311)	1.8 Å/(311)	<1,2> 74.7°	#75-0581	Cubic-CdS
Fig. S5c	4.0 Å/(112)	2.0 Å/(116)	2.3 Å/(204)	<1,3> 89.8°	#52-0868	Tetragonal CZTSSe
Fig. S5d	1.9 Å/(220)	1.9 Å/(022)	1.9 Å(202)	<1,2> 60.0°	#12-0175	Cubic-Cu ₂ S

Table S2 Measured distance and angle of corresponding planes of Fig. S5 (a-d).



Fig. S6 High resolution XPS spectra of Cu 2p, Zn 2p, Sn 3d core level on surface of CZTSSe absorber of RT and HT samples in groups A, B and C.

The specific band gap of CZTSSe:Cd is calculated as follows:

According to the previously reported works, the band gaps of CCTS and CCTSe are 1.07 and 0.8 eV.^[1,2] In addition, the Se/(S+Se) ratio in this work is 0.92, which is similar with our previous report.^[3] Furthermore, the band gaps of the CCTS_{1-x}Se_x and CZTS_{1-x}Se_x are linearly related to the concentration of Se,^[4] so we can calculate the band gaps of CCTS_{1-x}Se_x using below formulas:

$$E_g = 1.07 - 0.27_x \tag{1}$$

where x is Se/(S+Se). We calculated the band gap of CCTS0.08Se0.92 to be 0.822. In addition, the band gap of the RT absorber layer (CZTS_{0.08}Se_{0.92}) was estimated to be 1.075 eV by EQE. Based on the previously reported works,^[1,2] we can infer that the band gap of $CC_xZ_{1-x}TS_{0.08}Se_{0.92}$ has a linear relationship with the Cd content:

$$E_g = 1.075 - 0.253_x \tag{2}$$

where x is Cd/(Cd+Zn).



Fig. S7 The high-resolution XPS spectra of the Zn 2p and Cd 3d core levels of the depth profile of the HT sample.

Table S3 The Cd/(Cd+Zn) ratios of the HT sample obtained from XPS calculations and the band gap values at different depths of the absorber layer obtained by correlation calculations. Here, 1200 nm corresponds to the XPS on the back surface of the absorber layer.

	0 [nm]	10 [nm]	50 [nm]	100 [nm]	200 [nm]	1200 [nm]
Cd/(Cd+Zn)	0.446	0.197	0.166	0.117	0.023	0.011
Eg	0.962	1.025	1.033	1.045	1.069	1.072

AZO film is used as the transparent electrode and window layer of thin film solar cells, so its high conductivity (low square resistance), carrier concentration, mobility and transmittance are beneficial to improve the photovoltaic conversion efficiency of thin film solar cells. By optimizing the deposition parameters (sputtering power, pressure and sputtering time) to 150 W, 0.2 Pa, 90 minutes, a transparent conductive window layer material that basically meets the requirements of thin-film solar cells can be obtained at room temperature (RT). Further, we investigated the effect of depositing AZO films at 150 °C (HT) on their photovoltaic properties under the conditions of constant sputtering power, pressure and time. The Hall parameters, transmittance and crystallization quality are shown in Table S4 and Fig. S8, respectively. It can clearly be seen that as the temperature increases to 150 °C, the carrier concentration and mobility increase, and the sheet resistivity decreases (Table S4). This indicates that increasing the deposition temperature can effectively improve the electrical properties of AZO films. The transmission spectra of the AZO films were shifted toward the long-wavelength as the deposition temperature increased and there is a slight increase in transmittance at the short wavelength (400-500 nm). The maximum transmittance of the AZO film (Fig. S8a) in the visible light region is close to 90% with or without in-situ annealing. Fig. S8b shows the XRD patterns of AZO films for RT and HT, indicating crystalline quality is improved after increasing deposition temperature. When the deposition temperature is higher than room temperature, the source particles adsorbed on the surface of the substrate will have higher kinetic energy and their mobility will be enhanced, so it is easier to reach the lowest energy location. Therefore, the crystalline quality of AZO films deposited at 150 °C is higher than that at RT. By employing the in-situ annealing treatment during the AZO deposition process, the performance of the AZO film can be improved.

Sample	Sheet resistivity	Mobility	Concentration
	(Ω/□)	(cm ² V ⁻¹ S ⁻¹)	(×10 ²⁰ cm ⁻³)
RT	49.18	16.9	1.83
HT	24.82	26.5	2.44

Table S4 Sheet resistivity, mobility, carrier density of AZO films deposited at RT and HT.



Fig. S8 (a) Transmittance and (b) XRD patters of the AZO films with different deposition temperatures. The inset picture is full width at half maximum (FWHM) of (002) diffraction peak.





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Test and Calibration Center of New Energy Device and Module, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences (SIMIT) 235, Chengbei Road, Jiading, Shanghai, China

Measurement Report

Client Name	Guo Hongling	
Client Address	38 Tongyan Road, Jinnan Di	strict, Tianjin
Sample	Cu₂ZnSn(S,Se)₄ solar cell	OEN
Manufacturer	Institute of Photoelectronic NanKai University	Thin Film Devices and Technology,
Application	SIMITL72019111801	
Measurement Date	Nov. 18 th , 2019	
Performed by:	Qiang Shi Qiang Shi	Date: 11 / 18/2019
Reviewed by:	Birg Gao Bing Gao	Date: 2019-11-26
Approved by:	Shangelor R-	Date: 2014 - 11-26

The measurement report without signature and seal are not valid. This report shall not be

Zhengxin Liu

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Sample Information							
Cu ₂ ZnSn(S,Se) ₄ solar cell							
1							
GHL-2-1							
I-V characteristic							
25.5°C, 19.0%R.H							

Measurement of I-V characteristic

Reference cell	PVM1124 (NREL_ISO tracking#:2005)
Reference cell Type	mono-Si, WPVS
Calibration Value/Date of Calibration for Reference cell	145.2 mA/ Jul.2019
Measurement Conditions	Standard Test Conditions IEC 60904-3 Ed.2 AM 1.5G Irradiance: 1000 ± 100 W/m ² Temperature: 25 ± 2 °C
Measurement Method	Simulated Sunlight by Steady State Solar Simulator Class AAA based on IEC 60904-9 Ed.2
Spectral Mismatch Factor	SMM=1.004840

==== Measurement Result ====

Serial	Total Area	Active Area	lsc	Voc	Pmax	lpm	Vpm	FF
Number	(cm ²)	(cm ²)	(mA)	(mV)	(mW)	(mA)	(mV)	(%)
GHL-2-1	0.204	0.186	6.95	484.75	2.28	6.13	371.82	67.69

Measured after 3 minutes of light soaking at 100 mW/cm² and 3 minutes of cooling.

Report No.19TR111801

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Fig. S9 Certification report for the 12.25% efficiency of CZTSSe solar cell.



Fig. S10 The series resistance (*Rs*) and ideality factor (*A*) of devices RT and HT fitted by the dark *J-V* curves.



Fig. S11 The shunt conductance (G) of devices RT and HT fitted by the dark J-V curves.



Fig. S12 Reverse saturation current density (J_0) of devices RT and HT fitted by the dark *J-V* curves.



Fig. S13 *J-V* curves of high efficiency HT device measured under AM 1.5 (100 mW/cm²) after different storage times.

 Table S5 Detailed device performance parameters of HT device at different storage time.

Day after device fabrication	V _{oc} (V)	J _{sc} (mA/cm²)	FF (%)	PCE (%)
1 Day	0.484	37.41	66.83	12.1
180 Day	0.478	36.97	64.94	11.48



Fig. S14 C-V scan curve of devices RT (a) and HT (b).

The average lifetime τ_{avg} can be calculated with the equation:

$$\tau_{avg} = \frac{\left(A_1 \tau_1^2 + A_2 \tau_2^2\right)}{A_1 \tau_1 + A_2 \tau_2}$$

where A_1 and A_2 is the ratio of carrier lifetime $^{\tau_1}$ and $^{\tau_2}$, respectively.

Sample	τ ₁ (ns)	A ₁ (%)	τ_2 (ns)	A ₂ (%)	τ_{avg} (ns)
RT	3.16	47.94	0.81	52.06	1.94
HT	7.29	51.24	1.36	48.76	4.38

Table S6 The TRPL fitting results of RT and HT heterojunction samples.

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