Electronic Supplementary Information for:

A sputtered CdS buffer layer for co-electrodeposited Cu_2ZnSnS_4 solar cell with 6.6% efficiency

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Experimental

CZTS thin films were grown by sulfurization of co-electrodeposited CZTS precursors using a conventional three-electrode system with an Ag/AgCl reference electrode, a Pt foil counter electrode, and a Mo-coated glass substrate (Mo/glass) as a working electrode under potentiostatic control mode using a CHI660D electrochemical (CH Instrument, USA), as described in our previous work.[1-6] All raw chemicals are of analytical reagent grade (supplied by Sinopharm Chemical Reagent Co. Ltd., China). 10 mM $CuSO_4\cdot 5H_2O$, 20 mM $ZnSO_4\cdot 7H_2O$, 20 mM $SnSO_4\cdot 2H_2O$, 20 mM tartaric acid, 100 mM trisodium citrate and 10 mM $Na_2S_2O_3\cdot 5H_2O$ were simultaneously dissolved into deionized water under ca. 25 °C to produce a homogenous electrolyte. The precursors were co-electrodeposited at -1.15 V (vs. Ag/AgCl) for the following deposition times 5, 10, 20, 30 and 40 min at room temperature without stirring. After the deposition, the as-prepared films were then sealed in a rapid thermal process (RTP) furnace containing 500 mg of sulfur powder with a purity of 99%. The RTP process was heated up to 570 °C and subsequently maintained for 15 min at the pressure of 10 Torr. The sulfurized CZTS films deposited at different deposition times: 05, 10, 20, 30 and 40 min are hereafter denoted CZTS(05), CZTS(10), CZTS(20), CZTS(30) and CZTS(40), respectively.

The CZTS absorbers were employed for fabrication of a complete thin film solar cell with a standard structure of AZO/i-ZnO/sputtered CdS/CZTS/Mo/glass. The CdS (150 nm), i-ZnO (50 nm) and ZnO:Al (700 nm) layers were subsequently deposited by RF magnetron sputtering, respectively. Here, we make sure that the thin CdS layer is thick enough to prevent the damage caused during device fabrication, we increased the sputtered CdS layer thicknesses up to 150 nm. Finally, the samples were mechanically scribed into individual cells with a total area of 0.08 cm^2.

Characterizations

The structural properties of thus-obtained films were studied by X-ray diffraction (XRD) using a Bruker D8 Discover diffractometer with Cu Kα radiation (λ=1.5406 Å). Raman measurements were performed using a micro-Raman spectrometer. For excitation, an Ar^+ laser with 532 nm wavelength was used. The morphology and chemical composition were observed using a PhilipsS360 scanning electron microscope (SEM) attached to an energy-dispersive X-ray spectroscope (EDS). The element components were obtained as average values between two regions at the surface of the sulfurized films. Current density-voltage (J-V) characteristics of the devices were measured under AM 1.5 global spectrum with the irradiance set to 1000 W m^{-2} (Xe lamp; Newport). External quantum efficiency (EQE) measurements were performed by a single source illumination system (halogen lamp) combined with a monochromator. A calibrated Si-cell was used as reference for the J-V as well as for the EQE measurements.

Table S1. Chemical composition and composition ratios of the sulfurized CZTS thin films.

Sample ID	Elemental component (at %)				Composition ratio		
	Cu	Zn	Sn	S	Cu/(Zn+Sn)	Zn/Sn	S/Metal
CZTS(05)	9.77	5.52	3.79	80.92	1.05	1.46	4.24
CZTS(10)	16.85	12.08	8.32	62.75	0.83	1.46	1.68
CZTS(20)	22.25	15.37	11.72	50.66	0.82	1.31	1.03
CZTS(30)	23.44	16.58	11.88	48.10	0.82	1.40	0.93
CZTS(40)	25.45	19.13	11.14	44.28	0.84	1.72	0.80

Table S2. Photovoltaic parameters of the CZTS solar cells with a 150 nm-thick sputtered CdS.

Cells	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF (%)	R_s (Ω cm^2)	R_{sh} (Ω cm^2)	J_0 (mA cm^{-2})	η (%)
CZTS(05)	133.2	4.1	25.1	32.4	33.0	3.91×10^{-3}	0.1
CZTS(10)	453.1	15.2	47.1	9.9	117.3	2.56×10^{-4}	3.3
CZTS(20)	567.0	22.0	52.8	5.9	183.1	5.93×10^{-4}	6.6
CZTS(30)	581.4	19.9	57.2	5.3	282.8	9.33×10^{-5}	6.6
CZTS(40)	511.4	19.1	49.8	6.2	174.2	3.35×10^{-4}	4.9

Table S3. Photovoltaic parameters of the CZTS solar cells with a 170 nm-thick sputtered CdS**.**

Cells	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF (%)	R_s (Ω cm^2)	R_{sh} (Ω cm^2)	η (%)
CZTS(05)	115.6	1.40	35.1	41.3	66.5	0.1
CZTS(10)	343.2	12.2	42.6	10.3	155.1	1.8
CZTS(20)	517.1	18.2	53.8	6.2	219.6	5.1
CZTS(30)	555.3	15.8	55.0	6.5	252.6	4.9
CZTS(40)	467.2	14.7	47.5	7.4	158.4	3.3

Table S4. Device characteristics of the high performance CZTS(20) cells (C1-C10) and CZTS(30) cells (C11-C15).

Sample	Cells	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF (%)	R_s (Ω cm^2)	R_{sh} (Ω cm^2)	η (%)
CZTS(20)	C1	571.0	20.0	51.0	6.6	180.1	5.8
	C2	552.3	19.6	53.7	5.4	189.7	5.9
	C3	570.9	20.6	50.4	5.9	161.5	6.0
	C4	578.2	20.1	51.8	6.6	192.8	6.0
	C5	560.6	21.2	50.8	6.0	154.2	6.1
	C6	556.4	21.1	52.2	5.5	186.4	6.2
	C7	556.3	22.1	50.7	5.6	178.5	6.3
	C8	550.0	21.4	53.6	5.5	186.7	6.3
	C9	557.4	21.6	53.1	5.4	183.5	6.4
	C10	567.0	22.0	52.8	5.9	183.1	6.6
CZTS(30)	C11	576.9	18.2	57.4	5.4	311.2	6.1
	C12	581.8	19.2	57.2	5.5	287.4	6.4
	C13	589.2	19.2	57.1	5.4	279.7	6.5
	C14	576.1	19.4	57.8	4.9	281.7	6.5
	C15	581.4	19.9	57.2	5.2	282.8	6.6

The mini cells numbered by Cl-C10 and Cl1-C15 are coming from the same CZTS(20) and CZTS(30) samples, respectively.

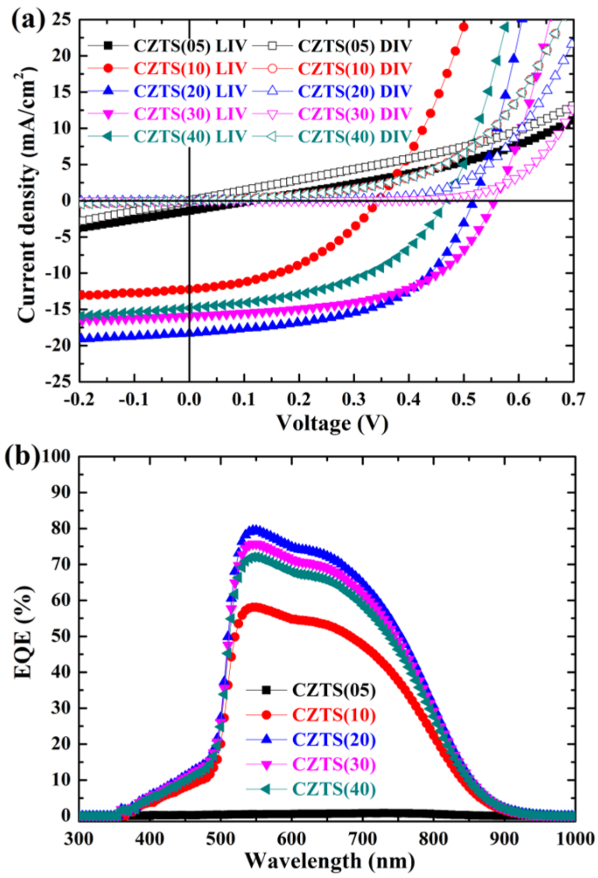

Figure S1(a) J-V characteristics of the CZTS solar cells with a 170 nm-thick sputtered CdS measured in dark and under AM1.5 simulated illumination. (b) EQE measurements of the corresponding CZTS solar cells.

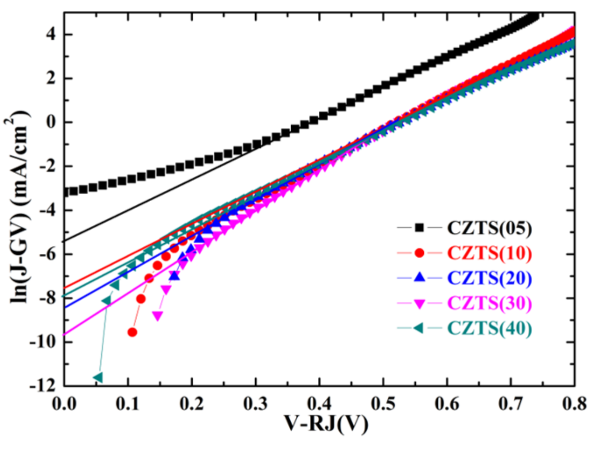

Figure S2. ln(J-GV) versus V-RJ with fit used to determine the reverse saturation current density (J_0) for CZTS solar cells

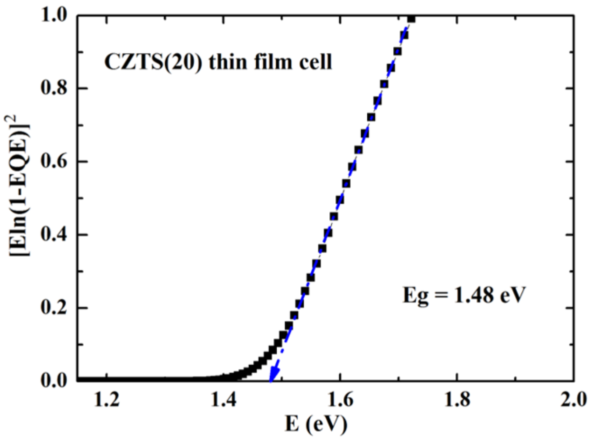

Figure S3. Band gap determination of the CZTS(20) cell from the EQE data.

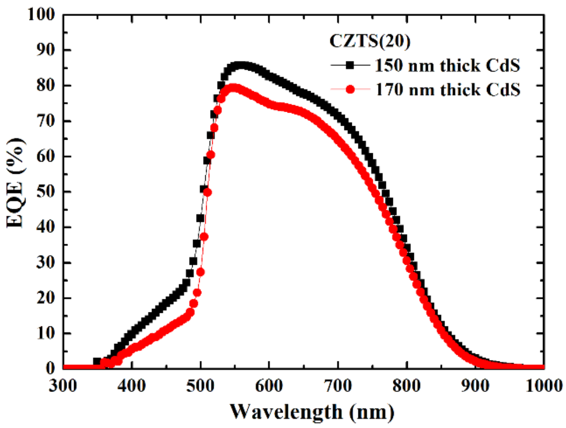

Figure S4.The comparison of EQE measurements for the CZTS(20) solar cells using two different thick sputtered CdS buffer layers (150 nm and 170 nm).

Reference

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