

Low-temperature Solution-Processed Kesterite Solar Cell Based on in Situ Deposition of Ultrathin Absorber Layer

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Supporting Information

Experimental Section

Chemicals:

Sources and purities of metal salts and other reagents were as follows: Copper(II) acetate monohydrate ($\text{Cu}(\text{CO}_2\text{CH}_3)_2 \cdot \text{H}_2\text{O}$; >99.99% from Aldrich), Tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, >99.99% from Aldrich), Zincchloride (ZnCl_2 , >99.99% from Alfa Aesar), Thioacetamide (CH_3CSNH_2 , >99% from Aldrich), dimethyl sulfoxide (DMSO, >99% from Merck). All chemicals were used as received without any further purification.

Preparation of CZTS precursor inks:

CZTS precursor was prepared by sequentially mixing 0.381 mol $\text{Cu}(\text{OAc})_2$, 0.262mol ZnCl_2 , 0.214 mol SnCl_2 and 1.143 mol TAA in 1 mL DMSO under an N_2 atmosphere in glove box. After stirring the mixture solution at room temperature for 10 min, a clear dark brown solution was obtained. CZTS precursors were directly coated on ITO-coated glasses, which were cleaned by ultrasonication for 10 min in acetone and then 10 min in Isopropyl alcohol. The prepared precursors were spin-coated at the spinning speed of 1300 rpm for 0.5 min followed by immediate annealing at 350 °C for 5 min on a hot plate inside a glove box. After the first coating, the second CZTS layer was deposited under the same temperaturebut annealed for 2 min. For the deposition of CdS layer, we applied a reported approach for CuInS_2 solar cell but with somemodifications. Typically, the CdS precursor solution was prepared by mixing CdCl_2 (0.1mmol) and thiourea (0.3mmol) with 1mL of 1-butylamine and 40 μL of 1-propionic acid. The CdS precursor solution was spin-cast directly onto the CZTS layer at 2500 rpm for 60s. Different from the slow annealing approach used in Ref 1 we immediately transferred the samples onto the preheated hotplate with a

temperature of 300 °C for 1 min. A second CdS layer was deposited under the same conditions, after which the device was heated for 5 min. Finally, to complete the device fabrication process, Al (80 nm) were thermally evaporated under vacuum (at a pressure of 10^{-6} Torr) and the whole devices were glass-encapsulated by an encapsulating binder called “DELO-Katiobond LP655”.

Materials Characterizations:

Scanning electron microscopy: Scanning electron microscopy (SEM) was performed in order to investigate the morphology of the films annealed at different temperatures. Top-view and cross-section pictures was characterized by ULTRATM 55 (Carl Zeiss AG, Germany) using an InLens detector operating at an accelerating voltage of 10 kV.

X-Ray diffraction analysis: Samples were prepared usually by spin-coating precursor solutions onto pieces of glass substrate and annealed at 300 °C and 350 °C respectively. X-Ray diffraction analysis Measurements were done with a Panalytical X'Pert powder diffractometer with Cu-K-alpha radiation. Tube parameters were: Voltage 40 kV, Current 35 mA. The measurement geometry was asymmetrical with a constant angle of incidence of 0.5° (to reduce signal from the substrate). On the primary beam side a goebel mirror produced (nearly) monochromatic and parallel radiation. The "mini-prop" proportional gas phase detector counted the diffracted x-ray photons. 2Theta range was 10-100° measured with an angle velocity of 0.05°/5s, which equals a total measurement time of 12.5 h.

X-ray photoelectron spectroscopy (XPS) depth profile measurements: Chemical characterization of CZTS films were carried out by X-ray photoelectron spectroscopy (PHI 5600, spectrometer, USA) using AlK α monochromatized radiation.

Raman spectroscopy: Raman spectra of CZTS nanocrystals were collected from a confocal micro Raman, (LabRam HR Evolution—HORIBA), using an excitation lasers of wavelengths 532.1 nm (Nd–YAG).

UV-vis absorption spectra: UV-Vis spectroscopy of CZTS films were carried out on a PerkinElmer's LAMBDA 950 UV-Vis spectrophotometer operated at a resolution of 1 nm.

The technique of photoinduced charge carrier extraction in a linearly increasing voltage (Photo-CELIV): In Photo-CELIV measurement, the device was illuminated with a 300 μ s laser pulse (405nm) of about one sun equivalent light intensity. Current transients were recorded across the internal 50 Ω resistor of our oscilloscope. We used a fast electrical switch to isolate the cell during the laser pulse and the delay time in order to prevent charge extraction or sweep out. After the variable delay time, the switch connected the solar cell to a Function Generator which applied a linear extraction ramp. The ramp was 20 μ s long and started with an offset matching the respective V_{oc} of the cell for each delay time.

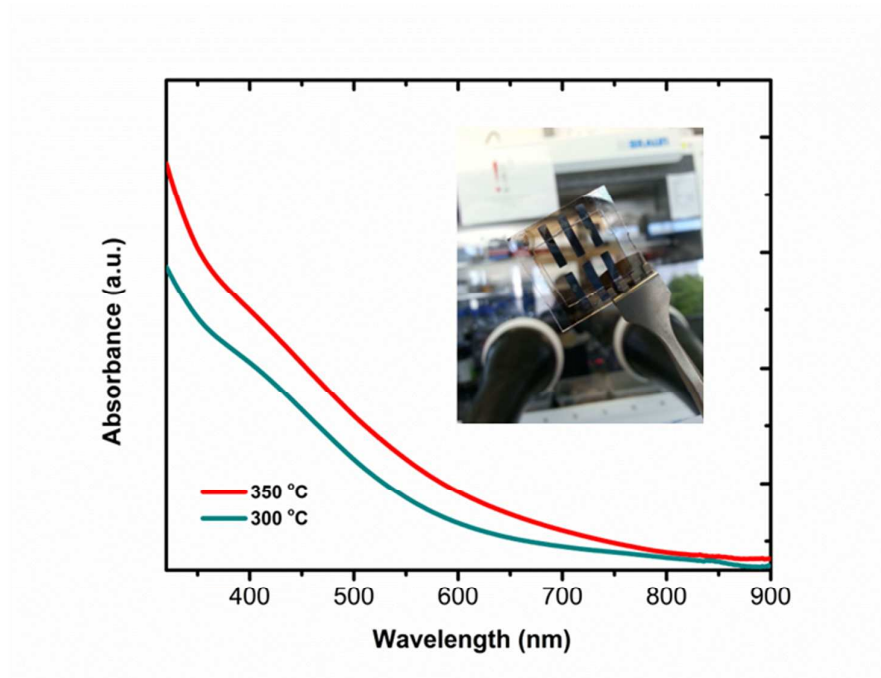


Figure S1 UV-Vis-NIR spectrum of CZTS films annealed at different temperatures, the insets showing the photo of the CZTS device.

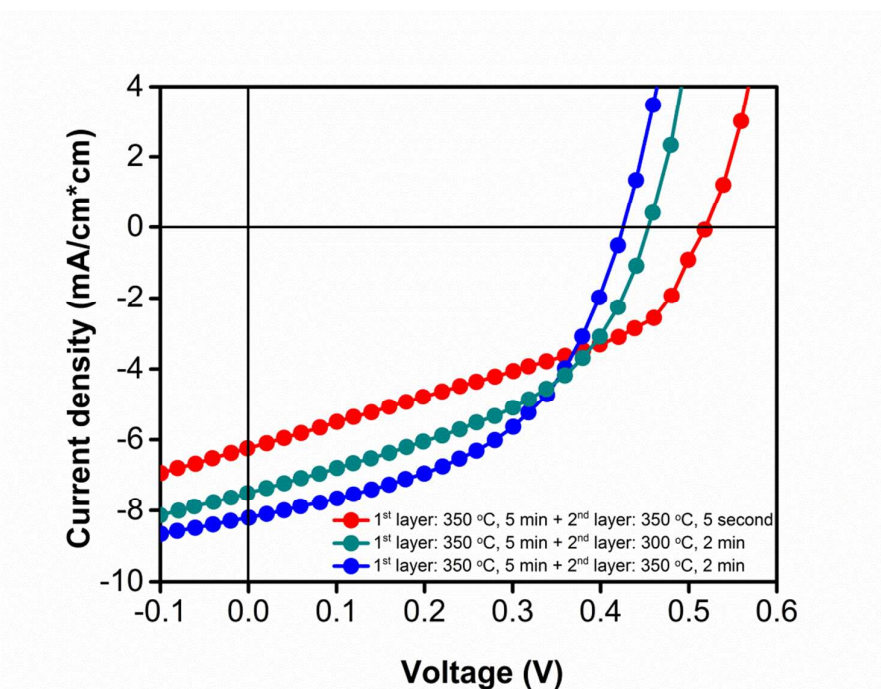


Figure S2 Current–voltage (I – V) curves of the three CZTS solar cells with different annealing recipes showing the increase of PCE, mainly due to the improved J_{sc} and FF, at longer annealing time and higher temperatures.

Furthermore, we also investigated the performance of solar cells fabricated with different annealing recipes (Figure S2 and Table S1). We found that the CZTS devices are also quite sensitive to their annealing recipes. By simple optimization of annealing temperature and annealing time of second CZTS layer, the FF. increase from 40.8% to 48.5% and the J_{sc} also enhanced from 6.24 mA/cm² to 8.20 mA/cm², although this accompanied by a loss of V_{oc} from 0.52 V to 0.43 V.

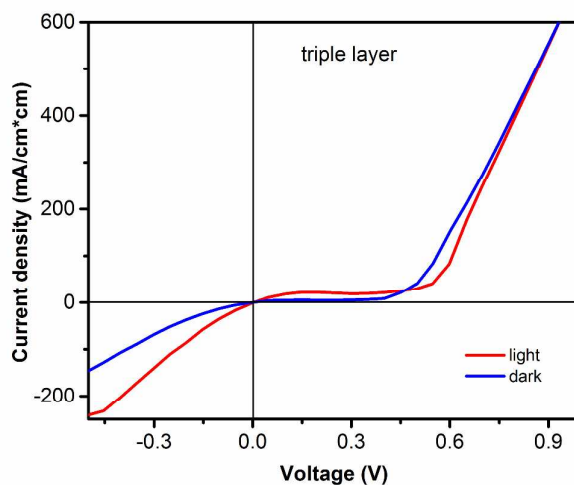


Figure S3. J - V characteristics of CZTS solar cells with thicknesses of 165 nm were measured under dark and illumination.

Table S1 Performance comparison of the three different annealing recipes for the deposition of second CZTS layer.

Annealing temperatures and time of the Second CZTS layer	J_{sc} [mA/cm ²]	V_{oc} [V]	FF. [%]	Eff. [%]
350 °C, 5 second	6.24	0.52	40.81	1.32
300 °C, 2 min	7.50	0.45	45.41	1.53
350 °C, 2 min	8.20	0.43	48.50	1.71

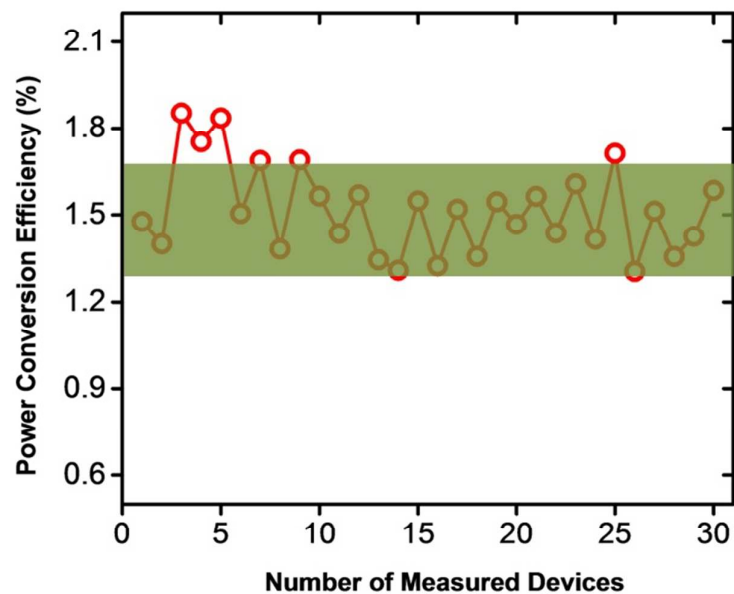


Figure S4. The results of 30 solar cells test showed that the average PCE of our low temperature processed CZTS solar cells reach at about 1.5%.

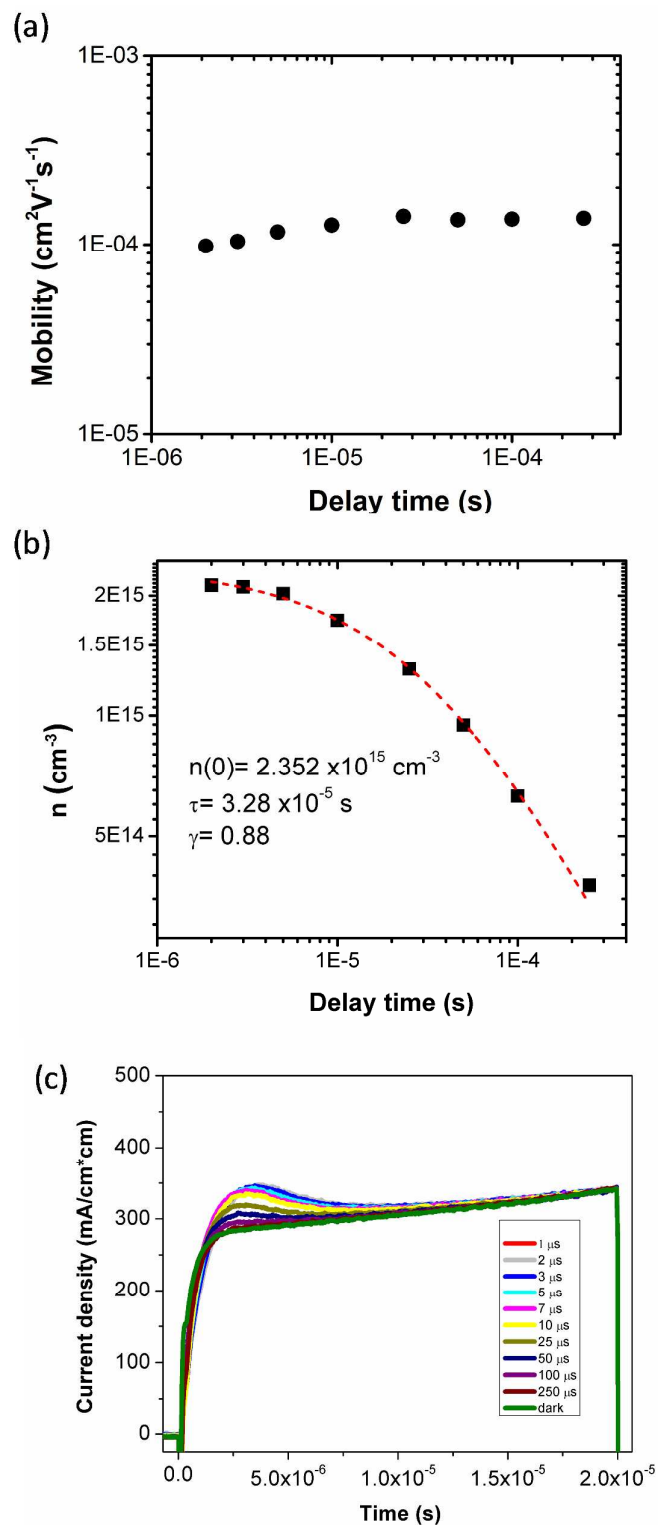


Figure S5. (a) Photo-CELIV mobility as a function of delay time; (b) the charge carrier concentration as a function of delay time and the fit. (c) Photo-CELIV traces of CZTS based solar cells with different delay time between the laser pulse and the extraction voltage ramp.

In photo-CELIV measurements, charge carriers are photogenerated in the bulk in the presence of a pulsed laser source and then extracted after an adjustable delay time (t_d) by simultaneously applying a triangular voltage pulse. Approximately twelve photo-CELIV transients, with different t_d were recorded (Figure S5) to calculate the charge carrier mobility (μ) using the following equation:

$$\mu = (2d^2) / (3At_{\max}^2 [1 + 0.36 \Delta j / (j(0))]) \quad \text{if } \Delta j \leq j(0), \quad (1)$$

where d is the device thickness, A is the voltage rise speed $A = dU/dt$, U is the applied voltage to the sample, t_{\max} is the time corresponding to the maximum of the extraction peak, and $j(0)$ is the displacement current.

$$n(t) = n(0) / (1 + (t / \tau_B)^\gamma), \quad (2)$$

Where $n(0)$ is the density of photogenerated carriers at $t=0$ and γ is a time-dependent parameter that characterizes the dispersion of charge carrier lifetimes.