A steady rise of kesterite Solar Cells

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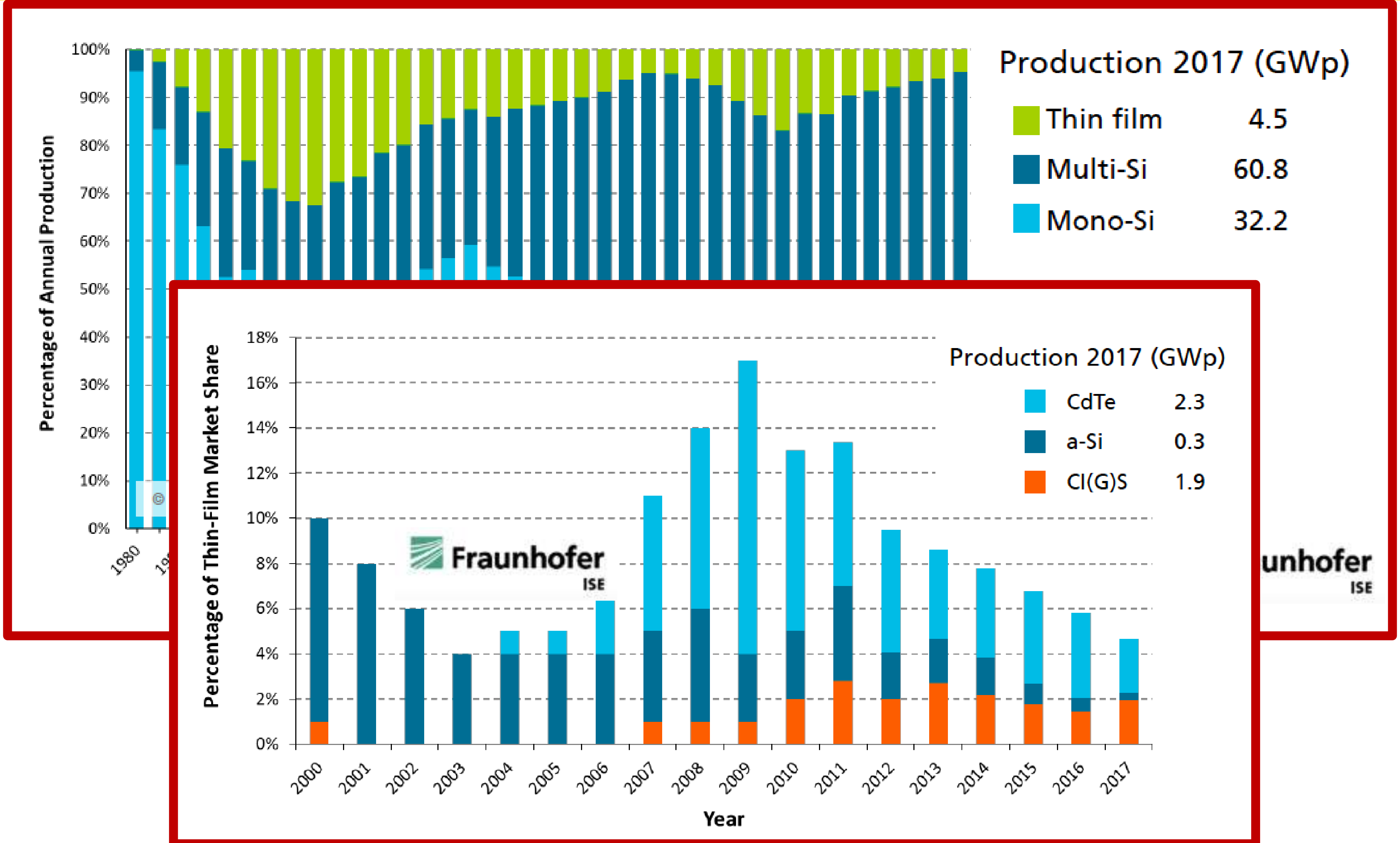
Never Stand Still | Faculty of Engineering | School of Photovoltaic and Renewable Energy Engineering

CIGS Solar Cell Market

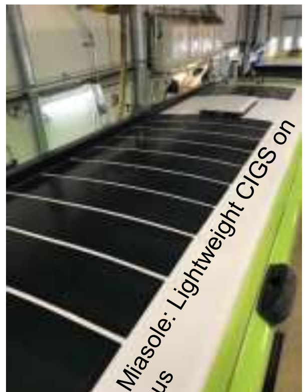


CIGS solar cell market

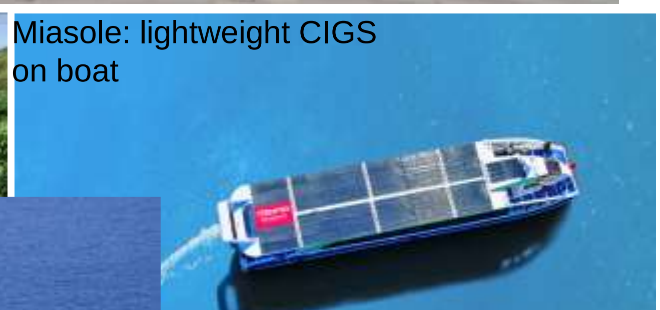
Light weight
Flexible /rigid
Better performance in weak light
Stable: serving long lifetime

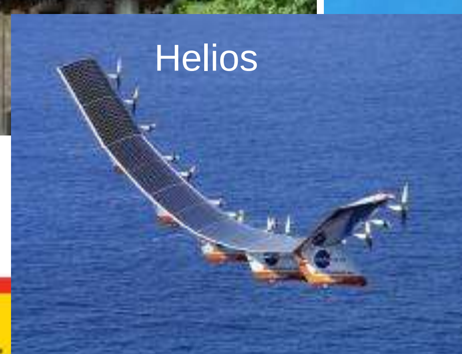
Cut and fit into tiny shap


Hanergy “Hantile”


Miasole: Lightweight CIGS on bus

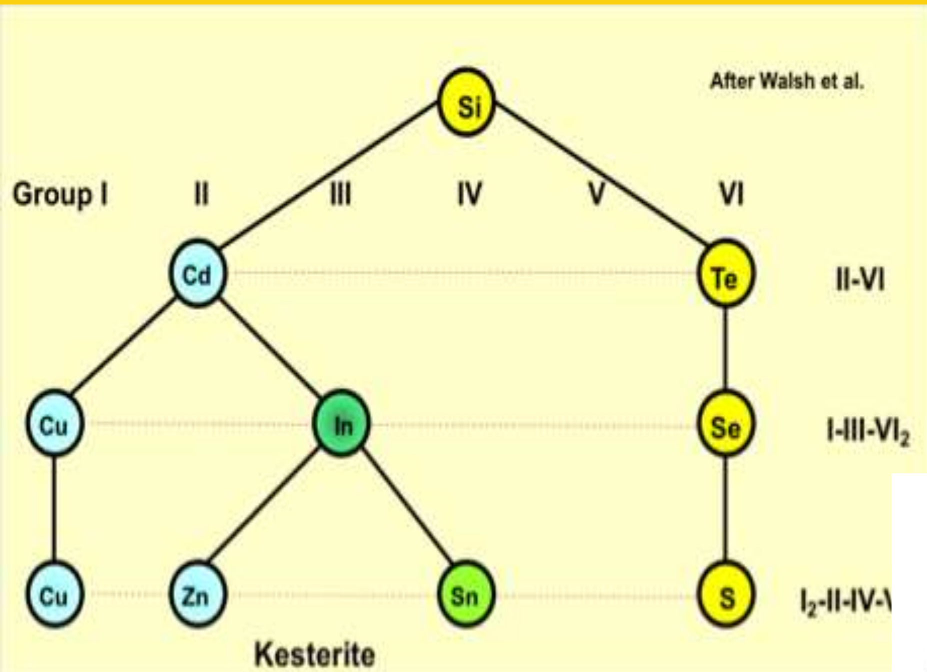

Miasole: lightweight CIGS on factory rooftop

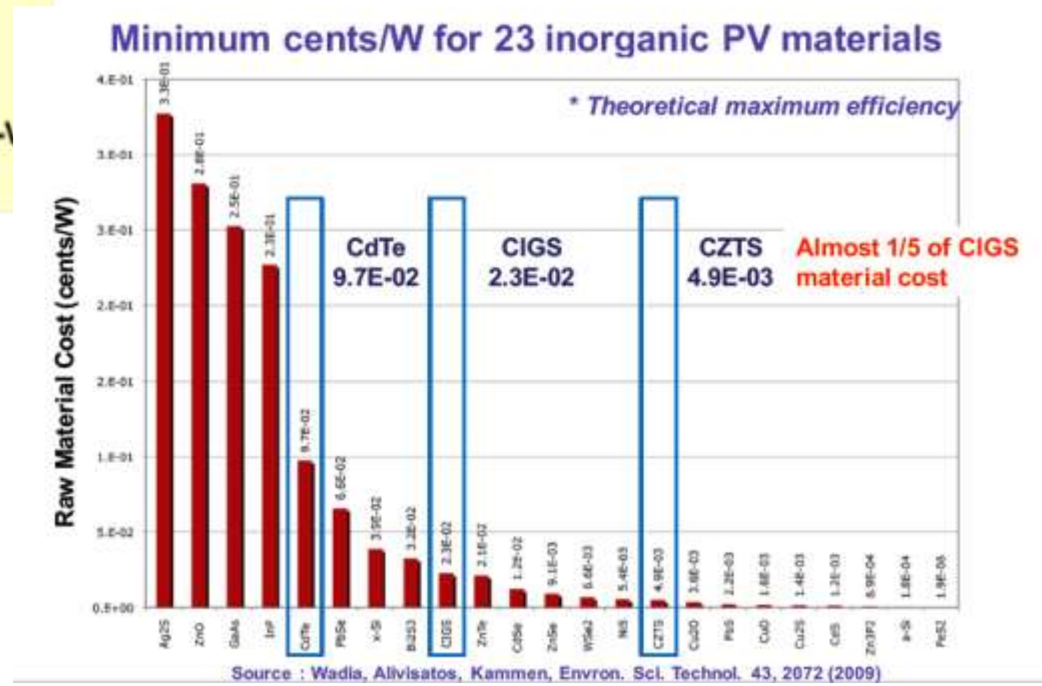

Miasole: lightweight CIGS on boat


Helios

Major running CIGS / CdTe players worldwide

Earth abundant and non-toxic kesterite CZTS

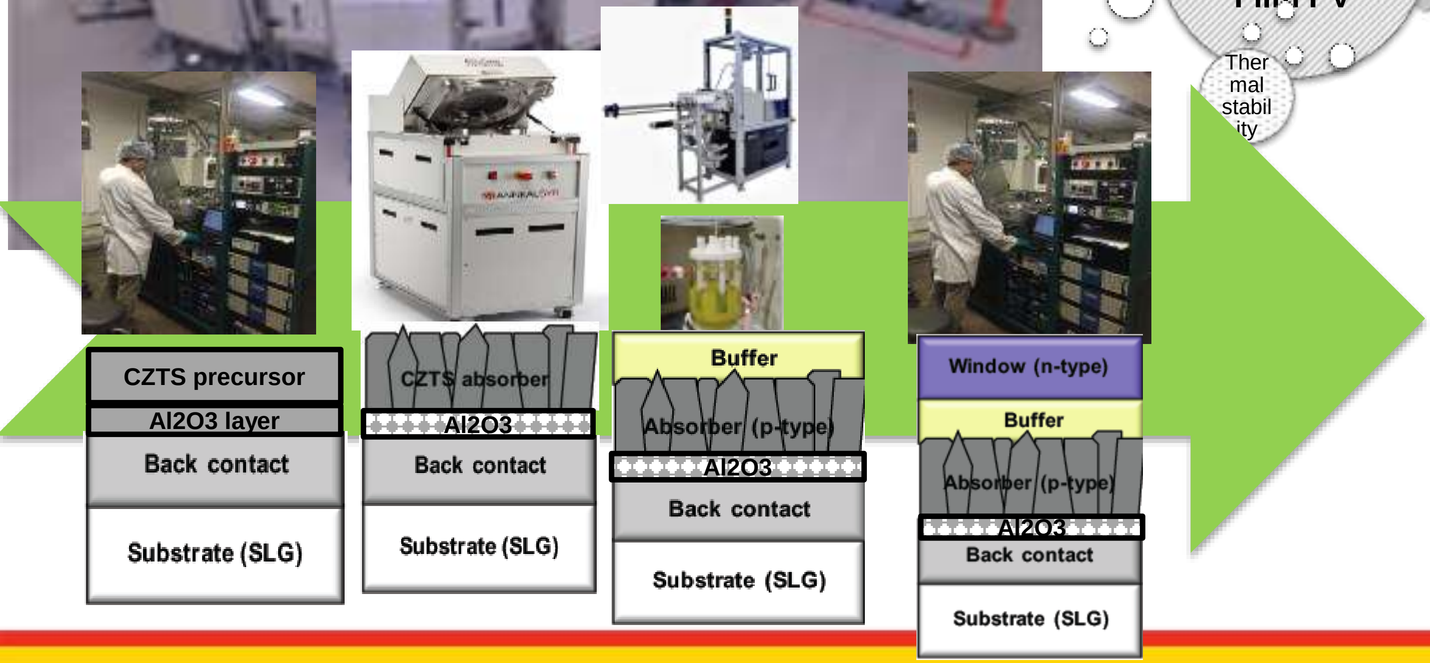


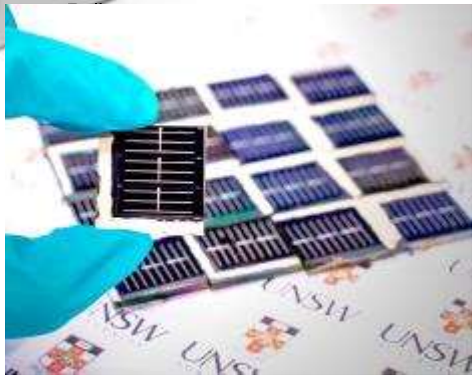


The manufacturing of CZTS solar cells

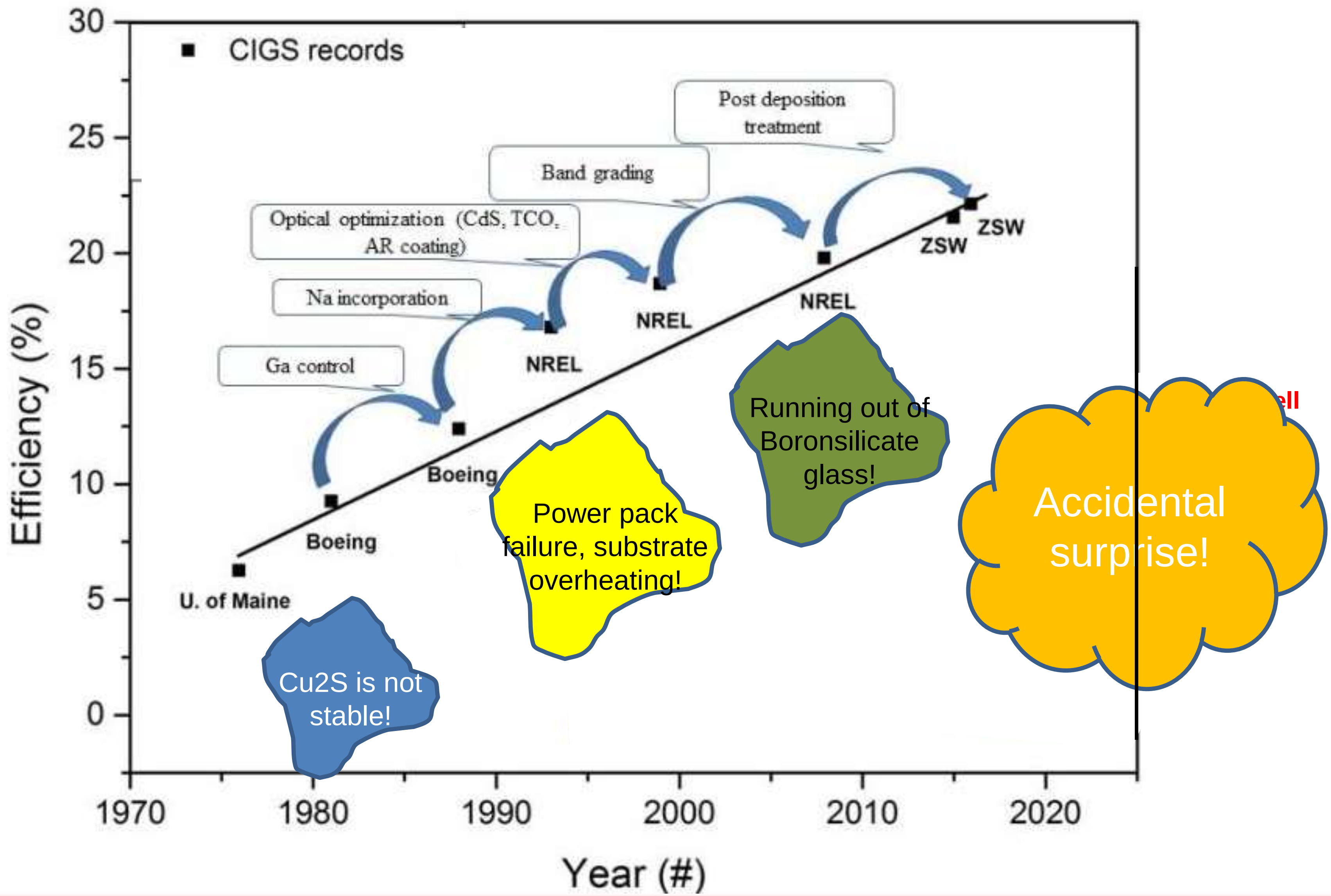
Current commercialized manufacturing for CIGS

Future up-scalable industrial scale for CZTS

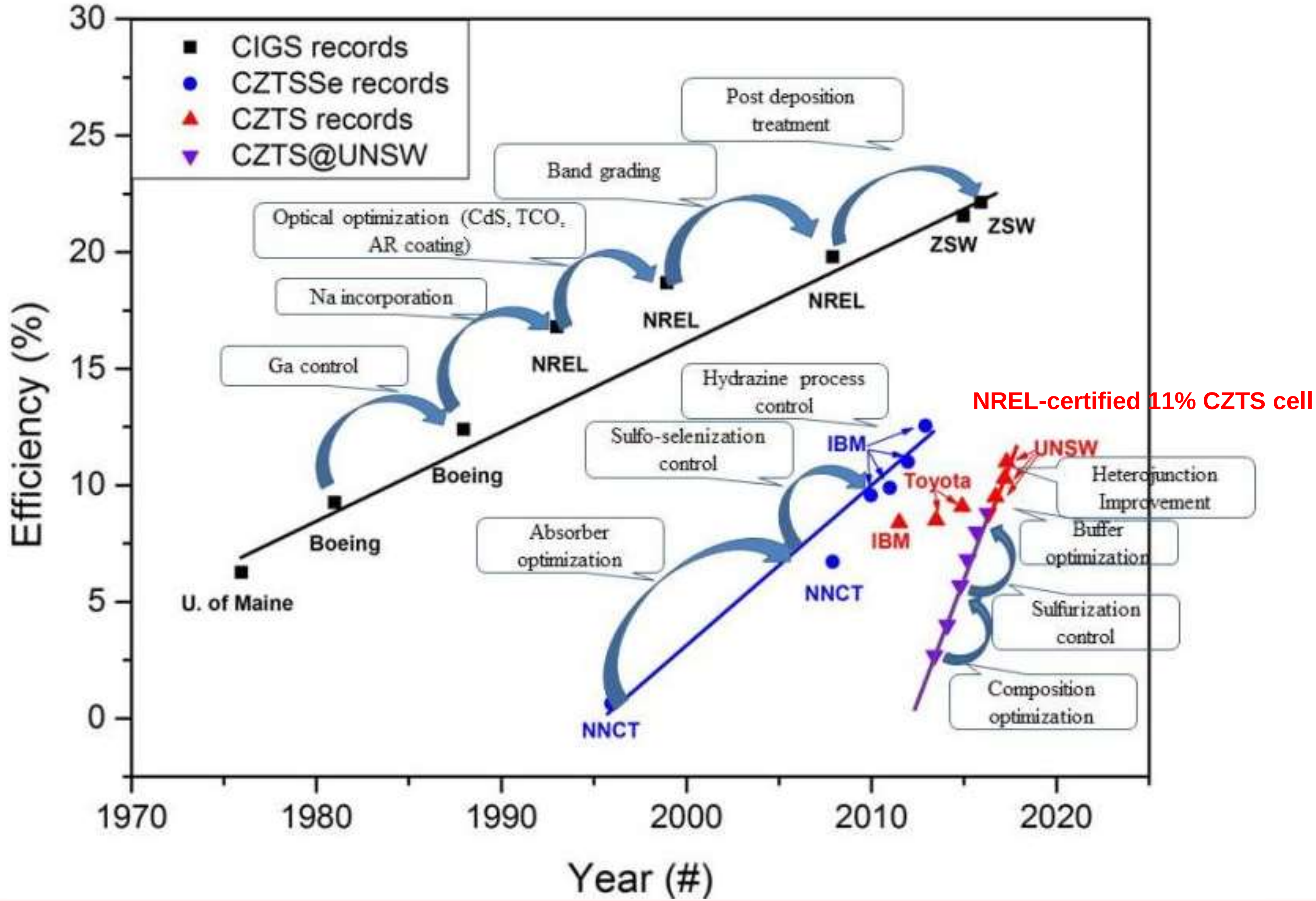




INNOVATION HIGHWAY: breakthrough milestones and key developments in CIGS

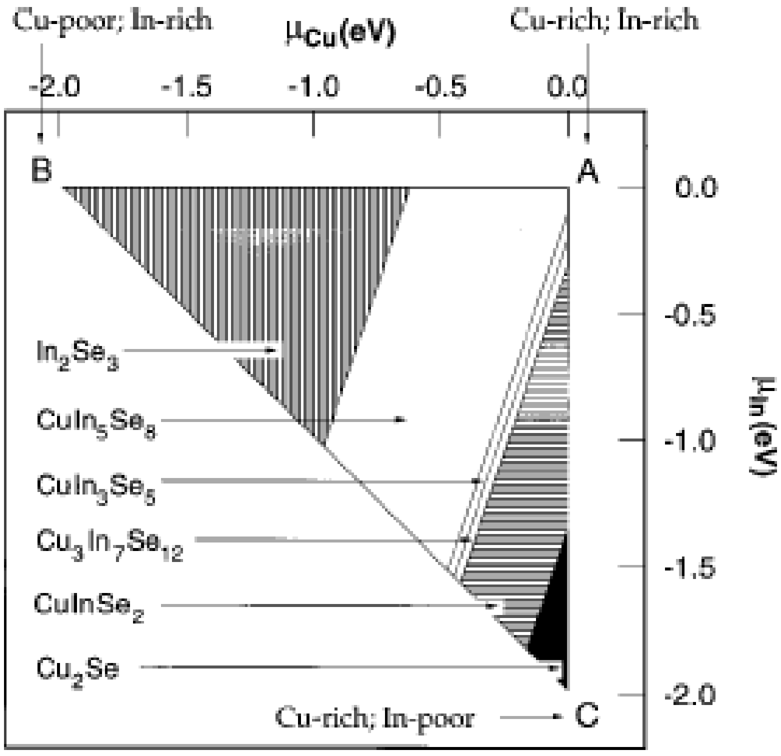


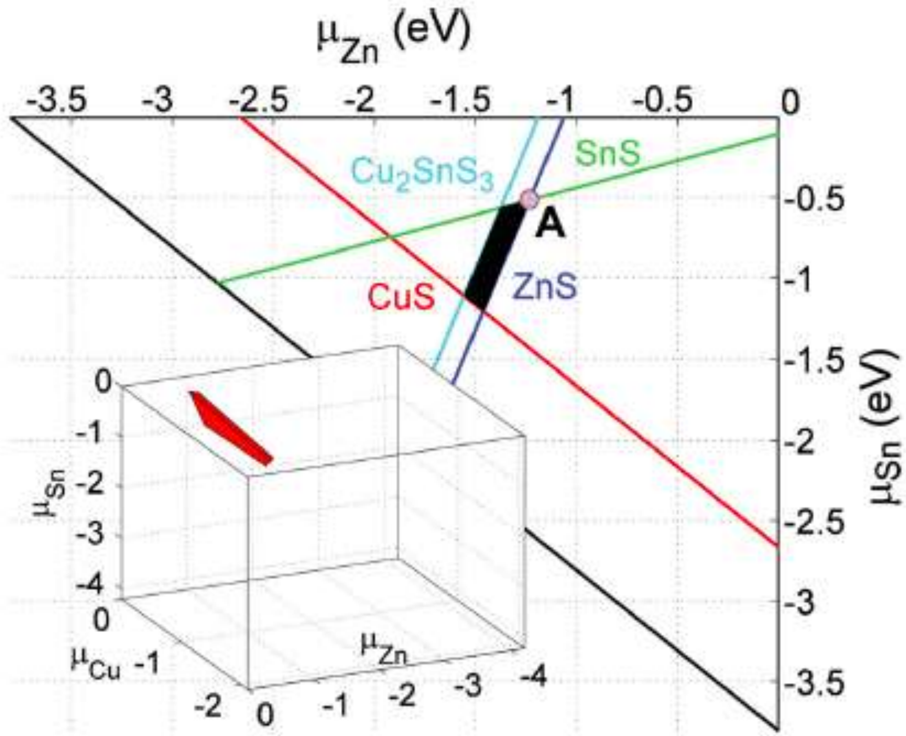
INNOVATION HIGHWAY: breakthrough milestones and key developments in CIGS and kesterite (CZTSSe and CZTS)



Challenges of CZTS solar cells: absorber

CIGS vs. CZTS

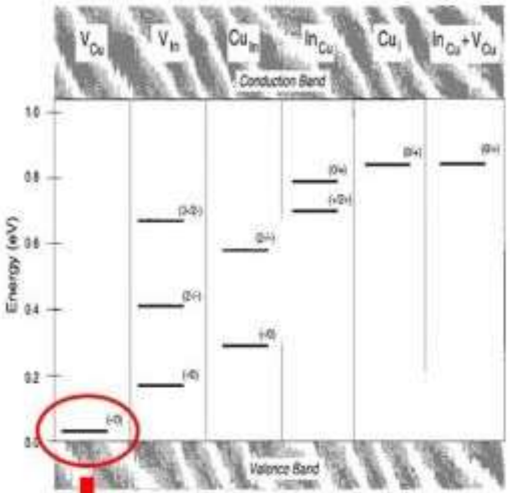




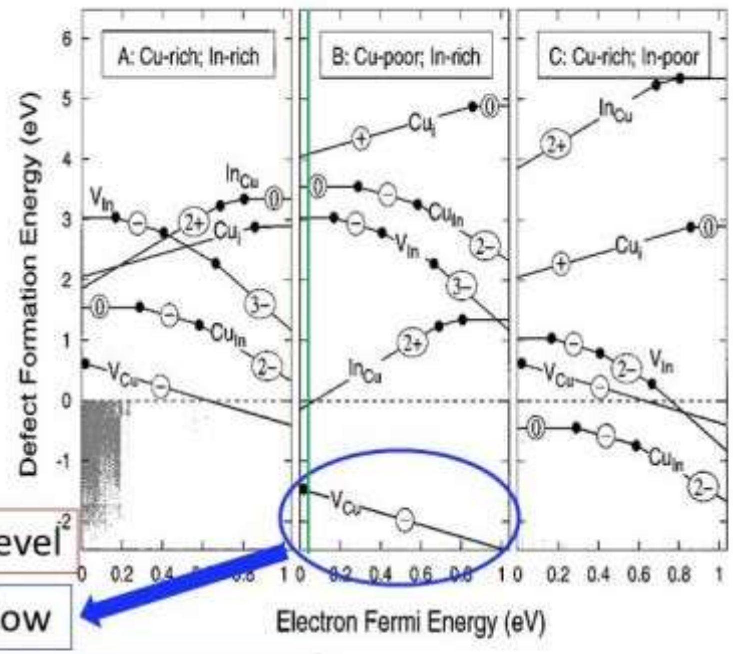
Source from "Physics Review B, Vol57, No.16, pp.9642" and "AEM, 2012,2.400-409"

CIGS

Defect transition energy level



Defect formation energy vs. Fermi energy

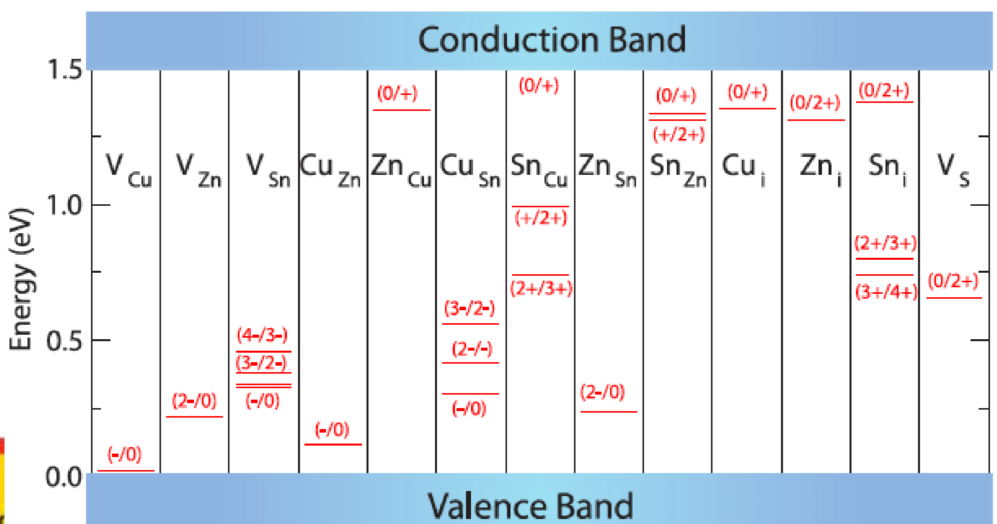


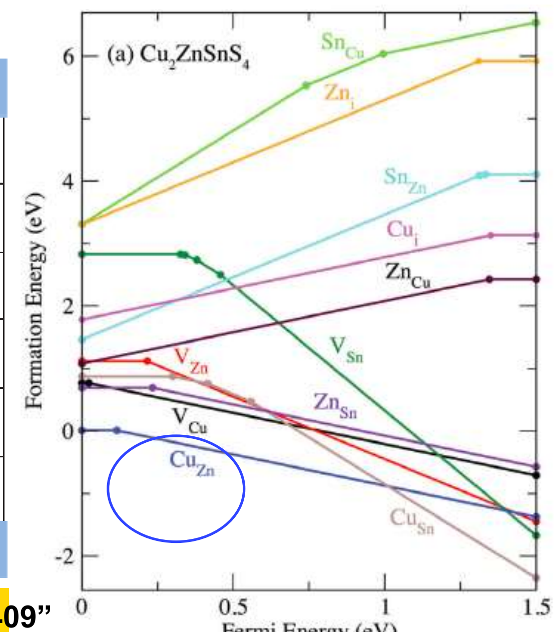
V_{Cu} has a shallow acceptor level

Formation energy of V_{Cu} is low

Formation energy of V_{Cu} & In_{Cu} are negative

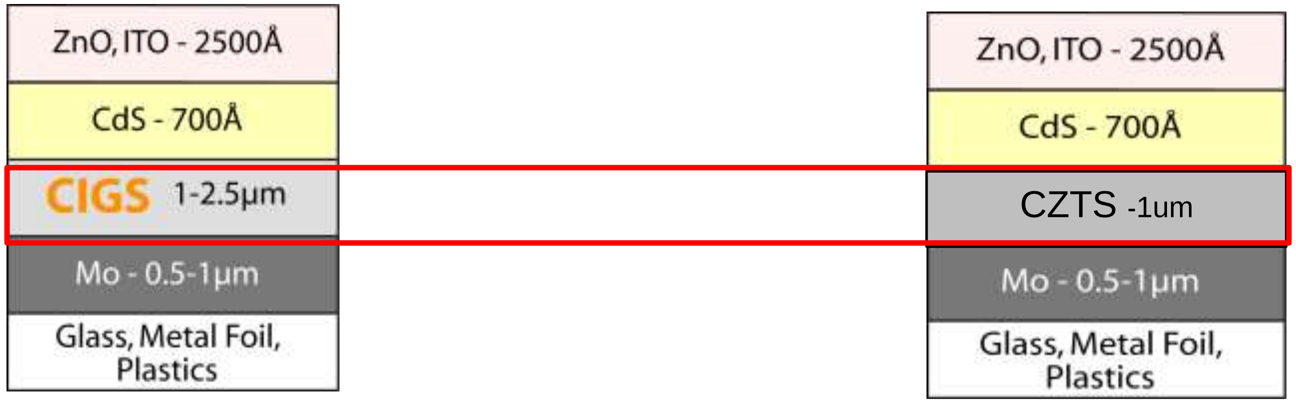
CZTS





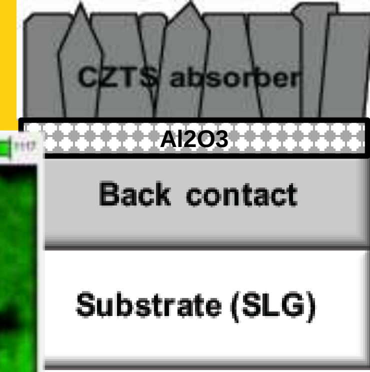
Source from "Physics Review B, Vol57, No.16, pp.9642" and "AEM, 2012,2.400-409"

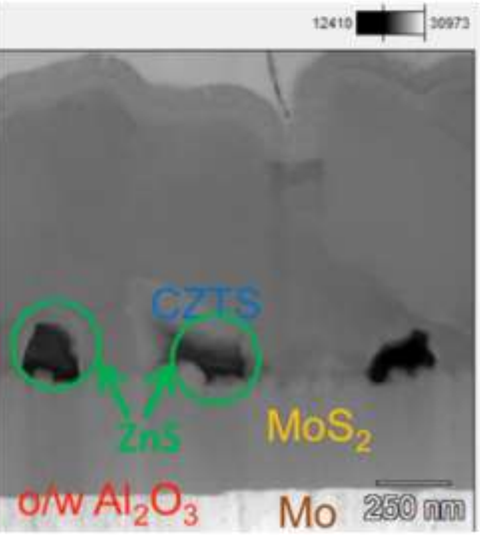
Interfaces of CZTS solar cells

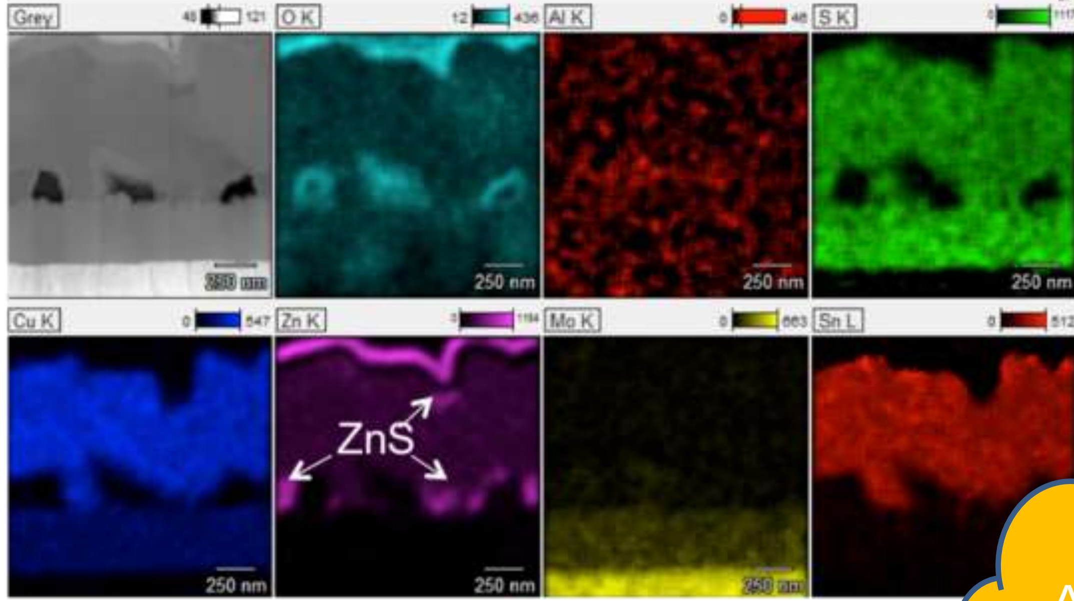


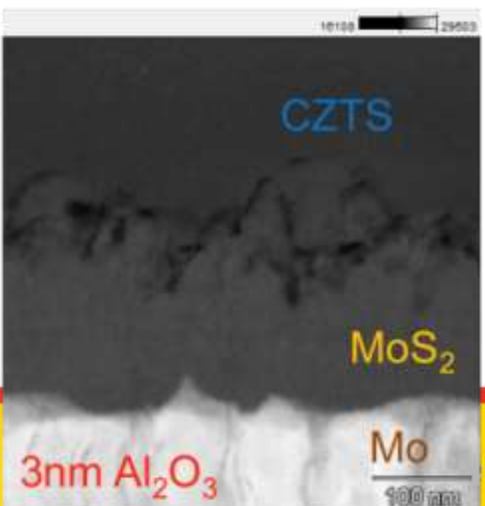
CZTS/Mo(S)$_2$ interface engineering

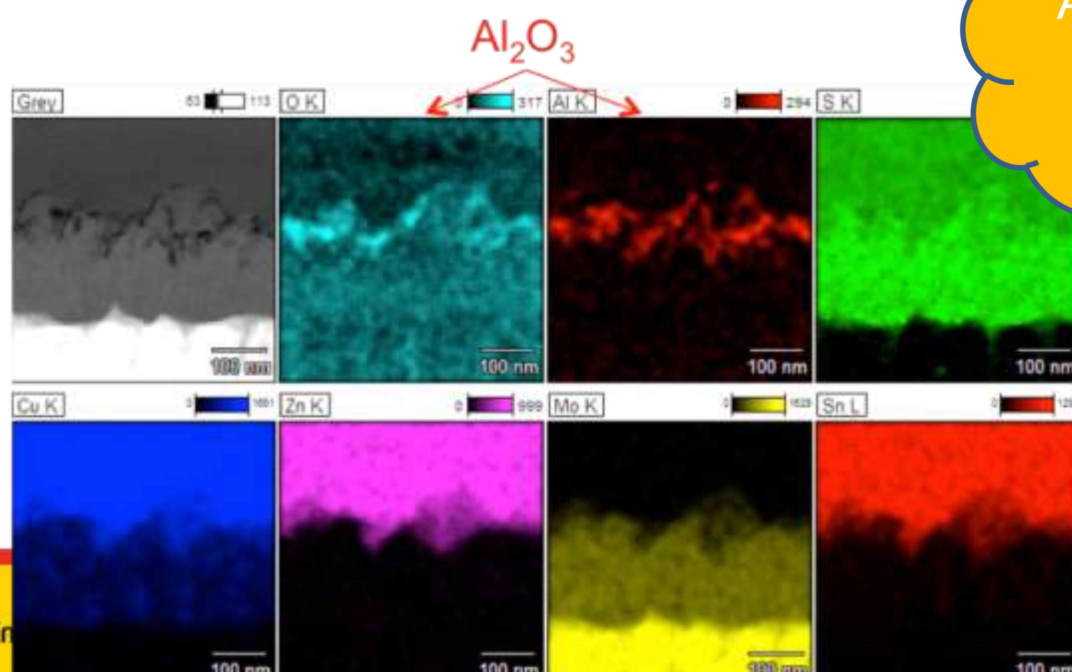
[UNSW, Liu F., NPG Asia Materials (2017) 9, e401; doi:10.1038/am.2017.103]





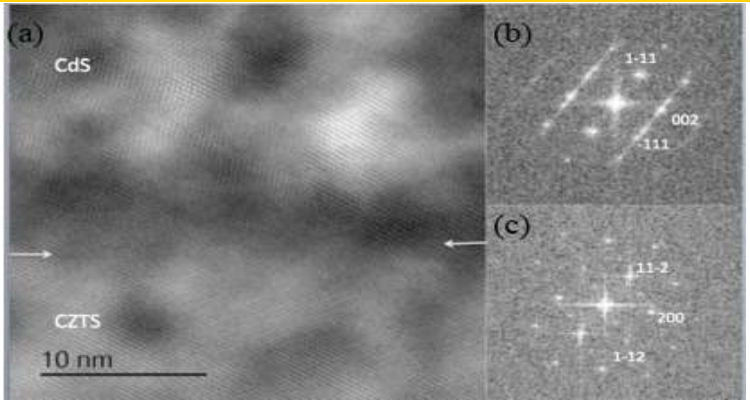




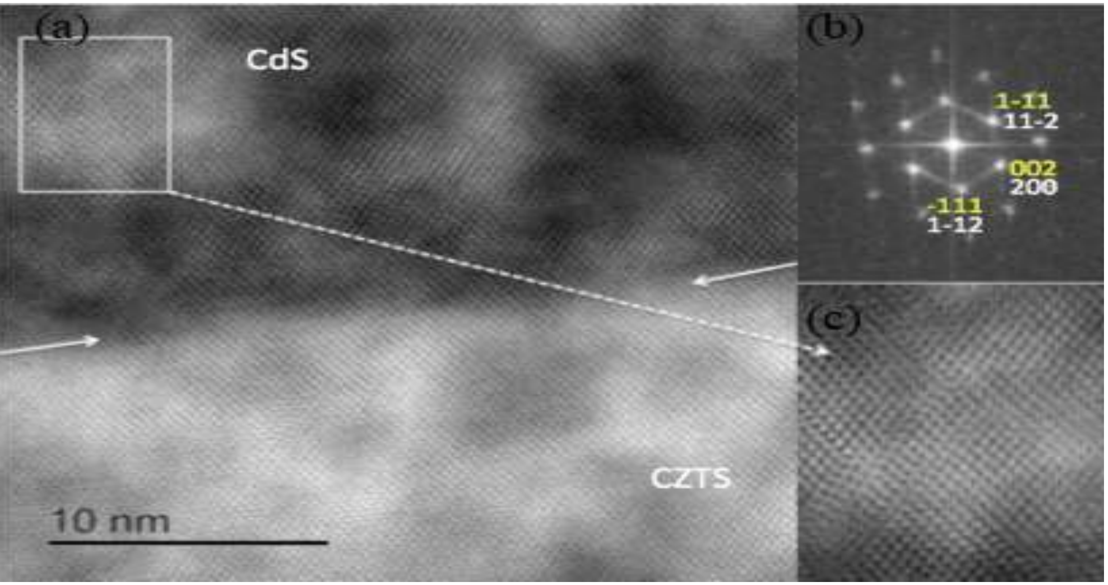


Accidental surprise!

CZTS/CdS interface
-sulfurization in a combined S and SnS atmosphere



- **Crystalline defective hetero-interface (CdS side)**
  - small size grains (a); extensive stacking faults and twins (b);



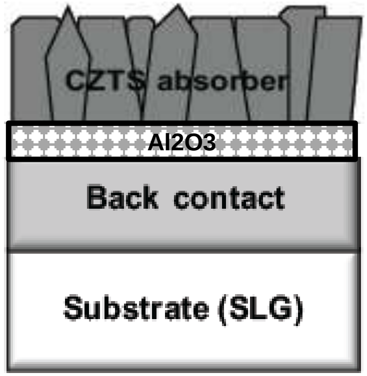
- **Suppress the Sn loss and remove the tens-nm sized small CZTS grains at the surface of CZTS absorber**

- **Realise localised "hetero-epitaxy" along the interface**
  - (111)CdS II (112) CZTS & (002)CdS II (200) CZTS

[**UNSW, Liu F.,Adv. Energy Mater., DOI: 10.1002/aenm.20160**

Major losses/problems of CZTS solar cells (baseline efficiency >8%)

- Interfaces: Interface recombination
  - Heterojunction interface recombination [SOLMAT 144(2016) 700-706, APL 104 (2014) 173901]
  - Back contact/bottom CZTS issue (*UNSW, Liu F., Hao X., NPG Asia Materials (2017) 9, e401; doi:10.1038/am.2017.103*)



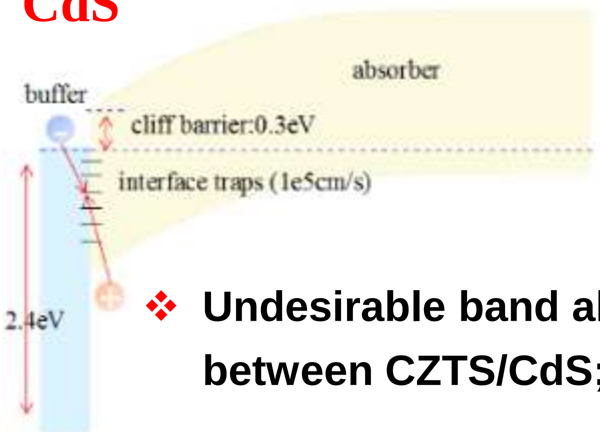
- Bulk:
  - Improved CZTS quality (sulfurization condition and back contact/absorber engineering) (*UNSW, Liu F. Hao X. and et al., NPG Asia Materials (2017) 9, e401; doi:10.1038/am.2017.103 & UNSW, Liu F., Hao X., and et al., Adv. Energy Mater., DOI: 10.1002/aenm.201600706*)

CZTS/CdS heterojunction interface engineering

UNSW, Kaiwen Sun, Xiaojing Hao et al., ***Advanced Energy Materials*** 6 (12), 1600046

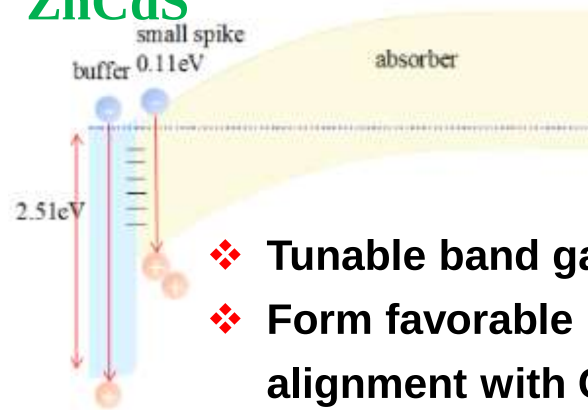
❑ Alternative ZnCdS buffer layer

CdS

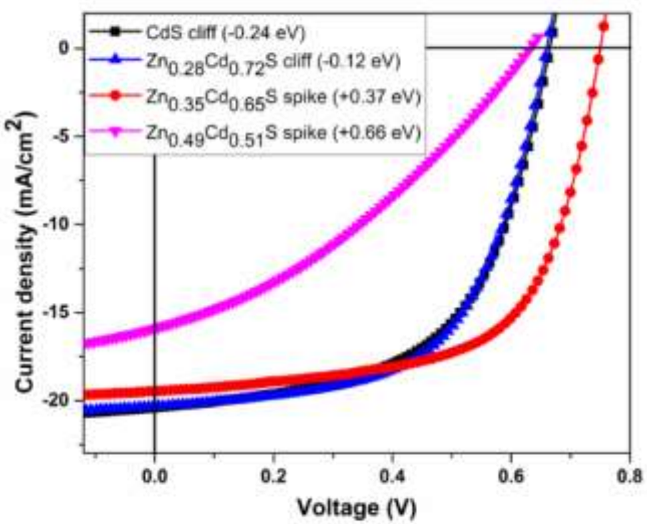


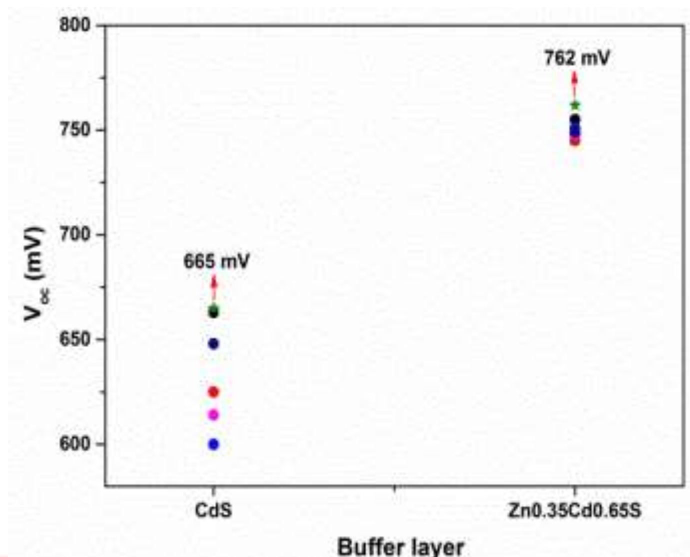
- **Undesirable band alignment between CZTS/CdS;**

ZnCdS



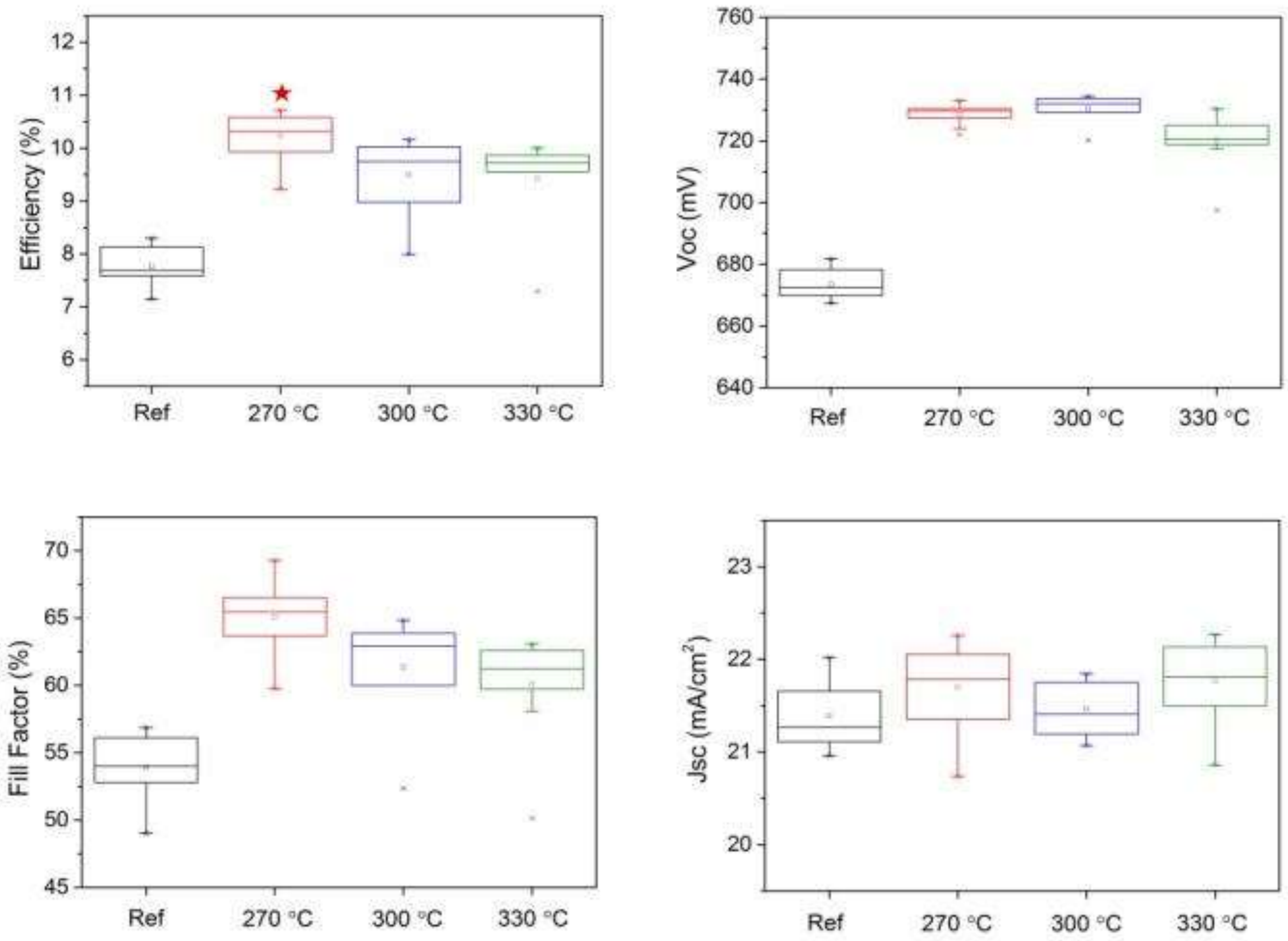
- **Tunable band gap of ZnCdS;**
- **Form favorable band alignment with CZTS.**





CZTS/CdS heterojunction-heat treatment

- Heterojunction heat treatment mainly affect Voc and FF



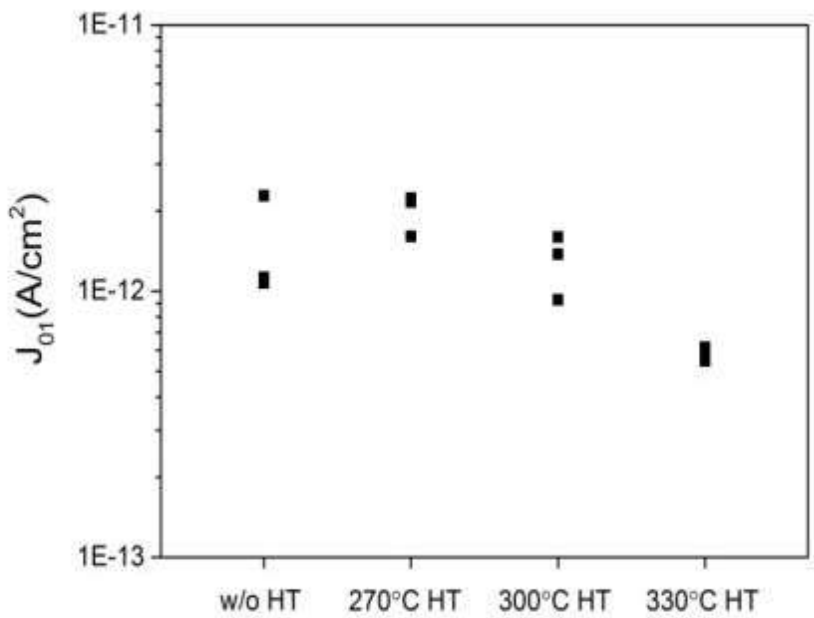
- Heat treatment at 270C boosts the efficiency from ~8% up to 11%

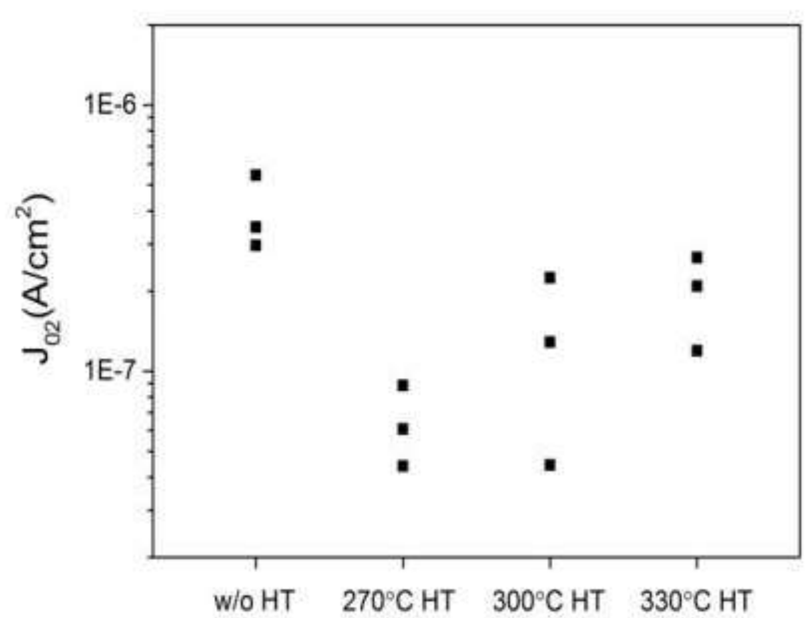
Yan C., Huang J., Sun K., and et al., **Nature Energy**, vol. 3, 2018, pp. 764 - 772

CZTS/CdS heterojunction-heat treatment

- Heterojunction heat treatment mainly affect heterojunction region

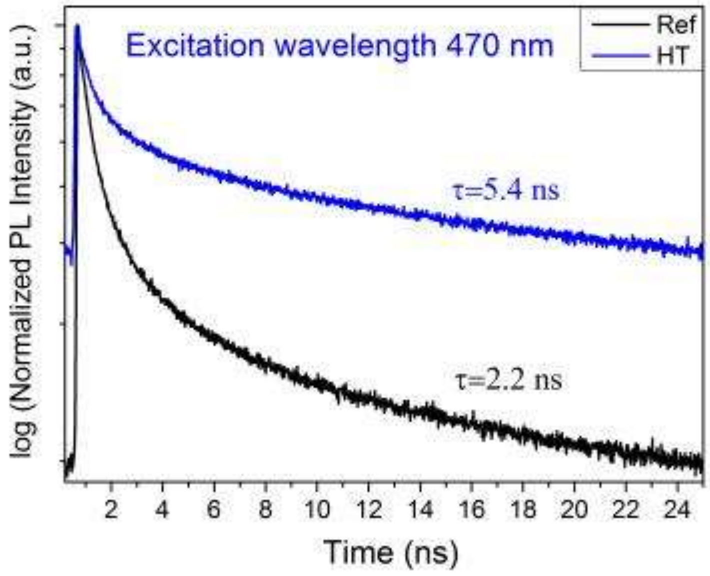
CZTS device	V_{OC} (mV)	Jsc (mA/cm²)	FF (%)	Eff(%)	$R_{S,L}$ (Ω cm²)	$G_{s,L}$ (mS cm⁻²)	A	J_0 (A/cm²)
W/o HT	672.5	20.65	56.29	7.82	4.40	0.56	2.61	9.0×10^{-7}
With HT	730.6	21.74	69.27	11.01	2.58	0.98	1.44	6.8×10^{-11}

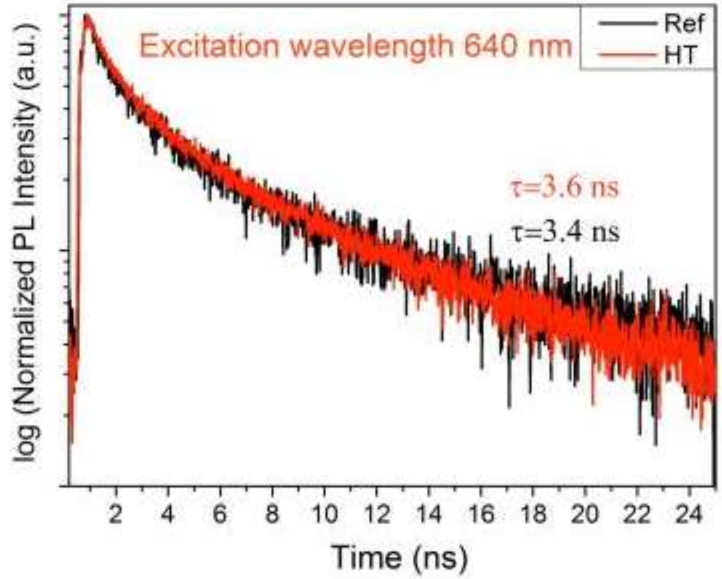


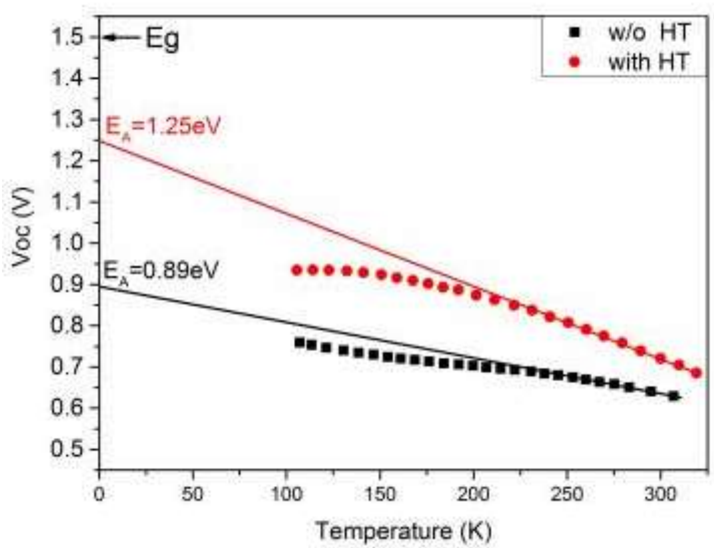


CZTS/CdS heterojunction-heat treatment

- Heterojunction heat treatment mainly affect heterojunction region



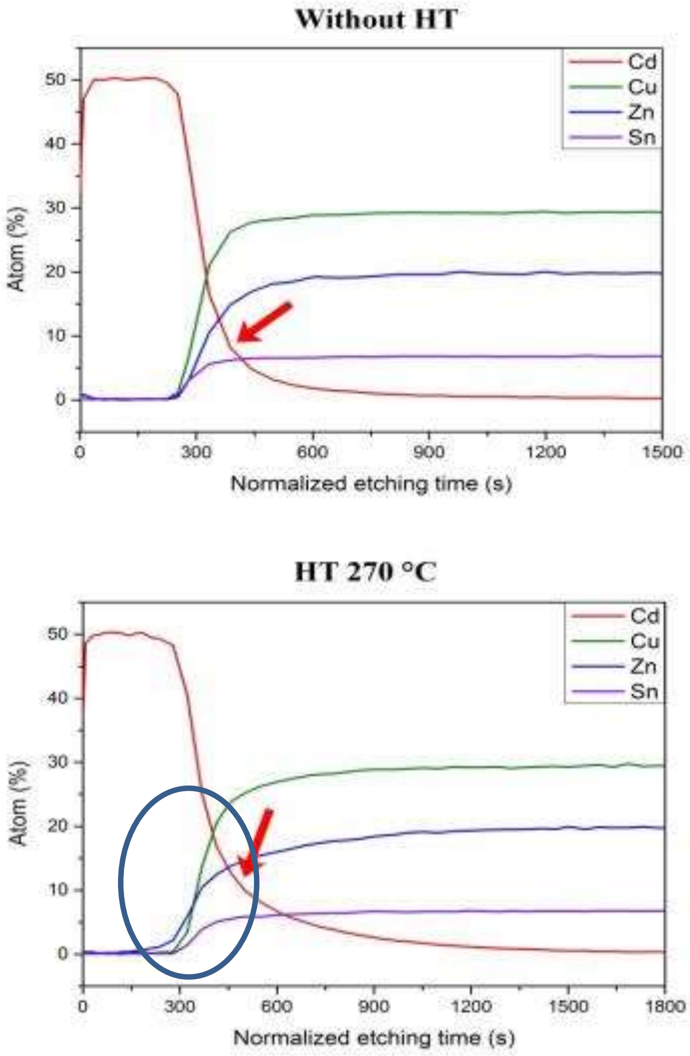




- Reduced non-radiative recombination is mainly located at heterojunction region.

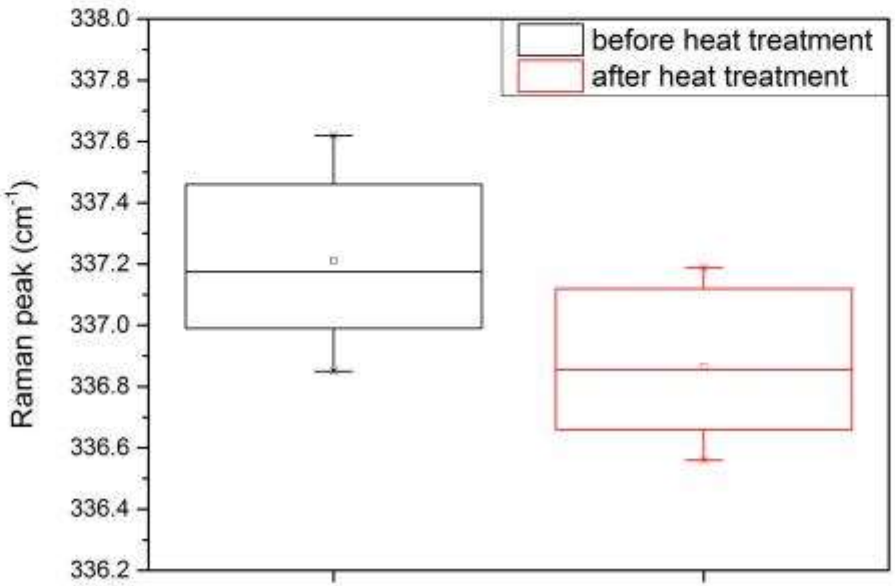
CZTS/CdS heterojunction-heat treatment

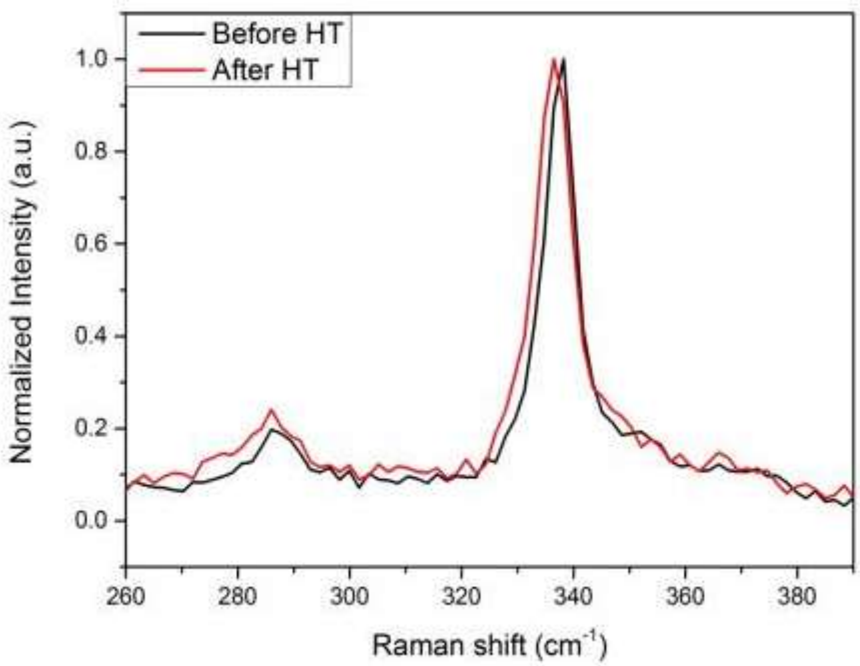
- Element inter-diffusion between CdS and CZTS: mainly Zn and Cd



CZTS/CdS heterojunction-heat treatment

- **Buffer side: Zn diffusion into CdS- ZnxCd1-xS**

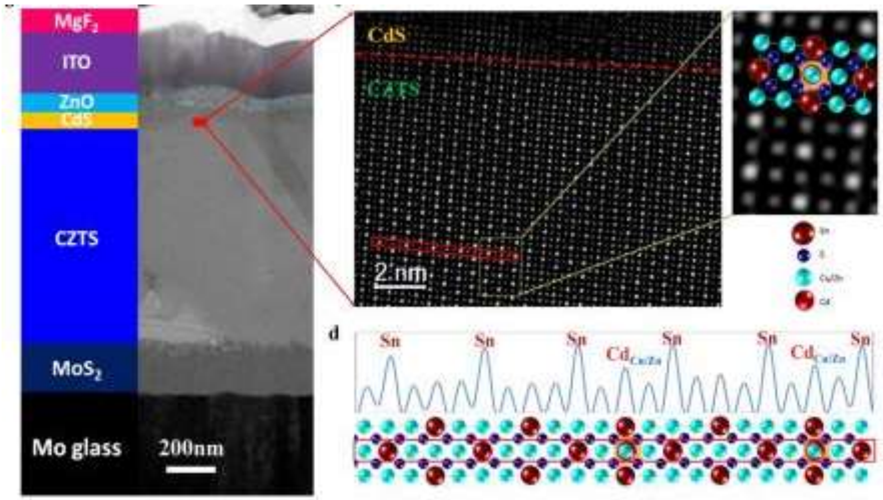


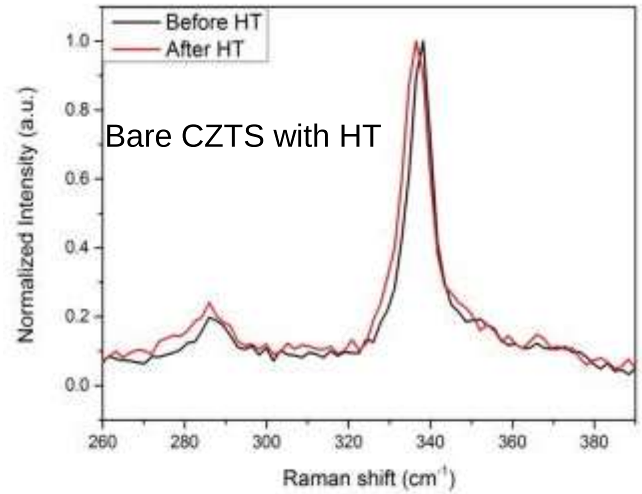


Yan C., Huang J., Sun K., and et al., **Nature Energy**, vol. 3, 2018, pp. 764 - 772

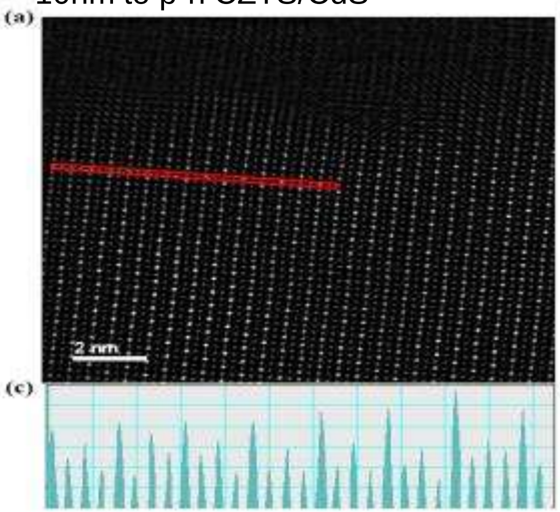
CZTS/CdS heterojunction-heat treatment

- **Absorber side: possible Cu2ZnxCd1-xSnS4 phase**

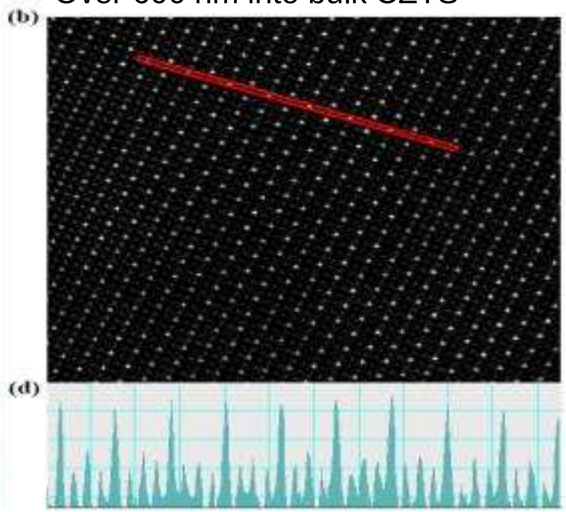


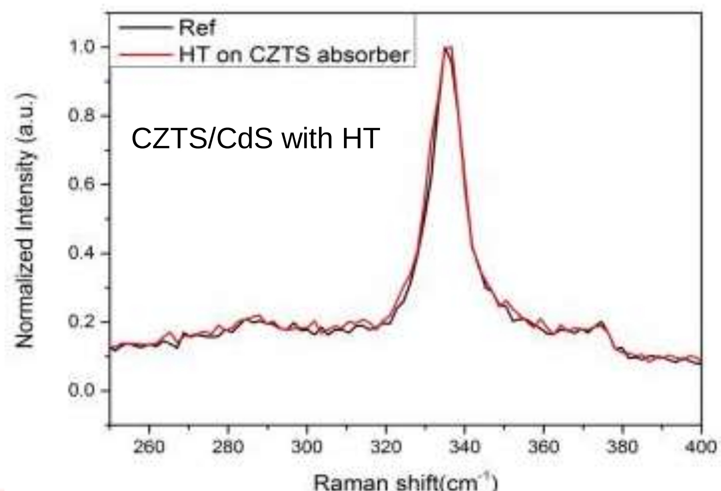


10nm to p-n CZTS/CdS



Over 600 nm into bulk CZTS

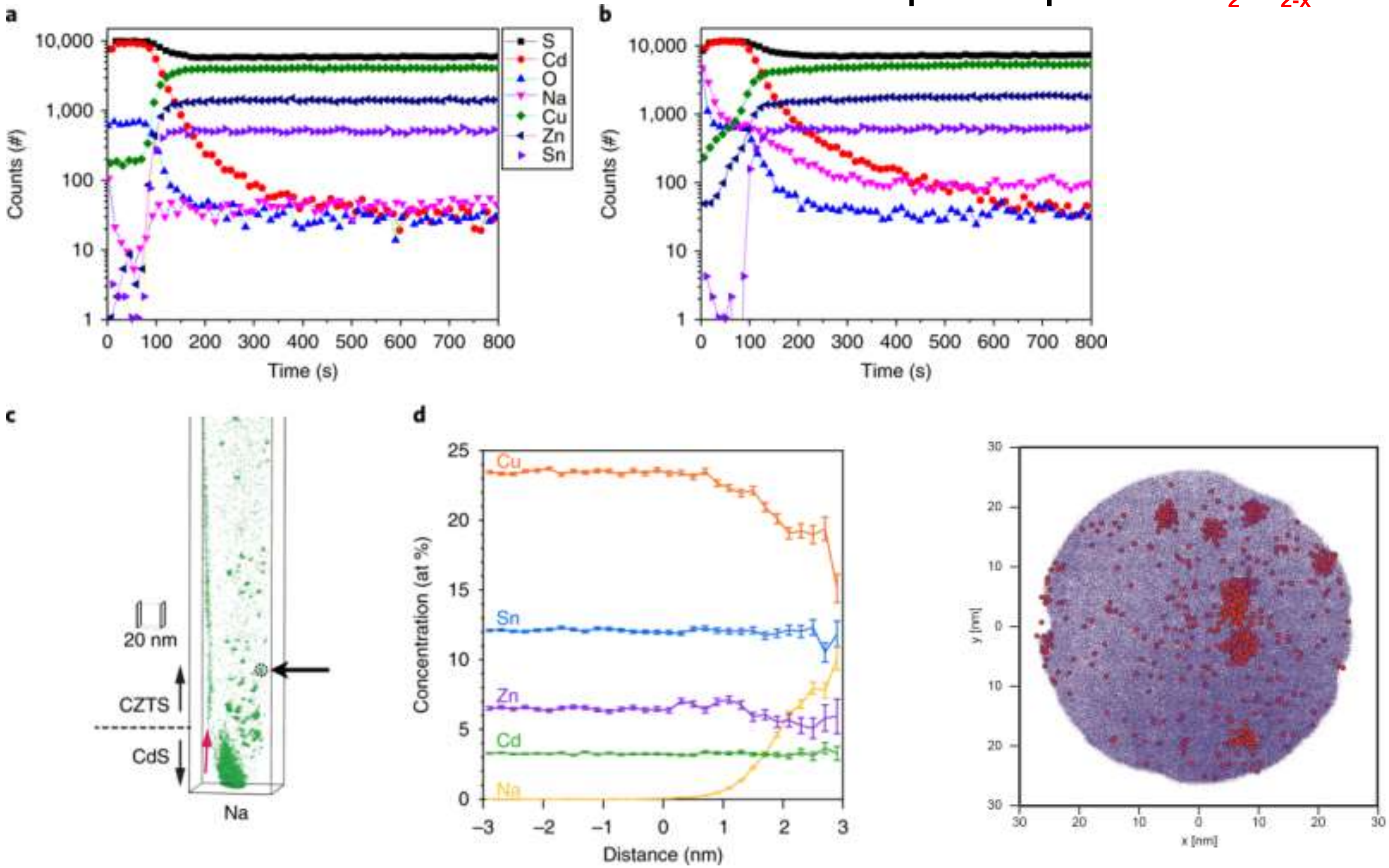




Yan C., Huang J., Sun K., and et al., **Nature Energy**, vol. 3, 2018, pp. 764 - 772

CZTS/CdS heterojunction-heat treatment

❑ **Absorber side: Na re-distribution and accumulation and possible phase of $Cu_2Na_{2-x}ZnSnS_4$ (Ave x:0.07)**

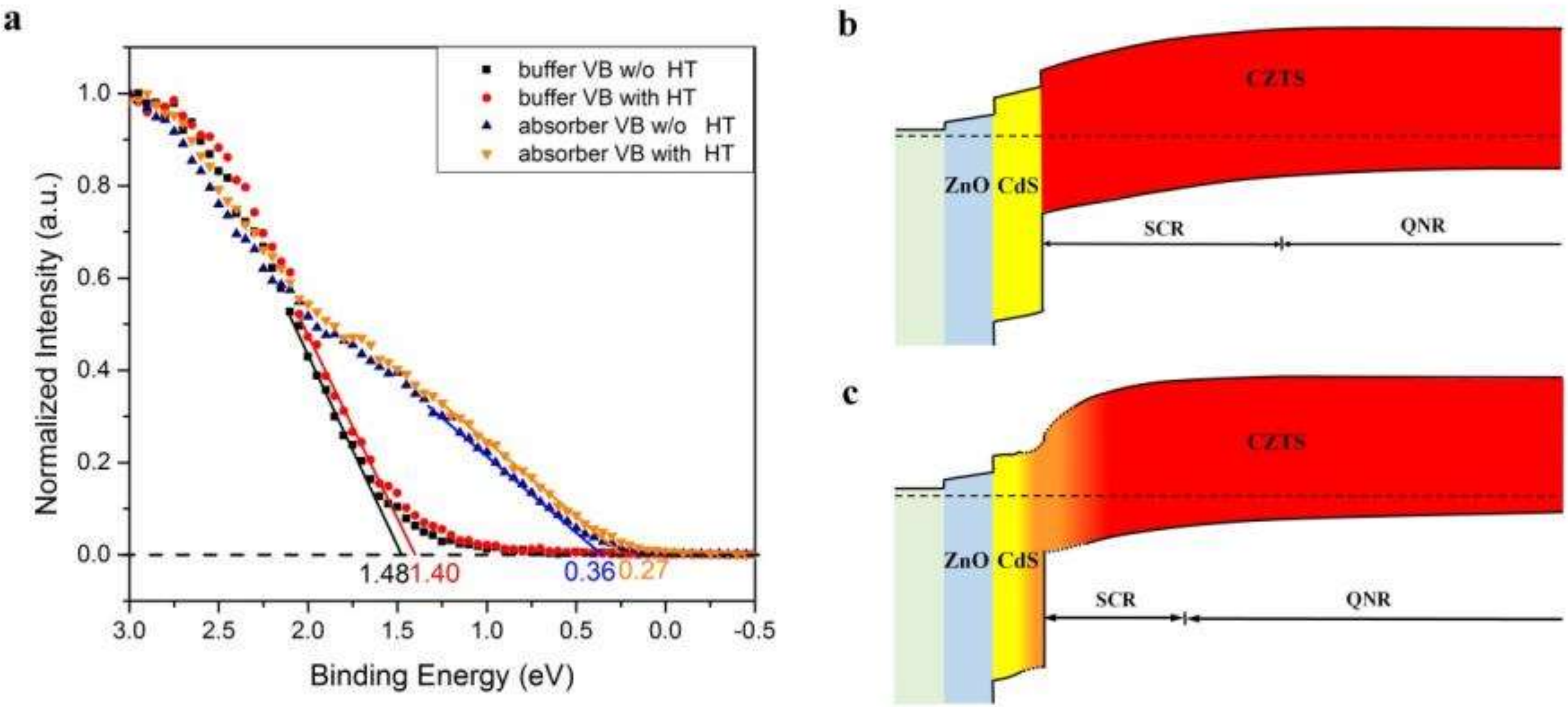


- **First principle calculations confirm the thermal-dynamical favorable formation of $Cu_2Na_{2-x}ZnSnS_4$ with low Na concentration (X<0.4)**

Yan C., Huang J., Sun K., and et al., **Nature Energy**, vol. 3, 2018, pp. 764 - 772

CZTS/CdS heterojunction-heat treatment

❑ Band alignment



- After HT, the Fermi Level gets closer to VBM.
- The CBO changed from (-0.13 eV) before HT to (-0.04eV) after HT assuming Eg of CdS and CZTS unchanged.

Yan C., Huang J., Sun K., and et al., **Nature Energy**, vol. 3, 2018, pp. 764 - 772

CZTS/CdS heterojunction-heat treatment

- Demonstrated 11% record efficiency sulphide kestertite CZTS solar cells.

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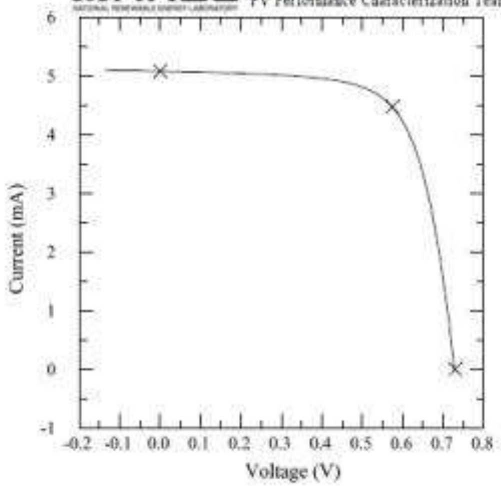
University of New South Wales (Australia)

CZTS Cell

Device ID: UNSW cell 3 170310
Mar 14, 2017 09:51
Spectrum: ASTM G173 global

Device Temperature: 24.6 ± 0.5 °C
Device Area: 0.2339 cm^2 ± 0.5 %
Irradiance: 1000.0 W/m^2

NREL X25 IV System
PV Performance Characterization Team



V_{oc} = 0.7306 V ± 0.2%
I_{sc} = 5.0854 mA ± 1.3%
J_{sc} = 21.744 mA/cm^2 ± 1.4%
Fill Factor = 69.27 % ± 0.4%

I_{max} = 4.4757 mA ± 1.3%
V_{max} = 0.5751 V ± 0.0%
P_{max} = 2.5739 mW ± 1.3%
Efficiency = 11.01 % ± 1.4%

After 10 minute soak at P_{max}, 5 minute cool.

page 5

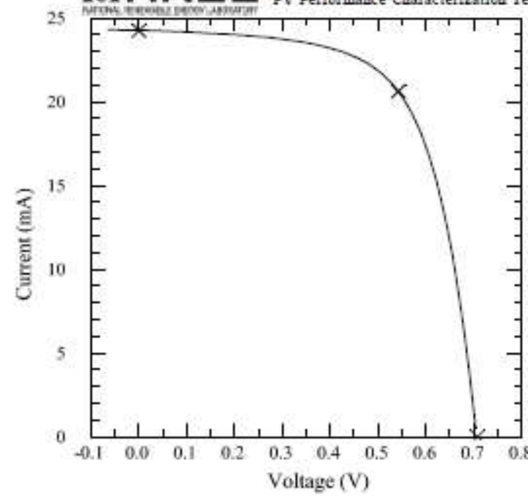
University of New South Wales

CZTS Cell

Device ID: UNSW Sample1 cell 2
Mar 27, 2017 14:28
Spectrum: ASTM G173 global

Device Temperature: 24.4 ± 0.5 °C
Device Area: 1.113 cm^2 ± 0.2 %
Irradiance: 1000.0 W/m^2

NREL X25 IV System
PV Performance Characterization Team



V_{oc} = 0.7083 V ± 0.2%
I_{sc} = 24.243 mA ± 1.0%
J_{sc} = 21.772 mA/cm^2 ± 1.0%
Fill Factor = 65.13 % ± 0.4%

I_{max} = 20.605 mA ± 1.0%
V_{max} = 0.5427 V ± 0.0%
P_{max} = 11.183 mW ± 1.0%
Efficiency = 10.04 % ± 1.0%

After 10 minute soak at P_{max}, 5 minute cool.

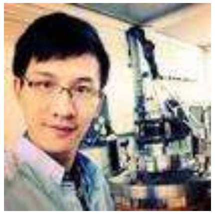
Yan C., Huang J., Sun K., and et al., **Nature Energy**, vol. 3, 2018, pp. 764 - 772

What's next?-Innovation highway of kesterite

- **Low conductivity**

V_{cu} or Cu_{Zn}

- **Cu$_{Zn}$ disorder pinned Fermi level**



Cu_{Zn} disorder

Defect Control

Sn-related?

S-related?

wrong bonds, dangling bonds

- **Other deep level defects /defects clusters?**


ADVANCED ENERGY MATERIALS

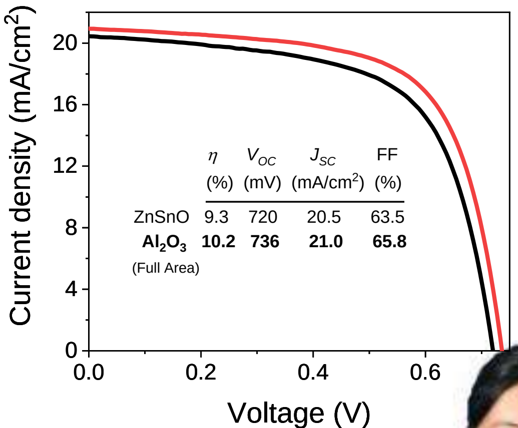
Communication

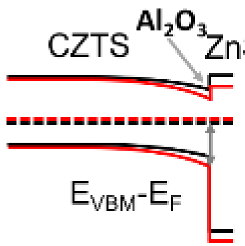
The Role of Hydrogen from ALD-Al_2O_3 in Kesterite Cu_2ZnSnS_4 Solar Cells: Grain Surface Passivation

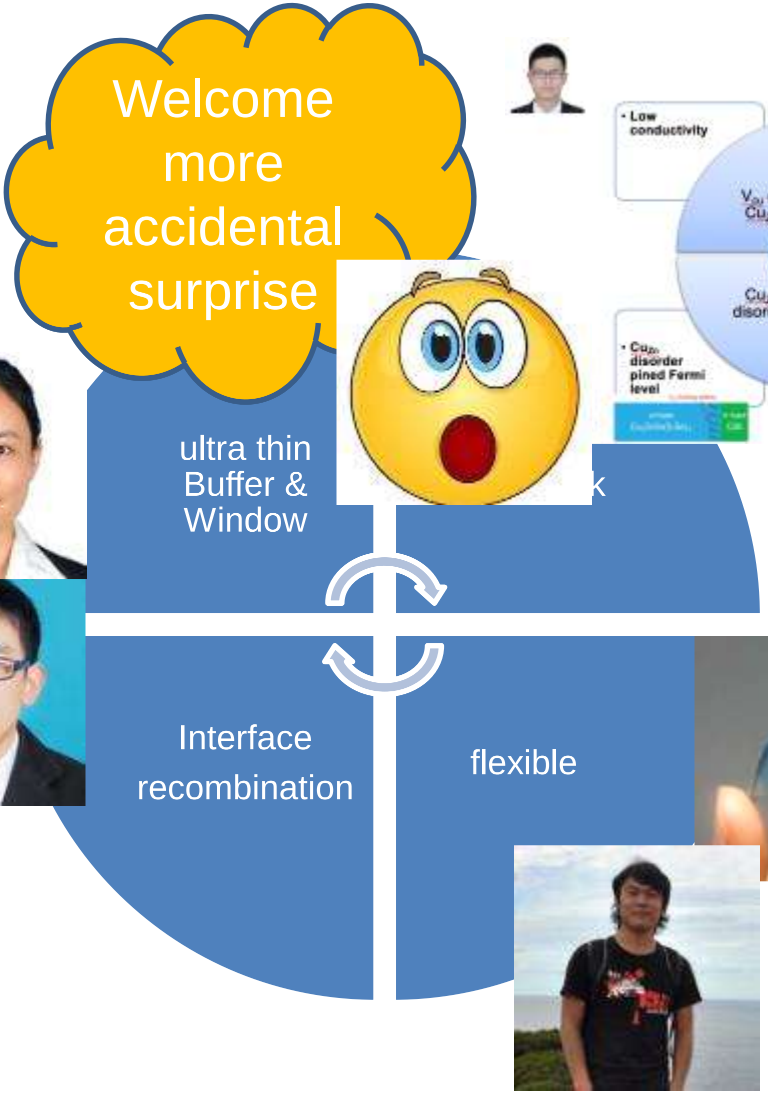
Jongsung Park, Jialiang Huang, Jaesung Yun, Fangyang Liu, Zi Ouyang, Heng Sun, Chang Yan, Kaiwen Sun, Kyung Kim, Jan Seidel, Shiyou Chen, Martin A. Green, Xiaojing Hao

- **Benign grain boundary?**
- **Passivation?**

What's next?-Innovation highway of kesterite







Fruitful exchange of ideas between labs globally

First Asia Pacific-European Kesterite workshop
(22 different countries in 5 continents)

Brainstorming se

Global competition & collaboration will make the kesterite to keep rising!

First Asia-Pacific Kesterite workshop in 2018

Continue on
2019, Xi'an, China
2020, Korea
2021, Sydney

China Nov 2018

What we learn here?

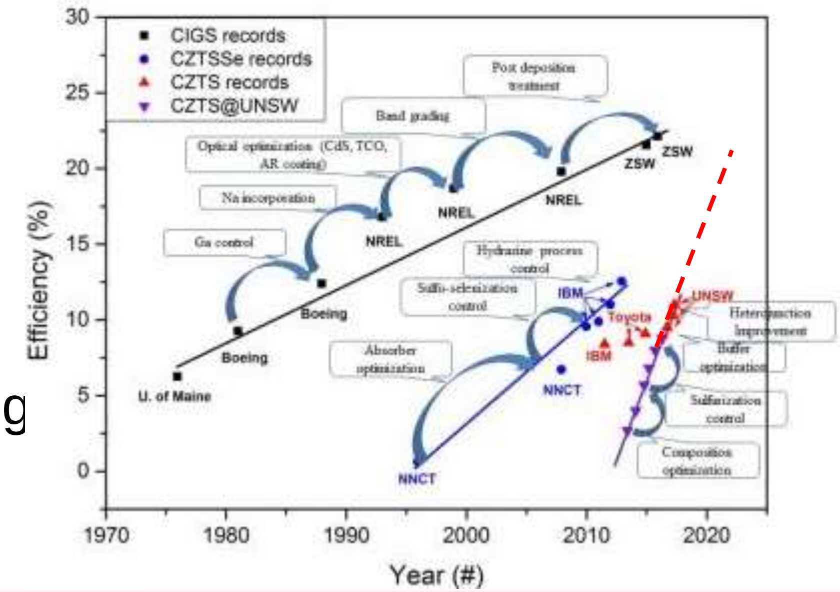
- Kesterite: high promise (earth-abundant & non-toxic & stable), challenging but full of fun.

- Demonstrated 11% efficiency CZTS solar cells

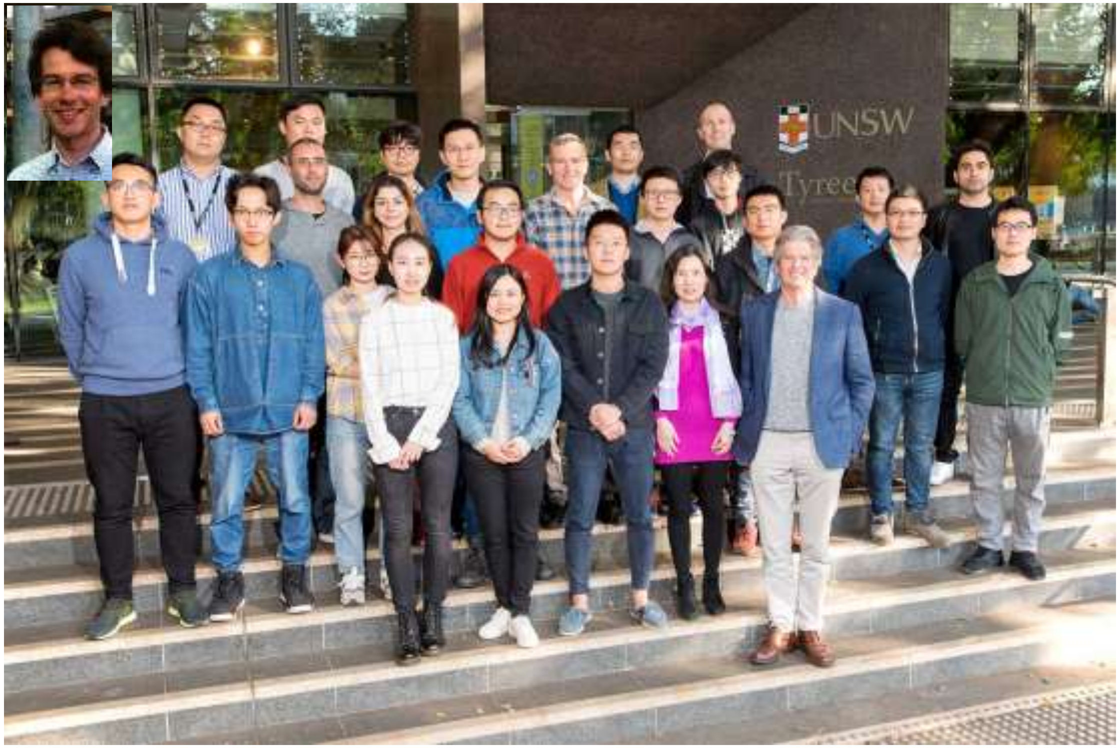
- Still a lot of unknowns about CZTS absorber materials & devices
  -interesting fundamentals
  -Never stand still!

- We are on the innovation highway!

- Global competition & collaboration
  will make the kesterite to keep rising



Acknowledgment



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ARENA

Australian Government

Australian Renewable Energy Agency

ACAP

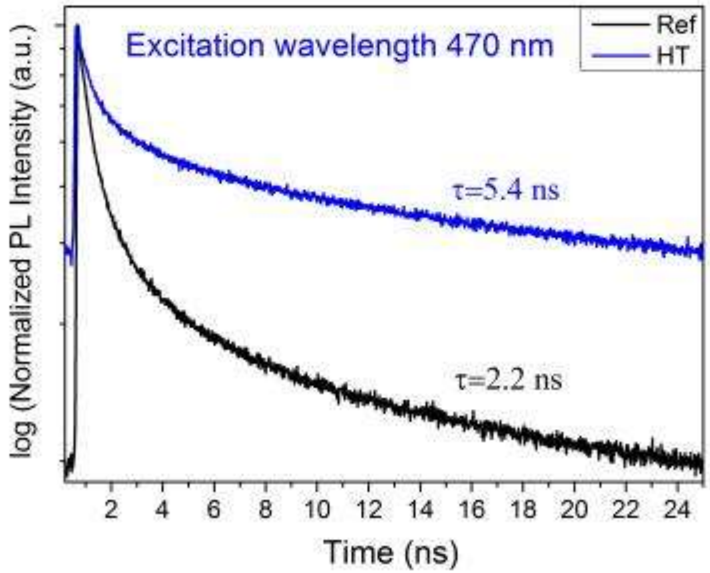
BAOSTEEL-AUSTRALIA

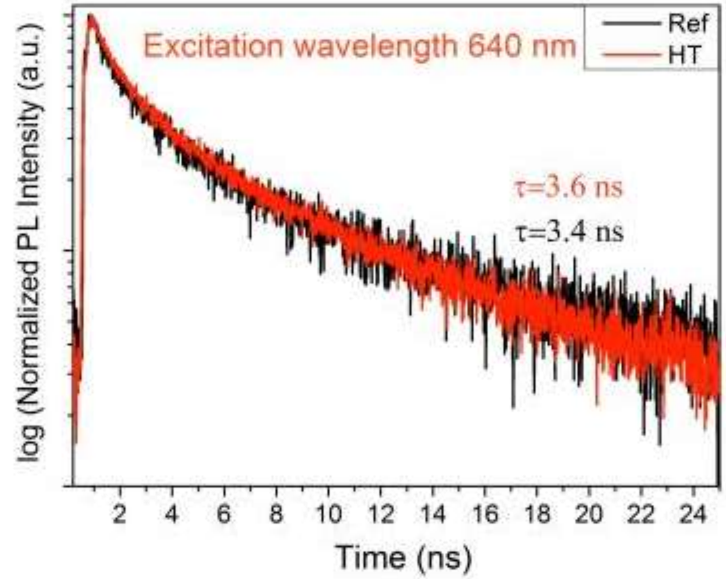
JOINT RESEARCH AND DEVELOPMENT CENTRE

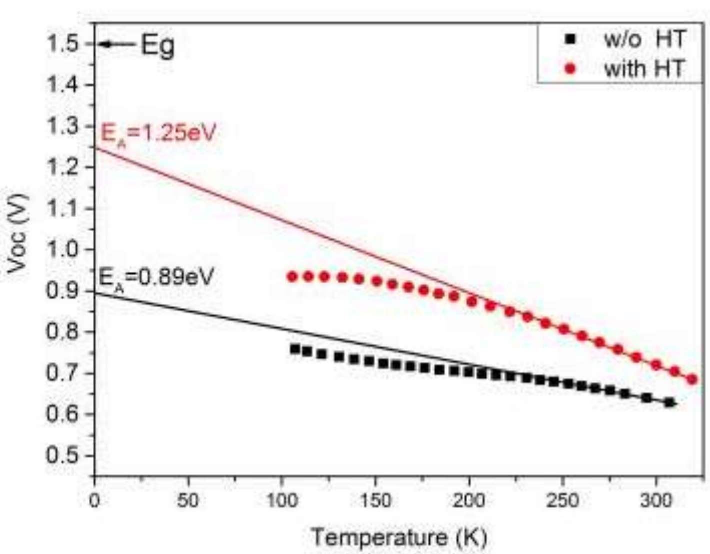
Questions and Thank You!

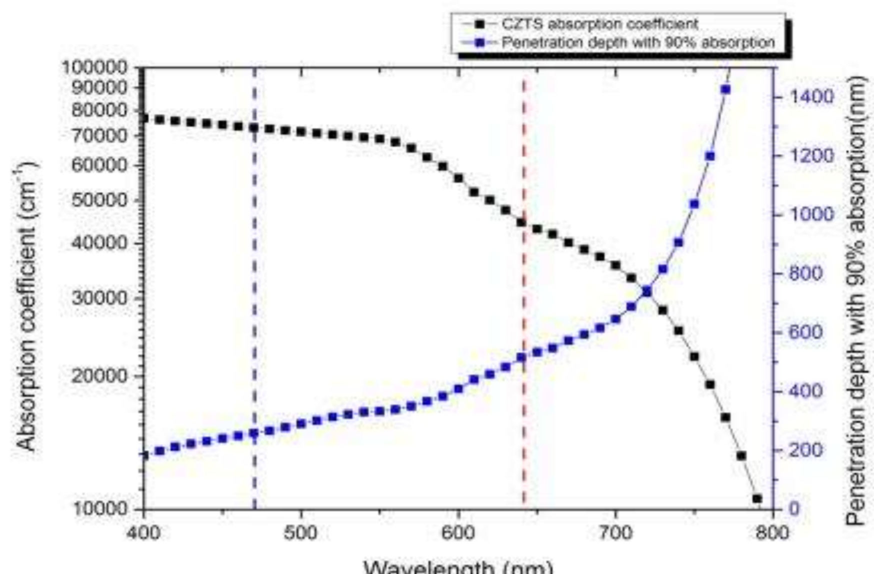
CZTS/CdS heterojunction-heat treatment

- **Heterojunction heat treatment mainly affect heterojunction region**





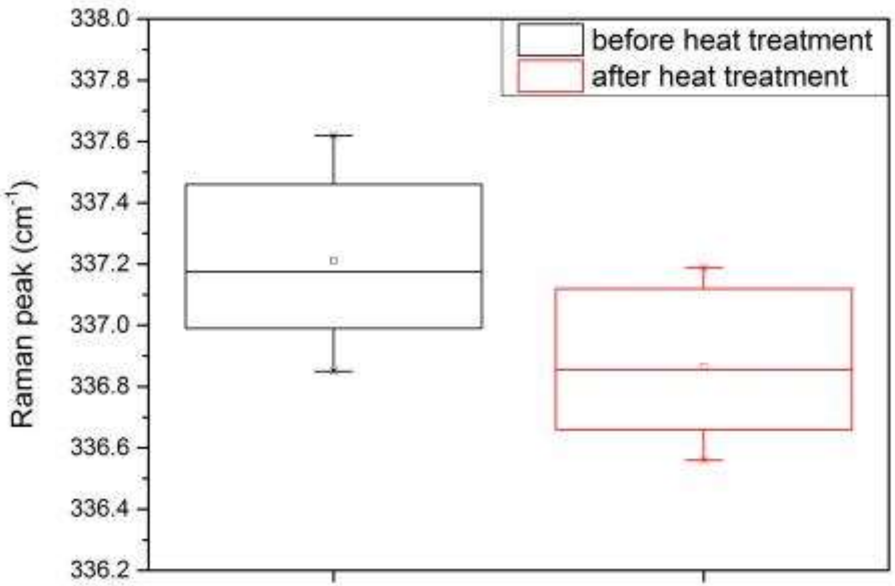


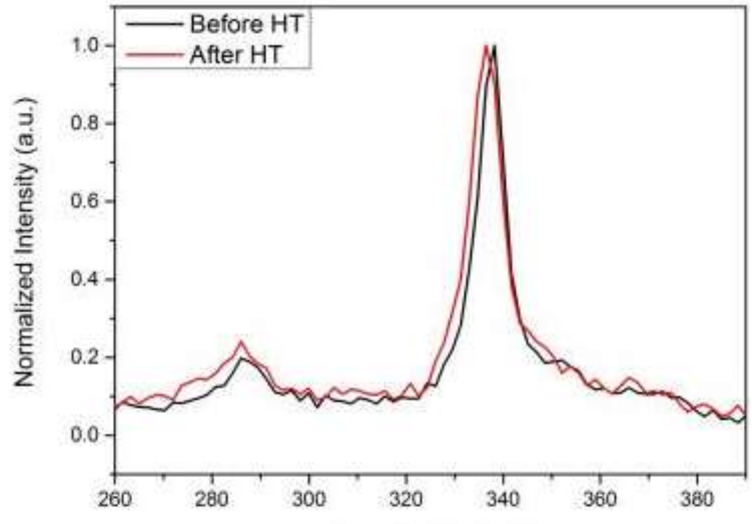


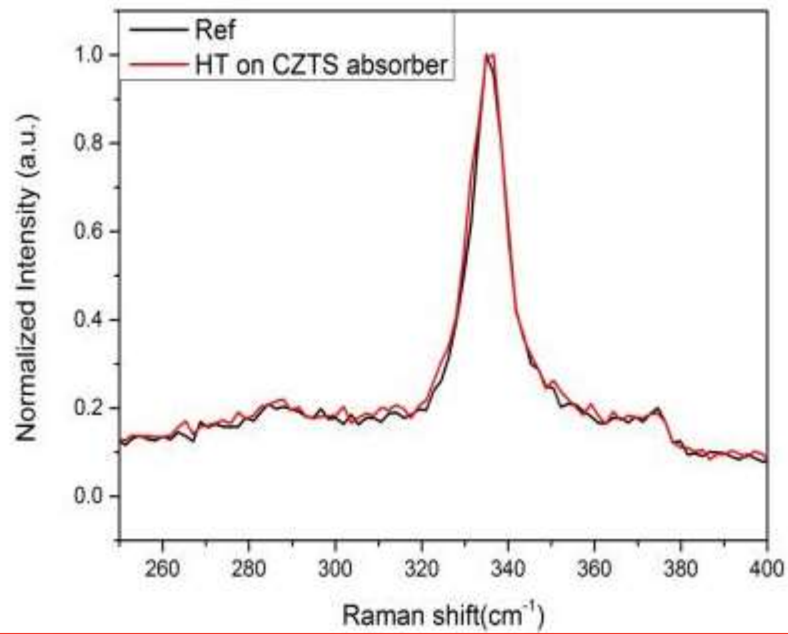
- Reduced non-radiative recombination is mainly located at heterojunction region.

CZTS/CdS heterojunction-heat treatment

- **Buffer side: Zn diffusion into CdS- ZnxCd1-xS**







Yan C., Huang J., Sun K., and et al., **Nature Energy**, vol. 3, 2018, pp. 764 - 772