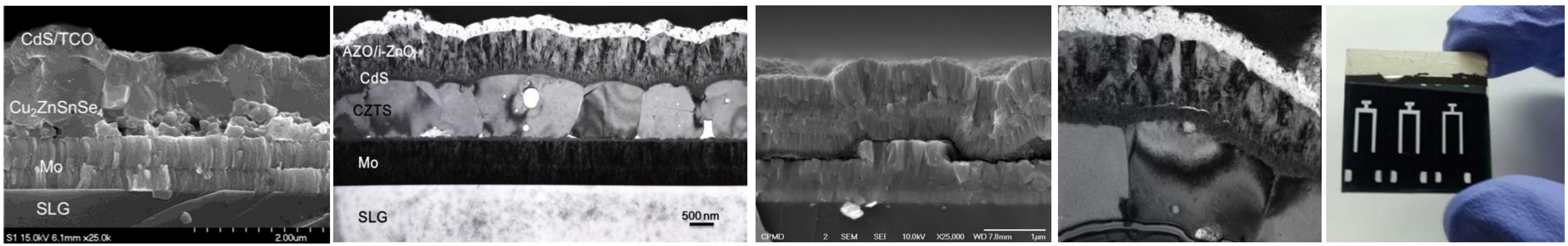
Developing Inorganic Thin Film Solar Cells using Earth-Abundant $Cu_2ZnSn(S,Se)_4$ Absorber Materials based on Sputtering Process



February 21. 2018

Jin Hyeok Kim

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Chonnam National University, South Korea

Acknowledgement

- GET-Future Project
- Lab Members
- KIER Thin Film Lab.
- KITECH & DGIST


PyeongChang 2018
Winter Olympic Games
Seoul
~ 10 hrs
Sydney


CHINA
KOREA
JAPAN
Seoul
Daejeon
Busan
Gwangju
Yeosu
3½ hours by car
2 hours by KTX
50 minutes by flight
전남대학교
CHONNAM NATIONAL UNIVERSITY
Started at 1952

Chonnam National University

Organization

(as of April 2017)

Student	Faculty	Staff	Alumni
33,296	1,183	568	196,654

16 Colleges & 11 Graduate Schools

Ranked 2nd or 3rd among National Universities
10th of 11th including Private Universities

Gwangju Campus

Agriculture and Life Sciences, Natural Science, Pharmacy, Medicine, Dentistry, Nursing, Veterinary Medicine, Law, Business Administration, Education, Humanities, Arts, Human Ecology, Engineering, Social Sciences

Yeosu Campus

Fisheries & Ocean Sciences, Culture & Social Sciences, Engineering Sciences

백두산
PC게임방
시대컴퓨터학원

CNU-Campus

CNU-Campus

http://www.jnu.ac.kr

Outline

Part 1

Overview

Part 2

Our Research Activity in CZTSSe TFSCs

Part 3

Technical Issues

Outline

Part 1

Overview

Part 2.

• Results in our Lab

Part 3.

• Technical issues

Global Warming

Glacier in Paragona, Argentina

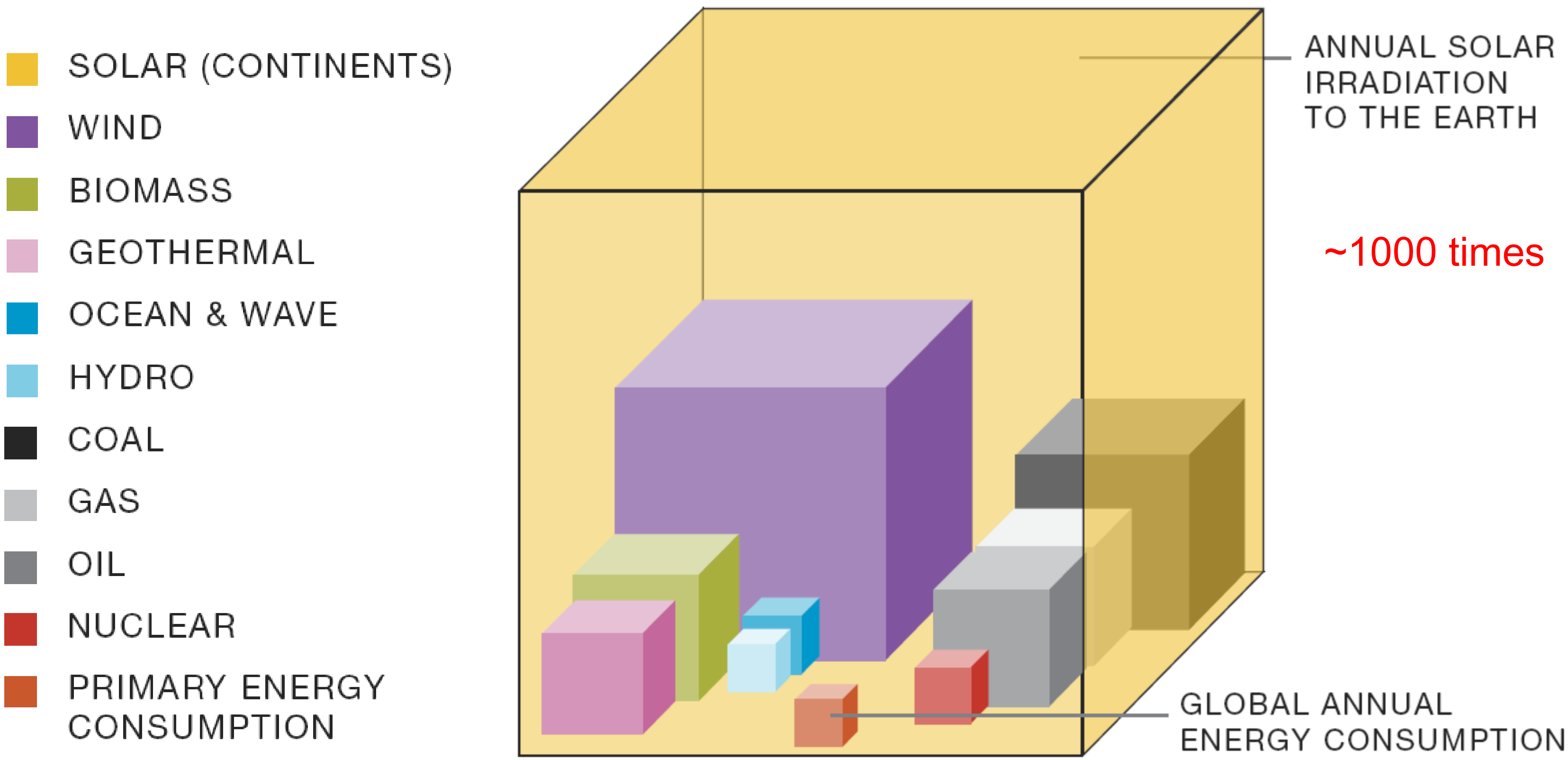
Year of 1928

Year of 2004

http://www.treehugger.com/slideshows/clean-technology/7-terrifying-global-warming-pictures/#slide-top

New & Renewable Energy

Solar Irradiation vs Established Global Energy Resources

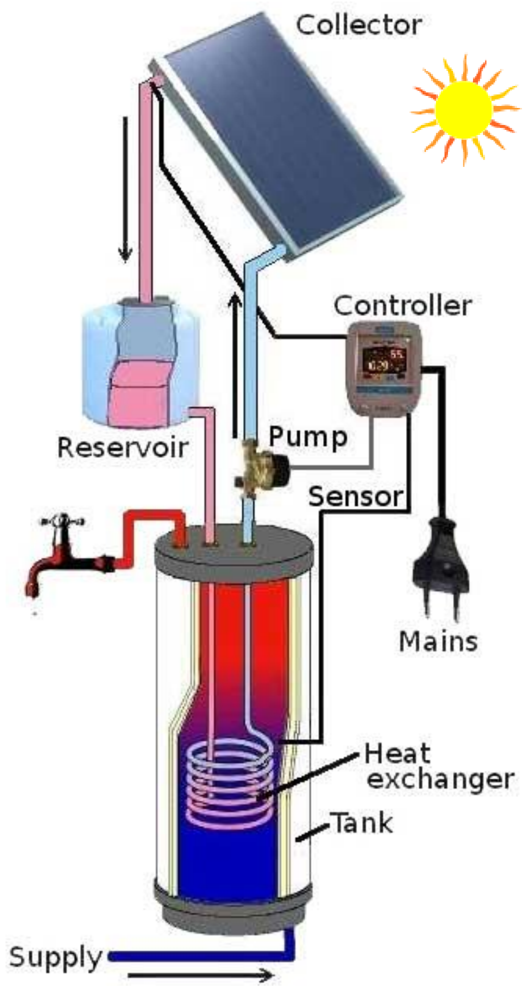


FOSSIL FUELS ARE EXPRESSED WITH REGARD TO THEIR TOTAL RESERVES WHILE RENEWABLE ENERGIES TO THEIR YEARLY POTENTIAL.

Source: "Solar Photovoltaic electricity empowering the world", EPIA, 2011 DLR, IEA WEO, EPIA's own calculations.

Utilization of Solar Energy

Solar Thermal

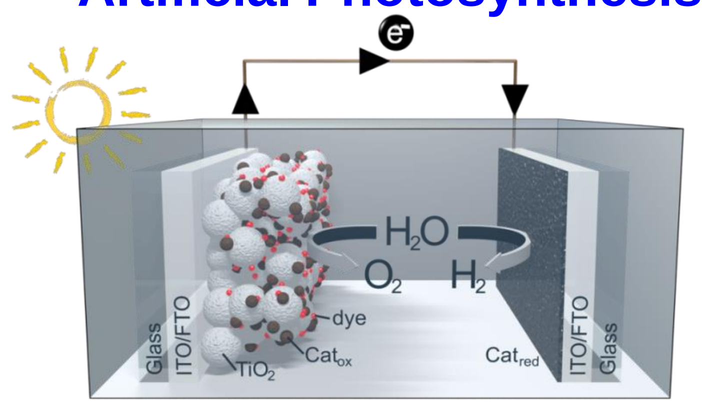


http://uk.solarcontact.com

Photovoltaic (Solar Cell)

http://ko.depositphotos.com/

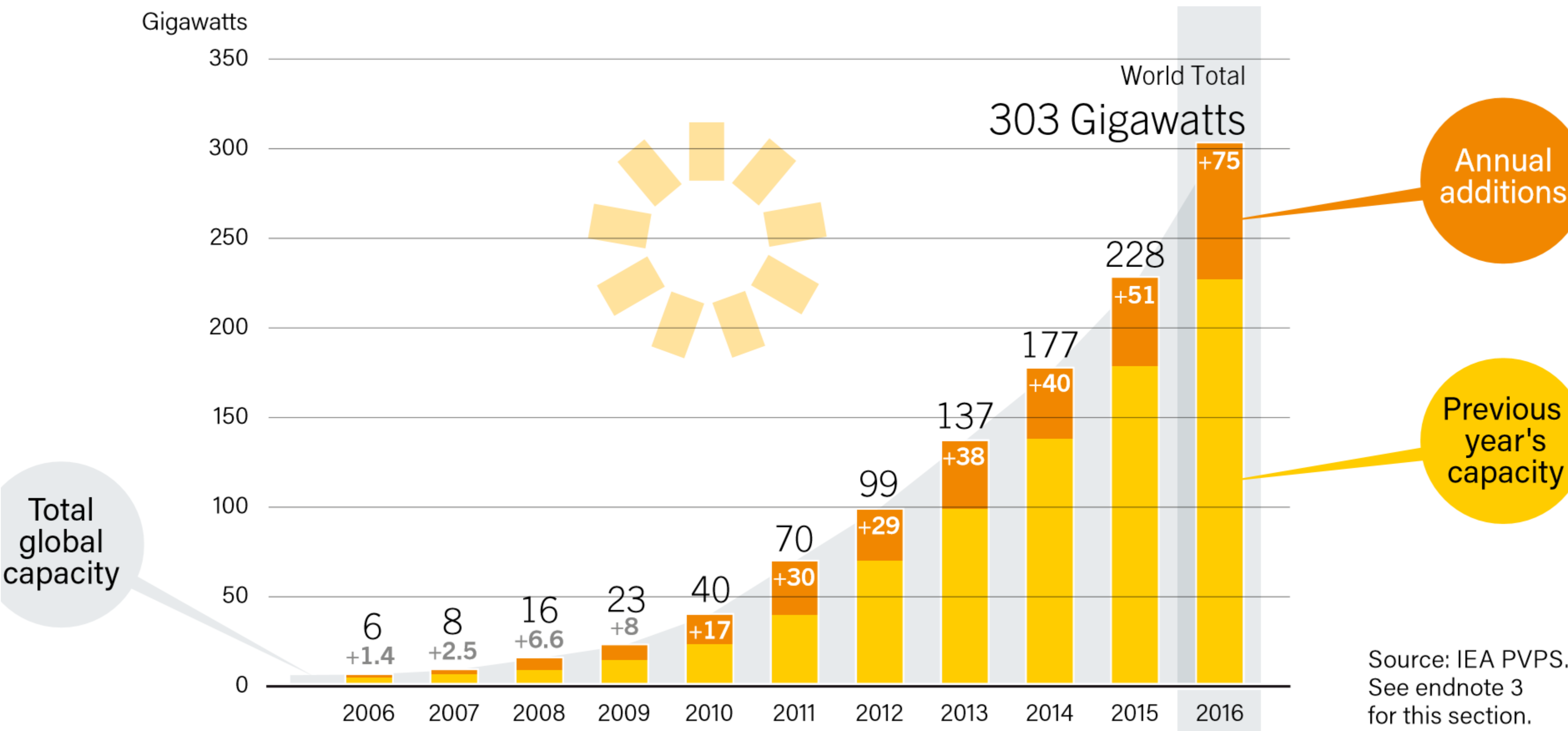
Artificial Photosynthesis



http://www.spicciagroup.net/img/water_splitting.png

Photovoltaic Overview

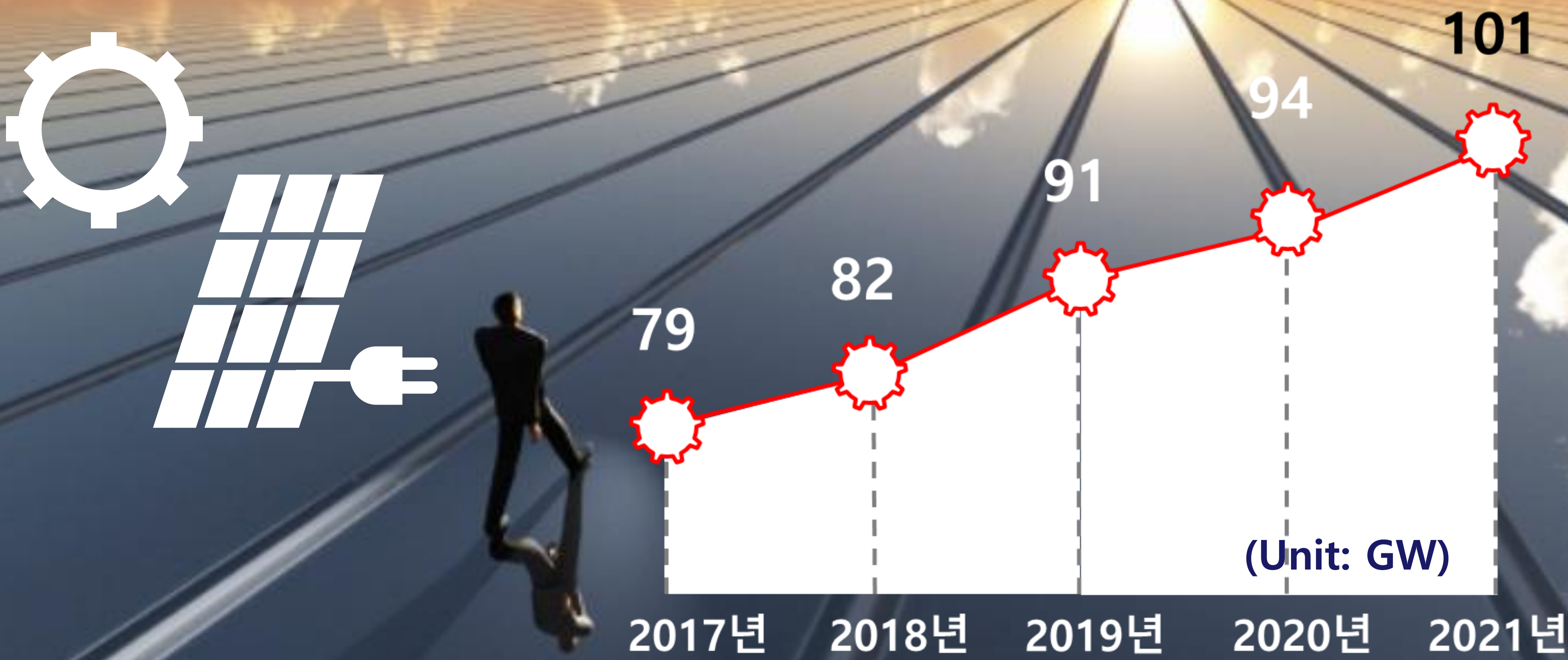
Solar PV Global Capacity and Annual Additions, 2006-2016



During 2016, at least 75 GW of solar PV capacity was added worldwide – equivalent to the installation of more than 31,000 SOLAR PANELS EVERY HOUR.

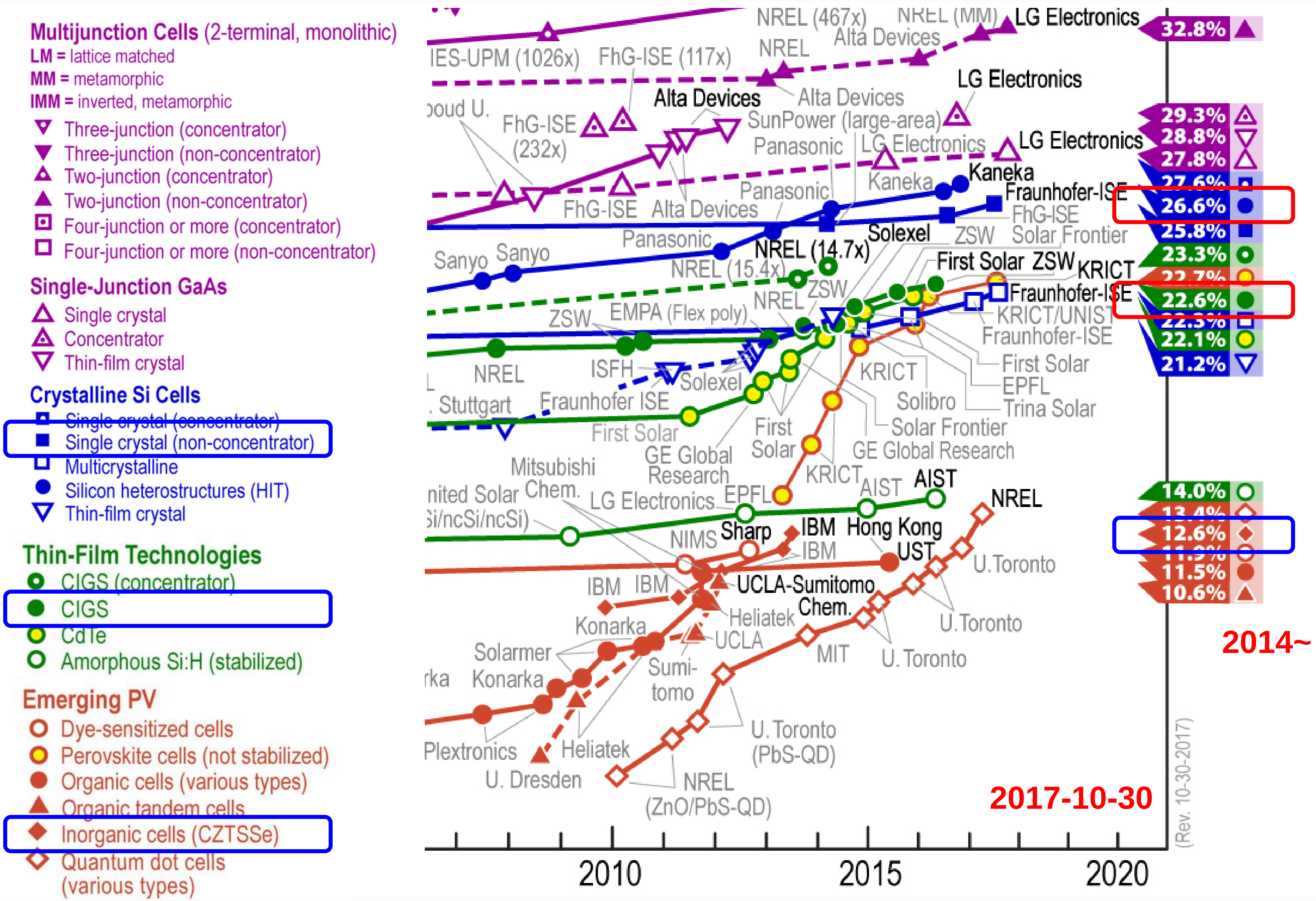
Source: *RENEWABLES 2017 GLOBAL STATUS REPORT*, REN21, 2017

Global PV Market Forecasting



Annual Installation Capacity (HIS, 2017)

Progress in Solar Cell Efficiency



Why $Cu_2ZnSn(S,Se)_4$ (CZTSSe)?

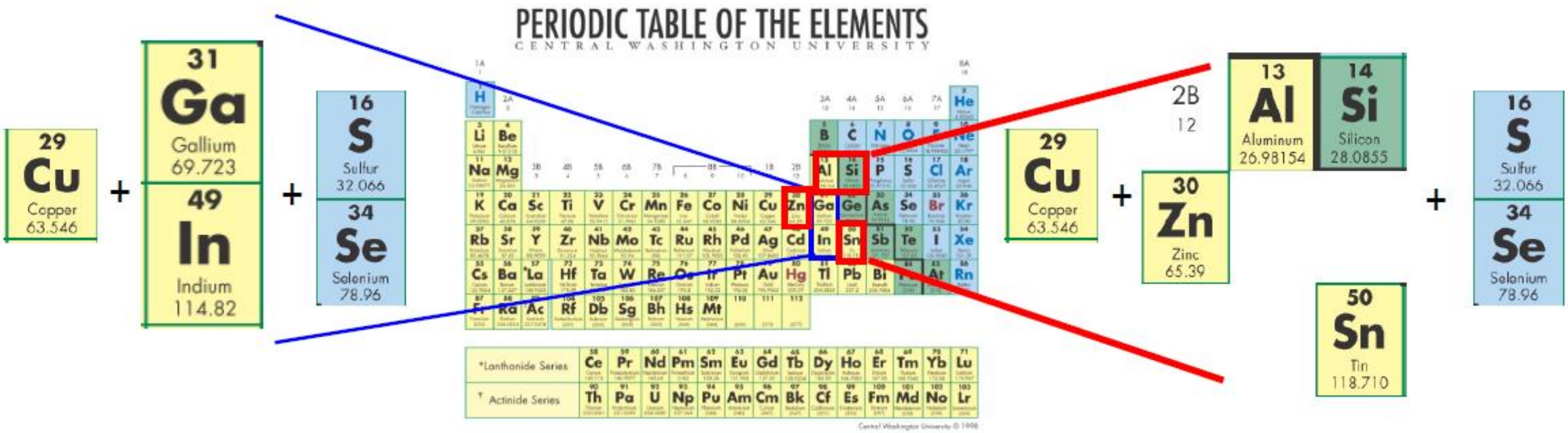
Issues in Inorganic Compound Thin Film Solar Cells

Expensive & Toxic

Low-cost and eco-friendly process with high efficiency

CdTe (η = 22.1%)
$Cu(In,Ga)(S,Se)_2$ (η =22.6%)

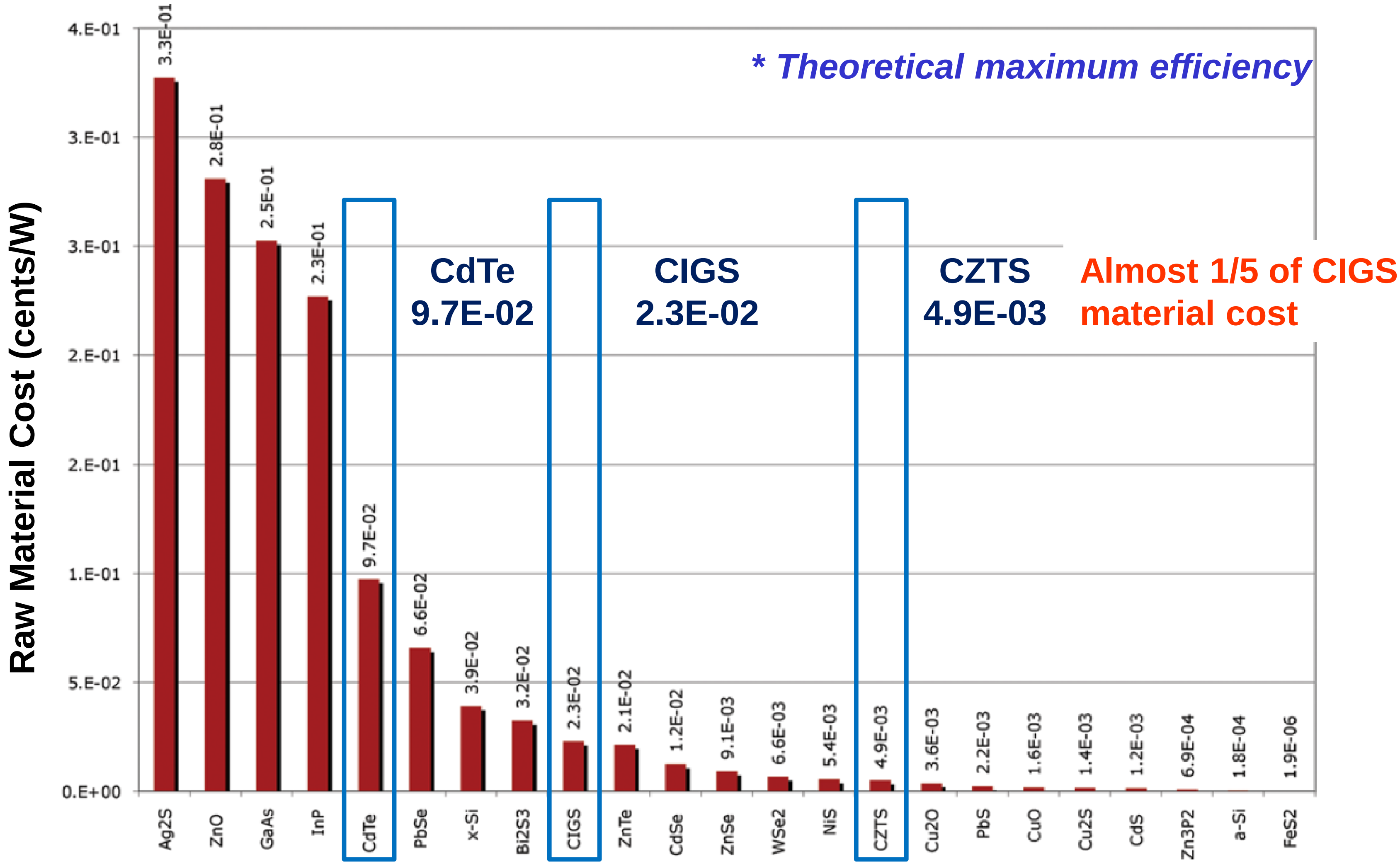
$Cu_2ZnSn(S,Se)_4$ (η =12.6%)



- High absorption coefficient (~10^4 cm^{-1})
- Suitable optical band-gap E of (1.0~1.5 eV)
- Environmental friendly (non-toxic)
- Chemical abundance

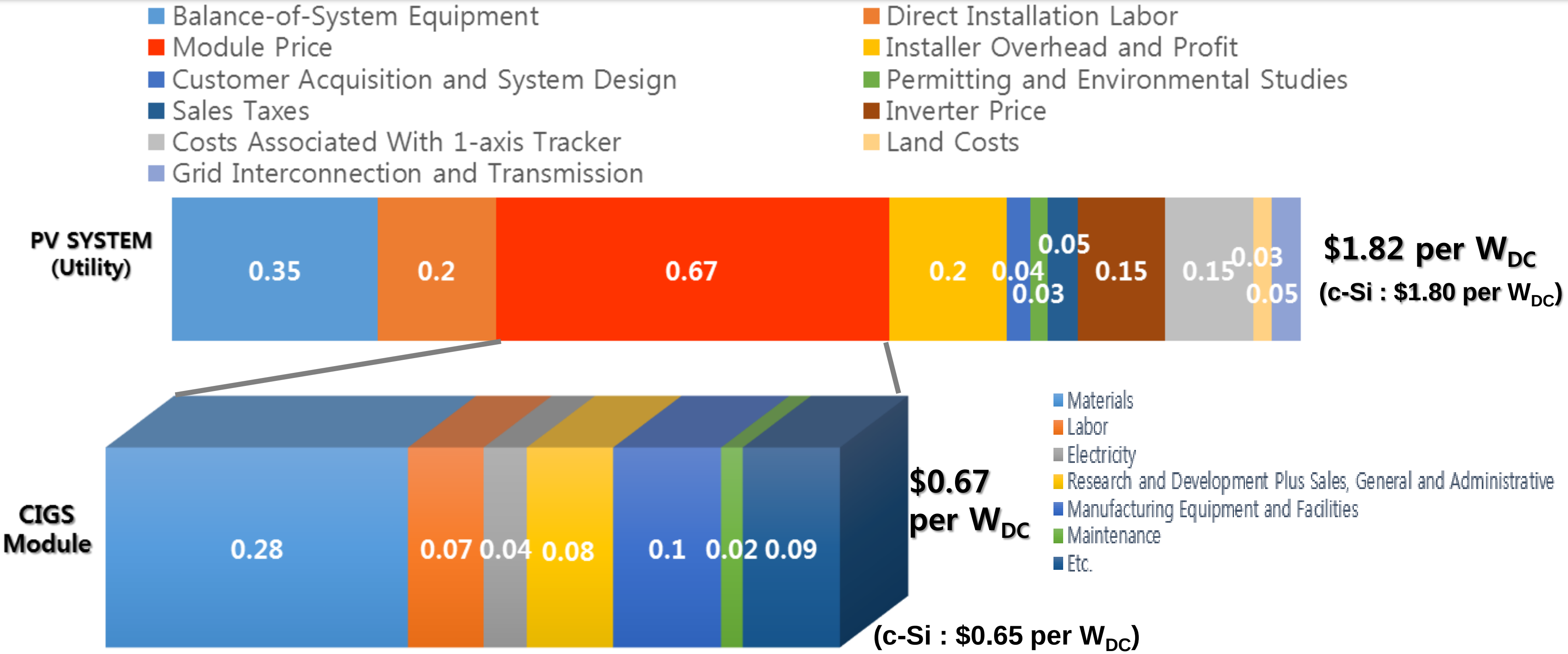
Why $Cu_2ZnSn(S,Se)_4$ (CZTSSe)?

Minimum cents/W for 23 inorganic PV materials



Source : Wadia, Alivisatos, Kammen, Envron. Sci. Technol. 43, 2072 (2009)

Cost for CIGS PV System



(Source : On the Path to SunShot – The Role of Advancements in Solar Photovoltaic Efficiency, Reliability, and Costs)

Materials Cost of CZTS $\cong \frac{1}{5}$ Materials Cost of CIGS

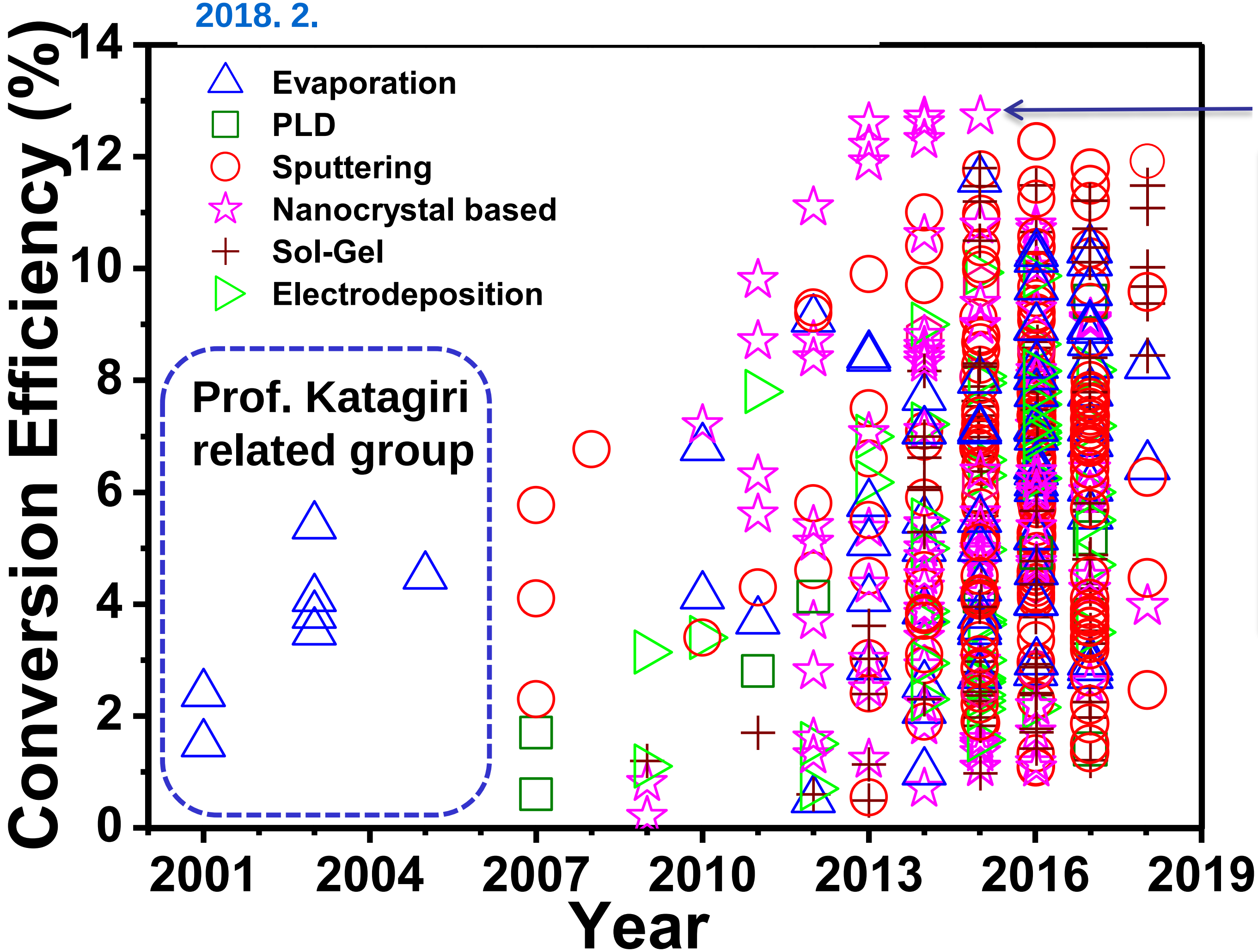
Environ. Sci. Technol. 43, 2072 (2009)

If **CIGS** is replaced with **CZTS**
the module cost will be decreased by **~10%**
the total PV system cost will be decreased by **~4%**

(Source: Materials Availability Expands the Opportunity for Large-Scale Photovoltaics Deployment)

Progress in Cell Efficiency in CZTSSe system

Results from Web of Science
Keywords: CZTS, CZTSe, Cu_2ZnSnS_4,..
2018. 2.



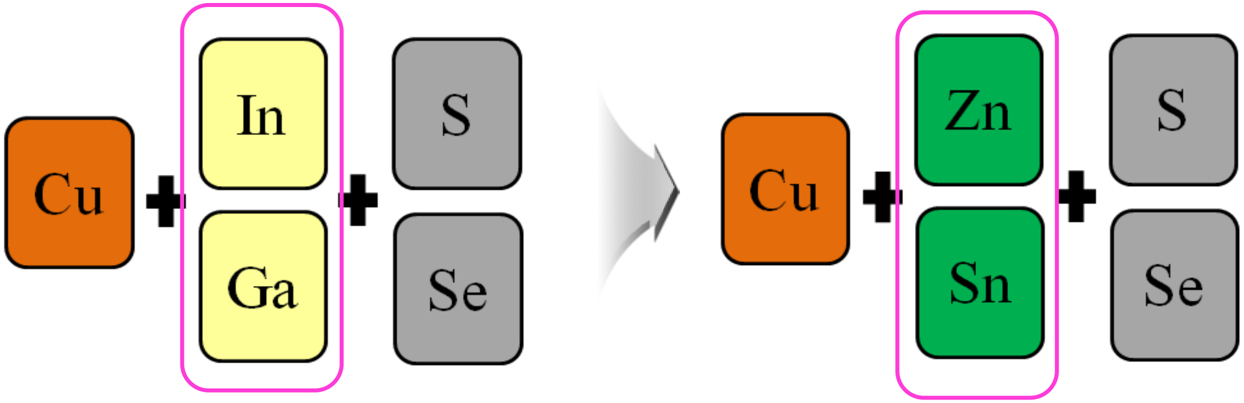
- W. Wang et al. IBM (USA)
- spin-coated precursor + annealing (540 °C)
- CZT(S,Se) absorber
- Hydrazine (pure solution)
- V_{OC}= 513.4 mV
- J_{SC}= 35.2 mA/cm^2
- *FF* = 69.8 %
- **Eff.**=12.6 %

Why $Cu_2ZnSn(S,Se)_4$ (CZTSSe)?

Still too low cell efficiency compare to CIGS!!

$Cu(In,Ga)(S,Se)_2$ (η = 22.6%)

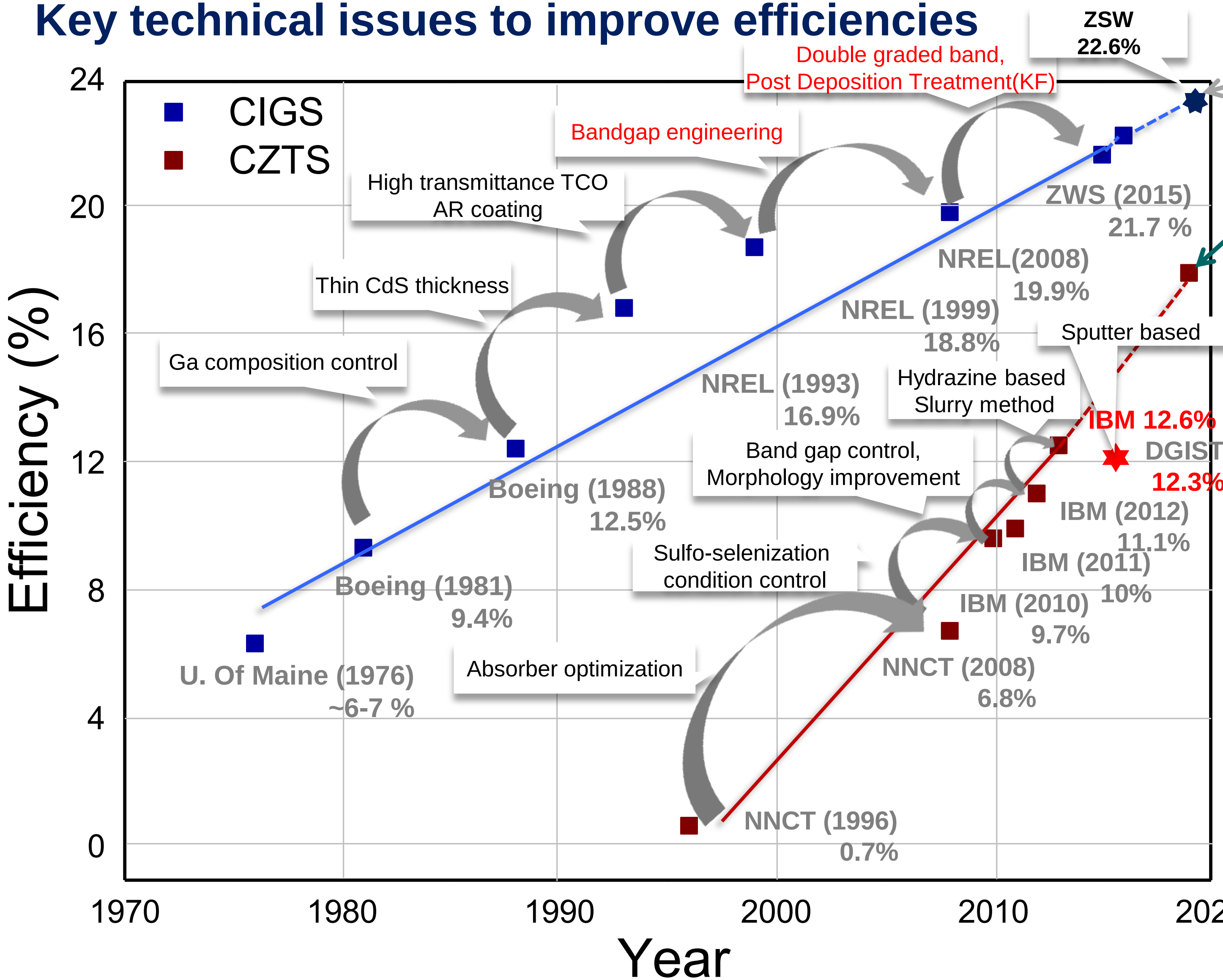
$Cu_2ZnSn(S,Se)_4$ (η = 12.6%)



Think about History on Technology Development!

Evolution of Cell Efficiencies in CIGS & CZTS

Key technical issues to improve efficiencies



World Best
22.6% (2016)

CZTS AIM
Efficiency: 15%
(2018)

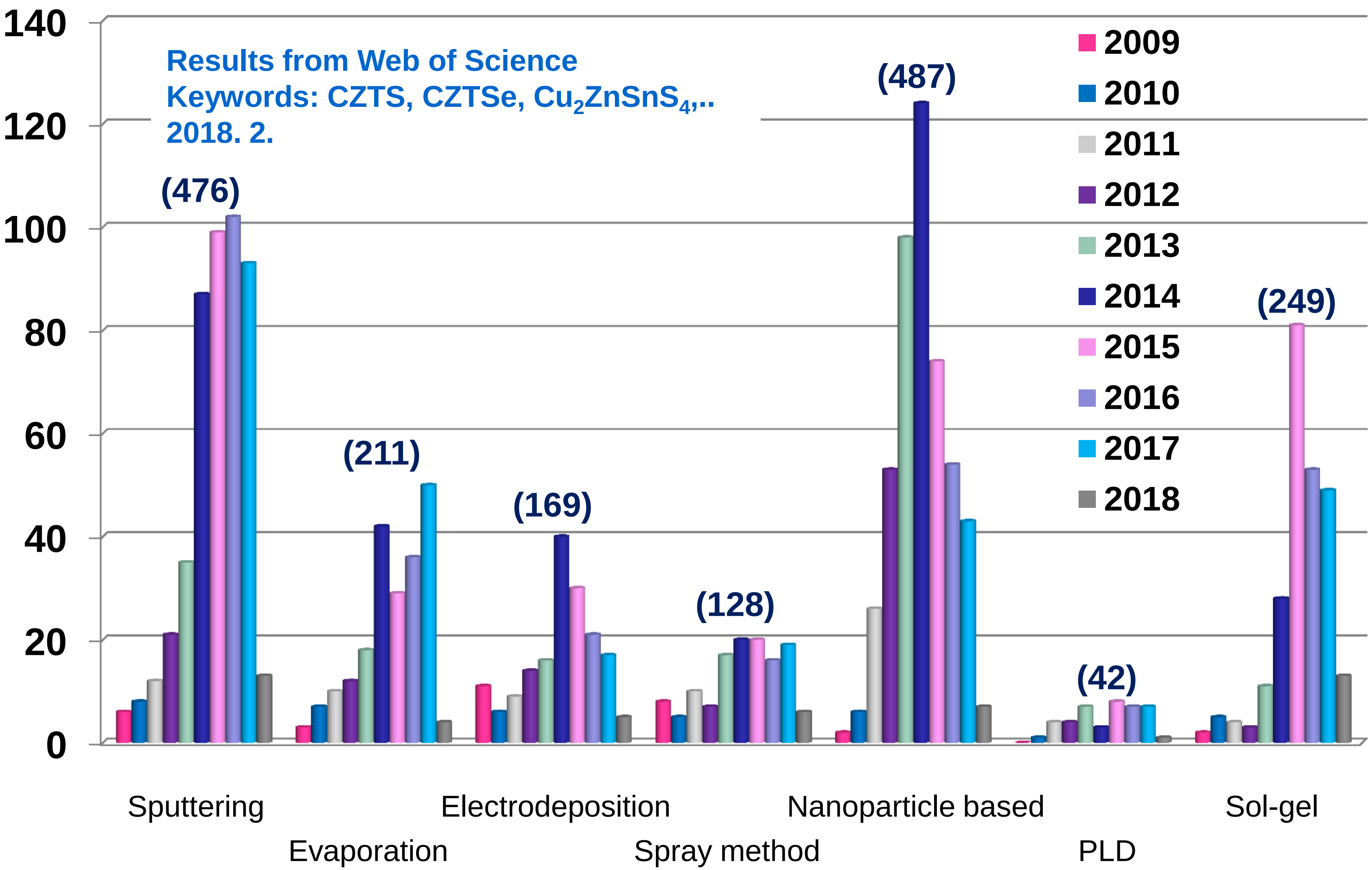
Following CIGS

- Bandgap engineering
- PDT treatment (Na, K)
- High transmittance TCO
- Band grading
- Wide band buffer

Progressing CZTS

- Enhancing the V_{oc}
- Control recombination
- Control absorption loss
- Elimination of defect (Bulk recombination)
- Harvesting extra photon

Recent Publications based on Methods



Major Results from World-Leading Groups

Institute	Materials	Process	Annealing condition	η (%)	Eg (eV)
Jilin University **Bin Yao**	CZTSSe	Sputtering	Sulfurization followed by selenization Ar atmosphere, 540 ℃, 30 min	11.53	1.16
	CZTSSe	Spin-coating	Control of selenization time and temperature N_2 atmosphere, 500-600 ℃, 5-30 min	7.48	1.05
Nankai University **Y. Zhang**	CZTSe	Sputtering	Different Se vapor composition Se & Ar atmosphere, 560 ℃, 15 min	10.41	1.03
	CZTSSe	Sputtering	Depletion region control Se & Ar atmosphere, 570 ℃, 15 min	10.23	1.13
	CZTSe	Electrodeposition	N_2 atmosphere, 500 ℃, 10 min	8.2	
IBM **David B. Mitzi** *Adv. Energy Mater.* **2014** , *4* , 1301465	CZTSe	Evaporation	Se & N_2 atmosphere, 590 ℃	11.6	1.00
	CZTSSe	Solution based	Hydrazine-based pure solution 500 ℃	12.6	1.13
IREC **Edgardo Saucedo** EES, DOI: 10.1039/c7ee02318a	CZTSe	Sputtering	Two step annealing process Se & Sn containing atmosphere 400 ℃, 30min. / 550 ℃, 15 min	10.1	1.04
	CZGTSe	Sputtering	Two step annealing process Se & Sn containing atmosphere 400 ℃, 30min. / 550 ℃, 15 min	11.8	
UNSW **Xiaojing Hao** ACS Energy Lett. 2017, 2, 930−936	CZCTS	Sputtering	Cd doping S & SnS atmosphere 560 ℃	11.5	13.8
	CZTS	Sputtering	$Zn_{1-x}Cd_xS$ buffer S atmosphere 560 ℃	9.2	1.50

Major Results from World-Leading Groups

6 WILEY PROGRESS IN PHOTOVOLTAICS GREEN ET AL.

TABLE 4 "Notable exceptions": "Top 10" confirmed cell and modu[...] (1000 Wm^{-2}) at 25°C (IEC 60904-3: 2008, ASTM G-173-03 global) [...]ım

"Top 10" confirmed cell and module results

Classification	Efficiency, %	Area, cm^2	V_{oc}, V	J_{sc}, mA/cm^2	Fill Factor, %	Test Centre (date)	Description
Cells (silicon)							
Si (crystalline)	25.0 ± 0.5	4.00 (da)	0.706	42.7[a]	82.8	Sandia (3/99)[b]	UNSW p-type PERC top/rear contacts[37]
Si (crystalline)	**25.8 ± 0.5[c]**	**4.008 (da)**	**0.7241**	**42.87[d]**	**83.1**	**FhG-ISE (7/17)**	**FhG-ISE, n-type top/rear contacts[38]**
Si (large)	26.6 ± 0.5	179.74 (da)	0.7403	42.5[e]	84.7	FhG-ISE (11/16)	Kaneka, n-type rear IBC[3]
Si (multicrystalline)	**22.0 ± 0.4**	**245.83 (t)**	**0.6717**	**40.55[d]**	**80.9**	**FhG-ISE (9/17)**	**Jinko solar, large p-type[39]**
GaInP	21.4 ± 0.3	0.2504 (ap)	1.4932	16.31[f]	87.7	NREL (9/16)	LG electronics, high bandgap[40]
GaInAsP/GaInAs	**32.6 ± 1.4[c]**	**0.248 (ap)**	**2.024**	**19.51[d]**	**82.5**	**NREL (10/17)**	**NREL, monolithic tandem**
Cells (chalcogenide)							
CIGS (thin-film)	22.6 ± 0.5	0.4092 (da)	0.7411	37.76[f]	80.6	FhG-ISE (2/16)	ZSW on glass[41]
CIGSS (cd free)	22.0 ± 0.5	0.512 (da)	0.7170	39.45[f]	77.9	FhG-ISE (2/16)	Solar frontier on glass[10]
CdTe (thin-film)	22.1 ± 0.5	0.4798 (da)	0.8872	31.69[g]	78.5	Newport (11/15)	First solar on glass[42]
CZTSS (thin-film)	12.6 ± 0.3	0.4209 (ap)	0.5134	35.21[h]	69.8	Newport (7/13)	IBM solution grown[43]
CZTS (thin-film)	11.0 ± 0.2	0.2339(da)	0.7306	21.74[e]	69.3	NREL (3/17)	UNSW on glass[12]
Cells (other)							
Perovskite (thin-film)	**22.7 ± 0.8[i]**	**0.0935 (ap)**	**1.144**	**24.92[d]**	**79.6**	**Newport (7/17)**	**KRICT[15]**
Organic (thin-film)	12.1 ± 0.3[k]	0.0407 (ap)	0.8150	20.27[e]	73.5	Newport (2/17)	Phillips 66

Progress in Phovoltaics DOI: 10.1002/pip.2978

Research Activities in Korea

Institute	Materials	Process	Annealing condition	η (%)	Eg (eV)
DGIST **J. Mater. Chem. A** **2016, 4, 10151**	CZTSSe	Sputtering	SeS_2/Se Graphite box 300˚C 1000sec. / 510˚C 1100sec.	**13.7** **12.3**	1.097
KAIST	CZTS	Sputtering	S vapor 580˚C 30min.	4.59	1.5
KIER	CZTSe	Co-evaporation	-	6.14	1.2
KIST **(SNU*)**	CZTSSe	Electrodeposition	Se powder H_2S gas 550˚C 15min.	9.9	1.14
Dongguk University	CZTSSe	Sputtering	S vapor 580˚C 5min	6.98	1.5
SKKU	CZTS	Co-sputtering	H_2S gas 550˚C 1 hour	6.75	-
Yeungnam University	CZTSe	Sputtering	Se vapor 500˚C 10min.	5.8	1.06
Yonsei University	CZTS	Hybrid ink-derived spin-coating	H_2S atmosphere, 550˚C, 30min	8.17	1.46
Chonnam National University Green Chem., 2016, 18, 700-711	CZTSSe	Sputtering	Controlling Chamber Pressure 500 Torr, S & Se vapor, 540˚C, 7min 30sec	**11.8**	1.0
	CZTSSe	Sputtering	Soft Annealing Process 300˚C 1hour, 580˚C 10min	**9.24**	0.99

*Present affiliation

Outline

Part 1

Photovoltaic Overview

Part 2

Our Research Activity in CZTSSe TFSCs

Part 3

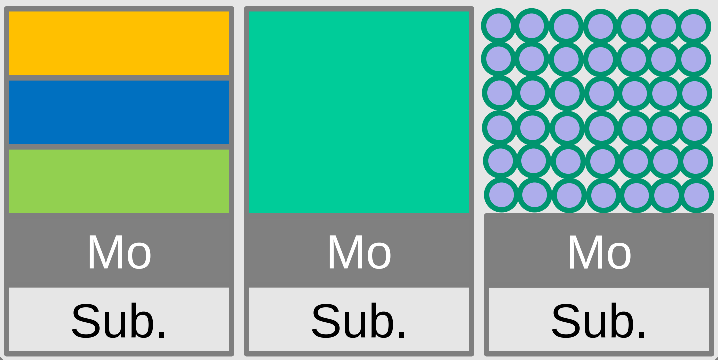
Technical Issues

Preparation of Absorber Layers

Precursor Preparation

Precursor Structure

Stacked layer | Co-deposition | Nano particle



Preparation Methods

Physical

- **Sputtering**
- Evaporation
- PLD

Chemical

- Electrodeposition
- Bath-based
- Sol-Gel
- Ink-Based
- CVD

Annealing process

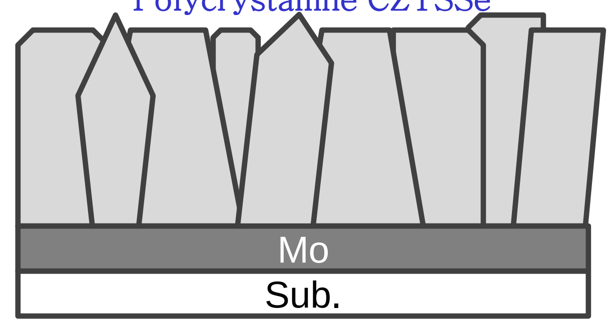
Pre-Treatment

- Elimination of C contained binder
- Homogeneous mixing of metal layers

Annealing Condition

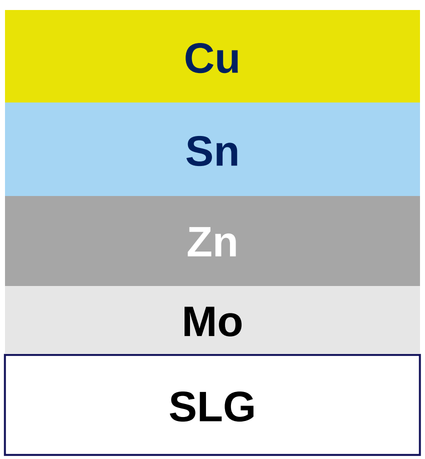
- Furnace & RTP Process
- S powder & Se pellet : 500 ~ 580 ^{o}C

Polycrystalline CZTSSe

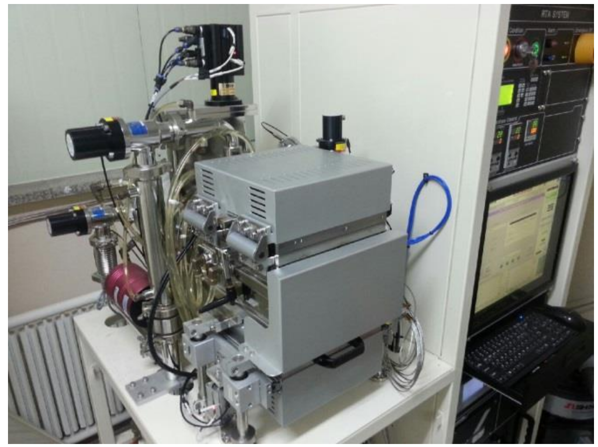


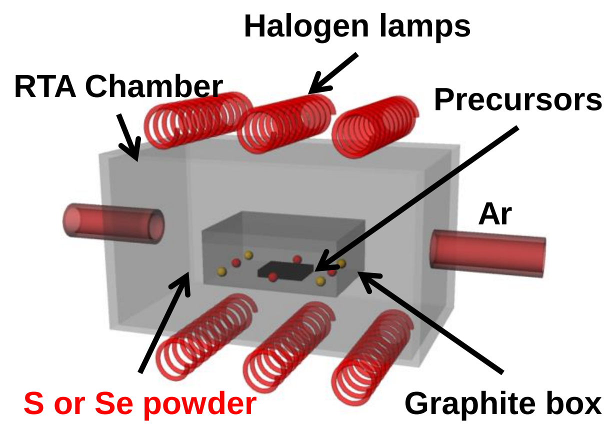
Preparation of Absorber Layers

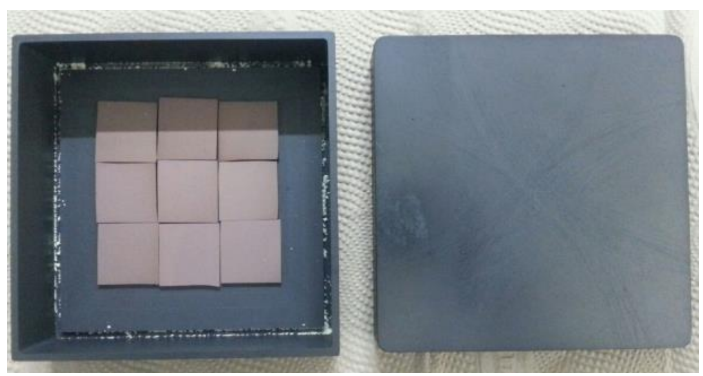
Sputtering

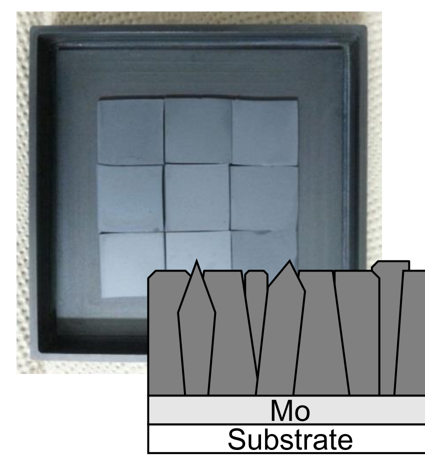


Sulfo-selenization using RTP



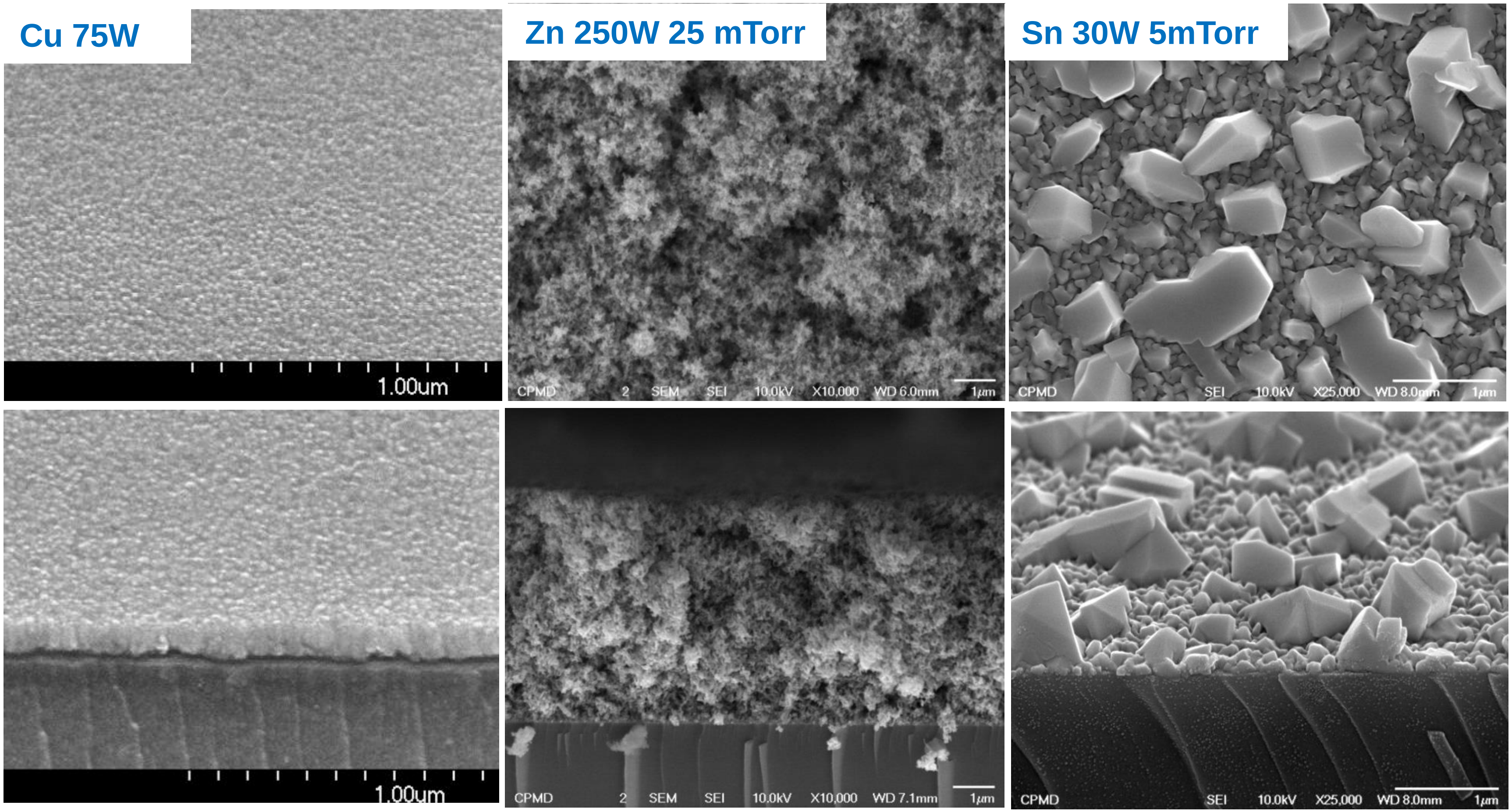






Preparation of Each Single Layers

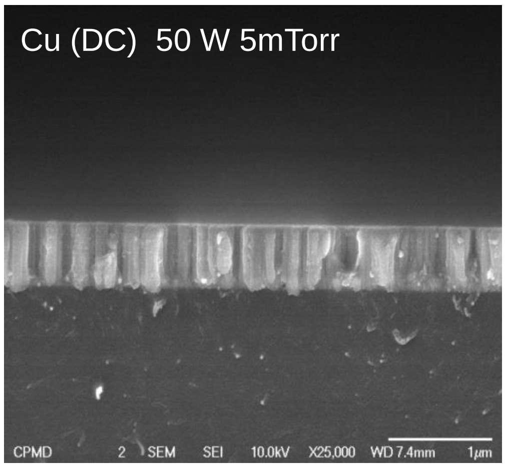
Single layer deposition using metal targets

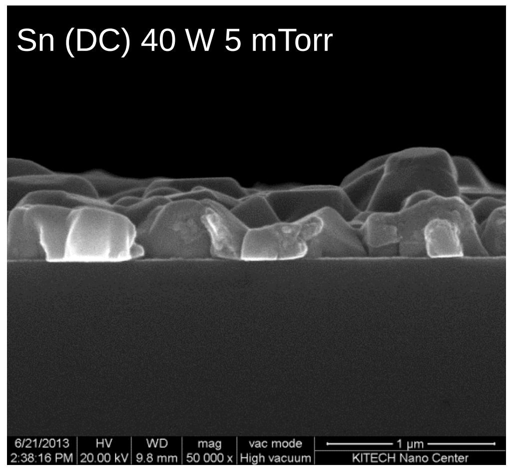


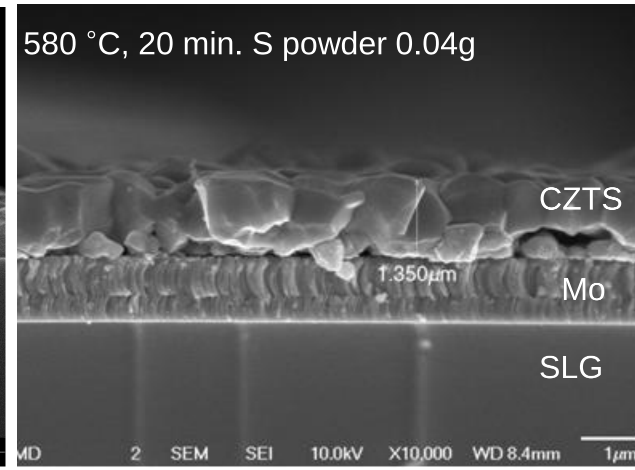
Difficult to control the uniformity of Zn and Sn unit layers by adjusting process parameters (power, pressure)

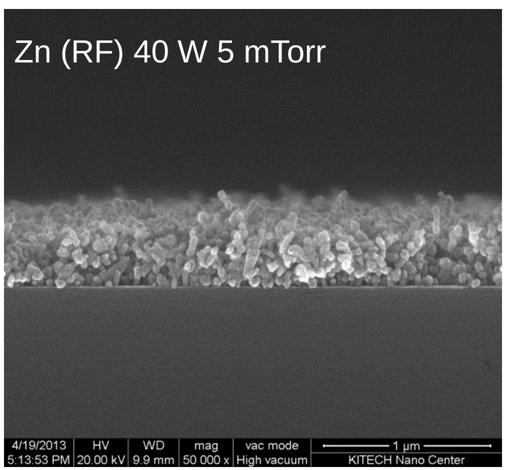
Preparation of Stacked Precursor Thin Films

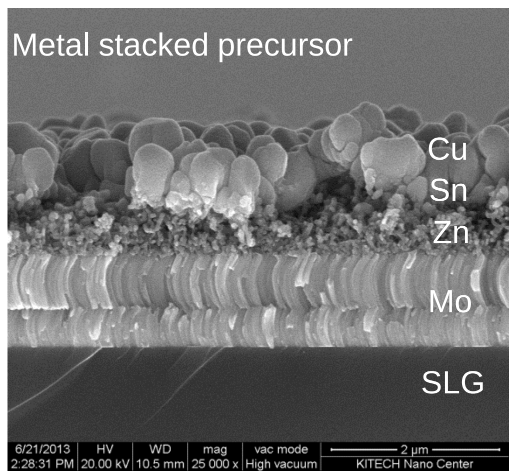
Reasonably possible to control the uniformity by adjusting process parameters (power, pressure, temperature)

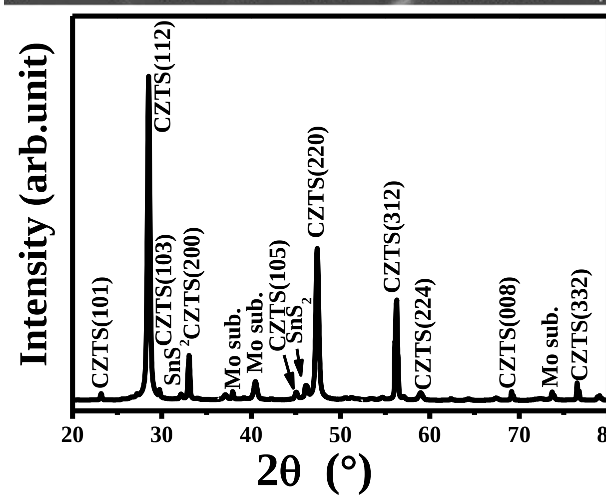










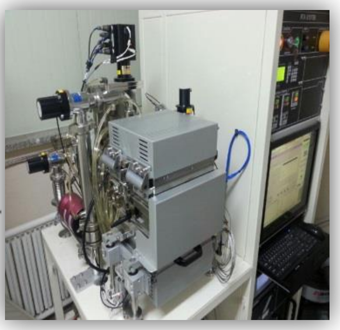


Solar Cell Fabrication Process

Solar Cell Fabrication in P&E ThinFilm Lab.

Sputtering

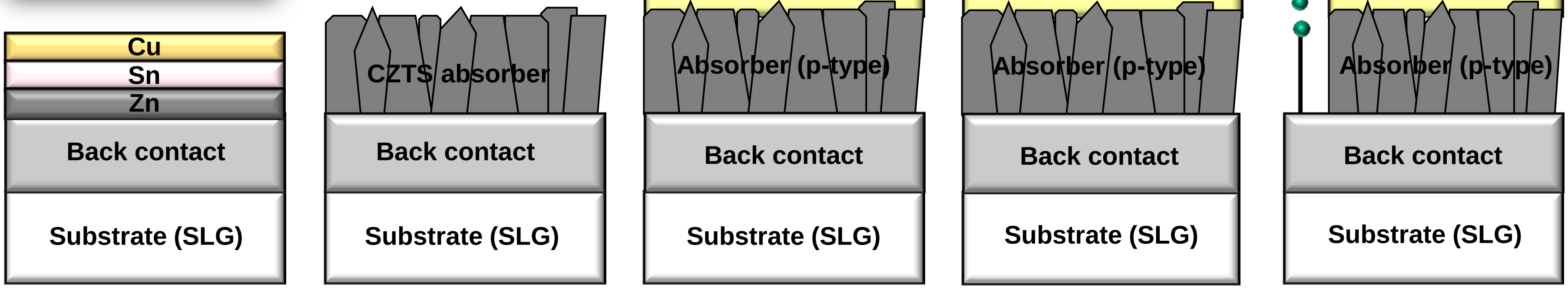
RTA



CBD

RF sputter

Evaporation



Precursor (~1㎛) | CZTS(~1㎛) | CdS (~60 ㎚) | n-AZO/i-ZnO (500㎚/50㎚) | Al (~1㎛)

Photo Images of Samples

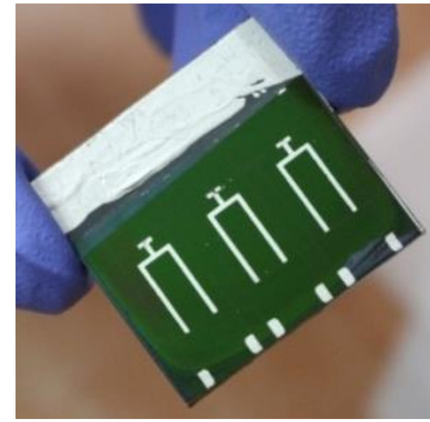
Precursor

2.5 cm

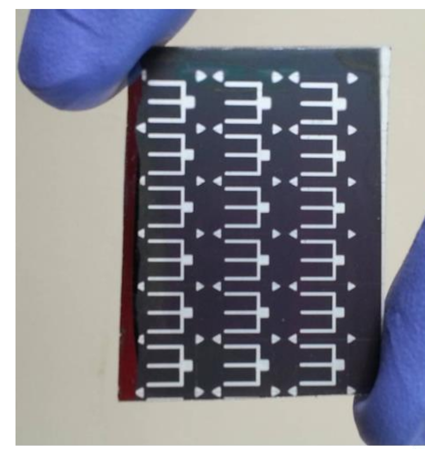
after
Sulfo-Selenization

after CdS

Final Cells



Cell size: 0.45 cm^2

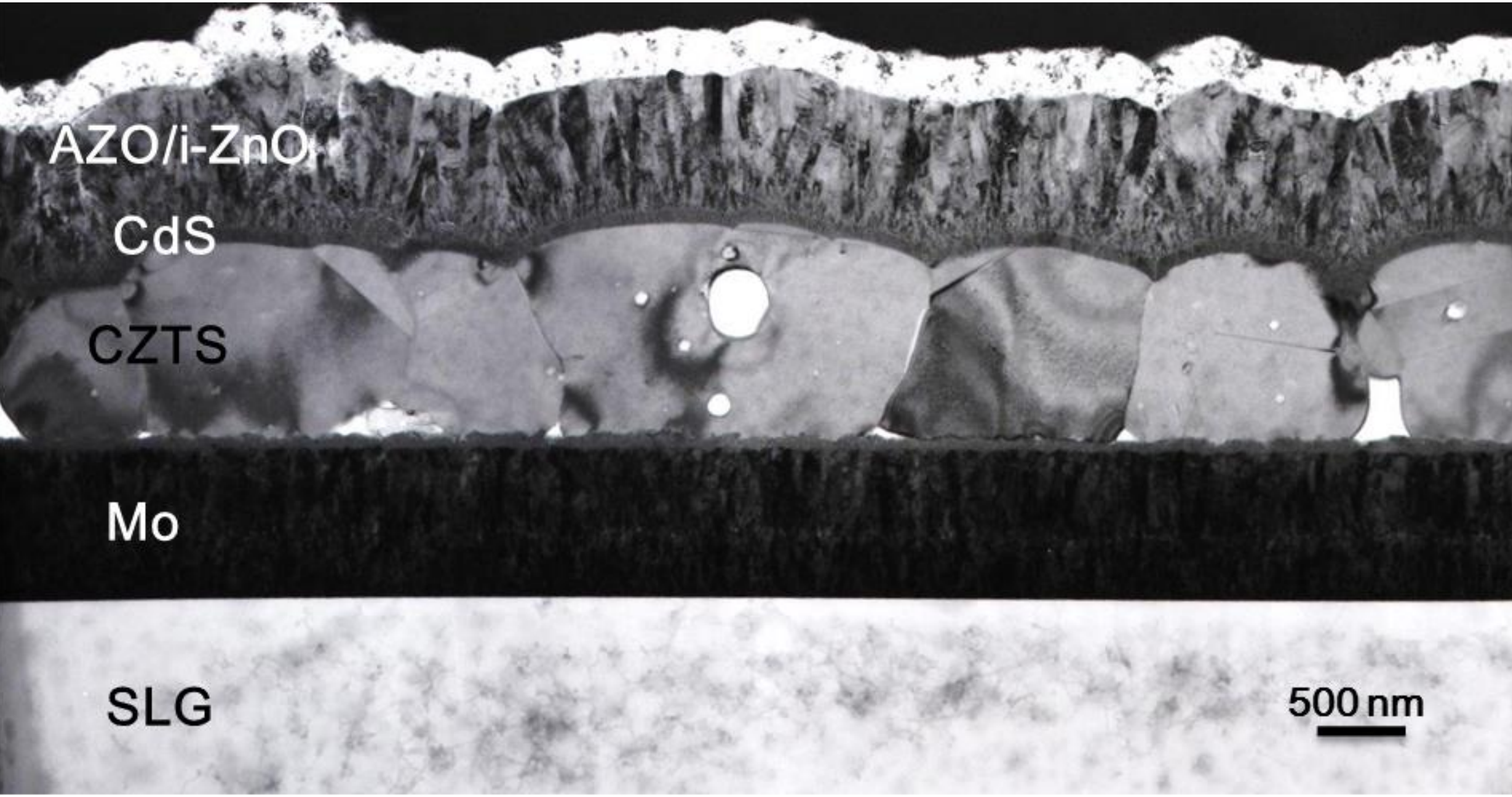


Cell size: 0.31 cm^2

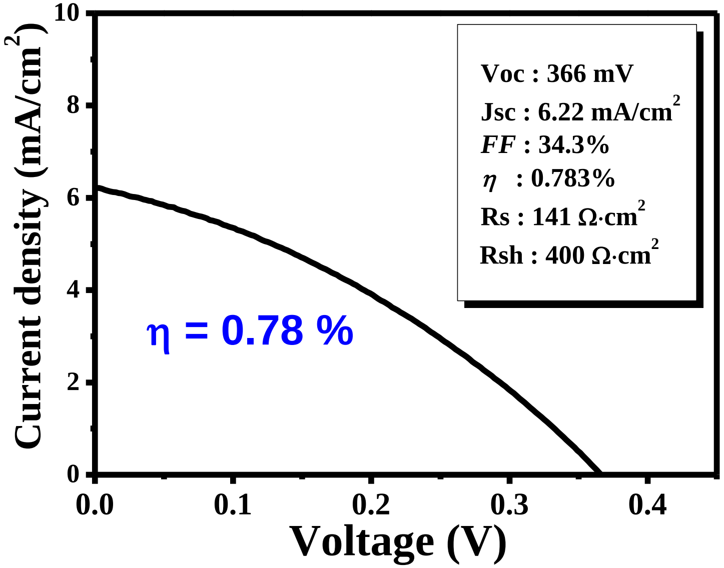
Reasonably Uniform Surface Morphology

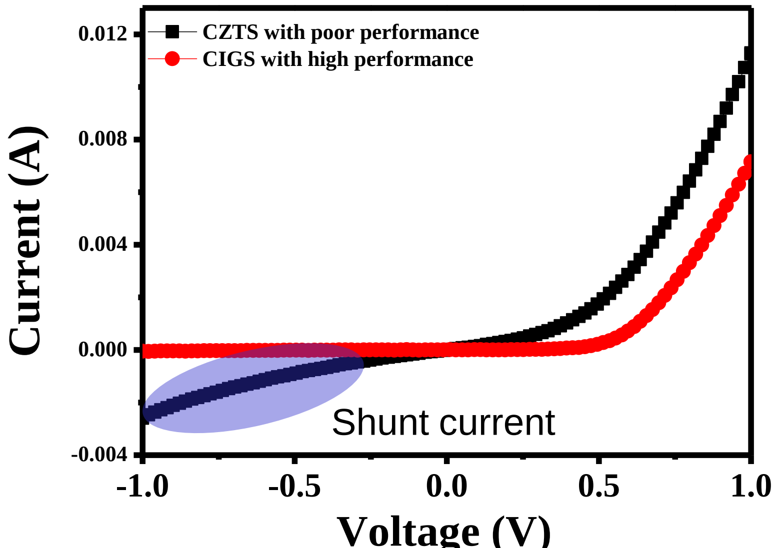
Fabrication of a CZTS TFSC

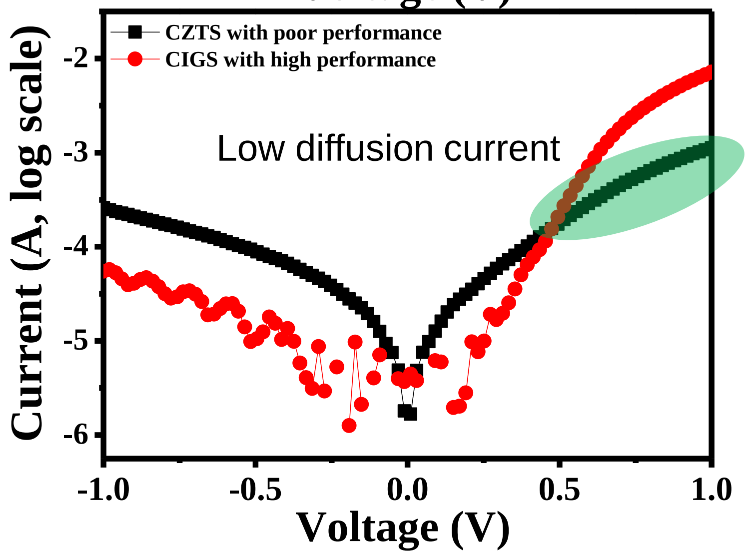
Cross-sectional TEM image



Cell efficiency of a CZTS TFSC



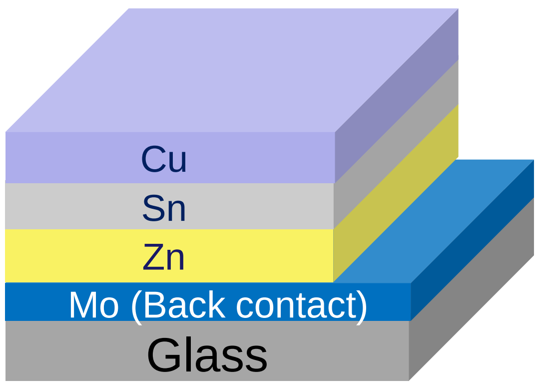




- Low shunt resistance
- Low diffusion current
- High recombination rate
- High series resistance

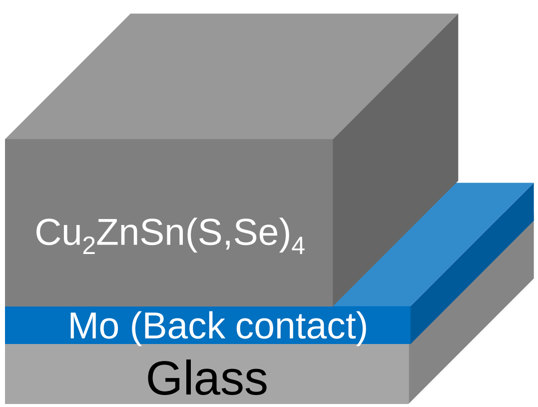
Processing Parameters to Be Controlled

Precursor Preparation



- Target material
- Thickness
- Stacking order
- Barrier layer

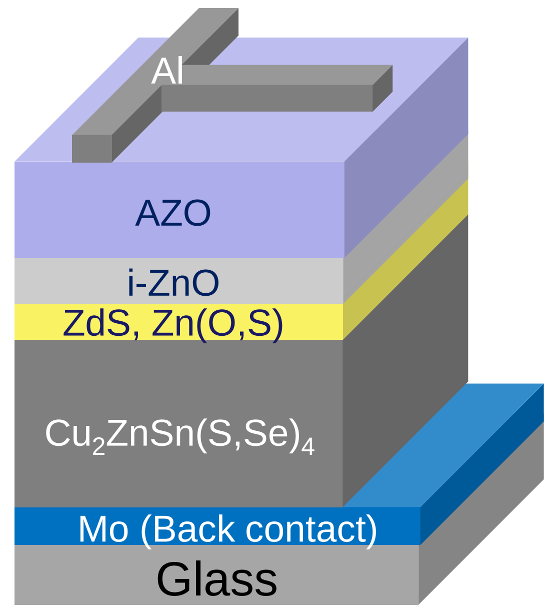
Sulfo-Selenization



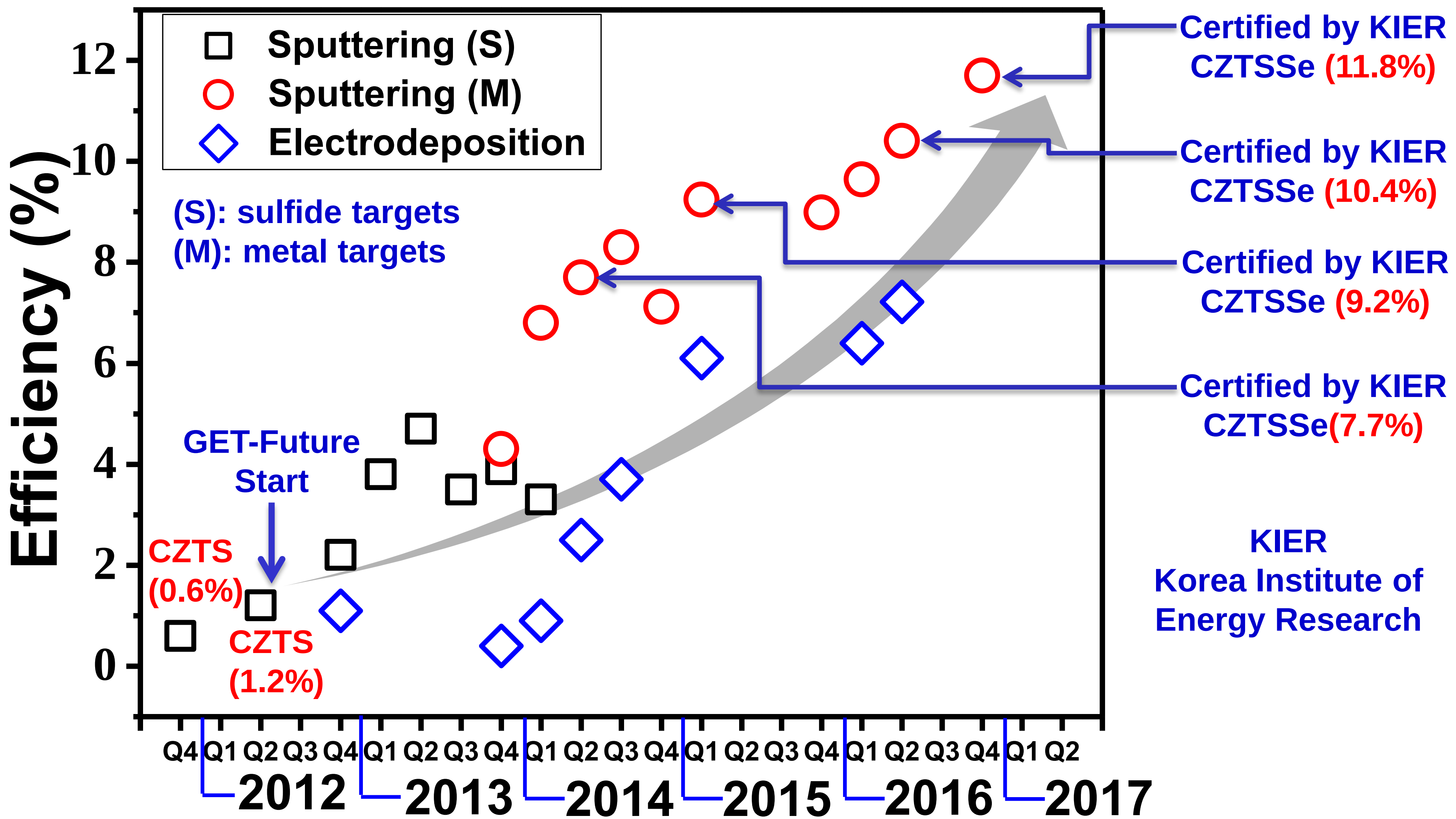
- Temperature
- Ramp Rate
- Duration Time
- Soft annealing
- Post annealing treatment
- Partial Pressure (S, Se)
- $MoSSe_2$ interfacial layer
- Alkali control

Cell Fabrication

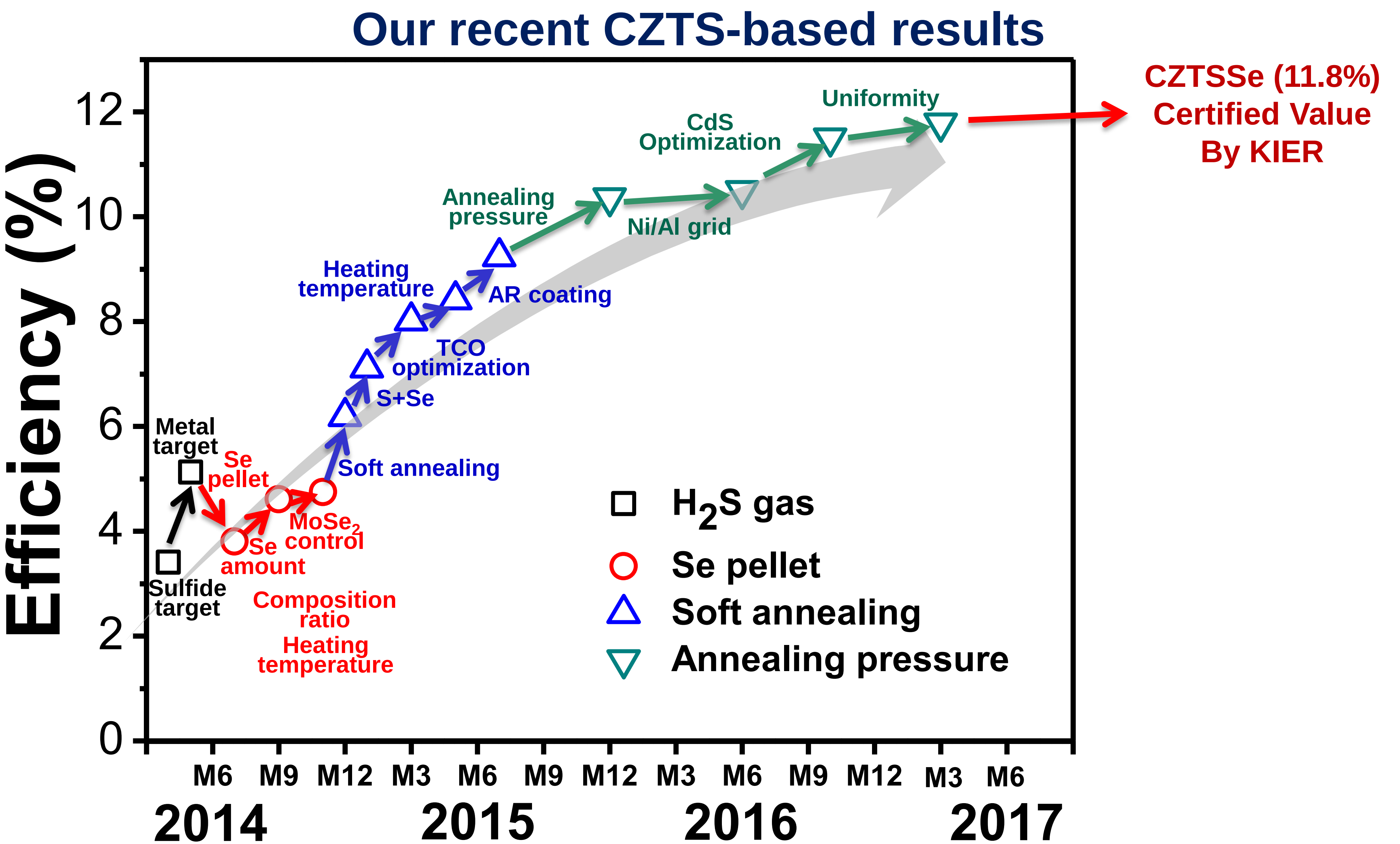
- Buffer thickness
- Cd-free buffer
- i-ZnO thickness
- AZO thickness
- Electrical properties of TCO layers
- Band gaps of n-type layers
- Deposition Temp. of n-type layers



Evolution of Cell Efficiency in our Lab.



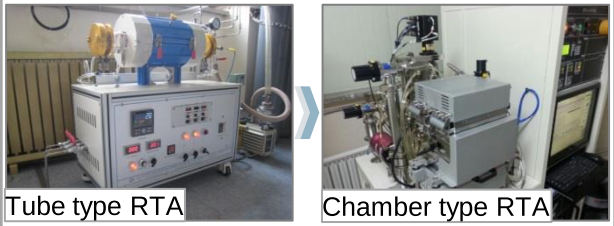
Key issues in improving Cell Efficiency



Major Three Steps in Improving Cell Efficiency

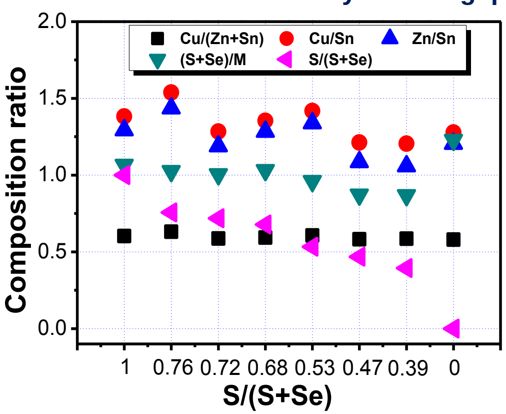
1 STEP

Reproducible Annealing Processing



- Easy to control annealing variation (Process pressure control, S/Se powder)
- Film uniformity
- High vacuum condition (pure atmosphere)

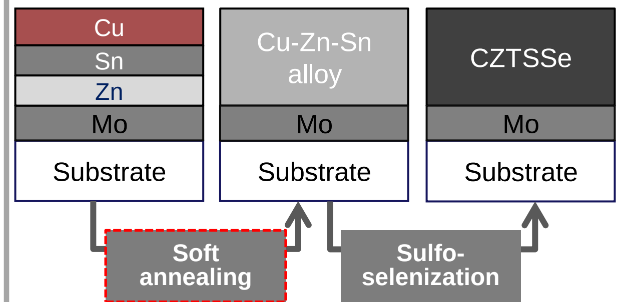
Control of absorber layer band gap



- Controlling band gap (S/Se ratio)

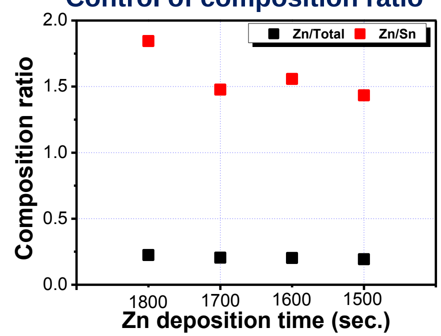
2 STEP

Introducing Soft Annealing Treatment



- Formation of metal alloy using the soft annealing process

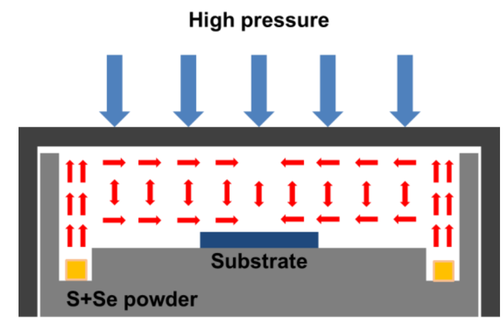
Control of composition ratio



- Controlling composition of absorber layer ratio using the precursor deposition time

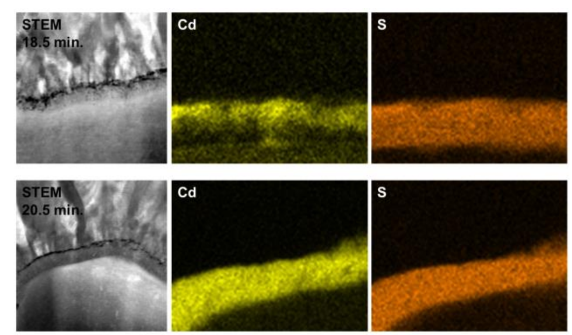
3 STEP

Controlling Annealing Pressure



- Optimization of annealing condition by varying external partial pressure

Optimization of CdS buffer layer

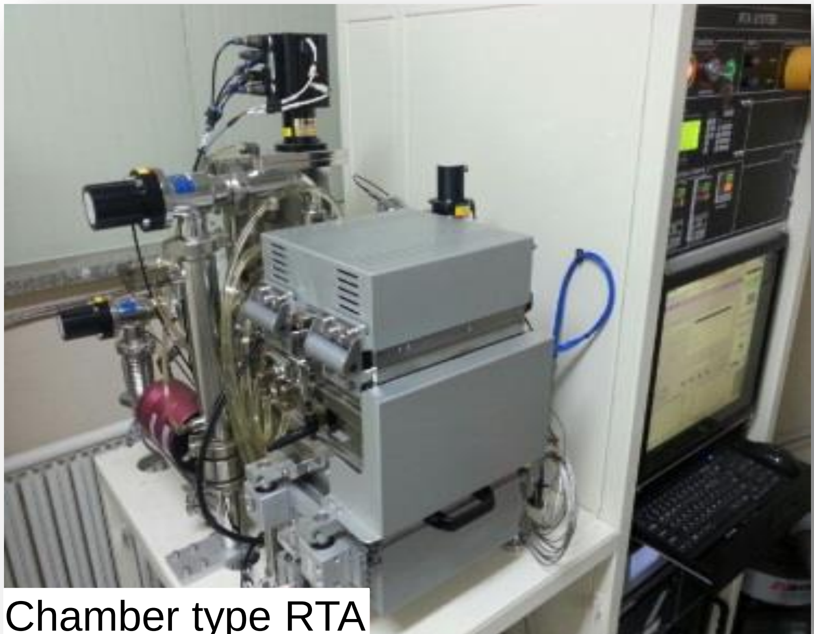


- Controlling deposition temperature and deposition time

Improving Reproducibility in Annealing Process

By introducing a chamber type RTA


Tube type RTA


Chamber type RTA

- Easy to control annealing parameters
  (Process pressure control, S/Se powder)
- Uniform film formation
- High vacuum condition (pure atmosphere)

Improving Reproducibility in Annealing Process

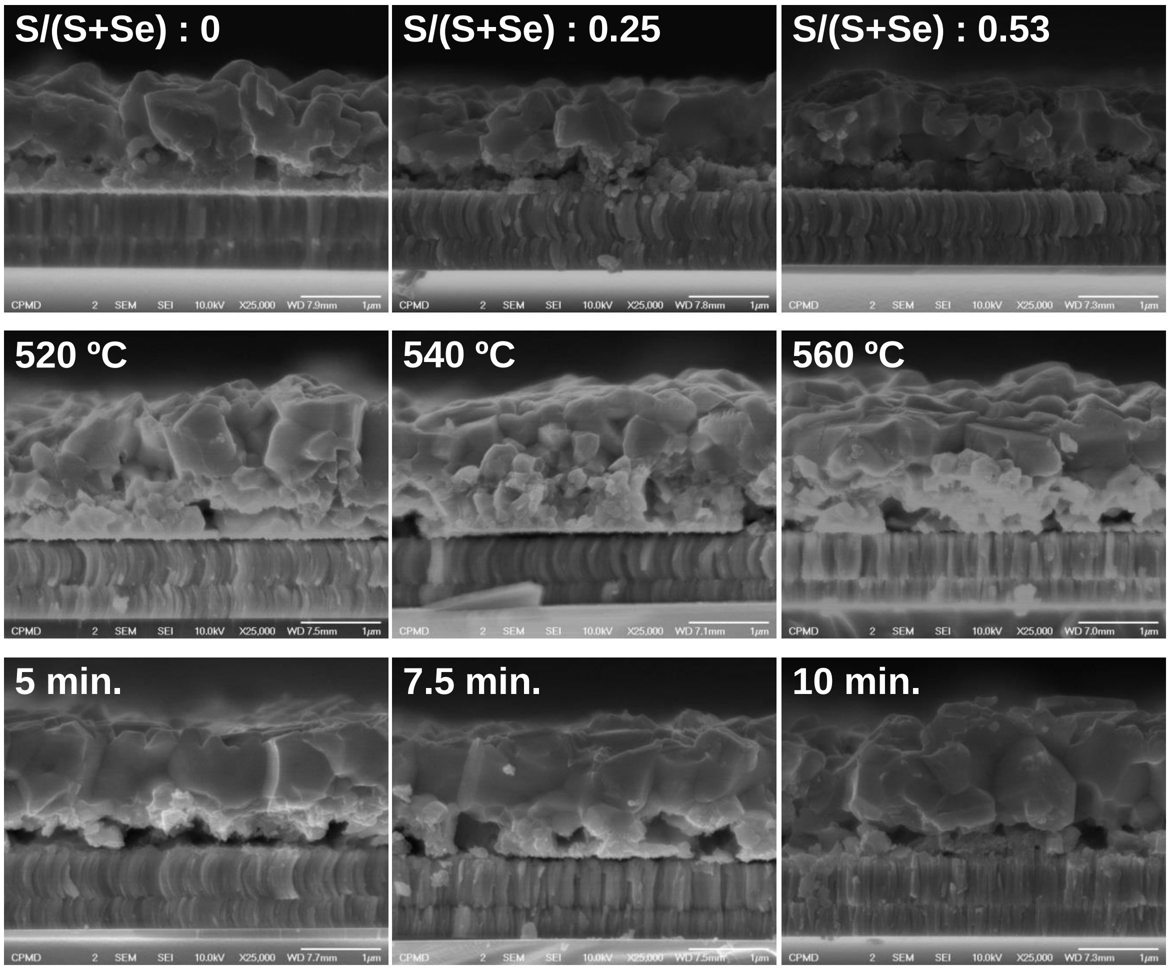
By introducing a chamber type RTA and Optimization

Annealing condition

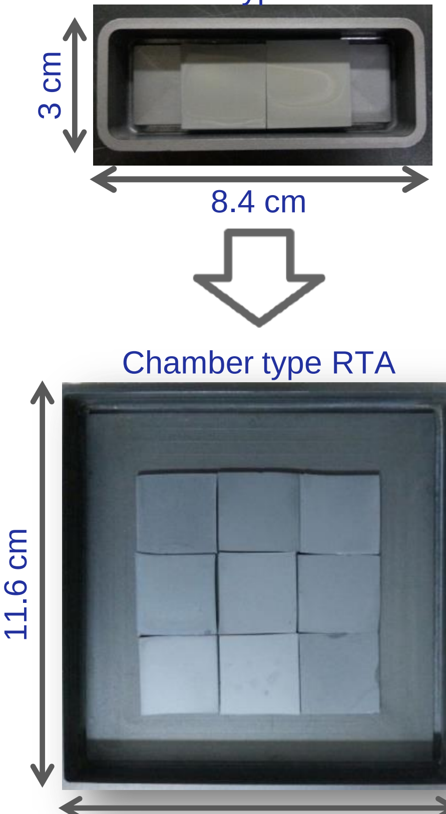
S/(S+Se) Ratio
520 ºC/10 min.

Annealing Temp.
10 min.
S:0.002g
Se:0.05g

Annealing Time
520 ºC
S:0.002g
Se:0.05g



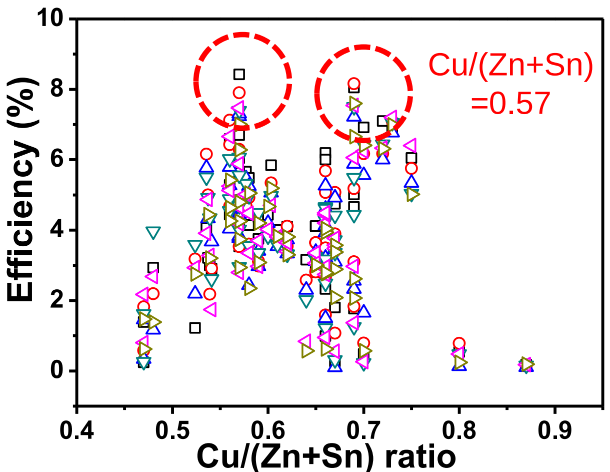
Uniformity

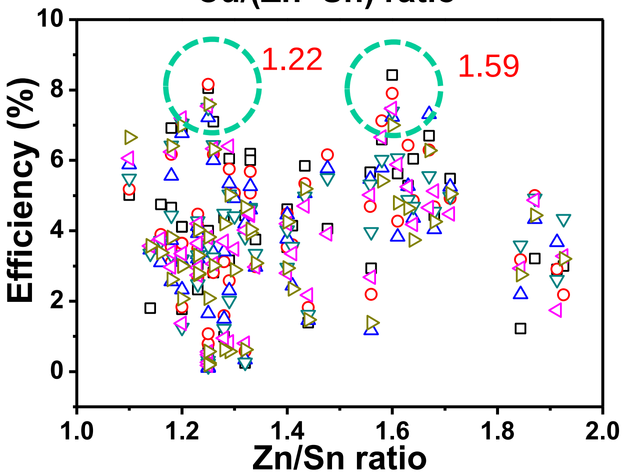


Optimization of Composition of Absorber Layers

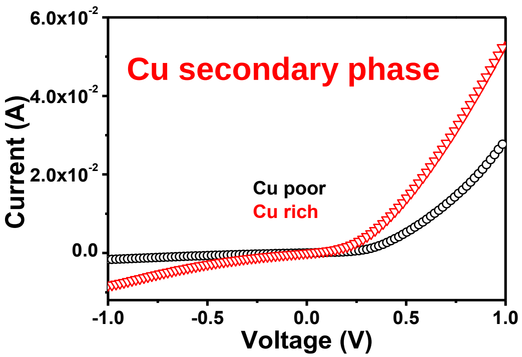
Controlling absorber layer composition ratio

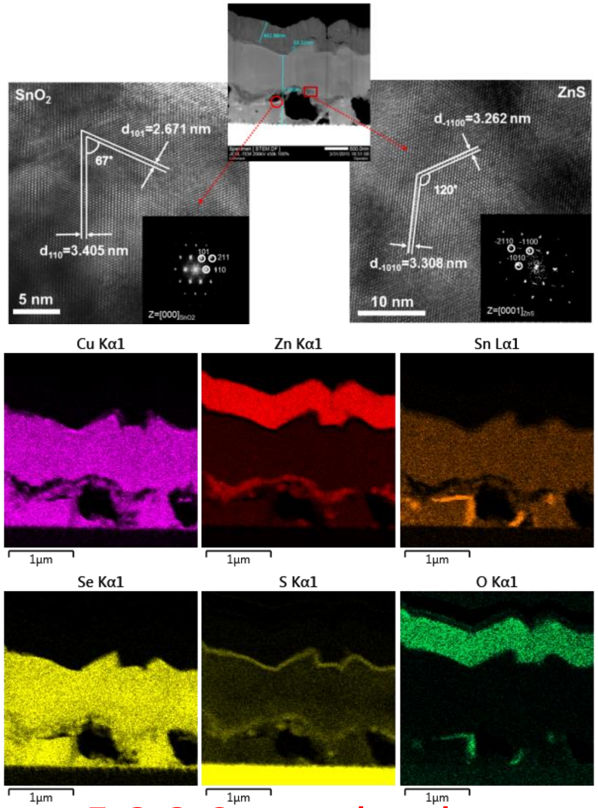
Precursor composition ratio



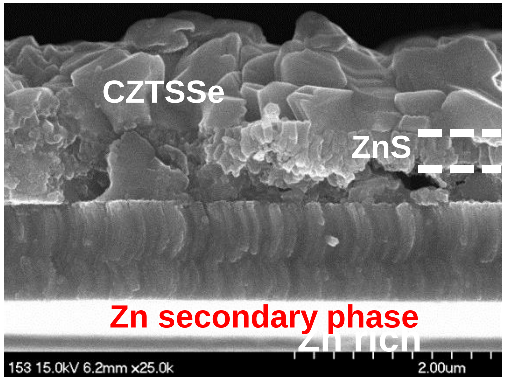


Examples on composition ratio changes



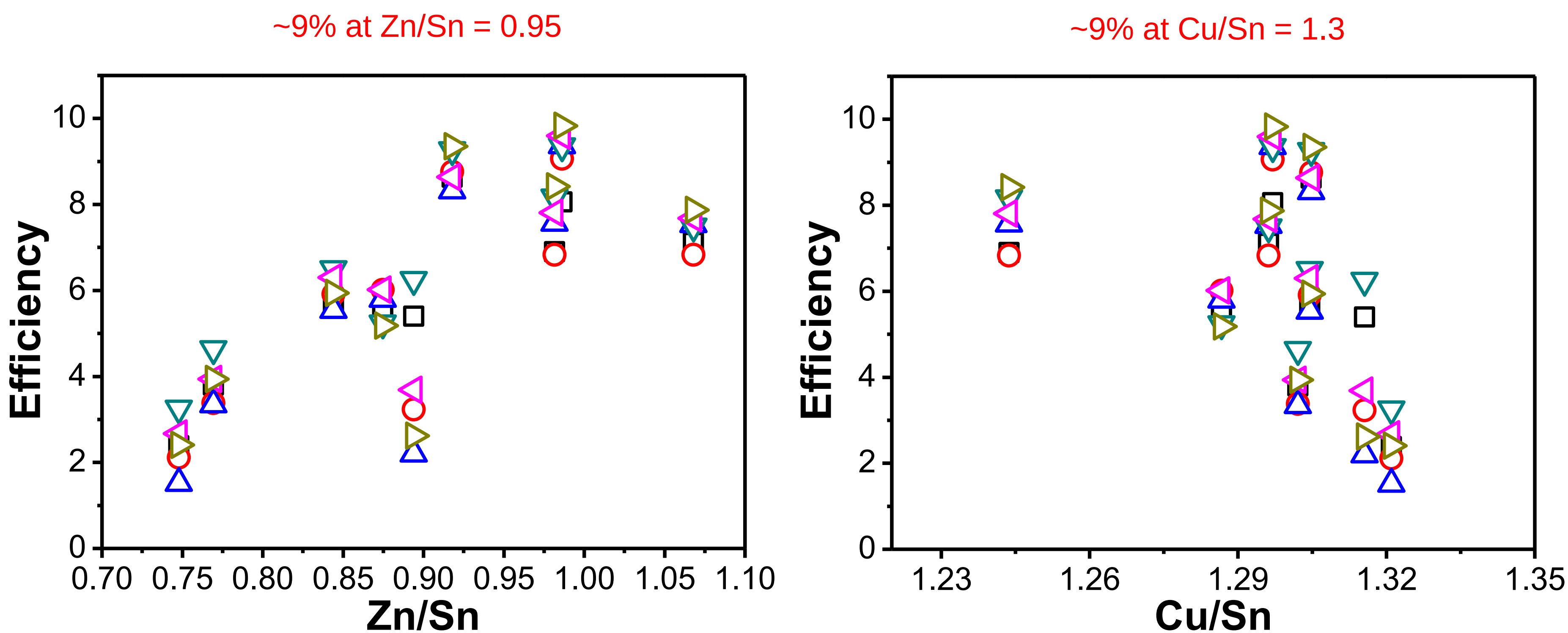


ZnS, SnO_2 secondary phase



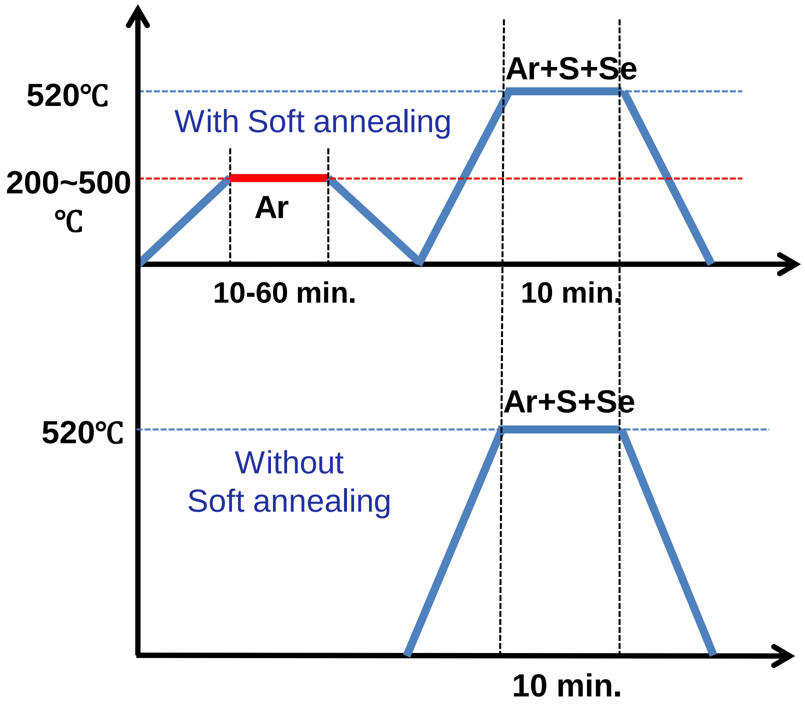
- Easy formation of secondary phases
- Small composition window for CZTSSe formation

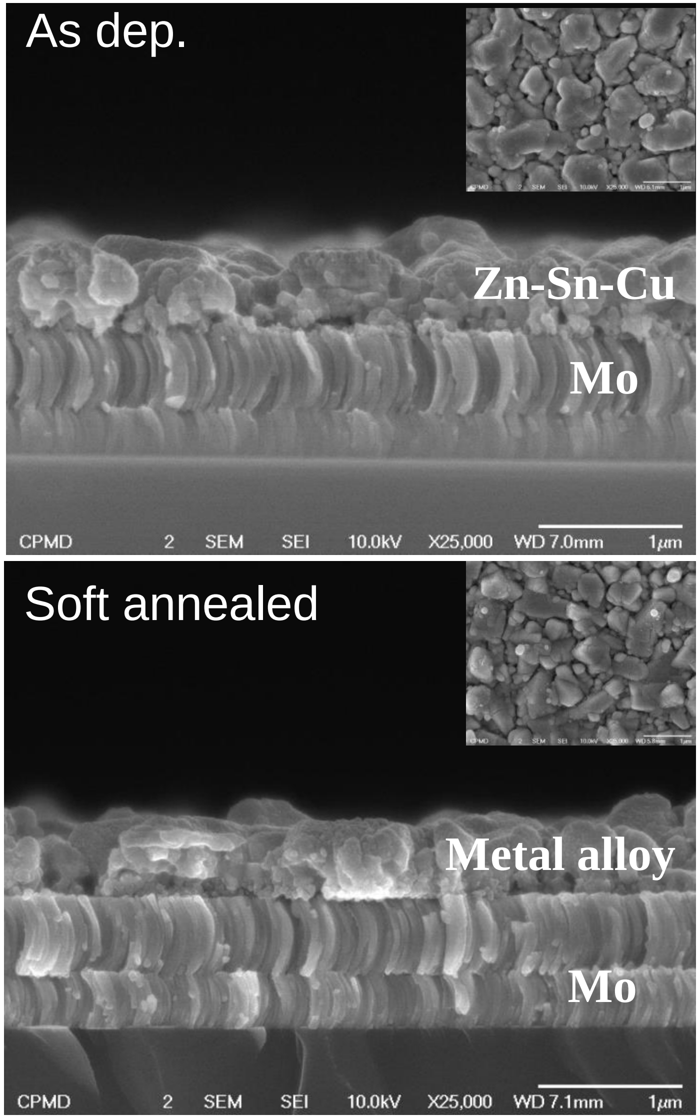
Optimization of Composition of Absorber Layers



Introducing Soft Annealing Process

Formation of metal alloy during the soft annealing process

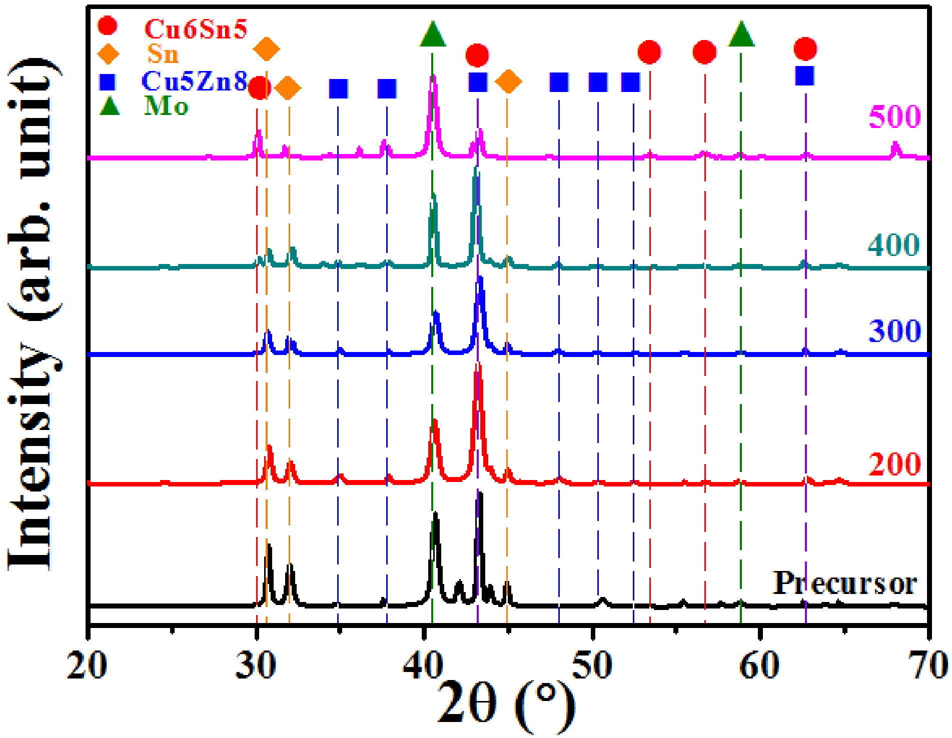




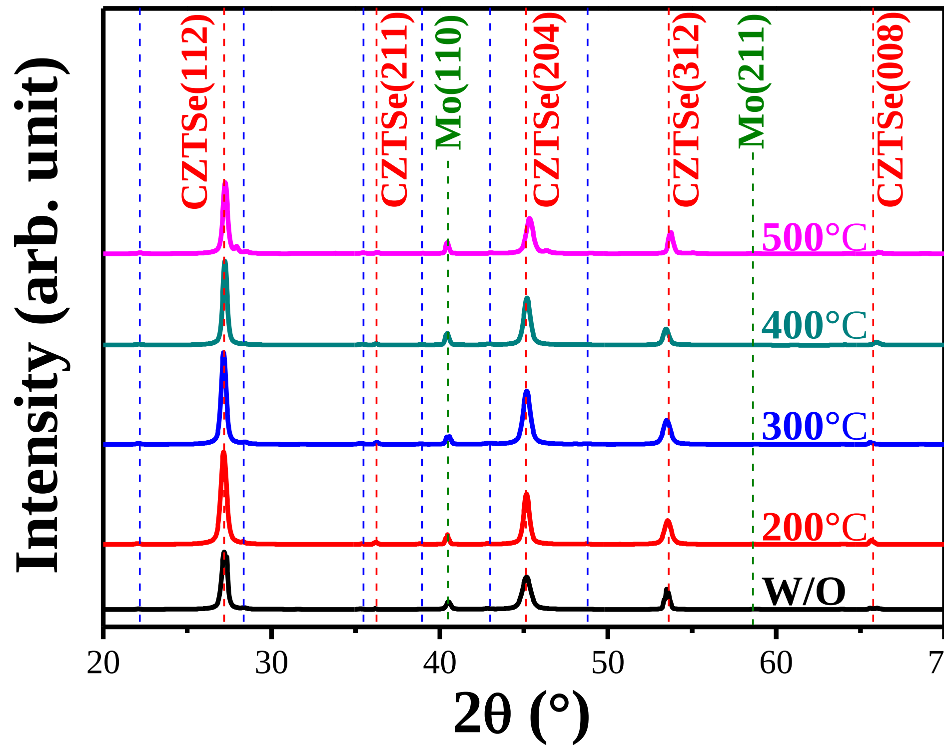
Green Chem., 2016, 18, 700–711

Introducing Soft Annealing Process

XRDP after soft annealing process

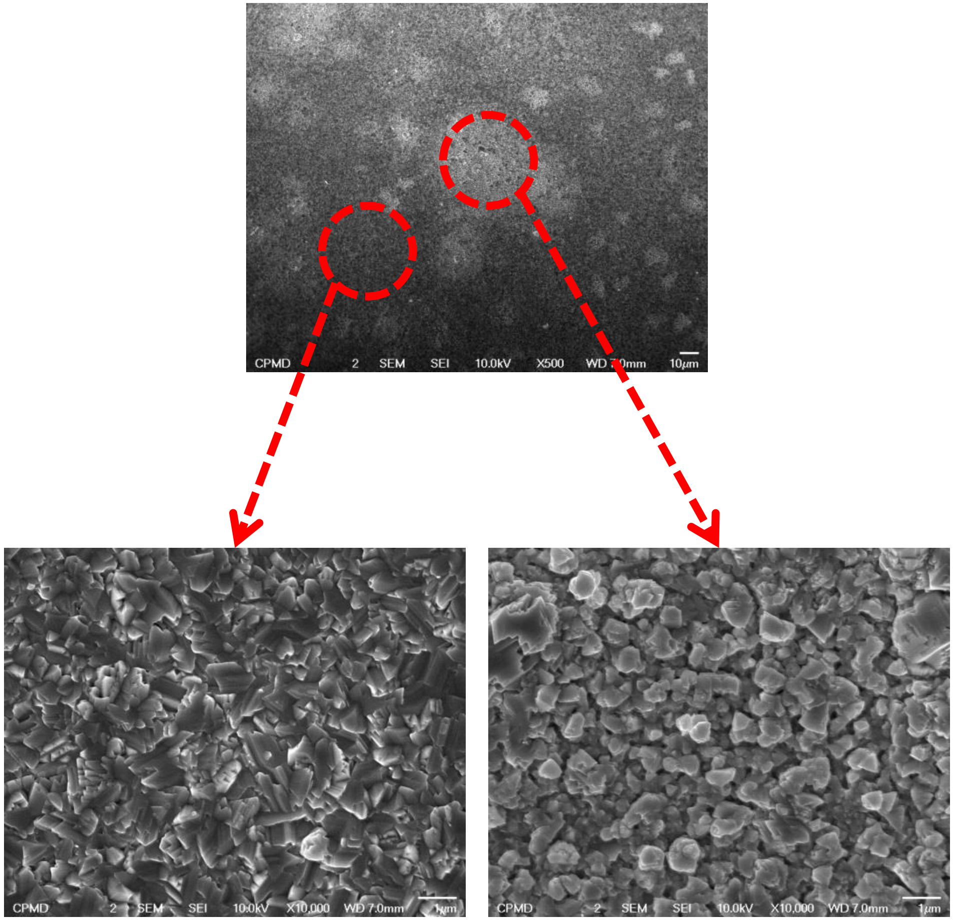


XRDP after sulfo-seenization process

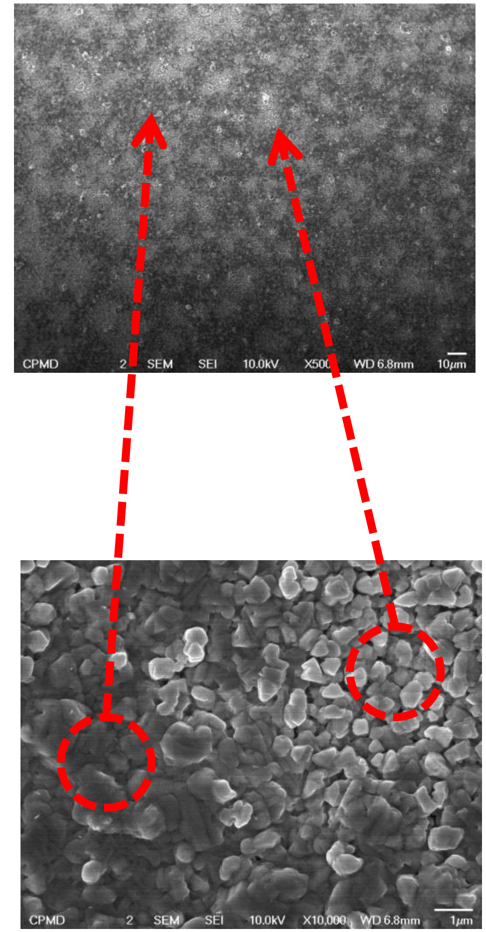


Introducing Soft Annealing Process

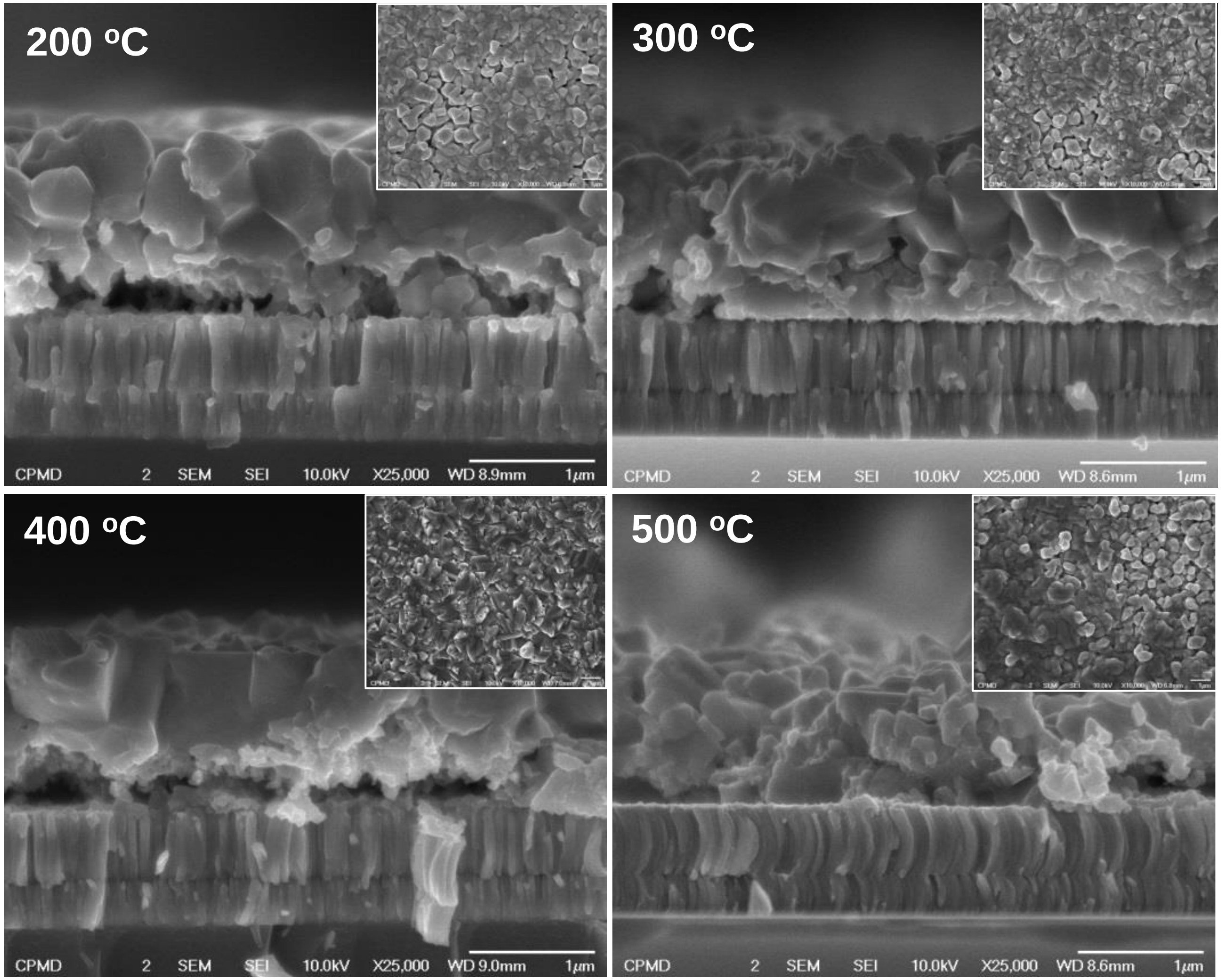
Preheating 400ºC



Preheating 500ºC



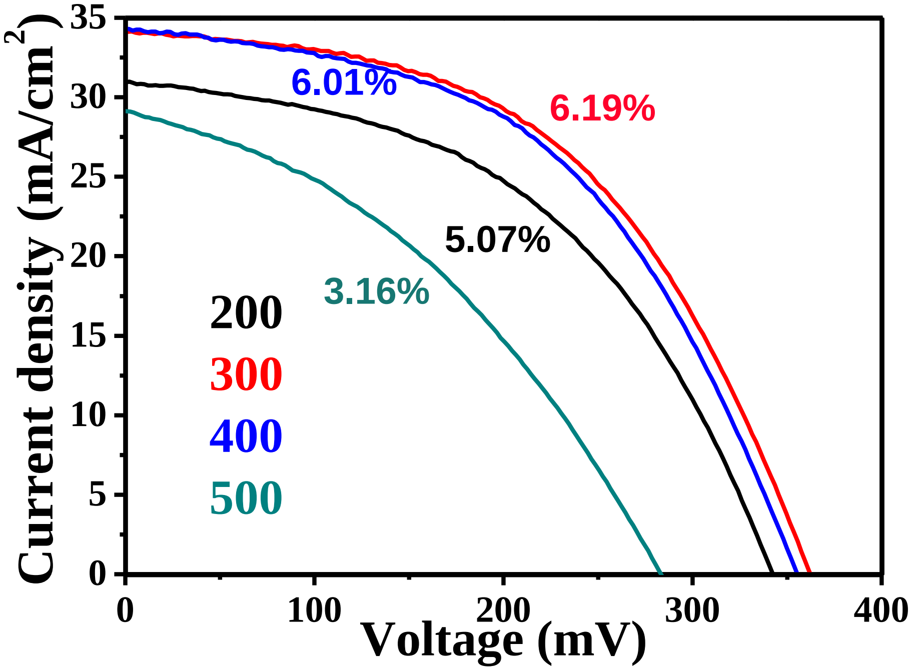
Introducing Soft Annealing Process

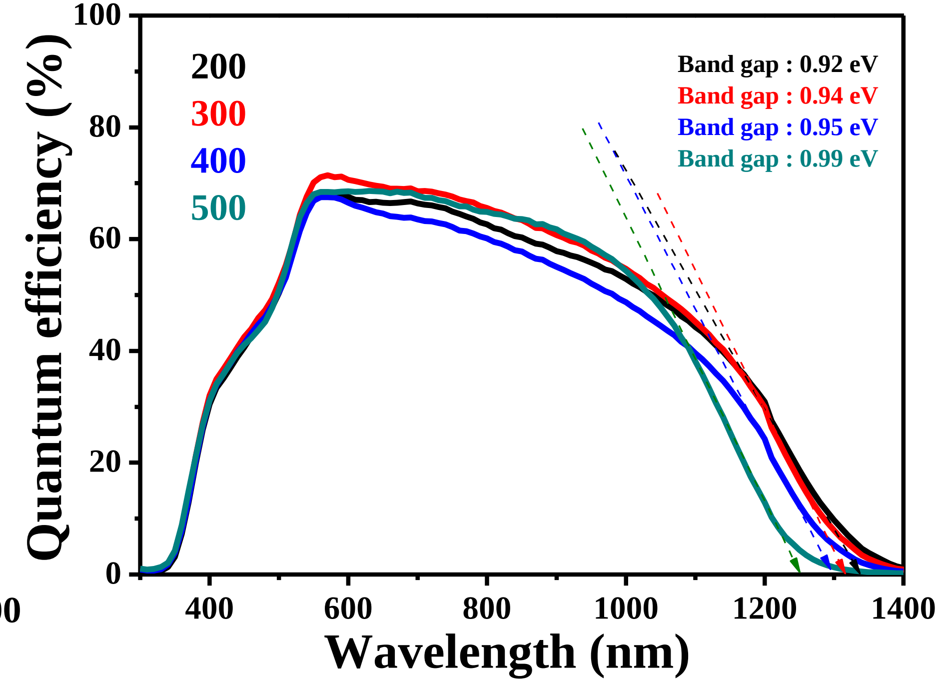


SEM images after sulfo-selenization process

Introducing Soft Annealing Process

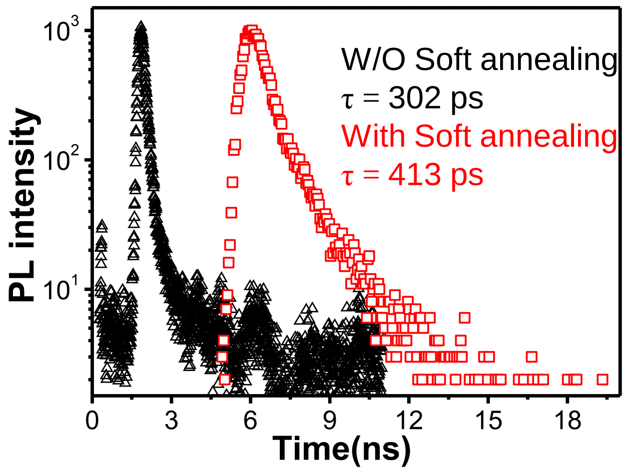
Cell Performance & EQE of CZTSSe TFSCs

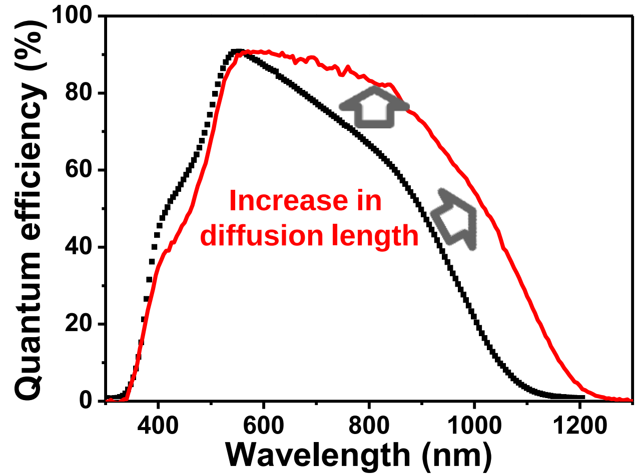


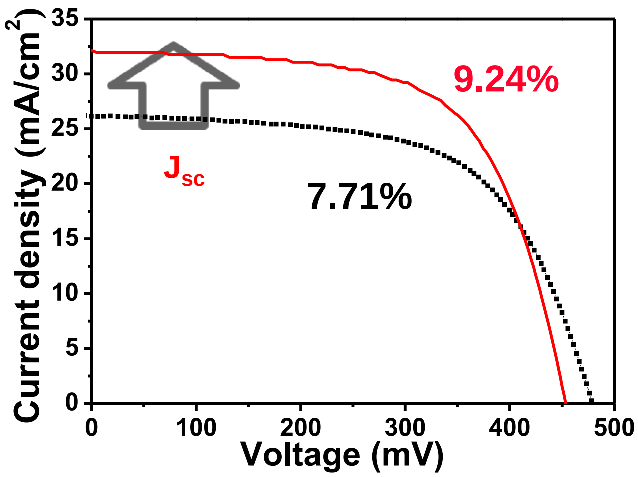


Introducing Soft Annealing Process

Comparison between two cells w/wo soft annealing

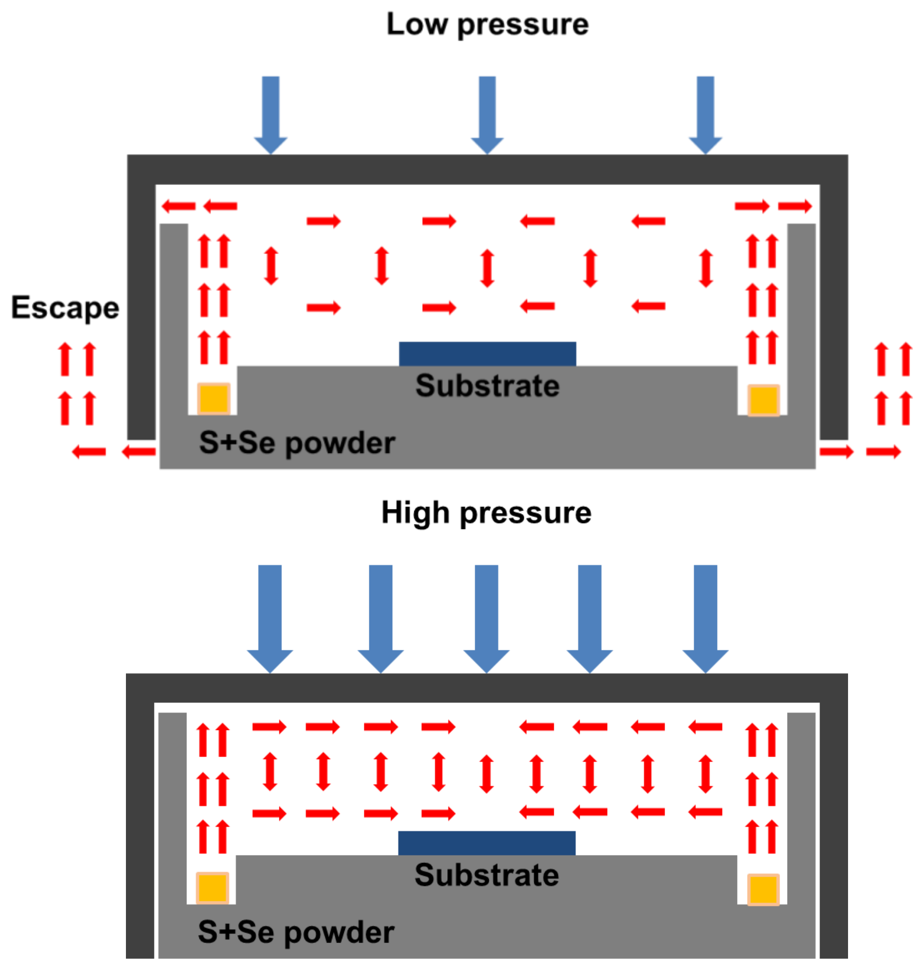




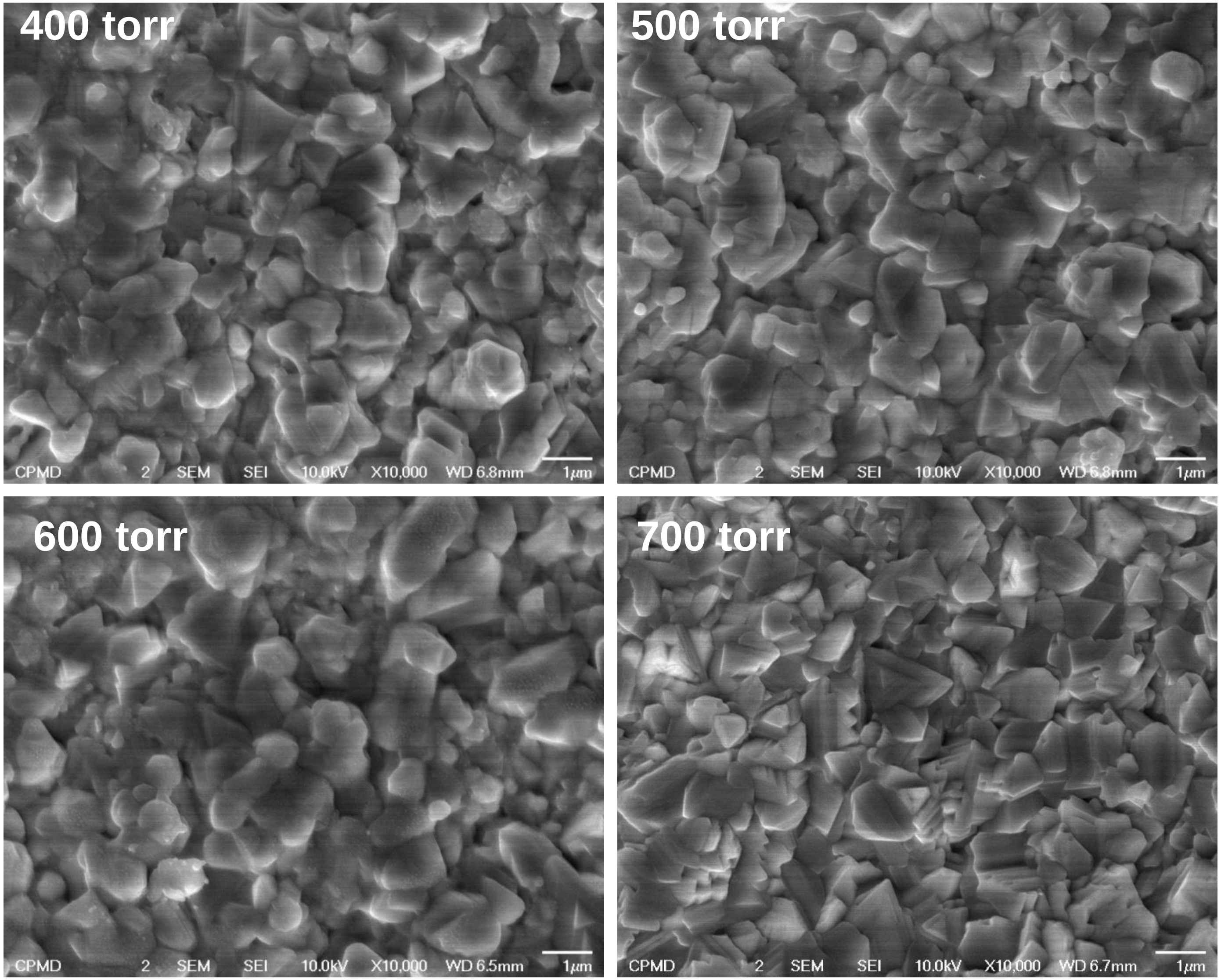


Controlling Partial Pressure during Sulfo-selenization

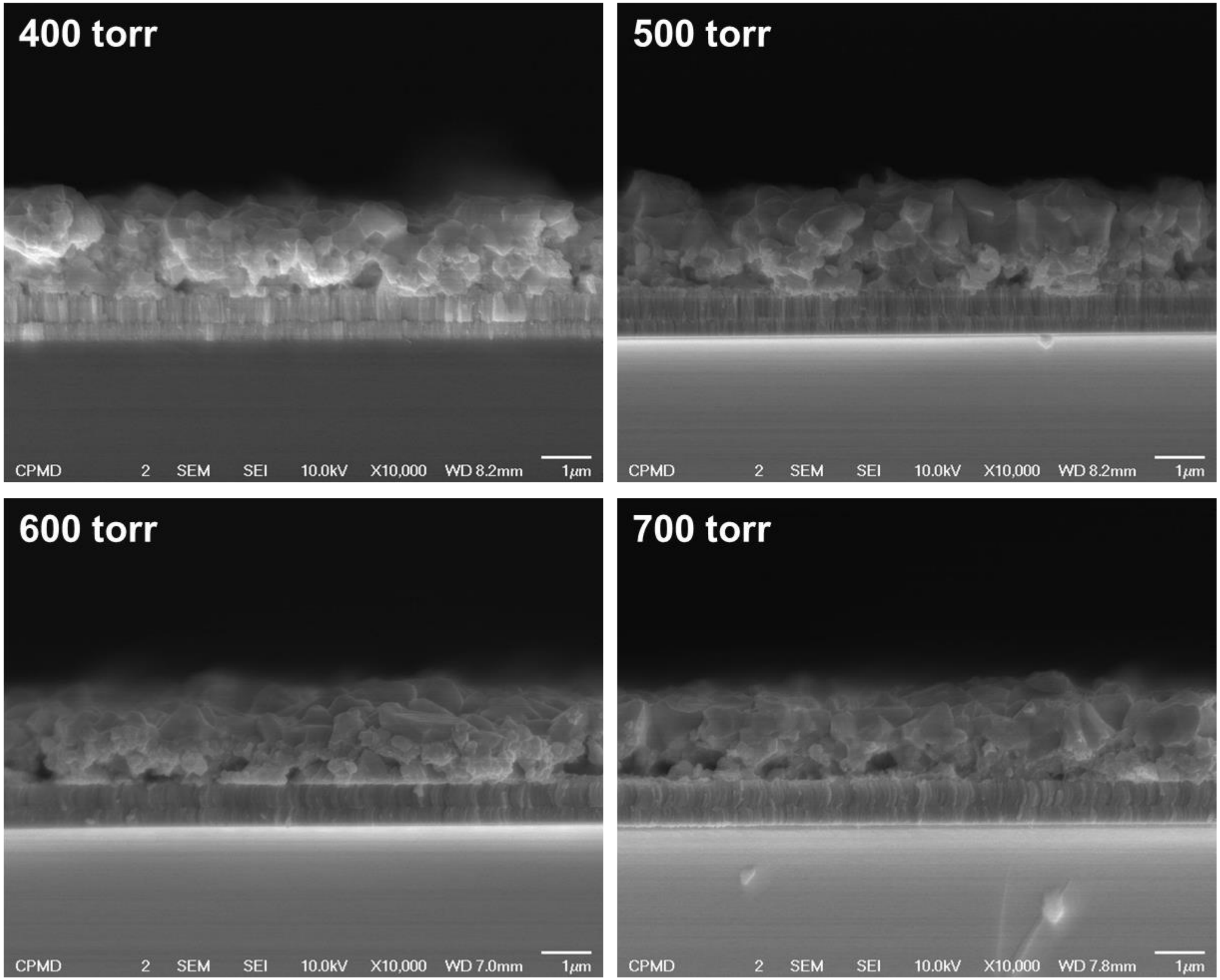
- S & Se vapor escapes easily in low external pressure condition
- Minimize Sn loss



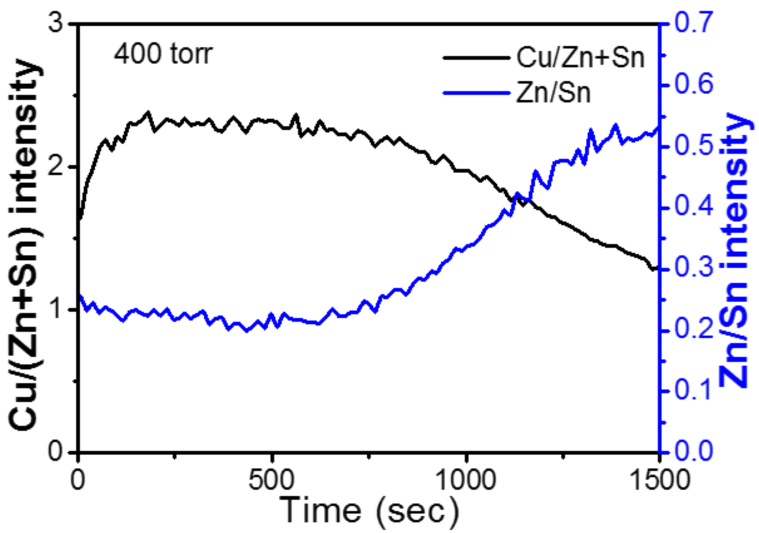
Controlling Partial Pressure during Sulfo-selenization

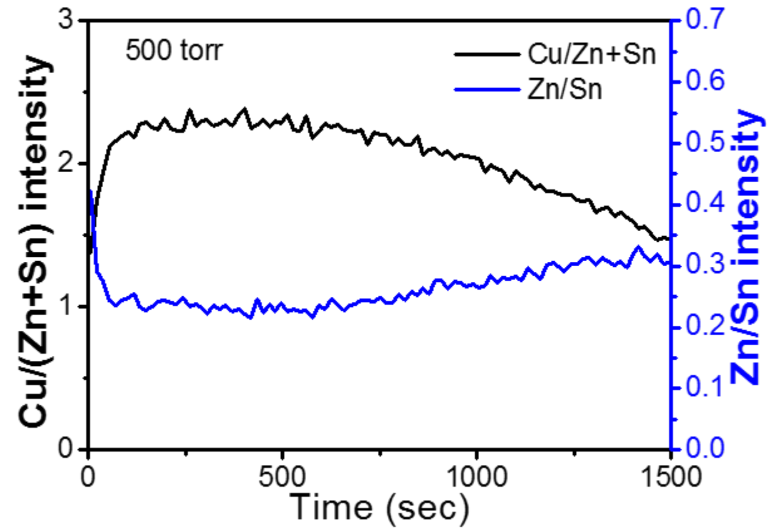


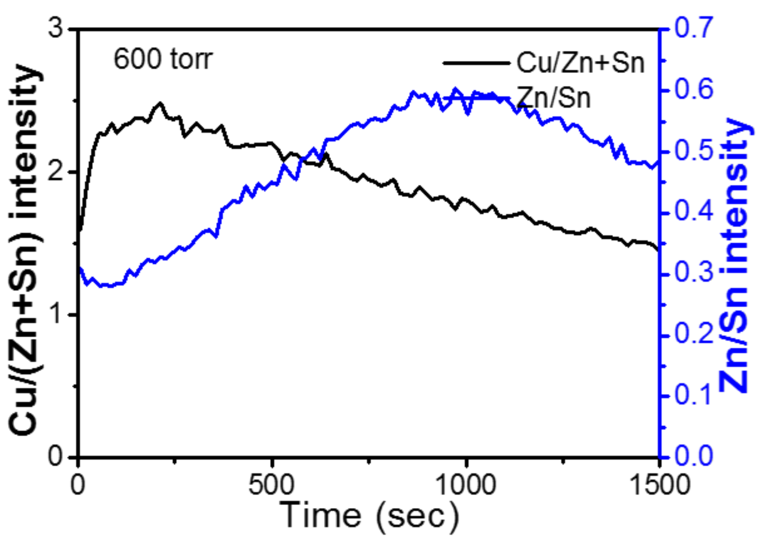
Controlling Partial Pressure during Sulfo-selenization

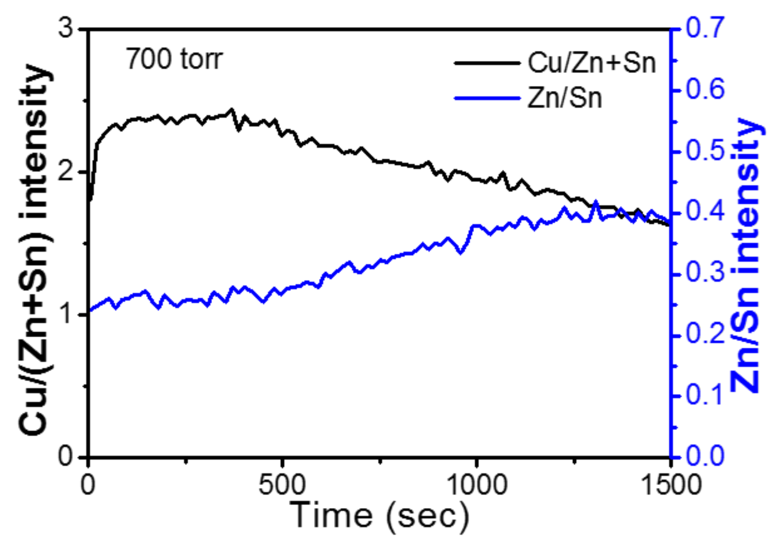


Controlling Partial Pressure during Sulfo-selenization

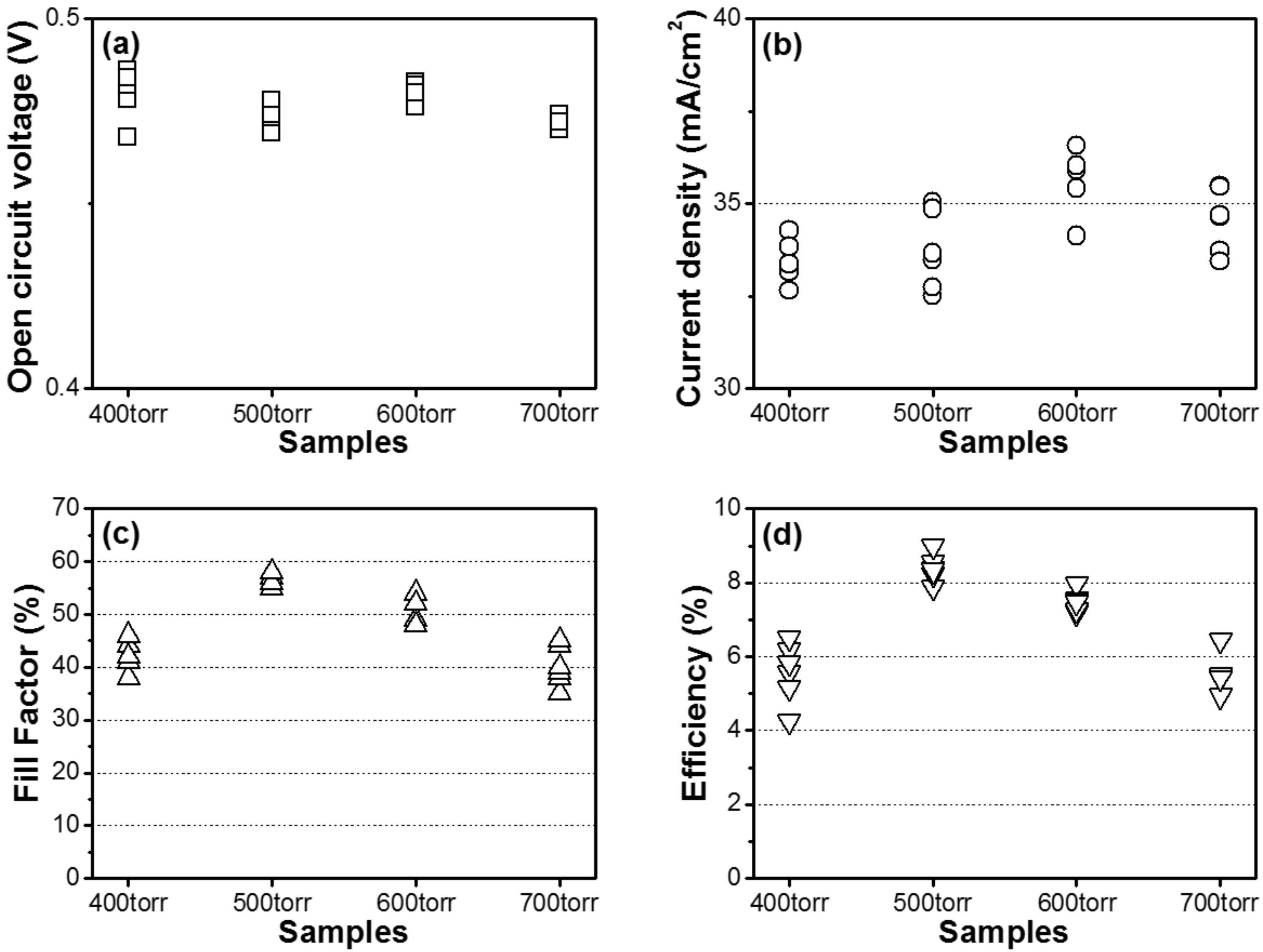




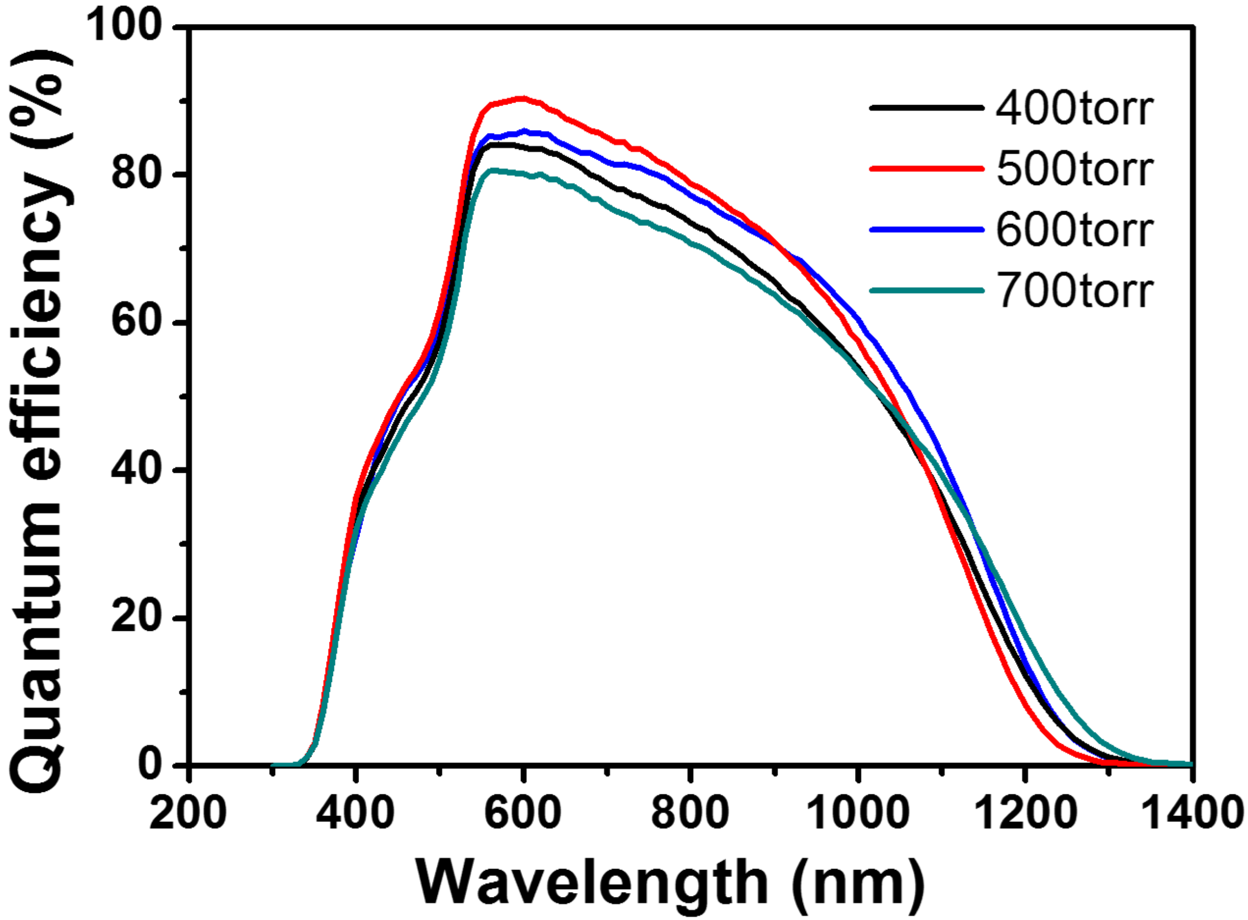




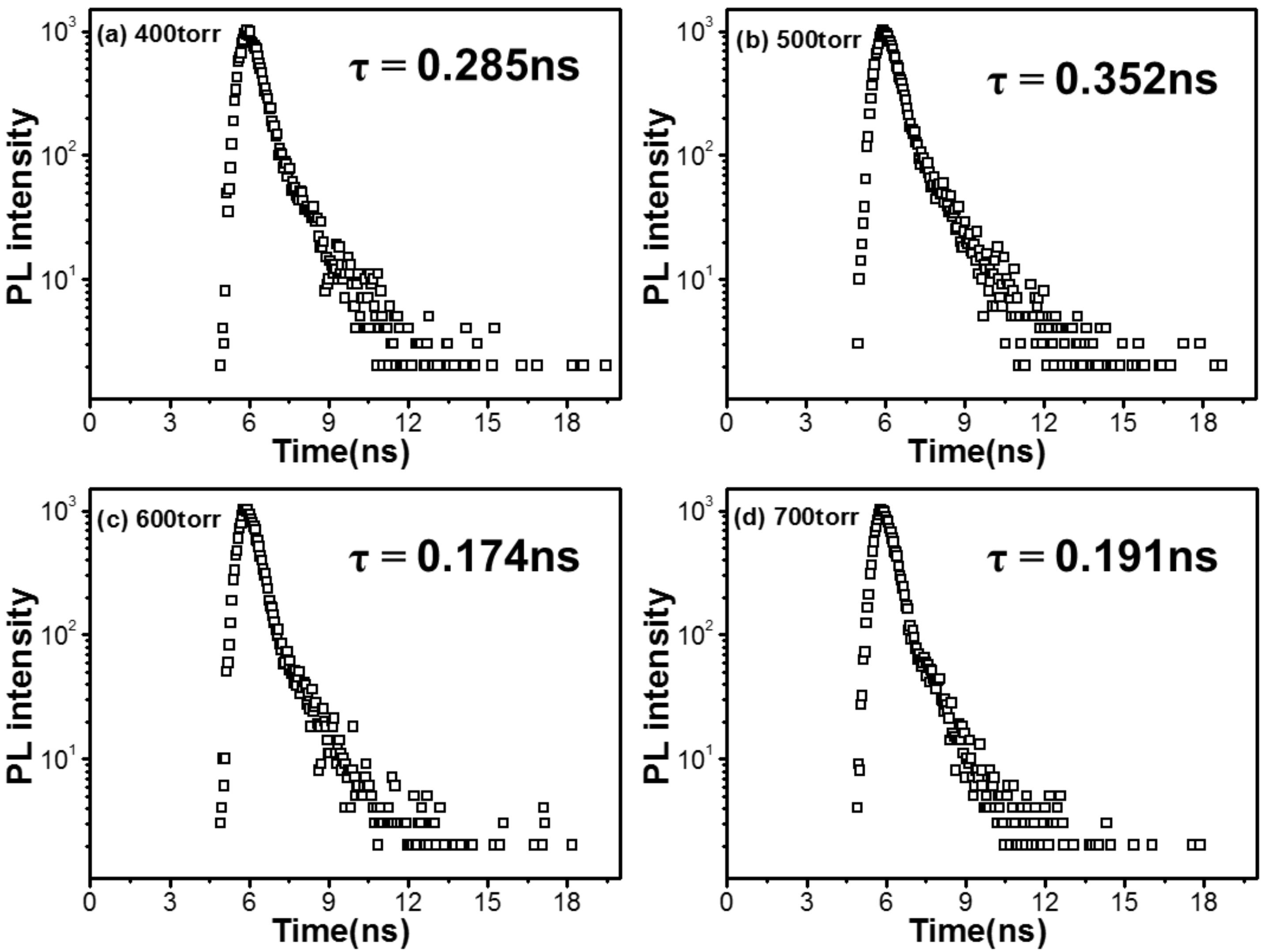
Controlling Partial Pressure during Sulfo-selenization



Controlling Partial Pressure during Sulfo-selenization



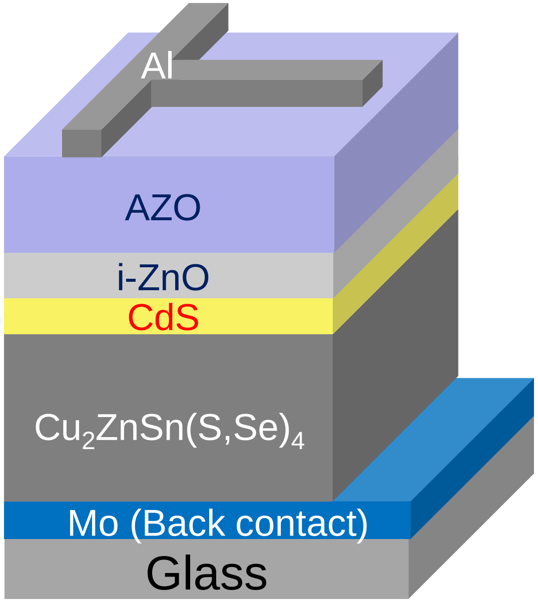
Partial Pressure Control during Sulfo-selenization Process



Fine Tuning on CdS Buffer Layer Process

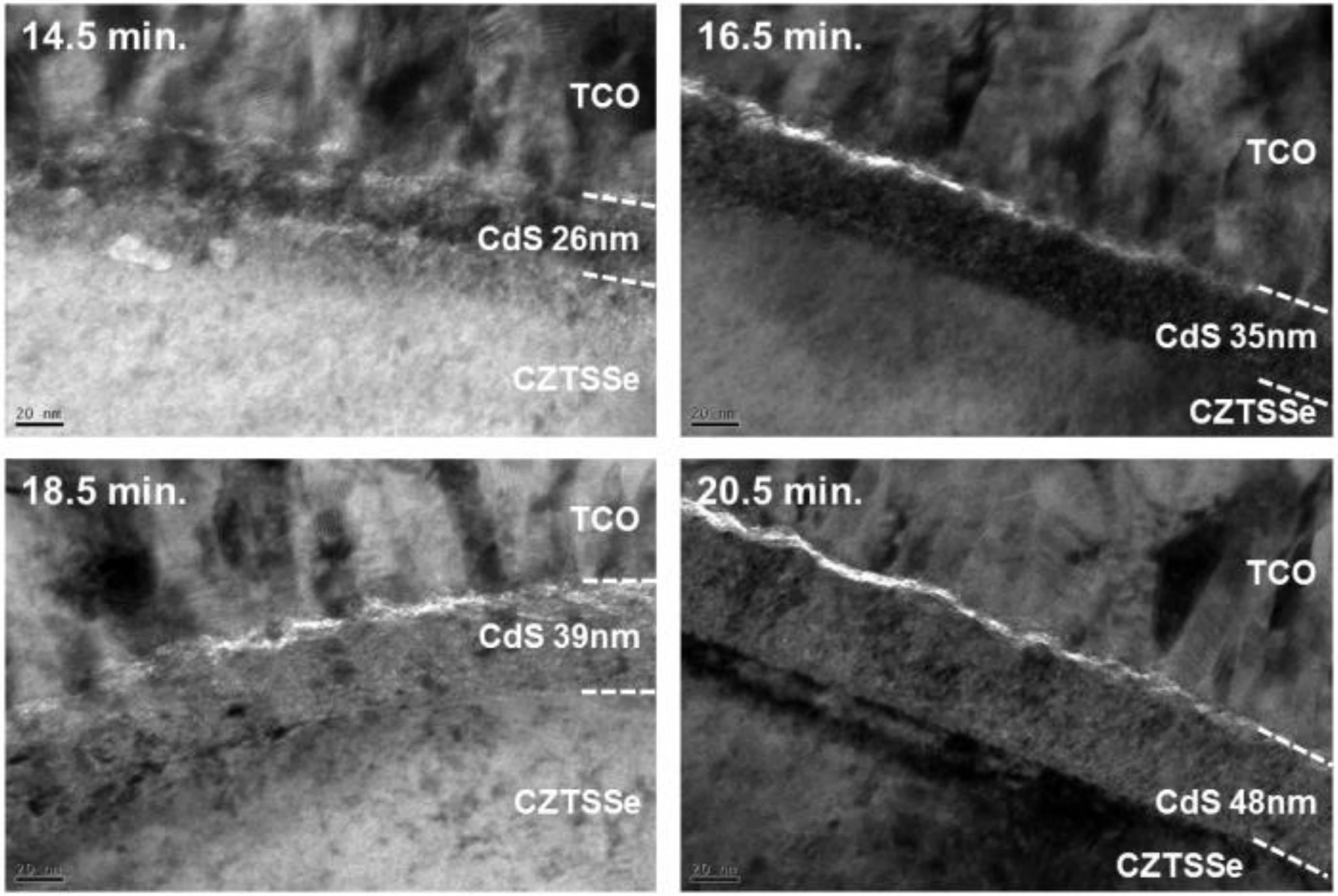
Varying deposition temperature and time

(60 ^oC & 80 ^oC)



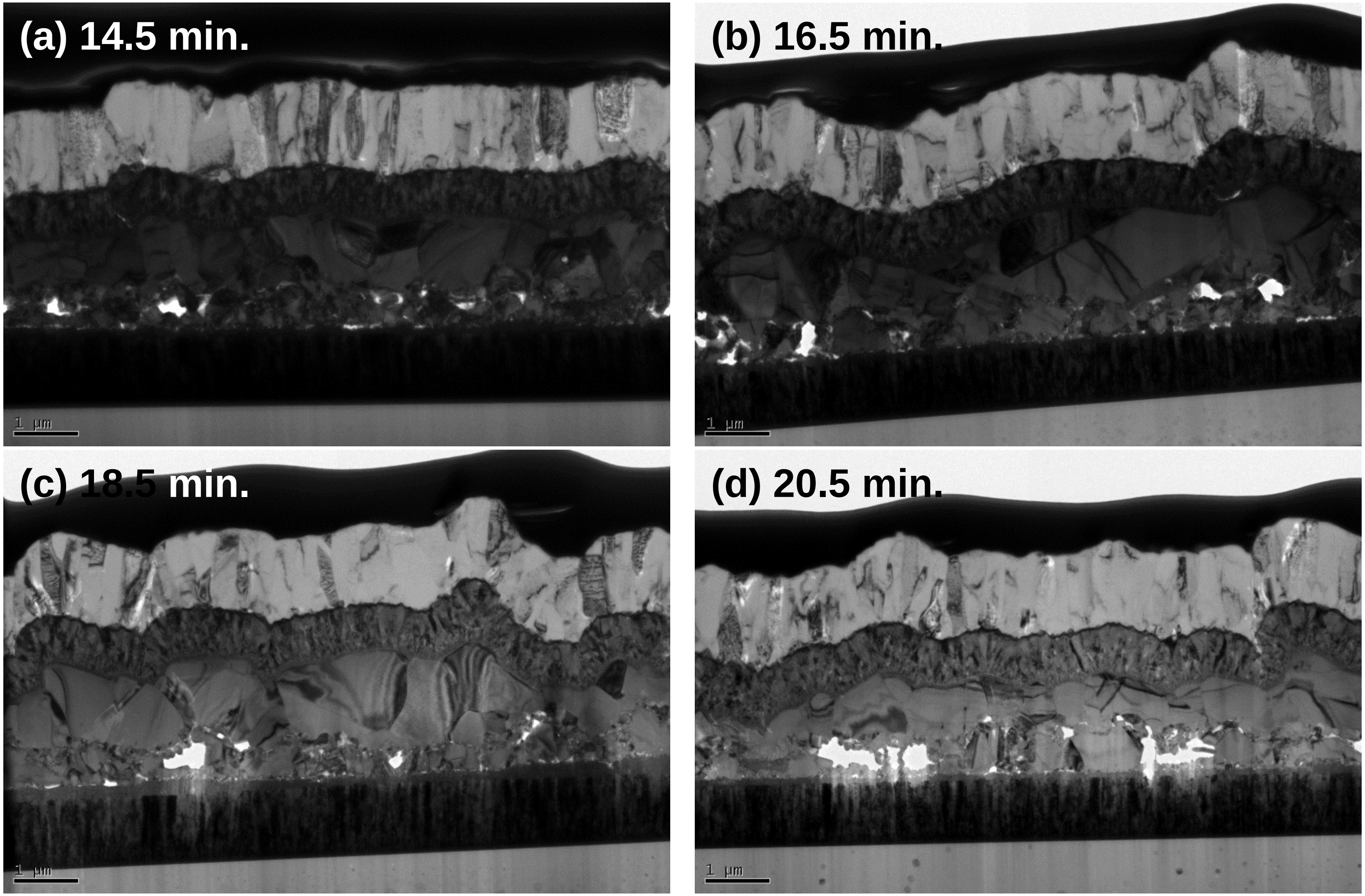
Fine Tuning on CdS Buffer Layers

Varying deposition time at T_{dep} = 60 ^oC

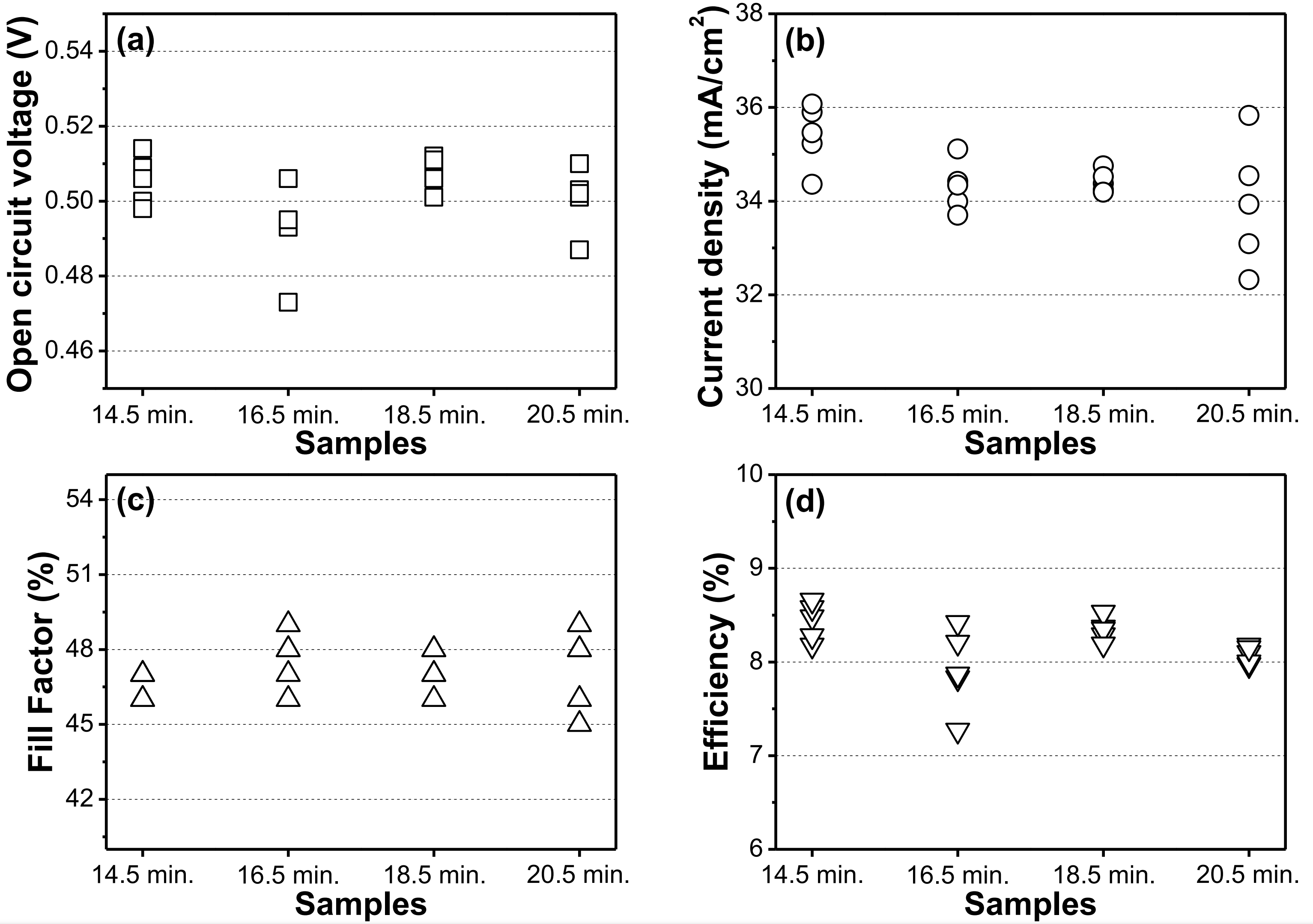


Optimization of CdS deposition time

Solar cell TEM image

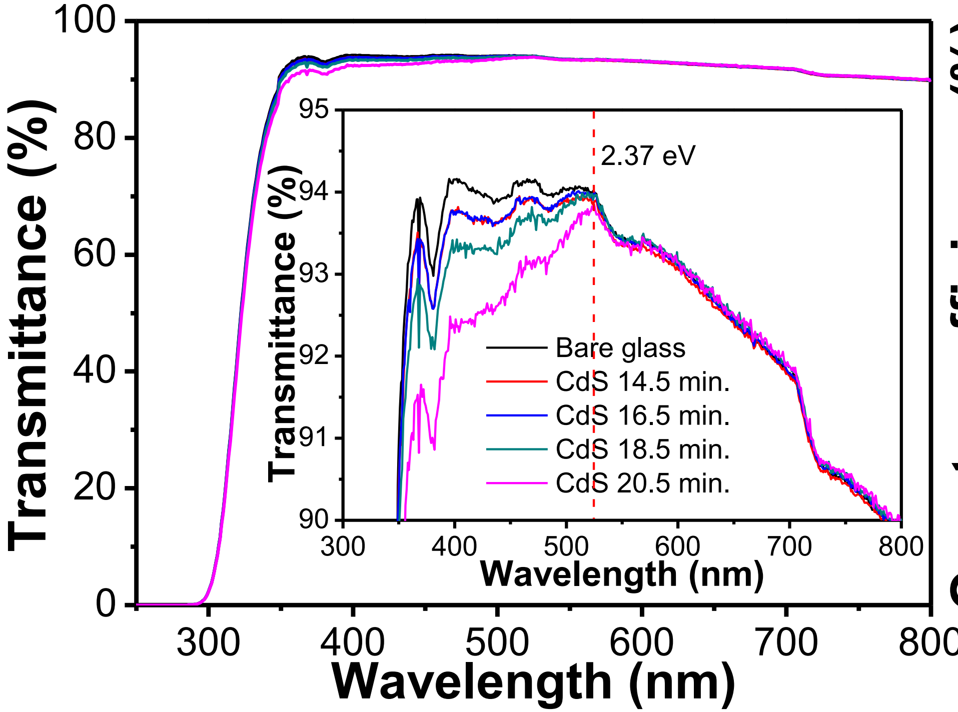


Solar cell efficiency

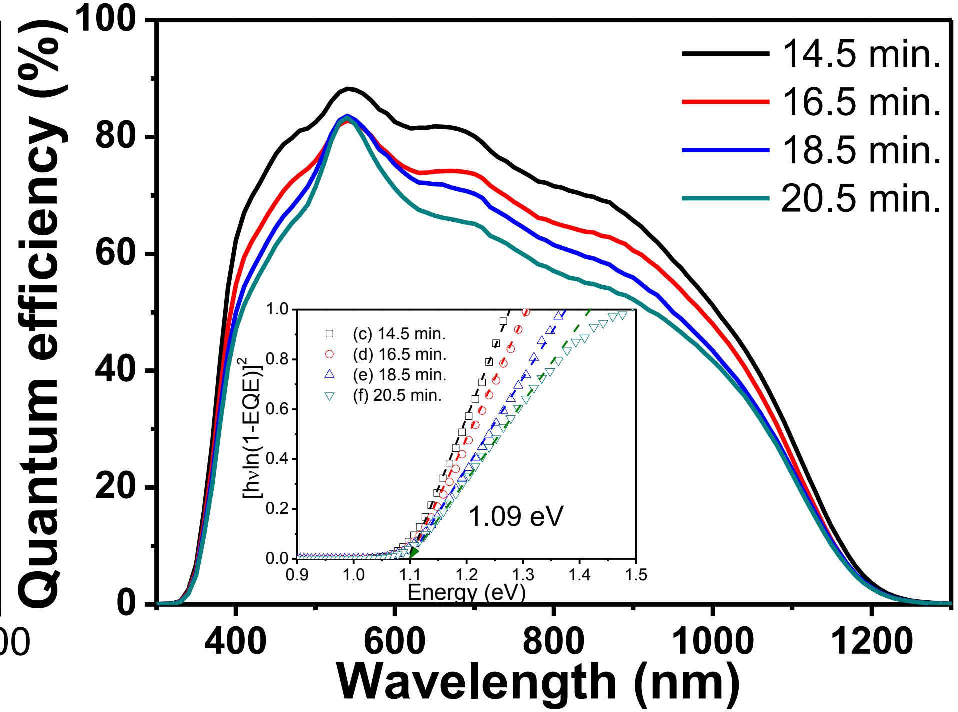


Fine Tuning on CdS Buffer Layers

- Optical transmittance spectra

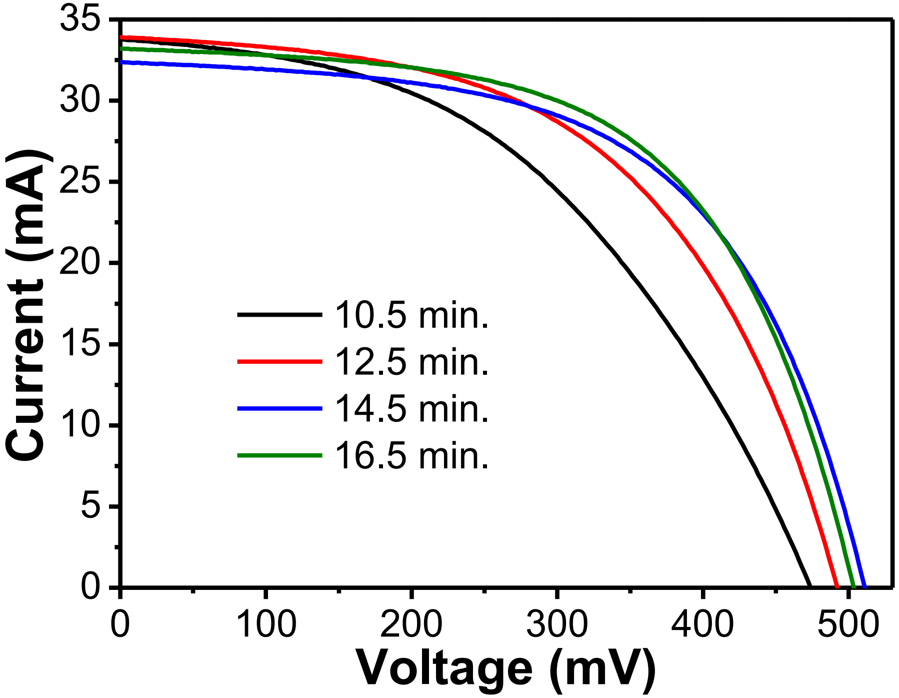


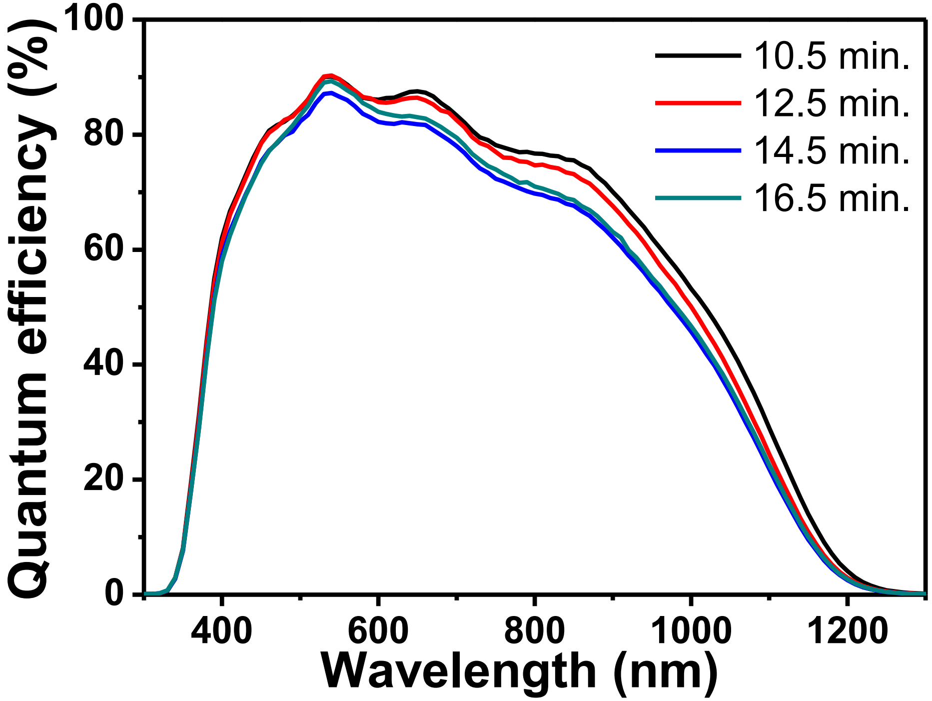
- Quantum efficiency



Fine Tuning on CdS Buffer Layers

Varying deposition time at T_{dep} = 60 °C

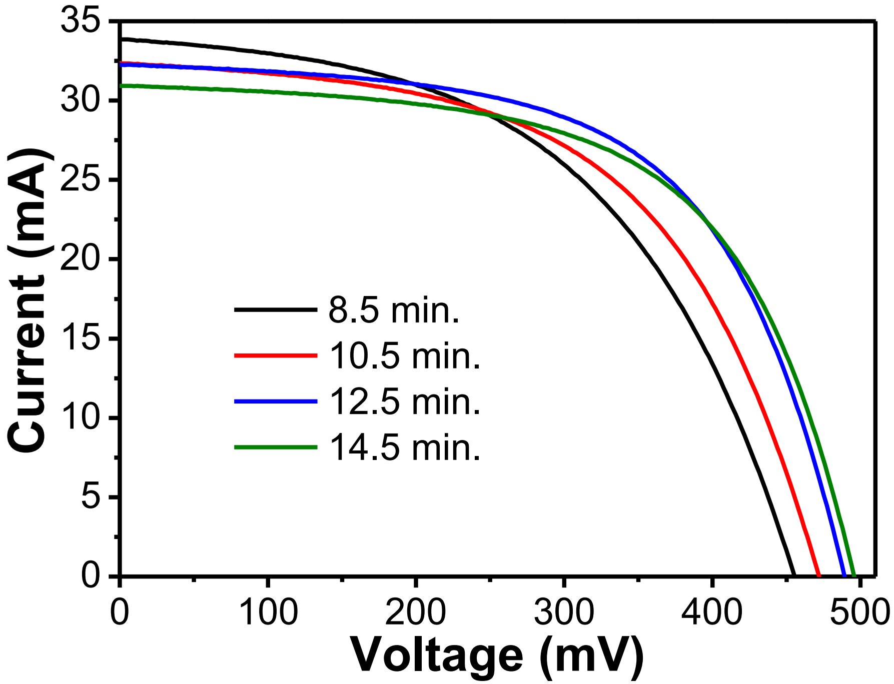


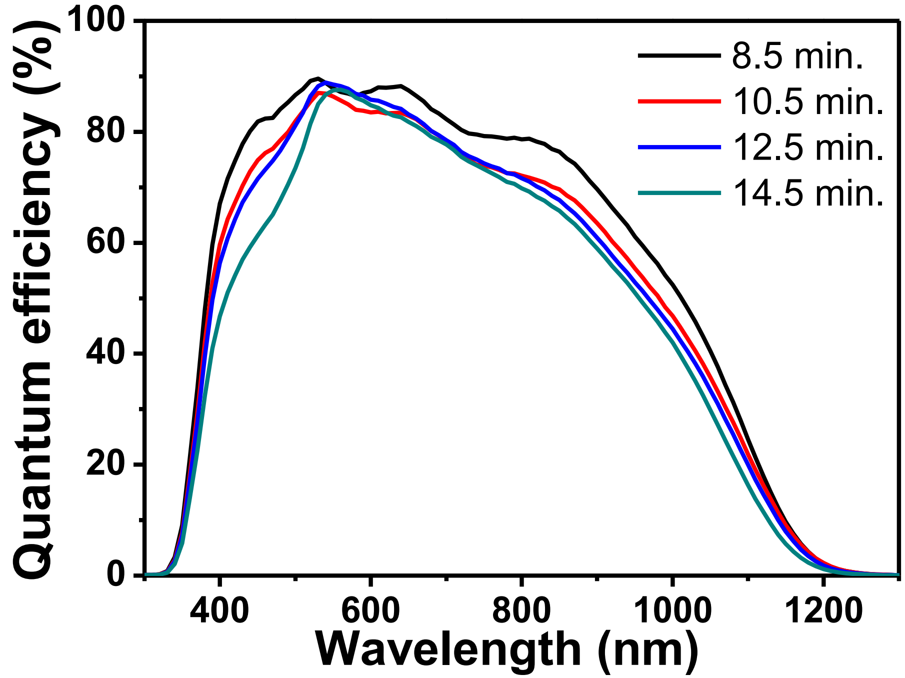


Deposition time	V_{oc} (V)	I_{sc} (mA)	J_{sc} mA/cm^2)	FF (%)	η(%)	R_s (ohm)	R_{sh} (ohm)
MG658-1 (10.5 min.)	0.473	10.13	33.78	0.45	7.34	15.64	500.00
MG659-1 (12.5 min.)	0.492	10.17	33.91	0.53	8.87	9.94	2000.00
MG660-1 (14.5 min.)	0.510	9.71	32.37	0.57	9.47	9.40	666.66
MG661-1 (16.5 min.)	0.503	9.95	33.19	0.58	9.70	8.93	-

Fine Tuning on CdS Buffer Layers

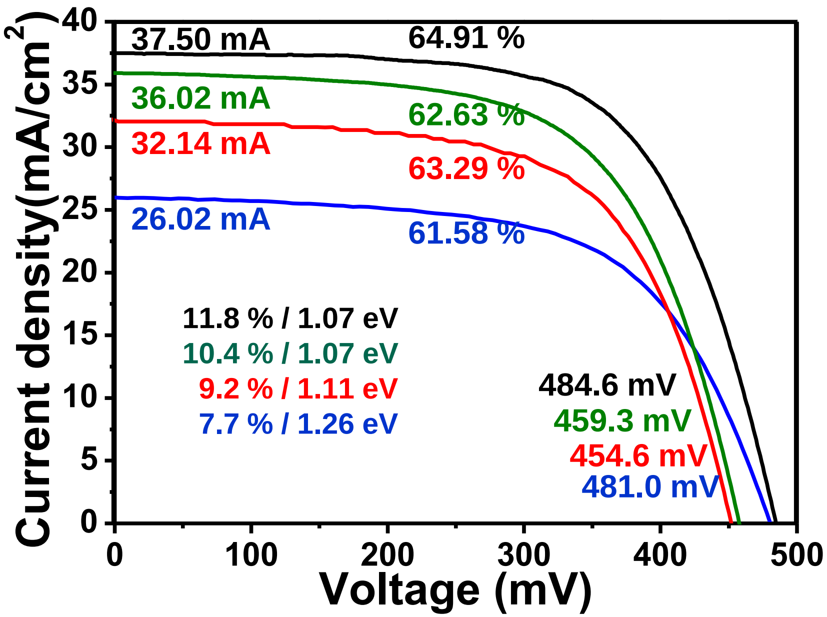
Varying deposition time at T_{dep} = 80 °C

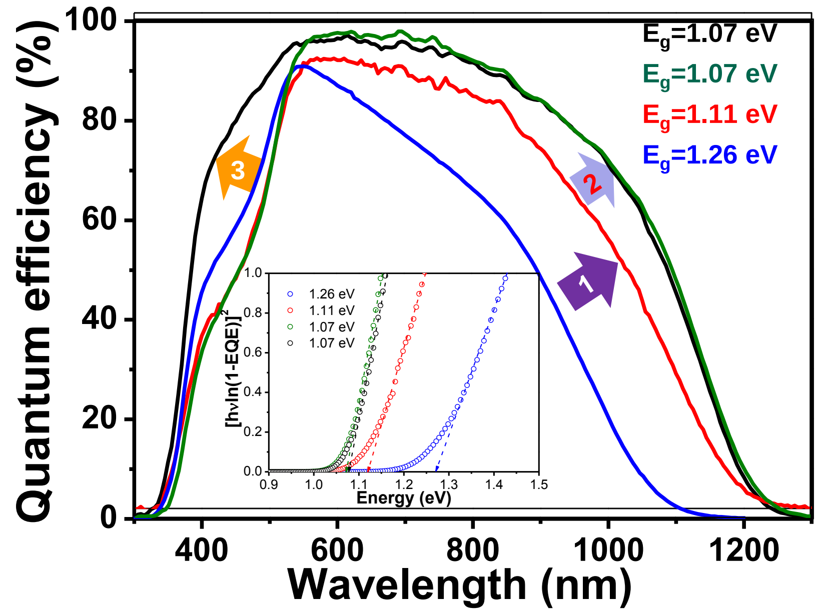




Deposition time	V_{oc} (V)	I_{sc} (mA)	J_{sc} (mA/cm²)	FF (%)	η(%)	R_s (ohm)	R_{sh} (ohm)
MG654-1 (8.5 min.)	0.455	10.16	33.86	0.50	7.79	11.35	666.66
MG655-1 (10.5 min.)	0.472	9.70	32.35	0.54	8.33	10.52	1000.00
MG656-1 (12.5 min.)	0.489	9.68	32.27	0.58	9.30	8.49	200.00
MG657-1 (14.5 min.)	0.495	9.27	30.91	0.59	9.12	8.37	2000.00

Comparison of J-V & EQE Results

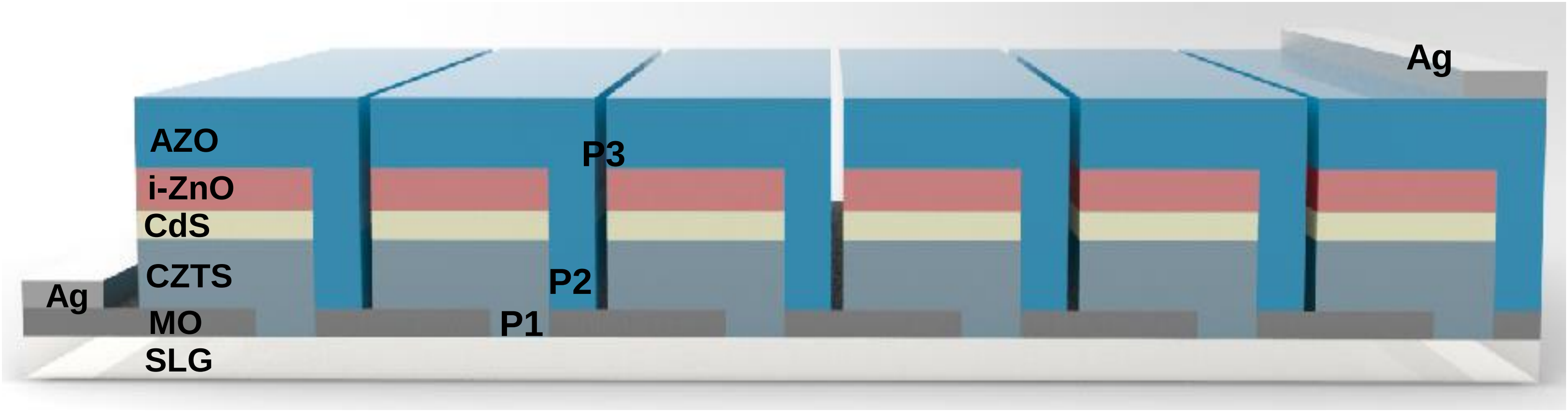




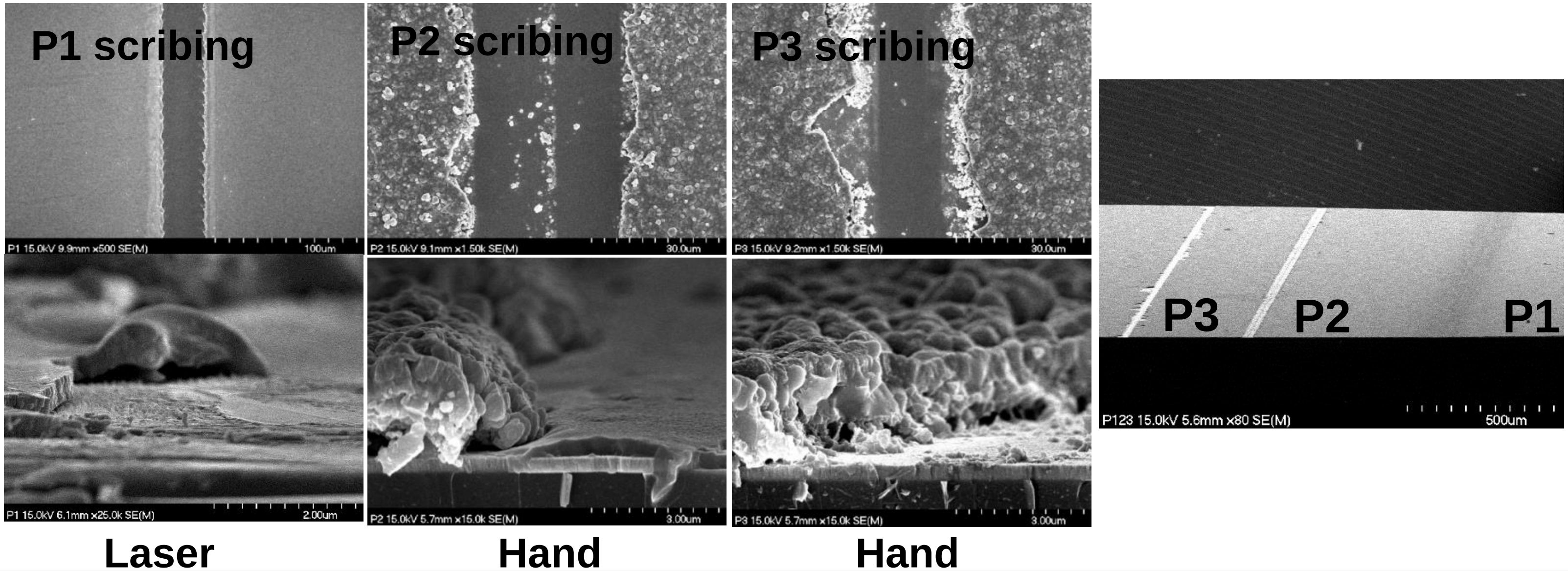
1. Band gap control (S/Se ratio)
2. Partial pressure control
3. Fine tuning on a CdS buffer layer

Fabrication of a CZTSSe Submodule

Cross-sectional schematic of a submodule

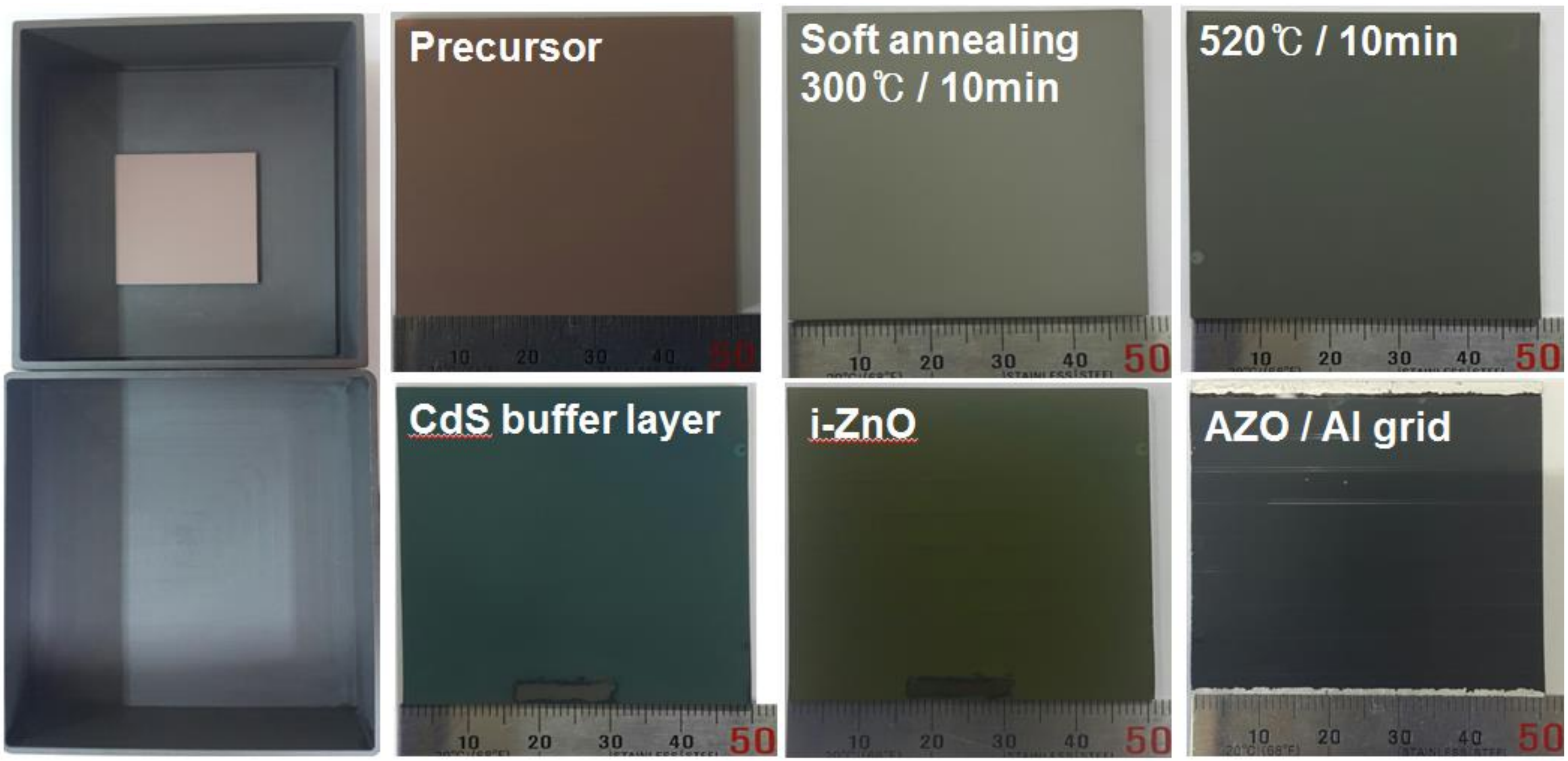


P1 : Mo, P2 : CZTS absorber, CdS and i-ZnO layers, P3 : AZO



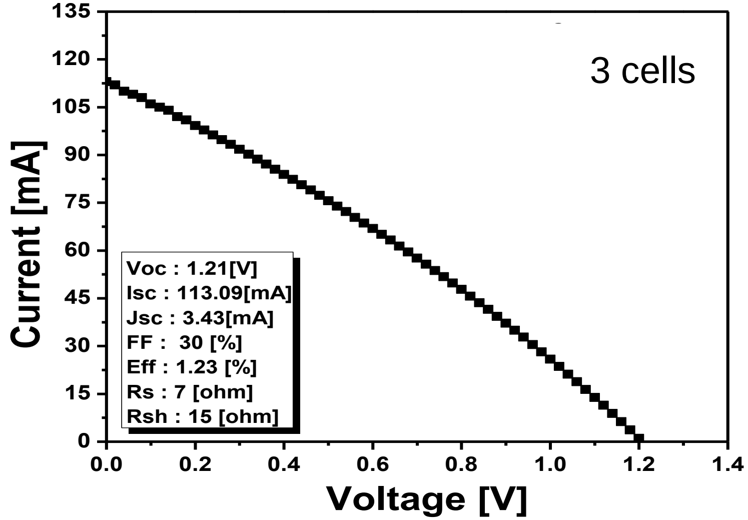
Fabrication of a CZTSSe Submodule

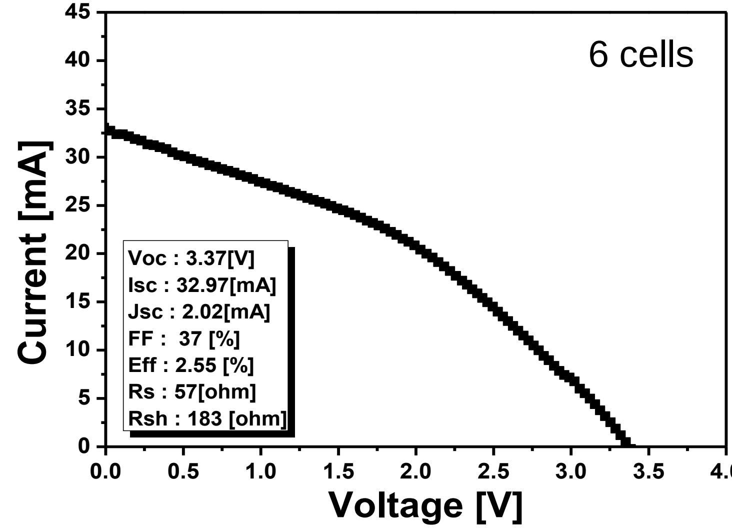
Sample size: 5 X 5 cm²

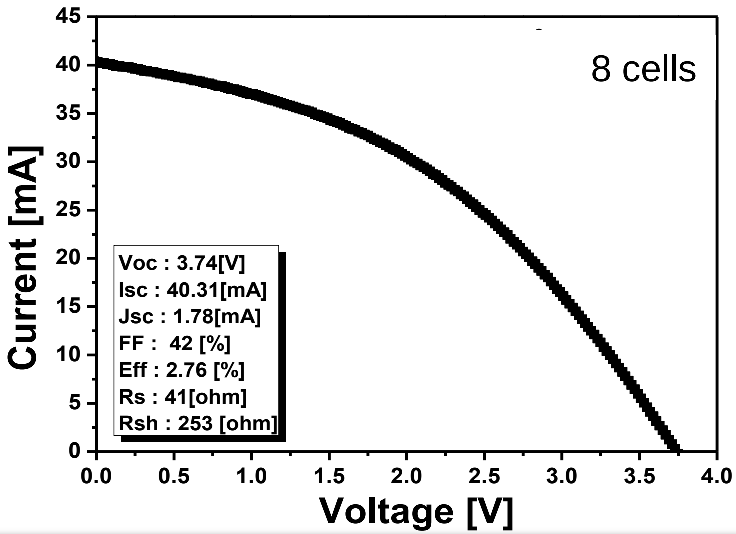


Fabrication of a CZTSSe Submodule

V_{oc} & I_{sc} could be controlled by changing module structure







# of cell	V_{oc} (V)	I_{sc} (mA)	J_{sc} (mA/cm^2)	FF (%)	η (%)
3	1.21	113.09	3.43	30	1.23
6	3.37	32.97	2.02	37	2.55
8	3.74	40.31	1.78	42	2.76

Size of a submodule is ~25 cm^2

Operation of a CZTSSe Submodule

Size of a submodule is 25 cm^2 (5X5 cm^2)

Outline

Part 1

Photovoltaic Overview

Part 2

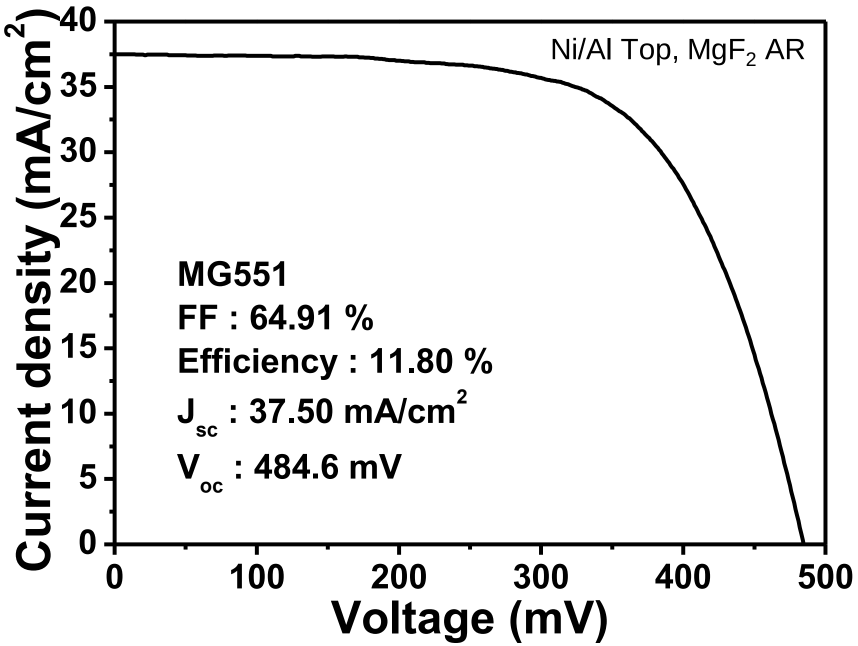
Our Results on CZTSSe TFSCs

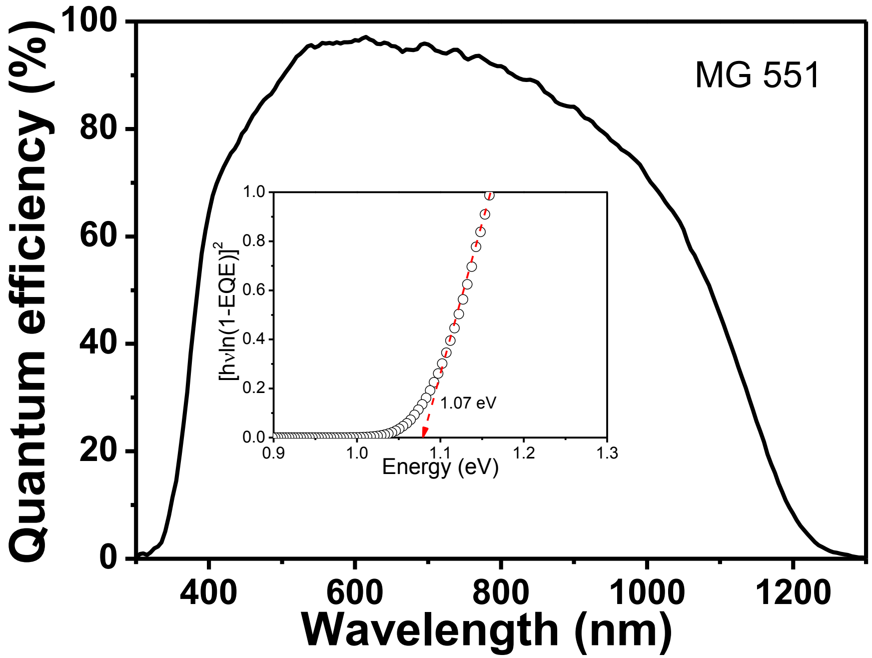
Part 3

Technical Issues

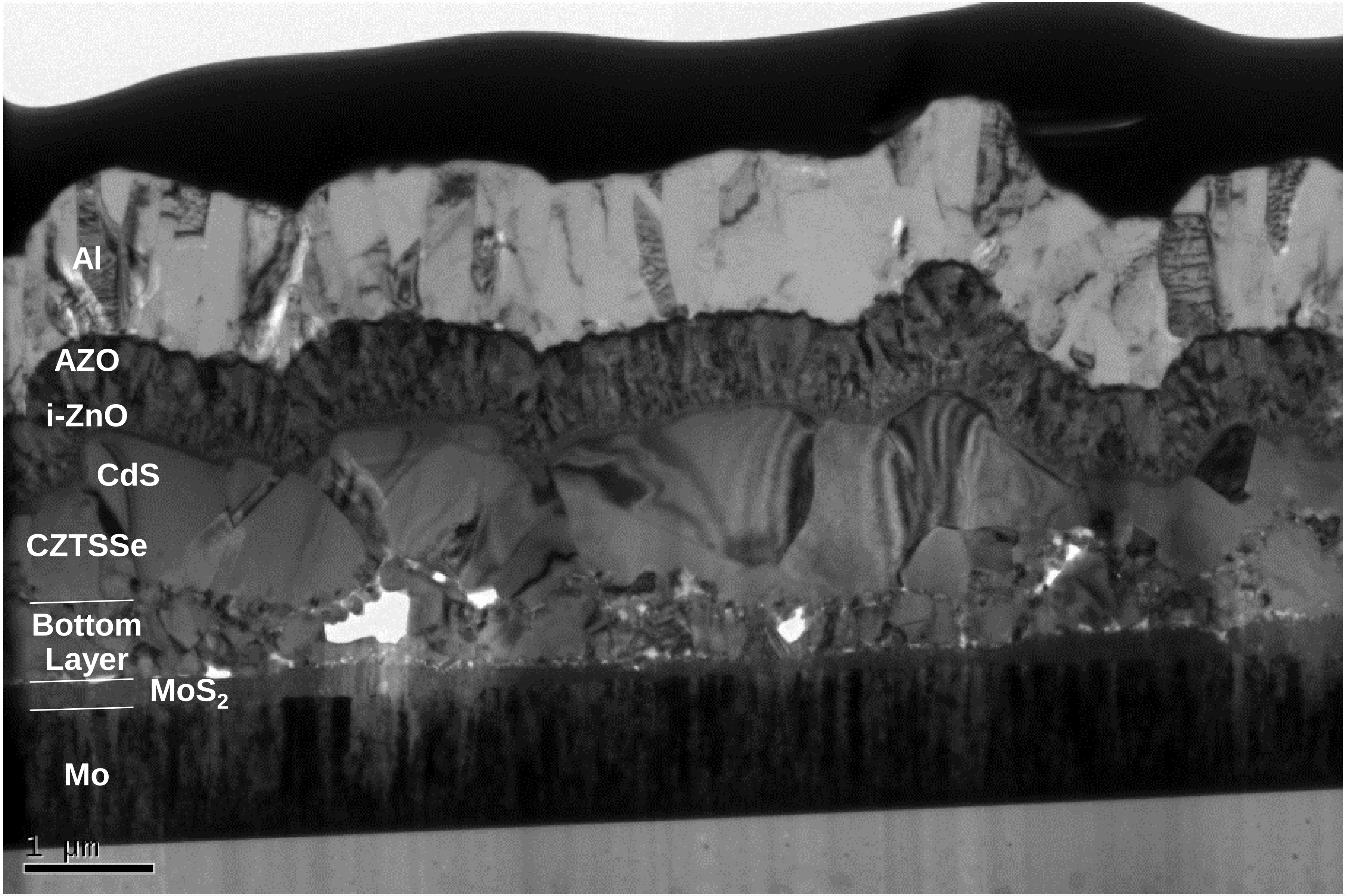
Fabrication of solar cell by sputtering

Best efficiency result

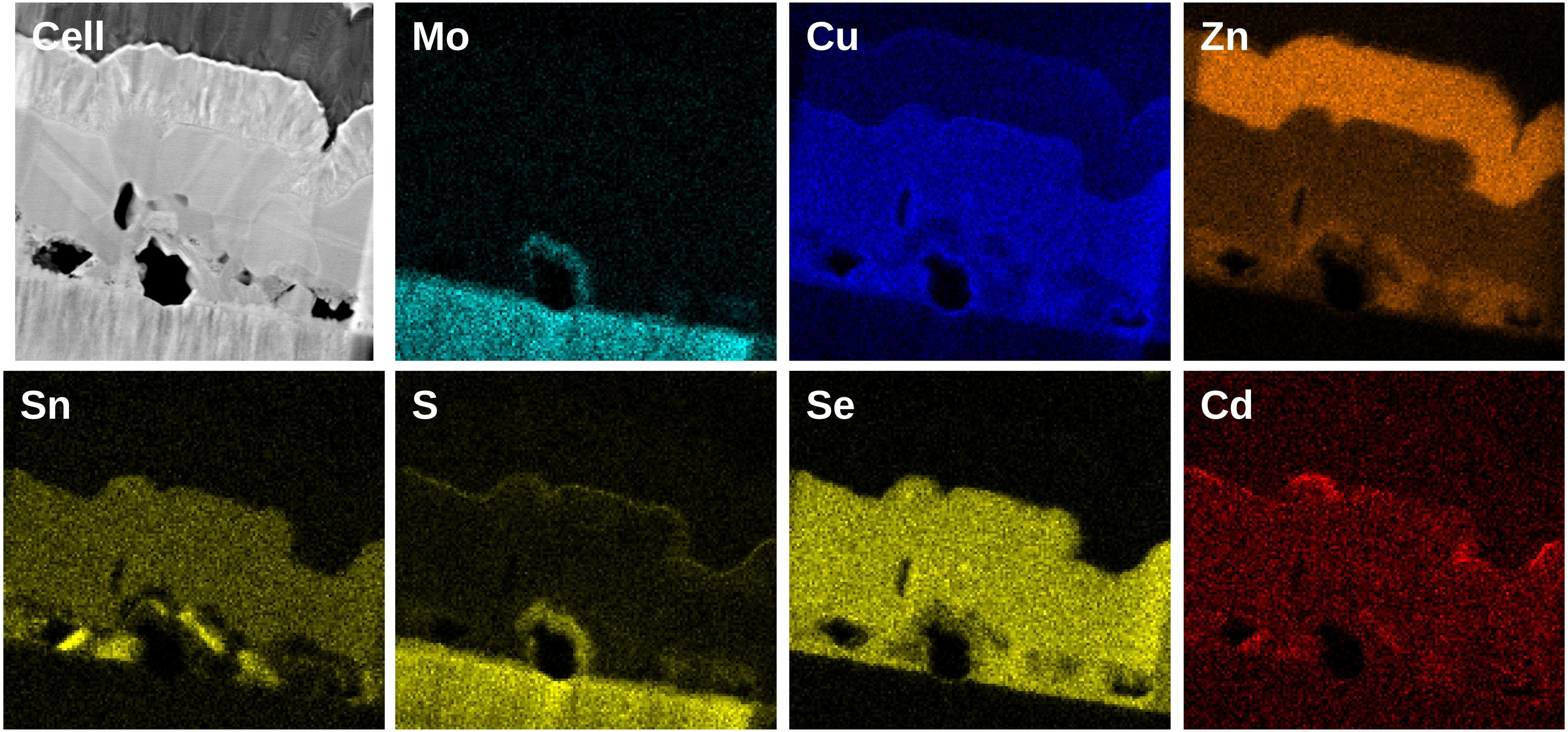




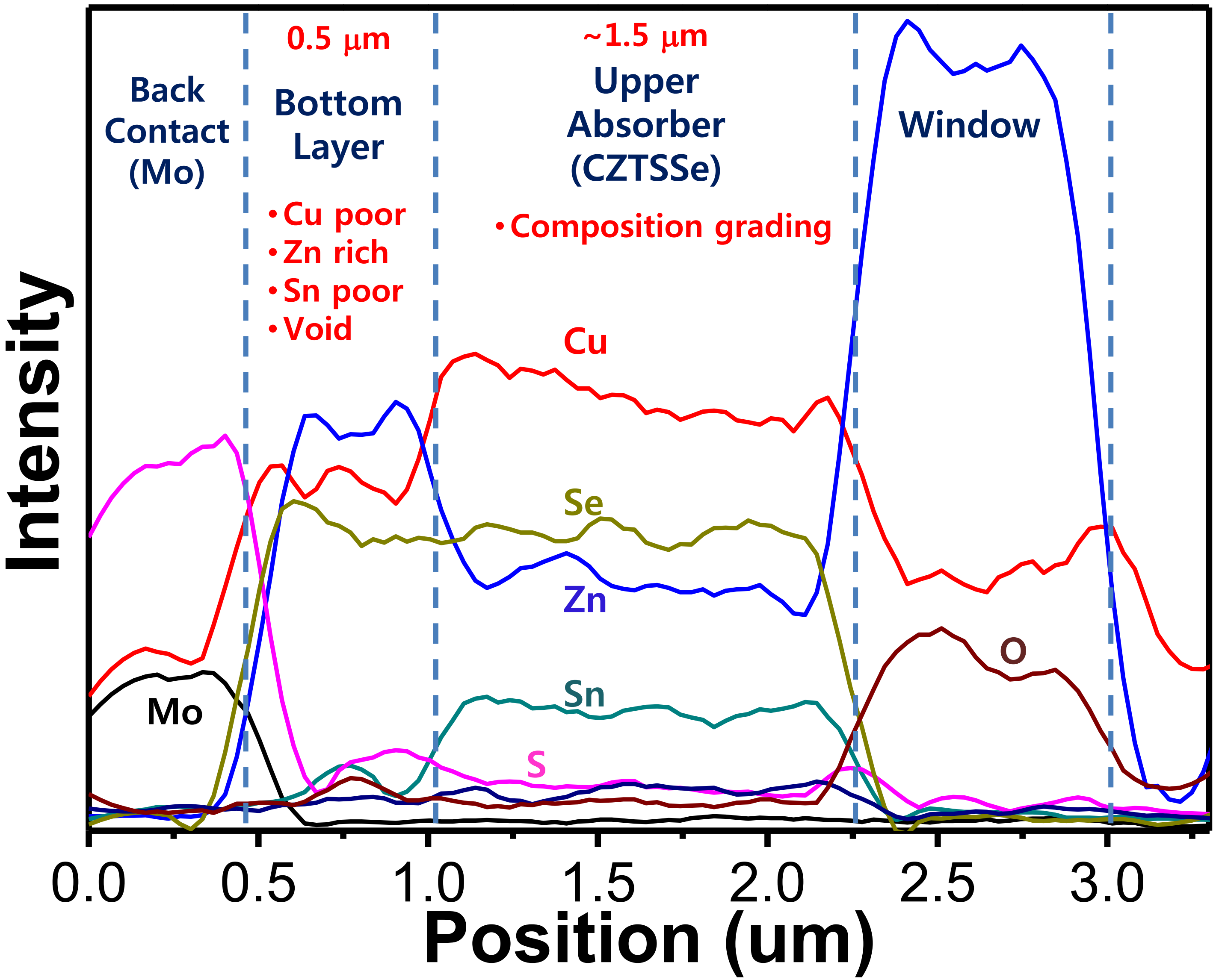
Cross-sectional BF-TEM image



STEM-HAADF Elemental Mapping Result

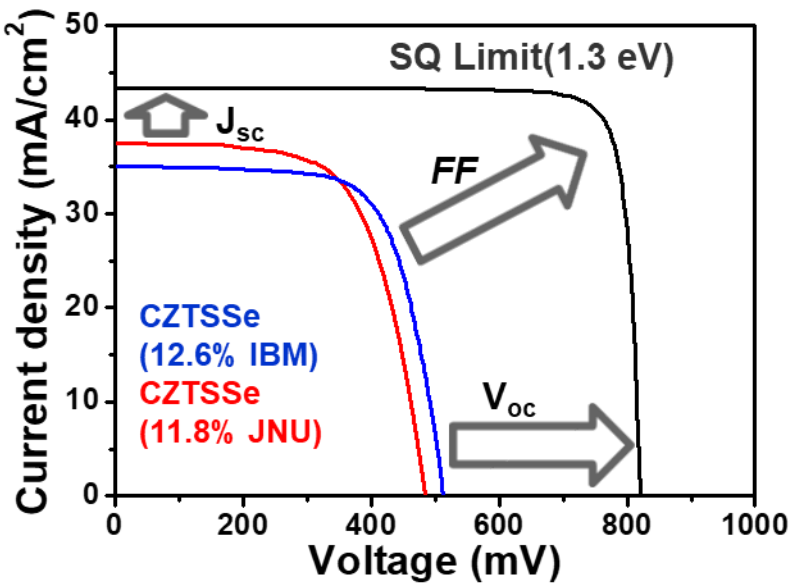


STEM EDS Line Scan Data



Technical Issues to Improve Cell Efficiency

IV characteristics for CZTSSe TFSCs



	SQ Limit	IBM	JNU	JNU/ SQ (%)
V_{oc} (mV)	820	513	485	59.0
J_{sc} (mA/cm²)	43.4	35.2	37.5	86.4
FF	86.0	69.8	64.9	75.4
η (%)	33.7	12.6	11.8	35.0

V_{oc}

Minimizing bulk recombination
- Cation disorders
- Grain boundaries

Minimizing interfacial recombination
- Absorber/Buffer
- Absorber/Mo interface

J_{sc}

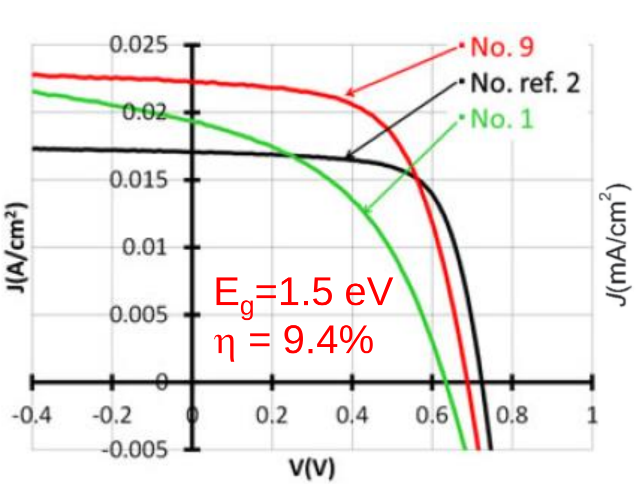
Minimizing photon loss
- Wide band-gap TCO
- Optimization of grid structure
- Cd-free Zn(O,S) buffer layer
- Thin buffer
- Anti-reflection coating

FF

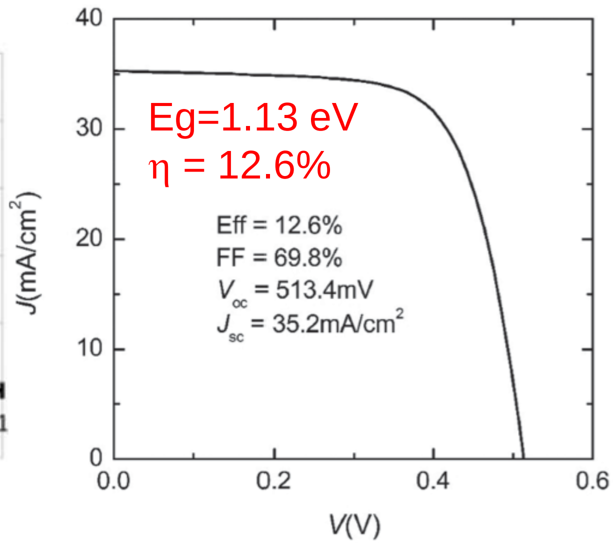
Optimization of R_s & R_{sh}
- Improving junction quality
- Carbon layer (Mo/CZTS)
- Diffusion barrier (Mo/CZTS)
- Defect control

V_{oc} deficit in CZTSSe devices

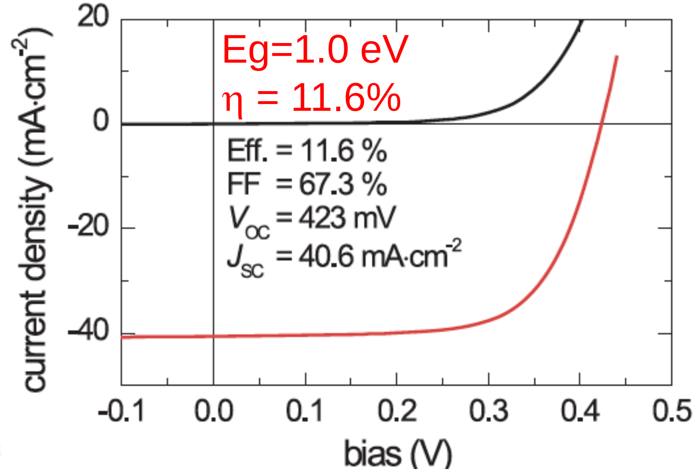
Pure sulfide	Mixed sulfo-selenide	Pure selenide



Tajima et al. Prog PV (2016), doi: 10.1002/pip.2837



Wang et al. Adv. Energy Mater., doi: 10.1002/aenm.201301465



Lee et al. Adv. Energy Mater., 1401372 (2014)

- $V_{oc}^{def} = E_g/q - V_{oc}$

Materials	CZTS	CZTSSe	CZTSe
V_{oc}^{def}	750~800	~620	~580

- V_{oc} deficit is the most performance-limiting factor

This slide is modified using a presentation material of Prof. B.H. Shin at KAIST

V_{oc} deficit in various PV technologies

Material	Eff. (%)	J_{sc} (mA/cm^2)	FF (%)	V_{oc} (mV)	E_g (eV)	V_{oc} deficit (mV)
Crystalline Si	25.6	41.8	82.7	740	1.1	360
GaAs	28.8	29.68	86.5	1122	1.42	298
CIGSe	22.6	37.8	80.6	741	1.1	359
CdTe	22.1	31.69	78.5	887	1.5	613
CdTe	13.6	21.7	61.7	1017	1.5	483
$(FA,MA)Pb(I,Br)_3$	22.1	24.97	80.3	1105	1.49	385

Material	Eff. (%)	J_{sc} (mA/cm^2)	FF (%)	V_{oc} (mV)	V_{oc} deficit (mV)	Year	Description
CZTSSe	12.6	35.2	69.8	513	617	2013	IBM, hydrazine
CZTS	8.4	19.5	65.8	661	789	2013	IBM, thermal co-evaporation
CZTSe	11.6	40.6	67.3	423	578	2014	IBM, thermal co-evaporation
CZTSe	8.65	30.89	61.3	457	543	2017	KAIST, co-evaporation*
CZTSSe	11.2	36.5	63.8	479	570	2015	EMPA, spin-coating
CZTSe	9.6	-	-	489	560	2016	IREC, sputtering
CZTSSe	10.3	31.6	64.6	505	525	2017	DGIST, Sputtering
CZTSSe	11.8	37.5	64.9	485	585	2016	JNU, Sputtering

This slide is modified version of Prof. B.H. Shins's at KAIST

*J. Kim, et al., PIP, 2017; 25:308–317

Two major origins for V_{oc} deficit

Interface

Absorber/Buffer

Absorber/Mo back contact

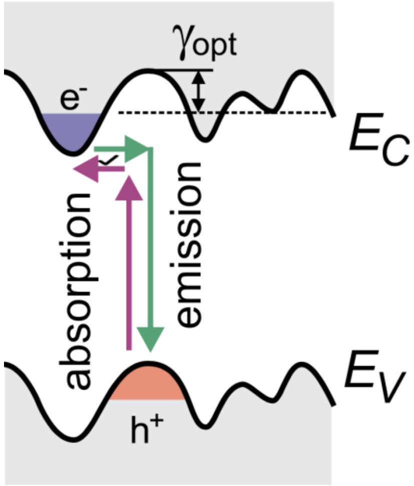
Defects

Bulk Defects: Cu_{Zn}^{+}, V_{Cu}^{+}, Zn_{Cu}^{-}, Sn_{Zn}^{2-}

Grain boundary

Secondary phases

Electrostatic Potential Fluctuation



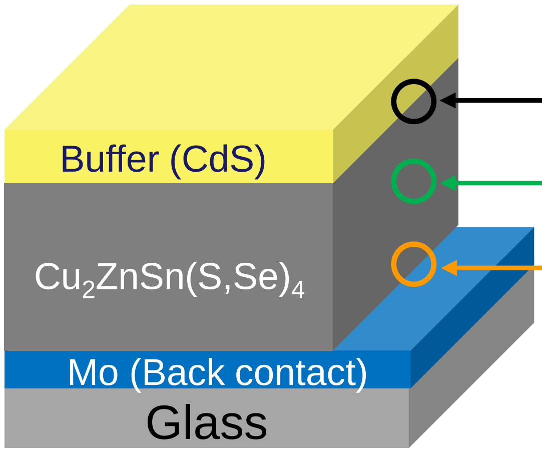
deep trap and band tail states

T. Gokmen et. al., APL103, 103506 (2013)

Various approaches to improve V_{oc} deficit

Origins of V_{oc} deficit: GBs, Interfaces, Defects

- Results in Low MCCLT, electrostatic potential fluctuations, and tail states
- Can be Minimized by Passivation, Doping, Post Annealing Treatment

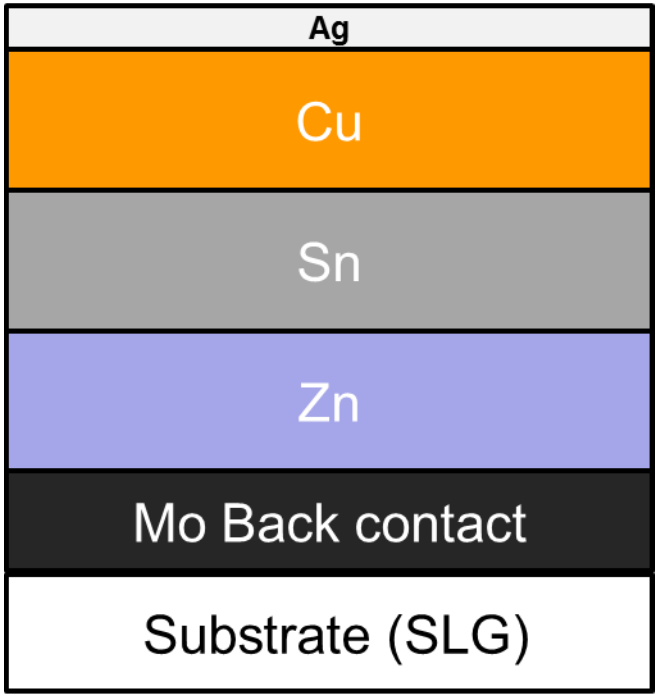


- ❑ Absorber/Buffer Interface
  - Alkaline (Na, K): surface passivation
  - Double emitter: increasing carrier density
  - Passivation with a dielectric layer
- ❑ Absorber Layer
  - Double grading: Band gap grading
  - Post air annealing: GB passivation
  - Doping: minimizing cation disorder (Cu_{Zn}^{-}, Zn_{Cu}^{+})
  - Doping: Depletion Region Width Control
- ❑ Absorber/Back-Contact Interface
  - Passivation with a dielectric layer
  - Optimizing sulfo-selenization process: (reducing secondary phases)

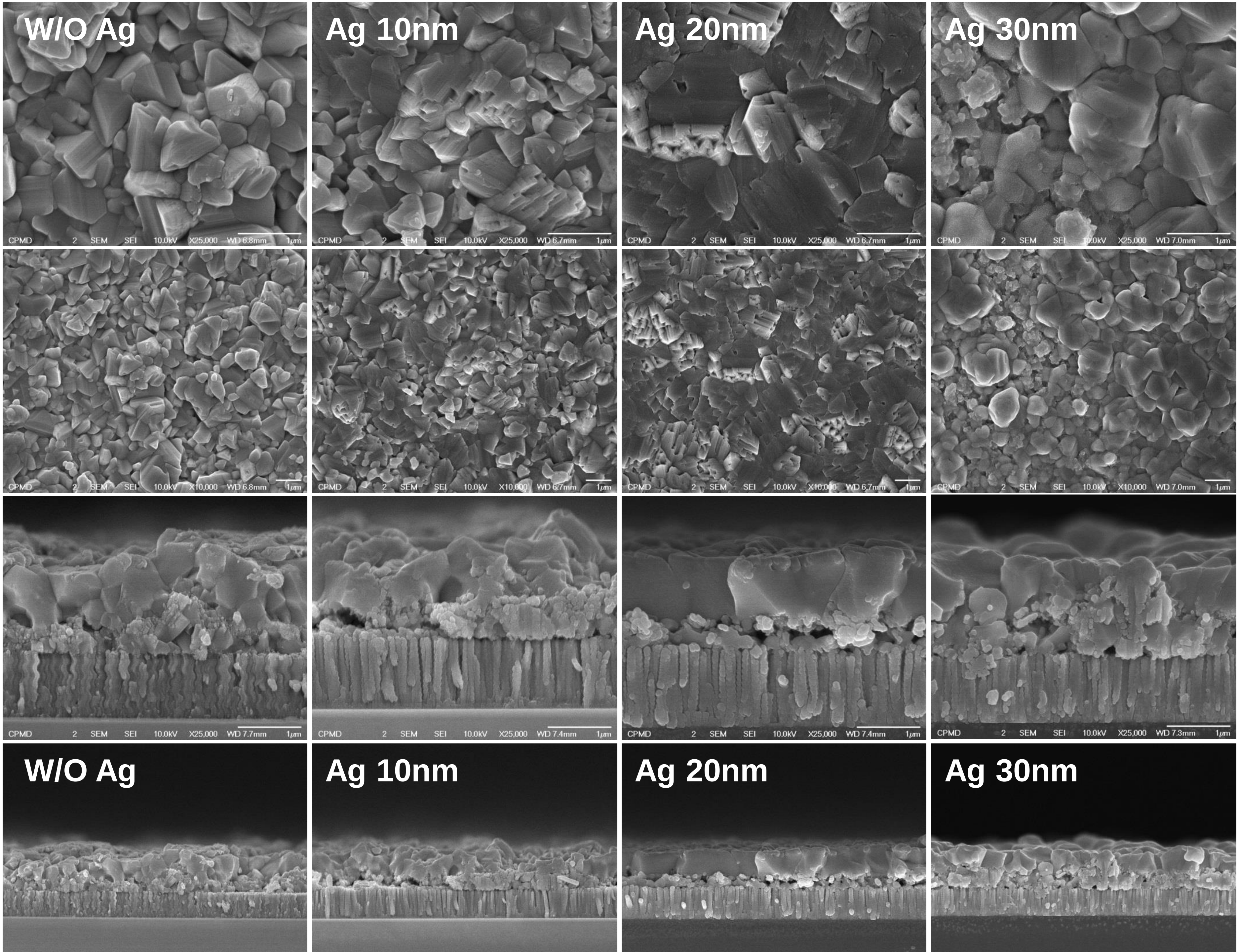
Ag doping Results

- Increasing grain size
- Reducing cation disorder (Cu_{Zn}^{+})

ACS Appl. Mater. Interfaces 2017, 9, 21243−21250
Sixin Wu
Henan University

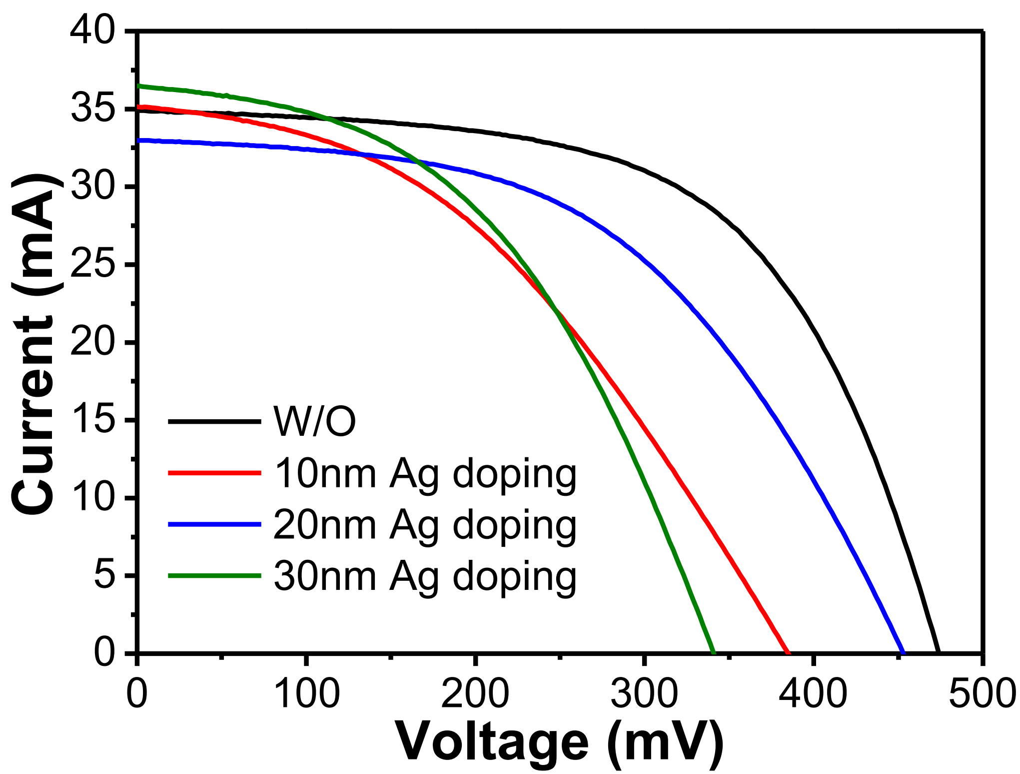


Deposition of Ag layer on precursors using e-beam evaporation (10, 20, 30, 40 nm)



W/O Ag
Ag 10nm
Ag 20nm
Ag 30nm
CPMD 2 SEM SEI 10.0kV X25,000 WD 6.8mm 1μm
CPMD 2 SEM SEI 10.0kV X25,000 WD 6.7mm 1μm
CPMD 2 SEM SEI 10.0kV X25,000 WD 6.7mm 1μm
CPMD 2 SEM SEI 10.0kV X25,000 WD 7.0mm 1μm
CPMD 2 SEM SEI 10.0kV X10,000 WD 6.8mm 1μm
CPMD 2 SEM SEI 10.0kV X10,000 WD 6.7mm 1μm
CPMD 2 SEM SEI 10.0kV X10,000 WD 6.7mm 1μm
CPMD 2 SEM SEI 10.0kV X10,000 WD 7.0mm 1μm
CPMD 2 SEM SEI 10.0kV X25,000 WD 7.7mm 1μm
CPMD 2 SEM SEI 10.0kV X25,000 WD 7.4mm 1μm
CPMD 2 SEM SEI 10.0kV X25,000 WD 7.4mm 1μm
CPMD 2 SEM SEI 10.0kV X25,000 WD 7.3mm 1μm
W/O Ag
Ag 10nm
Ag 20nm
Ag 30nm

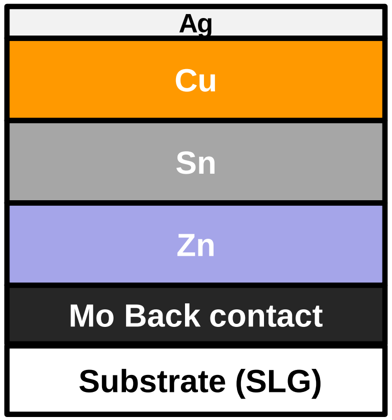
Ag doping Results



Deposition time	V_{oc} (V)	I_{sc} (mA)	J_{sc} (mA/cm^2)	FF (%)	η(%)	R_s (ohm)	R_{sh} (ohm)
MG651 (Without Ag)	0.474	10.46	34.89	0.58	9.71	8.82	1000.00
MG645 (Ag 10nm)	0.384	10.54	35.13	0.41	5.58	19.80	142.85
MG647 (Ag 20nm)	0.452	9.89	32.96	0.50	7.58	13.82	666.66
MG649 (Ag 30nm)	0.340	10.93	36.46	0.46	5.77	11.56	166.66

Ag doping Results

Need to change the amount of Cu



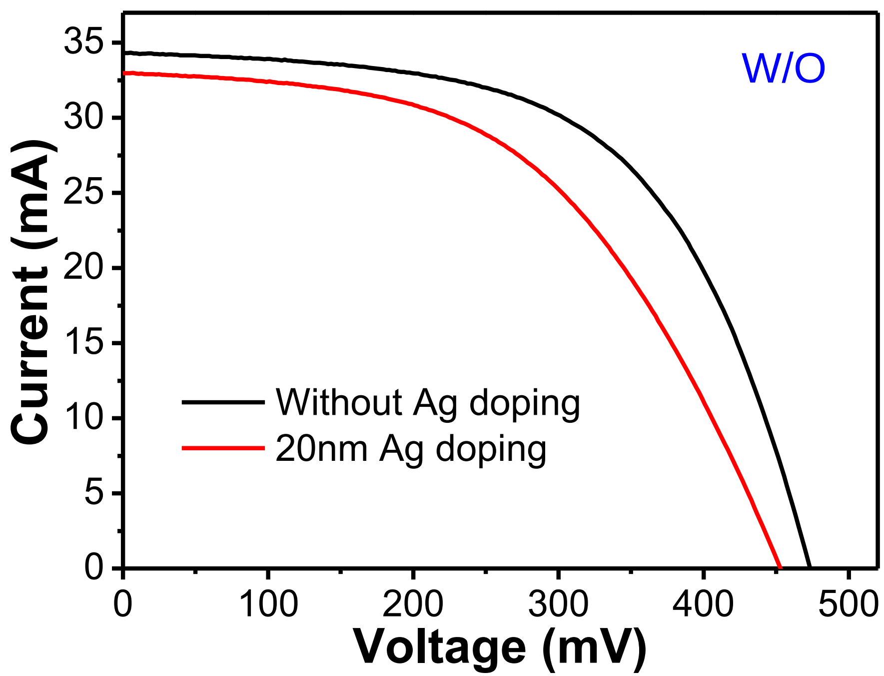
- ✓ Thickness of Ag : 20 nm

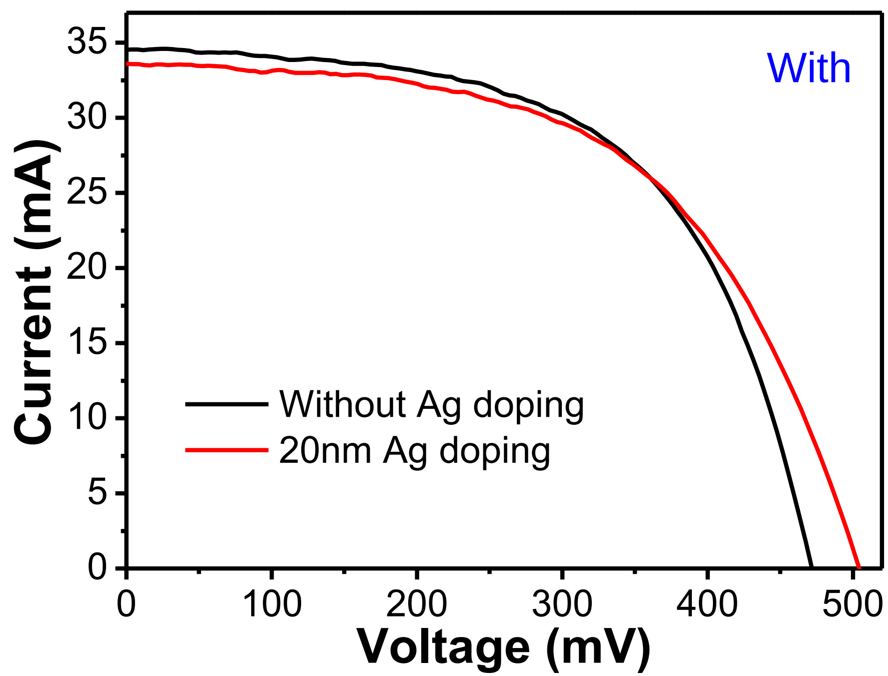
- ✓ Control of the Cu composition ratio

Sample Number	Gas flow	Process Power			Process pressure	Time (sec)		
	Ar	Zn	Sn	Cu		Zn	Sn	Cu
1								2812
2								2712
3	30sccm	30W	30W	30W	8mtorr	2006	2015	2612
4								2512
5								2412

Ag doping Results

Controlling the amount of Cu





Condition		V_{oc} (V)	I_{sc} (mA)	J_{sc} (mA/cm^2)	FF (%)	η(%)	R_s (ohm)	R_{sh} (ohm)
Standard	W/O	0.473	10.29	34.31	0.57	9.37	9.26	666.66
	Ag doping	0.452	9.89	32.96	0.50	7.58	13.82	666.66
Controlled	W/O	0.471	10.36	34.53	0.58	9.45	7.84	1333.33
	Ag doping	0.504	10.08	33.60	0.55	9.38	10.84	2000.00

Summary

11.8% CZTSSe thin film solar cells without additional treatment to minimize V_{oc} deficit could be fabricated successfully

NEXT STEP

- **Doping: minimizing bulk cation disorder**
- **Passivation: top and bottom interface of the absorber**
- **Band gap grading: minimizing recombination loss**
- **Harvesting: controlling the photon loss, carrier collection**

Fabrication of CZTSSe thin film solar cells with WORLD BEST efficiency !!

Photonic and Electronic Thin Film Laboratory - Windows Internet Explorer

http://pvsolar.chonnam.ac.kr/

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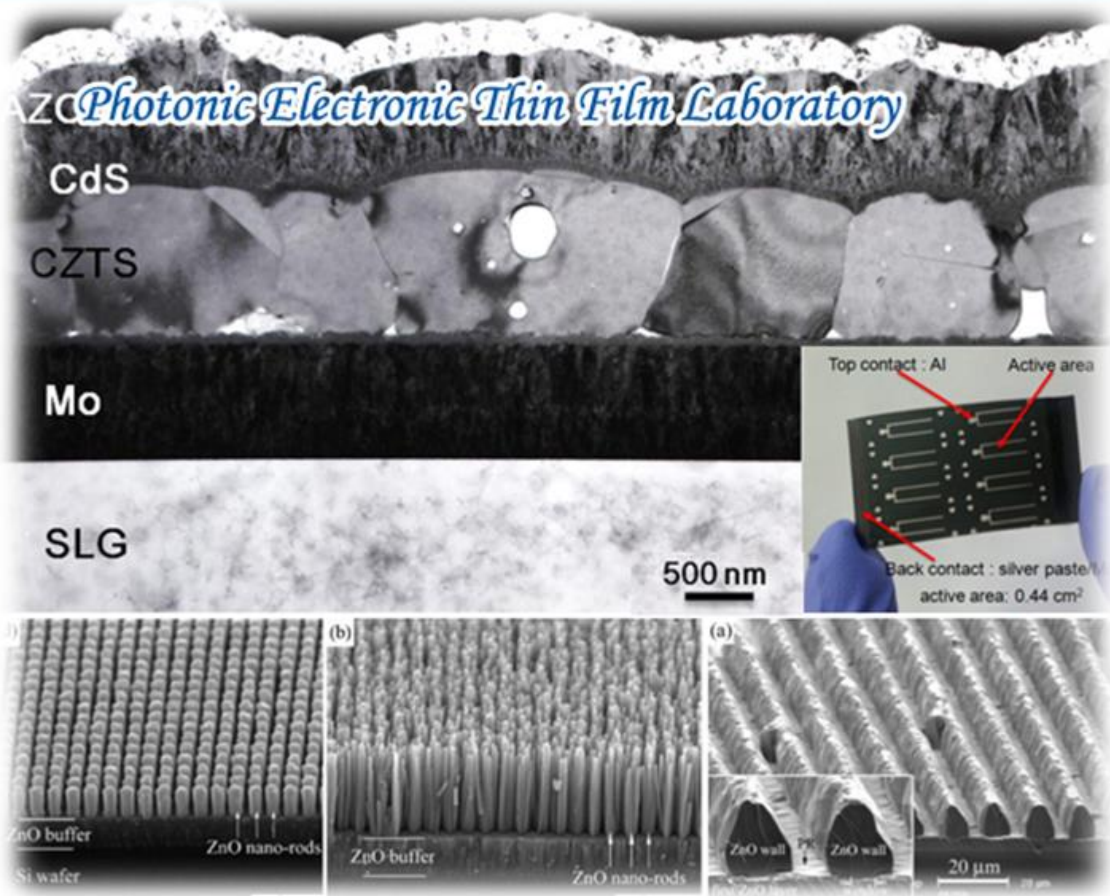
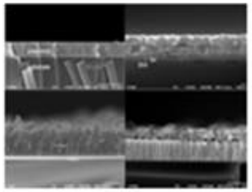


RESEARCH

CZTS Solor Cells



COMMUNITY +

(2016.7~2019.6)

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TEL : 82-62-530-1709 E-MAIL : jinhyeok@jnu.ac.kr

P&E Thin Film Lab.


Thank you

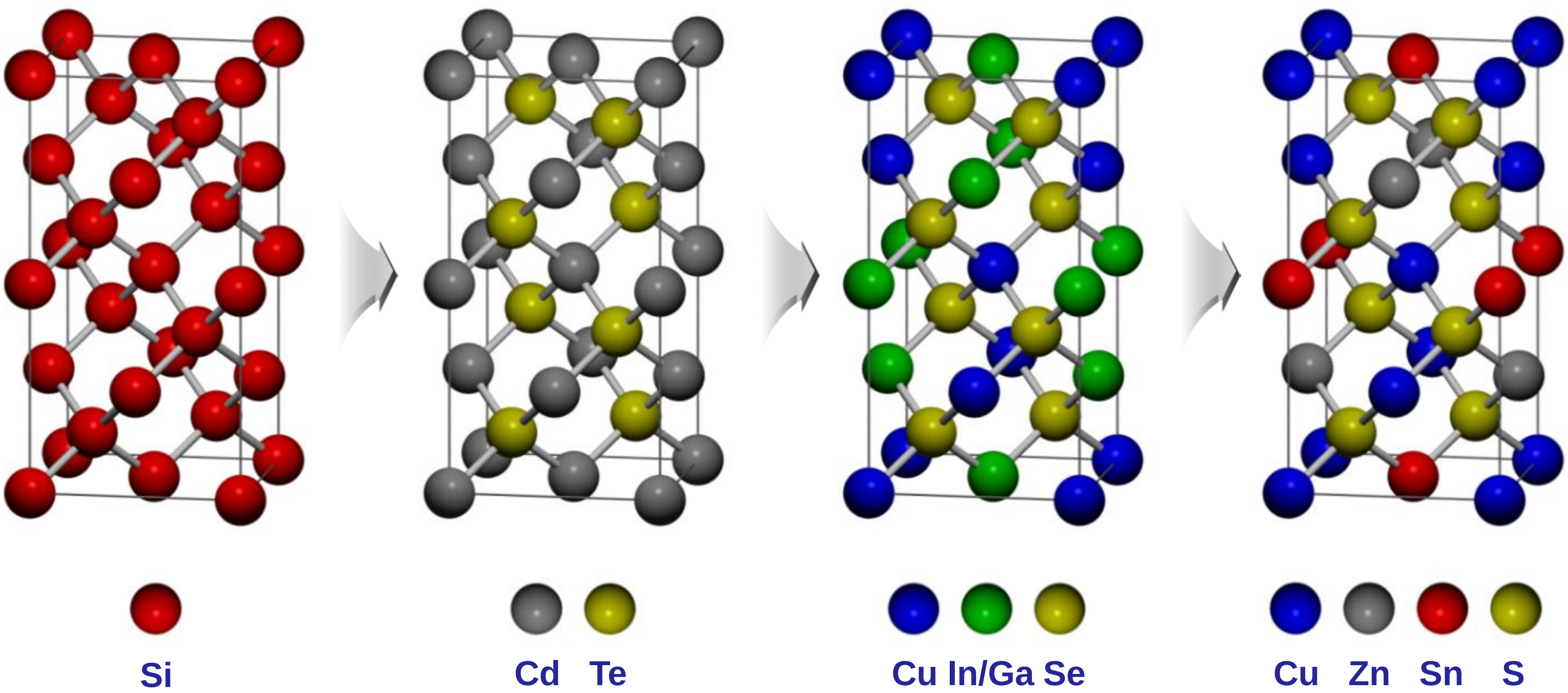
Why $Cu_2ZnSn(S,Se)_4$ (CZTSSe)?

Diamond Cubic
IV Silicon

Zincblende
II-VI CdTe
III-V GaAs

Chalcopyrite
I-III-VI_2 CIGSe

Kesterite
I-II-IV-VI_4 CZTS

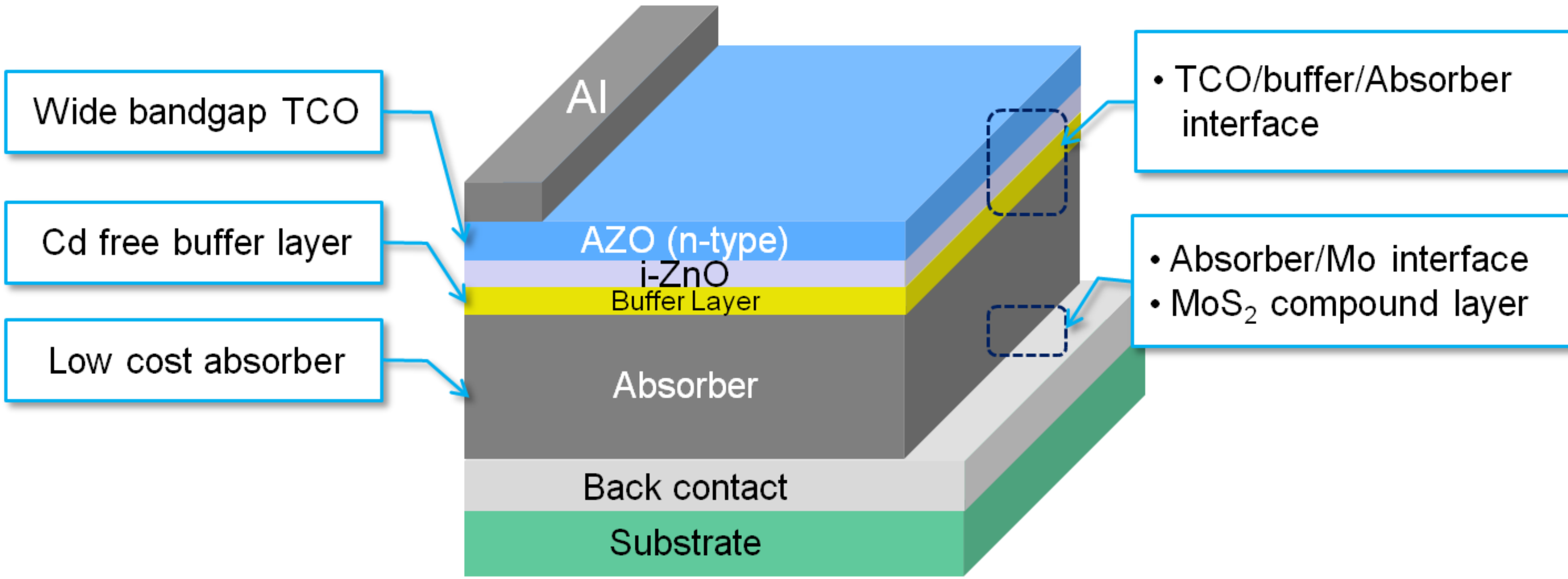


Crystal structures of semiconductor materials. (Courtesy of Dr. Bryce Walker)

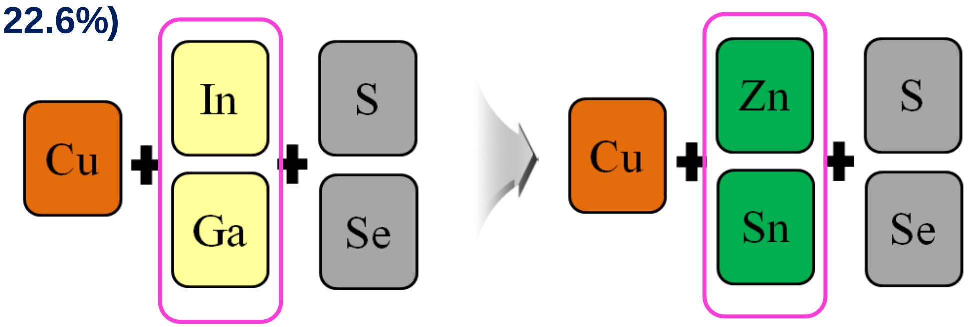
http://www.pveducation.org/es/fotovoltaica/czts

Issues in CIGSSe Thin Film Solar Cells

Low-cost and eco-friendly process with high efficiency



CdTe (η > 22.1%)
$Cu(In,Ga)(S,Se)_2$ (η > 22.6%)



$Cu_2ZnSn(S,Se)_4$ (η > 12.6%)

- High a (~10^4 cm^{-1})
- Suitable E_g of (1.0~1.5 eV)
- Non-toxic elements
- Earth-abundant elements