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Solution Route for Efficient Kesterite and Chalcopyrite Thin Film Solar Cells

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2026-4-07
UNSW Sydney

Outline

I. Motivation

II. Kesterite Solar Cells

CZTSSe

Absorber Engineering

Interface Engineering

Module

CZTS

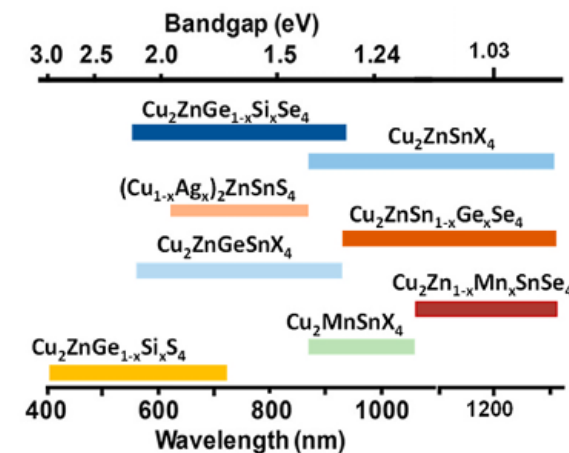
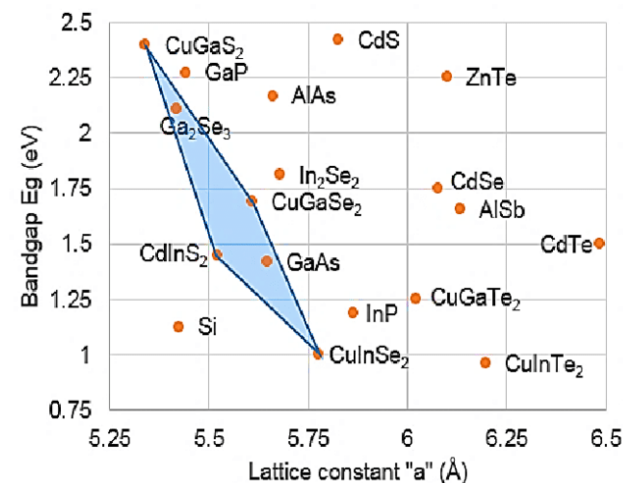
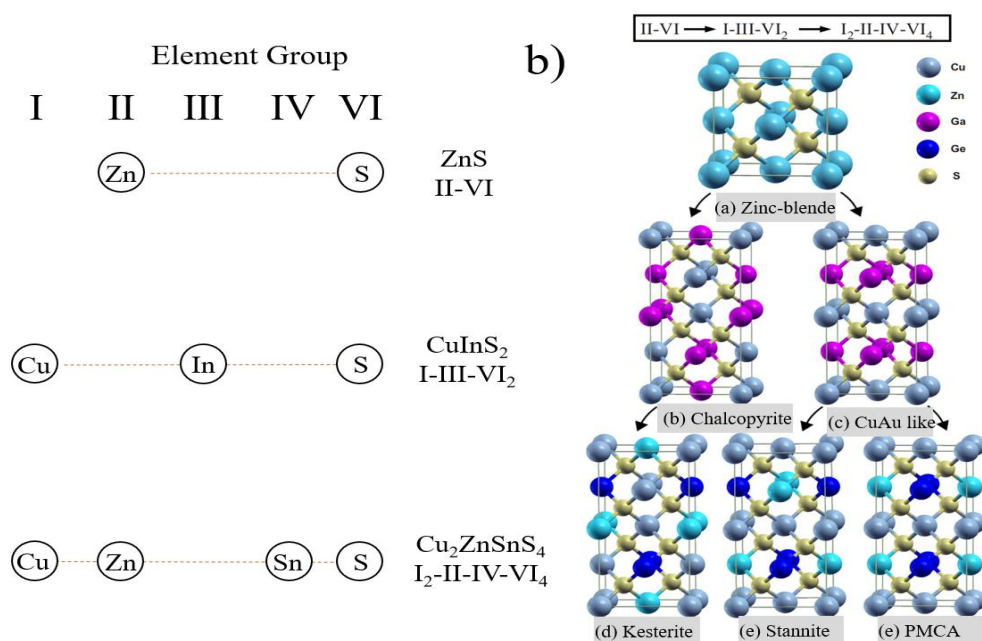
III. Chalcopyrite Solar Cells

CIGSSe

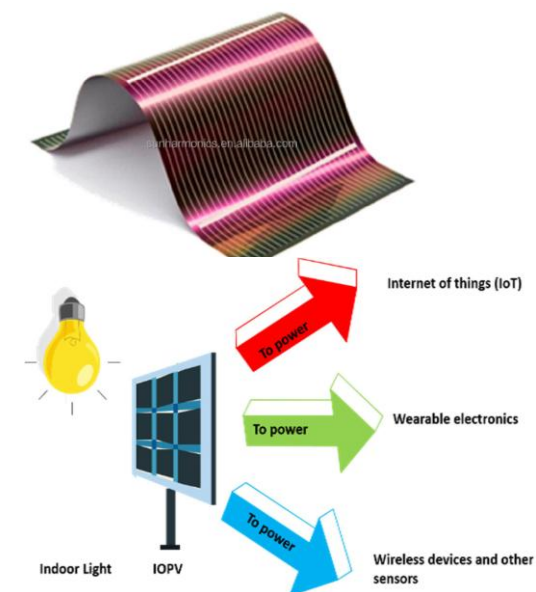
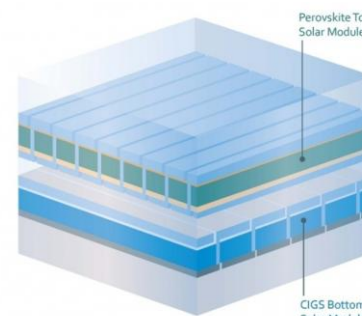
CIGS

V. Summary and Outlook

CIGS/CZTS Thin Film Solar Cells: Motivations



- High stability and non-toxic
- Tunable band gap: 0.90-2.5 eV (Top and bottom cell for tandem)
- On transparent substrate
- On flexible substrate



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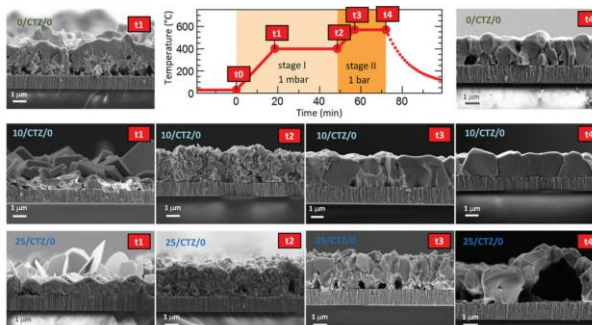
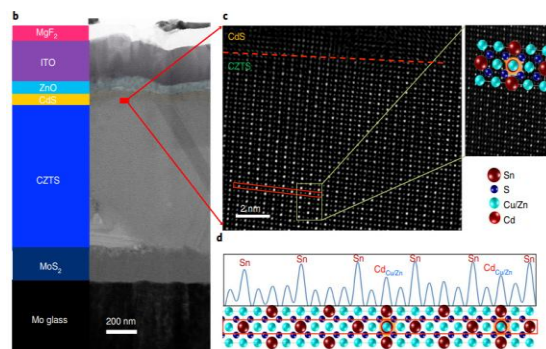
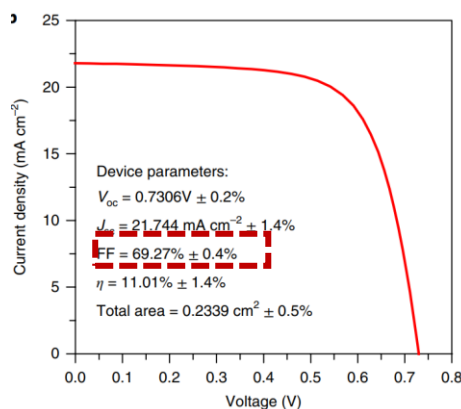
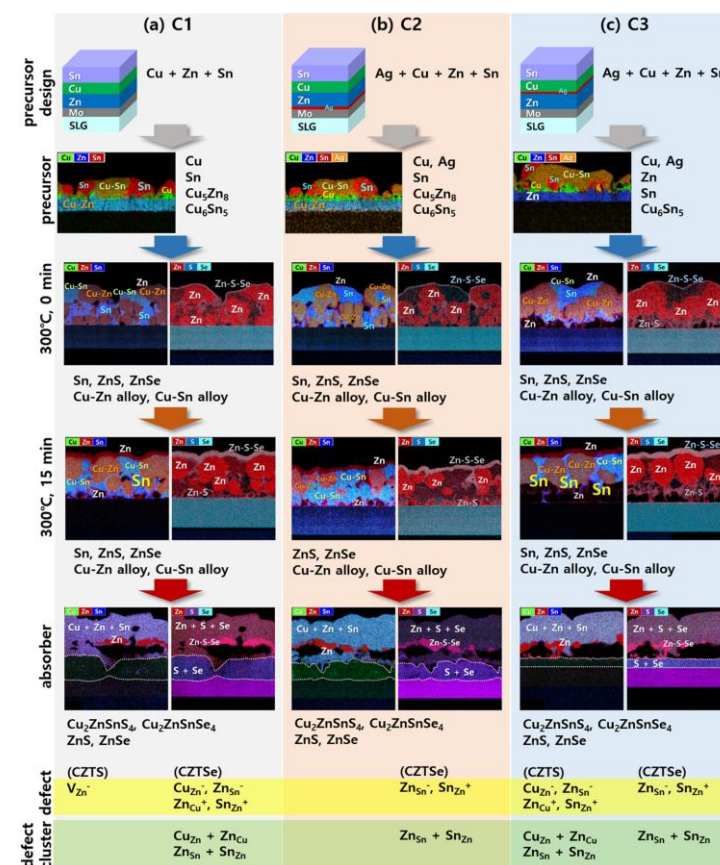
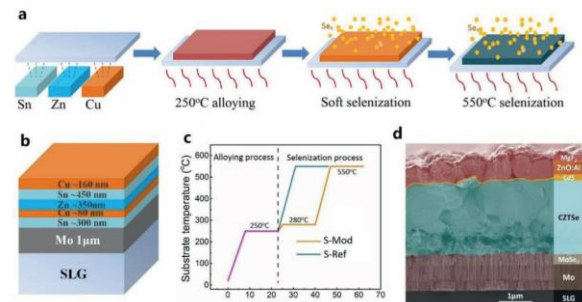
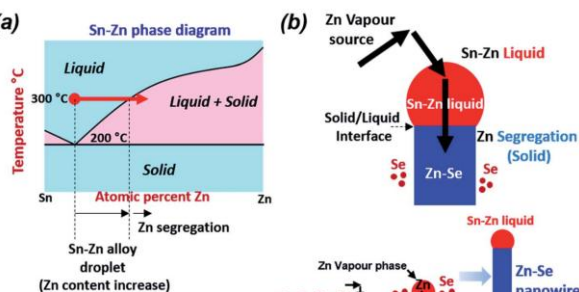
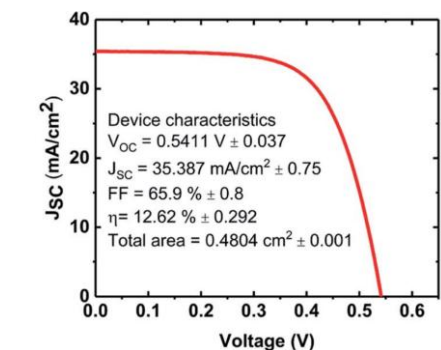
CIGS

V. Summary and Outlook

Fabrication of Kesterite: Vacuum vs Solution

NREL, UNSW, IREC, DGIST, JAIST, CNU, UPC, etc.

Precursors: Metal (Cu/Zn/Sn), sulfide/selenide (SnS, ZnS)



Son D H, Kim S H, Kim S Y, et al. Journal of Materials Chemistry A, 2019, 7, 25279.

Li J, Huang Y, Huang J, et al. Advanced Materials, 2020, 32, 2005268.

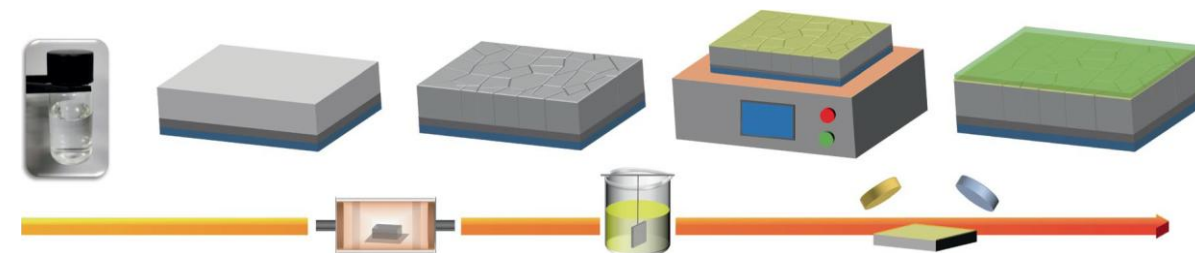
Kim, S, et al. EES, 2024, 17, 8609-8620. (DGIST)

Yan C, Huang J, Sun K, et al. Nature Energy, 2018, 3, 764.

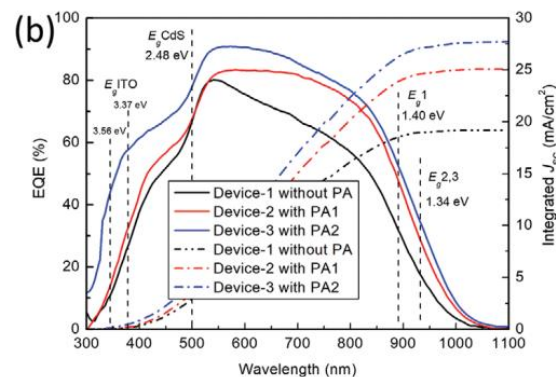
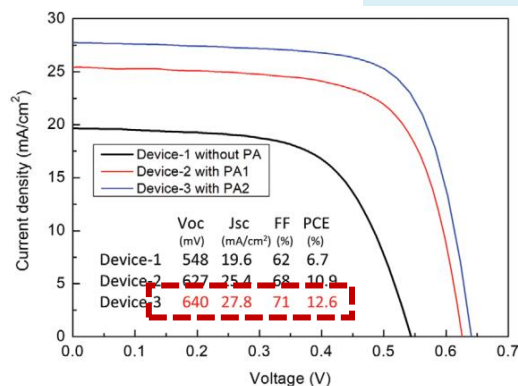
5 Giraldo S, Saucedo E, Neuschitzer M, et al. Energy & Environmental Science, 2018, 11, 582.

Fabrication of Kesterite: Solution

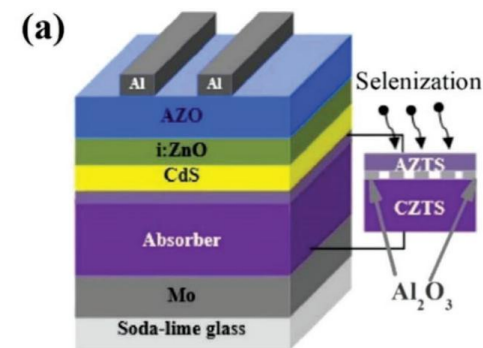
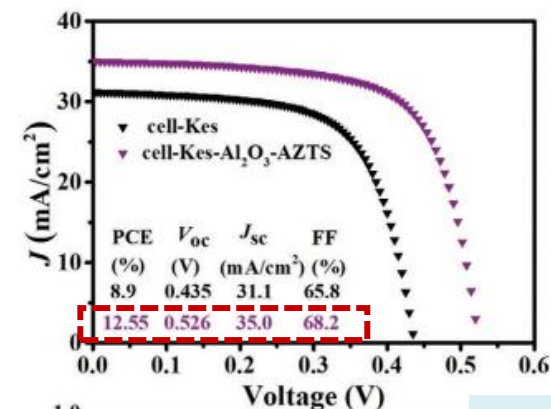
Precursors: metal oxides, metal salts + S source



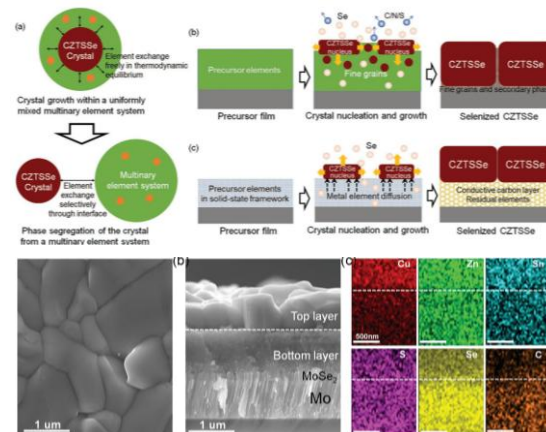
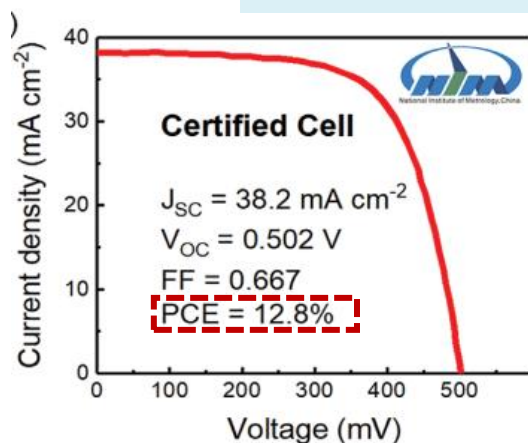
2-methoxyethanol (MOE)



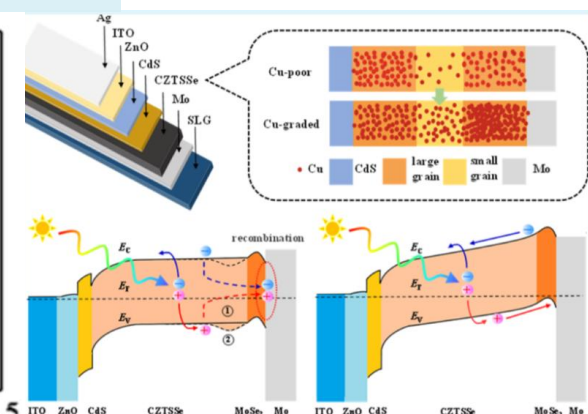
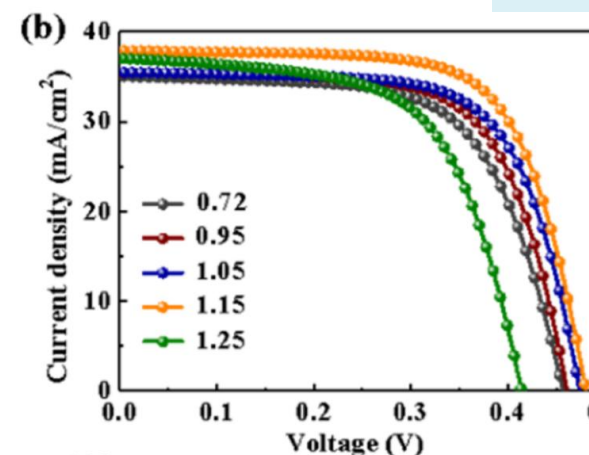
DMSO



TGA-ammonia



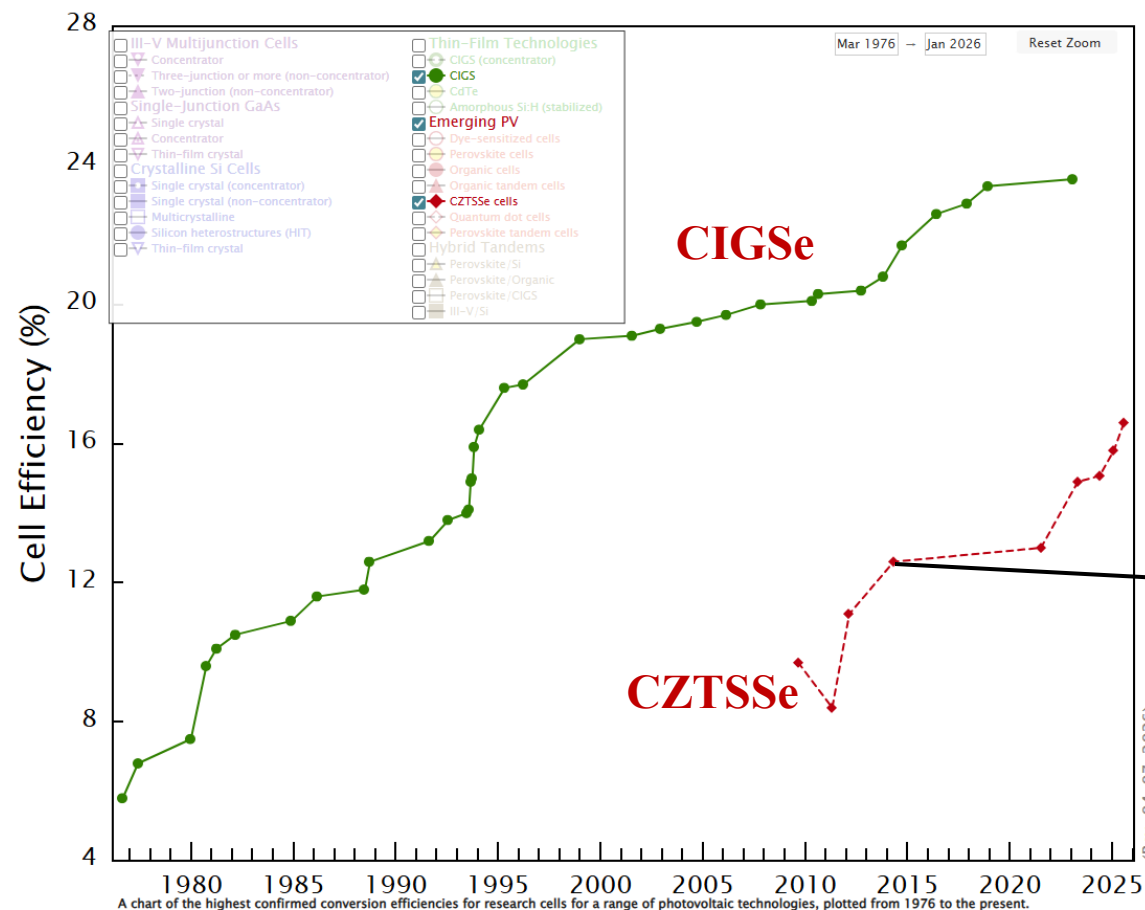
amine-thiol



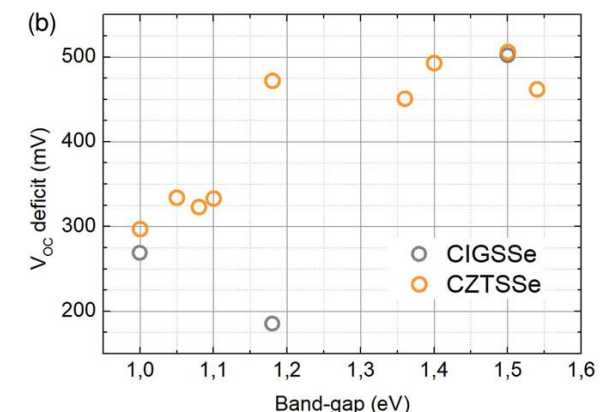
Kesterite Thin Film Solar Cells: Challenges

Large V_{oc} deficit: $V_{oc,def} = V_{oc}^{SQ} - V_{oc}$ V_{oc}/V_{oc}^{SQ}

Best Research-Cell Efficiencies

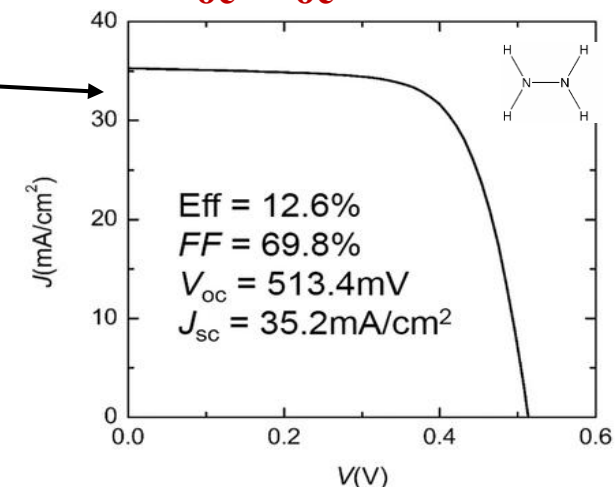


The chart displays record research cell efficiencies for five major technologies: crystalline silicon cells, single-junction gallium arsenide cells, multijunction cells, thin films, and emerging PV. Efficiencies have increased across all technologies over the last 50 years.



Giraldo, et al. *Adv. Mater.* 2019.

$V_{oc}/V_{oc}^{SQ} : 0.57$



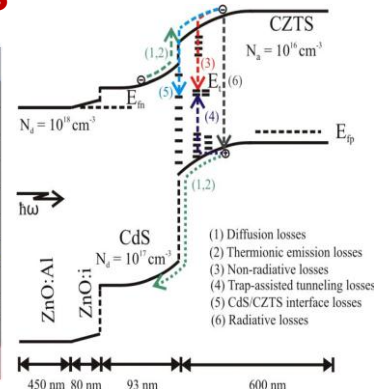
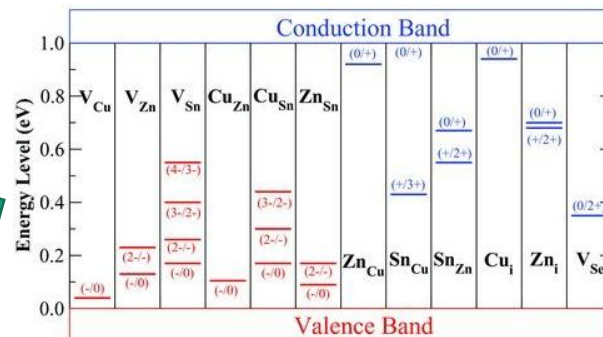
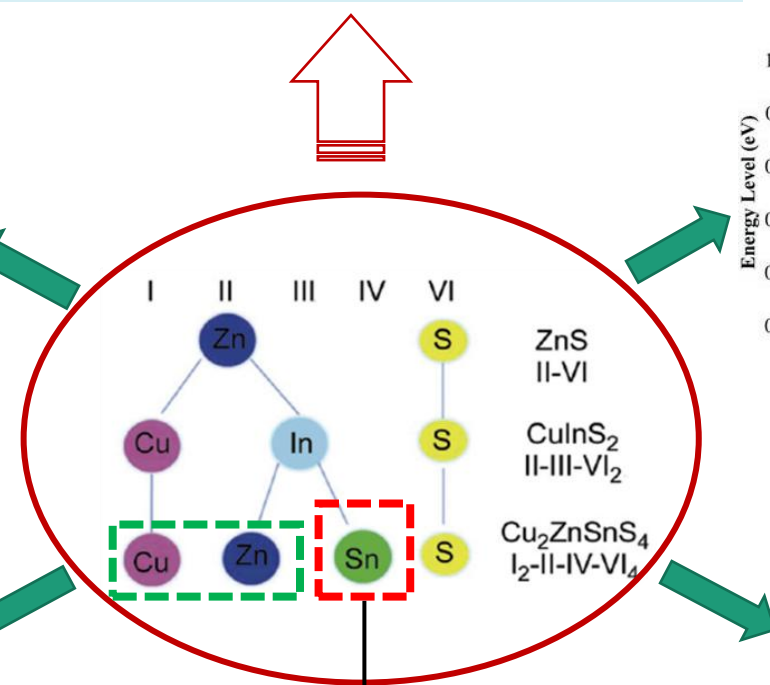
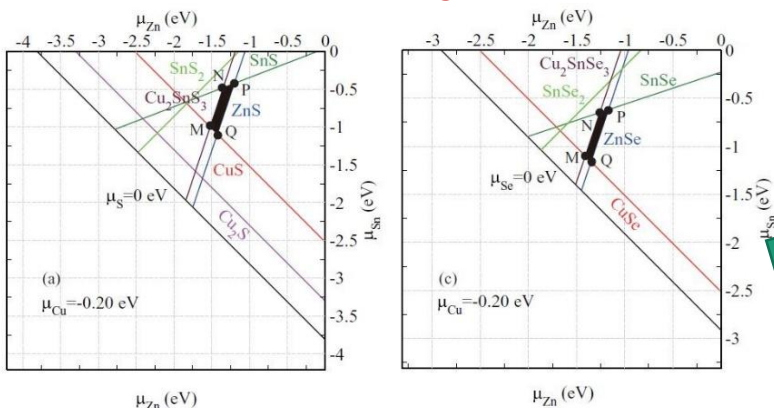
Mitzi, et al. *Adv. Energy Mater.* 2013.

Possible Reasons for Large V_{oc-def}

Absorber Fabrication
precursor film $\rightarrow$ absorber film

Secondary phases

Deep defects

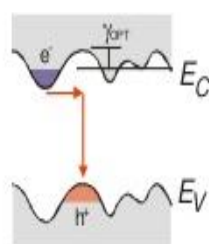
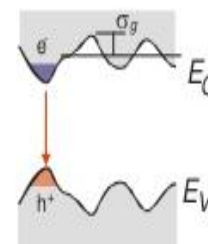


Cu-Zn disorder

Band tailing

Band gap Fluctuations

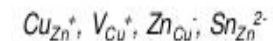
Electrostatic Potential Fluctuations



Cu/Sn: two oxidation states

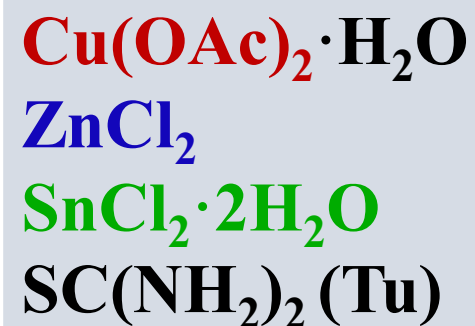
Causes : Competition between kesterite and stannite phase, secondary phases, non-uniform S/(S+Se), non-uniform strain

Causes : Charged defects

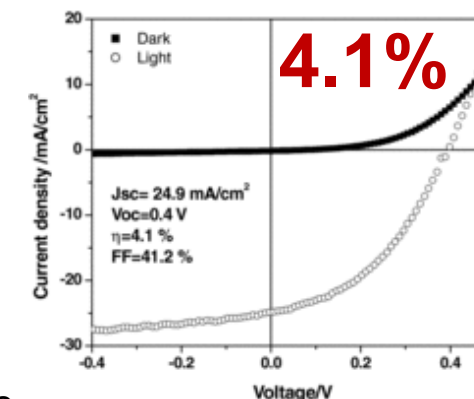
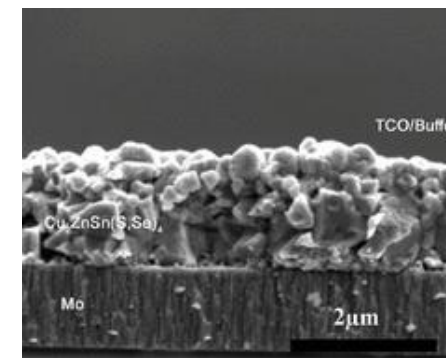


Absorber Engineering (DMSO Solution)

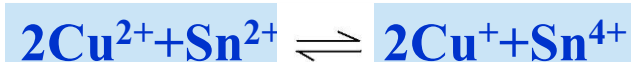
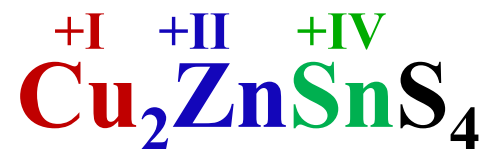
DMSO Molecular Precursor Solution Approach



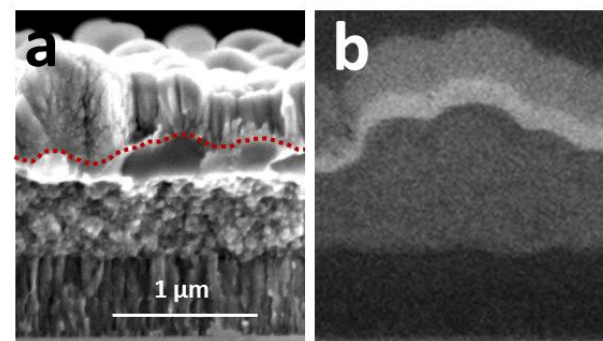
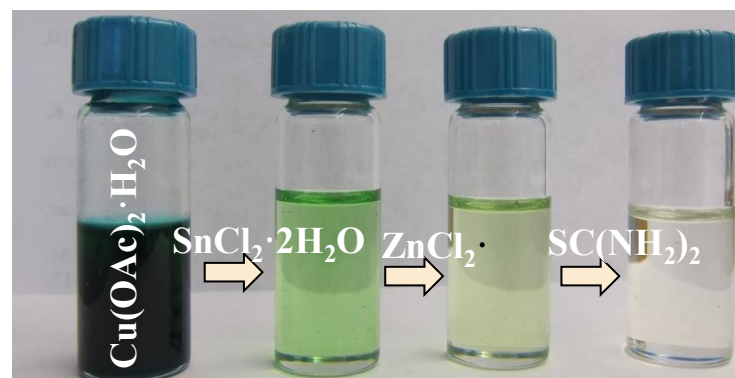
DMSO



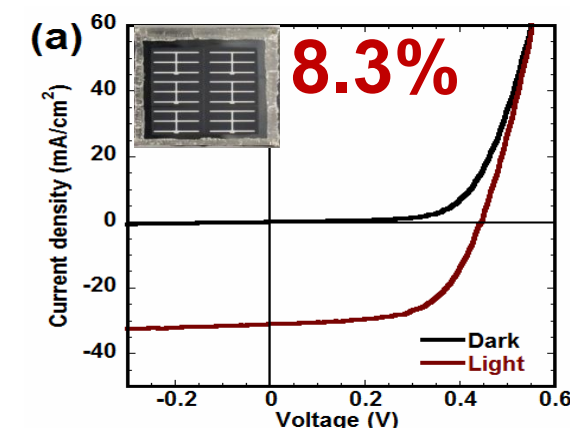
Ki and Hillhouse, *Adv. Energy Mater.* 2011, 732.



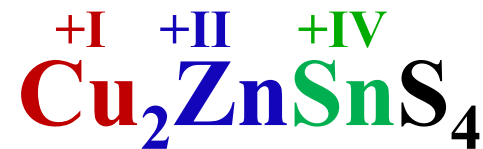
Controlling redox reaction



$V_{oc,def} : 0.424 \text{ V}$
 $V_{oc}/V_{oc}^{SQ} : 0.51$

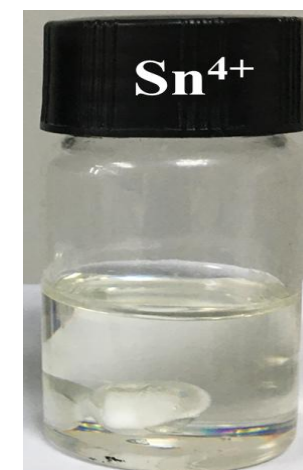


Controlling Tin Oxidation State: Sn^{2+} vs Sn^{4+}



CuCl , ZnCl_2 , $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, Tu

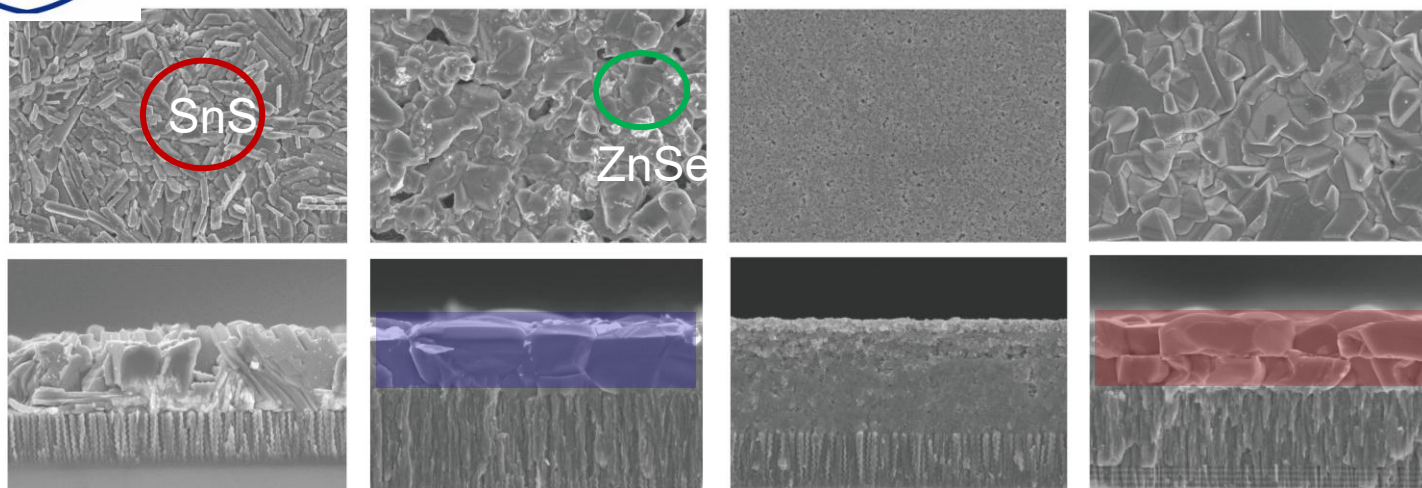
CuCl , $\text{Zn}(\text{OAc})_2$, SnCl_4 , Tu



Sn²⁺ vs Sn⁴⁺

Sn²⁺

Sn⁴⁺



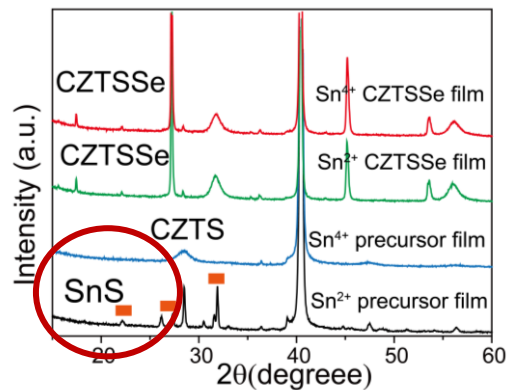
Sn²⁺ precursor film

Sn²⁺ CZTSSe film

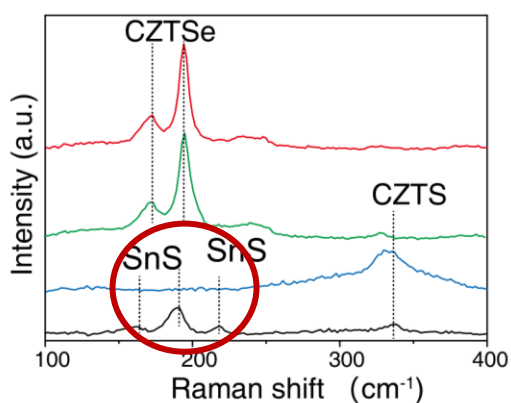
Sn⁴⁺ precursor film

Sn⁴⁺ CZTSSe film

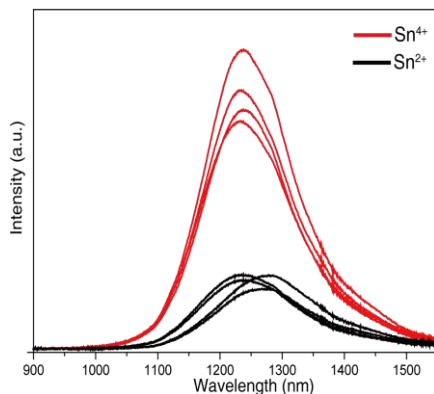
XRD



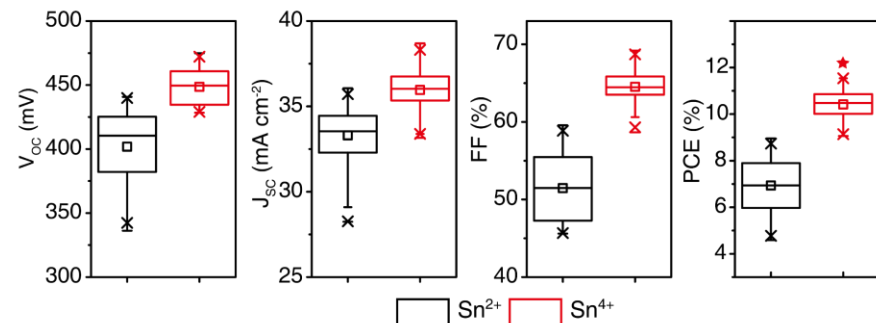
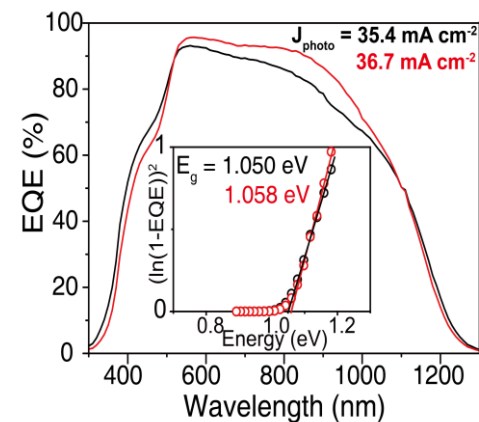
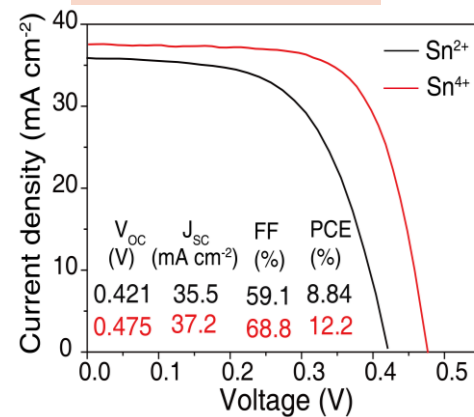
Raman



PL



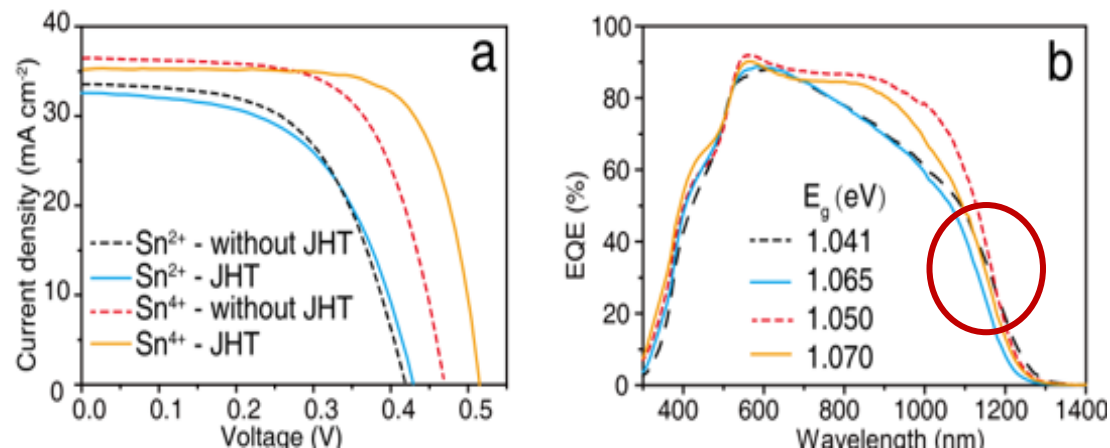
$\Delta V_{oc} = 54 \text{ mV}$



- Dramatic difference in composition and morphology of the precursor films
- Sn⁴⁺ shows high uniformity
- Sn⁴⁺ device has much high V_{oc}

Junction Heat Treatment (JHT)

JHT (200°C/20 h, vacuum)



Sn²⁺

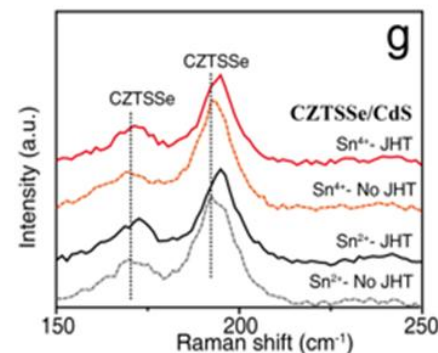
E_g : increase 24 meV
 J_{sc} : decrease
 V_{oc} : equal to E_g increase
FF: no obvious change

Sn⁴⁺

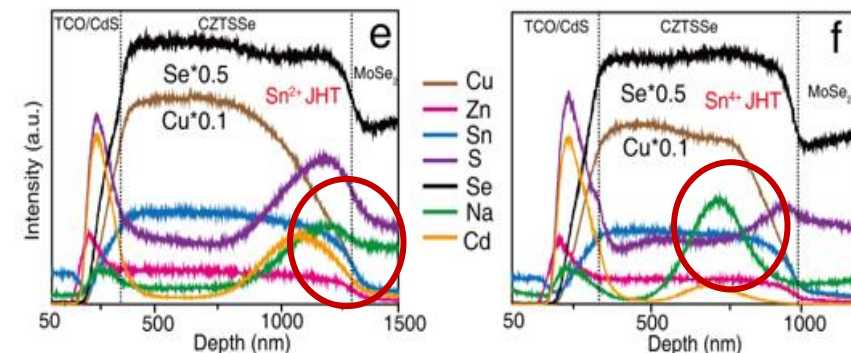
E_g : increase 20 meV
 J_{sc} : decrease
 V_{oc} : enhance 50 mV
FF: increase

V_{oc} directly related to the oxidation state of the Sn precursor

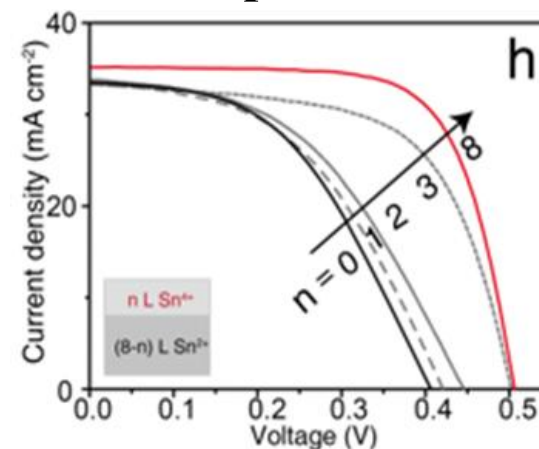
Raman



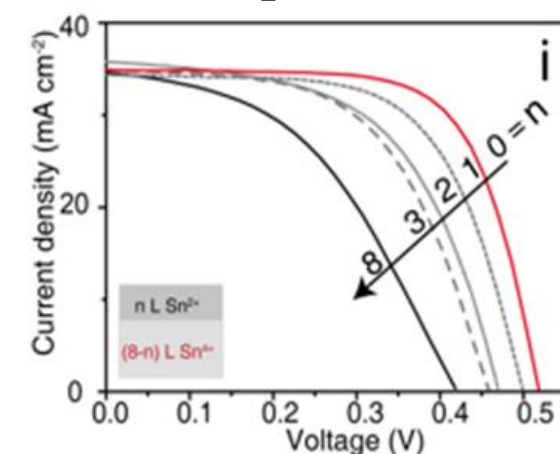
GDOES



Top Sn⁴⁺

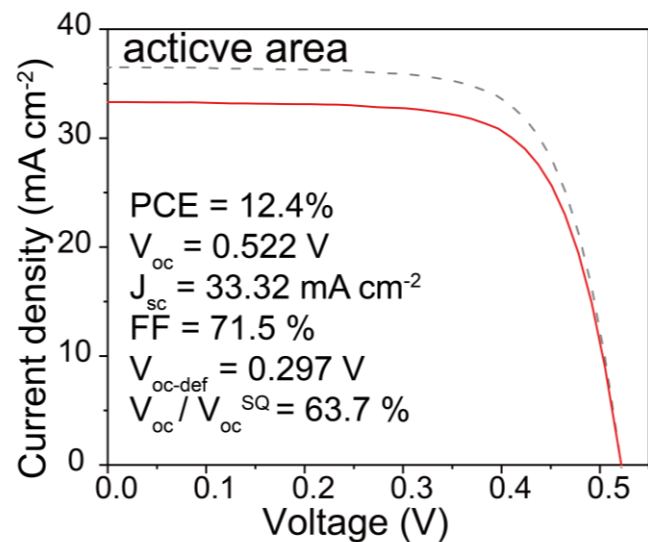


Top Sn²⁺



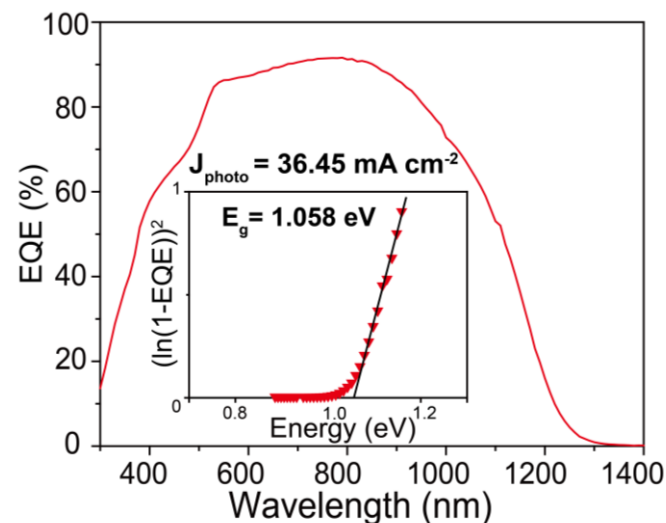
- Order level similarly improved upon JHT
- Large Cd and S diffuse into film
- **Surface property is more important**

Champion CZTSSe Device from Sn^{4+} DMSO Solution



Total area: 12.4%
Active area: 13.6%

$V_{oc,def} : 0.297 \text{ V}$
 $V_{oc}/V_{oc}^{SQ} : 63.7\%$



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CZTSSe Cell

Device ID: NUPT-1

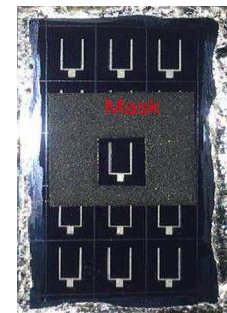
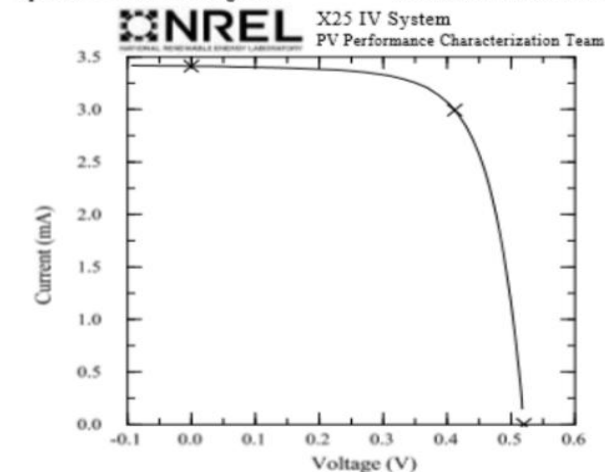
Nov 01, 2018 16:29

Spectrum: ASTM G173 global

Device Temperature: $24.5 \pm 0.6 \text{ }^\circ\text{C}$

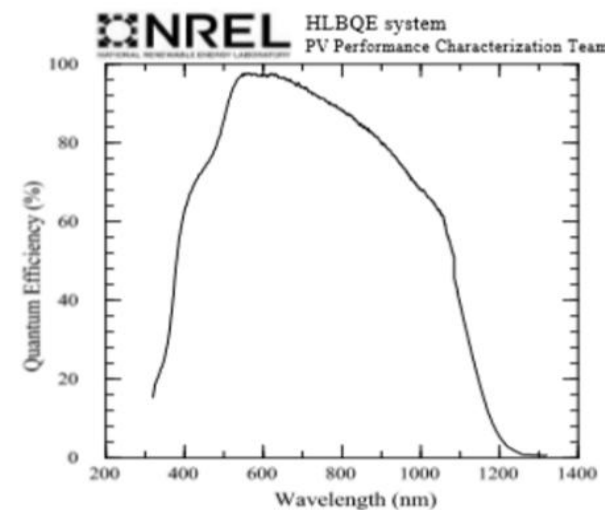
Device Area: $0.1066 \text{ cm}^2 \pm 0.4 \%$

Irradiance: 1000.0 W/m^2



Total area: 11.56%
Active area: 13.22%

$V_{oc,def} : 0.332 \text{ V}$
 $V_{oc}/V_{oc}^{SQ} : 0.61$



Identify the Origin of the V_{oc} deficit

Energy &
Environmental
Science



PAPER

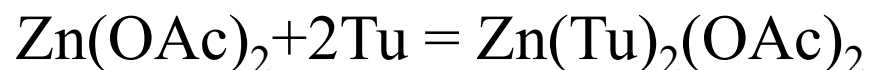
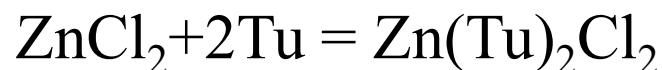
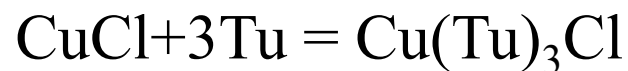
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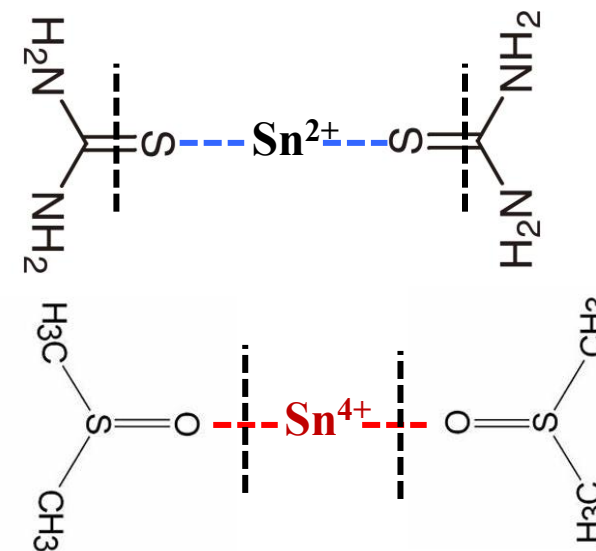
Cite this: *Energy Environ. Sci.*,
2021, 14, 2369

Identifying the origin of the V_{oc} deficit of kesterite solar cells from the two grain growth mechanisms induced by Sn^{2+} and Sn^{4+} precursors in DMSO solution†

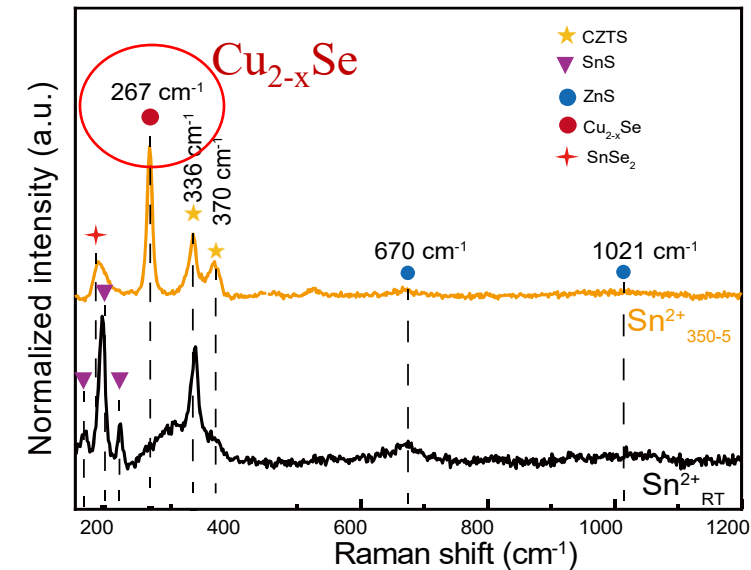
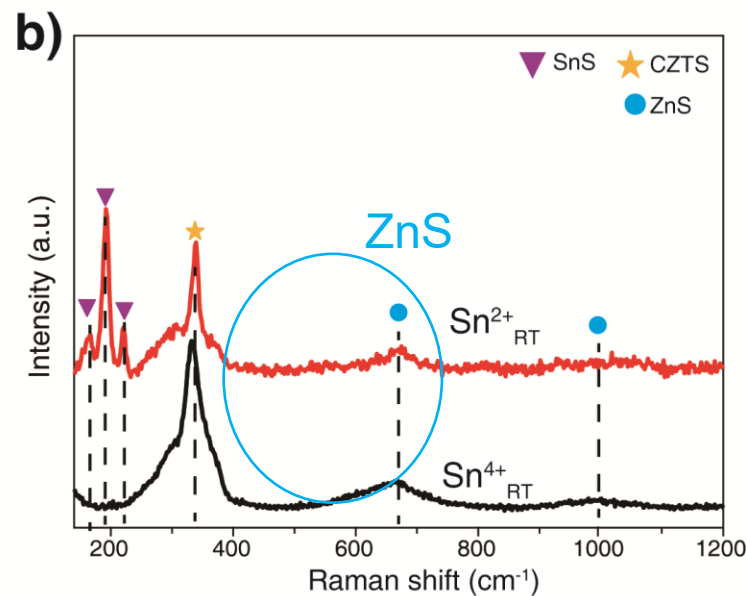
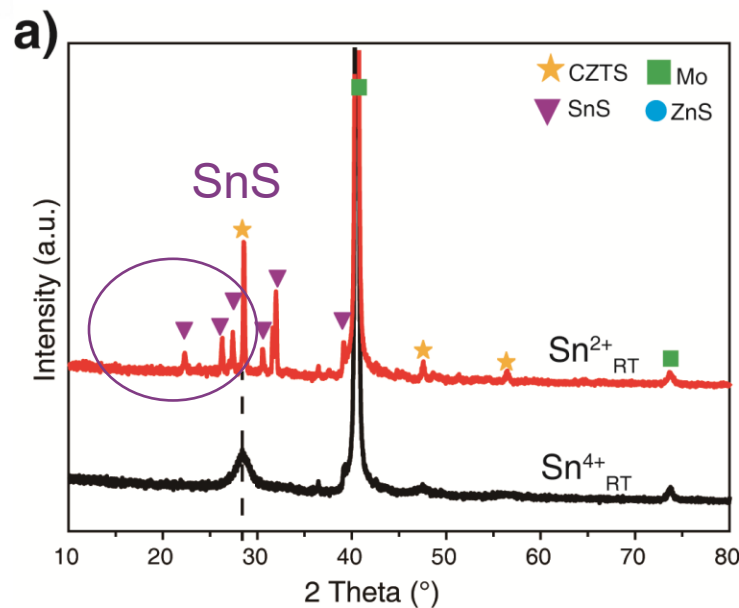
Reaction of each precursor in the DMSO solution with Tu



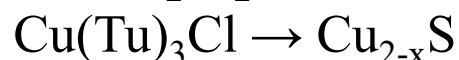
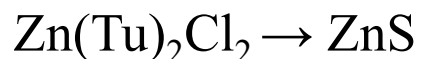
Reaction from solution to solid film



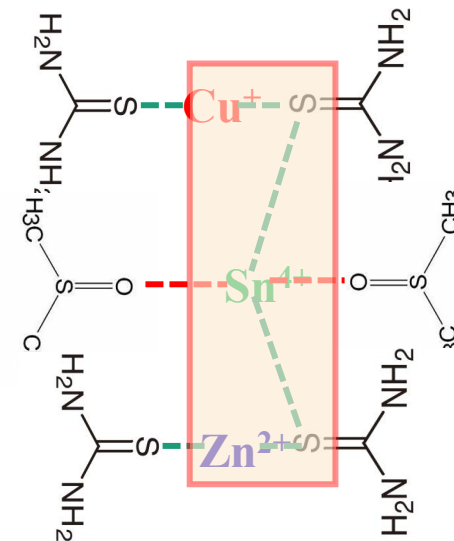
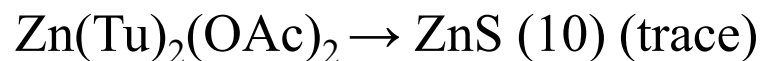
Reaction Paths from Solution to Precursor films



Sn²⁺ solution

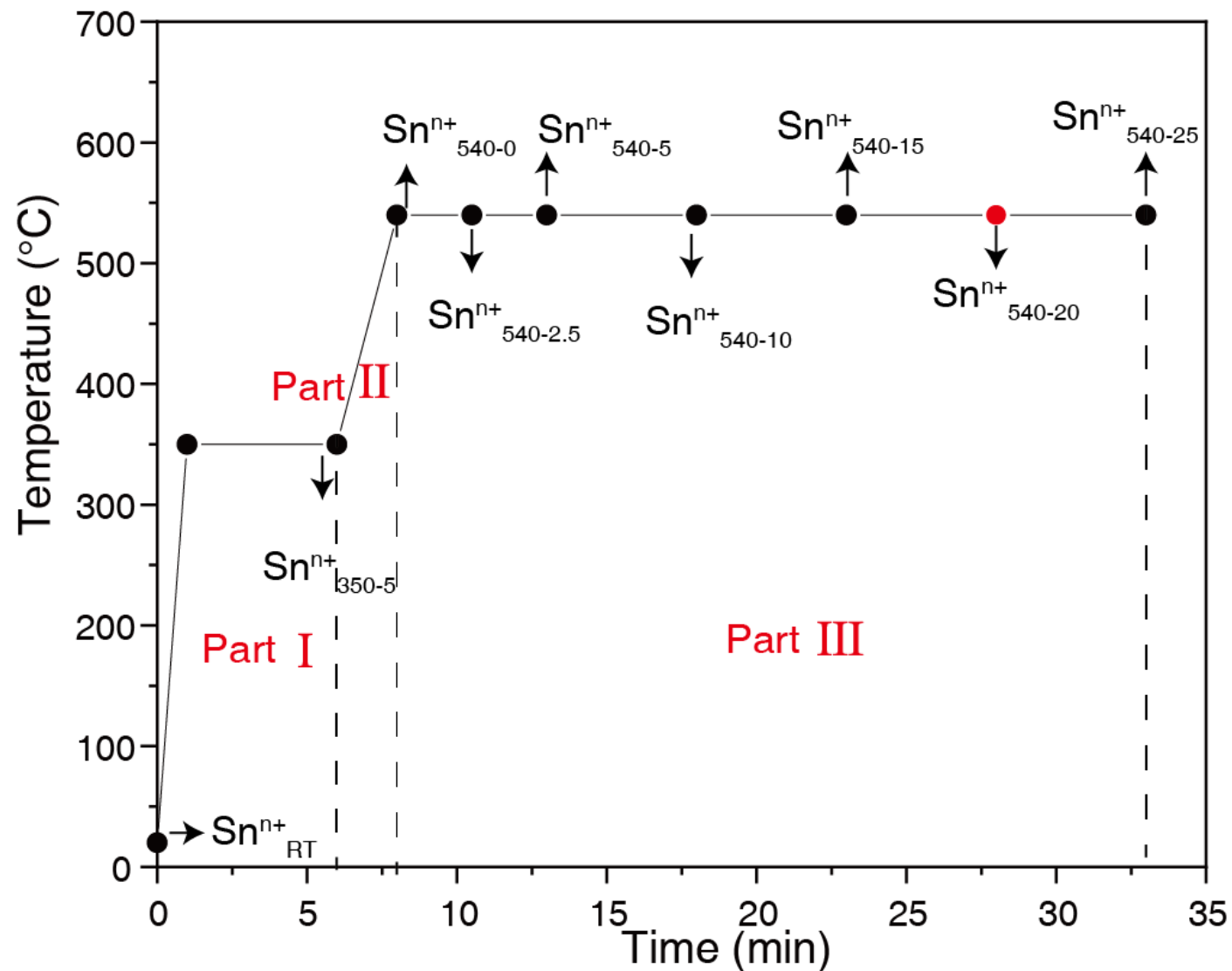


Sn⁴⁺ solution



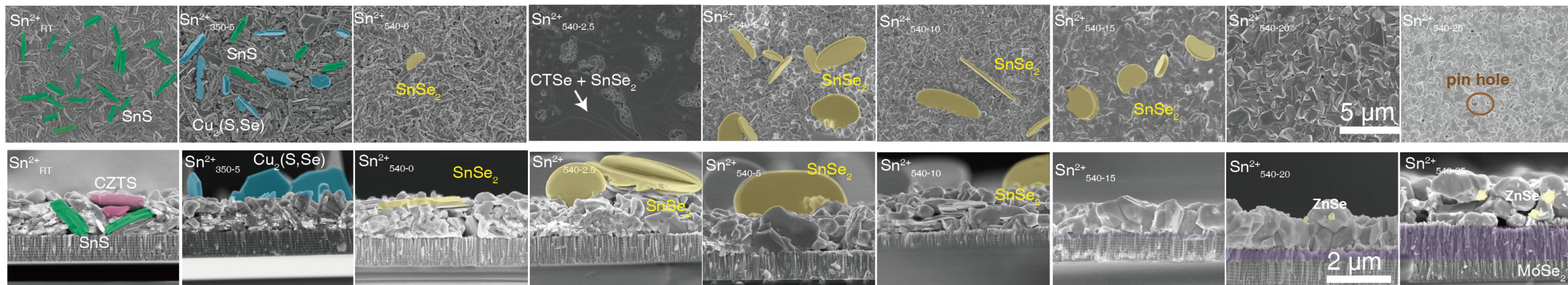
Grain Growth from Precursor Film to Absorber

Selenization profile

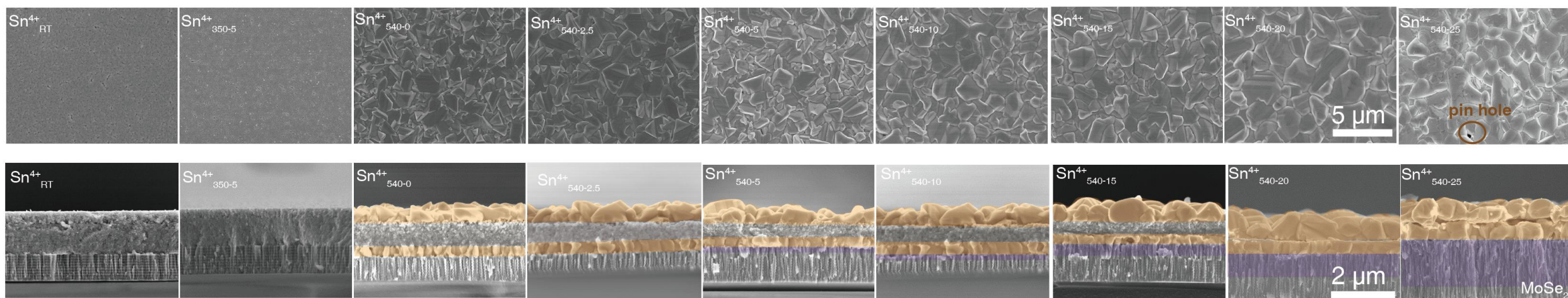


Grain Growth from Precursor Film to Absorber

Sn^{2+}

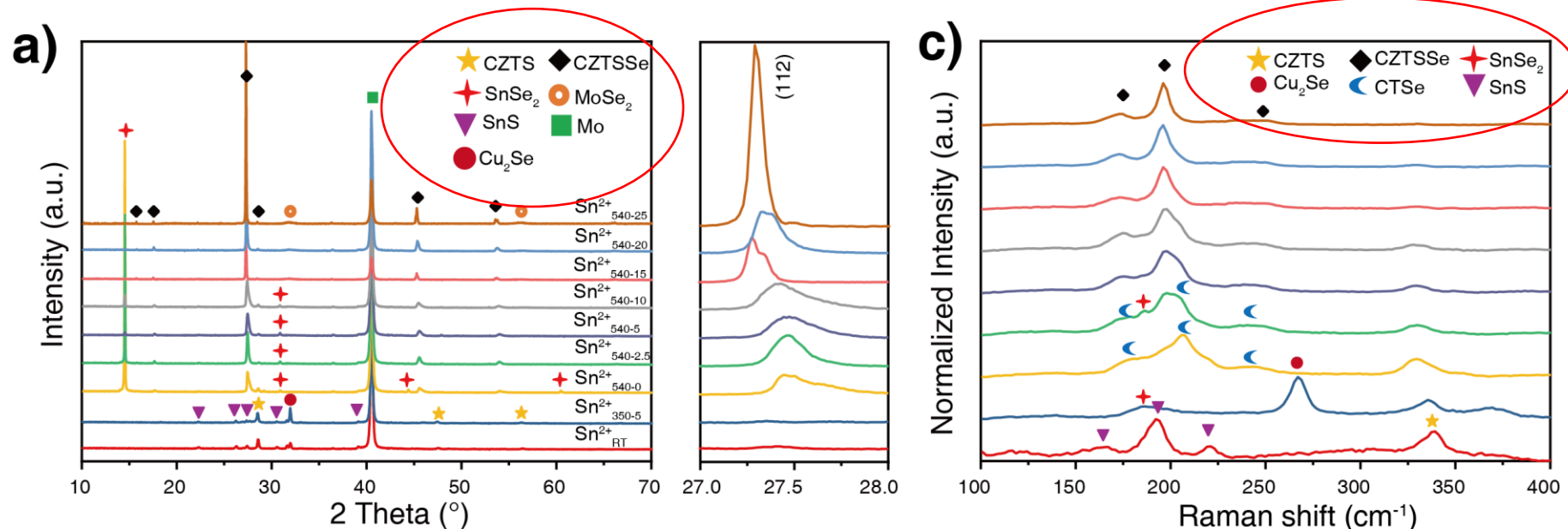


Sn^{4+}

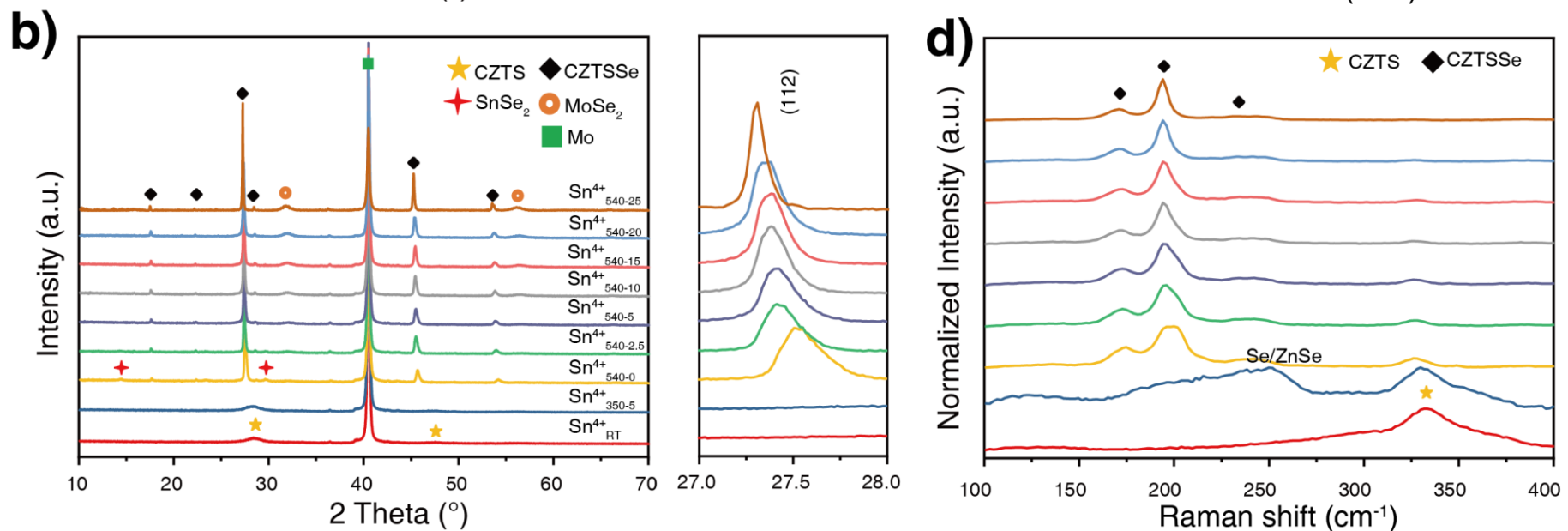


Grain Growth from Precursor Film to Absorber

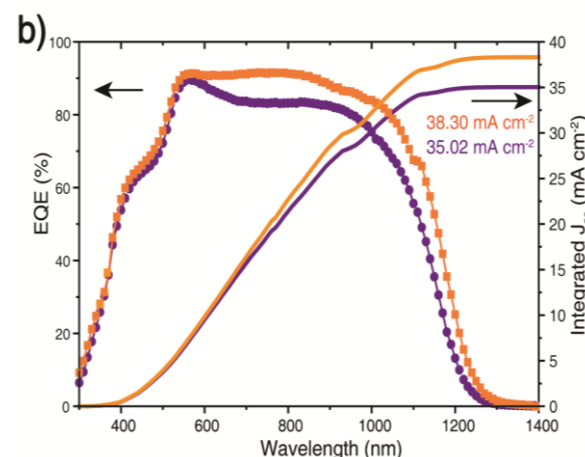
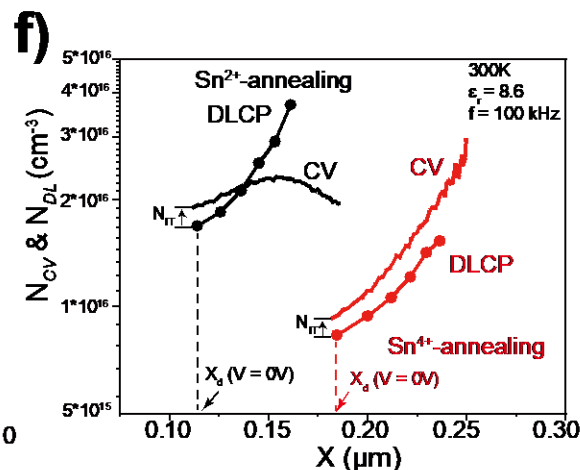
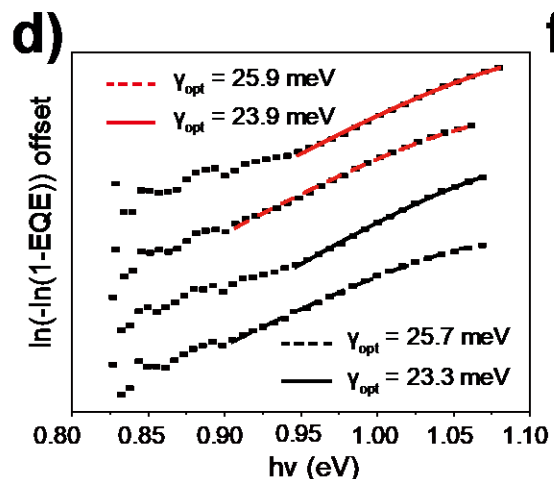
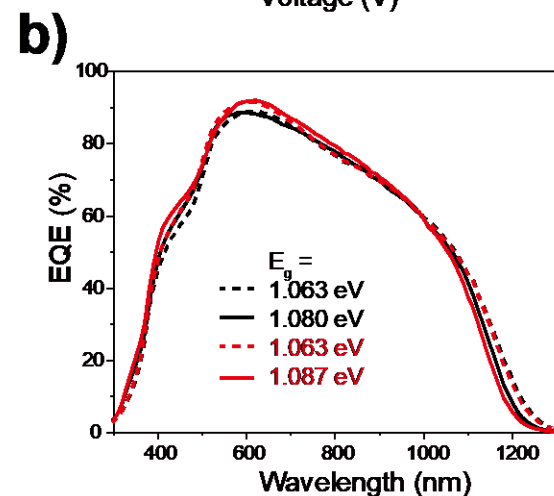
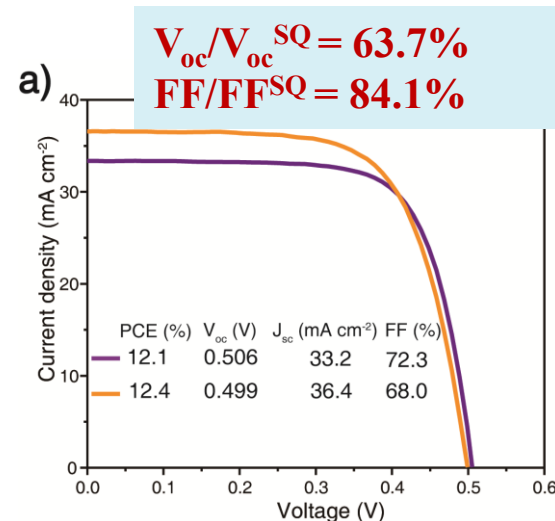
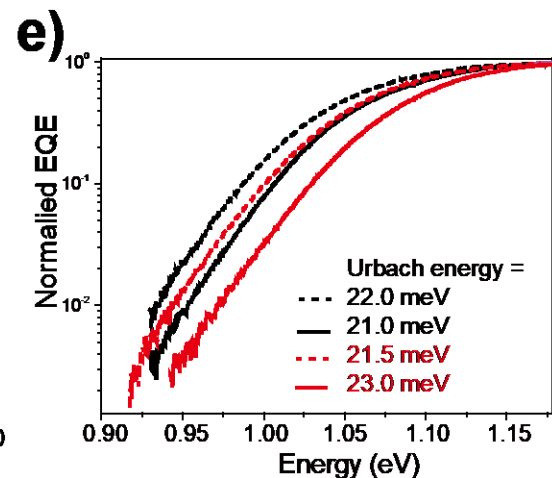
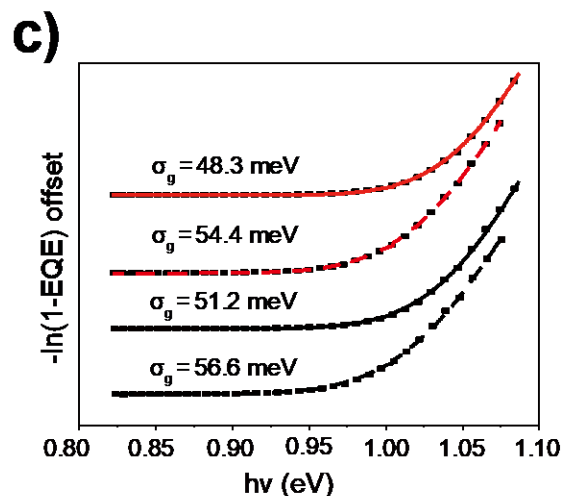
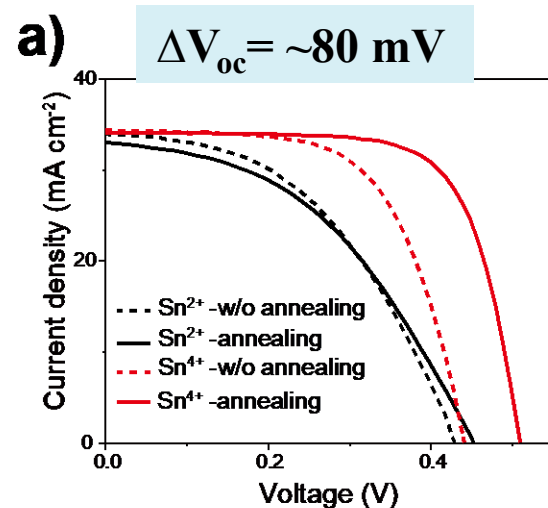
Sn^{2+}



Sn^{4+}



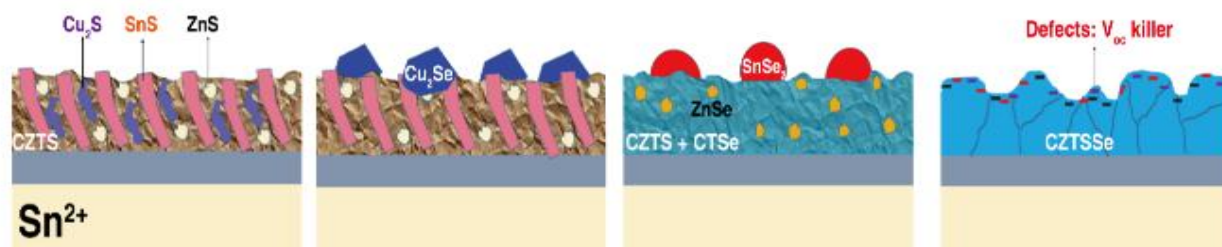
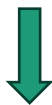
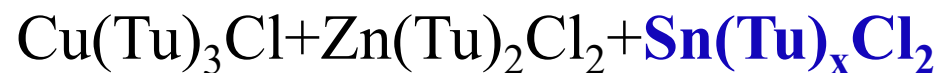
JHT on the Electronic Property of the Absorbers



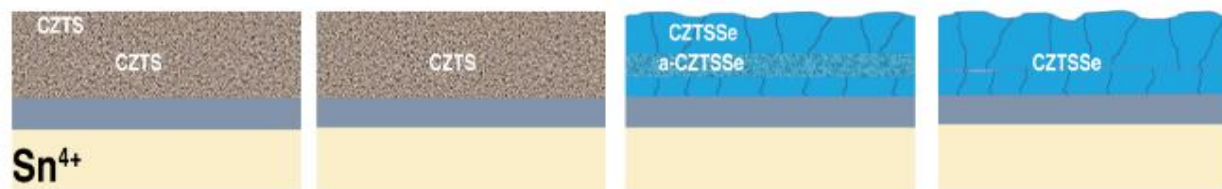
- Band gap (order level) similarly improved upon JHT
- Band tailing (E_U) does not show correlation to V_{oc}
- Charge carrier concentration (especially surface defects) significantly reduced
- Multi phase fusion grain growth produce defects (especially near the surface)

Two Reaction Paths to Absorber

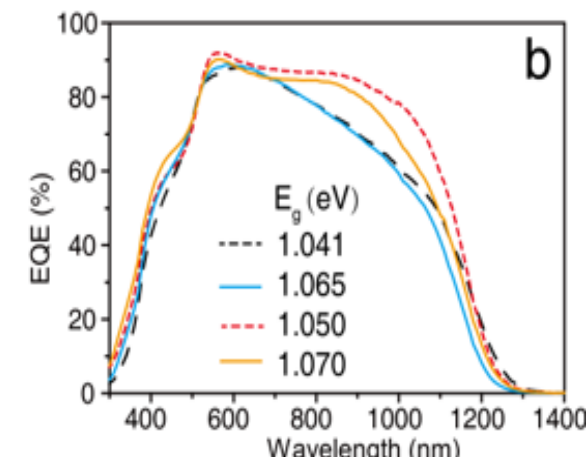
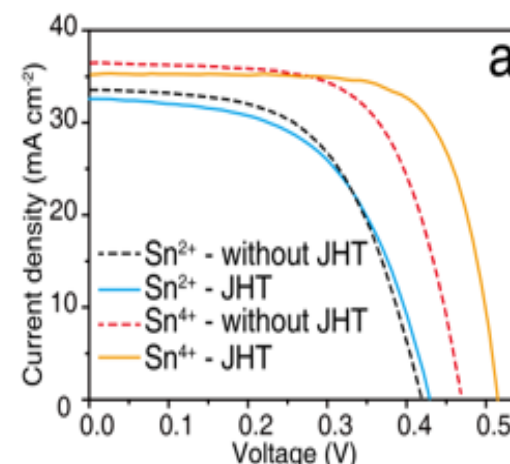
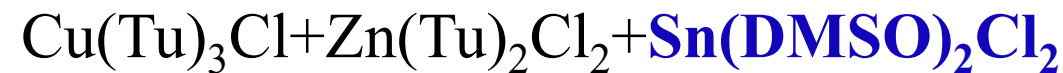
Sn²⁺: multi-phase fusion



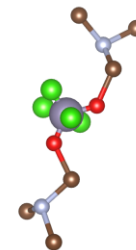
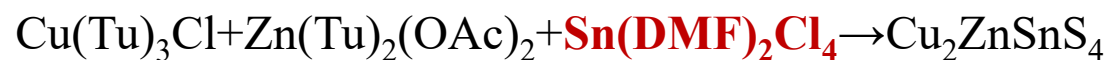
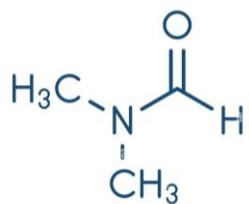
VS



Sn⁴⁺: direct phase transformation



Universal of the Direct Phase Transformation



Sn
O
Cl

Journal of
Materials Chemistry A

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Cite this: *J. Mater. Chem. A*, 2021, 9, 12981

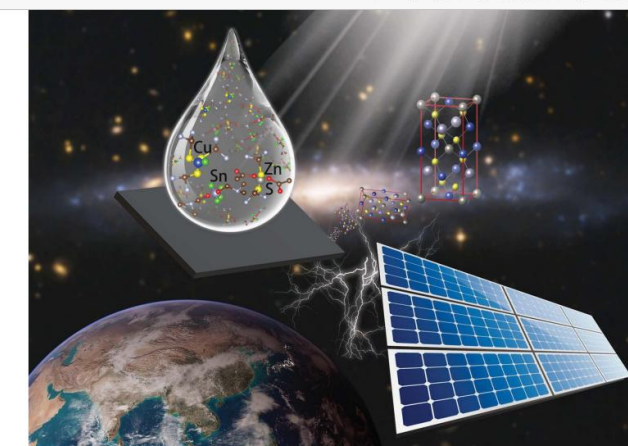
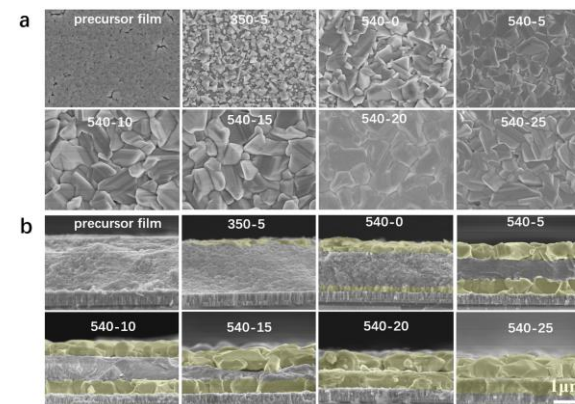
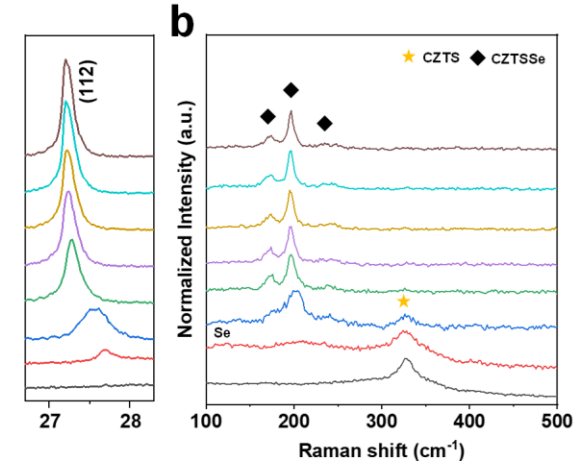
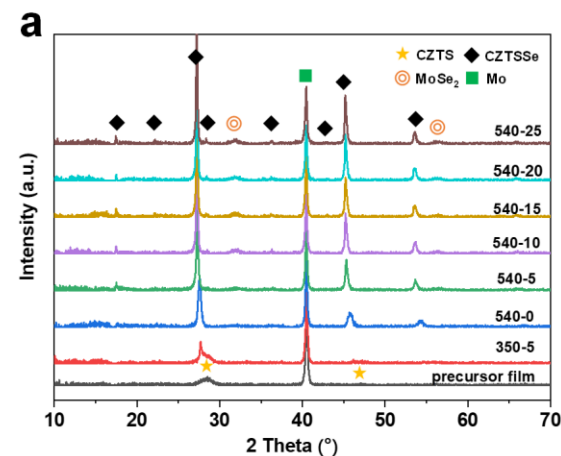
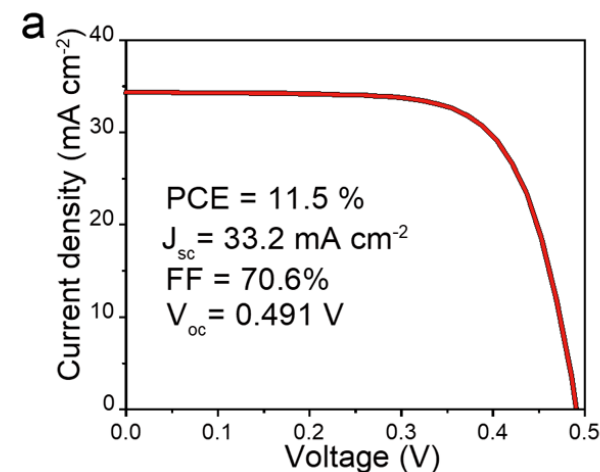
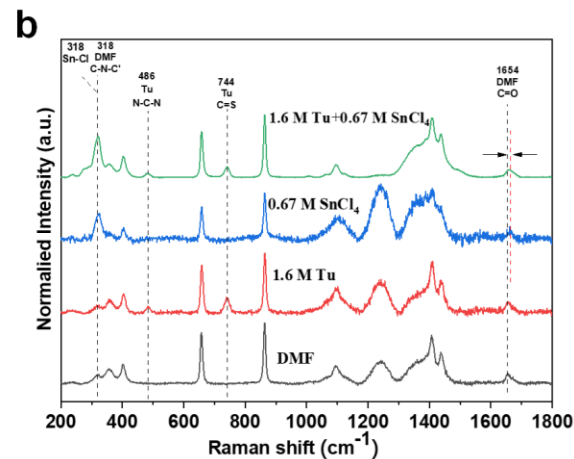
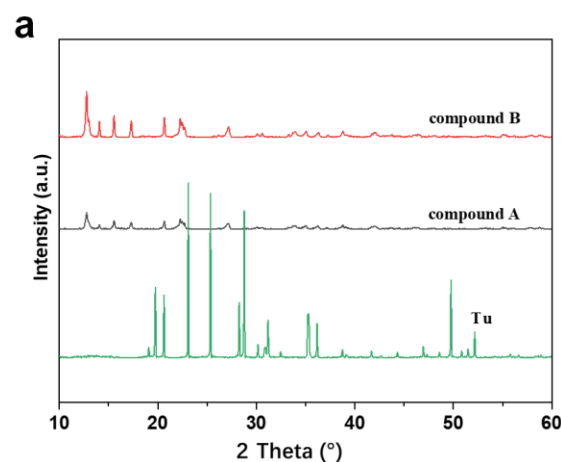
Received 3rd March 2021
Accepted 29th April 2021

DOI: 10.1039/d1ta01871j

rsc.li/materials-a

11.5% efficient $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ solar cell fabricated from DMF molecular solution†

Chuanyou Niu,[‡] Yuancai Gong,[‡] Ruichan Qiu, Qiang Zhu, Yage Zhou, Shasha Hao, Weibo Yan,* Wei Huang and Hao Xin^{‡*}

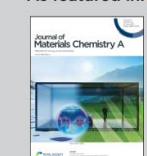


Highlighting a study on a solution processed kesterite solar cell by Prof. Hao Xin's group from Nanjing University of Posts and Telecommunications.

11.5% efficient $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ solar cell fabricated from DMF molecular solution

Efficient CZTSSe thin film solar cells are fabricated from N, N-dimethylformamide (DMF) solution. Studies of chemical reactions of precursors $\text{CuCl}_2\text{Zn}(\text{OAc})_2$, SnCl_4 , and Thiourea (Tu) in the DMF solution and the reaction path from solution to CZTSSe absorber material show a kesterite structured CZTS precursor film was formed due to the coordination of SnCl_4 with DMF, which enables direct phase transformation grain growth mechanism and thus high quality CZTSSe absorber materials. A champion device with an efficiency of 11.5%, a V_{oc} of 0.491 V, and a FF of 70.6% has been achieved, the highest performance of CZTSSe solar cells fabricated from DMF molecular solution.

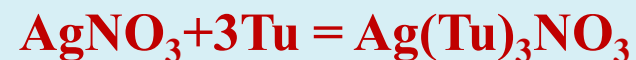
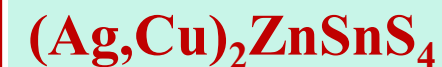
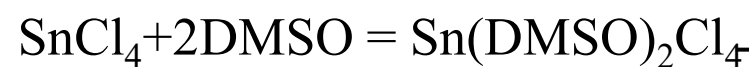
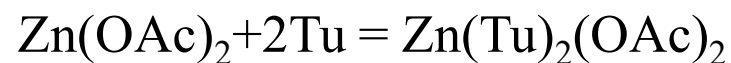
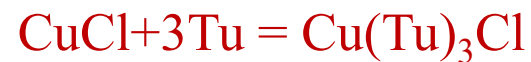
As featured in:



See Weibo Yan, Hao Xin et al., *J. Mater. Chem. A*, 2021, 9, 12981.

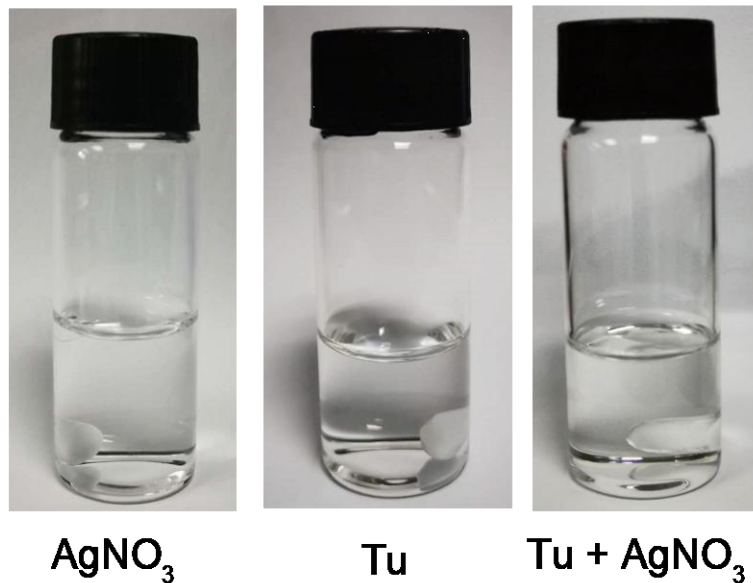
Ag Incorporation with Controlled Grain Growth Enables 12.5% Efficient Kesterite Solar Cell with Open Circuit Voltage Reached 64.2% Shockley–Queisser Limit

Yuancai Gong, Ruichan Qiu, Chuanyou Niu, Junjie Fu, Erin Jedlicka, Rajiv Giridharagopal, Qiang Zhu, Yage Zhou, Weibo Yan, Shaotang Yu, Jingjing Jiang, Sixin Wu,* David S. Ginger,* Wei Huang,* and Hao Xin*

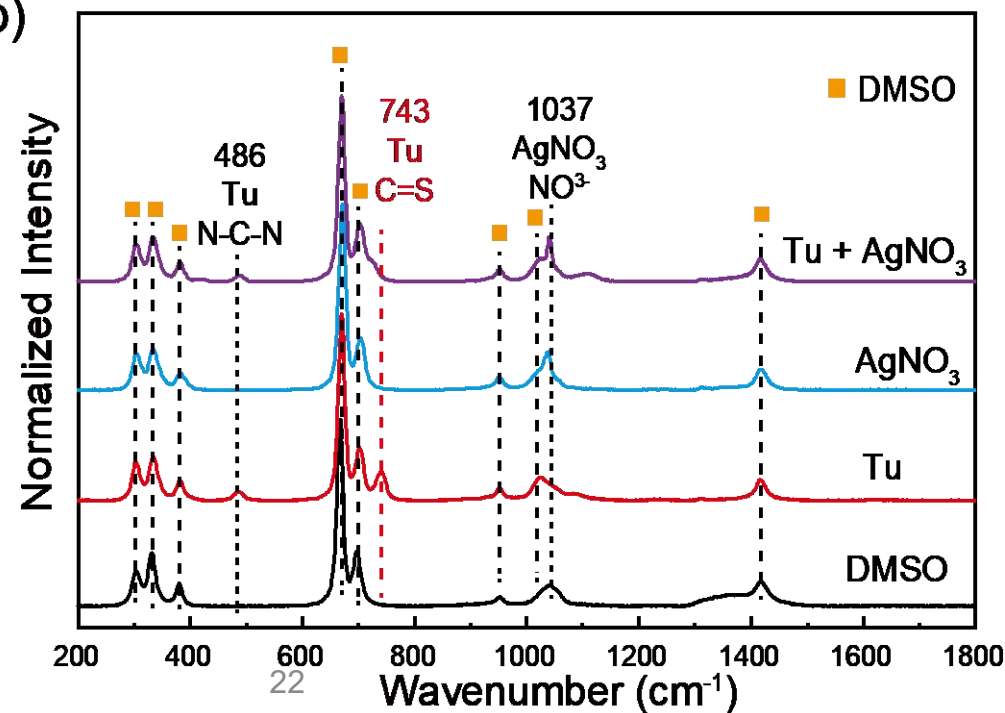


Ag^+ coordinates with Tu as Cu^+

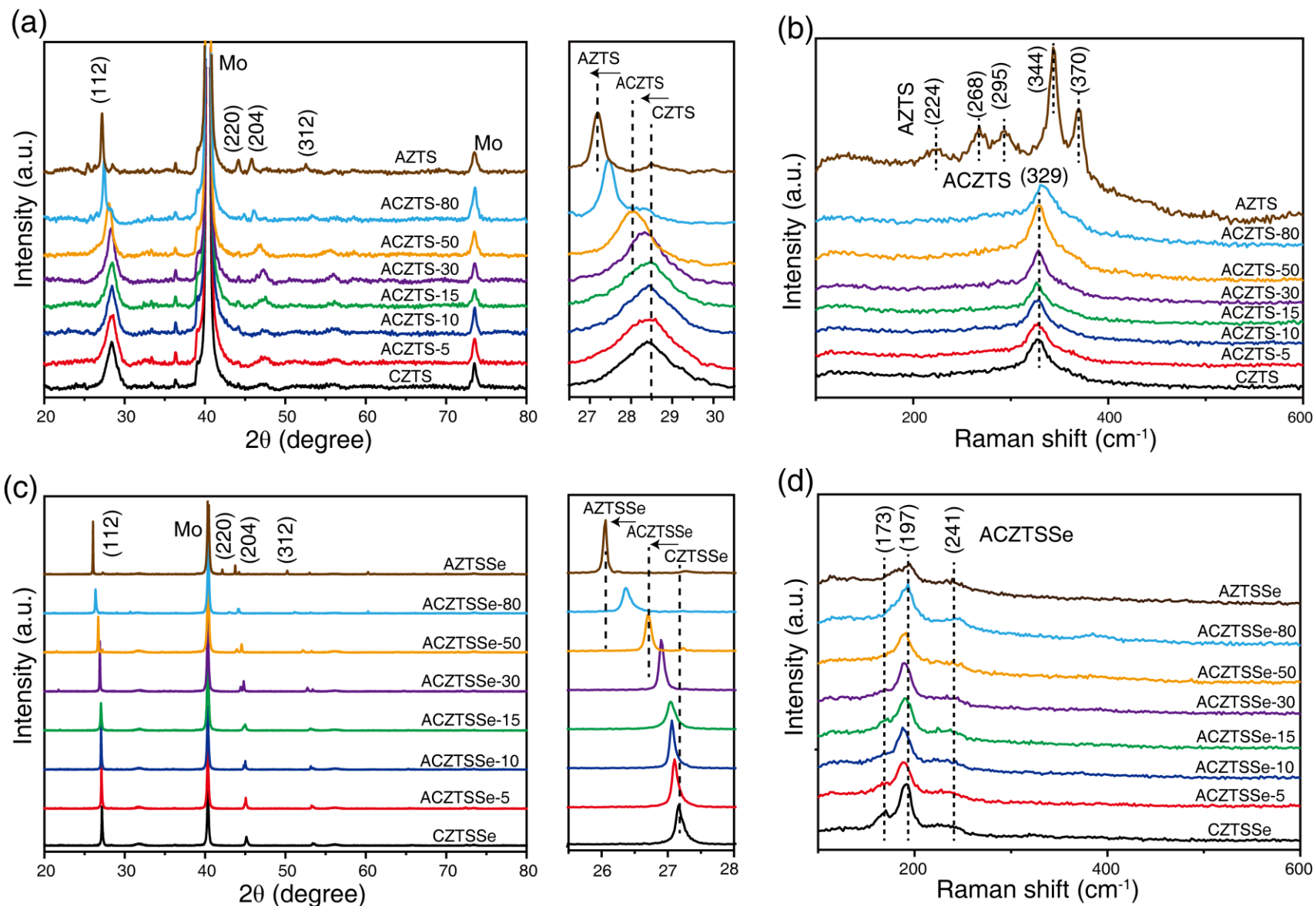
(a)



(b)

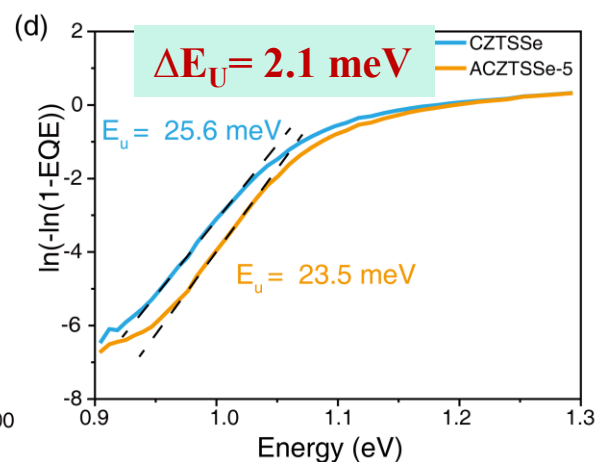
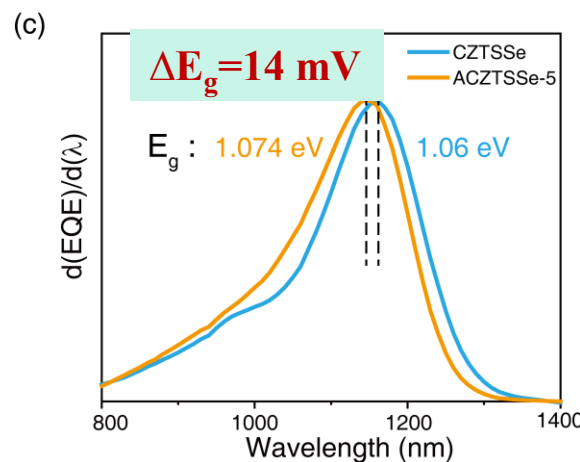
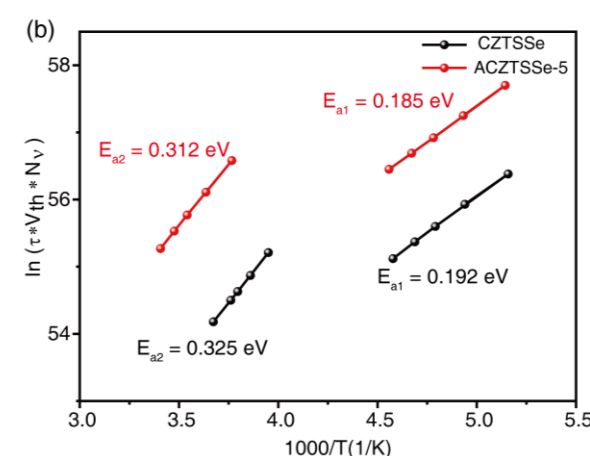
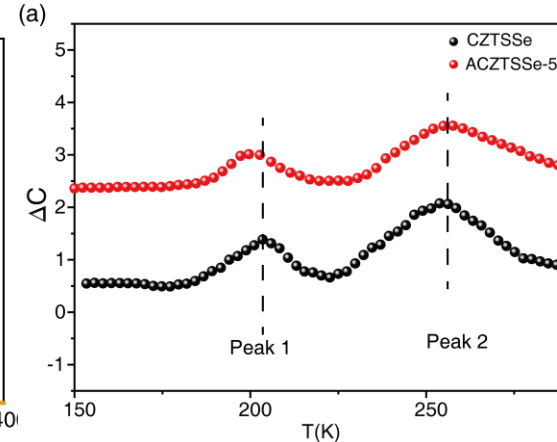
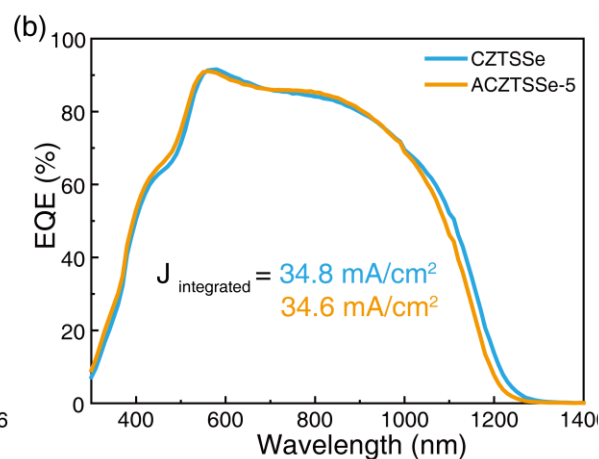
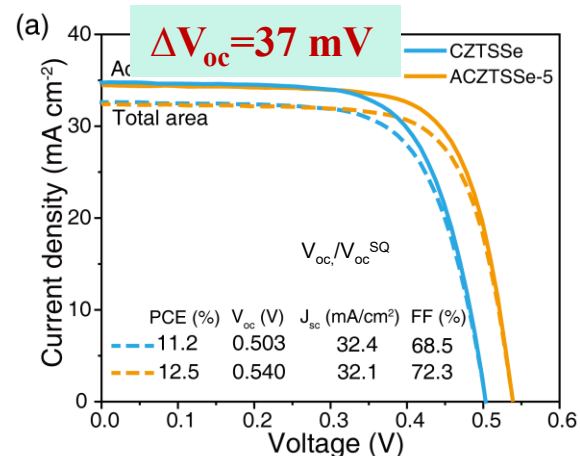


Ag Incorporation Through DMSO Solution



$(\text{Ag}_x, \text{Cu}_{1-x})_2\text{ZnSnS}_4$ ($x=0-1$) successfully fabricated.

Ag (5%) Alloying on Defect Property



Device	Defect	$N_T (\text{cm}^{-3})$	Lowest reported
No Ag	Cu_{Zn}	2.84×10^{13}	5.79×10^{13}
	Cu_{Sn}	2.22×10^{13}	8.32×10^{13}
Ag (5%)	Cu_{Zn}	5.12×10^{12}	1.50×10^{13}
	Cu_{Sn}	1.48×10^{13}	3.25×10^{13}

Total area: 12.5%
Active area: 13.5%

$$V_{oc}/V_{oc}^{SQ} = 64.2\%$$

- Suppresses Cu_{Zn} and Cu_{Sn}
- E_U decreased 2.1 meV, V_{oc} increased 23 mV

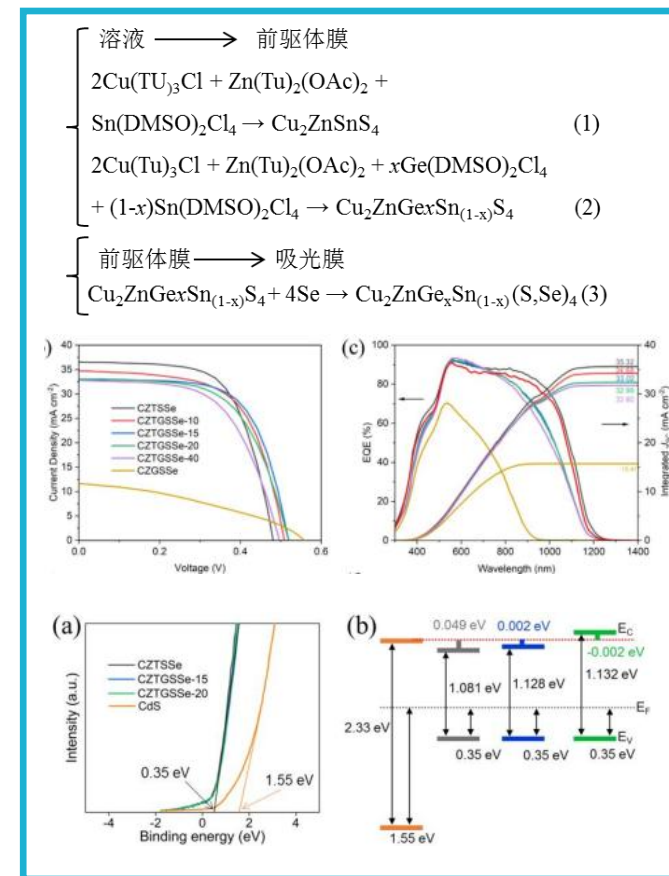
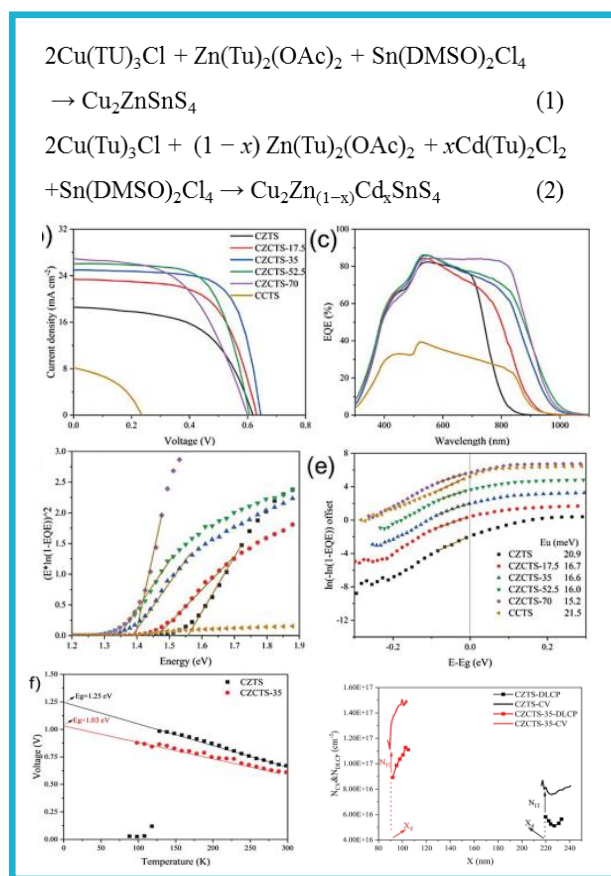
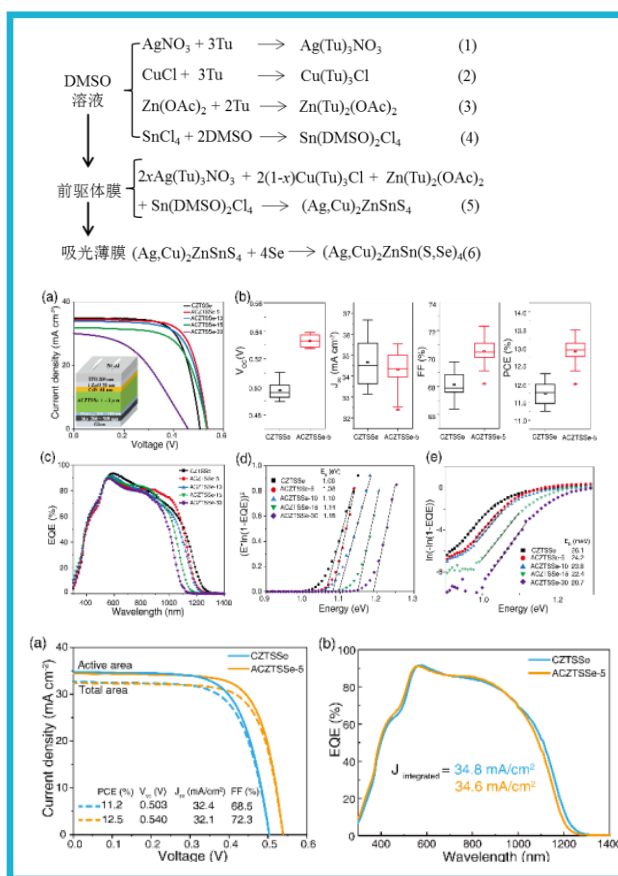
Absorber Engineering: Alloying via DPT



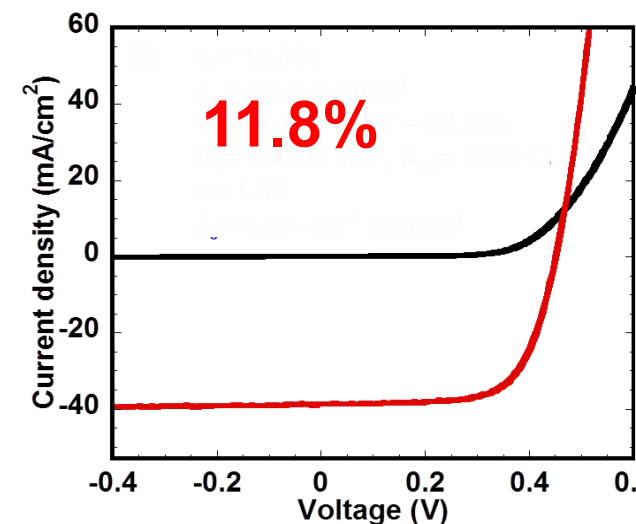
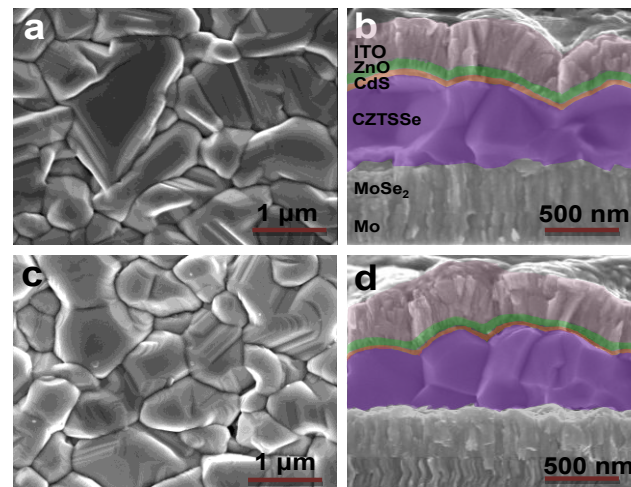
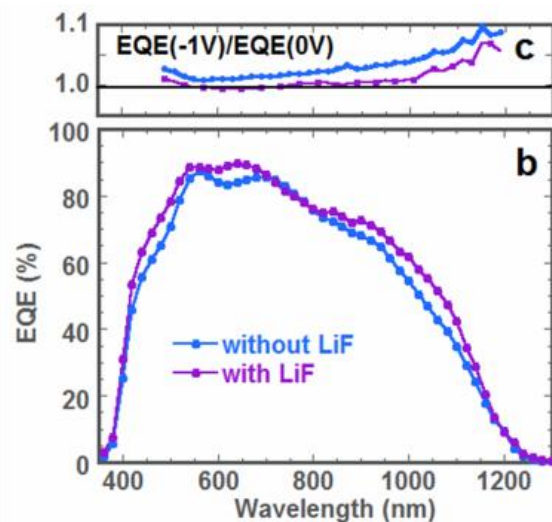
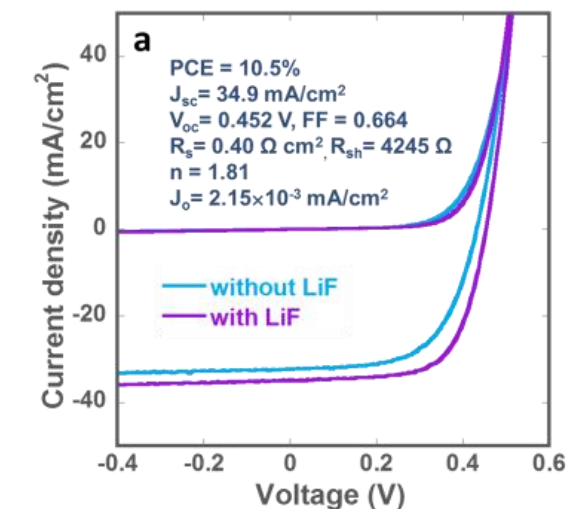
Ag alloying

Cd alloying

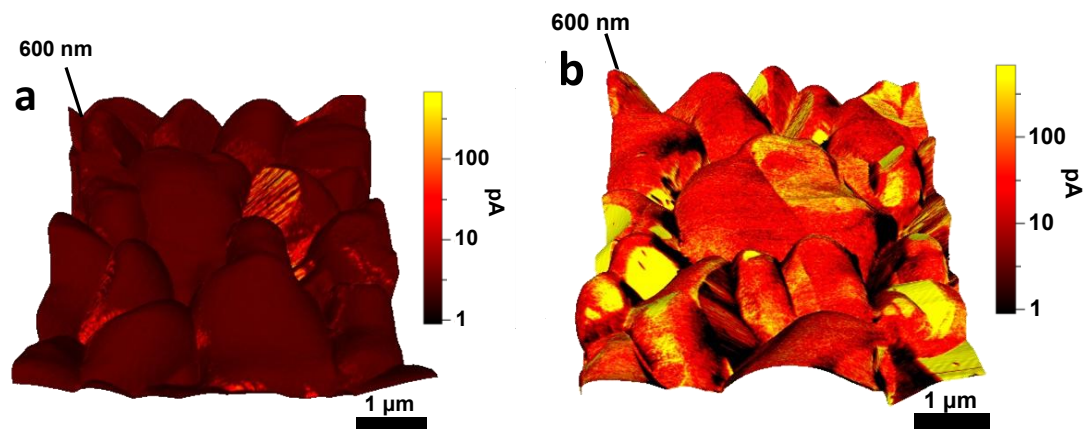
Ge alloying



Absorber Engineering: Li Doping



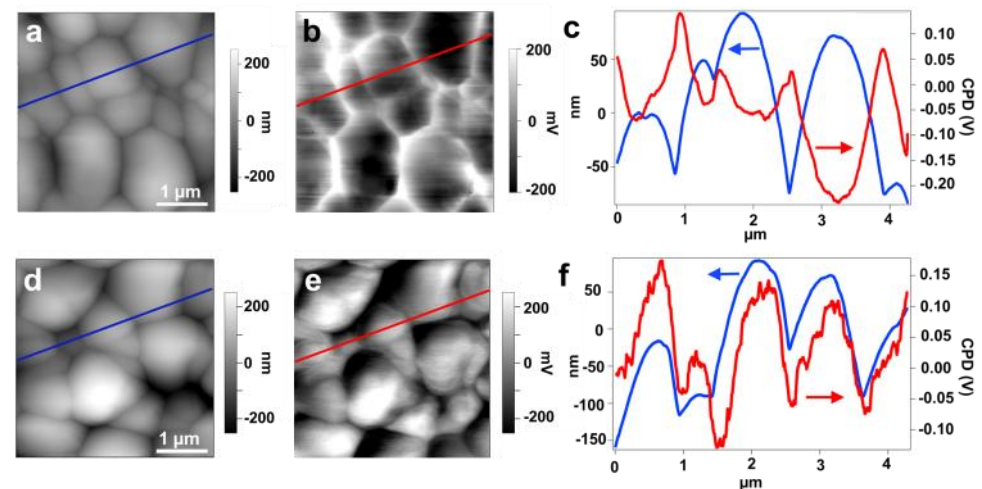
cAFM



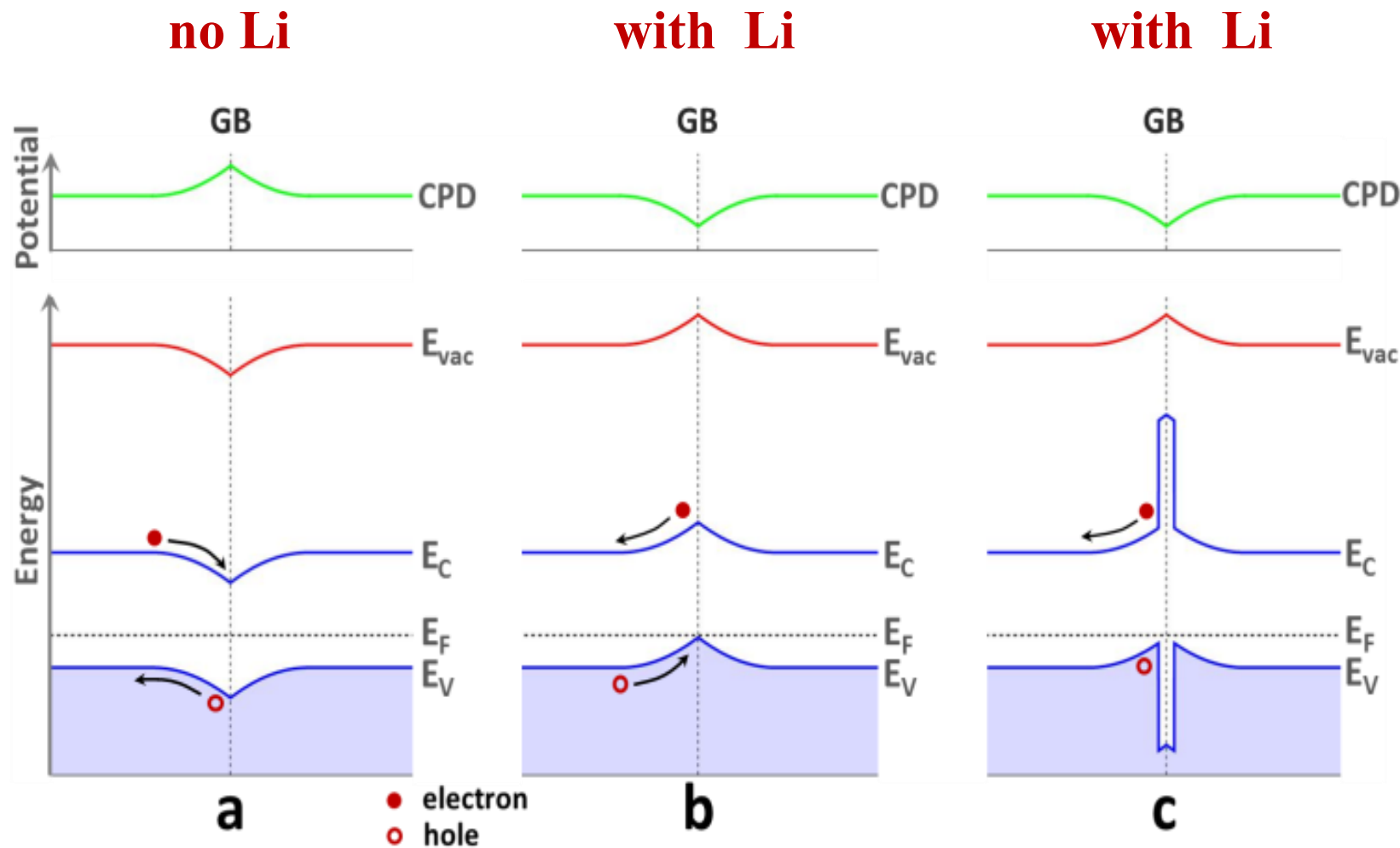
AFM

SKPM

Line Scan

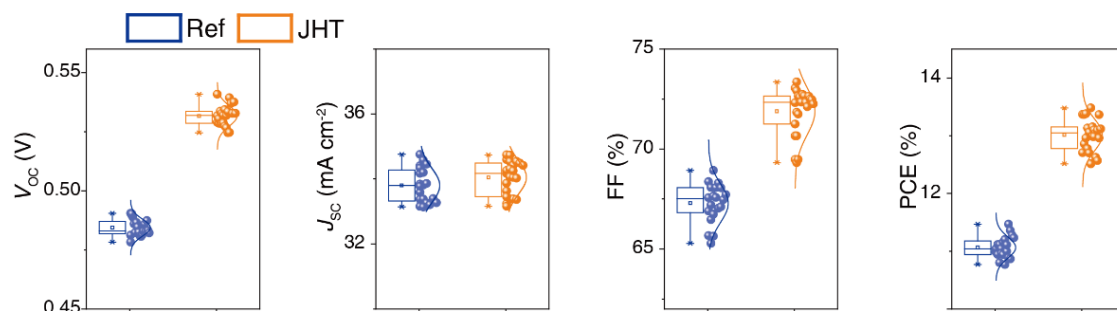
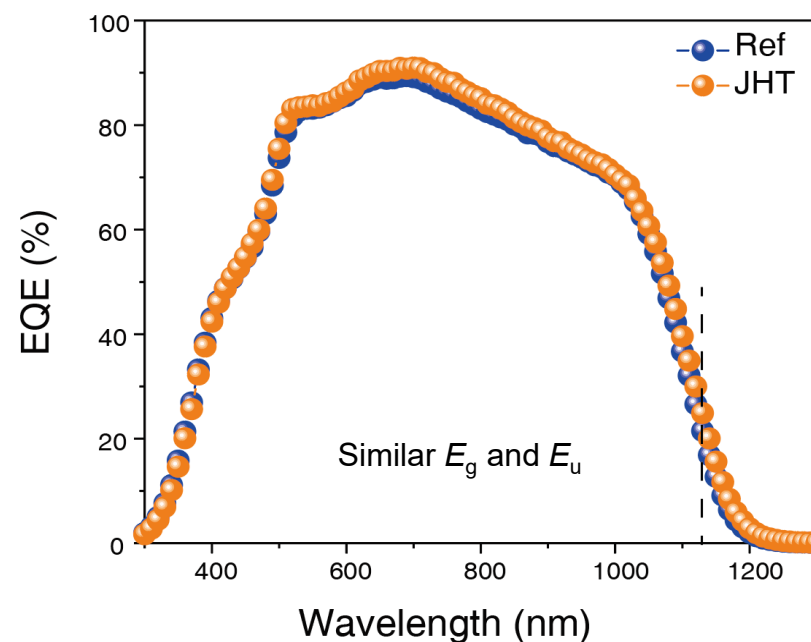
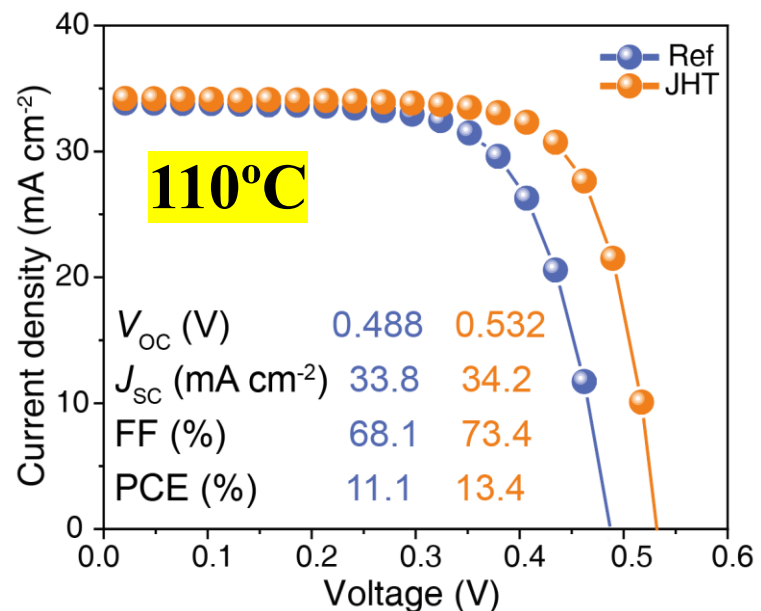


Band Diagrams Cross a Grain Boundary



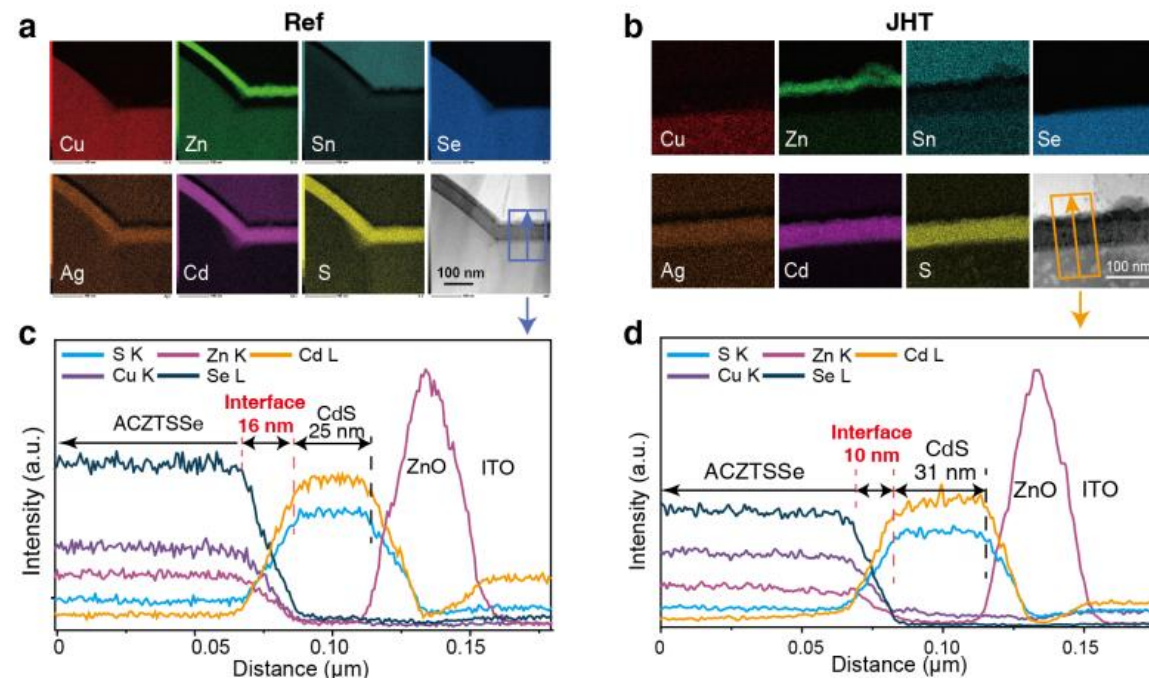
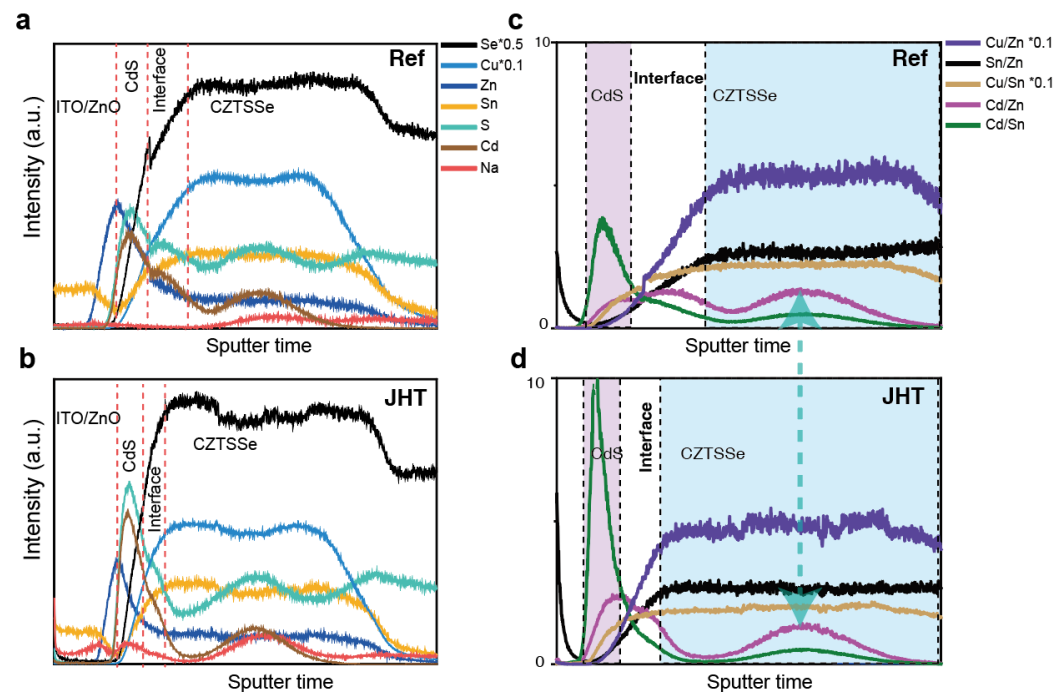
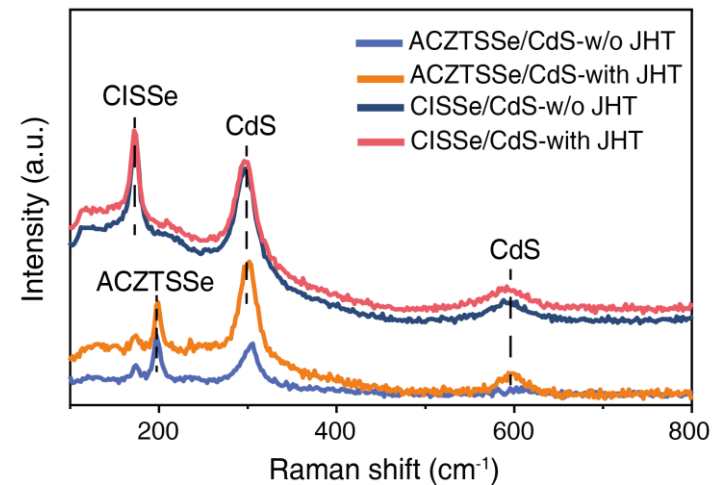
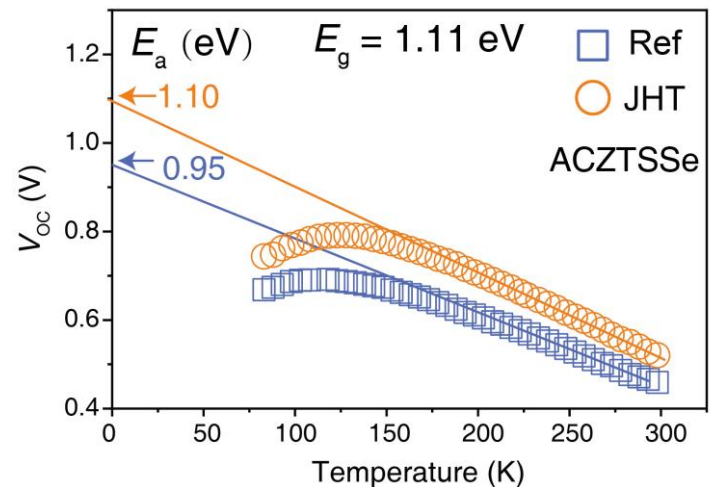
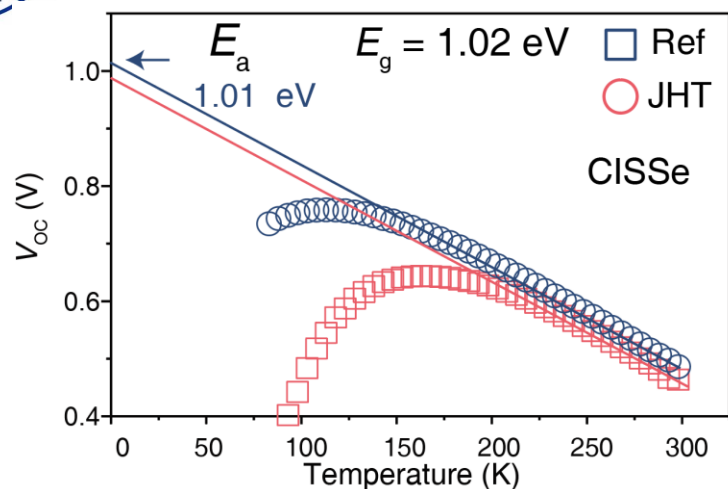
- Without Li, a downward band bending at GBs, higher recombination
- With Li, upward band bending at GBs, repelling minority carriers and reduce recombination

Low-Temp Junction Heat Treatment (LT-JHT)

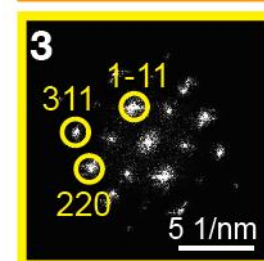
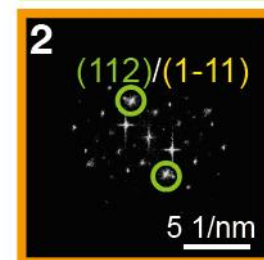
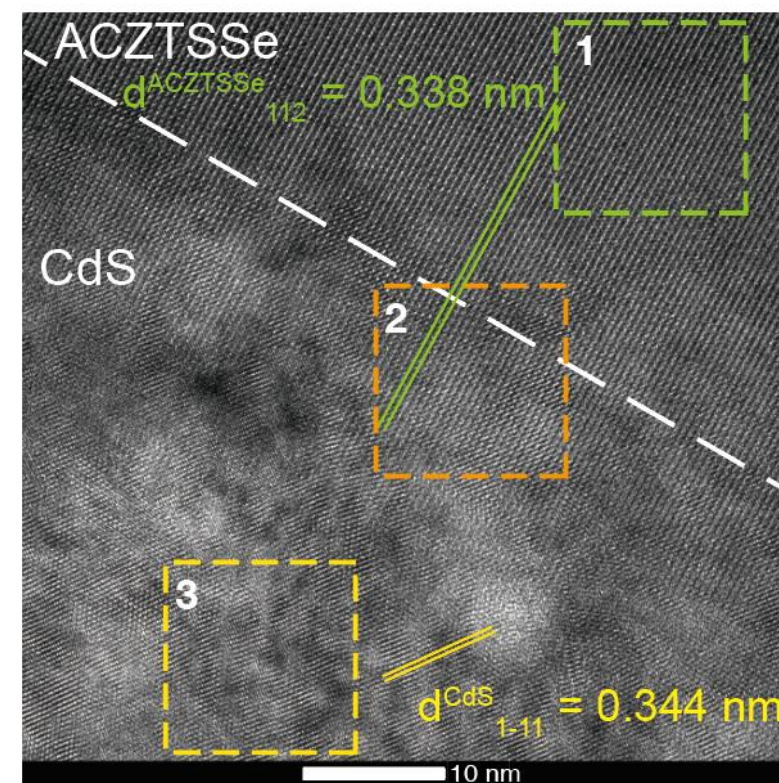
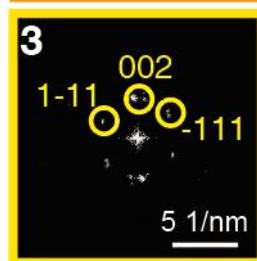
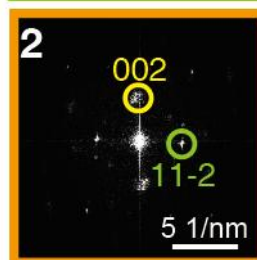
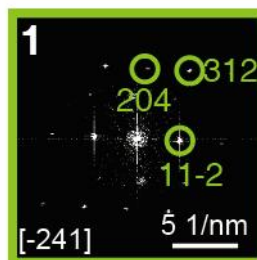
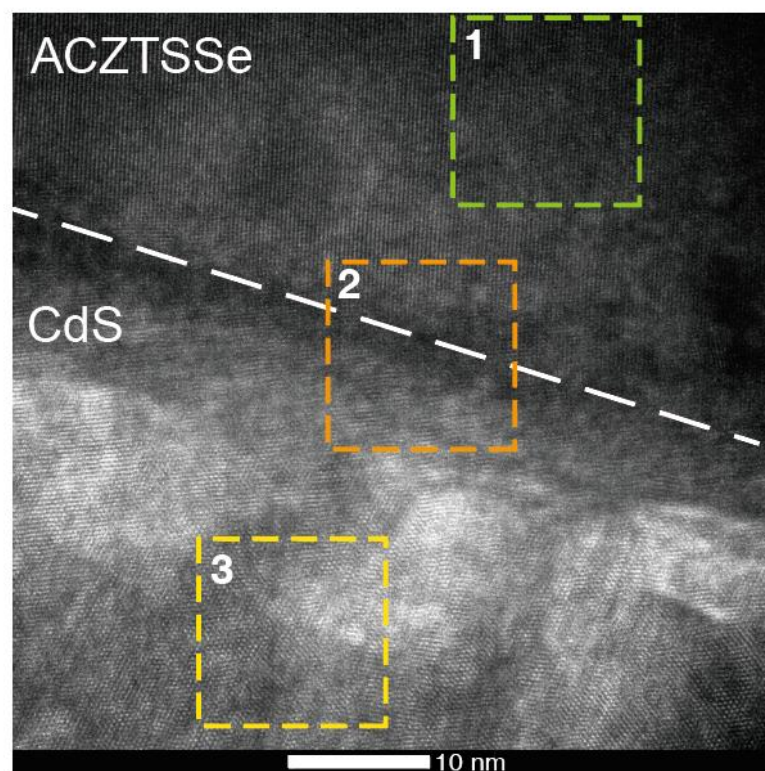


- No change on band gap, same E_u
- No obvious improvement on absorber bulk
- Improvement comes from heterojunction

LT-JHT on CZTSSe/CdS Interface



Elemental Di-mixing Enables Epitaxial Interface

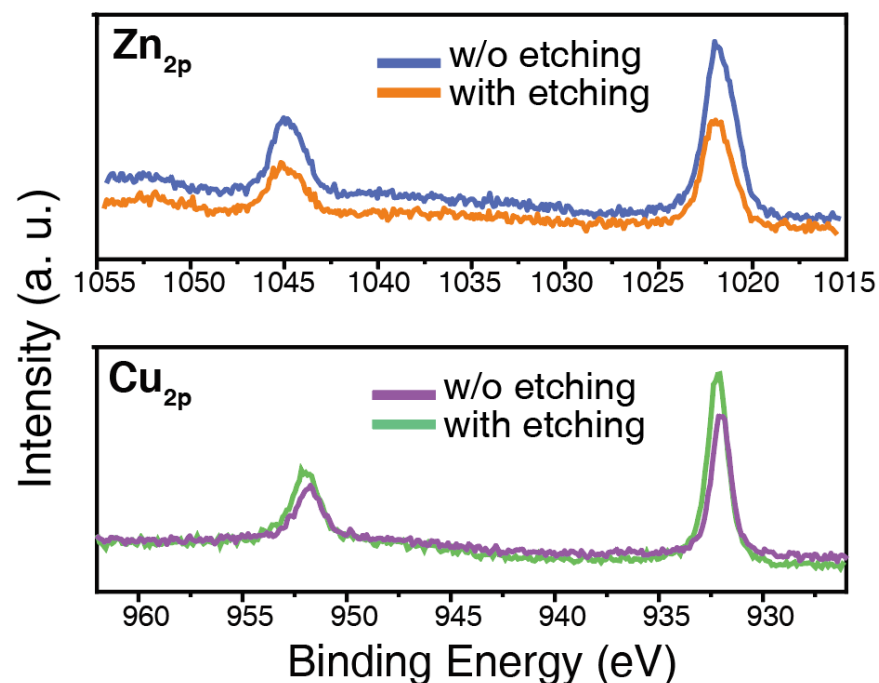


- Low crystallinity of CZTSSe and CdS
- Defective and non-coherent interface

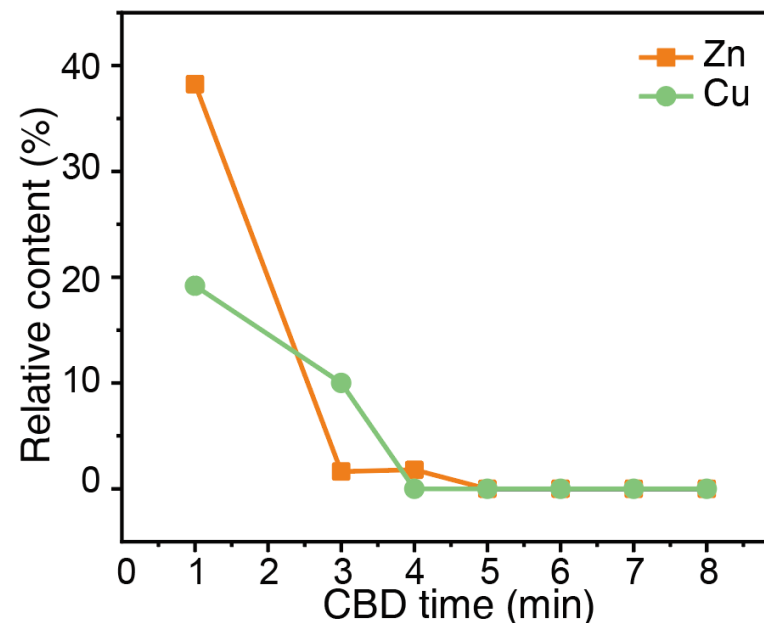
- Improved crystallinity for CZTSSe and CdS
- Coherent interface: CZTSSe(112)||CdS(111)

Construction of CZTSSe/CdS Interface

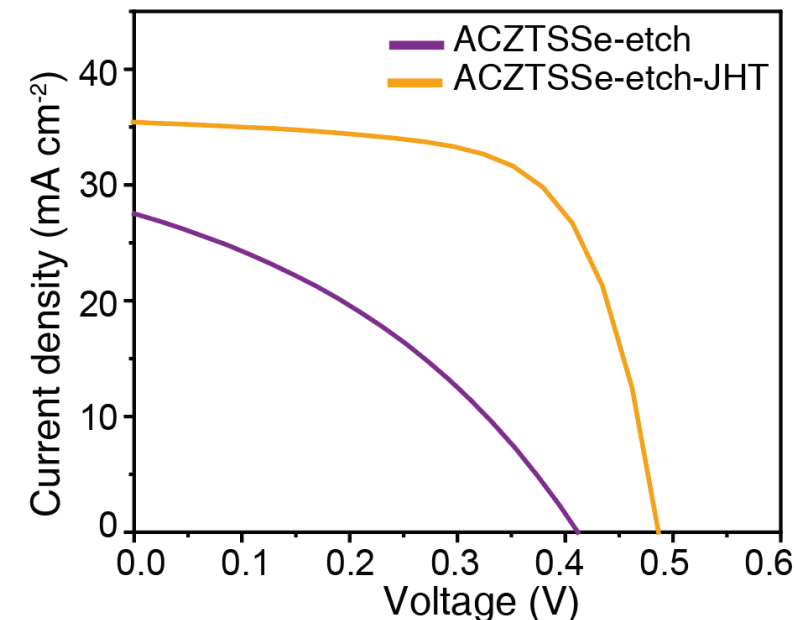
NH₄OH etching



Zn Cu intensity change



Device with etching and JHT



$$K = 8.2 \times 10^{-40}$$



$$K = 1.48 \times 10^{-17}$$

- Zn dissolves with etching (during CBD)
- Cu poor/Zn-rich surface
- CdS constructed on Zn-poor surface (not Cu-poor as in CIGS)
- Zn re-deposition into CdS
- JHT recovers interface: Zn moves towards surface

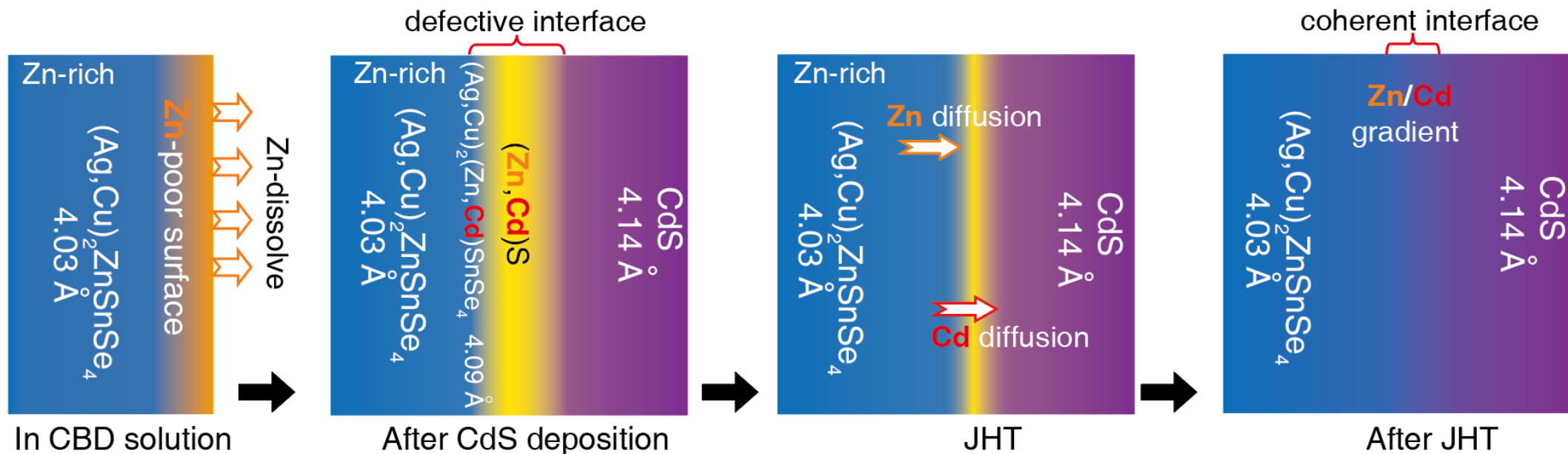
CZTSSe/CdS Interface: Defective to Epitaxial

nature energy

Article

<https://doi.org/10.1038/s41560-022-01132-4>

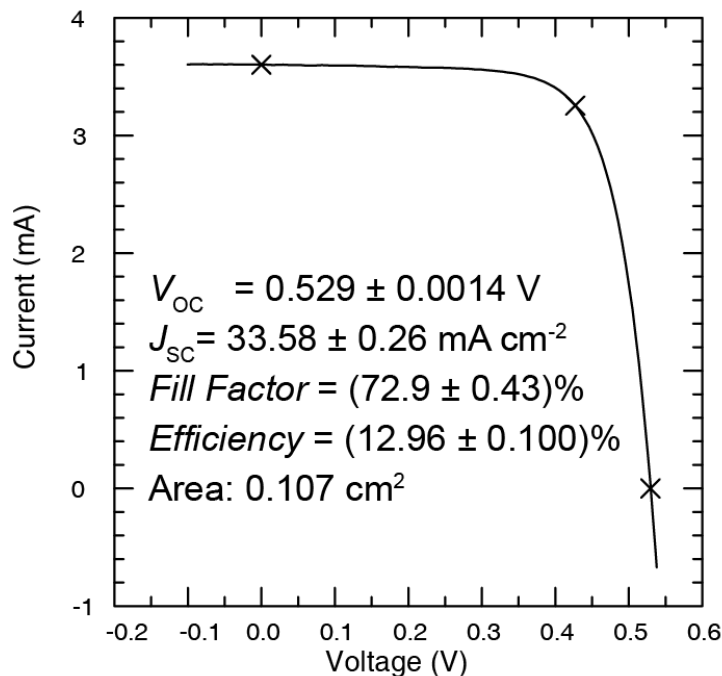
Elemental de-mixing-induced epitaxial kesterite/CdS interface enabling 13%-efficiency kesterite solar cells



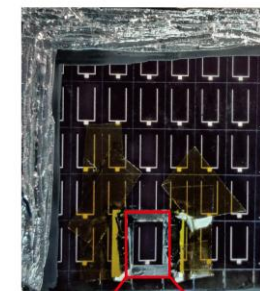
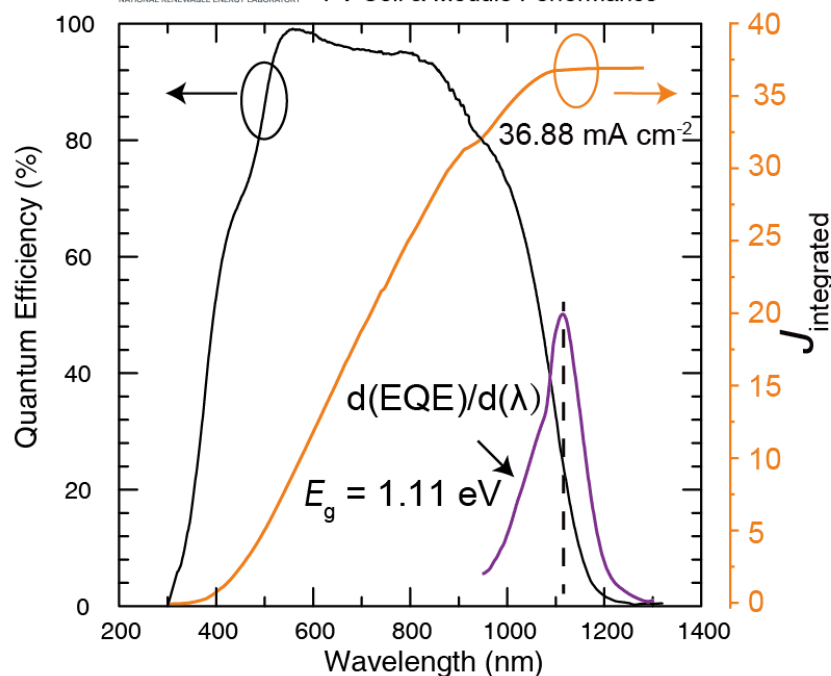
- Cd in CZTSSe and Zn in CdS are observed in Ref sample
- Interface narrows and sharpens upon low-temperature JHT
- Elemental de-mixing: Cd and Zn back to original position
- Interface moves toward CdS layer

Record Efficiency Device via LT JHT

NREL X25 IV System
PV Cell & Module Performance



NREL HLB QE system
PV Cell & Module Performance

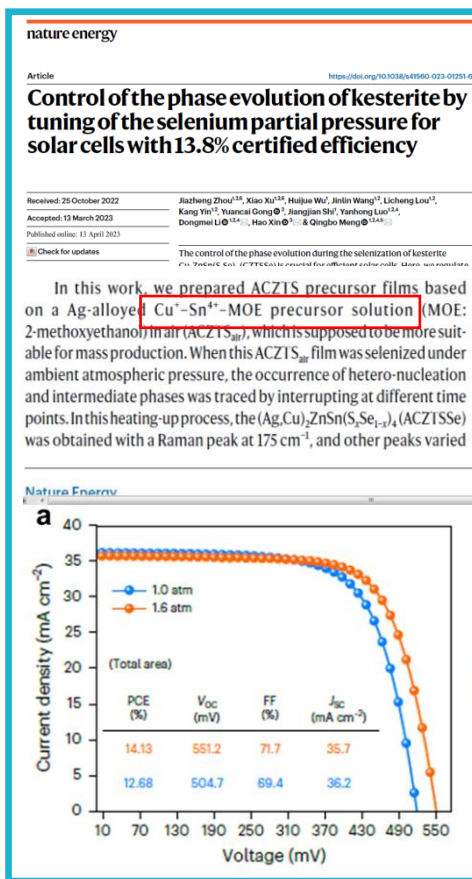
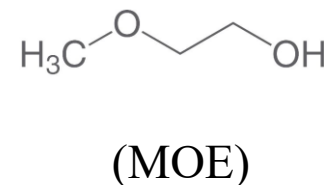
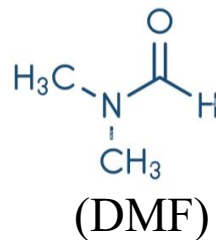
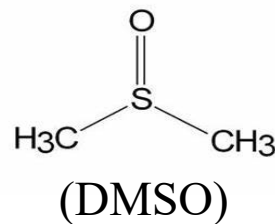


0.107 cm² Cell

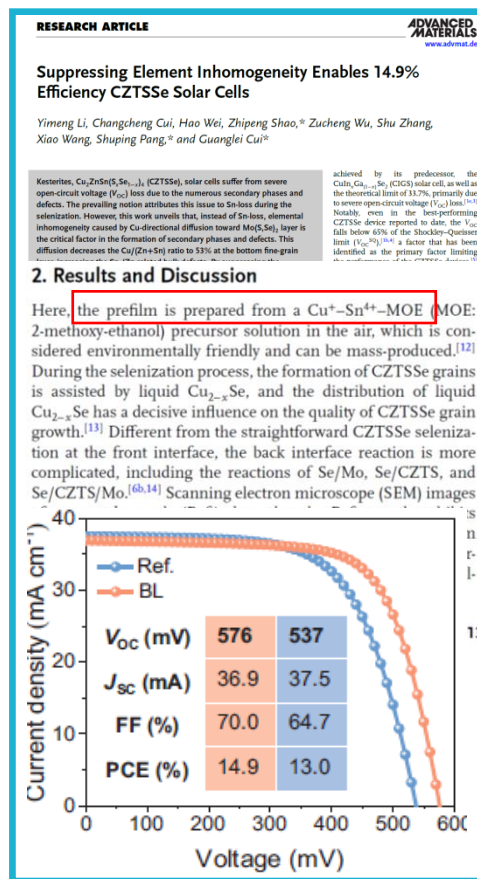
Aperture area: 12.96%
Active area: 14.22%

Device	Absorber	Area (cm ²)	V _{OC} (V)	J _{SC} (mA/cm ²)	FF (%)	Eff. (%)	n	J ₀ (A/cm ²)	R _s	E _g (eV)	V _{OC-def} (V)	Certifying Center
This work	ACZTSSe*	0.107	0.529	33.7	72.9	13.0	1.35	8.2×10 ⁻⁹	0.35	1.11	0.337	NREL
IBM cell ⁶	CZTSSe	0.420	0.513	35.2	69.8	12.6	1.45	7.0×10 ⁻⁸	0.72	1.13	0.373	Newport
DGIST cell ⁷	CZTSSe	0.480	0.541	35.4	65.9	12.6	1.88	9.6×10 ⁻⁷	0.87	1.13	0.345	Newport
UNSW cell ²	CZTS	0.233	0.730	21.7	69.3	11.0	1.44	6.8×10 ⁻⁸	2.58	1.50	0.500	NREL
IBM cell ²⁷	CZTSe	0.43	0.423	40.6	67.3	11.6	1.57	1.3×10 ⁻⁶	0.32	1.00	0.342	Newport

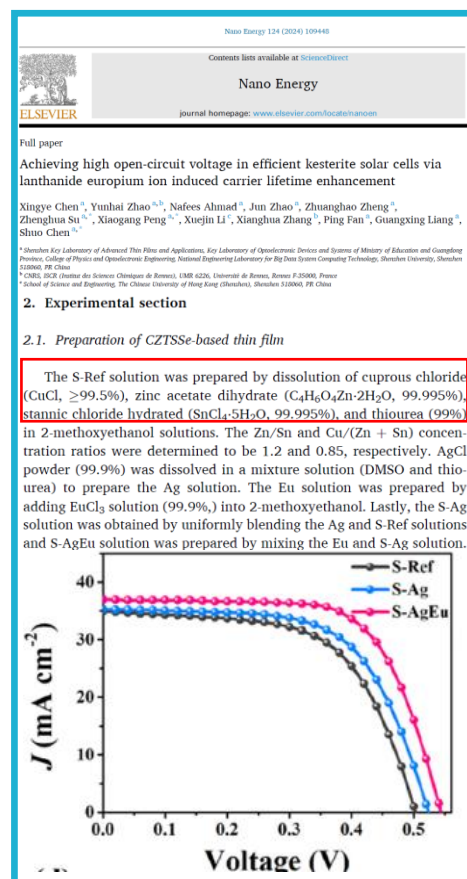
Universal of Cu^+ - Sn^{4+} Precursors and LT-HJT



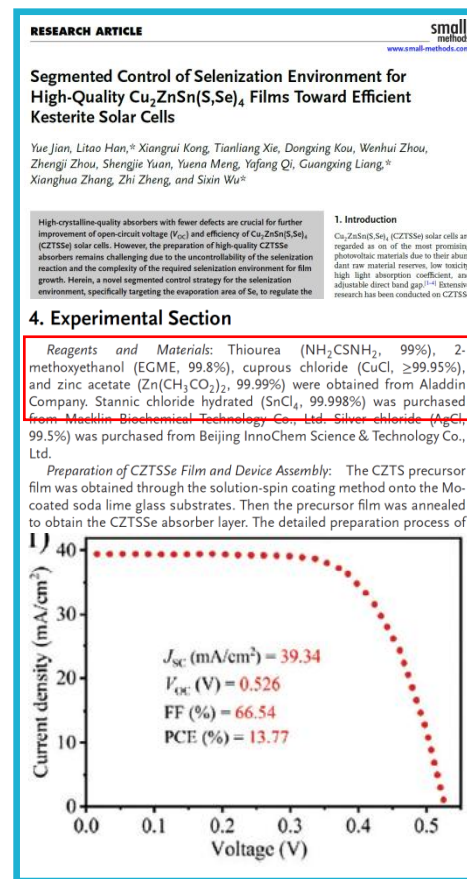
Nat. Energy, 2023, 8, 526-535



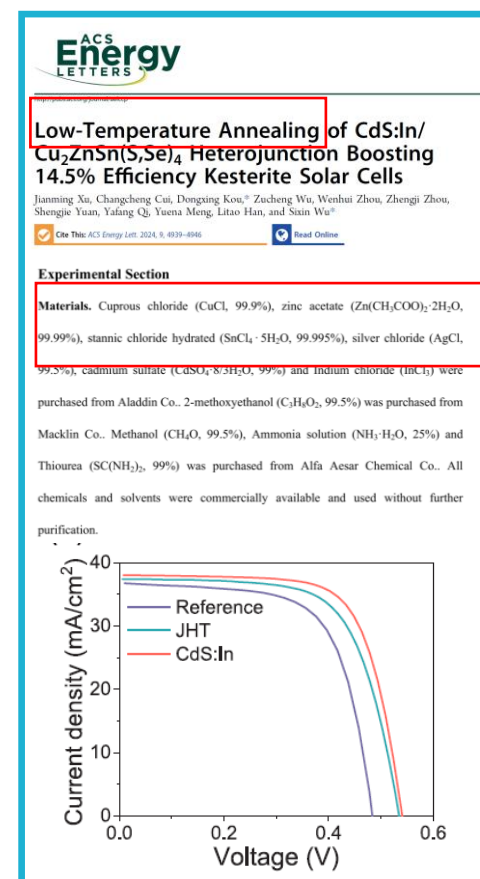
Adv. Mater., 2024, 36, 2400138



Nano Energy, 2024, 124, 109448

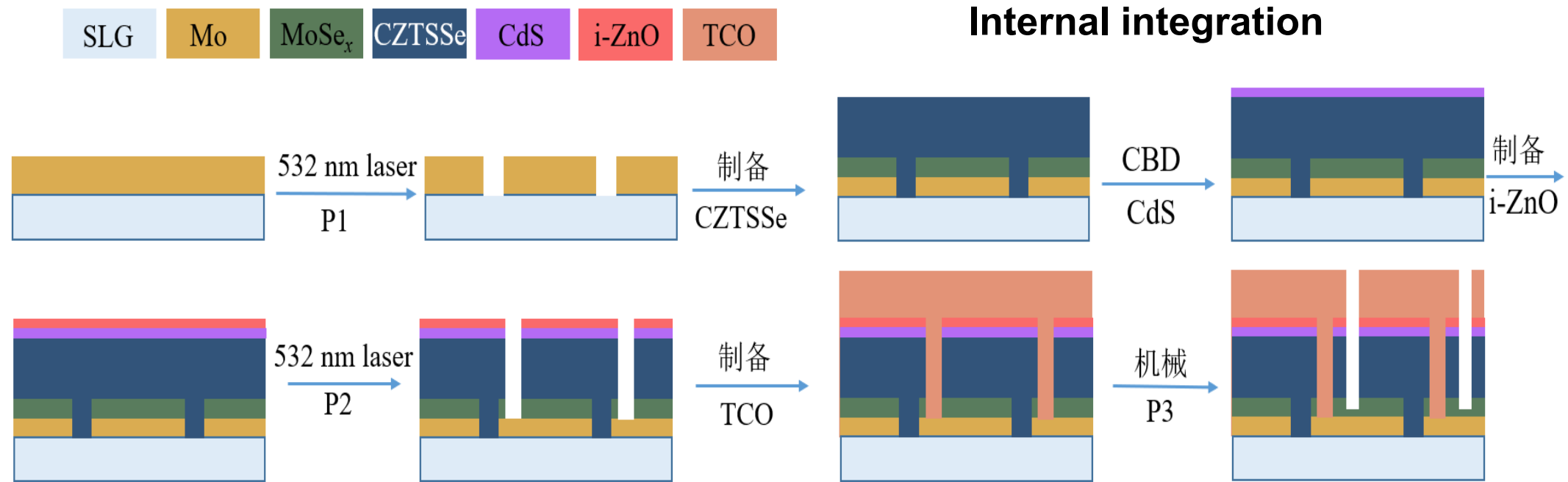


Small Methods, 2024, 2400041



ACS Energy Lett. 2024, 9, 4939-4946

Fabrication of CZTSSe Module

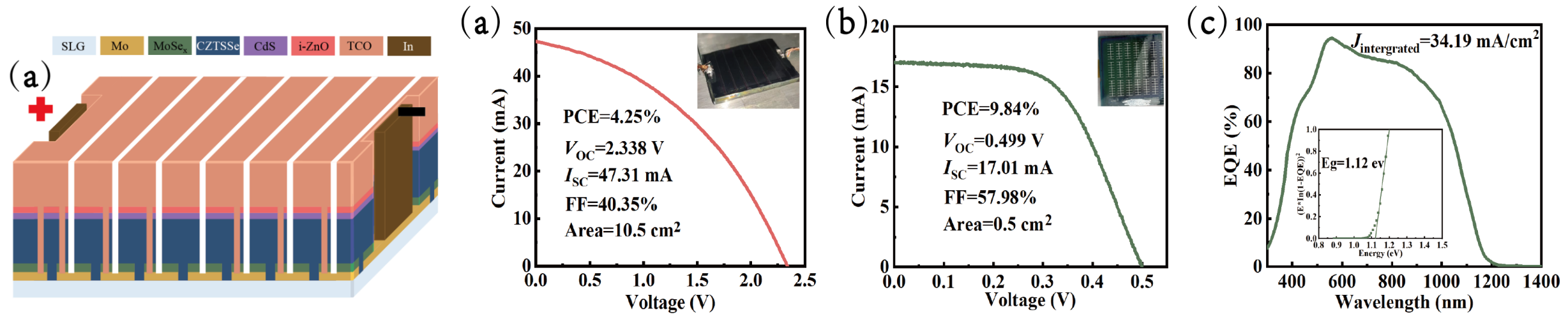


P1: isolate the Mo back contacts

P2: create connecting channel between top and bottom contacts

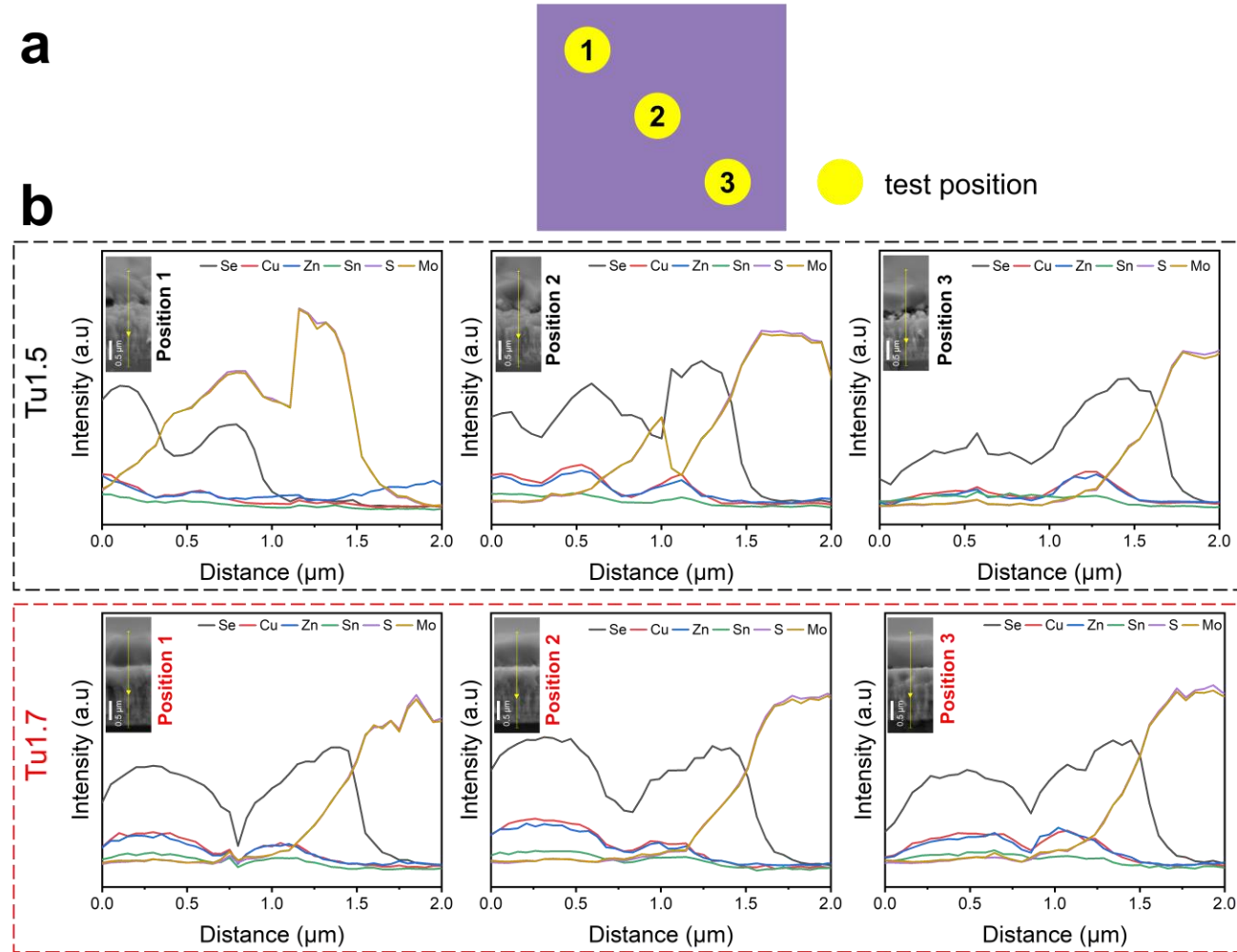
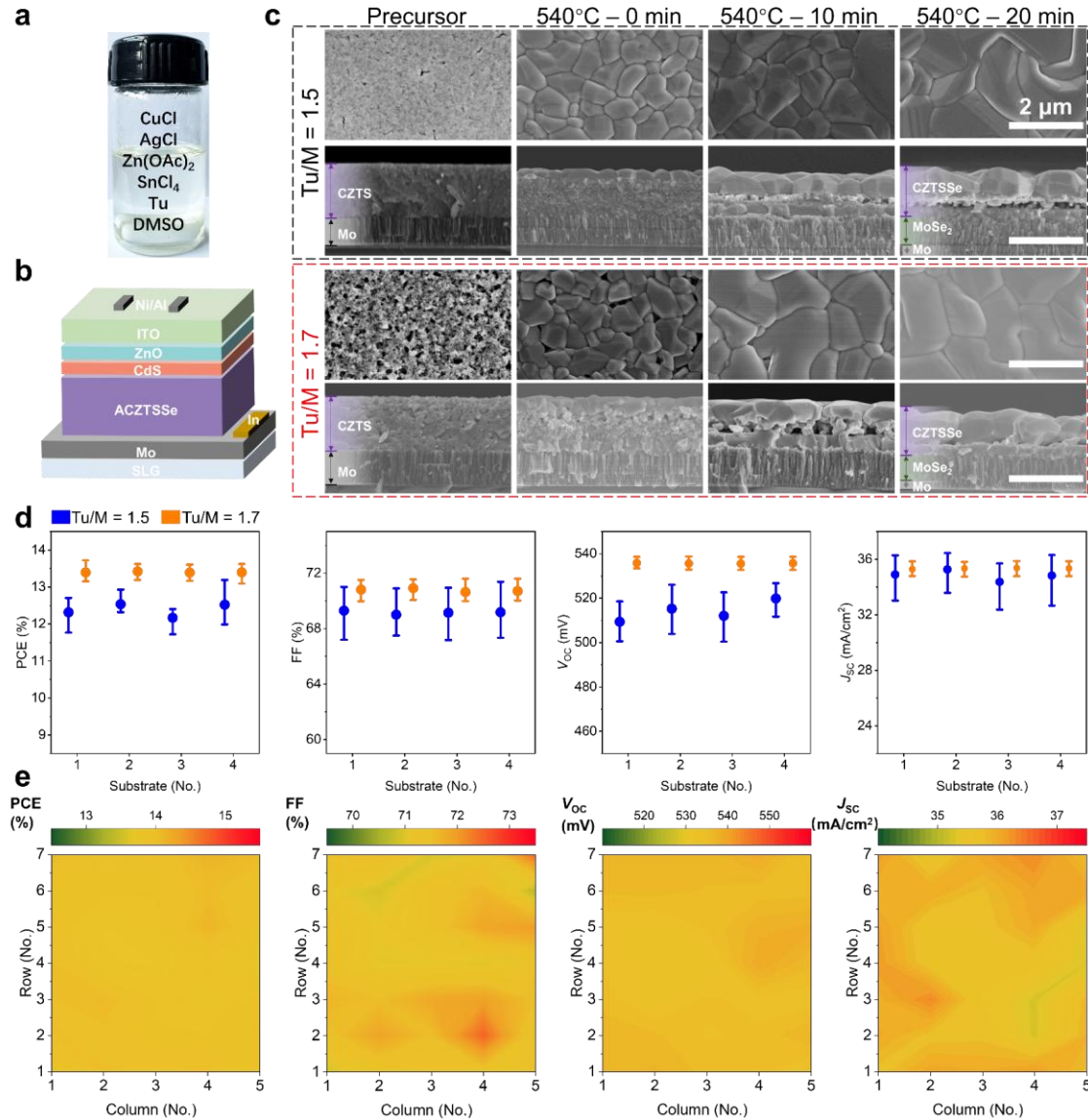
P3: separate aluminum doped zinc oxide (AZO) top contacts

Module Performance



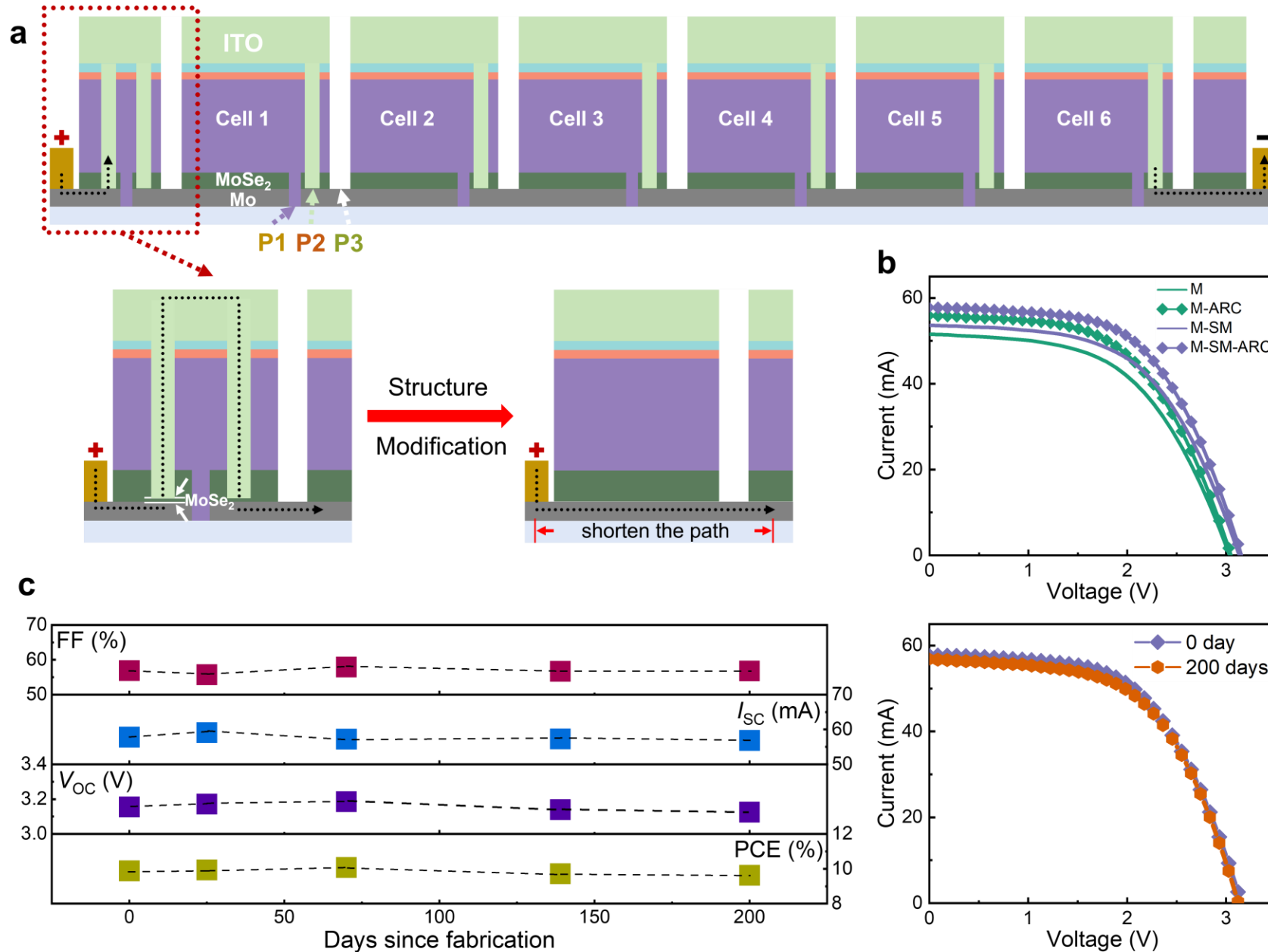
	Module	Ref	CTM loss
V_{OC} (V)	2.338	0.499	21.84%
J_{SC} (mA/cm ²)	27.03	34.02	20.55%
FF (%)	40.35	57.98	30.41%
PCE (%)	4.25	9.84	56.81%

Composition Regulation to Improve Uniformity

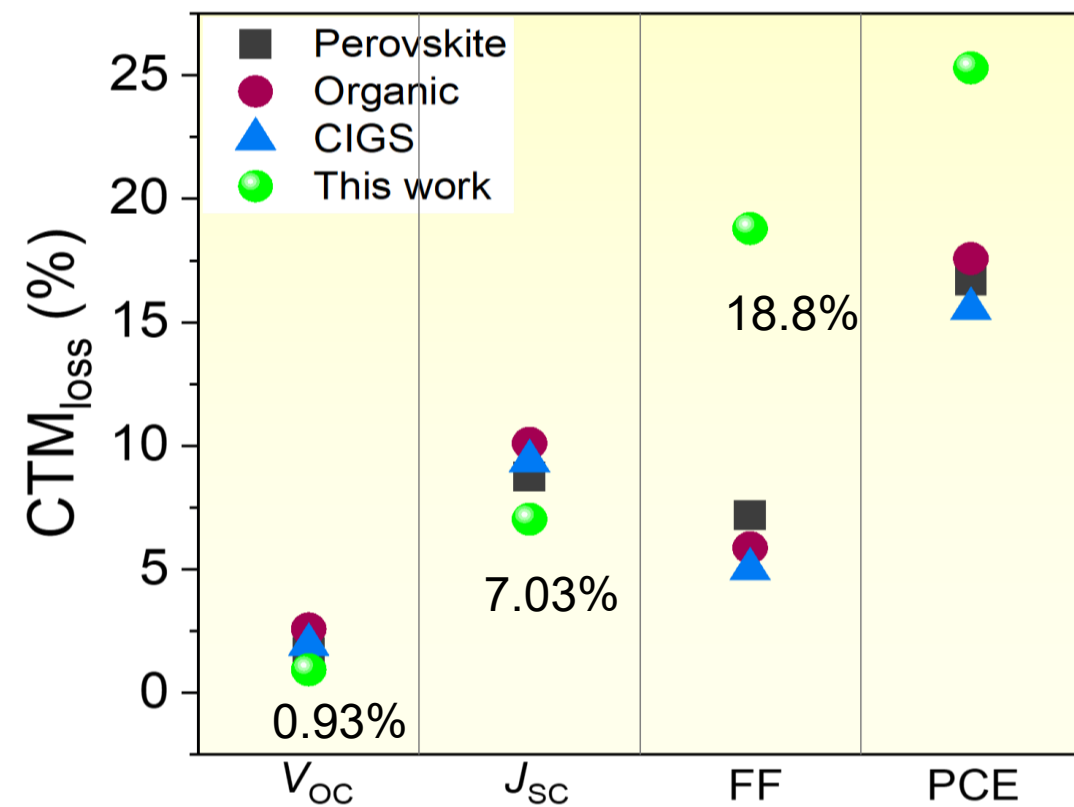
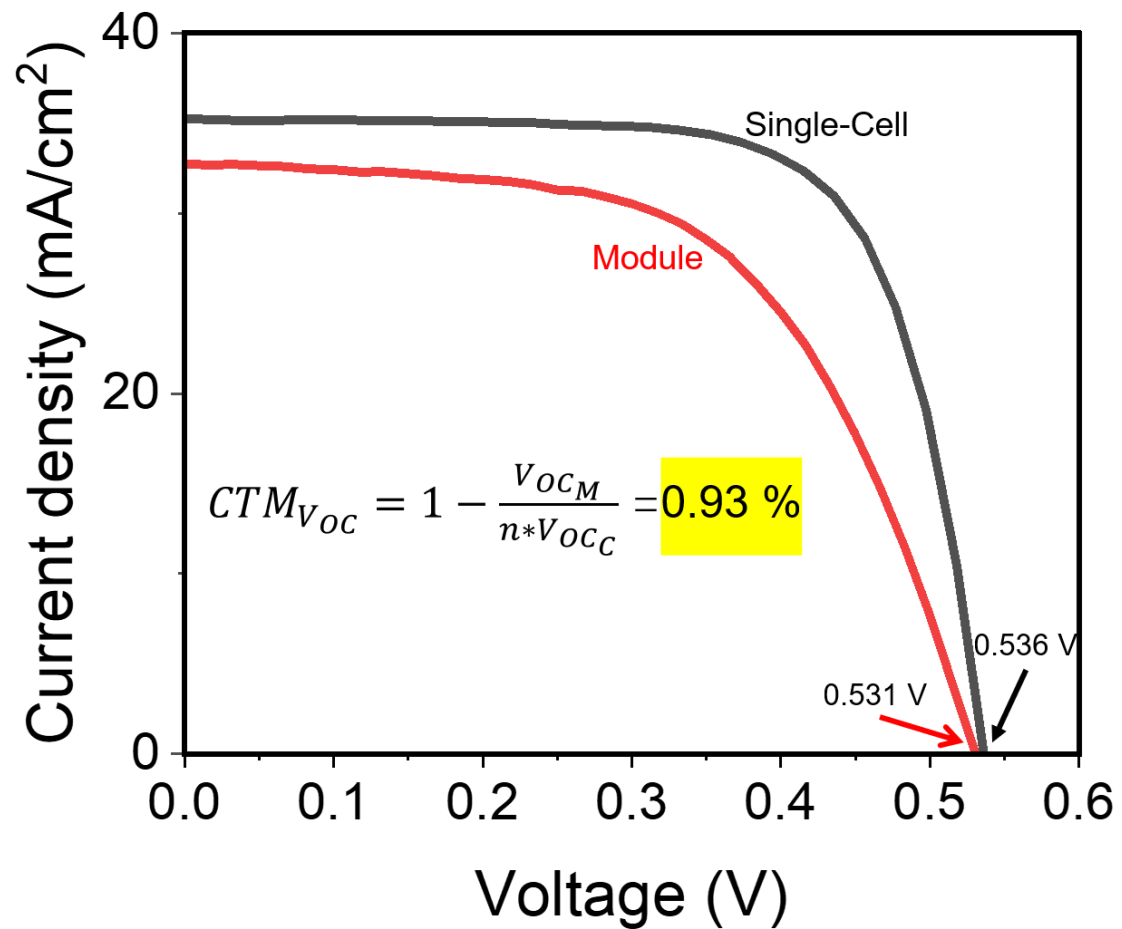


Nature Energy, 2025, 10, 1315–1322.

Module Structure Modification and Stability



Cell to Module (CTM) Loss



Nature Energy, 2025, 10, 1315–1322.

First Record Efficiency Kesterite Solar Module

Received: 14 May 2024 | Accepted: 3 June 2024
DOI: 10.1002/pip.3831

SHORT COMMUNICATION

PROGRESS IN
PHOTOVOLTAICS WILEY

Solar cell efficiency tables (Version 64)

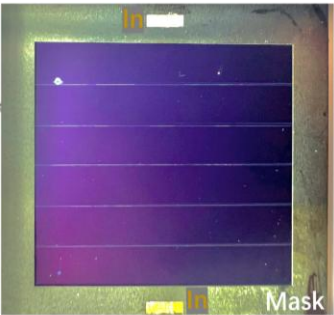
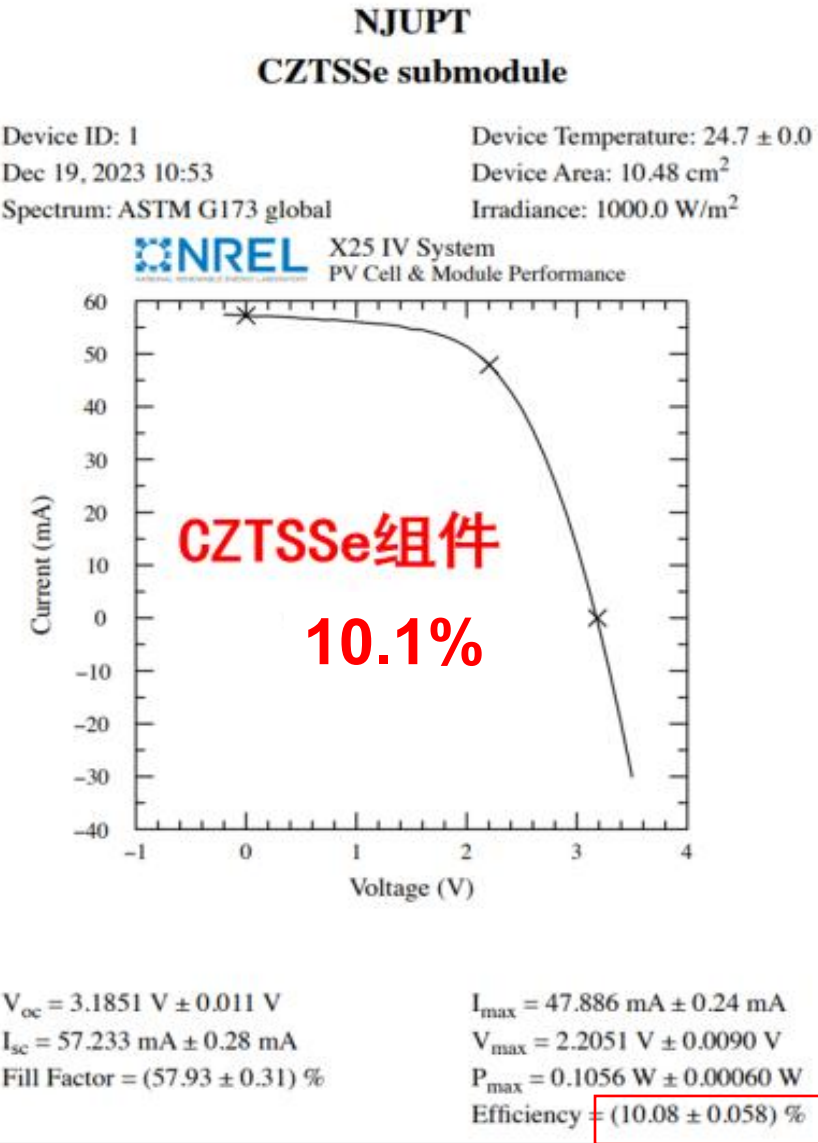
Martin A. Green¹ | Ewan D. Dunlop² | Masahiro Yoshita³ |
Nikos Kopidakis⁴ | Karsten Bothe⁵ | Gerald Siefer⁶ | David Hinken⁵ |
Michael Rauer⁶ | Jochen Hohl-Ebinger⁶ | Xiaojing Hao¹

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TABLE 1 Confirmed single-junction terrestrial cell and submodule efficiencies measured under the global AM1.5 spectrum (1000 W/m²) at 25°C (IEC 60904-3: 2008 or ASTM G-173-03 global).

Classification	Efficiency (%)	Area (cm ²)	V _{oc} (V)	J _{sc} (mA/cm ²)	Fill factor (%)	Test centre (date)	Description
Silicon							
Si (crystalline cell)	27.3 ± 0.4 ^a	243.1 (da)	0.7434	42.60 ^b	86.2	ISFH (12/23)	LONGi, n-type HBC ⁴
Si (thin transfer submodule)	21.2 ± 0.4	239.7 (ap)	0.687 ^c	38.50 ^{c,d}	80.3	NREL (4/14)	Solexel (35 µm thick) ⁵
Si (thin film minimodule)	10.5 ± 0.3	94.0 (ap)	0.492 ^c	29.7 ^{c,e}	72.1	FhG-ISE (8/07)	CSG Solar (<2 µm on glass) ⁶
III-V cells							
GaAs (thin film cell)	29.1 ± 0.6	0.998 (ap)	1.1272	29.78 ^f	86.7	FhG-ISE (10/18)	Alta Devices ⁷
GaAs (multicrystalline)	18.4 ± 0.5	4.011 (t)	0.994	23.2	79.7	NREL (11/95)	RTI, Ge substrate ⁸
InP (crystalline cell)	24.2 ± 0.5 ^g	1.008 (ap)	0.939	31.15 ^h	82.6	NREL (3/13)	NREL ⁹
Thin film chalcogenide							
CIGS (cell) (Cd-free)	23.35 ± 0.5	1.043 (da)	0.734	39.58 ⁱ	80.4	AIST (11/18)	Solar Frontier ¹⁰
CIGSSe (submodule)	20.3 ± 0.4	526.7 (ap)	0.6834	39.55 ^{c,j}	75.1	NREL (5/23)	Avancis, 100 cells ¹¹
CdTe (cell)	21.0 ± 0.4	1.0623 (ap)	0.8759	30.25 ^d	79.4	Newport (8/14)	First Solar, on glass ¹²
CZTSSe (cell)	13.45 ± 0.3	1.101 (da)	0.5109	37.90 ^b	69.5	NPVM (4/24)	IoP/CAS ¹³
CZTSSe (minimodule)	10.1 ± 0.3	10.48 (da)	0.5309 ^c	32.77 ^{c,k}	57.9	NREL (1/24)	NJUPT, 6 serial cells ¹⁴
CZTS (cell)	10.0 ± 0.2	1.113 (da)	0.7083	21.77 ^h	65.1	NREL (3/17)	UNSW ¹⁵
Amorphous/Microcrystalline							
Si (amorphous cell)	10.2 ± 0.3 ^{g,k}	1.001 (da)	0.896	16.36 ^d	69.8	AIST (7/14)	AIST ¹⁶
Si (microcrystalline cell)	11.9 ± 0.3 ^g	1.044 (da)	0.550	29.72 ^h	75.0	AIST (2/17)	AIST ¹⁷

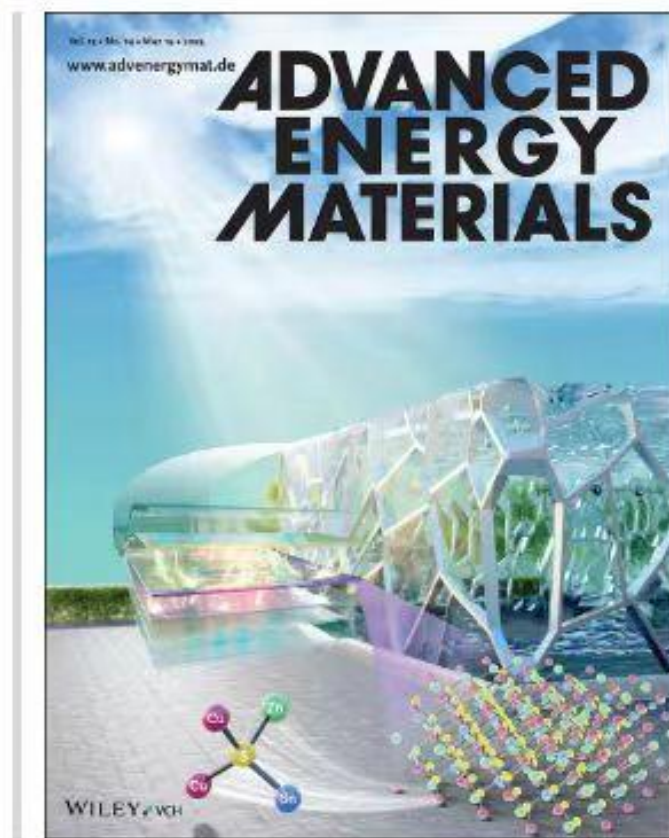


Kesterite Solar Cell on Transparent Electrode

11.4% Efficiency Kesterite Solar Cells on Transparent Electrode (Adv. Energy Mater. 19/2023)

Yage Zhou, Chunxu Xiang, Qi Dai, Sitong Xiang, Ran Li, Yuancai Gong, Qiang Zhu, Weibo Yan, Wei Huang, Hao Xin

First Published: 19 May 2023



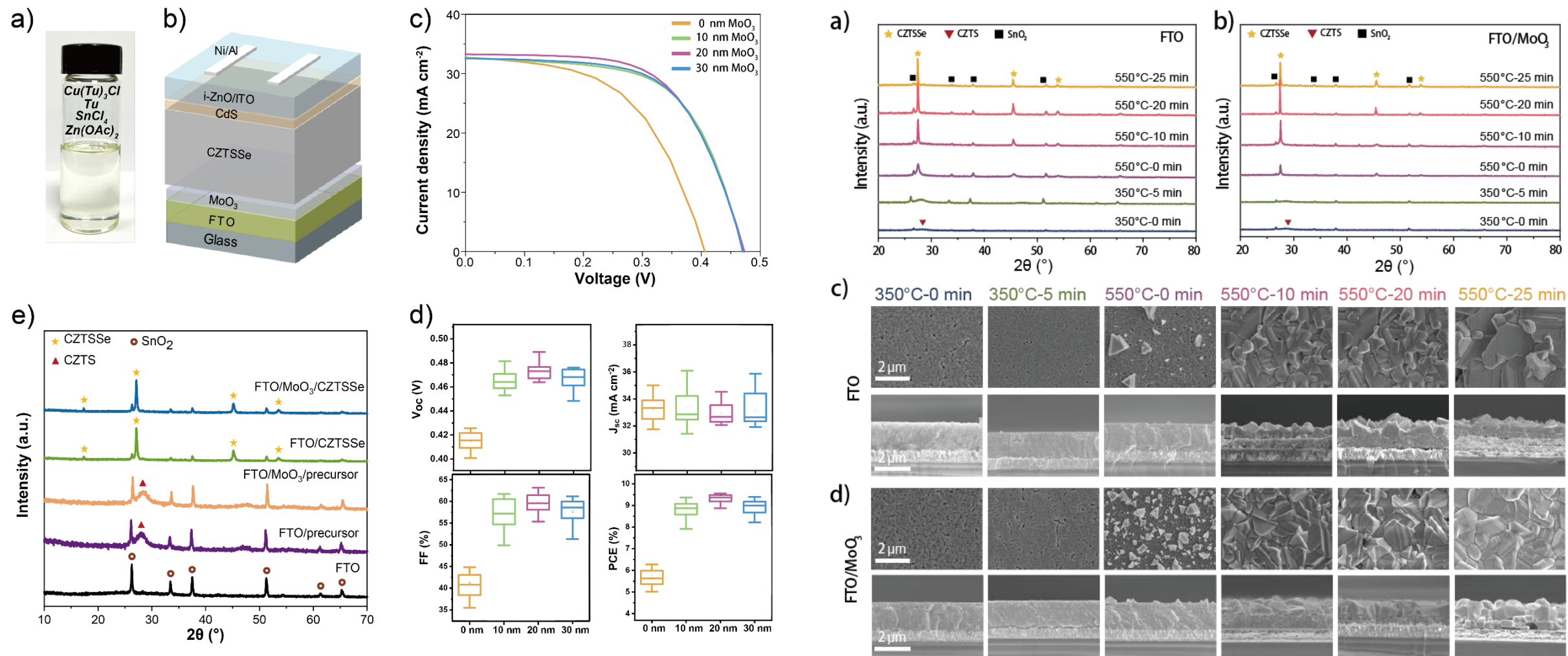
Kesterite Solar Cells

The image representing article number [2300253](#) by Wei Huang, Hao Xin, and co-workers depicts the architectural photovoltaic integration inspired by the Chinese building Water Cube. The work of this article is illustrated by the device structure of a kesterite solar cell on a translucent substrate applied to the building facade and the crystal structure of its absorber layer.

Adv. Energy Mater. 2023, 13, 202300253.

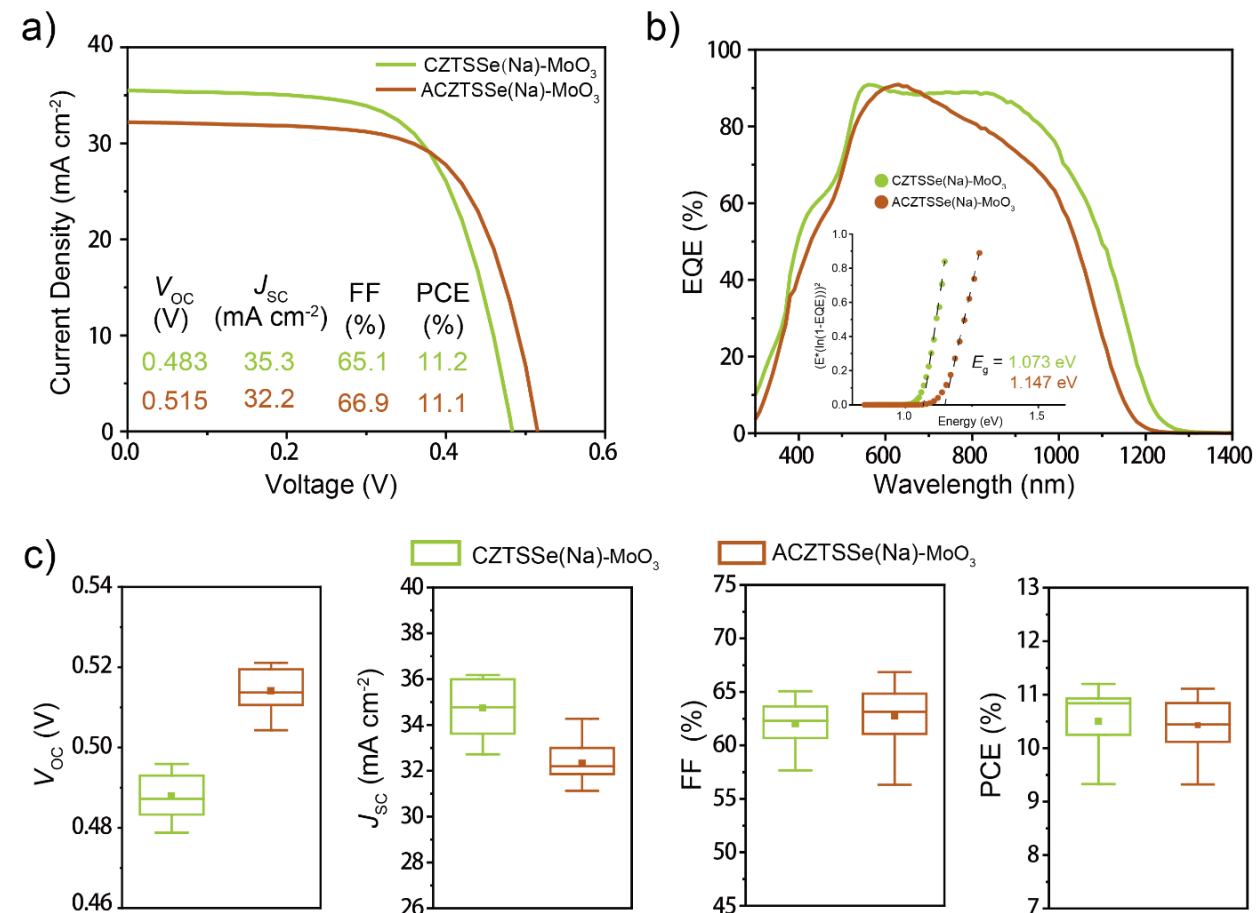
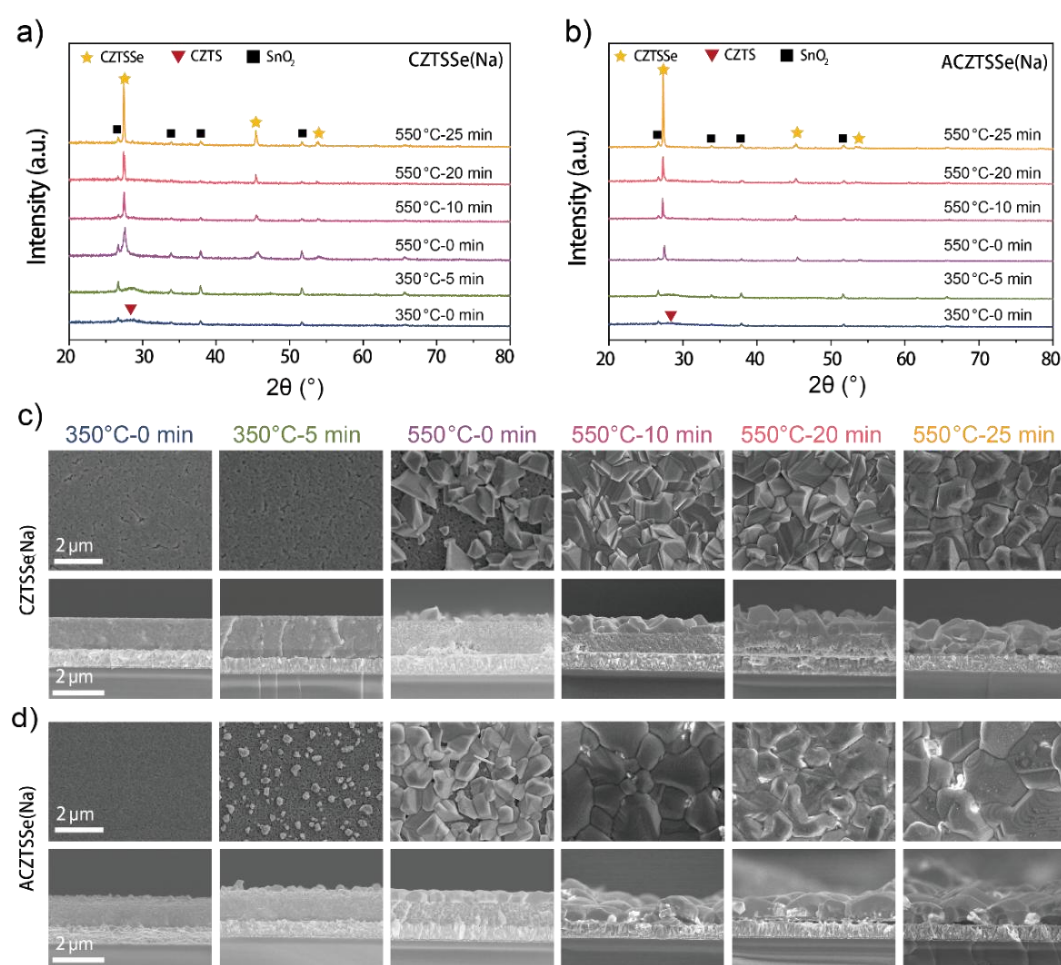
CZTSSe Solar Cell on Transparent Electrode

MoO₃ interfacial layer: selenized to MoSe₂, initiates grain growth at back contact

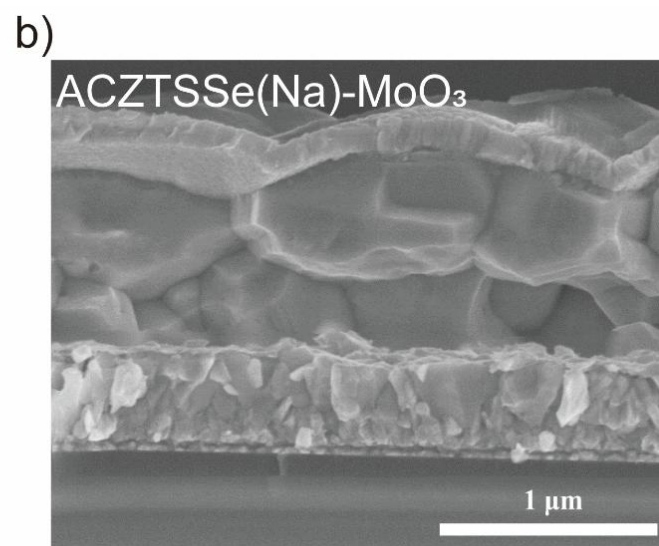
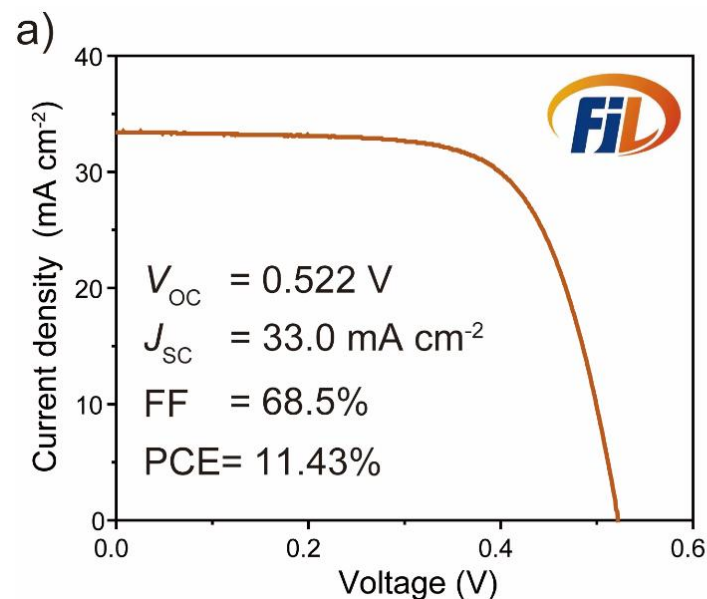


CZTSSe Solar Cell on Transparent Electrodes

Na doping and Ag alloying



CZTSSe Solar Cell on Transparent Electrodes



福建省计量科学研究院
FUJIAN METROLOGY INSTITUTE
(国家光伏产业计量测试中心)
National PV Industry Measurement and Testing Center

报告编号: 21Q3-00177

检测结果/说明:

Results of Test and additional explanation:

- Standard Test Condition (STC): Total Irradiance: 1000 W/m²
Temperature: 25.0 °C
Spectral Distribution: AM1.5G

2 Measurement Data under STC

Test Times	I_{SC} (mA)	V_{OC} (V)	I_{MPP} (mA)	V_{MPP} (V)	P_{MPP} (mW)	FF (%)	η (%) total area	η (%) effective area (with subtracted busbars area)
1	3.297	0.5226	2.931	0.4029	1.181	68.54	10.36	11.47
2	3.294	0.5222	2.927	0.4021	1.177	68.43	10.32	11.43
3	3.290	0.5210	2.919	0.4017	1.173	68.43	10.29	11.39
Average Value	3.294	0.5219	2.926	0.4022	1.177	68.47	10.32	11.43

Mismatch factor: 1.014

3 I-V & P-V Characteristic Curves under STC

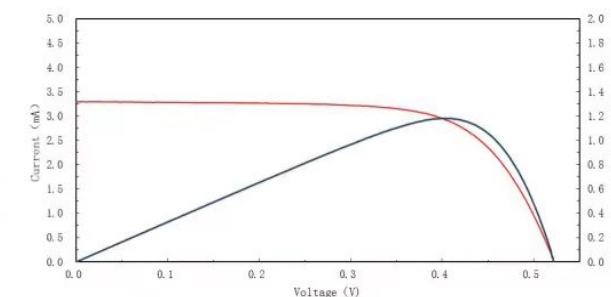
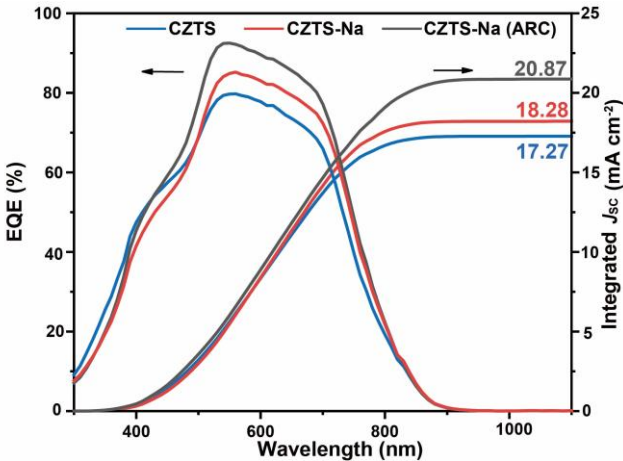
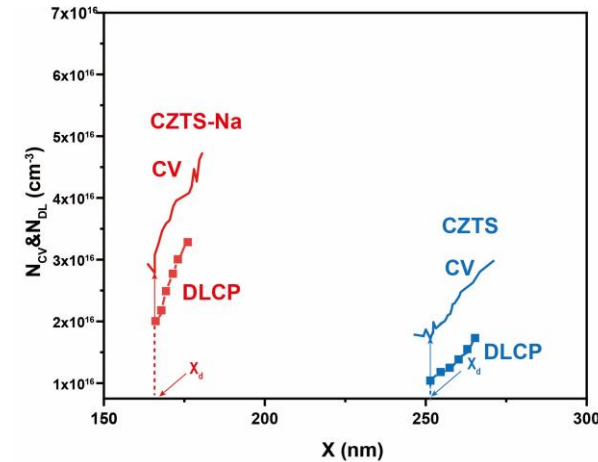
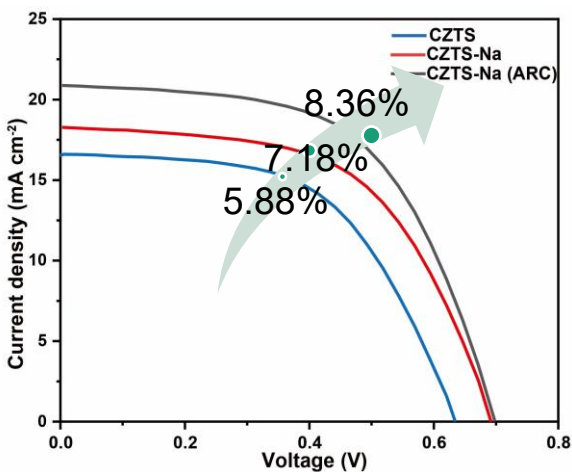
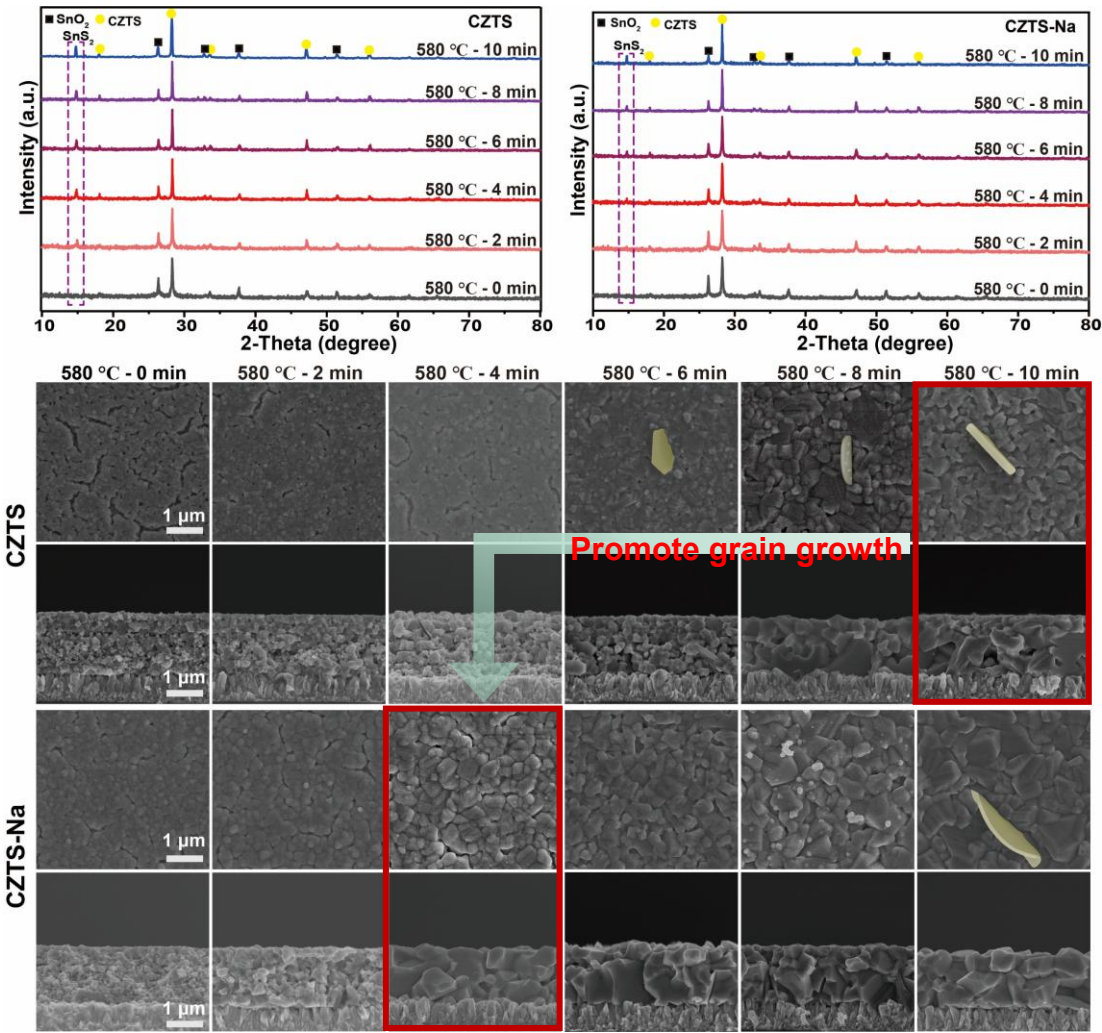


Figure 1. I-V and P-V characteristic curves of the measured sample under STC

Device*	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	n	R_s ($\Omega \text{ cm}^2$)	R_{sh} ($\Omega \text{ cm}^2$)	J_0 (A cm^{-2})	E_U (meV)	σ_g (meV)	V_{opt} (meV)
CZTSSe/FTO	0.406	32.7	52.9	7.02	2.20	2.65	115	2.85×10^{-5}	24.6	55.6	23.3
CZTSSe/MoO ₃ /FTO	0.473	33.4	60.5	9.56	2.00	2.95	607	3.44×10^{-6}	24.1	52.3	22.8
CZTSSe(Na)/MoO ₃ /FTO	0.483	35.5	65.1	11.2	1.77	1.73	982	1.11×10^{-6}	24.1	47.5	22.3
ACZTSSe(Na)/MoO ₃ /FTO	0.515	32.2	66.9	11.1	1.57	2.42	1082	8.33×10^{-8}	23.1	55.9	23.7
CZTSSe(Na)/Mo	0.483	37.4	66.2	12.0	1.68	1.80	2729	1.70×10^{-7}	23.9	50.51	23.9
ACZTSSe(Na)/Mo	0.531	34.8	67.0	12.4	1.53	1.74	5449	2.71×10^{-8}	23.5	48.3	22.2

CZTS Solar Cell on FTO Electrodes

Na doping



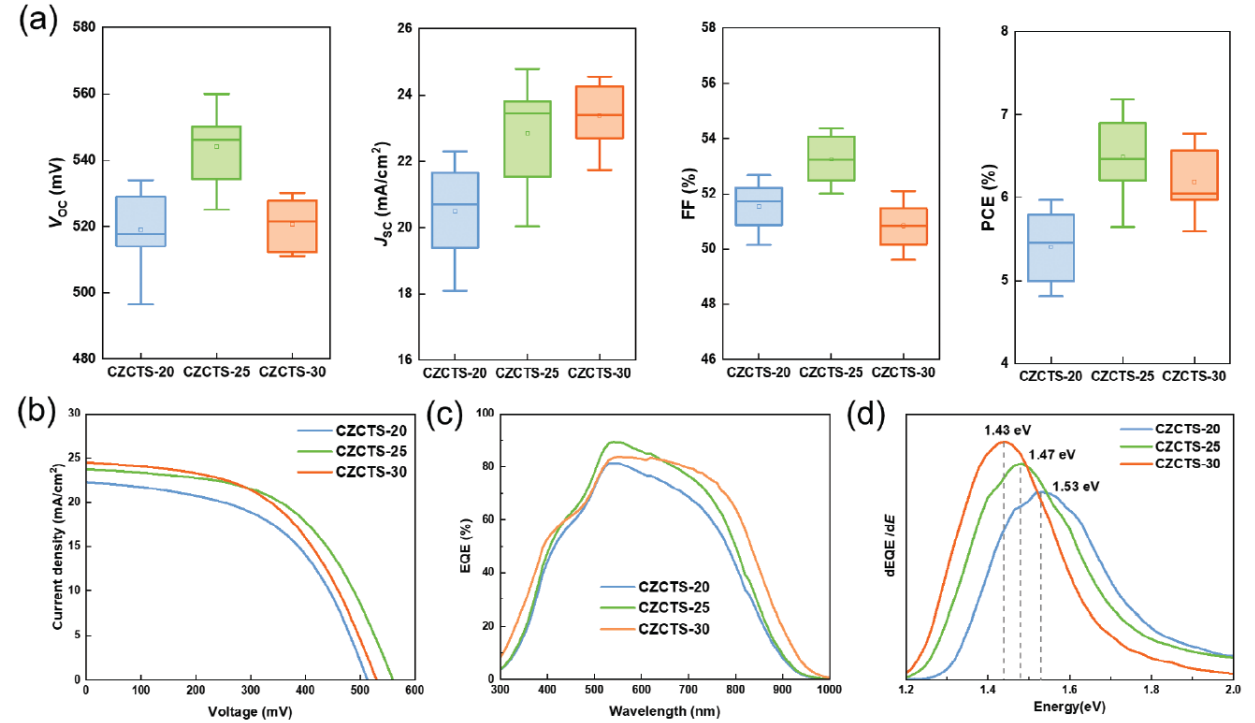
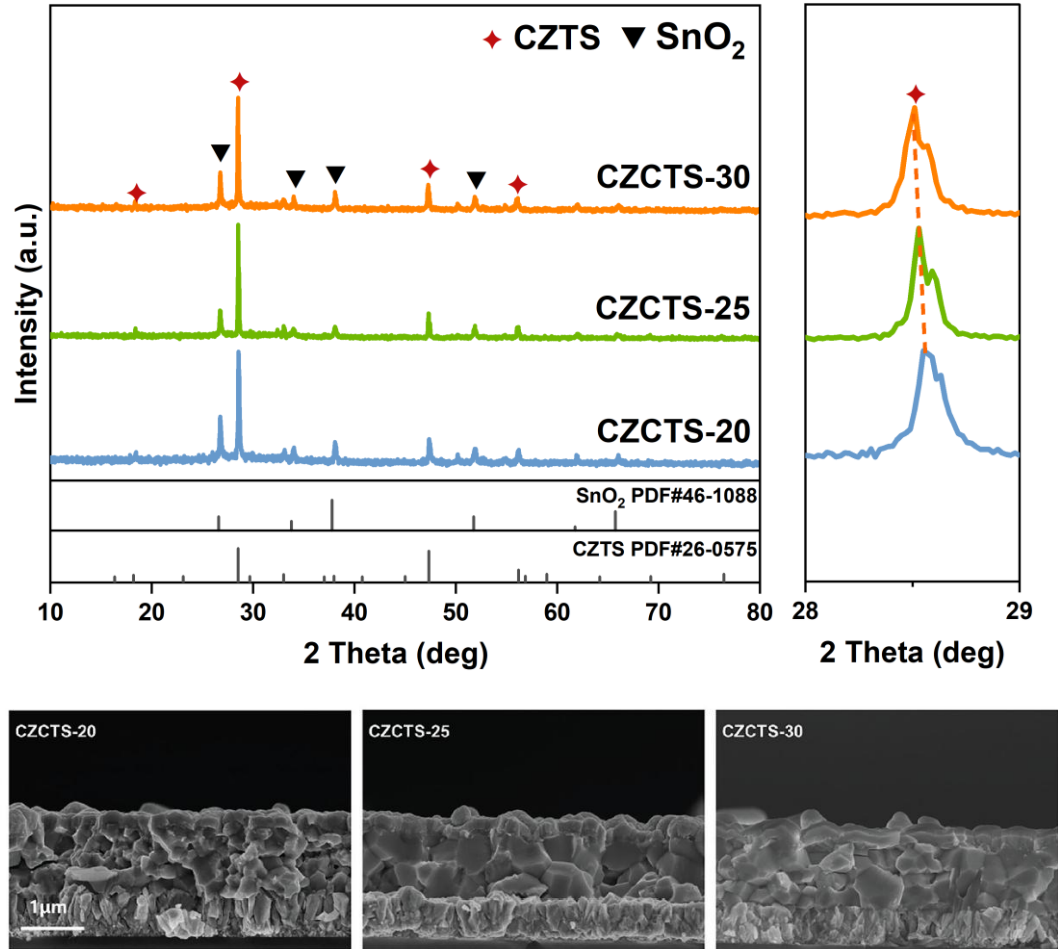
Mitigated absorber and HJ interface defects

$E_g = 1.61 \text{ eV}$

Device	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF [%]	PCE [%]	R _s [Ω cm ²]	R _{sh} [Ω cm ²]	n	J ₀ [A cm ⁻²]	E _g [eV]	V _{oc} /V _{oc} ^{SQ} [%]	N _{CV} [cm ⁻³]	N _{DLCP} [cm ⁻³]	N _{IT} [cm ⁻³]	X _d [nm]
CZTS	0.638	16.62	55.48	5.88	12.90	571	3.46	4.23 × 10 ⁻⁶	1.62	47.20	1.90 × 10 ¹⁶	1.11 × 10 ¹⁶	7.90 × 10 ¹⁵	252
CZTS-Na	0.696	18.27	56.46	7.18	8.62	701	2.38	9.52 × 10 ⁻⁸	1.61	52.41	2.66 × 10 ¹⁶	2.00 × 10 ¹⁶	6.60 × 10 ¹⁵	165
CZTS-Na (ARC)	0.700	20.88	57.20	8.36	7.67	839	2.27	7.64 × 10 ⁻⁸	1.61	52.48	-	-	-	-

CZTS Solar Cell on FTO Electrodes

Cd alloying: improved grain growth, suppressed Cu_{Zn}

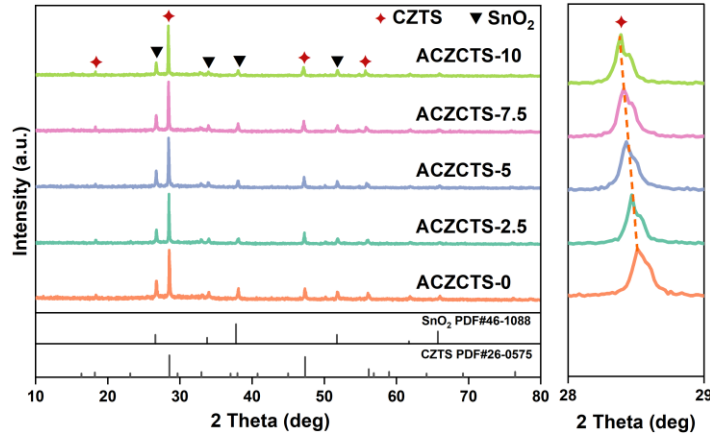


Cell	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]	R_s [Ω m ²]	R_{sh} [Ω m ²]	n	$V_{\text{oc}}/V_{\text{oc}}^{\text{SQ}}$ [%]	E_g [eV]	E_u [meV]
CZCTS-20	0.513	22.3	52.2	5.97	27.2	1865	2.5	41.1	1.53	27.6
CZCTS-25	0.560	23.7	54.1	7.18	33.7	2739	2.6	46.7	1.47	28.3
CZCTS-30	0.530	24.6	52.1	6.77	31.0	2531	2.8	45.1	1.43	31.4

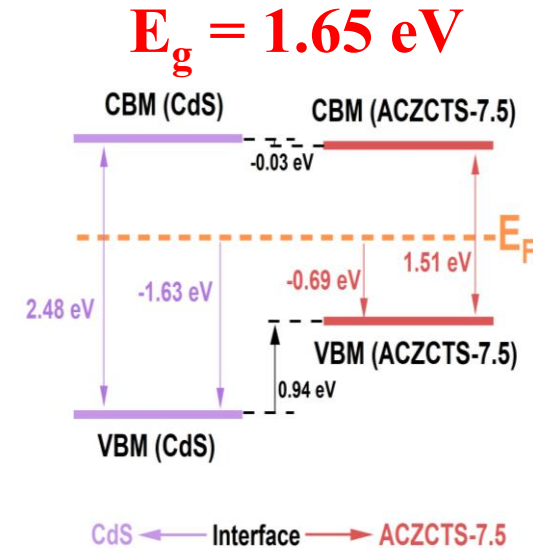
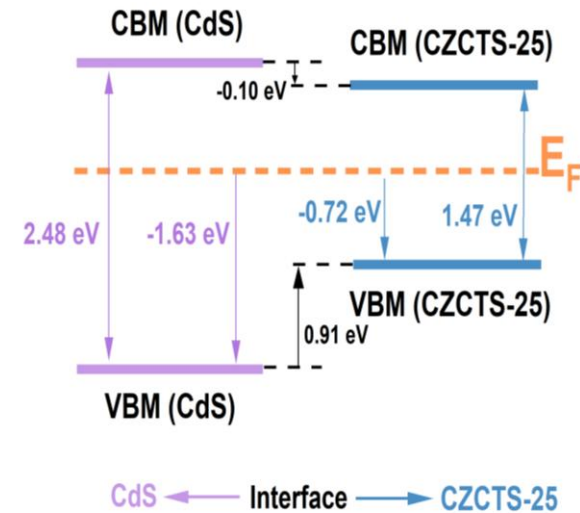
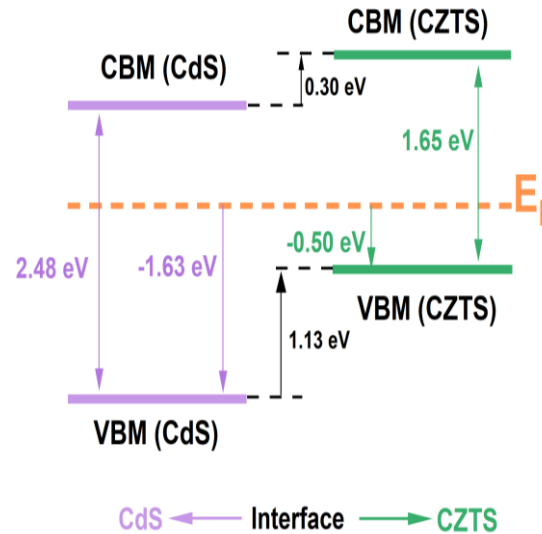
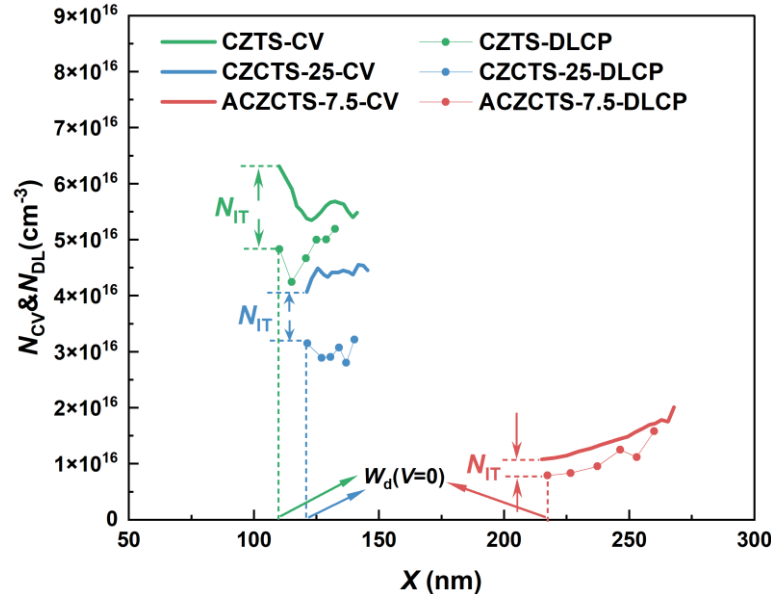
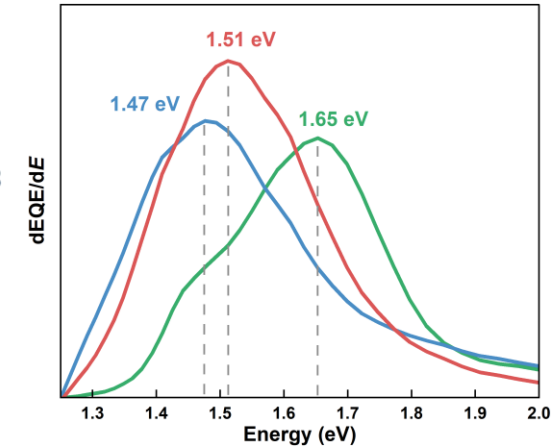
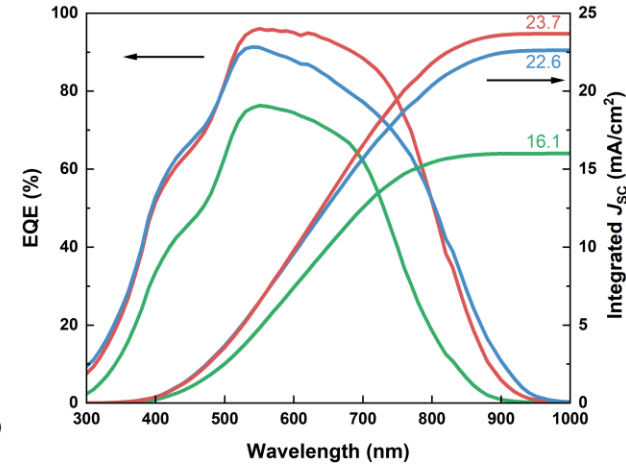
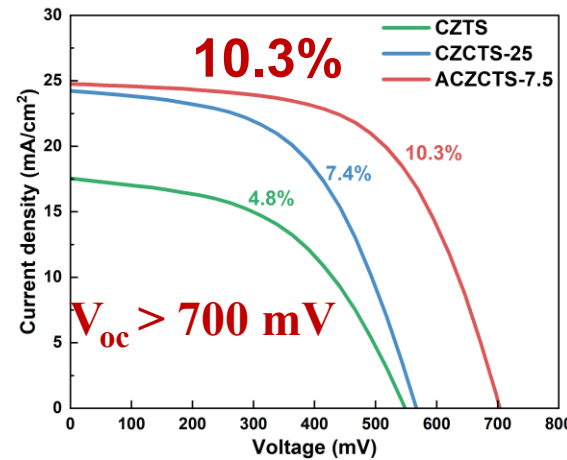
Cd/(Cd+Zn)=25% $E_g = 1.47$ eV

CZTS Solar Cell on FTO Electrodes

Ag/(Ag+Cu)=7.5%

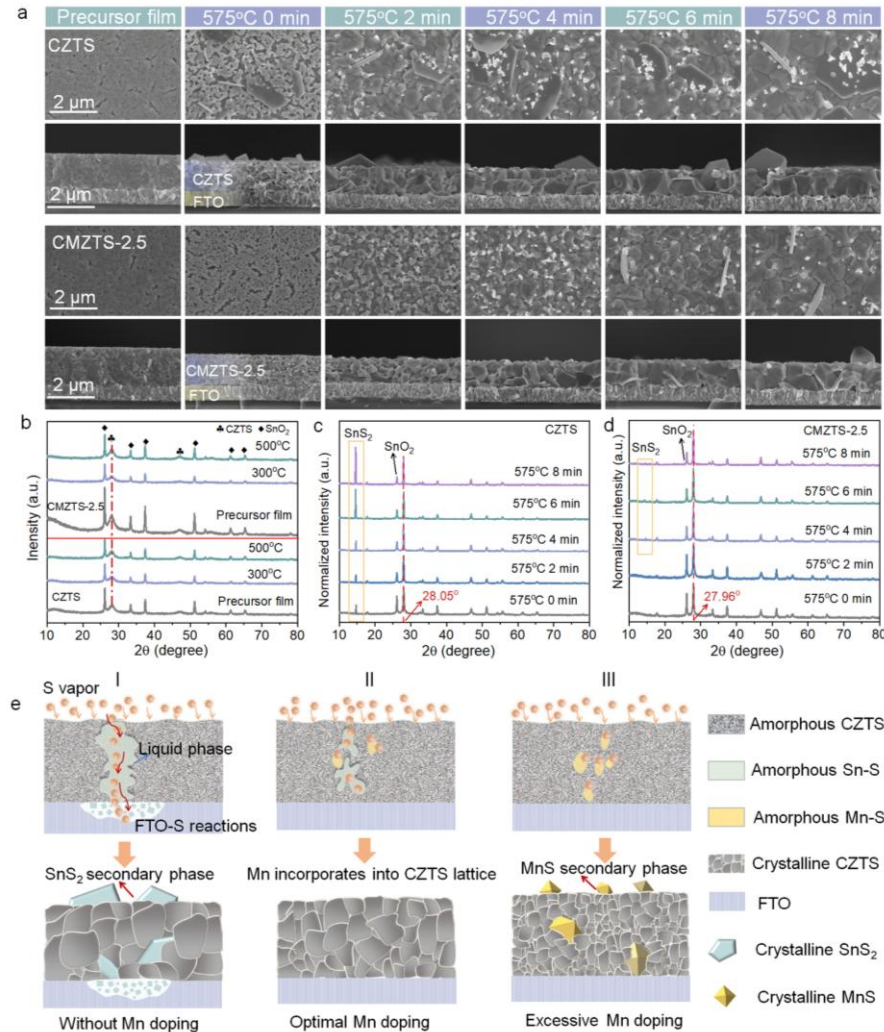


Ag-Cd co-alloying: CBO: Cliff to Spike

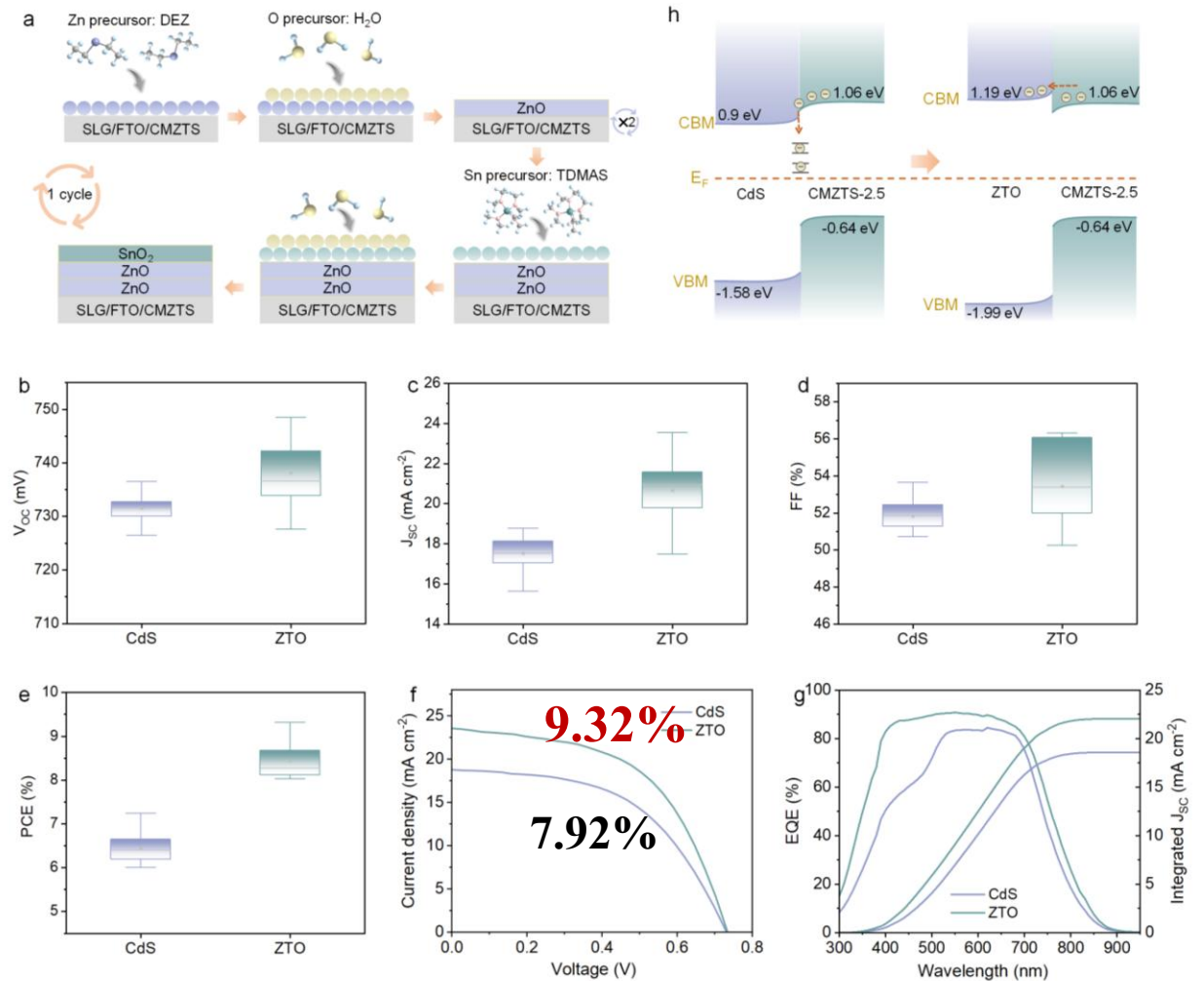


Cd-free CZTS on FTO Electrode

Mn-Mediated Phase Engineering



ZnSnO buffer layer



Outline

I. Motivation

II. Kesterite Solar Cells

CZTSSe

Absorber Engineering

Interface Engineering

Module

CZTS

III. Chalcopyrite Solar Cells

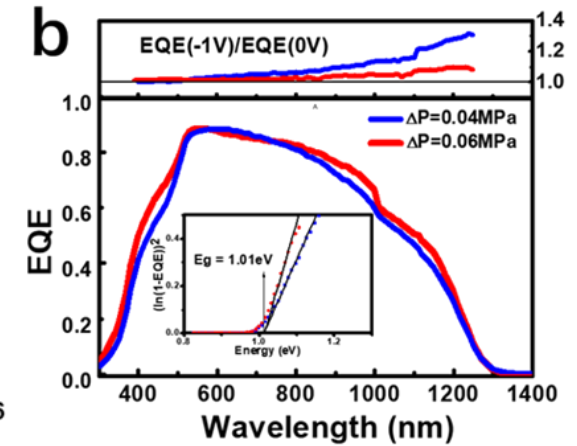
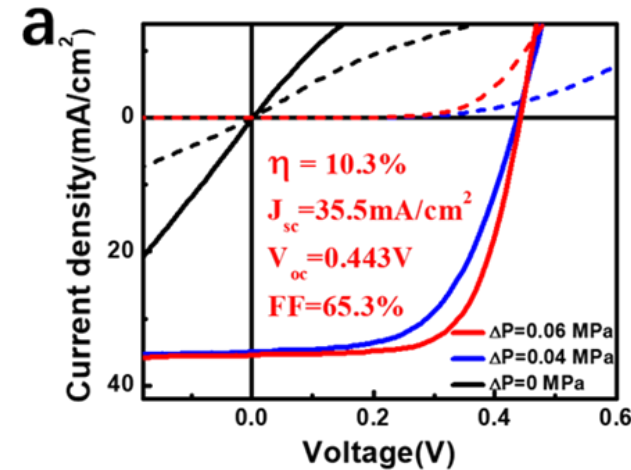
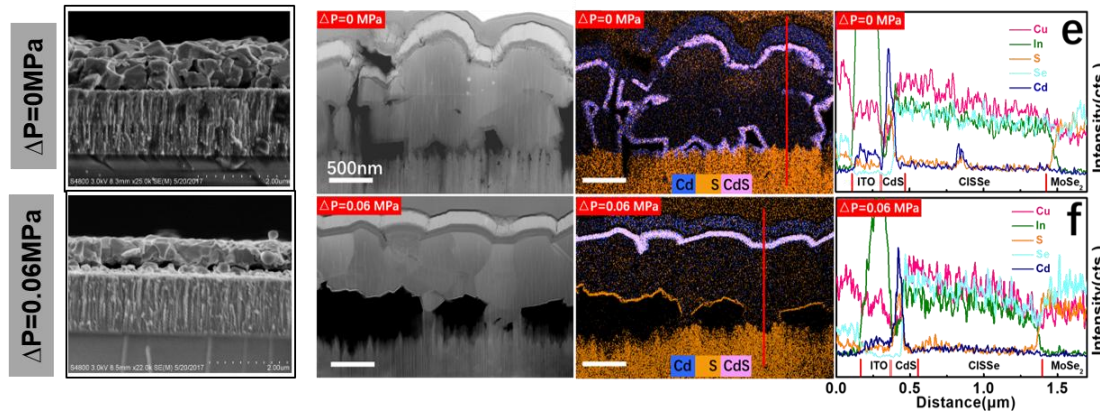
CIGSSe

CIGS

V. Summary and Outlook

CIGSSe: High Pressure Selenization

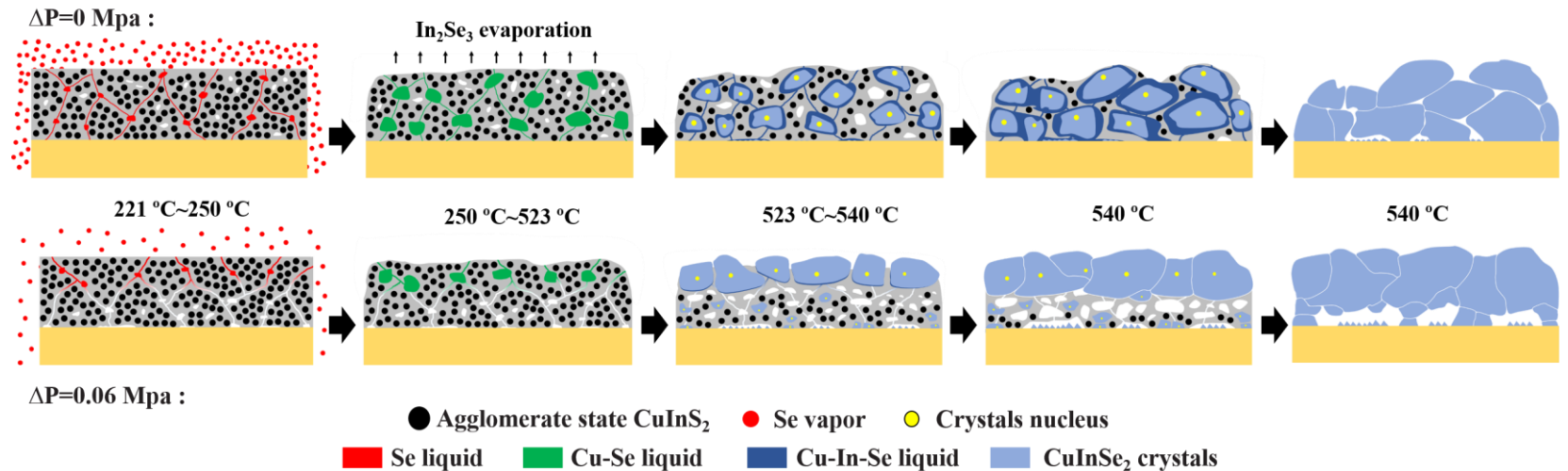
Cu/In=0.85, no etching treatment



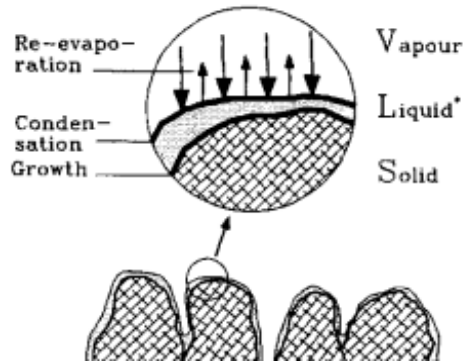
ΔP=0 MPa: loose grains, CdS into the film, Cu-rich near surface

ΔP=0.06 MPa: dense top grains, CdS only on surface, uniform composition

- Dissolve all precursors at room temperature.
- Long-time stability
- PCE=10.3%



High Pressure Selenization: Cu-rich Absorber



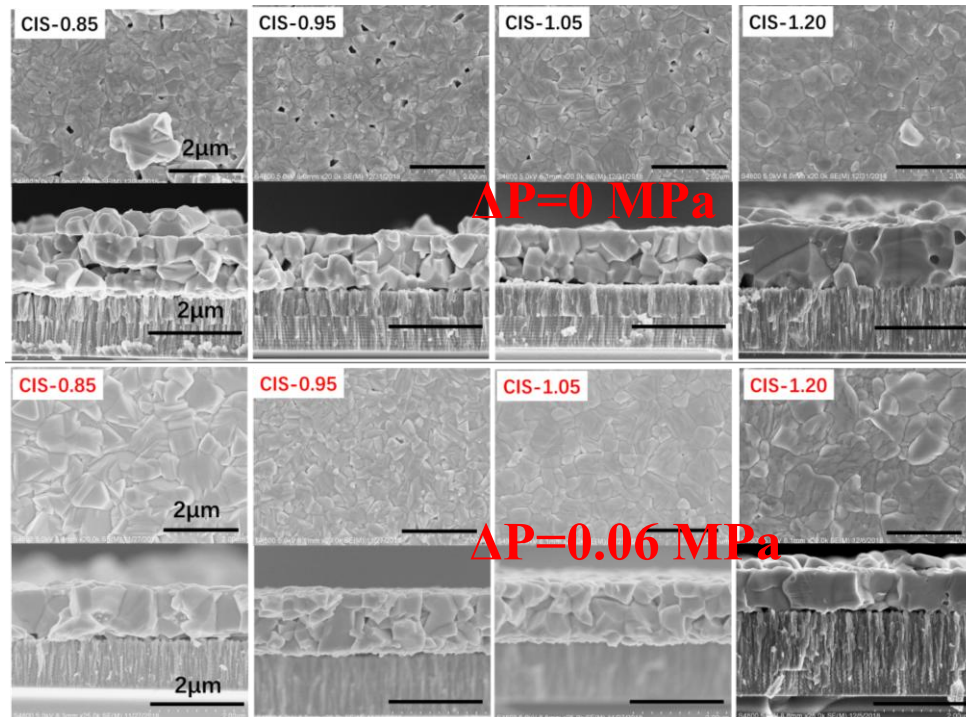
Cu-poor ($\text{Cu}/(\text{In}+\text{Ga}) < 0.9$)

- State-of-the-art composition
- Avoid Cu_{2-x}Se impurity (KCN etching is still needed)
- Order-defect-compound (ODC) layer

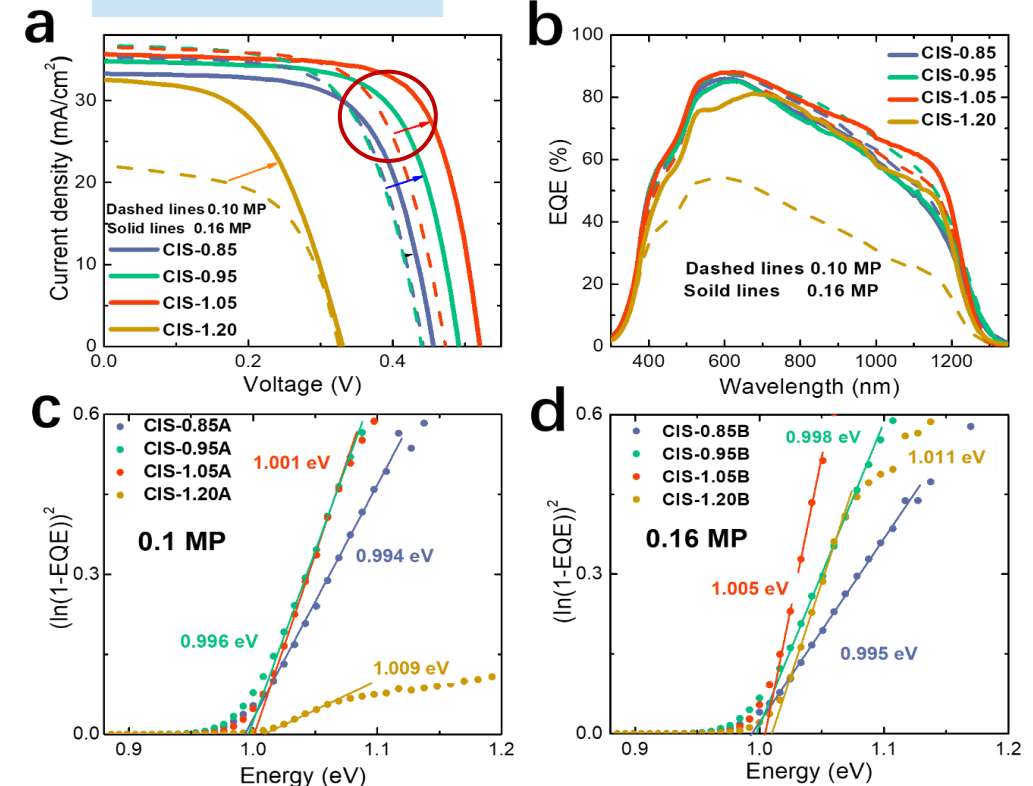
Cu-rich

- Lower defect
- Potentially High V_{oc}
- Cu_{2-x}Se impurity
- High performance not achieved yet

$\text{Cu}/\text{In} = 0.85, 0.95, 1.05, 1.20$

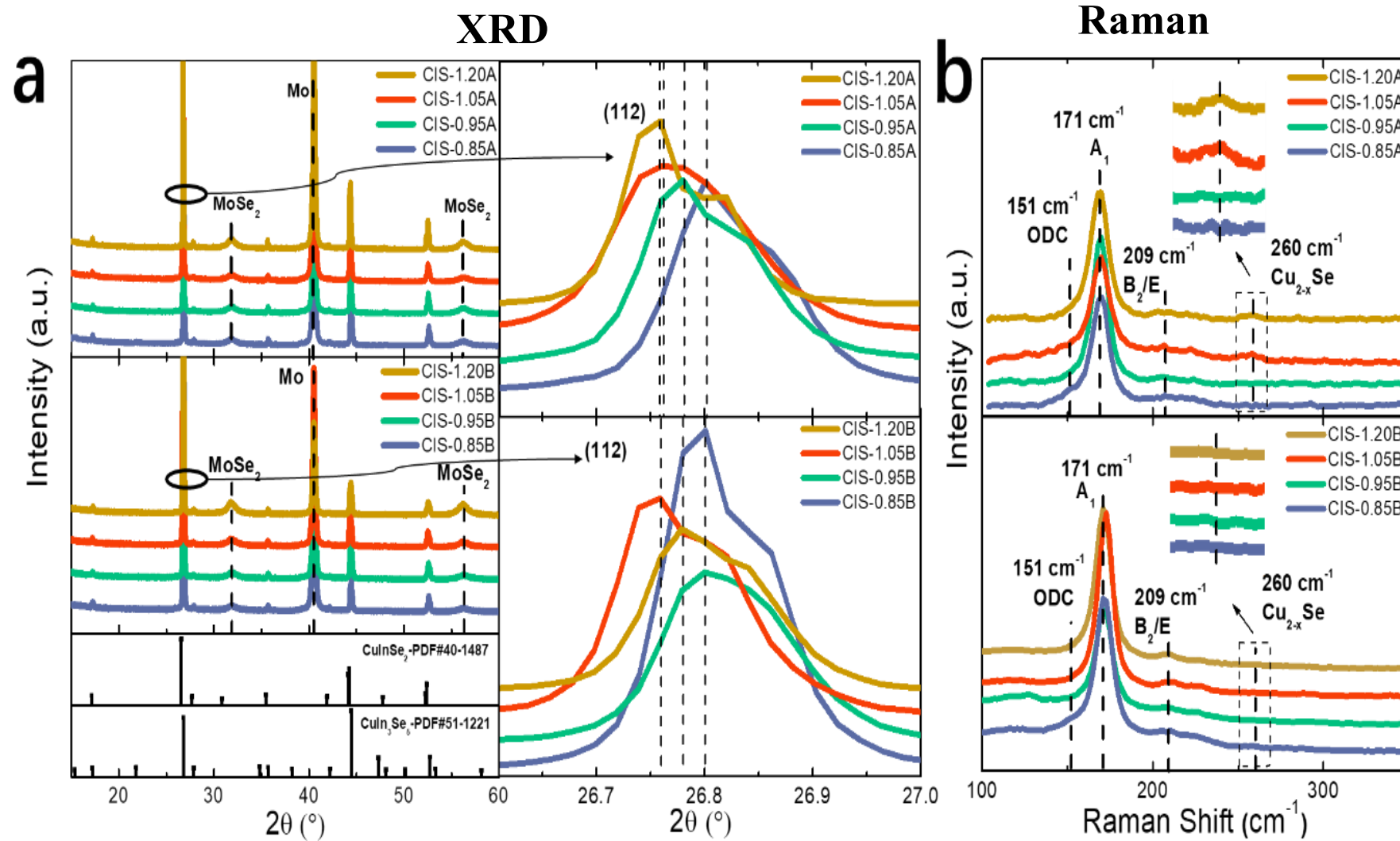


$\text{Cu}/\text{In} = 1.05$



Cu_{2-x}Se -free Cu-Rich Absorber

With $(\text{NH}_4)_2\text{S}$ etching, Cu_{2-x}Se on surface can be removed

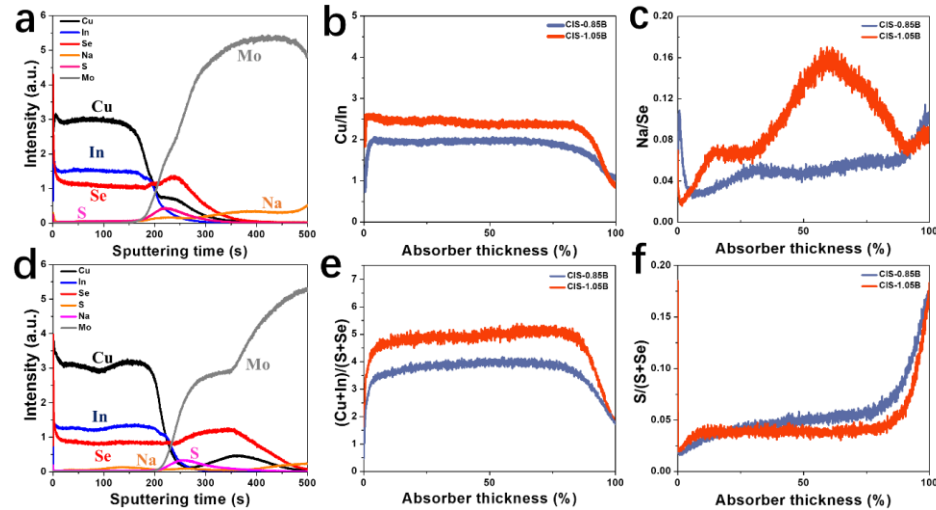


Cu_{2-x}Se exists in
Cu-rich films

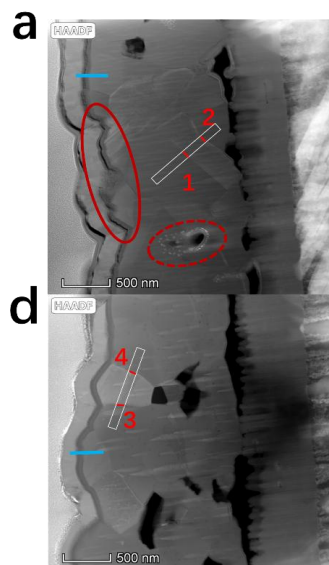
Cu_{2-x}Se free

Cu-rich CIS: Optoelectronic Properties

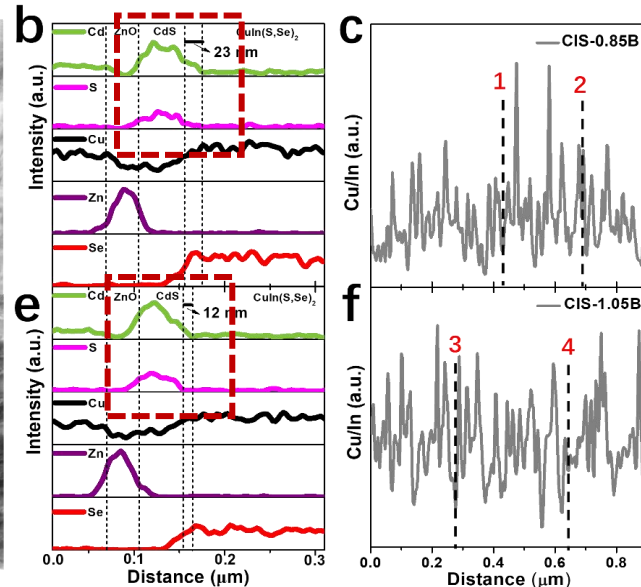
GDEOS



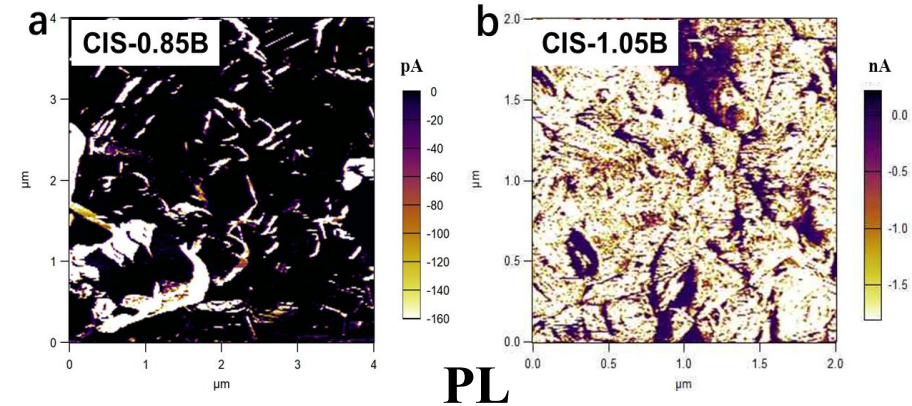
TEM



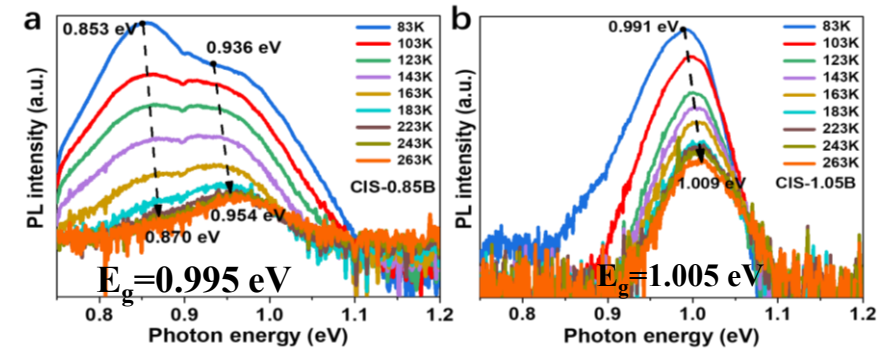
EDX



c-AFM

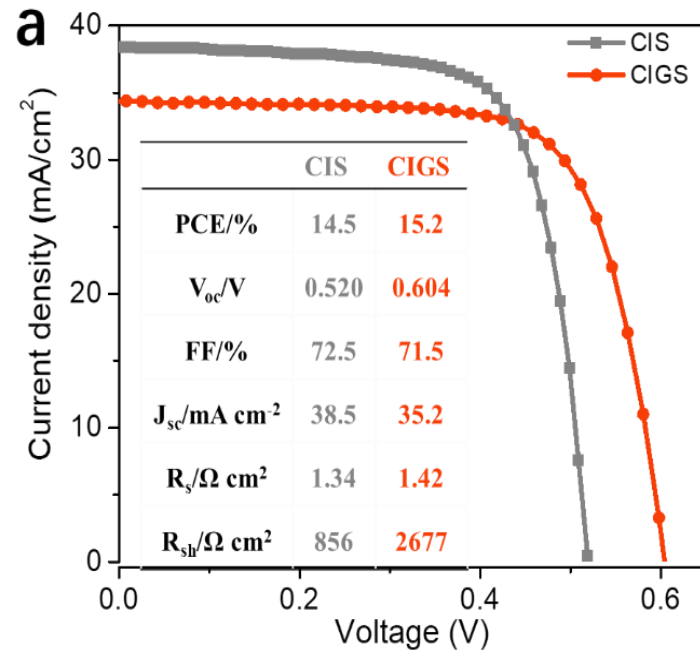


PL



- **Cu-rich composition**
- **Shorter Cd diffusion into absorber**
- **Epitaxial like interface**
- **Higher and more uniform conductivity**
- **Higher PL peak position**

Champion Cu-rich CIS/CIGS Device from DMF Solution



PCE=14.5%

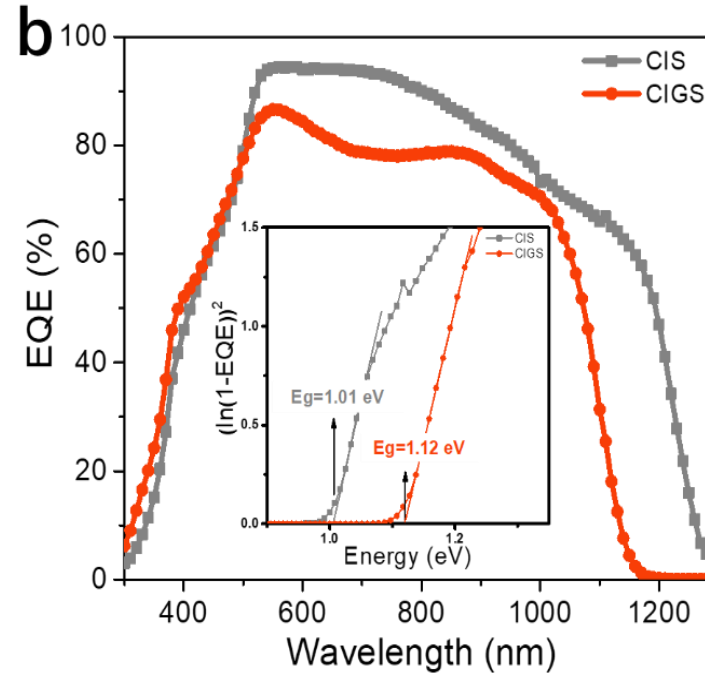
V_{oc} =520 mV

J_{sc} =38.5 mA/cm²

FF=72.5%

$V_{oc,def}$ =0.235V

V_{oc}/V_{oc}^{SQ} =67%



PCE=15.2%

V_{oc} =604 mV

J_{sc} =35.2 mA/cm²

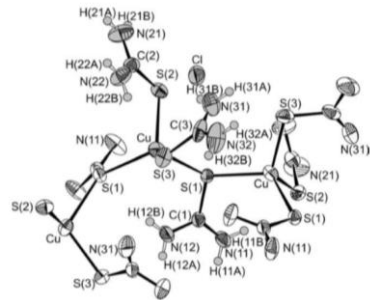
FF=71.51%

$V_{oc,def}$ =0.273 V

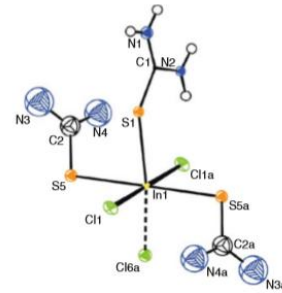
V_{oc}/V_{oc}^{SQ} =69%

H₂O Solution: Complexes as Precursors

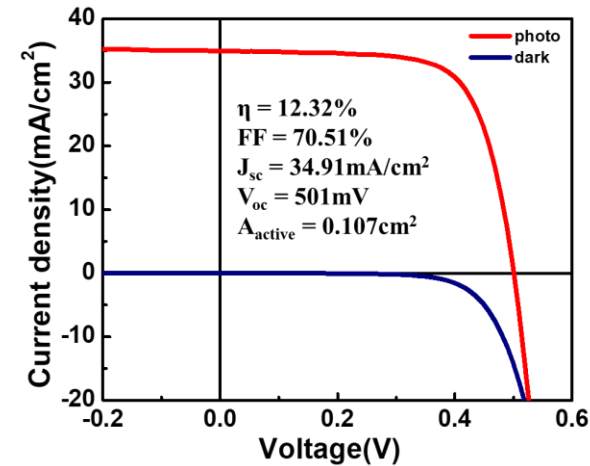
- Challenges: Hydrolysis, Impurities originating from starting materials, Oxidation



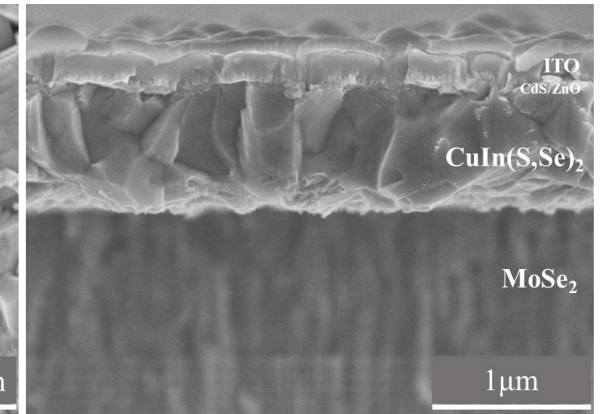
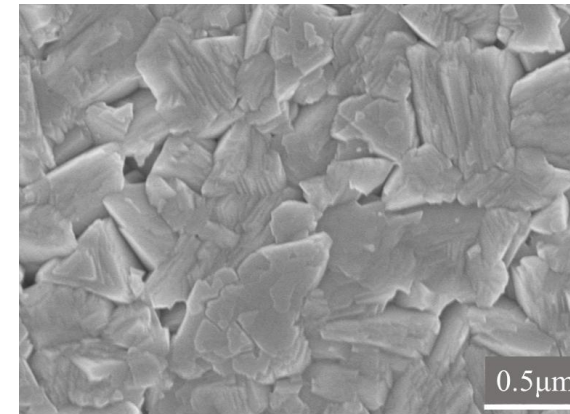
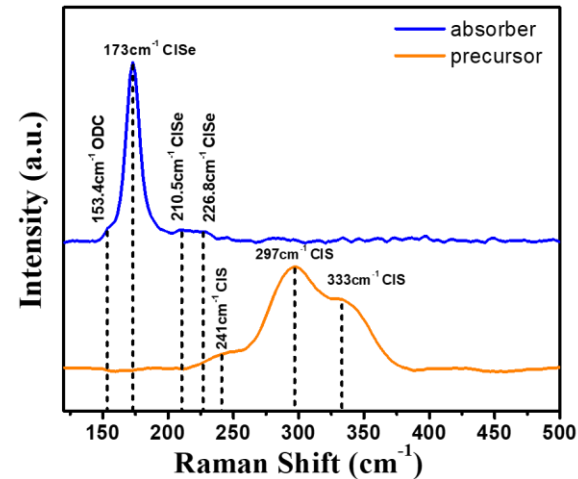
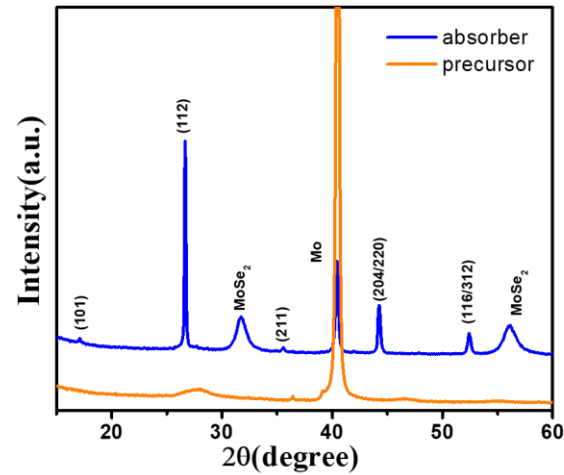
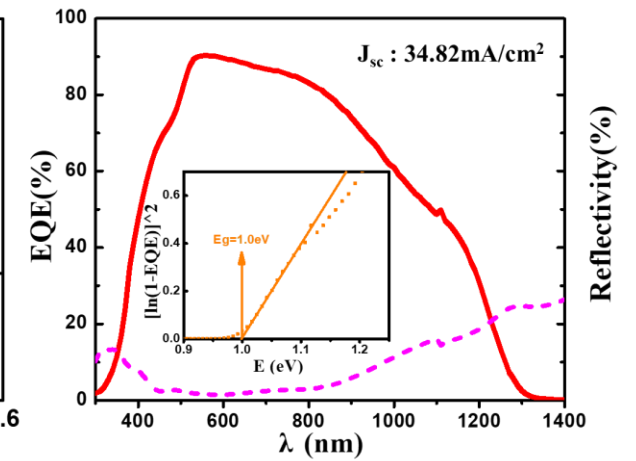
P. Bombicz et al. Inorg.Chim. Acta 357 (2004) 513.



J Therm Anal Calorim (2011) 83.



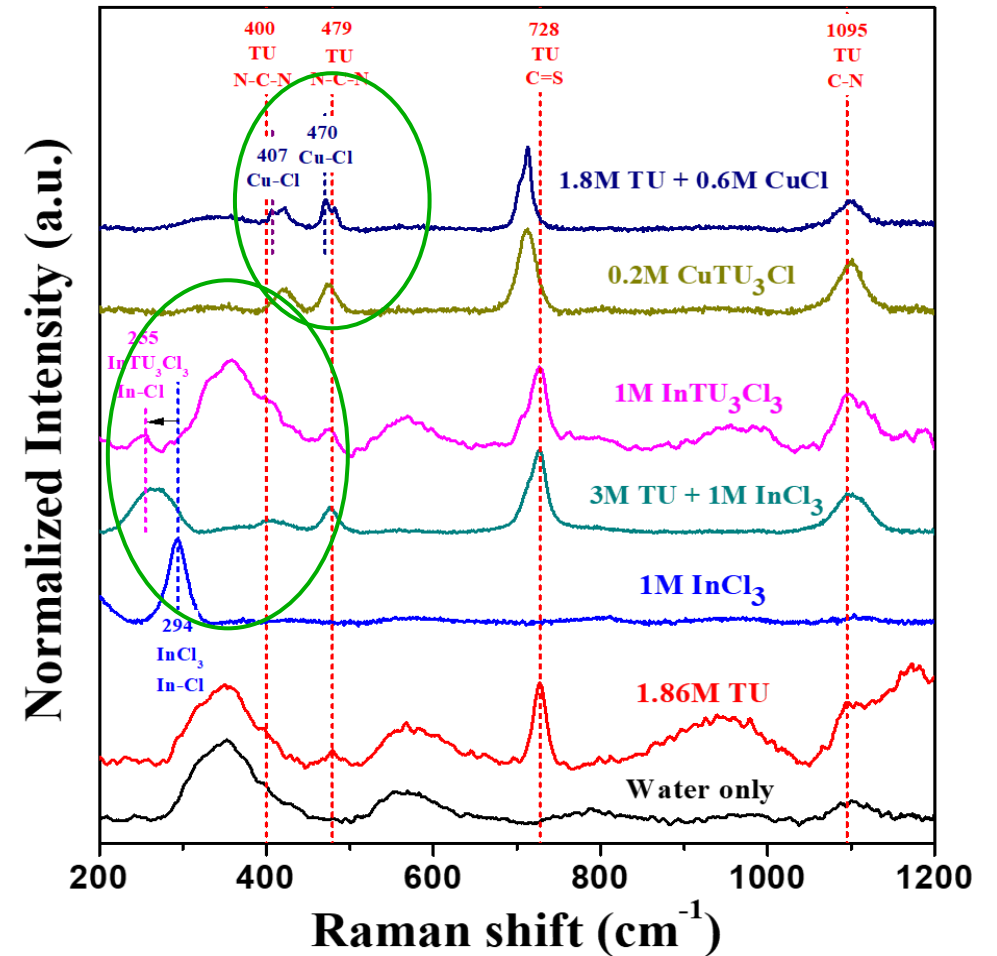
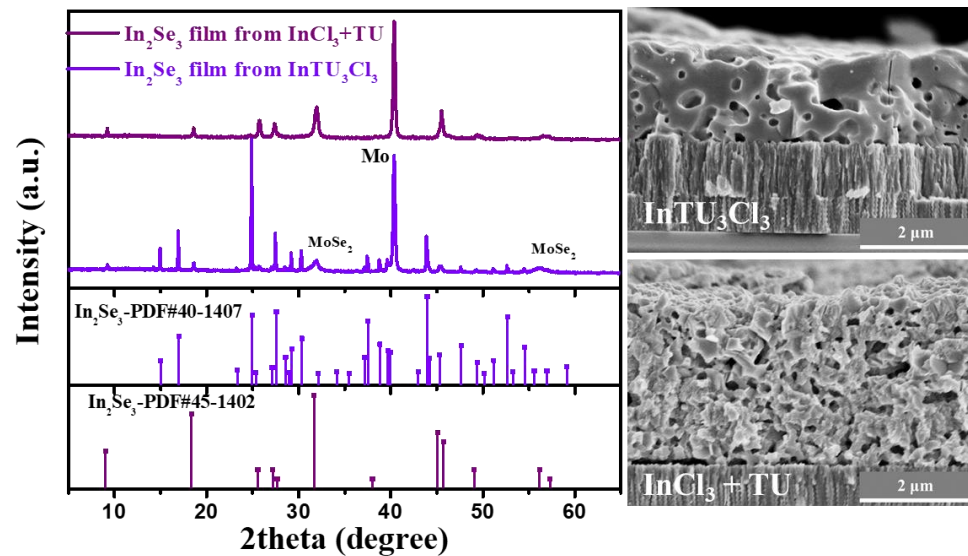
12.3% CIS



Chemistry in Aqueous Solution

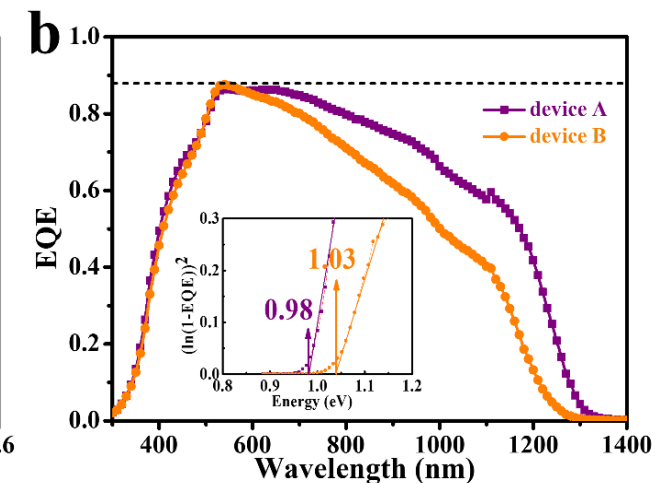
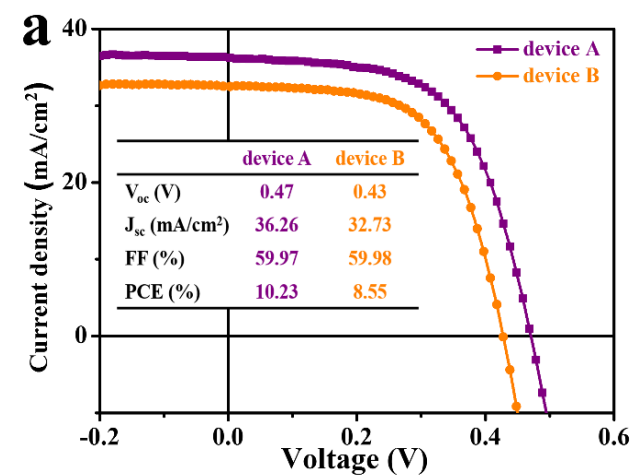
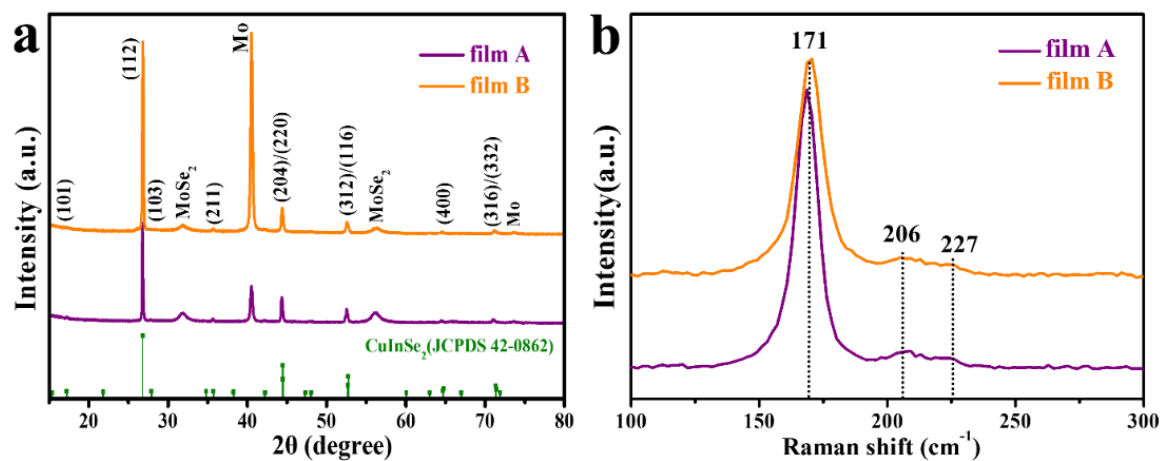
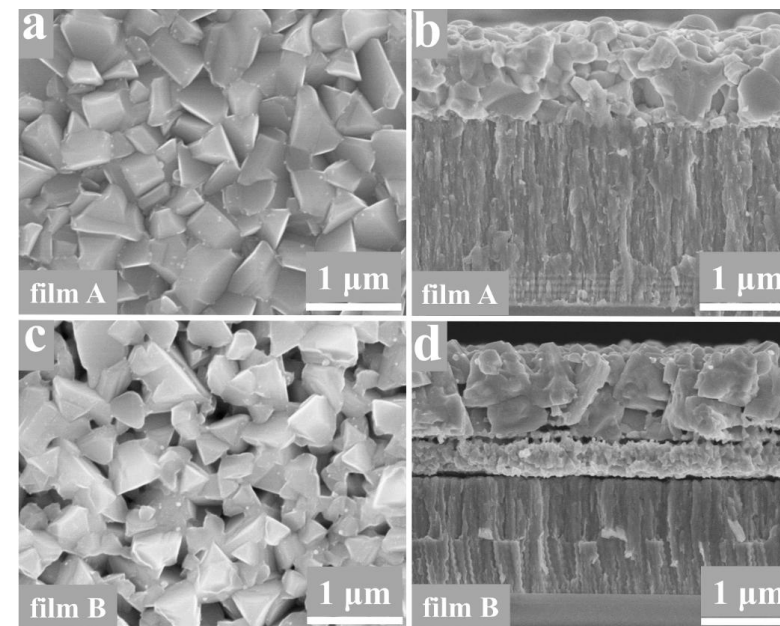
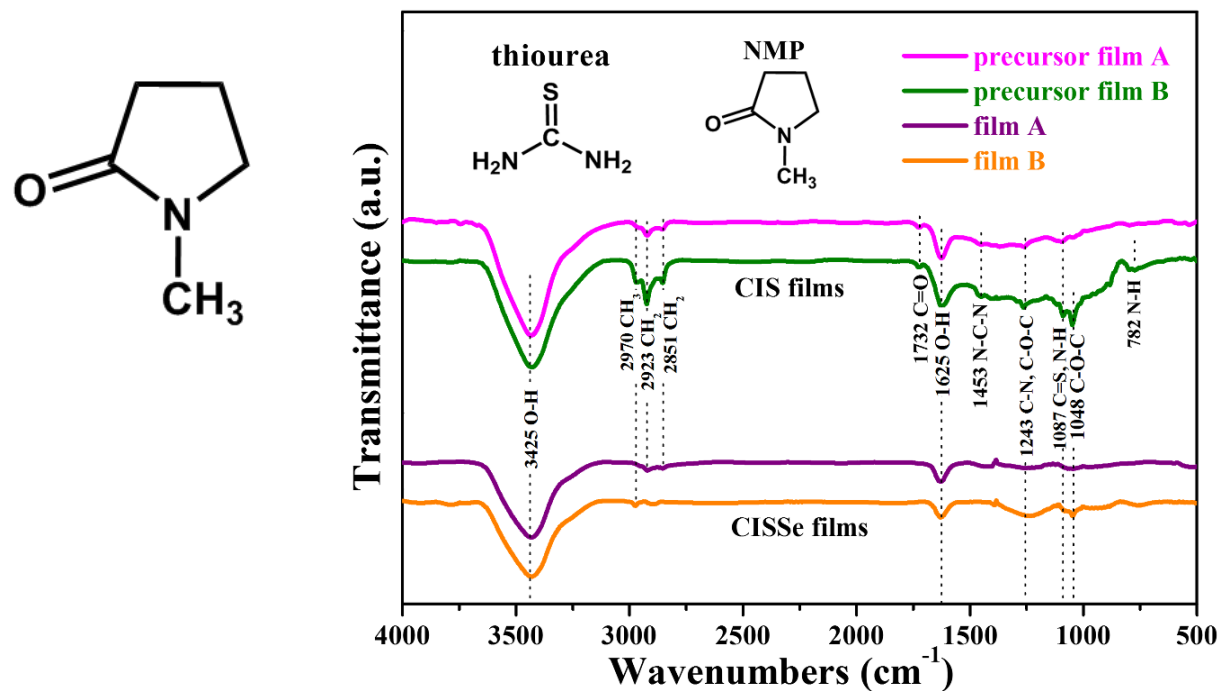


All the solutions prepared by mixing TU and InCl_3 became unclear.



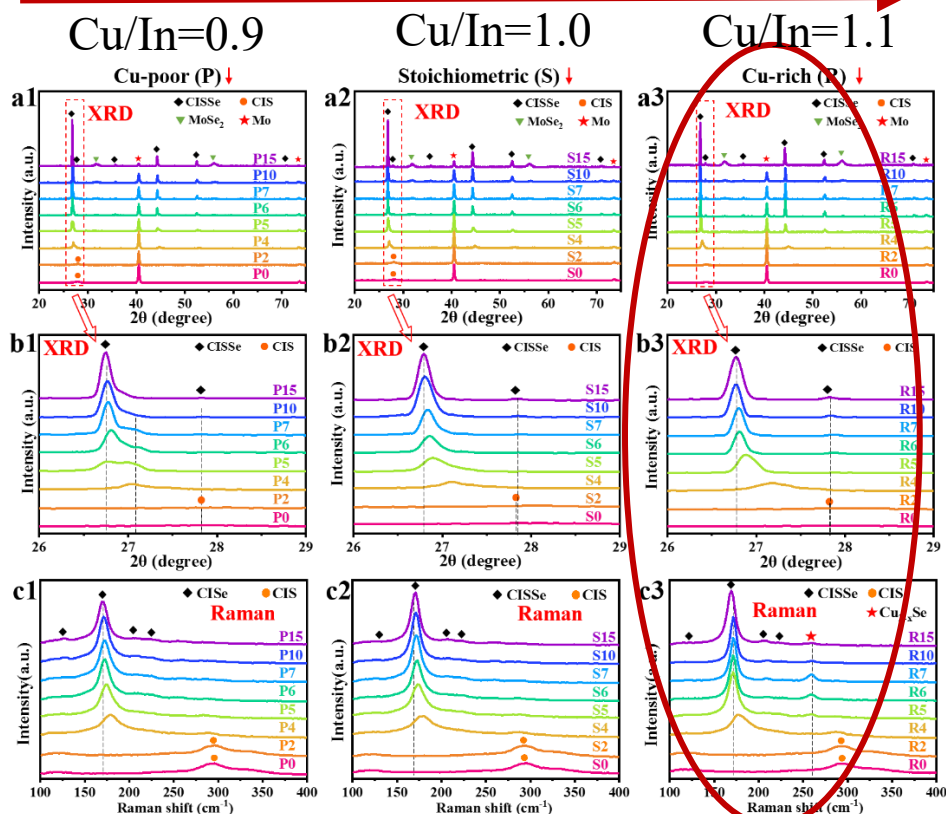
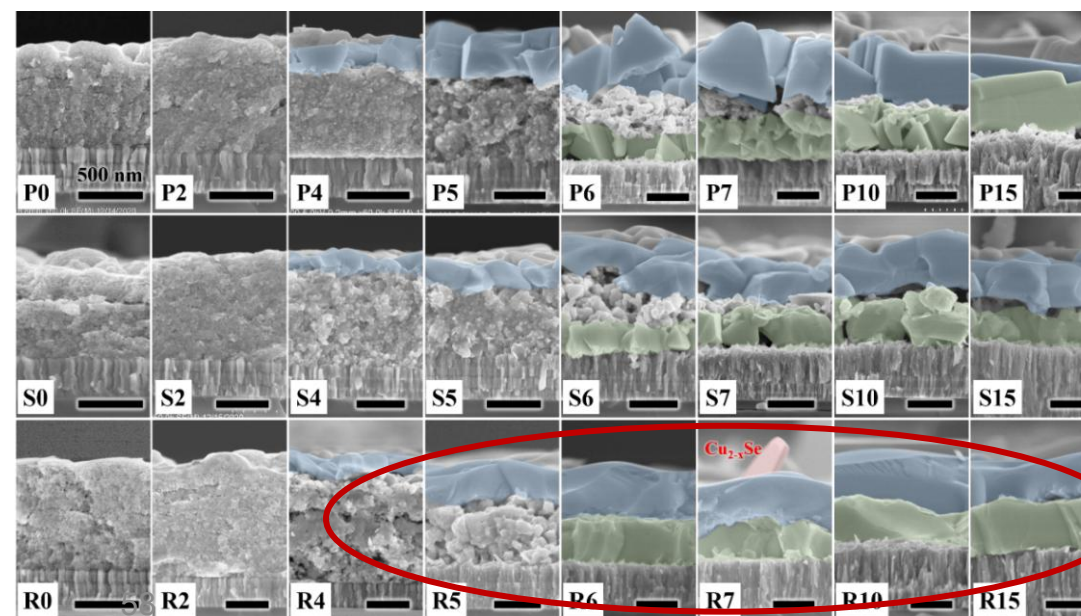
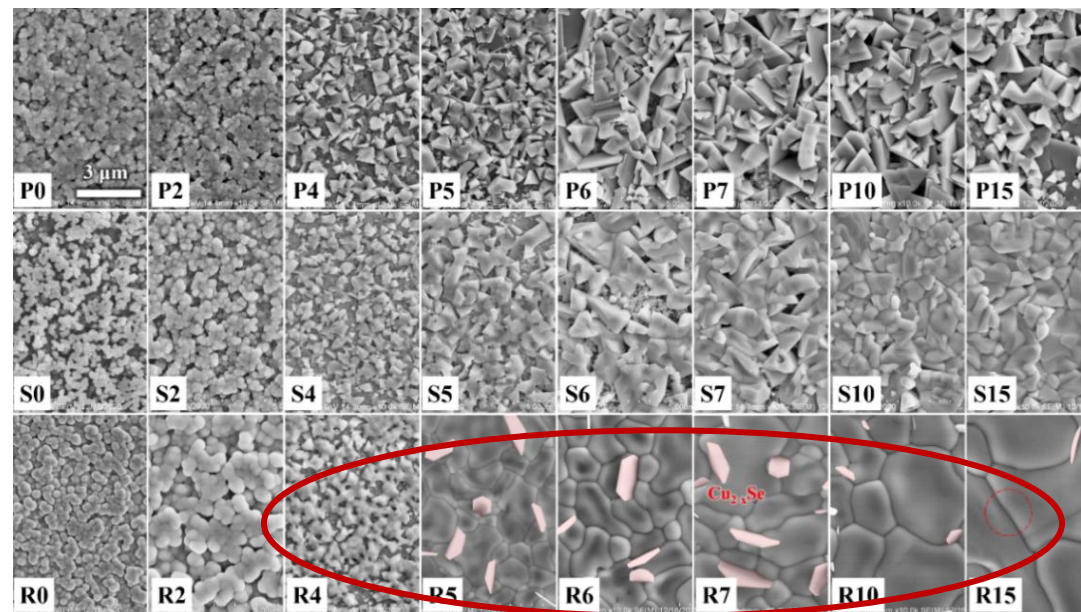
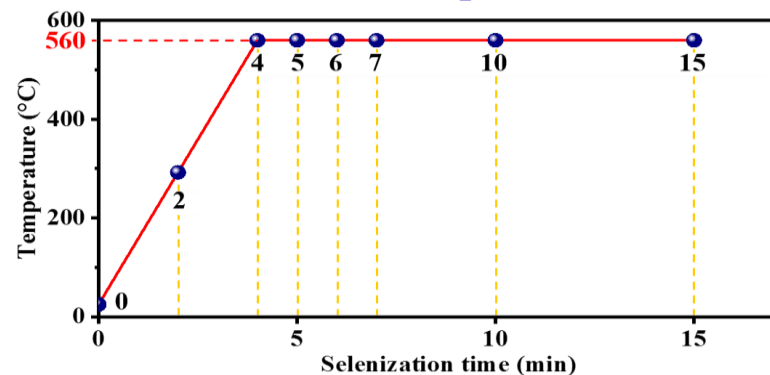
The direct bonding of all metal ions with sulfur in the precursor solution is the key for high quality absorber film.

NMP Solution: Annealing in Air vs Inert Atmosphere



Grain Growth of Solution Processed CIS absorber

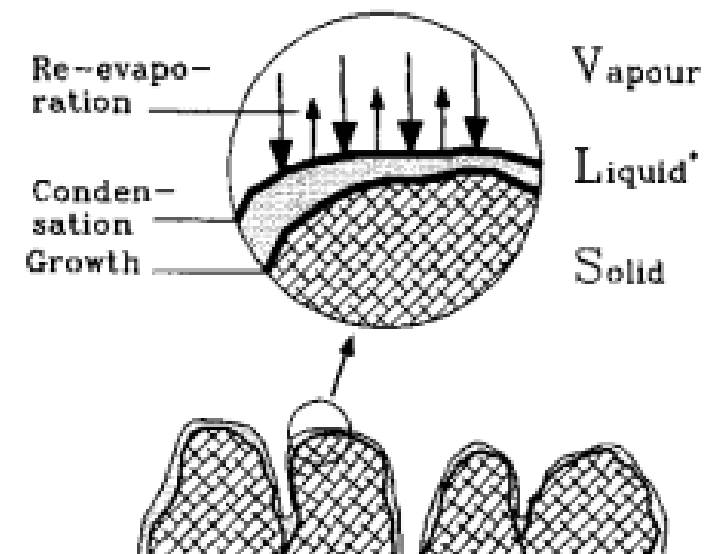
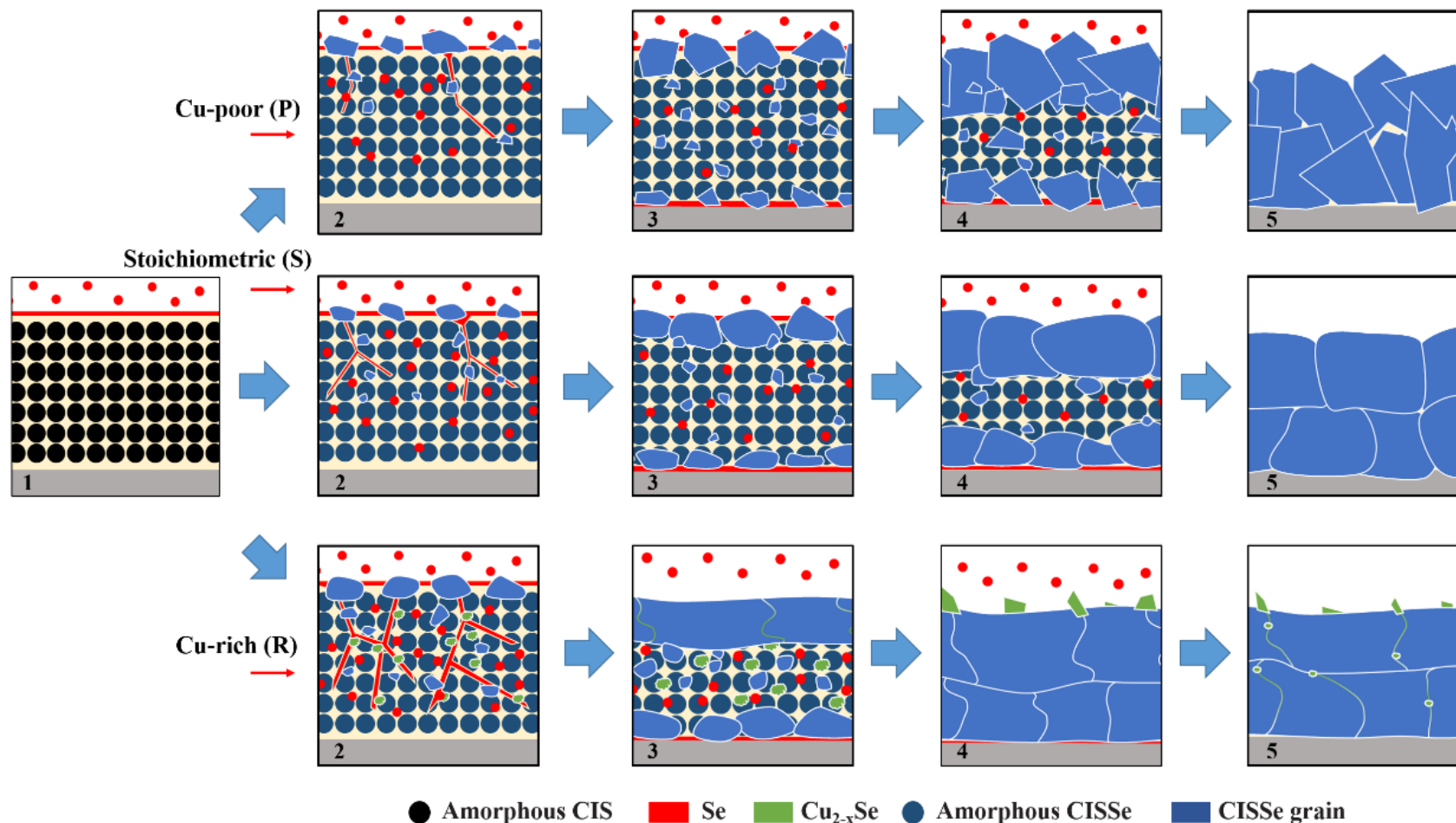
Selenization profile



Grain Growth of Solution Processed CIS absorber

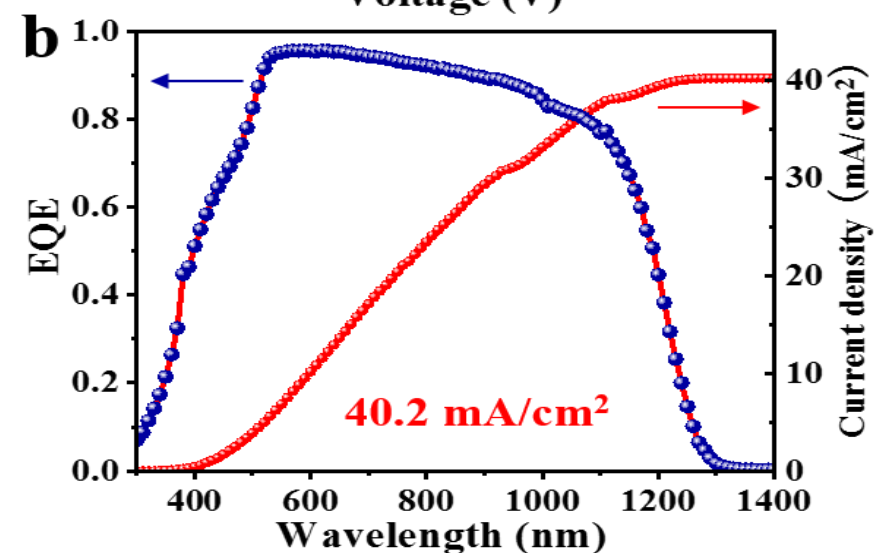
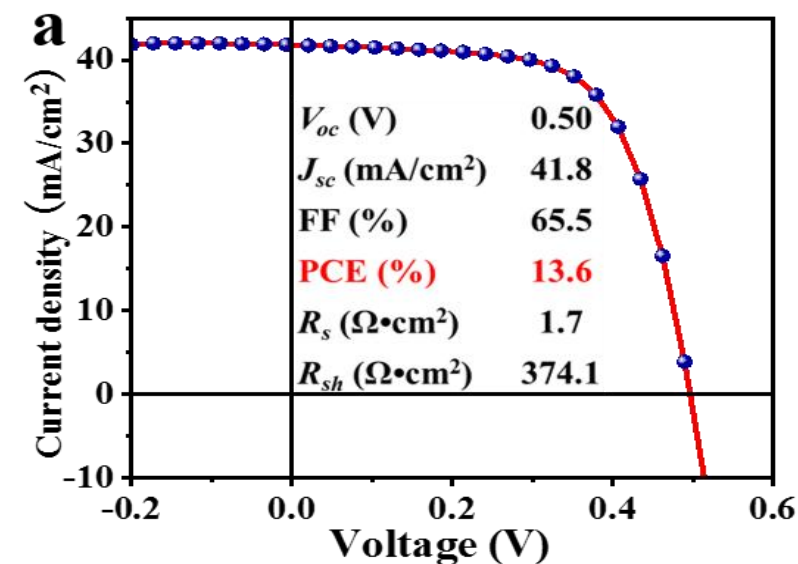
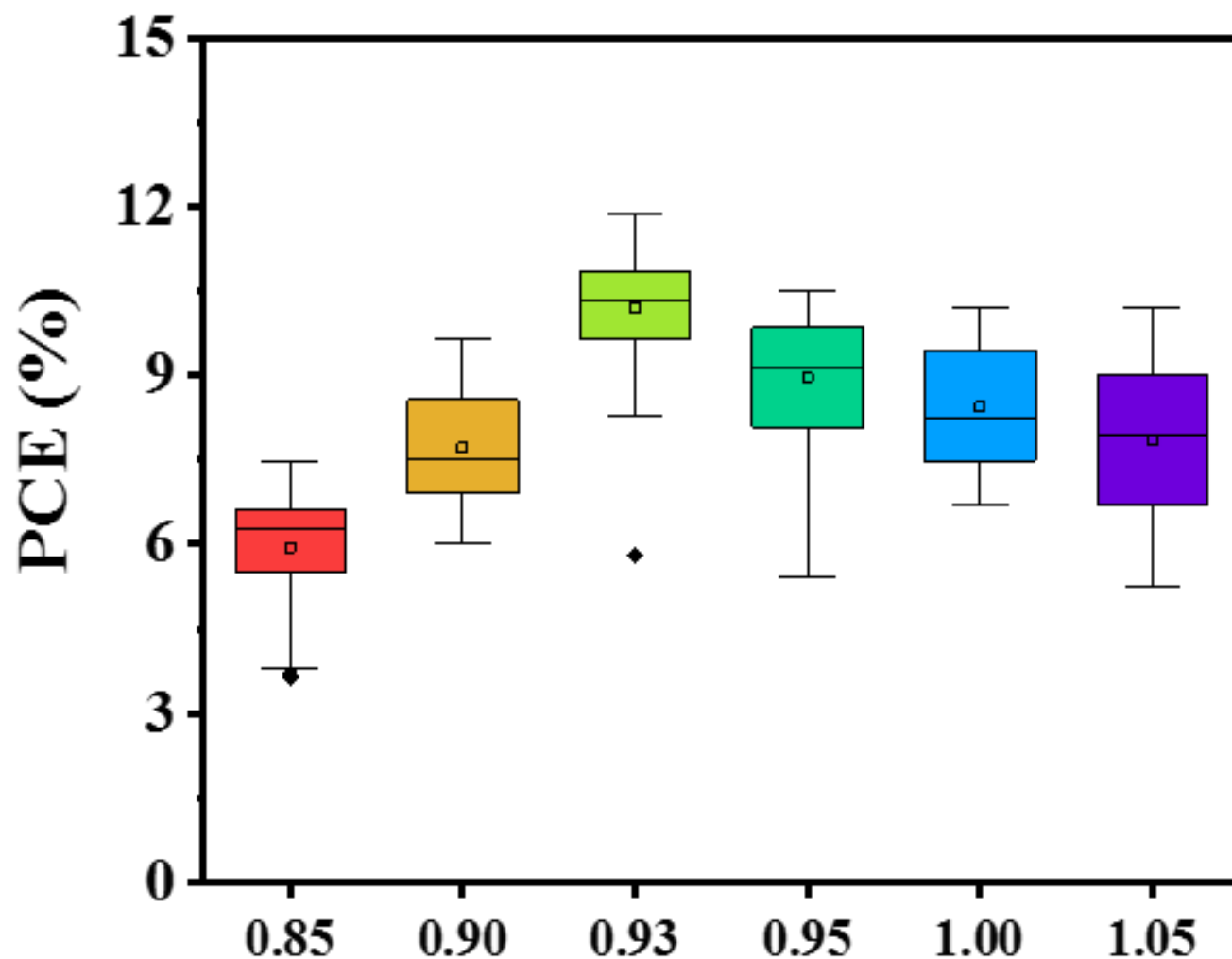
Direct phase transformation grain growth

Liquid (Cu_{2-x}Se) phase assisted grain growth

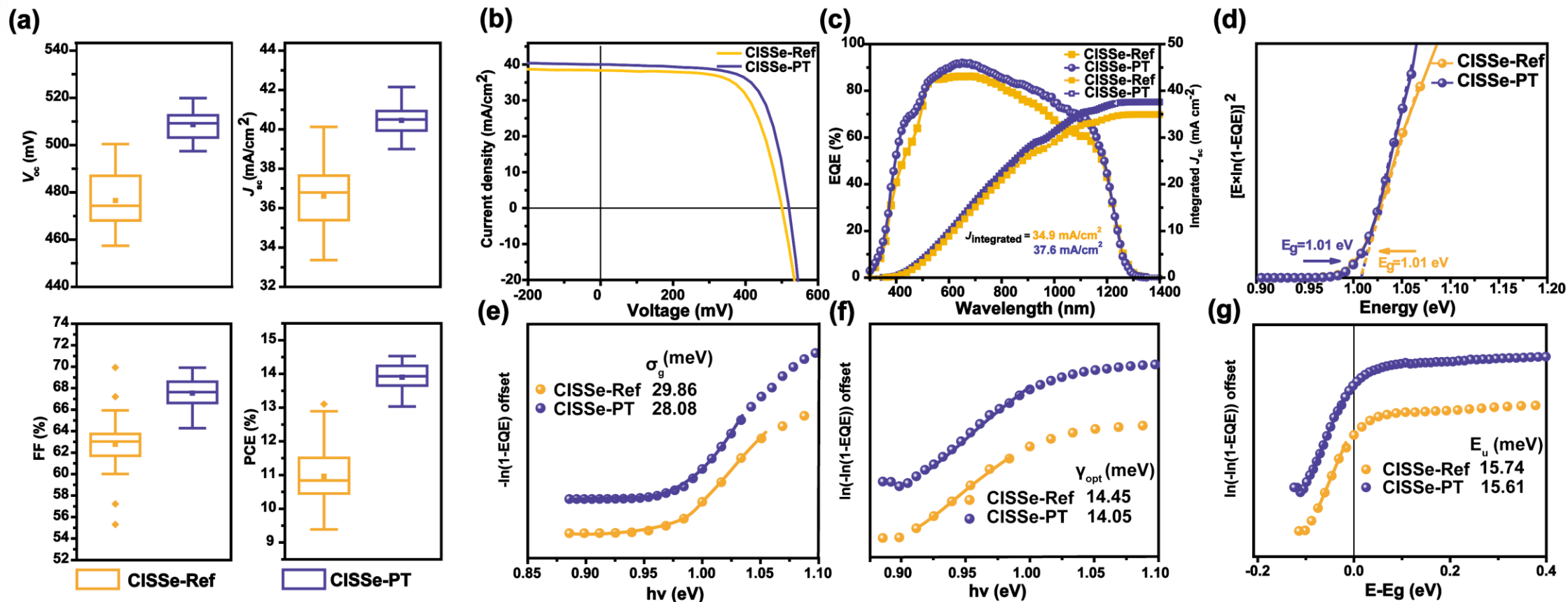


Solution route

High Tolerance to Composition Near Stoichiometry



CISSe Back Contact: Plasma Treatment

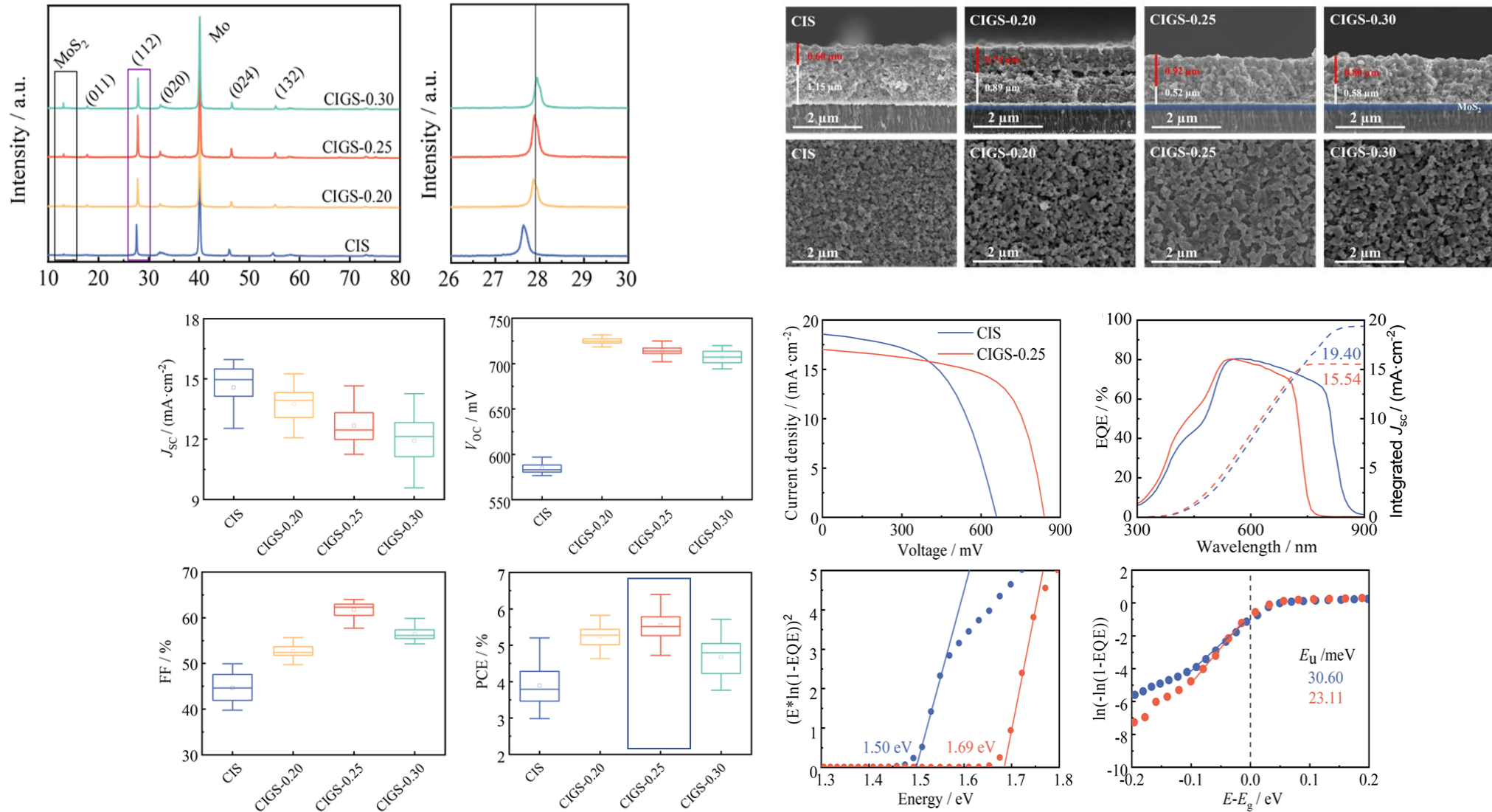


Device	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)	R_s ($\Omega \cdot \text{cm}^2$)	R_{sh} ($\Omega \cdot \text{cm}^2$)	n	J_0 (A·cm ⁻²)	E_g (eV)	E_u (meV)	σ_g (meV)	γ_{opt} (meV)
CISSe-Ref	500	38.33	67.21	12.89	0.83	647	1.60	2.1×10^{-7}	1.01	15.74	29.86	14.45
CISSe-PT	520	40.00	69.87	14.53	0.40	861	1.57	1.08×10^{-7}	1.01	15.61	28.08	14.05

An efficiency of **14.53%** is achieved from the champion CISSe-PT device. *Adv. Funct. Mater.* 2023, 2310124.

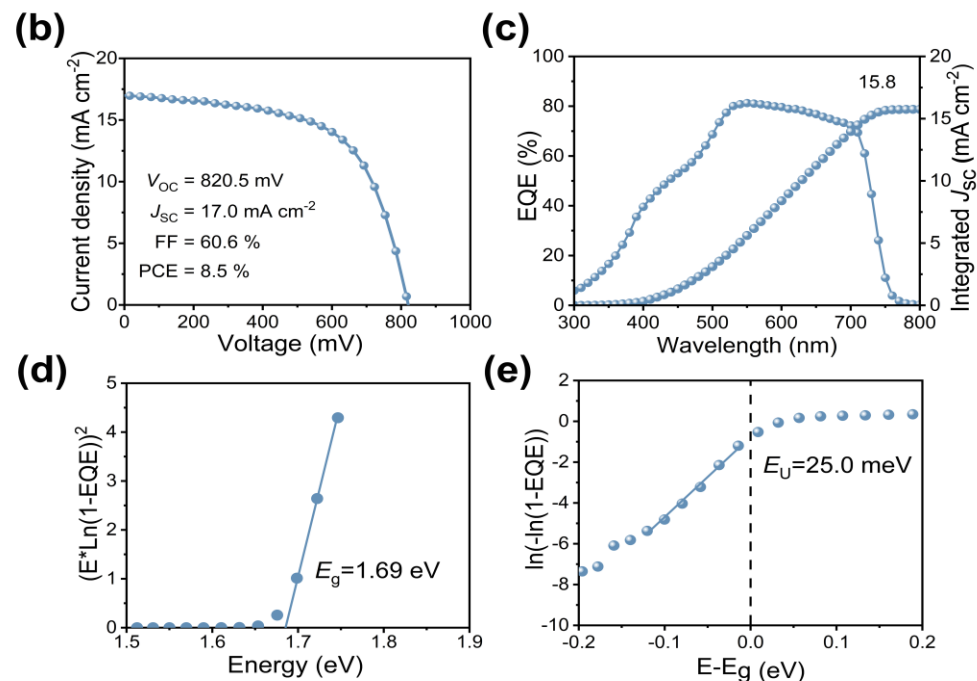
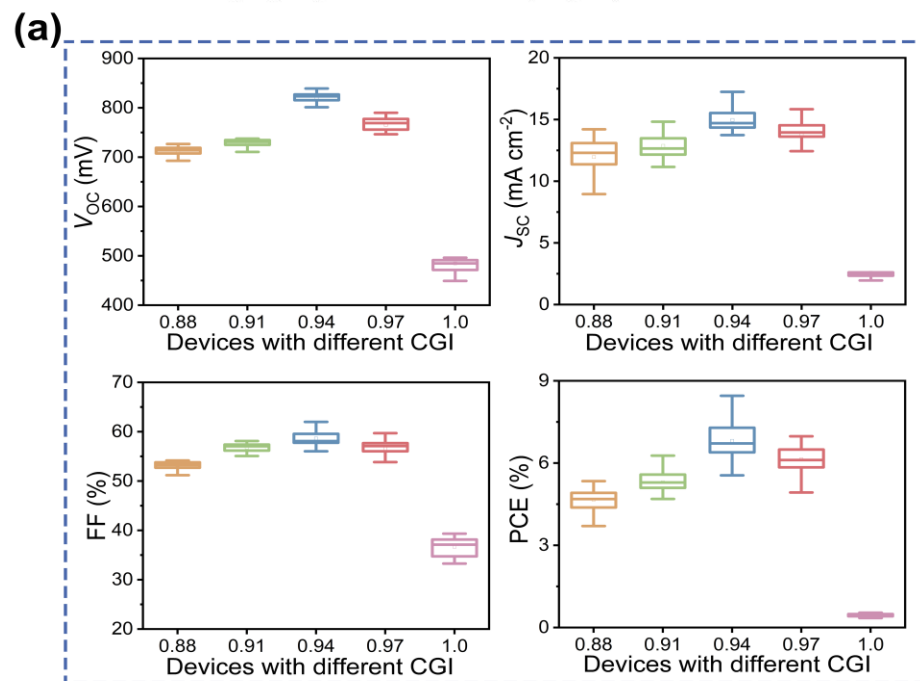
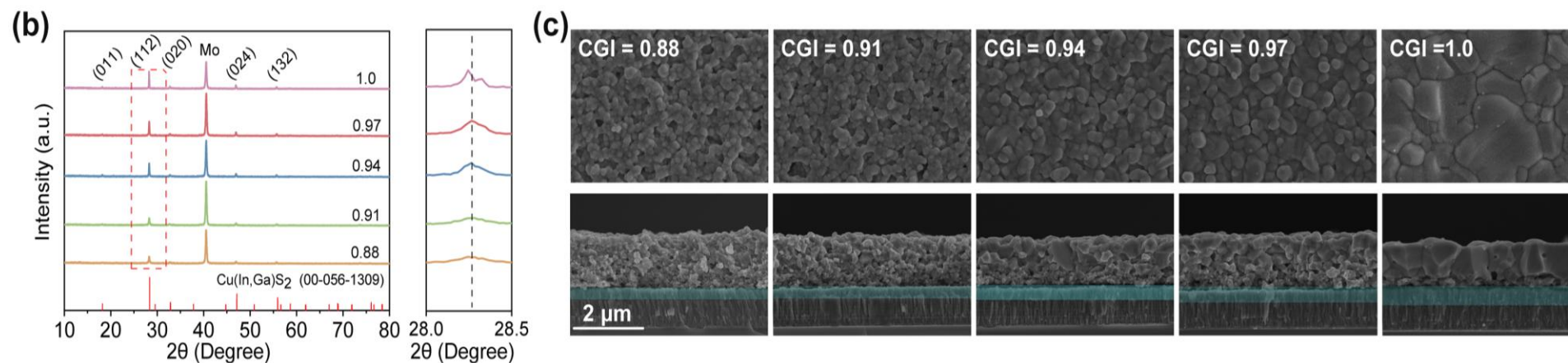
Wide Bandgap CIGS

Optimization of GGI



Wide Bandgap CIGS

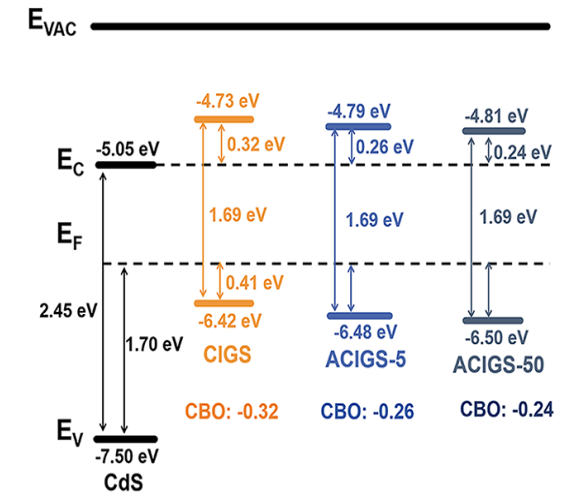
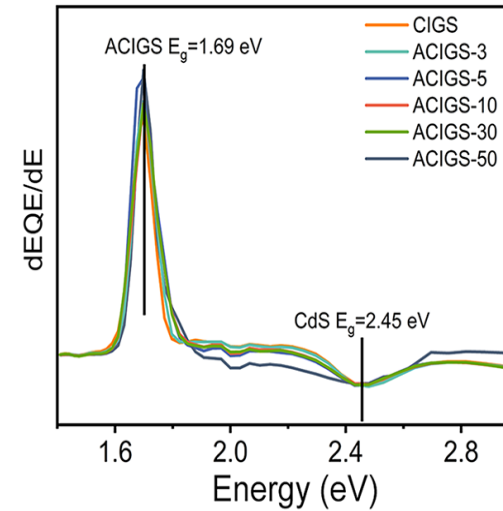
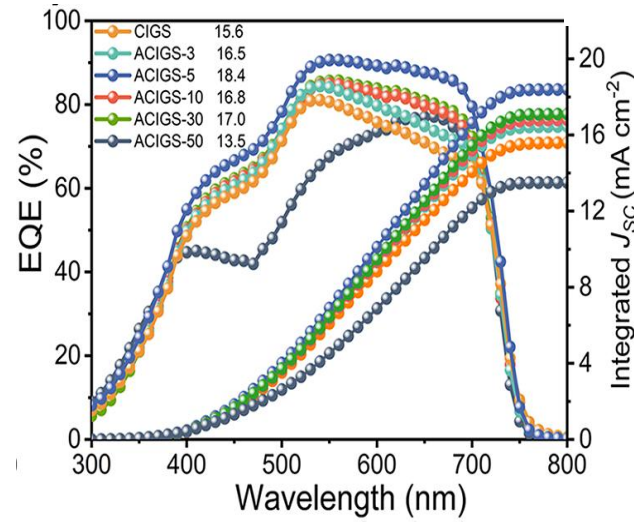
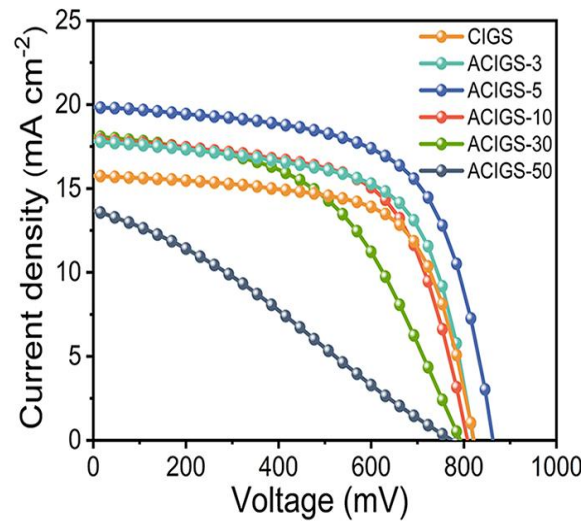
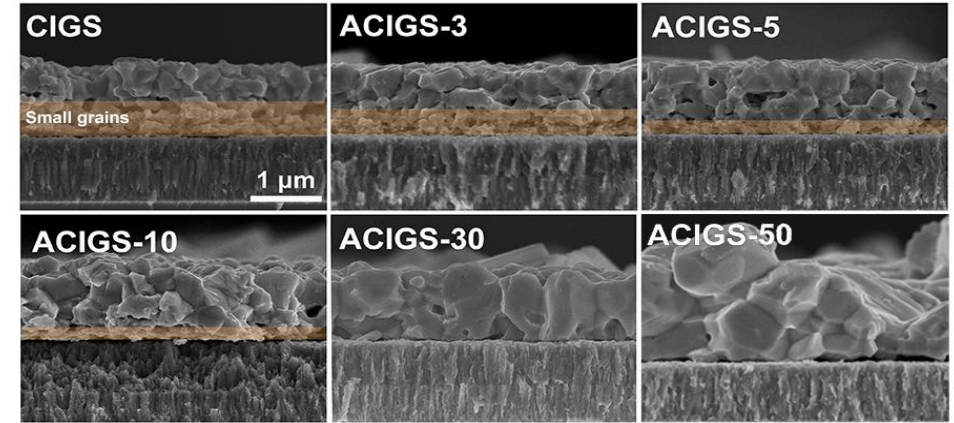
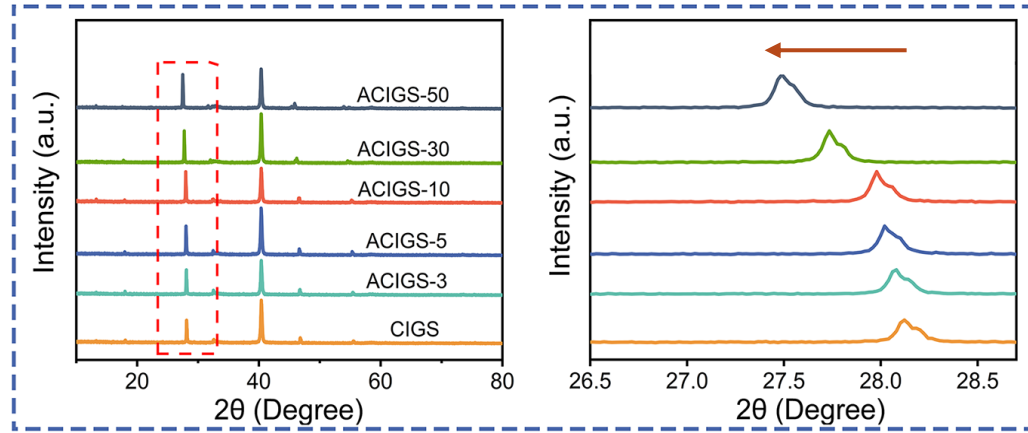
Optimization of CGI: 0.88, 0.91, 0.94, 0.97



CGI=0.94, PCE=8.5%

Wide Bandgap CIGS: Ag Alloying

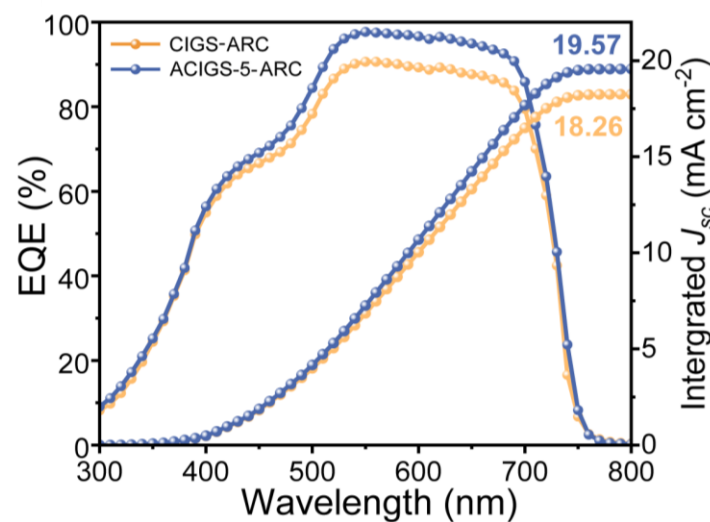
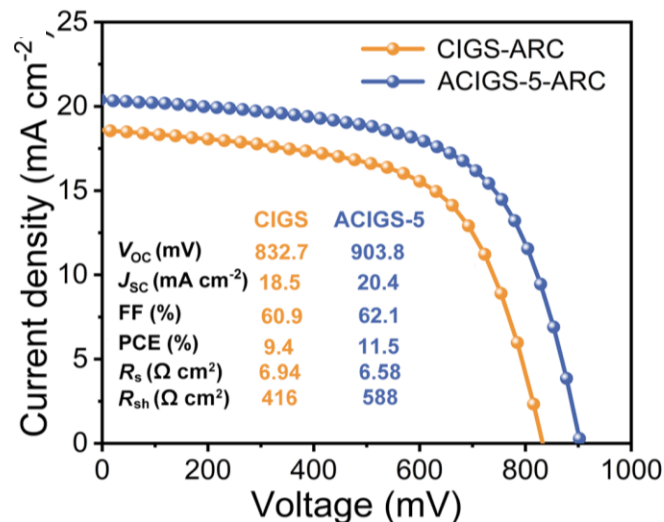
Ag/(Ag+Cu)=0, 3, 5, 10, 30, 50%



Nano Research, 2025, 18(10) 94907972

Wide Bandgap CIGS: Ag Alloying

$E_g=1.69$ eV PCE=11.5%



$E_g=1.70$ eV PCE=12.94%



报告编号: 26Q3-00162

检测结果/说明:

Results of Test and additional explanation.

1. 标准测试条件 Standard Test Condition (STC):

总辐照度 Total Irradiance: 1000 W/m²

被测电池温度 Temperature: 25.0 °C

光谱分布 Spectral Distribution: AM1.5G

2. STC条件下测量数据 Measurement Data and I-V/P-V Curves under STC

正扫 Forward Scan

I_{sc} (mA)	V_{oc} (V)	I_{MPP} (mA)	V_{MPP} (V)	P_{MPP} (mW)	FF (%)	η (%)	A (cm ²)
1.788	0.9675	1.537	0.8111	1.247	72.09	12.86	0.097

反扫 Reverse Scan

I_{sc} (mA)	V_{oc} (V)	I_{MPP} (mA)	V_{MPP} (V)	P_{MPP} (mW)	FF (%)	η (%)	A (cm ²)
1.787	0.9671	1.527	0.8222	1.255	72.62	12.94	0.097

失配因子 Mismatch factor: 1.024

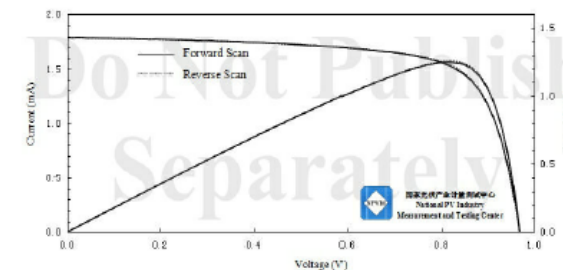
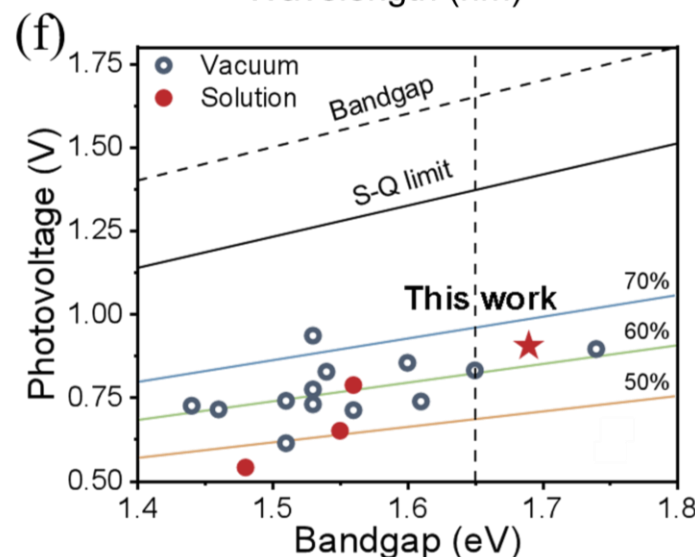
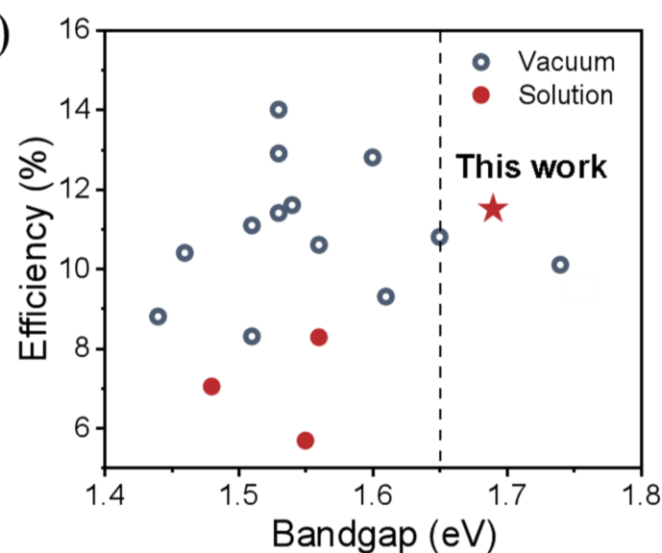
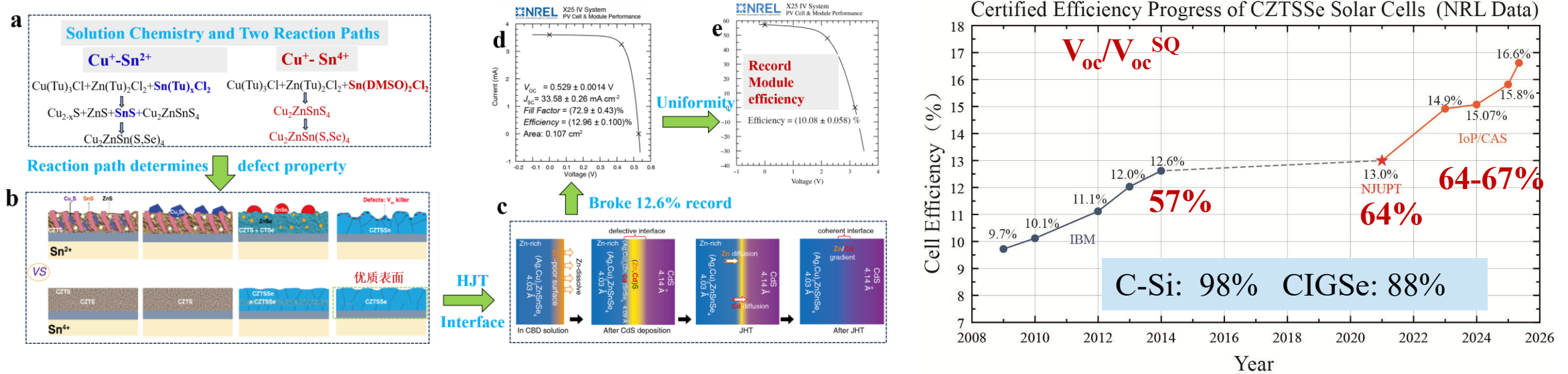


图1 STC下电流-电压特性曲线和功率-电压特性曲线

Figure 1. I-V and P-V characteristic curves of the measured sample under STC



Summary and Outlook

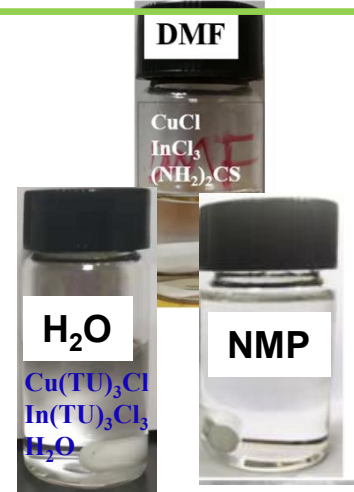


- ◆ The killer defects: multiphase fusion reaction path
- ◆ $\text{Cu}^+\text{-Sn}^{4+}$ molecular solution enables direct phase transformation grain growth
- ◆ Unveils the kesterite/CdS heterojunction is constructed on a Zn-poor surface
- ◆ Low temperature JHT induces elemental di-mixing, reconstructing epitaxial interface.
- ◆ 10.1% module with low J_{sc} and V_{oc} CTM loss
- ◆ New strategy is required to further mitigate V_{oc} loss

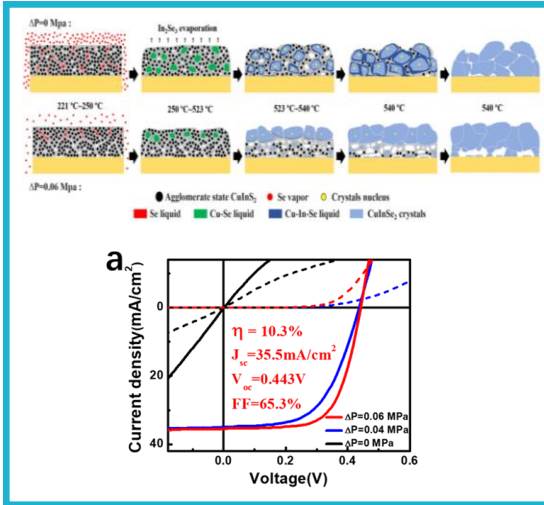
Summary and Outlook: Chalcopyrite



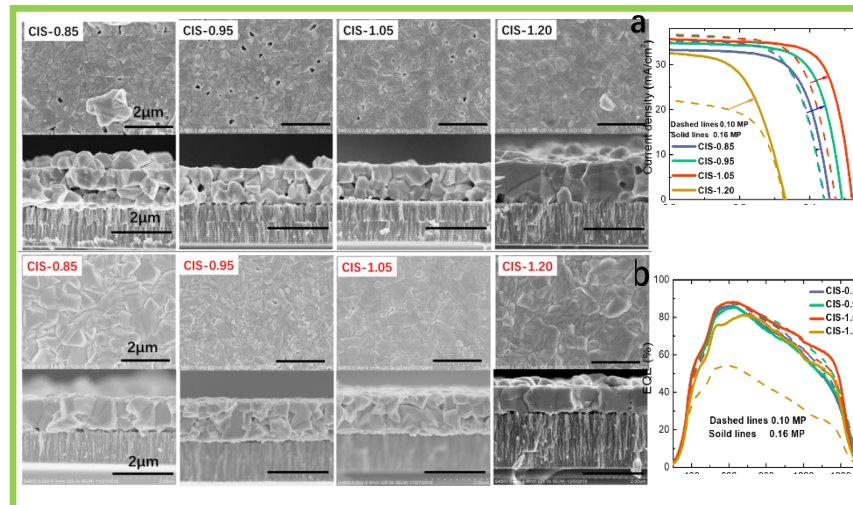
3 Solvent Systems



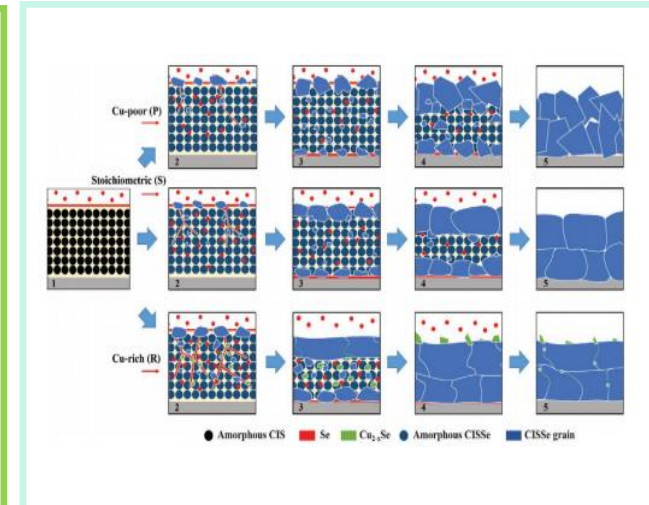
High-pressure selenization



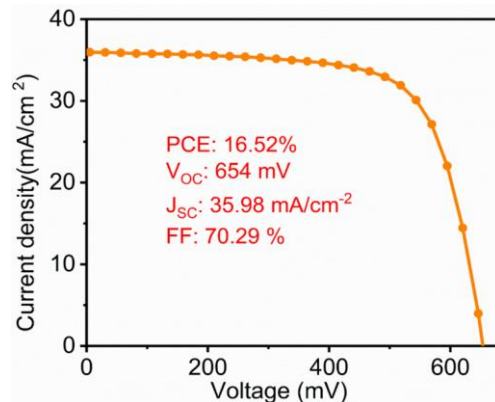
Cu-Rich CIGS Absorber



Grain Growth Mechanism



Doctor-blading in air



Unpublished data

- For the first time performed selenization under high pressure to fabricate better absorber
- Achieved highly efficient Cu-rich CIGS solar cells without KCN etching
- Different grain growth mechanism to that of vacuum-based approach
- >18% efficiency via doctor-blading in air

Publications

- Sol. RRL 2018, 2, 1800044.
- Sol. RRL 2019, 1900052.
- Nano Energy 2019, 62, 818.
- Nano Energy 2020, 69, 104438.
- Sol. Energy 2021, 220, 796-801.
- Adv. Energy Mater. 2021, 12, 2103644.
- ACS Appl. Energy Mater. 2022, 5, 10, 12336.
- Adv. Energy Sustain. Res. 2022, 2200006.
- Sol. RRL 2022, 2200150.
- Nano Research, 2025, 18(10) 94907972.

Patents

- Four issued China patents
- 1 PCT patent.

Acknowledgements

Prof. David S. Ginger
Prof. Hugh W. Hillhouse
Dr. Rajiv Giridharagopal
Prof. Xiaojing Hao
Prof. Martin Green
Prof. Qingbo Meng
Prof. Sixin Wu
Prof. Chunlei Yang
Dr. Zhenghua Su
Dr. Junjie Fu

Dr. Weibo Yan
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Ruichan Qiu
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