

Fabrication of CZTS Solar Cells with 5.1% Efficiency Via Thermal Decomposition and Reaction of Non-toxic Sol-gel Route

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SUPPORTING INFORMATION

Precursor sol solution preparation:

The precursor solution was prepared by dissolving Cu(CH₃COO)₂·H₂O (0.4 mol/L, AR), Zn(CH₃COO)₂·2H₂O (0.25 mol/L, AR), SnCl₂·2H₂O (0.2 mol/L, AR) and SC(NH₂)₂ (1.6 mol/L, AR) into in 2-methoxyethanol (AR) while stirring at 50 °C for several hours to get dark yellow solution. After aging at room temperature in air for several days, the prepared precursor solution was converted into sol solution and then proper Monoethanolamine (1% molar concentration) was added and stirred to avoid cracks during spin coating. All chemical reagent were purchased from Sinopharm Chemical Reagent Co., Ltd.

CZTS thin film preparation:

The precursor sol solution was spin coated on molybdenum coated sodalime glass (SLG) substrate at 3000 rpm for 30 s followed by annealing at 200 °C for 5 min on a hot plate in air. This coating step was repeated ten times to get thick CZTS precursor thin film. After that, the prepared precursor thin film was annealed at 560 °C in sulfur atmosphere (evaporation of solid sulfur) for one hour to obtain desired crystallinity.

Na-doping preparation:

Three different concentration of Na-doping (0.5%, 1% and 2%) were adopted in the formation of CZTS precursor solution. In this paper only the concentration of 1% Na-doping was reported.

HCl etching preparation:

To show the improvement of device performance, one annealed Na-doping CZTS thin film was etched with the solution of HCl (5% v/v, 75 °C) for 300 s to remove the superficial ZnS.

In-depth Raman Spectroscopy measurement

The CZTS thin film sample was put on the area of target and etched by using RF magnetron sputtering for different time to get different in-depth for CZTS thin films.

CZTS solar cell device fabrication:

Firstly, CdS buffer layer was deposited on prepared CZTS/Mo/SLG at 80 °C for 10 min using chemical bath depo-

sition (CBD). The solution of CBD consisted of deionized H₂O (160 mL), NH₄OH (25%, 20 mL), 0.3 M CdSO₄ (10 mL, AR) and 1.5 M thiourea (10 mL, AR). Next, 50 nm i-ZnO followed by 600 nm ZnO:Al layer were deposited by RF and DC magnetron sputtering. Finally Ni followed by Al was thermally evaporated on ZAO layer to form top contact fingers via shadow mask.

Characterization and analysis:

The surface and cross-section morphology of thin films were characterized by SEM (FEI Quanta-200 and NOVA NanoSEM 230) and Atomic Force Microscopy (Veeco NanoMan VS). The X-ray diffraction (XRD) data, Raman spectra and TGA data were collected by using Rigaku3014, LabRAM ARAMIS and DSC-TGA (SDT Q600, TA Instruments-Waters LLC, containing 10% Oxygen) respectively. Energy Dispersive Spectrometer (EDS, EDAX-GENESIS60S) and X-ray photoelectron spectroscopy (XPS K-Alpha 1063) were used to check the elemental composition and valence states of CZTS thin films. Current density-voltage (I-V) characterization for solar cells were performed using Xe-based light source solar simulator (Newport, 91160 and KEITHLEY 2400) to provide simulated 1 sun AM 1.5G illumination which was calibrated with a standard Si reference cell, traceable to the National Renewable Energy Laboratory. The EQE were measured by 7SCSpec series spectrum performance testing system of solar cells.

Additional Tables and Figures

			EDS		XPS	
	Composition		No Doping	1% Na doping	No Doping	1% Na doping
Precursor solution	Cu/Zn+Sn		0.85	0.85		
	Zn/Sn		1.25	1.25		
Annealed thin films	Cu/Zn+Sn		0.84	0.86		
	Zn/Sn		1.21	1.22		
	S/metal		1.08	1.09		
Impurities content	C				5.25%	1.13%
	O				0.73%	1.17%
	Cl				0.74%	0.64%
	Na				0.65%	1.91%
Binding Energy (eV)	Cu	2p _{3/2}			932.3	932.5
		2p _{1/2}			952.1	952.3
	Zn	2p _{3/2}			1021.5	1021.7
		2p _{1/2}			1044.5	1044.7
	Sn	3d _{5/2}			486.1	486.4
		3d _{3/2}			494.6	494.8
	S	2p			161.7	161.9

Table S1. The EDS and XPS data of CZTS thin films and precursor solution

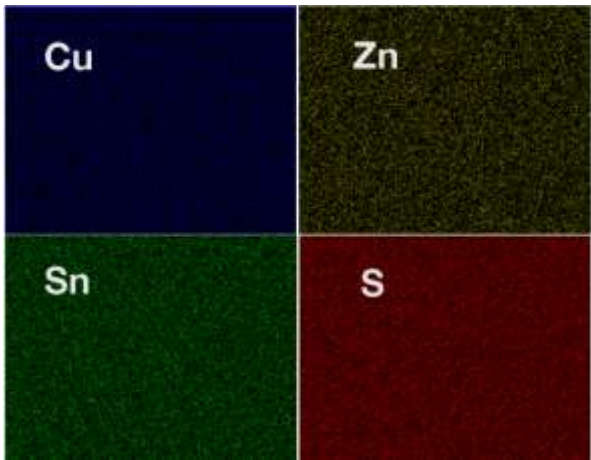


Figure S1. The Element Mapping images analysis of CZTS thin film without Na-doping

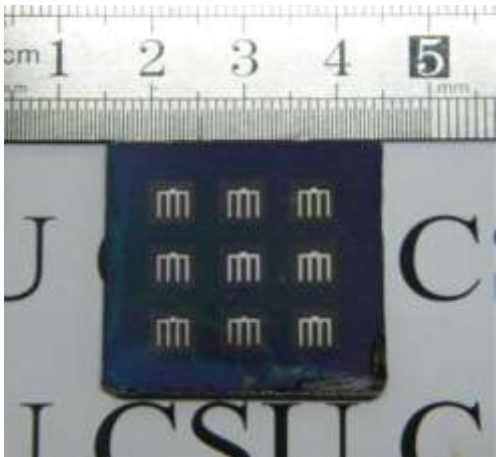


Figure S2. The completed CZTS solar cell device with structure of Ni:Al/ZAO/i-ZnO/CdS/CZTS/Mo/glass

The device parameters are calculated based on total device area (0.25 cm²) which include areas shaded by Ni:Al fingers , and the active area is about 0.20 cm²

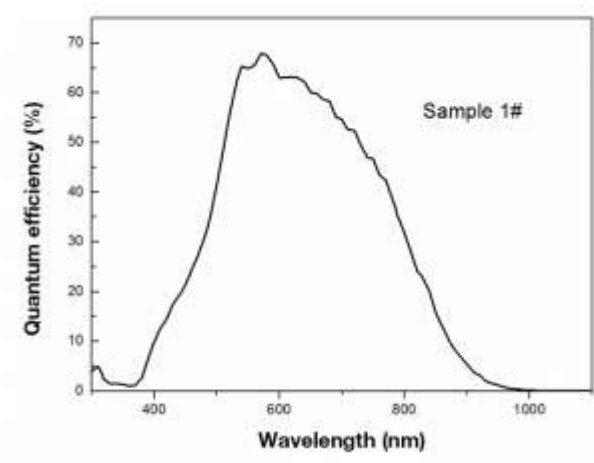


Figure S3. The quantum efficiency of Sample 1# cell