

Supporting Information

Surface and Interface Engineering for Highly Efficient Cu₂ZnSnSe₄ Thin Film Solar Cells Via In-Situ Formed ZnSe Nanoparticles

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Experimental details

Stacked Metallic precursor preparation

The metallic stacked precursors with different stacking orders were prepared on 1 μm thick Mo-coated soda lime glass (SLG) substrates using a direct current (DC) magnetron sputtering technique at room temperature. The 2.5 x 2.5 cm^2 Mo-coated SLG were ultrasonically cleaned using isopropyl alcohol and deionized water for 10 min., and then the substrates were placed in the sputtering chamber. The 3-inch Cu, Zn, and Sn metallic targets with 99.999 % purity (TASCO, USA) were used. The DC sputtering conditions of each metallic stacked layer were as follows; Cu: 3.10 W/cm^2 , 8 mTorr, Sn: 3.10 W/cm^2 , 8 mTorr, and Zn: 3.10 W/cm^2 , 8 mTorr, respectively. The substrate holder was cooled using a homemade cooling chuck system and the substrate temperature was maintained near 5 $^\circ\text{C}$ to improve the morphologies and microstructures of the as-deposited Zn and Sn layers through controlling the growth rate. The substrates were rotated at 5 rpm during the DC sputtering process. Total thicknesses of stacking precursors are kept approximately 580 nm. The detailed deposition conditions and sample names of the metallic precursors with different stacking orders are listed in the Table S1.

CZTSe thin film preparation

The different stacking ordered precursor thin films were annealed at and Se atmosphere to prepare high quality of $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) absorber layer. Se powders were purchased from Sigma Aldrich (99.999%). The different stacking ordered precursor thin films were placed in a graphite box, which was subsequently placed into a tube type rapid thermal annealing system, which allows accurate control of the chalcogenide vapor pressure during the annealing process. Annealing process was performed by using two-step annealing process on metallic precursors. First dwelling stage is performed at 350 $^\circ\text{C}$ for 5 min, and second dwelling stage is performed at 490 $^\circ\text{C}$ for 10 min. Both two stages are termed as low temperature (LT) stage for the first stage and as high temperature (HT) stage for the second stage. The annealing temperature was increased at a rate of 2.5 $^\circ\text{C s}^{-1}$ for all annealing processes, measured on the right-hand side of the graphite box using a thermocouple. The volume of the graphite box was 142.6 cm^3 . All the annealing processes were carried out under an Ar atmosphere inside the quartz tube. After finishing the annealing process, the graphite box naturally cooled down.

The composition ratios of four CZTSe thin films are shown with values of $\sim 0.64 \pm 0.01$ for $[\text{Cu}]/([\text{Zn}]+[\text{Sn}])$ and $\sim 1.09 \pm 0.04$ for $[\text{Zn}]/[\text{Sn}]$, as measured by X-ray fluorescence spectrometer (XRF).

CZTSe/ZnSe layer preparation for calculation of band alignment

For the angled resolved XPS measurement, a ZnSe layer on the CZTSe thin film is prepared by DC sputtering and post annealing process. After finishing the synthesis of the CZTSe thin film, ~ 20 nm of metallic Zn layer was sequentially deposited on the CZTSe thin film by DC sputtering technique at 5°C . Afterward, the CZTSe thin film was put in the graphite box together with Se powder and was annealed at 280°C for 10 min. The thickness of synthesized ZnSe layer on a CZTSe film was approximately ~ 30 nm, confirmed by FE-SEM measurement.

Device fabrications

The CZTSe solar cell devices were fabricated with a configuration of Al-Ni/AZO/*i*-ZnO/CdS/CZTSe/Mo/SLG without anti-reflection coating. Before deposition of CdS buffer layer, each CZTSe thin films were etched with 0.2 M potassium cyanide at room temperature for 120 s and rinsed using DI water for 60 s. The 50 nm CdS buffer layers were deposited onto the absorber layers via the chemical bath deposition method using a precursor solution consisting of 0.0015 M CdSO_4 , 2.871 M ammonia, and 0.05 M thiourea at 60°C for 14.5 min. After deposition of thin CdS layer, the samples were dried for 1 h. The 80 nm *i*-ZnO thin film with high resistivity was prepared using the RF magnetron sputtering technique at room temperature, with an RF power of 50 W, and at a working pressure of 1 mTorr under Ar and O_2 mixed plasma. The 580 nm Al doped ZnO (AZO) layer was deposited using the RF sputtering technique at room temperature, with an RF power of 70 W, and at a working pressure of 1 mTorr under Ar plasma. Finally, the Al-Ni top grid was deposited using the DC sputtering technique $\sim 2 \mu\text{m}$ by keeping the active area of the fabricated solar cells up to 0.3 cm^2 .

Characterizations of thin film and devices

The structural properties of thin films were measured by using high-resolution XRD (X'pert PRO, Philips, Eindhoven, Netherlands) operated at 40 kV and 100 mA and analyzed using Raman scattering spectroscopy with micro-Raman spectrometer (HORIBA, JOBIN-YVON HR 800) with a spectral resolution around 0.35 cm^{-1} and a confocal resolution of $100 \mu\text{m}$ under the back scattering

geometry at room temperature. The 514 nm line of an Ar⁺ ion laser source was used for excitation and the incident laser power on the sample surface was around 10 mW. Specifically, Raman microscope was equipped with an intensified charge coupled device with a focal length of 50 cm. Raman scattering spectra were collected in the backscattering geometry. The scattered light was collected and filtered to remove the contributions at the excitation wavelength, and the detection range was 200 to 950 nm with a resolution of 0.02 nm. The compositional ratio of CZTSSe and ACZTSSe thin films were characterized by a XRF (Axios Minerals PANalytical Netherlands). Internal standard equipment calculation process software was used to calibrate compositional ratio in the XRF (Axios Minerals PANalytical Netherlands) system. The surface morphology of the thin films was characterized by a using field emission scanning electron microscope (FE-SEM, Model: JEOL JSM-6701F, Japan). The transmission electron microscopy (TEM) was obtained using a JEOL-3010 at an operating voltage of 300 kV. TEM samples for CZTSe solar cell devices were prepared by focused ion beam (FEI, Helios G3 CX) at an operating voltage of 30 kV onto Ni TEM grids. Ga ion used as milling source. The elemental distribution and mapping were obtained by energy dispersive X-ray spectroscopy (EDS, Oxford INCA system) using a Technai G2 F30 equipped with TEM. The band alignment near the interface between CZTSe and CdS layers are investigated by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Co., USA) depth profiling. The sample is sputtered from CdS to CZTSe side by an Ar ion gun (2kV, 1uA) with a sputter rate of 0.2 nm/s of SiO₂. Field emission electron probe micro analyzer (FE-EPMA, JXA-8530F, JEOL Ltd, Japan) is used to observe the elemental distribution on a surface of annealed film during annealing process. The room temperature photoluminescence (RTPL) of the thin films were characterized by avalanche photodiode equipment (SH-4 and USA) at Korea Basic Science Institute (KBSI). The excitation source was an Ar ion laser operating at the wavelength of 514 nm. The power conversion efficiency (PCE) and EQE spectra for solar cell devices were characterized by a class AAA solar simulator (WXS-155S-L2, WACOM, and Japan) with the condition of AM 1.5G, 100 mW/cm², and 25 °C and with an incident photon conversion efficiency (IPCE) measurement unit (PV measurement, Inc., USA), respectively. Room temperature capacitance (C) vs voltage (V) plot of the solar cell devices were collected from -2.5 V to

1 V DC bias voltage by using 30 mV and 100 kHz alternating current (AC) signal. An impedance analyzer (Hewlett Packard, HP4284) is used to perform the C-V measurement.

Calculation of free carrier concentrations and junction depletion widths in the device

The junction depletion width (W) is extracted from the C-V plot shown in Fig. 3(a), following equation (Equation (1)).

$$C = \frac{\epsilon_0 \epsilon_r A}{W} \quad \text{Equation (1)}$$

where ϵ_0 is free space permittivity, and ϵ_r is relative dielectric constant of CZTSSe. The value of C is obtained from Fig. 3(a) at $V = 0$. The ϵ_r value of 8.2 is obtained from earlier published paper¹. The area (A) of solar cell device is used with the number of $3 \times 10^{-5} \text{ m}^2$. Afterward, free carrier concentration (N) is calculated following Equation (2).

$$N = \frac{-2}{q \epsilon_0 \epsilon_r A^2} \left[\frac{d(C^{-2})}{dV} \right]^{-1} \quad \text{Equation (2)}$$

where q is the electronic charge. The value for $(d(C^{-2})/dV)^{-1}$ is taken from the slope of $1/C^2-V$, as described in Fig. S3.

Calculations for band alignments

To construct the band alignment between (i) CZTSe/CdS, (ii) CZTSe/ZnSe NPs/CdS, (iii) CZTSe/ZnSe layer/CdS, angle resolved XPS characterizations of CZTSe, CdS, ZnSe, CZTSe/CdS, CZTSe/ZnSe NPs, CZTSe/ZnSe NPs /CdS, CZTSe/ZnSe layer, and CZTSe/ZnSe layer/CdS were performed.

(i) CZTSe/CdS interface

The valance band offset (VBO, ΔE_v) for CZTSe/CdS sample is determined by Kraut method through core level offset for XPS spectra following Equation (3).

$$\Delta E_v = (E_{\text{Cu } 2p \ 3/2}^{\text{CZTSe/CdS}} - E_{\text{Cd } 3d \ 5/2}^{\text{CZTSe/CdS}}) - (E_{\text{Cu } 2p \ 3/2}^{\text{CZTSe}} - E_{\text{VBM}}^{\text{CZTSe}}) + (E_{\text{Cd } 3d \ 5/2}^{\text{CdS}} - E_{\text{VBM}}^{\text{CdS}}) + V_{\text{bb}} \quad \text{Equation (3)}$$

where E_{VBM} is the valence band maximum of bulk CZTSe and CdS, $E_{Cu\ 2p\ 3/2}^{CZTSe/CdS}$ and $E_{Cu\ 2p3/2}^{CZTSe}$ are binding energies of the Cu core levels in CZTSe and CZTSe/CdS, $E_{Cd\ 3d\ 5/2}^{CZTSe/CdS}$ and $(E_{Cd\ 3d\ 5/2}^{CdS})$ are binding energies of the Cd core levels in CZTSe and CZTSe/CdS, and V_{bb} is the band bending, respectively. The value of band bending (V_{bb}) for CZTSe/CdS is obtained by Equation (4).

$$V_{bb} = (E_{Cd\ 3d\ 5/2}^{CdS} - E_{Cd\ 3d\ 5/2}^{CZTSe/CdS}) + (E_{Cu\ 2p3/2}^{CZTSe} - E_{Cu\ 2p3/2}^{CZTSe/CdS}) \text{ Equation (4)}$$

The value conduction band offset (CBO, ΔE_c) can be calculated by following Equation (5).

$$\Delta E_c = ((E_g^{CdS}) - (E_g^{CZTSe}) - \Delta E_v) \text{----- Equation (5)}$$

where E_g^{CdS} and E_g^{CZTSe} are band gap energies of CdS and CZTSe, respectively.

(ii) CZTSe/ZnSe NPs/CdS interface

The ΔE_v of CZTSe/ZnSe NPs/CdS sample is determined through core level offset for XPS spectra following Equation (6).

$$\Delta E_v = (E_{Cu\ 2p\ 3/2}^{CZTSe/ZnSe\ NPs/CdS} - E_{Cd\ 3d\ 5/2}^{CZTSe/ZnSe\ NPs/CdS}) - (E_{Cu\ 2p3/2}^{CZTSe/ZnSe\ NPs} - E_{VBM}^{CZTSe/ZnSe\ NPs}) + (E_{Cd\ 3d\ 5/2}^{CdS} - E_{VBM}^{CdS}) + V_{bb} \text{--- Equation (6)}$$

where E_{VBM} is the valence band maximum of bulk CZTSe/ZnSe NPs and CdS, $E_{Cu\ 2p\ 3/2}^{CZTSe/ZnSe\ NPs/CdS}$ and $E_{Cu\ 2p3/2}^{CZTSe/ZnSe\ NPs}$ are binding energies of the Cu core levels in CZTSe/ZnSe NPs and CZTSe/ZnSe NPs/CdS, $E_{Cd\ 3d\ 5/2}^{CZTSe/ZnSe\ NPs/CdS}$ and $(E_{Cd\ 3d\ 5/2}^{CdS})$ are binding energies of the Cd core levels in CZTSe/ZnSe NPs/CdS and CdS, respectively. The value of V_{bb} for CZTSe/ZnSe particle/CdS is obtained by Equation (7).

$$V_{bb} = (E_{Cd\ 3d5/2}^{CdS} - E_{Cd\ 3d5/2}^{CZTSe/ZnSe\ NPs/CdS}) + (E_{Cu\ 2p3/2}^{CZTSe/ZnSe\ NPs} - E_{Cu\ 2p3/2}^{CZTSe/ZnSe\ NPs/CdS}) \text{----- Equation (7)}$$

The value of CBO of CZTSe/ZnSe NPs/CdS is calculated by following Equation (8).

$$\Delta E_c = ((E_g^{CdS}) - (E_g^{CZTSe/ZnSe\ NPs}) - \Delta E_v) \text{----- Equation (S8)}$$

where E_g^{CdS} and $E_g^{CZTSe/ZnSe\ NPs}$ are band gap energies of CdS and CZTSe/ZnSe NPs, respectively.

(iii)-1 ZnSe layer/CdS layer interface for CZTSe/ZnSe layer/CdS layer

The ΔE_v of ZnSe layer/CdS sample is determined through core level offset for XPS spectra following Equation (9).

$$\Delta E_v = (E_{Zn\ 2p3/2}^{ZnSe\ layer/CdS} - E_{Cd\ 3d\ 5/2}^{ZnSe\ layer/CdS}) - (E_{Zn\ 2p3/2}^{ZnSe\ layer} - E_{VBM}^{ZnSe\ layer}) + (E_{Cd\ 3d\ 5/2}^{CdS} - E_{VBM}^{CdS}) + V_{bb} \text{----- Equation (9)}$$

where E_{VBM} is the valence band maximum of bulk ZnSe layer and CdS, $E_{Zn\ 2p3/2}^{ZnSe\ layer/CdS}$ and $E_{Zn\ 2p3/2}^{ZnSe\ layer}$ are binding energies of the Zn core levels in ZnSe layer/CdS and ZnSe layer, $E_{Cd\ 3d5/2}^{ZnSe\ layer/CdS}$ and $(E_{Cd\ 3d5/2}^{CdS})$ are binding energies of the Cd core levels in ZnSe layer/CdS and CdS, respectively. The value of V_{bb} for ZnSe layer/CdS is obtained by Equation (10)

$$V_{bb} = (E_{Cd\ 3d5/2}^{CdS} - E_{Cd\ 3d5/2}^{ZnSe\ layer/CdS}) + (E_{ZnSe\ 2p3/2}^{ZnSe\ layer} - E_{ZnSe\ 2p3/2}^{ZnSe\ layer/CdS}) \text{----- Equation (10)}$$

The value of CBO of ZnSe layer/CdS is calculated by following Equation (11).

$$\Delta E_c = ((E_g^{CdS}) - (E_g^{ZnSe}) - \Delta E_v) \text{----- Equation (11)}$$

where E_g^{CdS} and E_g^{ZnSe} are band gap energies of CdS and ZnSe layer, respectively.

(iii)-2 CZTSe/ZnSe layer interface for CZTSe/ZnSe layer/CdS layer

The ΔE_v of CZTSe/ZnSe layer sample is determined through core level offset for XPS spectra following Equation (12).

$$\Delta E_v = (E_{Zn\ 2p3/2}^{CZTSe/ZnSe\ layer} - E_{Cu\ 2p5/2}^{CZTSe/ZnSe\ layer}) - (E_{Zn\ 2p3/2}^{CZTSe/ZnSe\ layer} - E_{VBM}^{ZnSe\ layer}) + (E_{Cu\ 2p3/2}^{CZTSe} - E_{VBM}^{CZTSe}) + V_{bb} \text{----- Equation (12)}$$

where E_{VBM} is the valence band maximum of bulk ZnSe layer and CZTSe, $E_{Zn\ 2p3/2}^{CZTSe/ZnSe\ layer}$ and $E_{Zn\ 2p3/2}^{ZnSe\ layer}$ are binding energies of the Zn core levels in ZnSe layer and CZTSe/ZnSe layer, $E_{Cu\ 2p3/2}^{CZTSe/ZnSe\ layer}$ and $(E_{Cu\ 2p3/2}^{CZTSe})$ are binding energies of the Cu core levels in CZTSe/ZnSe layer and CZTSe respectively. The value of V_{bb} for CZTSe/ZnSe layer is obtained by Equation (13)

$$V_{bb} = (E_{Zn\ 2p3/2}^{ZnSe} - E_{Zn\ 2p3/2}^{CZTSe/ZnSe\ layer/CdS}) + (E_{Cu\ 2p3/2}^{CZTSe} - E_{Cu\ 2p3/2}^{CZTSe/ZnSe\ layer/CdS}) \text{----- Equation (13)}$$

The value of CBO of CZTSe/ZnSe layer is calculated by following Equation (14).

$$\Delta E_c = ((E_g^{\text{ZnSe}}) - (E_g^{\text{CZTSe}}) - \Delta E_v) \text{----- Equation (14)}$$

where E_g^{ZnSe} and E_g^{CZTSe} are band gap energies of CdS and ZnSe layer, respectively.

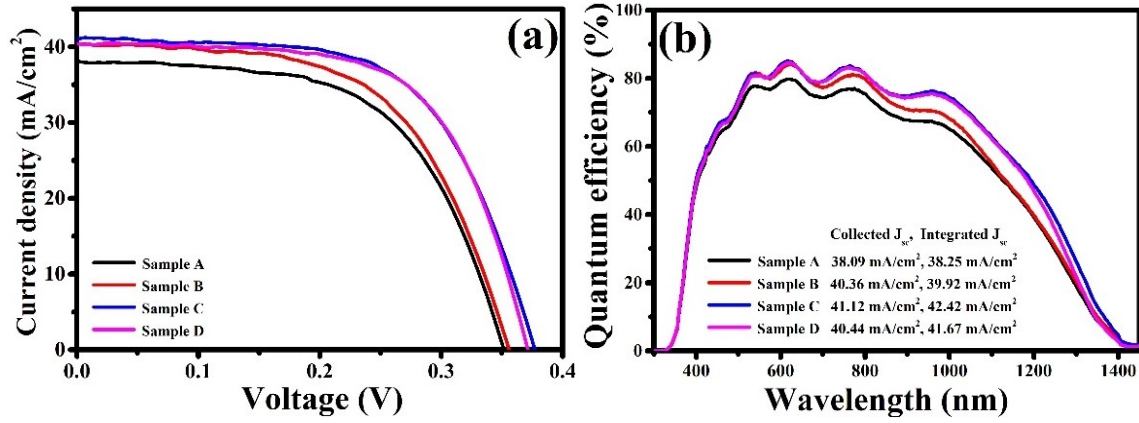


Fig. S1. The best performances of (a) J-V curves, (b) EQE spectra with integrated current densities in CZTSe solar cells with different stacking orders.

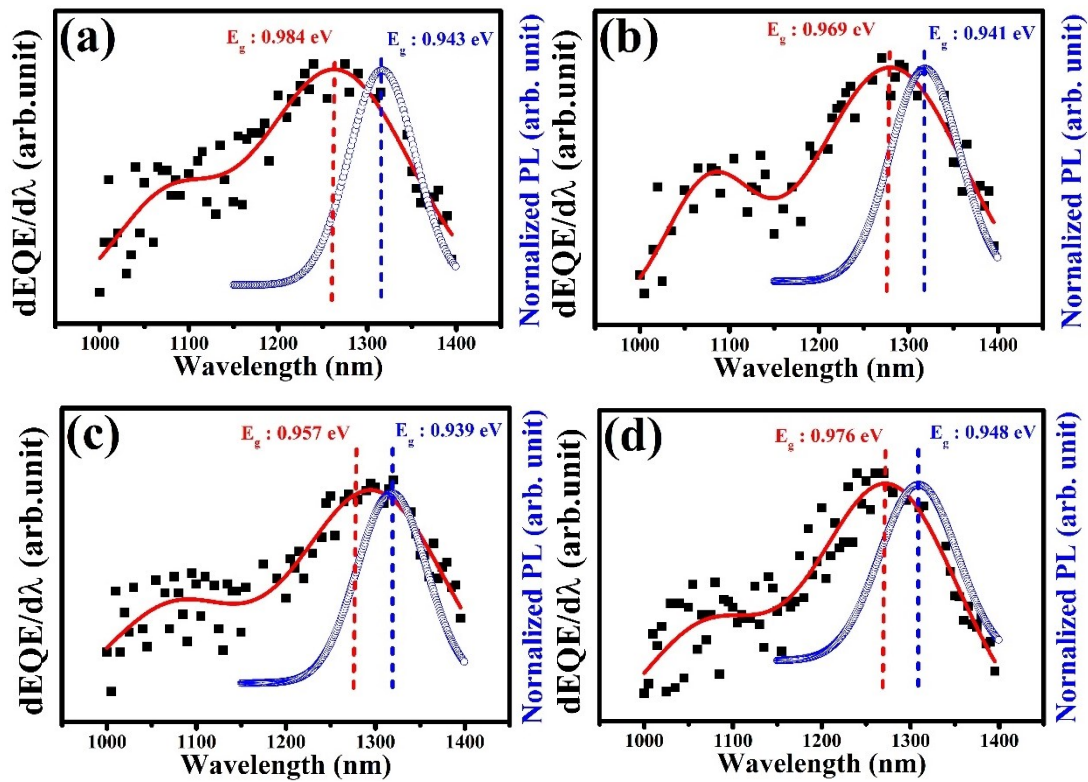


Fig. S2. EQE spectra vs. energy from dEQE/dλ (black square), fitted dEQE/dλ (red line), and fitted RTPL spectrum (blue circles) for the champion performance of CZTSe solar with different stacking orders; (a) Sample A, (b) Sample B, (c) Sample C, and (d) Sample D, respectively.

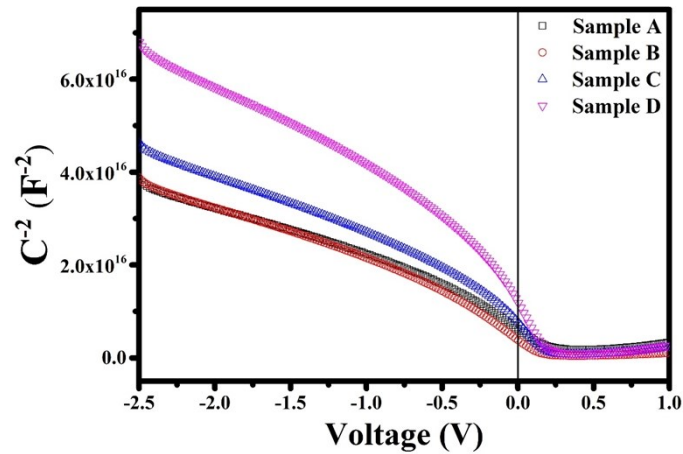


Fig. S3. Plots of $1/C^2$ vs voltage for CZTSe solar cells with different stacking orders measured under dark condition.

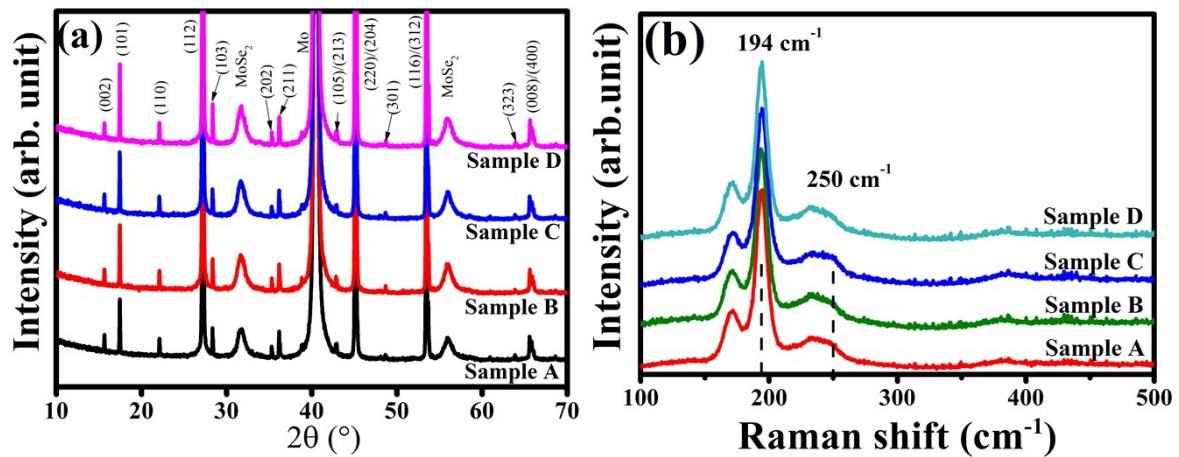


Fig. S4. (a) XRD patterns and (b) Raman spectra of the CZTSe thin films with different stacking orders. The diffraction peak from CZTSe structure are marked as '*' in Fig. S4(a).

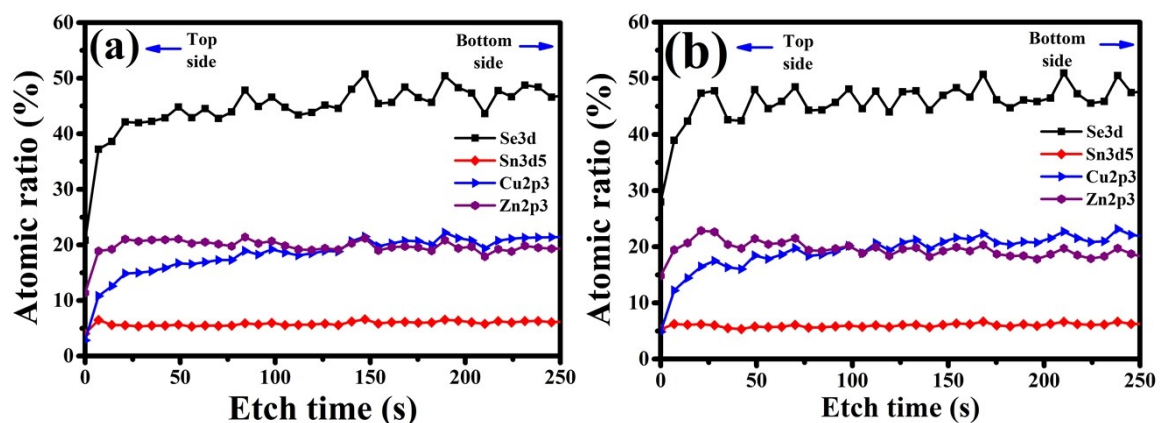


Fig. S5. Quantitative XPS depth profiles for Samples A (a, CZTSe) and D (b, CZTSe/ZnSe NPs) by Ar ion etching process. Inserted top region is large sized grain from FE-SEM images in the Fig. 3.

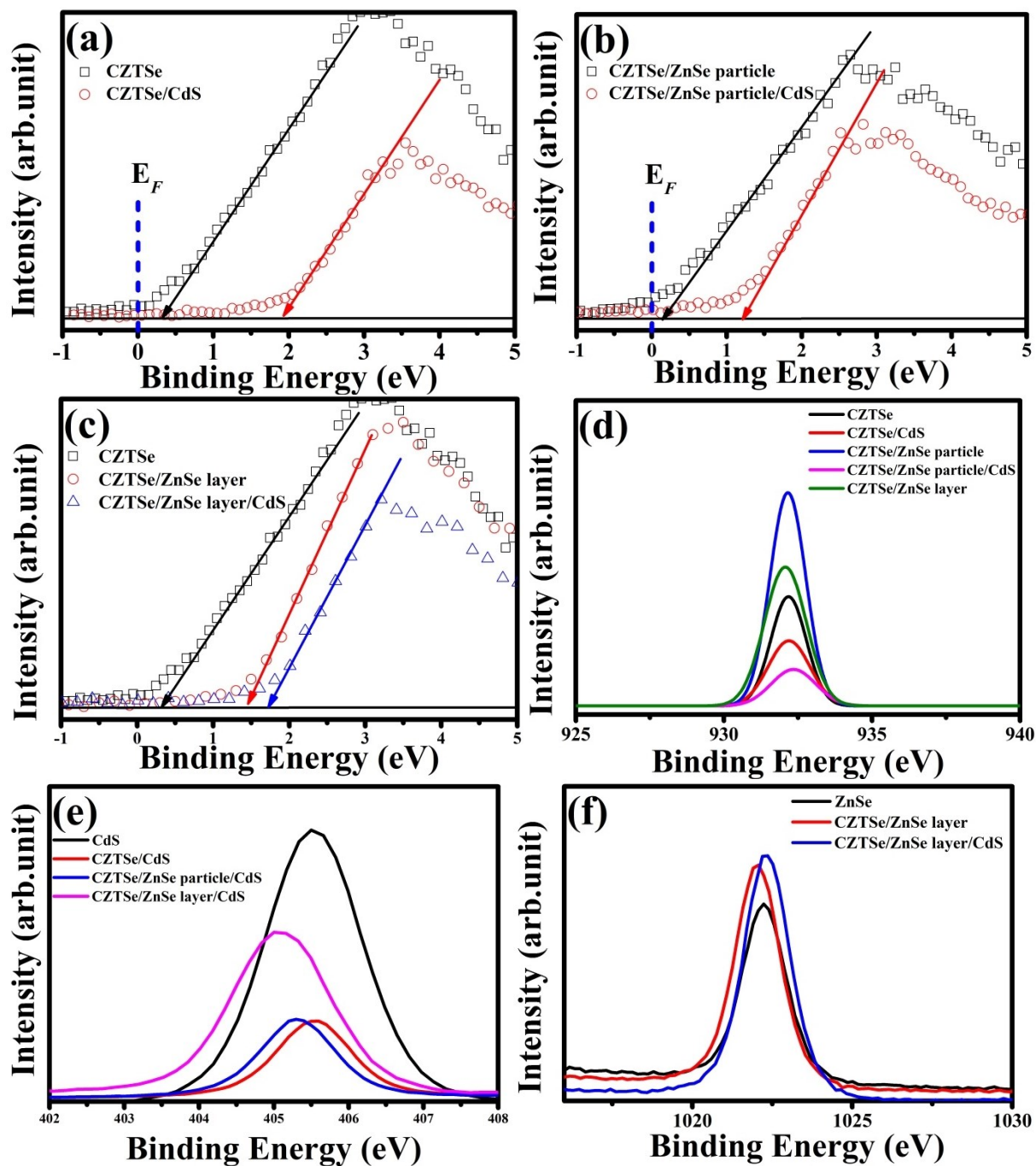


Fig. S6. ((a)~(c)) Valance band XPS spectra, (d) Cu $2p$ core levels, (e) Cd $3d$ core levels, and (f) Zn $2p$ core levels of CZTSe, CZTSe/CdS, CZTSe/ZnSe NPs, CZTSe/ZnSe NPs/CdS, CZTSe/ZnSe layer, CZTSe/ZnSe layer/CdS from the Samples A and D.

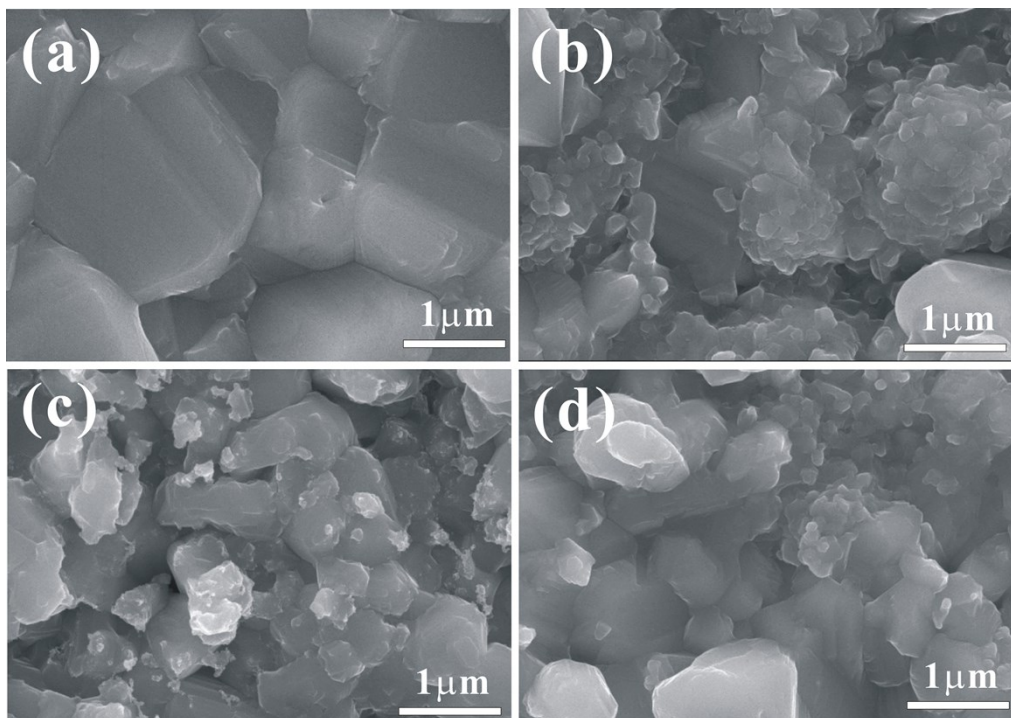


Fig. S7. Surface FE-SEM images of CZTSe thin films using Zn located on top of metallic precursors with different thickness of top Zn layer; (a) 0 nm (Sample A), (b) 20 nm (Sample C) (c) 50 nm, and (d) 75 nm, respectively.

Table S1. Sample names with different type of stacking orders.

Sample names	Thickness of each layer
A (Cu/Sn/Zn/Mo)	Mo/Zn(~180 nm)/Sn(~230 nm)/Cu(~170 nm)
B (Cu/Sn/Zn/Sn/Cu/Mo)	Mo/Cu(~10 nm)/Sn(~13 nm)/Zn(~180 nm)/Sn(~217 nm)/Cu(~160 nm)
C (Zn/Cu/Sn/Zn/Mo)	Mo/Zn(~160 nm)/Sn(~230 nm)/Cu(~170 nm)/Zn(~20 nm)
D (Zn/Cu/Sn/Zn/Sn/Cu/Mo)	Mo/Cu(~10 nm)/Sn(~13 nm)/Zn(~160 nm)/Sn(~217 nm)/Cu(~160 nm)/Zn(~20 nm)

Table S2. The compositional ratio for CZTSe thin films after annealing process determined from XRF characterization

Sample names	Cu/ (Zn+Sn)	Cu/Sn	Zn/Sn
A	0.63	1.34	1.13
B	0.64	1.35	1.10
C	0.65	1.35	1.08
D	0.63	1.31	1.06

Table S3. Summarized and calculated parameters for each sample obtained from XPS characterizations, optical band gap energies from EQE and UV-vis characterizations, and calculated of E_{VBM} , ΔE_{V} , V_{bb} , and ΔE_{C} , respectively.

Materials	$E_{\text{Cu}} 2p_{3/2}$ (eV)	$E_{\text{Cd}} 3d_{5/2}$ (eV)	$E_{\text{Zn}} 2p_{3/2}$ (eV)	E_{g} (eV)	E_{VBM} (eV)	V_{bb} (eV)	ΔE_{V} (eV)	ΔE_{C} (eV)
Bulk CZTSe	932.17	.	.	0.984	0.34	.	.	.
Bulk CdS	.	405.5	.	2.4	1.927	.	.	.
Bulk ZnSe	.	.	1022.26	2.7	1.44	.	.	.
CZTSe/CdS	932.26	405.59	.	.	.	-0.18	-1.407	+0.01
CZTSe/ZnSe NPs	932.14	.	.	0.954	0.144	.	.	.
CZTSe/ZnSe NPs/CdS	931.99	405.55	.	.	.	+0.1	-1.186	+0.26
ZnSe layer/CdS	.	405.5	1022.38	.	1.63.	-0.3	+0.11	-0.3
CZTSe/ZnSe layer	932.63	.	1022.06	.	.	-0.38	+0.74	+0.976

Reference

1. Y.-F. Qi, D.-X. Kou, W.-H. Zhou, Z.-J. Zhou, Q.-W. Tian, Y.-N. Meng, X.-S. Liu, Z.-L. Du and S.-X. Wu, *Energy Environ. Sci.*, 2017, **10**, 2401-2410.