Thin Film Photovoltaics: Advances in Earth Abundant Chalcogenide Technologies

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Preface

HZB Helmholtz Zentrum Berlin

Martin-Luther University
Halle-Wittenberg

PEOPLE

MARIE CURIE ACTIONS

IREC

Institut de Recerca en Energia de Catalunya
Catalonia Institute for Energy Research

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OUTLINE

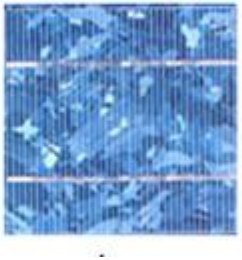
Current PV Technologies

Wafer-based Si

- Rigid (Si-wafer)
- Cut out of blocks (ingots)
- Technology mature, long lifetimes

mono-crystalline

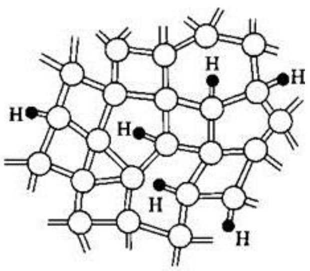
poly-crystalline



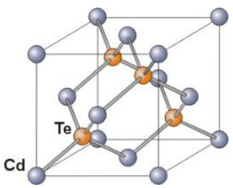
Thin Film PV

- Deposition of thin films, choice of substrate
- High cost reduction potential
- Low energy payback times

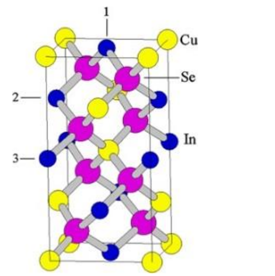
amorphous Si



CdTe



Cu(In,Ga)(S,Se)$_2$

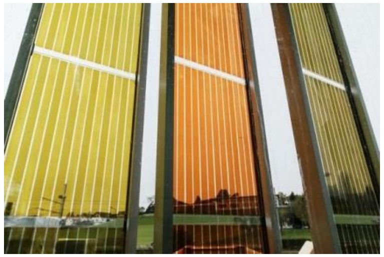


Emerging PV

[3]

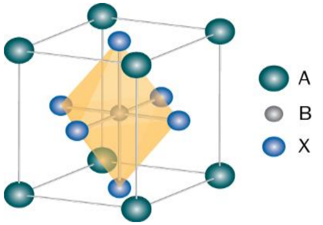
- Promising, but still immature technologies
- New materials and concept
- Efficiency or stability not yet proven

OPV/DSSC/QD



[1]

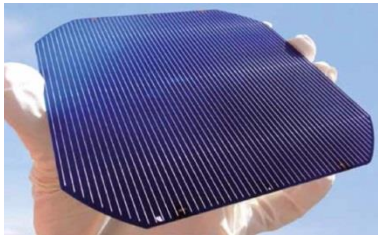
Perovskites

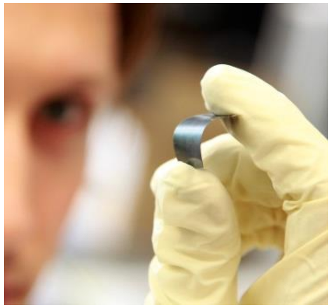


[2]

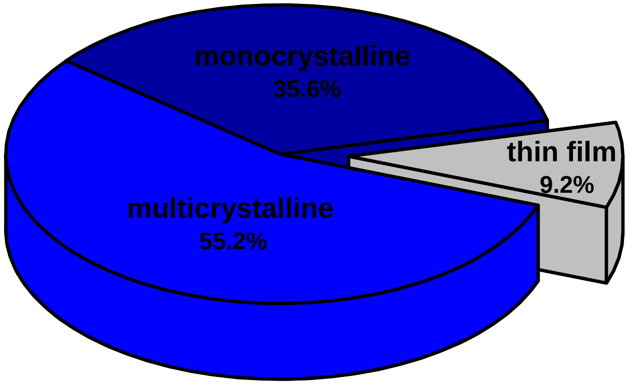
PV Technologies

	Record lab cell efficiency	Record module efficiency	Highest commercial module eff. 2016	Global production in 2014+ [GW_p]	Energy payback time* [years]
Silicon technology					
monocrystalline	25.6%	22.8%[a]	21.5%[a]	16.9 (35.6%)	4.1±2.0
multicrystalline	21.3%	19.2%.[b]	16.1%[b],16.2%[c]	26.2 (55.2%)	3.1±1.3
Thin film technology					
CdTe	22.1%	18.6%	16.4%[d]	1.9 (4.0%)	1.0±0.4
CIGS	22.6%	16.5%[f]	14.9%[e]	1.7 (3.6%)	1.7±0.7
a-Si	13.6%	10.9%	9.8%[g]	0.8 (1.6%)	2.3±0.7





Market share 2014



Thin film PV technology

- Minimal use of high purity martial
- Low energy payback time
- Extendable to flexible substrates
- Module price of 0.40€/W_p achievable although lower production capacity than Si

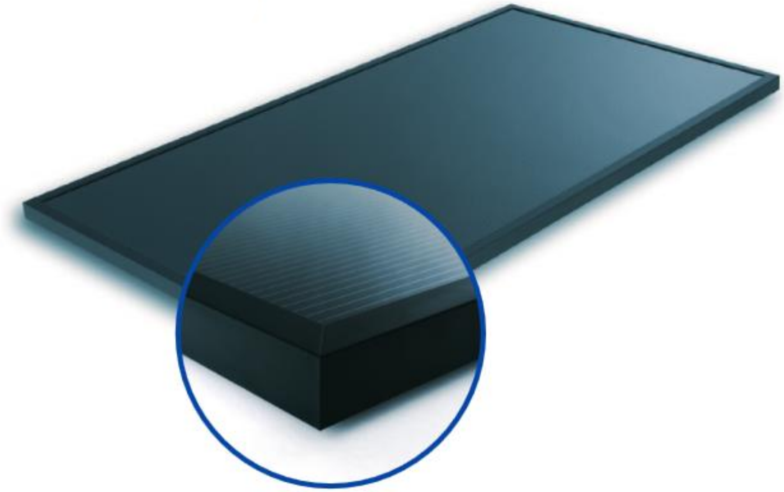
Green, M. A.et al. Solar Cell Efficiency TablesProg. Photovolt. Res. Appl. 2016, 24 (1), 3–11.
[a]Sunpower; [b]TrinaSolar; [c]SUNTECH; [d]FirstSolar; [e]Solibro; [f]TSMC (exited the solar industry in 2015); [g]Kaneka Solar Energy - Hybride between thin film mc-Si and a-Si; – status April 2016, +Fraunhofer ISE: Photovoltaics Report, updated: 11 March 2016
*Bhandari et al.[12] an insolation of 1700kWh/m^2/year (corresponds to southern Europe) and 30 years of lifetime for the calculations.

Why Thin Film?

High aesthetic value

Integration of CIGS solar modules in a BIPV façade developed by Manz CIGS Technology (www.manz.com)

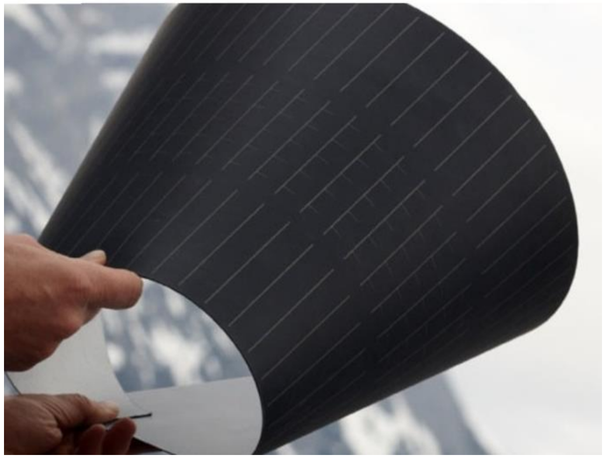
- **Design-driven projects**
- **BIPV**



Linion-F CIGS module from Soltecture (www.soltecture.com)

Why Thin Film?

Choice of substrate (low weight, flexible substrates)



http://www.sunplugged.at

- Glass
- Stainless steel
- Aluminum
- Polymers
- Ceramics

Solé Power Tile by SRS Energy.

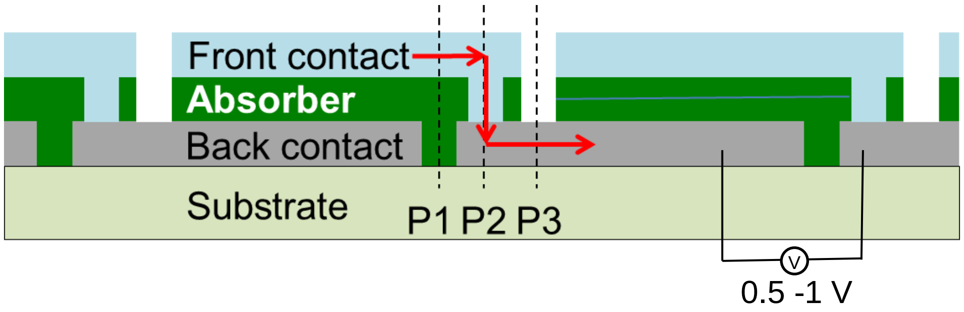
Uni-Solar photovoltaic sheet modules

Integration of CIGS flexible modules on metal roofs (http://sunplugged.at)

Why Thin Film PV?

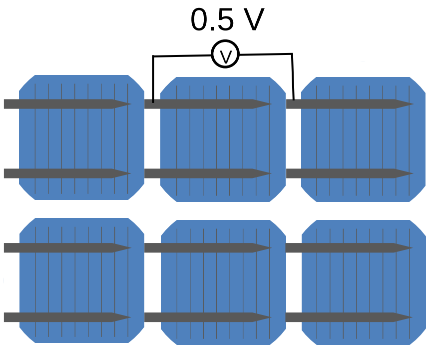
High cost reduction potential with low-cost technologies

Monolithic integration

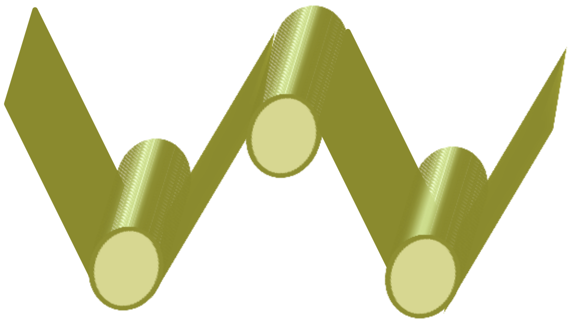


vs.

Wafer integration



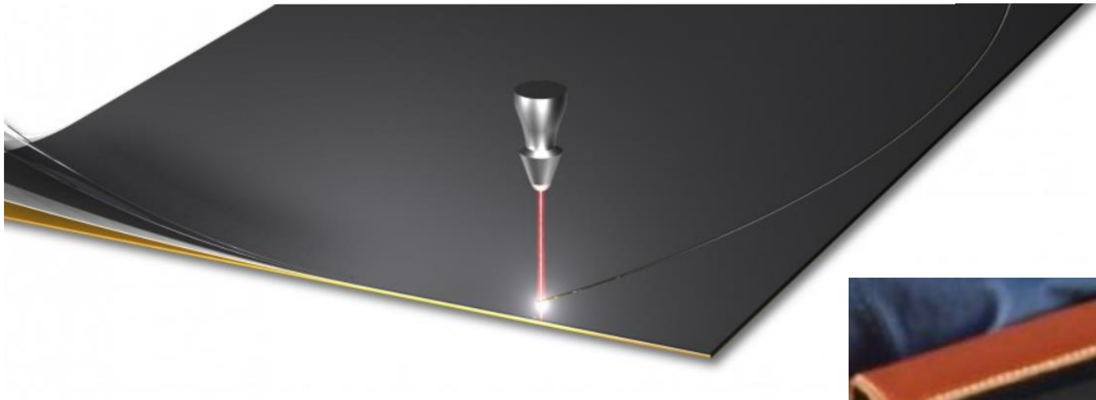
Roll-to-Roll Processing

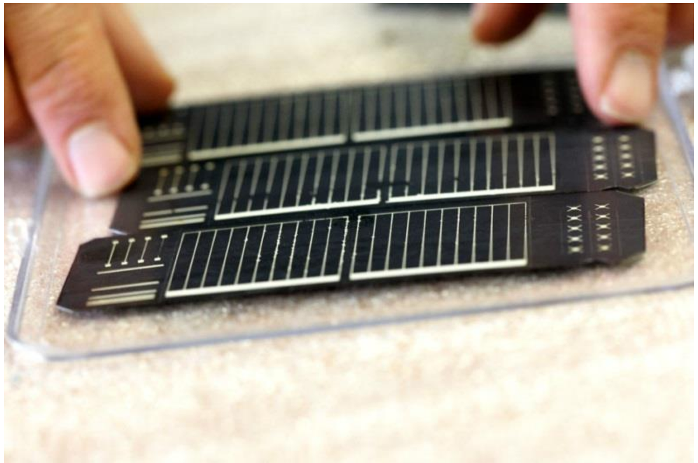


- **Low material consumption**
- **Large area deposition**
- **Monolithic integration**
- **Possibly Roll-to-Roll production**

Why Thin Film PV?

Flexibility of module size and shape – possibility to design of customised modules

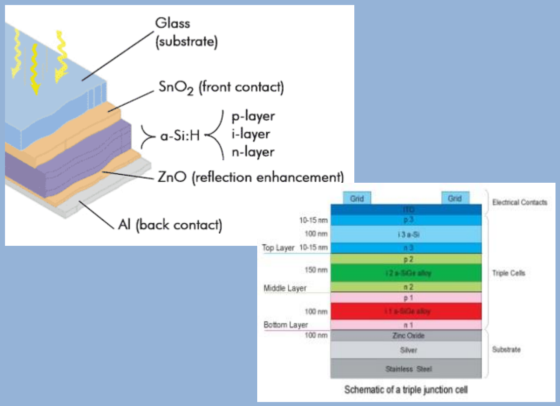




http://www.sunplugged.at/

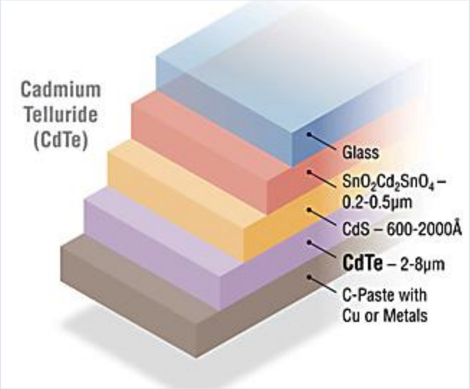
Thin Film PV – Main Commercial Technologies

a-Si (superstrate)



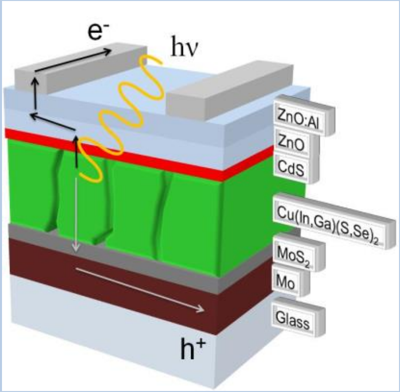
- *Low cost demonstrated*
- *Earth abundant elements*
- *Instability*
- *Medium efficiencies demonstrated for multi-junction cells*

CdTe (superstrate)



- *High efficiency*
- *Low cost has been demonstrated*
- *Te is a scarce element*
- *Cd is toxic and contaminant*

CIGS (substrate)



- *High efficiency*
- *Relatively low cost*
- *In an Ga are scarce element*
- *CZTSSe good alternative material*

SEMS at IREC

1. **Thin Film Photovoltaics**
   - PV Technologies(CIGS / CdTe/ a-Si)
   - Why Thin Film PV?
   - Technologies
2. **The Solar Energy Materials and Sytems group at IREC**
   - Presentation of the group and institute
   - Main research lines
   - Examples
3. **The kesterite solar cell**
   - Standard process and device architecture
   - The absorber material
   - Challenges
4. **Ge boosting CZTS cell efficiencies**
   - Experimental – Ge layer optimization
   - Growth model and impact on crystal grains/grain boundaries
   - Bifacial crystallisation and Ge-Na interaction

5. **Conclusions**

Catalonia Institute for Energy Research

Founded in 2008, and located in Barcelona, Spain:

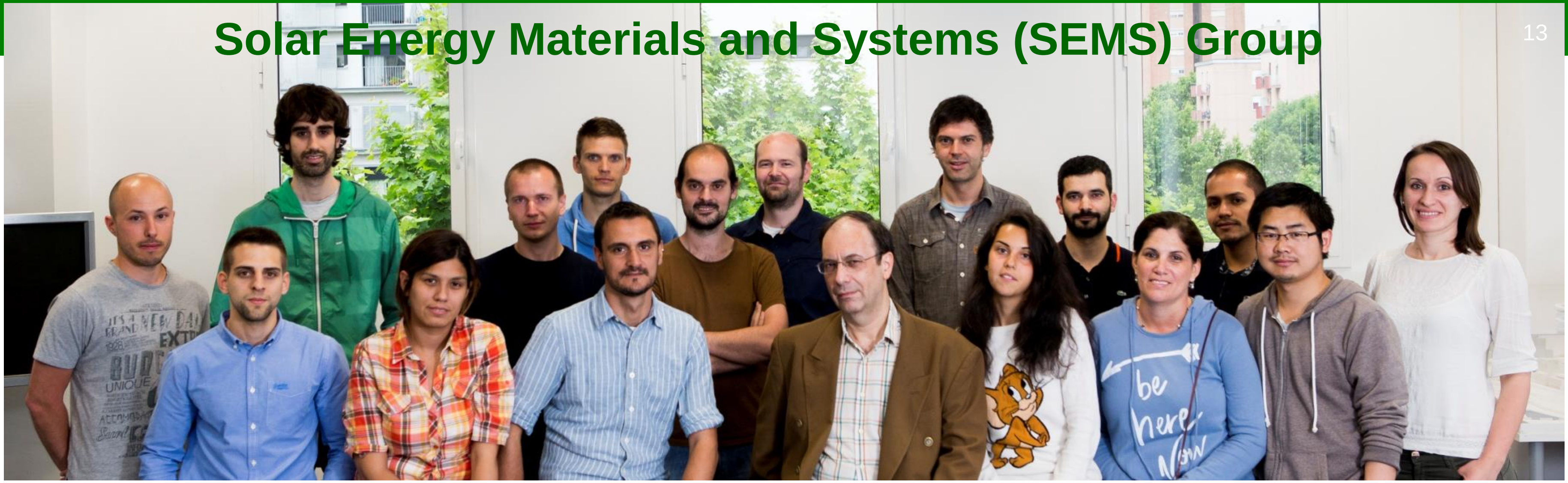
Aim: "..to contribute to the objective of creating a more sustainable future for energy usage and consumption, keeping in mind the economic competitiveness and providing society with the maximum level of energy security…"

Main activity: Research for Technology Development

Six main areas:

- **Advanced materials for energy**
  - **Solar Energy Materials and systems**
  - Functional nanomaterials
  - Materials and catalysts
  - Nanoionics and fuel cells
  - Energy storage and harvesting
- Lighting
- Offshore wind energy
- Electrical engineering
- Bioenergy and biofuels
- Thermal energy and building performance

Solar Energy Materials and Systems (SEMS) Group



Group leader: Prof. Alejandro Pérez-Rodríguez
Head of processes lab.: Dr. Edgardo Saucedo
Head of characterization lab.: Dr. Victor Izquierdo-Roca

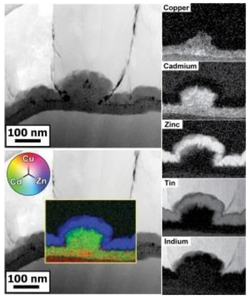
- **6 Experienced researchers**
  - Dr. Paul Pistor (Marie Curie)
  - Dr. Marcel Placidi (Mineco PosDoc)
  - Dr. Mónica Colina (Flexart)
  - Dr. Florián Oliva (Scalenano)
  - Dr. Moisés Espíndola (Novazolar)
  - Dr. Markus Neuschitzer

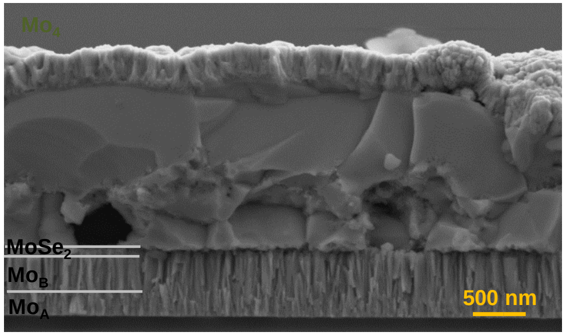
- **6 PhD Students**
  - Haibing Xie (China council fellow)
  - Sergio Giraldo (FPI Sunbeam)
  - Laura Acebo (IREC fellow)
  - Ignacio Becerril (Ecoart)
  - Laia Arqués (Novacost)
  - Alejandro Hernández (FPI Nascent)

- **2 Laboratory Technicians**
  - Dr. Diouldé Sylla (Electrochemistry and Safety)
  - Yudania Sánchez (Chemistry)

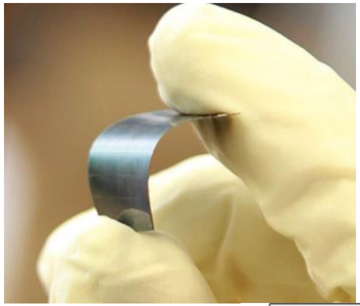
Main Research Lines

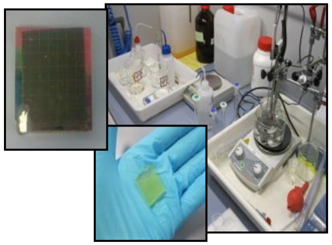
Development of high efficiency kesterite devices: *Engineering of the different device components for high effficiency kesterite thin film solar cells ($Cu_2ZnSnSe_4$, Cu_2ZnSnS_4 and $Cu_2ZnSn(S,Se)_4$*



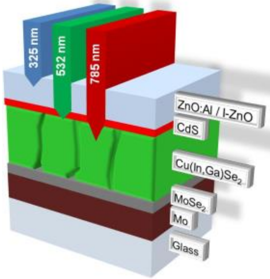


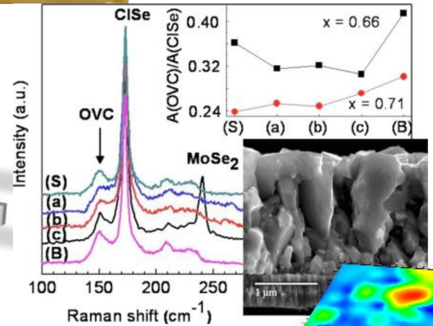
New materials and device concepts: *Cu-based chalcogenides, new absorber alloys, alternative buffer layers, alternative substrates, bifacial/semi-transparent concepts*

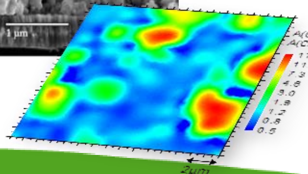




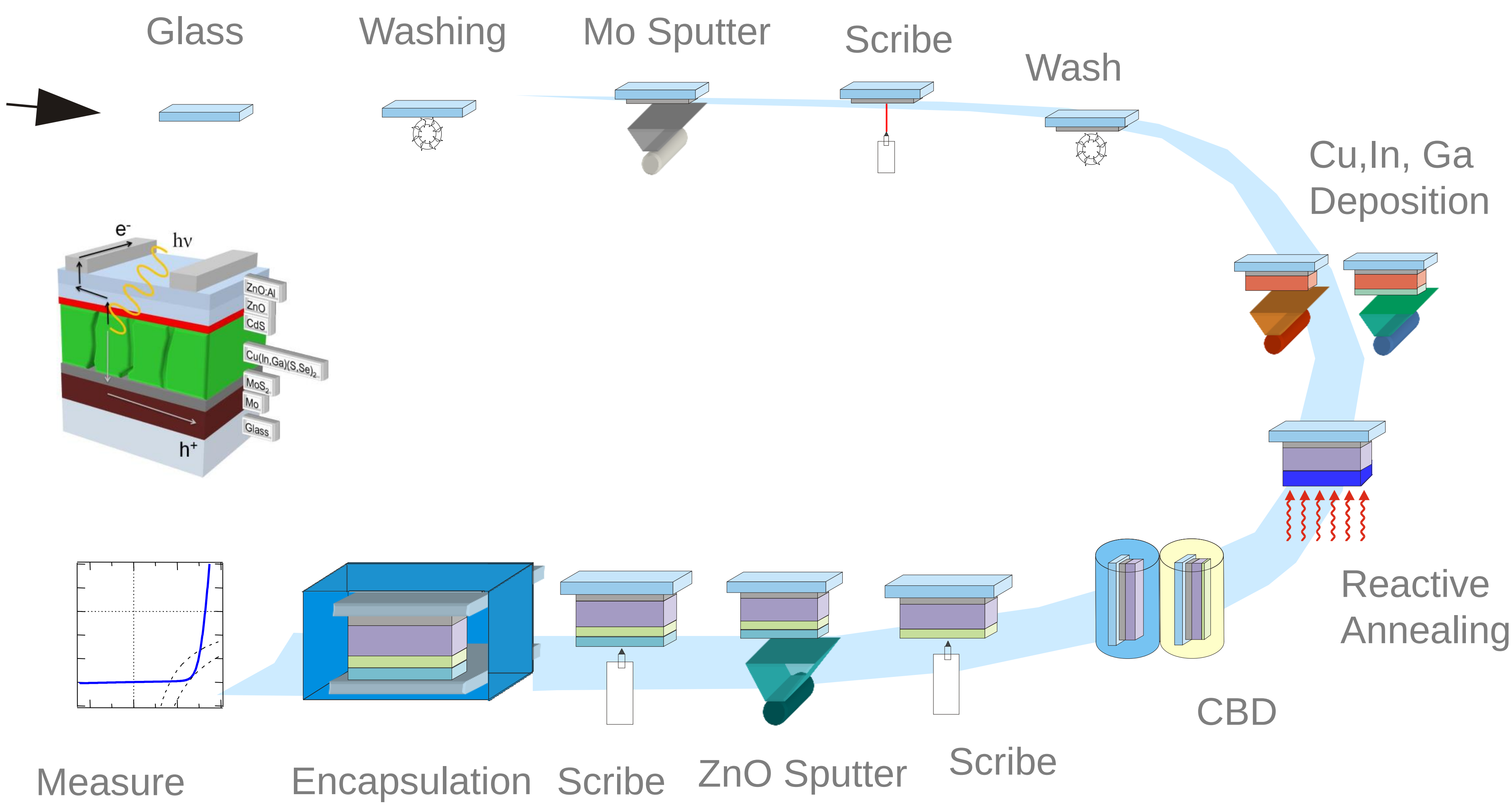
Advanced characterisation processes in thin film PV technologies: *Development of techniques suitable for Quality Control & Process Monitoring (Raman spectroscopy, other light scattering based methods)*







Process and Quality Control



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Catalonia Institute for Energy Research

Picture adapted from Roland Scheer, Martin-Luther-University Halle

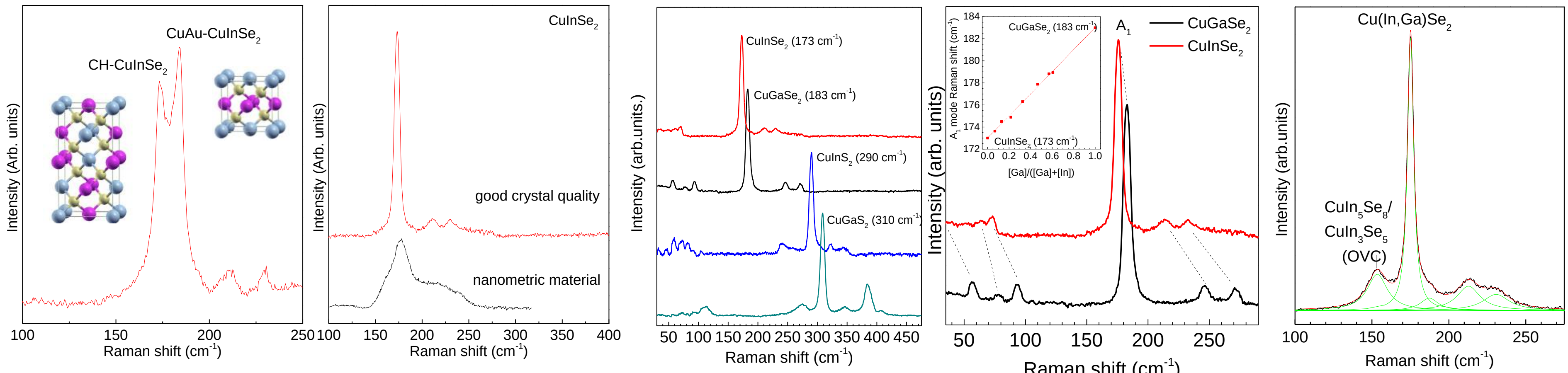
Process and Quality Control

Raman Spectroscopy

Probes atomic vibrations in a crystal (phonons)

Sensitive to:
Crystal structure, composition, secondary phases, defects, stress (thickness)

Crystalline structure | Crystalline Quality/stress/strain | Atomic/alloy Composition | Secondary phases



Interest in Raman scattering for non-destructive, contact-less, fast assessment of the different layers in the solar cell

Alternative substrates

Substrates and applications

Soda-lime Glass

- Mechanical properties
- Thermal properties
- Alkali (Na, K)

High efficiency traditional modules
WR 12.6%
IREC 10.6%

Alternative

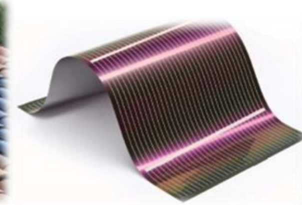
Ceramic
- Non-flat
- No alkali
- Impurities

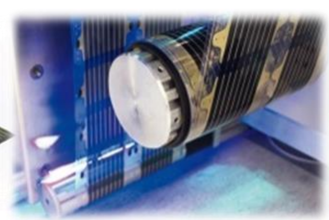
Steel
- Rough
- No alkali
- Impurities

Polyimide
- Non-rigid
- No alkali
- Low T

Numerous applications!

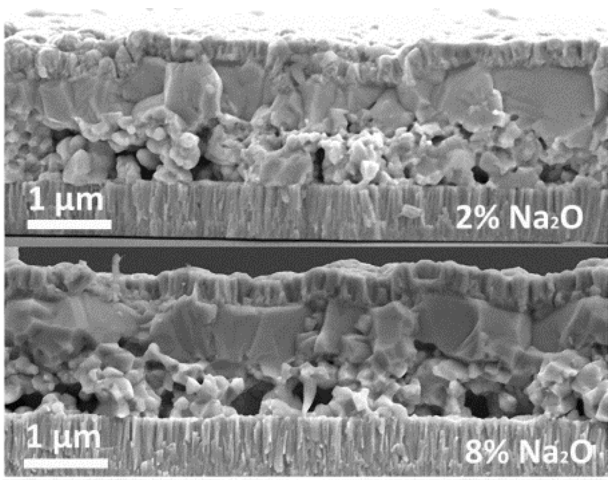
Building-integrated PV | Roll-to-roll | Flexible modules

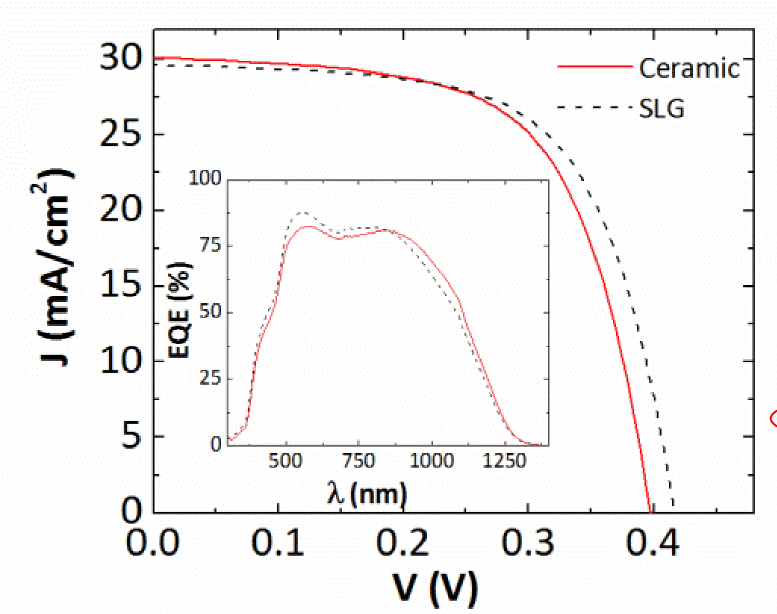


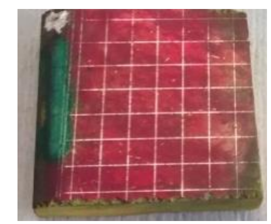


Kesterite solar cells on ceramic tiles

- Solar cells fabricated on ceramic substrates with an **vitreous enamel**: **smooth surface, barrier for impurities and alkali source**.
- In a first attempt, samples with good crystalline quality and efficiencies of up to 4.6% were achieved → no clear relation of results with Na_2O%
- Further optimization led to a record **7.5% efficiency** cell showing the huge potential of these substrates





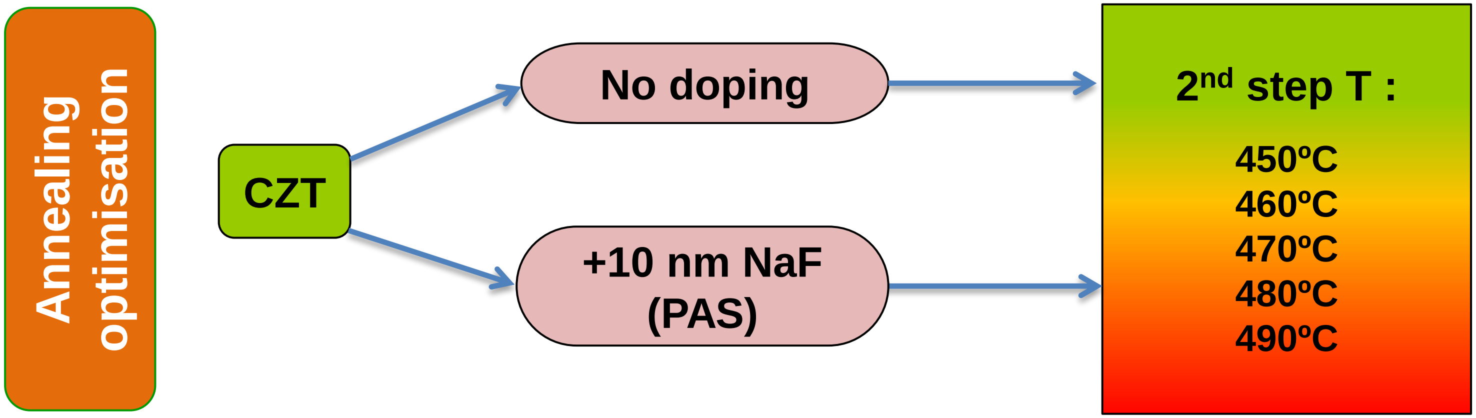


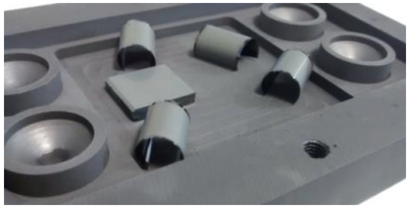
Ceramic	**7.5%**
SLG ref	7.9%
IREC record	10.6%

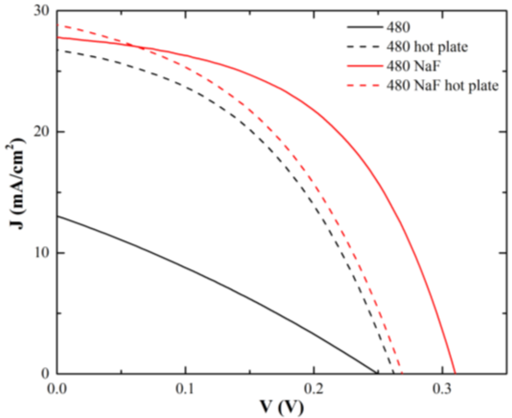
I. Becerril et al., Solar Energy Materials and Solar Cells, 154, pp. 11-17 (2016)

Polyimide

- Extremely **light** and **flexible**
- Low surface roughness (Ra < 3 nm)
- N**o metallic impurities**
- Good chemical and mechanical **stability**
- Efficiencies > 20% have been obtained for CIGS
- **No alkaline dopants (Na, K)**
- **Process temperature limit: 500ºC**







New records CZTSe on polyimide foil
4.4% efficiency (Na-doped)
3.1% efficiency (undoped)

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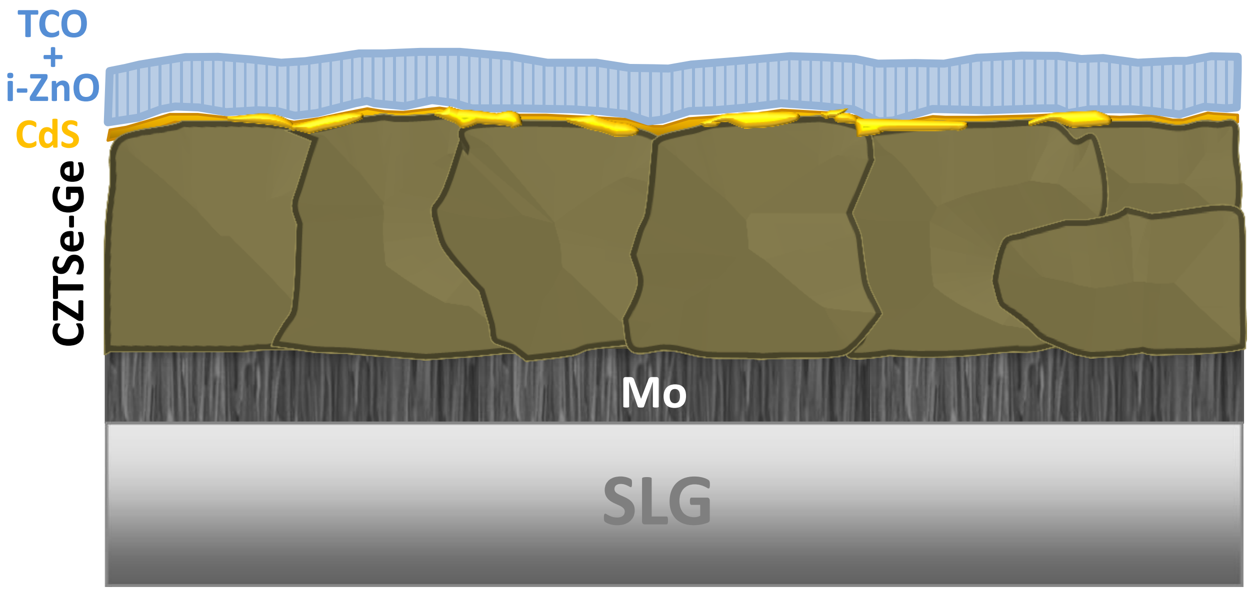
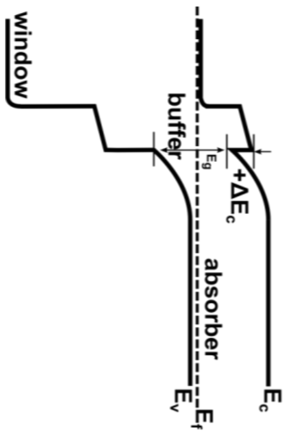
Device architecture



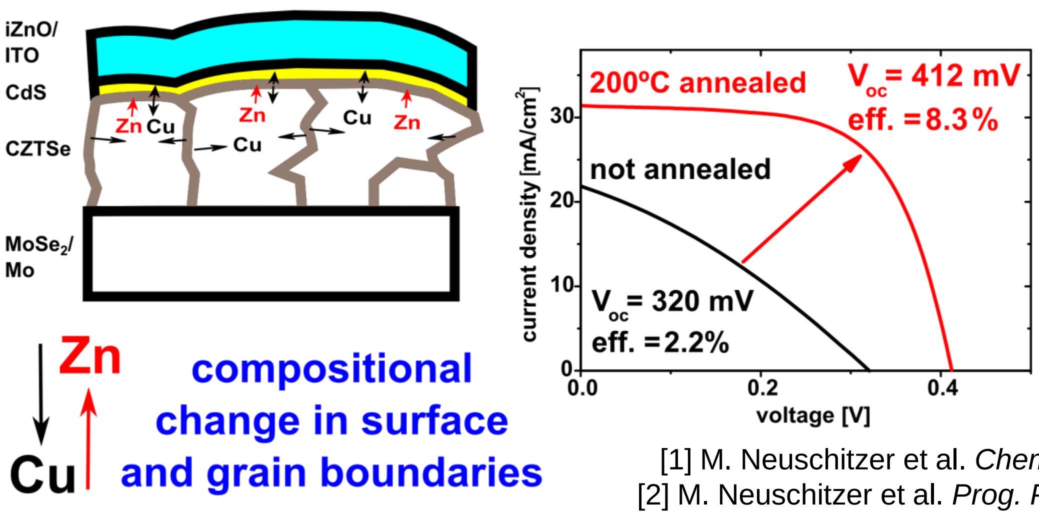


- So far, same structure than CIGS based solar cells
- Some technological problems associated to this structure that need to be solved in order to increase the conversion efficiency of Kesterites
- Problems at the interfaces (buffer/absorber, back contact, secondary phases)

Through an intense, combined work at IREC concerning the interfaces, high efficiencies of up to 8.3 % could be obtained:

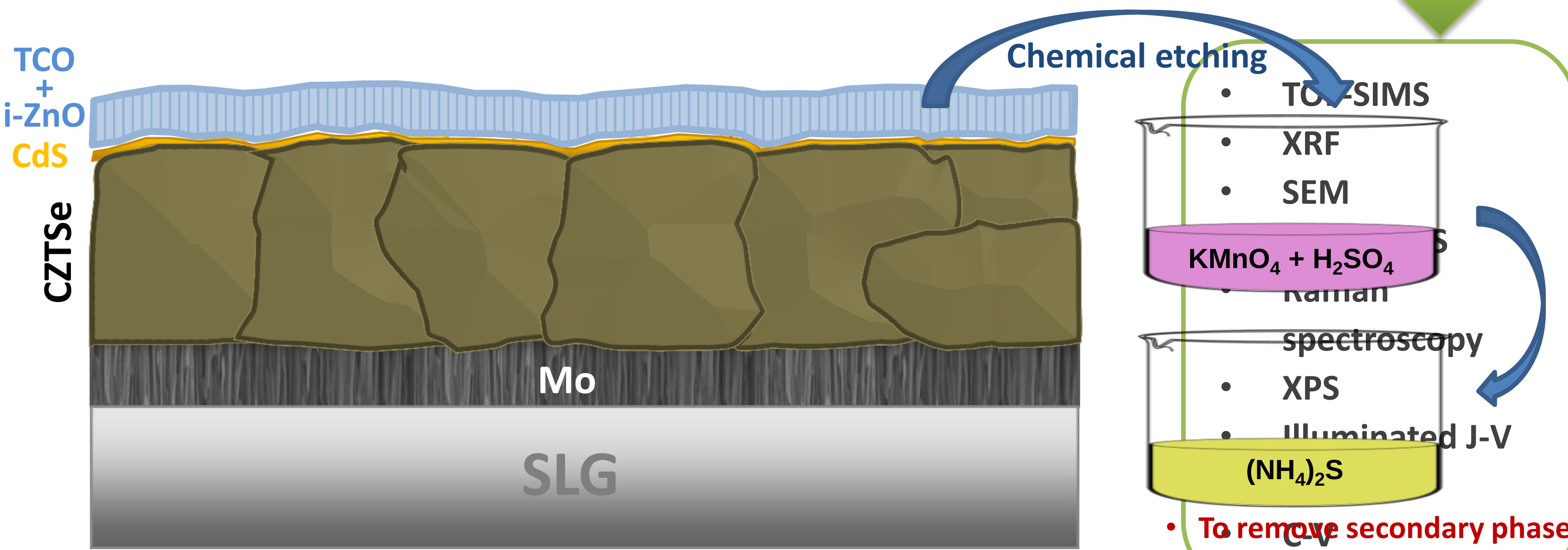
- Etching processes to remove secondary phases and to passivate the absorber surface[1]
- Thermal induced re-ordering of Cu-Zn at the absorber surface (Post Deposition Annealing)[2]
- Buffer layer optimization ($Cd(NO_3)_2$ precursors)[3]
- Back contact engineering (Multi-layer Mo to avoid overselenization and CZTS decomposition[4]

200ºC annealing of CZTSe solar cells



[1] M. Neuschitzer et al. *Chemistry of Materials 2015 27 (15), 5279-5287*
[2] M. Neuschitzer et al. *Prog. Photovolt: Res. Appl., 2015, 23: 1660–1667*
[3] S. Lopez-Marino et al. *Chem. - Eur. J.* 2013, 19, 14814
[4] Lopez-Marino, et al. *Nano Energy* 2016, DOI:10.1016/j.nanoen.2016.06.034

Solar cell processing



- **To remove secondary phases, mainly ZnSe [1,2]**
- **To passivate the surface [2]**

[1] S. Lopez-Marino et al. Chem. - Eur. J. 2013, 19, 14814
[2] H. Xie et al. ACS Appl. Mater. Interfaces 2014, 6, 12744

The CZTS crystal structure

Characteristics of the kesterite structure….

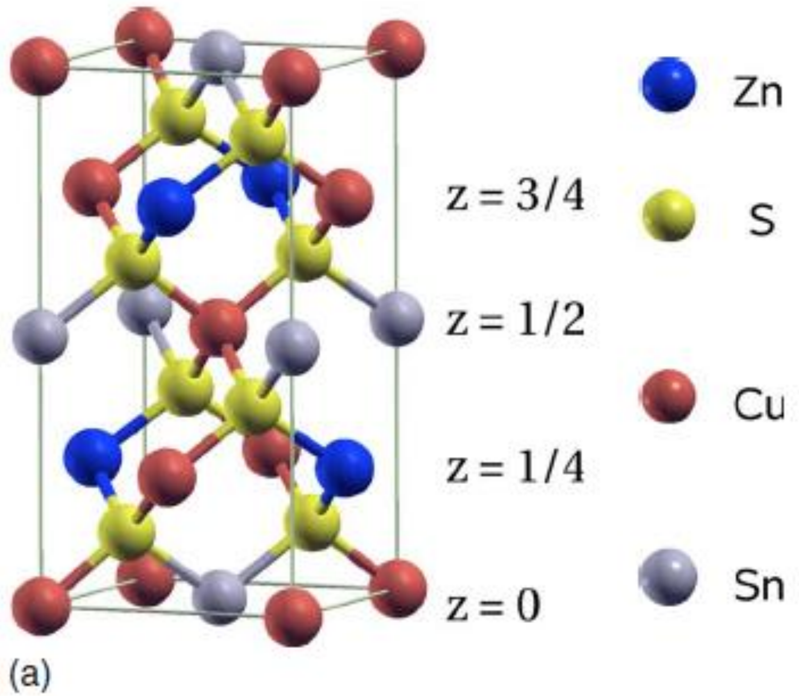
Cu-Sn plane

Cu-Zn plane

Cu-Sn plane

Cu-Zn plane

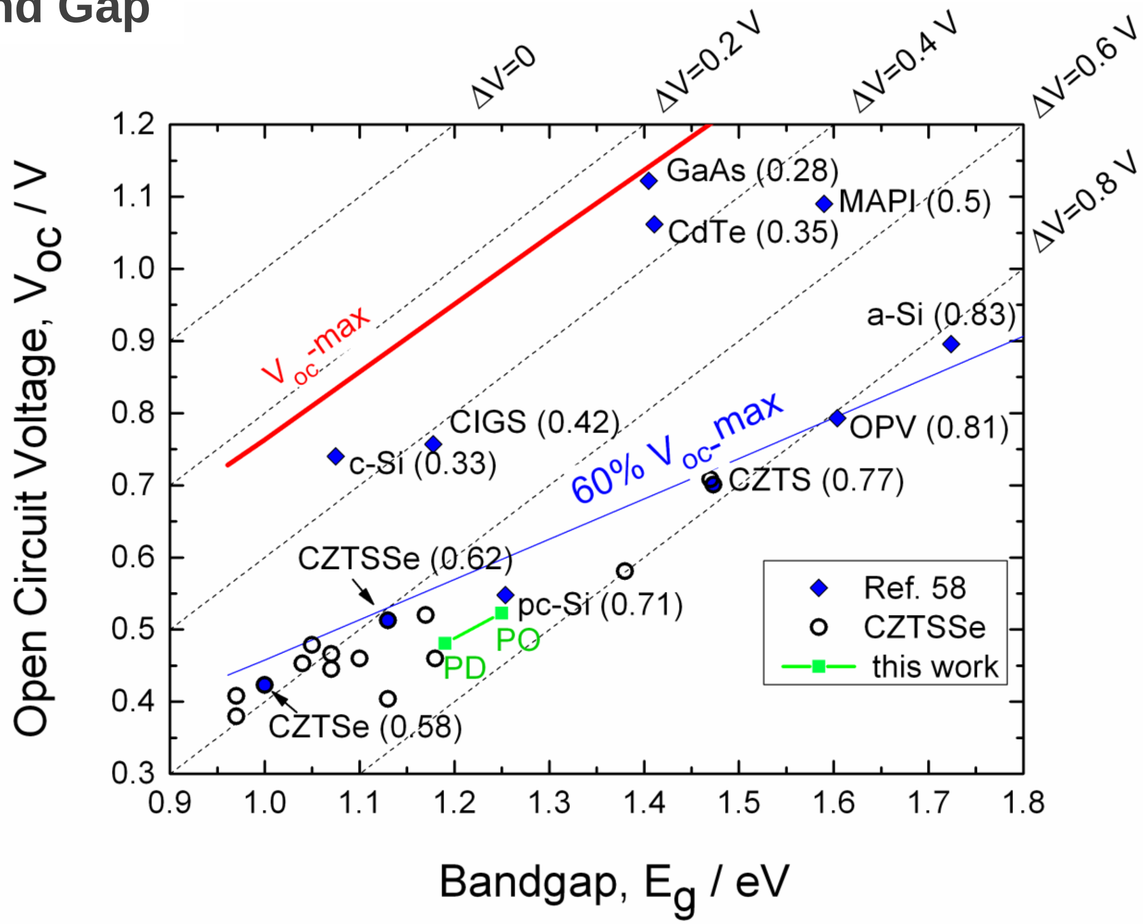
Cu-Sn plane



- ❖ Exchange of Cu and Zn atoms in the CuZn planes costs only very small energy
- ❖ Cu and Zn exchange can introduce disorder in the lattice

J. Paier et al, Phys. Rev. B 79, 2009, 115126.

V_{OC} vs Band Gap



- Voltage deficit for kesterites between 0.55-0.80 V
- Voltage deficit of 0.42 V for CIGS, 0.35 for CdTe and 0.33 V for c-Si

[1] S. Bourdais et al., Adv. Energy Mater. 2016, DOI: 10.1002/aenm.201502276.

Voltage deficit

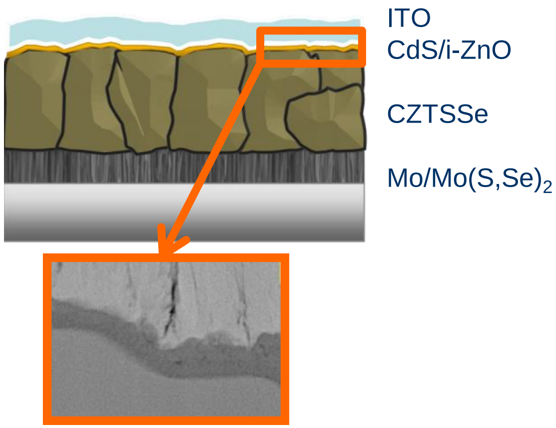
➤ **What are the possible origins of this large V_{OC} deficit?**

Three main reasons for V_{oc} deficit

Interface recombination

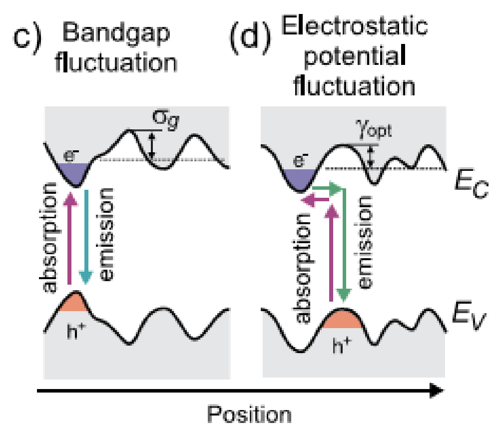
Front interface (CdS/CZTSSe)[3] due to:

- Wrong band-alignment
- Un-passivated surface
- Secondary phases



Bandgap/electrostatic potential fluctuation [4]:

Cu/Zn disorder is one of the most probable reasons



Bulk recombination [5]

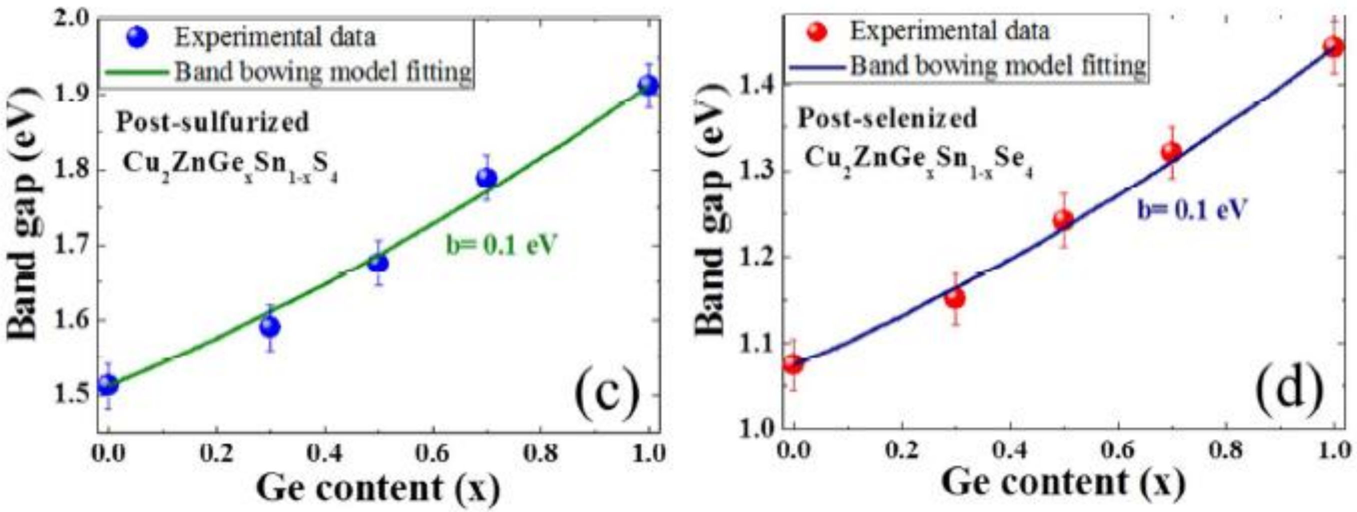
- Deep defects
- Secondary phases inclusions/network
- GBs recombination

[1] Ph. Jackson et al. Phys Status Solidi rrl 9(1) (2014) 28-31 [2] W. Wang et al. Adv. Energy Mater. 4 (2014) 1301465
[3] F. Liu et al. Adv. Energy Mater. (2016) 1600706. [4] T. Gokmen et al. Appl. Phys. Lett. 103, (2013) 103506. [5] T. Gokmen et al. . Adv. Energy Mater. 4, (2014) 1300543.

Band gap tuneability

At least in part, the high efficiencies obtained for CIGS and CdTe are assigned to carefully tuned band gap gradients within the absorber, enhancing charge carrier collection and reducing interface recombination

- Band gap can be easily tuned for kesterites between 1.0 eV to 3.6 eV by changing both, cations (mainly in Sn-site) and anions[1]



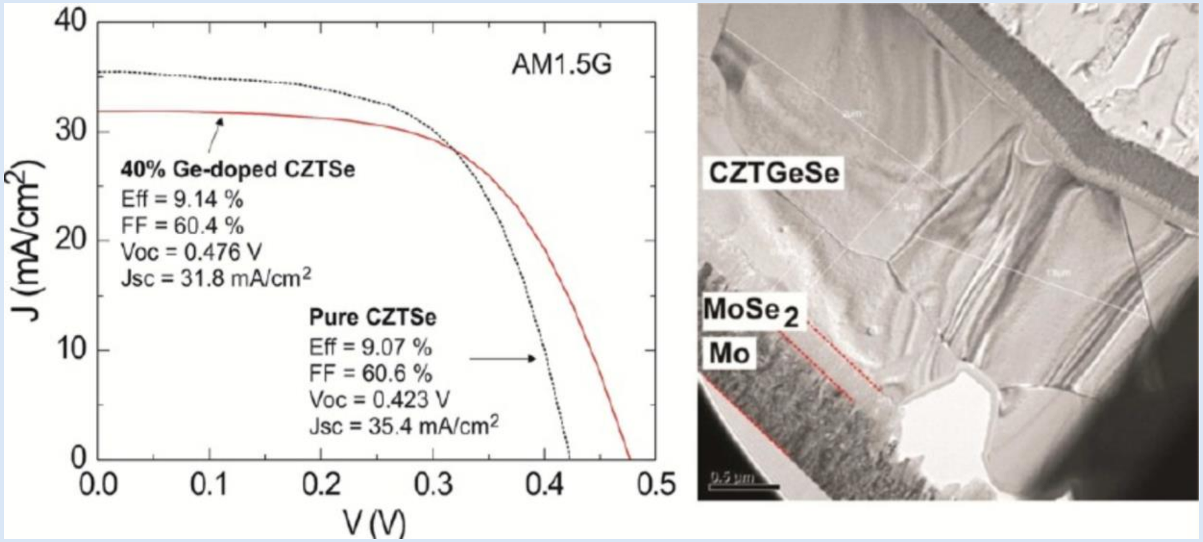
- **$Cu_2ZnSn(S_{1-y}\text{-}Se_y)_4$ – 1.00 – 1.45 eV**
- **$Cu_2Zn(Sn_{1-x}Ge_x)(S_{1-y}\text{-}Se_y)_4$ – 1.00 – 2.85 eV**
- **$Cu_2Zn(Sn_{1-x}Si_x)(S_{1-y}\text{-}Se_y)_4$ – 1.00 – 3.6 eV**
- **$Cu_2(Zn_{1-x}Cd_x)Sn(S_{1-y}\text{-}Se_y)_4$ – 0.96 – 1.45 eV**
- **$(Cu_{1-x}Ag_x)_2ZnSn(S_{1-y}\text{-}Se_y)_4$ – 1.00 – 2.01 eV**

[1] D. B. Khadka, J. Kim, *J. Phys. Chem. C* **2015**, *119*, 1706

1. **Thin Film Photovoltaics**
   - PV Technologies(CIGS / CdTe/ a-Si)
   - Why Thin Film PV?
   - Technologies
2. **The SEMS group at IREC**
   - Presentation of the group and institute
   - Main research lines
   - Examples
3. **The kesterite solar cell**
   - Standard process and device architecture
   - The absorber material
   - Challenges
4. **Ge boosting CZTS cell efficiencies**
   - Experimental – Ge layer optimization
   - Growth model and impact on crystal grains/grain boundaries
   - Bifacial crystallisation
5. **Conclusions**

Ge in CZTSSe: Alloying based strategies

IBM (S. Bag et al, Chem. Mater. 24 (2012) 4588–4593. DOI:10.1021/cm302881g)



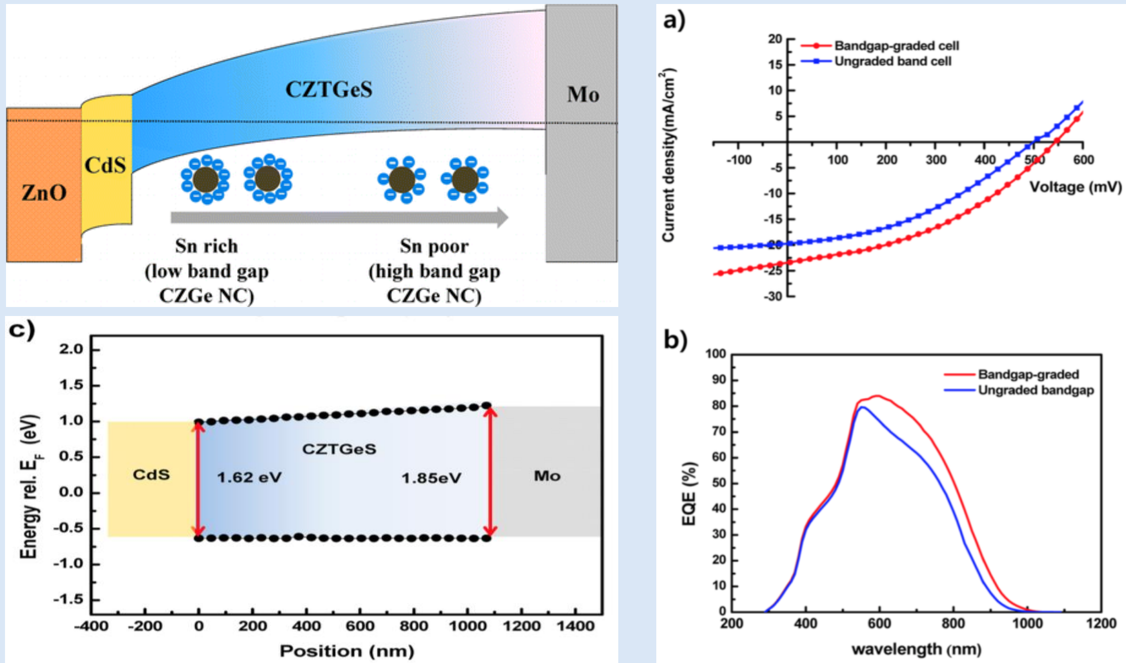
First device reported with Ge-alloying in **hydrazine-processed** CZTSe:

- **40% Ge-substituted** absorber
- **9.14%** power conversion **efficiency** (versus 9.07%)
- **Higher open-circuit voltage** (0.476 Vs 0.423)
- However: **no improvement of Voc deficit** (Voc increase related mainly to Eg increase)

➔ *Promising results indicating an alternative way to **tailor the band gap** of the CZTSSe absorber and demonstrating compatibility of Ge with CZTS state of the art processes*

Ge in CZTSSe: Alloying based strategies

Yonsei University (Korea) (in colab. with KIMM, KRICT, Univ. of Washington)
(I. Kim et al, Chem. Mater. 26 (2014) 3957-3965. DOI 10.1021/cm501568d)



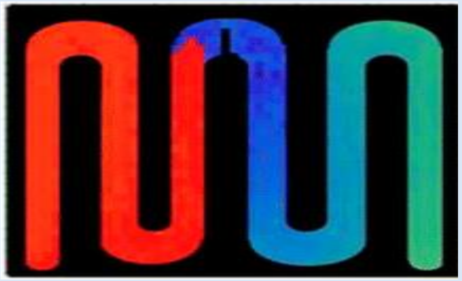
First demonstration of Bandgap-grading using CZTGeS alloying:

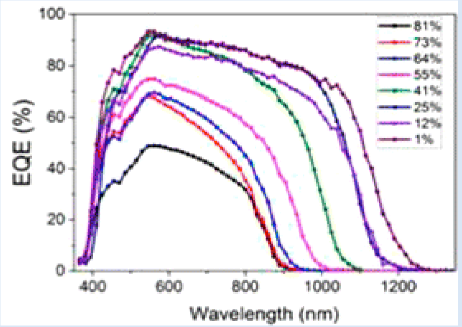
- ➢ Based on metal chalcogenide complex (MCC) ligand capped nanocrystals (NCs)
- ➢ Higher short circuit current (23.3 mA/cm^2 vs 19.5 mA/cm^2) and Voc (0.52 V vs 0.48 V) in relation to the constant band gap case
- ➢ Power conversion **efficiency** of **6.3% (vs 4.8% for constant band gap absorber)**
- ➢ Variation of the bandgap from 1.85 eV (back) to 1.62 eV (front)

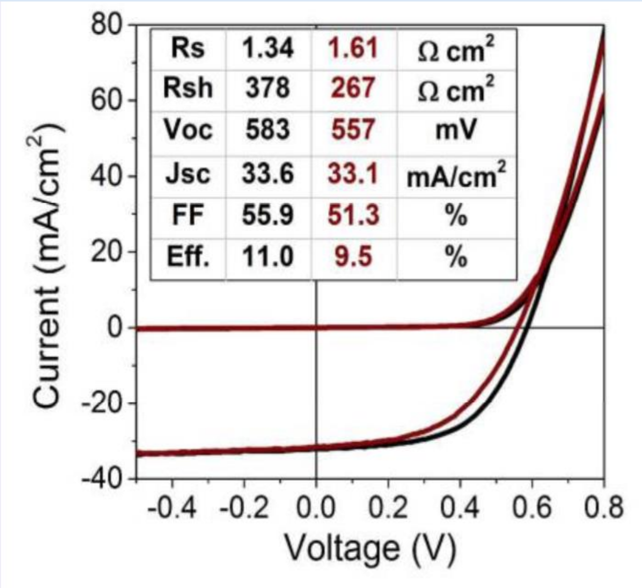
Ge in CZTSSe: Alloying based strategies

Univ. of Washington

(A.D. Collord, H.W. Hillhouse. Chem. Mater. (2016). DOI:10.1021/acs.chemmater.5b04806.







Study of CZTGeSSe devices as function of Ge/(Ge+Sn) rel. content in broad composition range (from 0% to 90%) using spray coated absorbers with molecular inks:

- **Increase of Eg up to 1.3 eV for Ge/(Ge+Sn) up to 50% without any loss in optoelectronic material quality**
- **Highest efficiency: 11.0% with 25%Ge relative content** (band gap of about **1.2 eV**) with **reduction of Voc deficit** (63% of theoretical Voc as compared to 58% for the current record device without Ge)

In summary: Ge alloying has demonstrated…

- **Increased V_{OC}** but in some cases linked to **higher band-gap**
- Potential for **graded band-gap concepts**
- **Improvement** of **grain growth** and **crystallinity**
- **Increased** minority charge **carrier lifetime**
- Large potential to **reduce V_{OC} deficit** in current kesterite technology

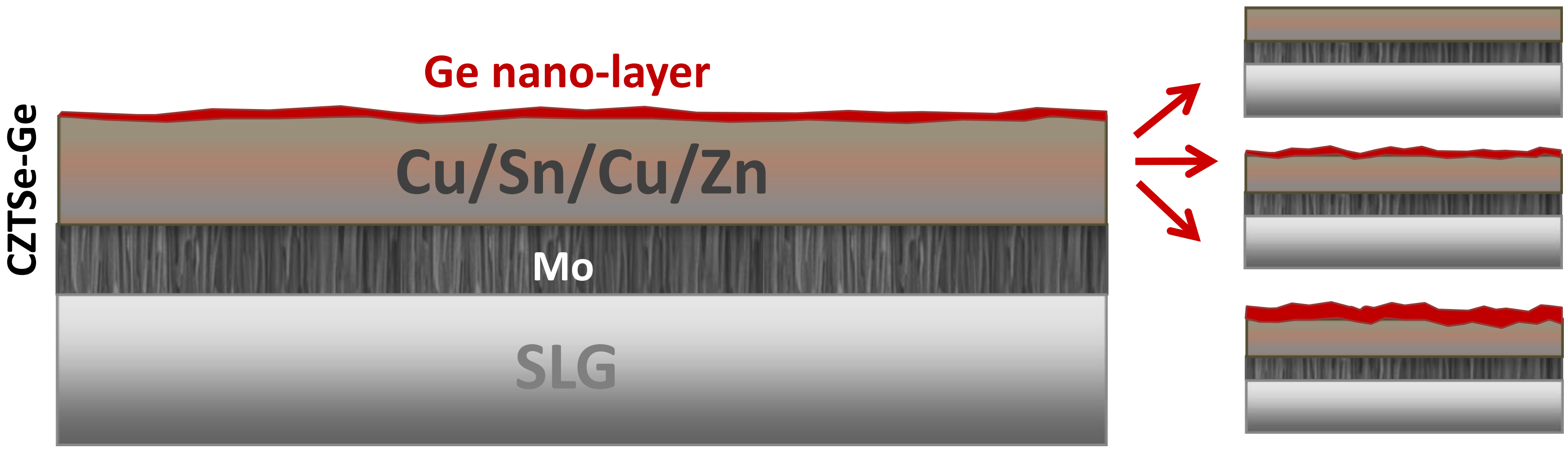
INVOLVING **RELATIVELY LARGE AMOUNT OF Ge (20-40% Ge-substitution)**
Univ. of Washington

IREC Approach: deposition of a Ge nanolayer on top of the metallic precursors, before selenisation.

[1] A.D. Collord, H.W. Hillhouse. Chem. Mater. (2016). DOI:10.1021/acs.chemmater.5b04806

First approach: Ge nanolayer variation

Different Ge thicknesses
(0, 1 ,2 ,5 ,7.5 ,10 , 12.5, 15, 25, 50 nm)



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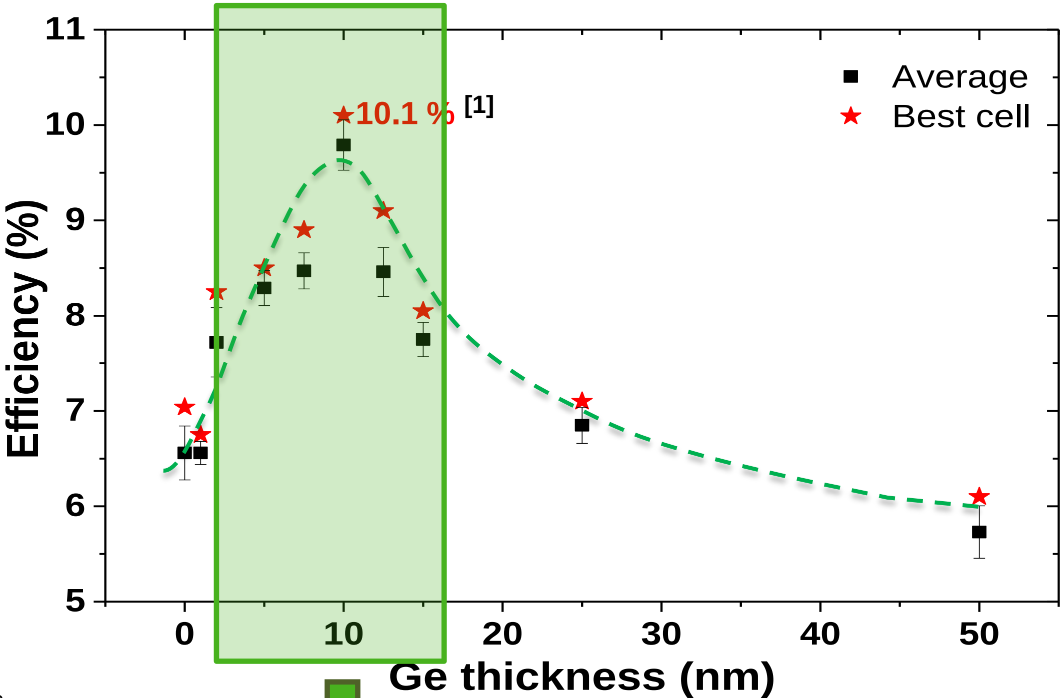
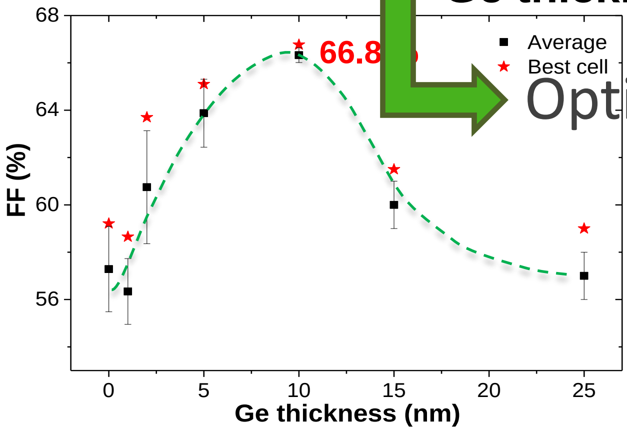
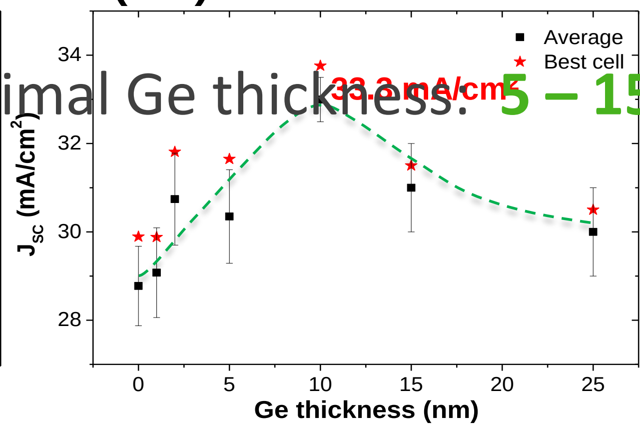
Ge thickness optimization (Optoelectronic properties)

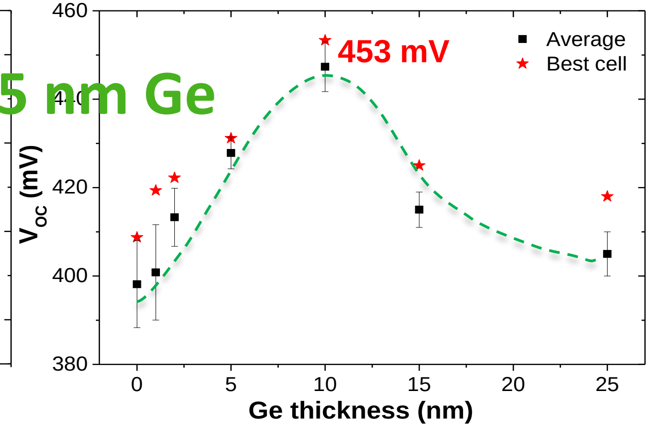


Sample	Ge thickness (nm)	Nominal Ge/(Ge+Sn) (%)
Ref	0	0
Ge1	1	0.44
Ge2	2	0.87
Ge5	5	2.2
Ge7.5	7.5	3.3
Ge10	10	4.4
Ge12.5	12.5	5.5
Ge15	15	6.6
Ge25	25	10.9
Ge50	50	21.8

Optimal Ge thickness: **5 – 15 nm Ge**







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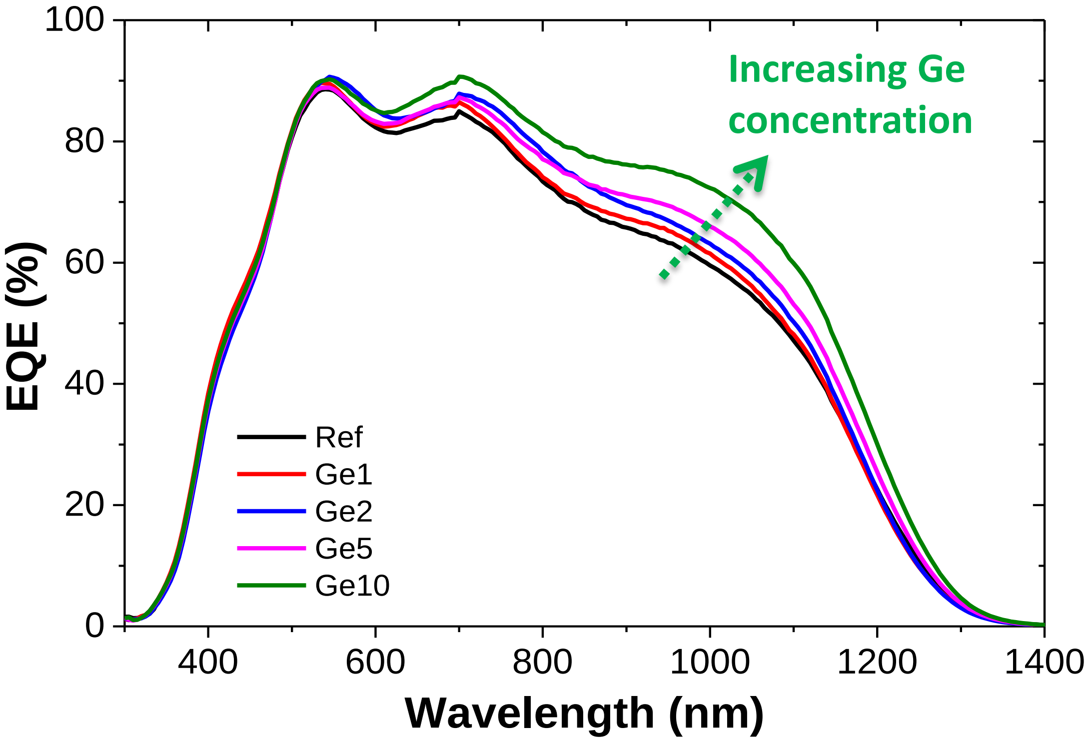
[1] S. Giraldo et al. Adv. Energy Mater. 5, 2015, 1501070.

Optoelectronic properties



EQE shows improvement in the photogenerated current collection

Sample	Ge thick. (nm)	E_G (eV)
Ref	0	**1.04**
Ge1	1	**1.05**
Ge2	2	**1.05**
Ge5	5	**1.05**
Ge10	10	**1.04**
Ge15	15	**1.03**
Ge25	25	**1.02**

- **No remarkable changes in the band gap value**

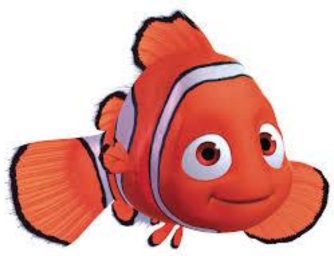
Does this mean that Ge was not incorporated into the absorber?

[1] S. Giraldo et al. Adv. Energy Mater. 5, 2015, 1501070.

Optoelectronic properties

1. Where is Ge located?
2. Why can such low amount of Ge lead to this large efficiency improvement?

Finding Germanium...



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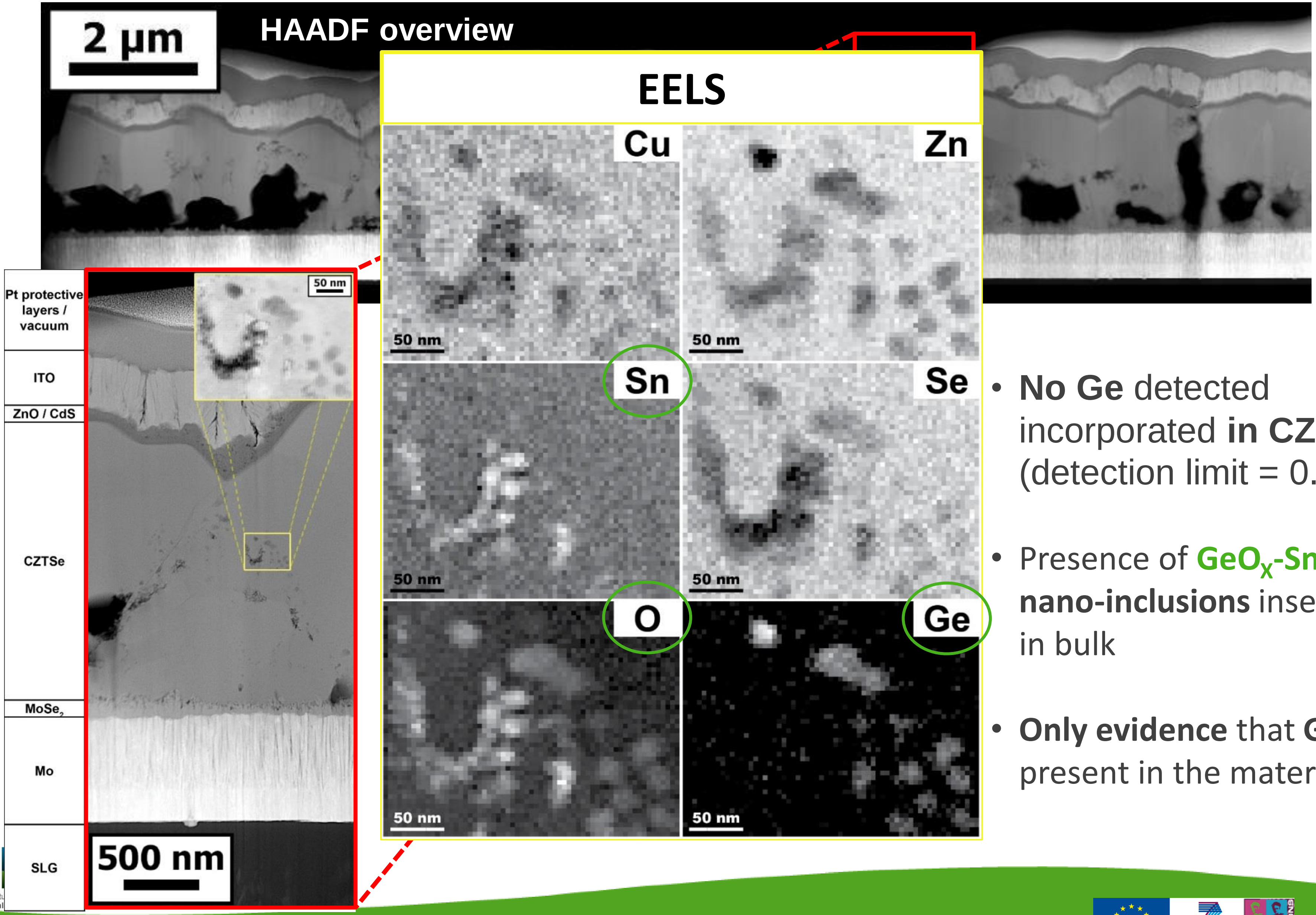
[1] S. Giraldo et al. Adv. Energy Mater. 5, 2015, 1501070.

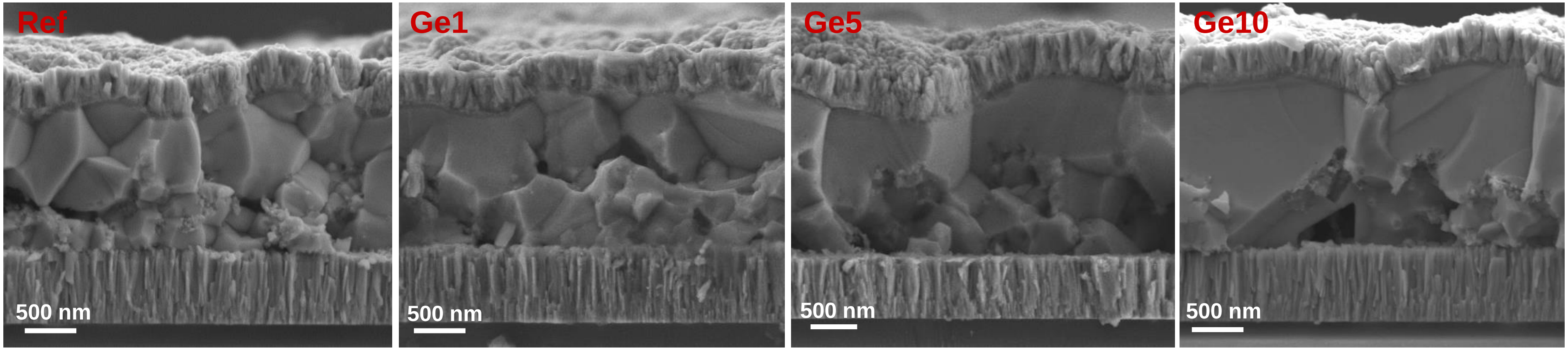
Finding Germanium…



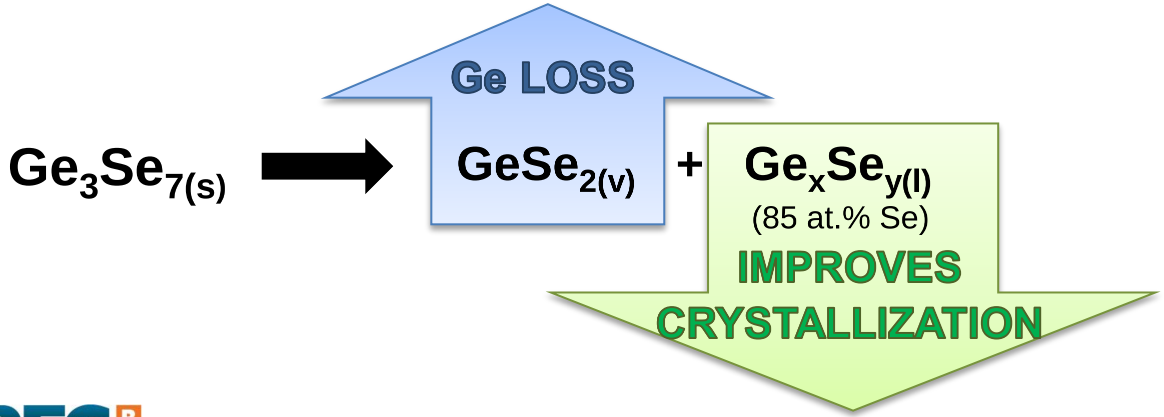
- **No Ge** detected incorporated **in CZTSe** (detection limit = 0.2%)
- Presence of **GeO_X-SnO_X nano-inclusions** inserted in bulk
- **Only evidence** that **Ge** is present in the material

[1] S. Giraldo et al. Adv. Energy Mater. 5, 2015, 1501070.

SEM: Impact on CZTSe grains morphology



- **Large grains** and **reduced density of grain boundaries** are observed with increasing Ge concentration
- **Ge-Se liquid phase** might **assist** the **CZTSe crystallization process:**



This reaction would explain:

- **Ge loss**
- **Improved crystallization** of CZTSe

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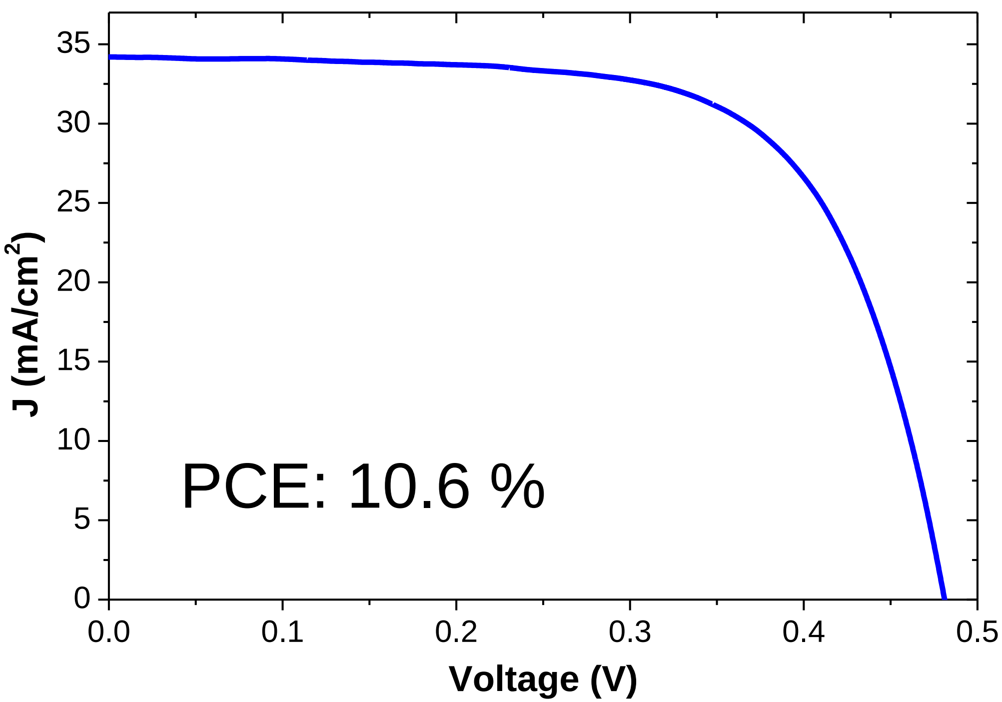
[1] S. Giraldo et al. Adv. Energy Mater. 5, 2015, 1501070.

PEOPLE
MARIE CURIE ACTIONS

Best efficiency obtained so far

Ge superficial layer allows achieving **10.6% efficiency** devices (with ARC + metallic grid) with **the lowest V_{OC} deficit** reported so far for this technology!!



Cell#	Cell Area (cm²)	Voc (V)	Jsc - 1sun (mA/cm²)	Eff (%)	FF (%)
IREC_01	0.231	**0.475**	35.1	**10.3**	61.7
IREC_02	0.230	**0.467**	34.6	**10.4**	64.5
IREC_03	0.233	**0.455**	34.7	**10.4**	66.2
IREC_04	0.238	**0.431**	35.4	**9.8**	64.4
IREC_05	0.228	**0.476**	34.0	**10.2**	62.8
IREC_06	0.228	**0.473**	34.3	**10.6**	65.1
IREC_07	0.229	**0.466**	34.2	**10.6**	66.4
IREC_08	0.236	**0.446**	35.1	**10.1**	64.8
IREC_09	0.241	**0.480**	34.2	**10.5**	63.9
IREC_10	0.245	**0.465**	34.1	**10.5**	66.2
IREC_11	0.246	**0.456**	34.9	**10.6**	66.5
IREC_12	0.247	**0.444**	34.8	**10.0**	64.5
IREC_13	0.232	**0.475**	34.5	**10.1**	61.5
IREC_14	0.239	**0.463**	34.0	**10.2**	64.7
IREC_15	0.239	**0.452**	34.6	**10.4**	66.1
IREC_16	0.237	**0.438**	35.5	**9.9**	63.8

In collaboration with IMRA EUROPE S.A.

[1] S. Giraldo et al. Progress in Photovolt., 2016, DOI: 10.1002/pip.2797.

Lowest voltage deficit reported so far

Material	Eff (%)	V_{OC} (mV)	Band-gap (eV)	V_{OC} deficit (mV)	Ref
CISe	15,0	491	1,00	**509**	[2]
CZTS	8,5	708	1,45	**742**	[1]
CZTSSe	12,6	513	1,13	**617**	[1]
CZTSe	11,6	423	1,00	**577**	[3]
CZTSSe	11,2	479	1,05	**571**	[4]
This work (CZTSe)	**10.6**	**480**	**1,03**	**550**	**-**

1. The formation of **Ge_3Se_7 phase** that incongruently decomposes into **volatile $GeSe_2$** and a **Se-rich liquid phase** which assists the crystallization of CZTSe.

2. The presence of Ge **reduces** the probability of **formation of Sn^{+2}** that are commonly associated to deep defects that deteriorate the cell voltage.

3. The only evidence we found for an incorporation of Ge into the CZTSe absorber is the presence of **GeO_x nanoclusters** inserted in the grains bulk, that might act as **electron back reflectors**, enhancing the voltage of the solar cells.

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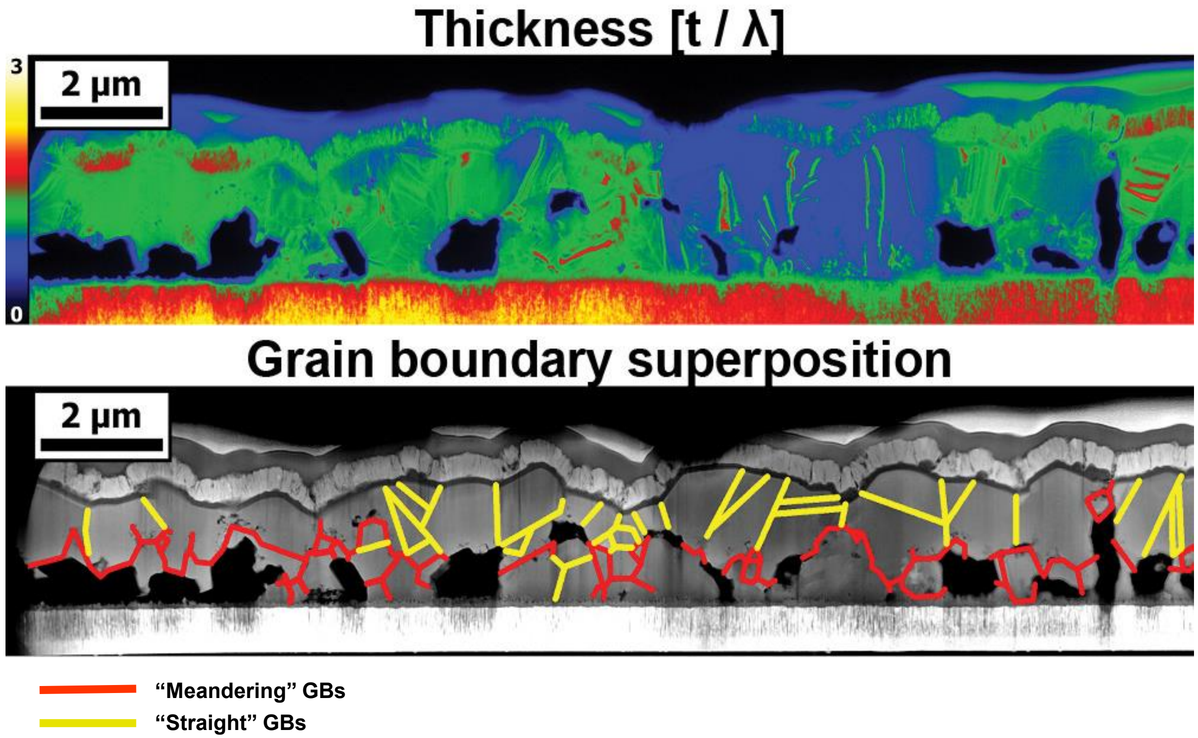
[1] M. A. Green et al. Prog. Photovolt. Res. Appl. 23, 2015, 1-9
[2] J. AbuShama et al. 31st IEEE PVSC, 2005
[3] Y. S. Lee et al. Adv. Energy Mater. 5, 2015, 1401372
[4] S. G. Haass et al. Adv. Energy Mater. 2015. DOI: 10.1002/aenm.201500712

Impact on morphology and grain structure

Impact on the **grain boundaries (GBs)** structure is currently under investigation by **HRTEM** / **EELS** / **EDX**



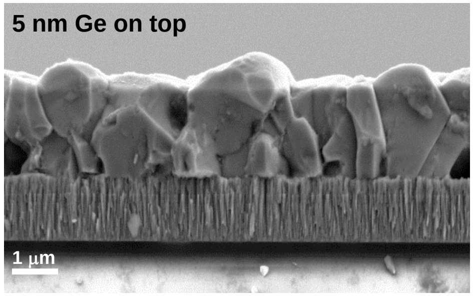
Two types of GBs were found:

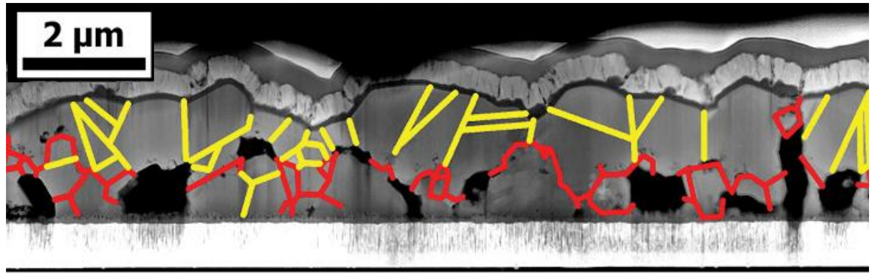
- **"Meandering" GBs:** mainly horizontal, connecting the pores, most located in the bottom half part of the absorber (Na, Cd, S)
- **"Straight GBs":** mainly vertical, connecting the surface to the pores, most located in the upper half part of the absorber (Cu-enriched)

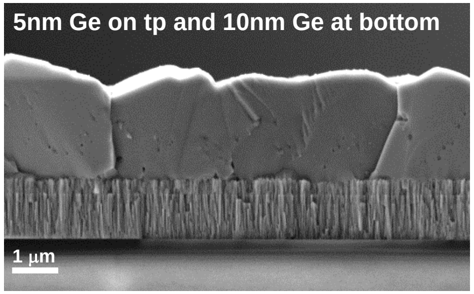
[1] T. Thersleff et al., submitted to Adv. En. Mat.

Top and bottom Ge nanolayers

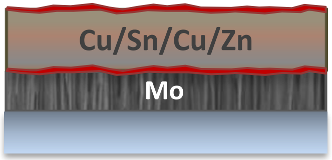
Impact on the **grain boundaries (GBs)** structure is currently under investigation by **HRTEM** / **EELS** / **EDX**



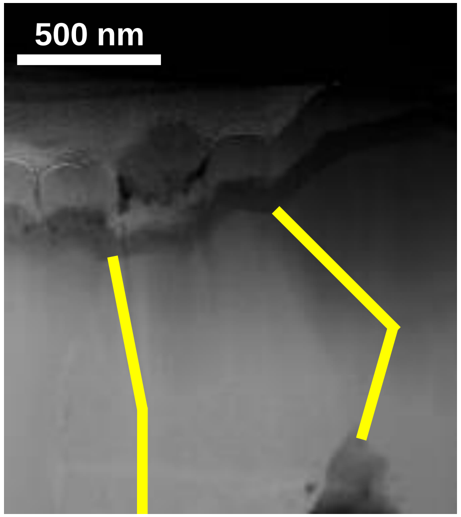




Ge on top



Ge on top and bottom

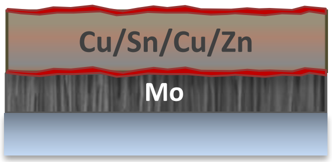


➔ The introduction of **Ge at the bottom** drastically **reduces** the presence of **meandering GBs**

➔ **Large grains extended over the whole thickness confirmed by TEM**

[1] S. Giraldo et al., under preparation.

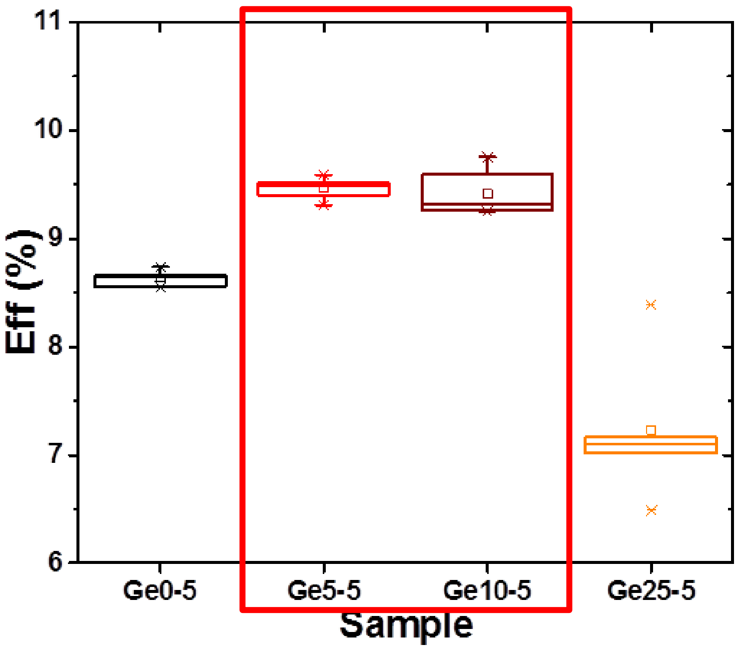
Top and bottom Ge nanolayers

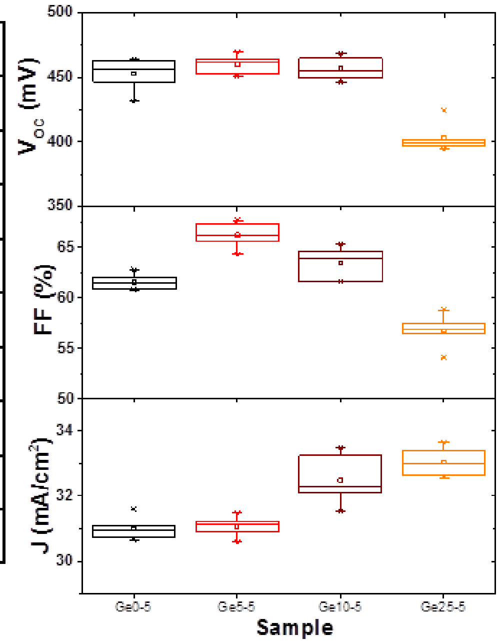


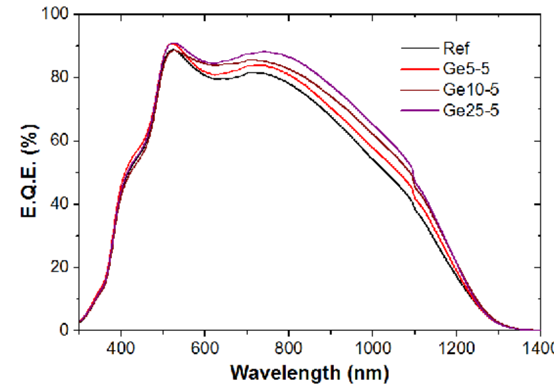
Ge: 5 nm

Ge: 0, 5, 10, 25 nm

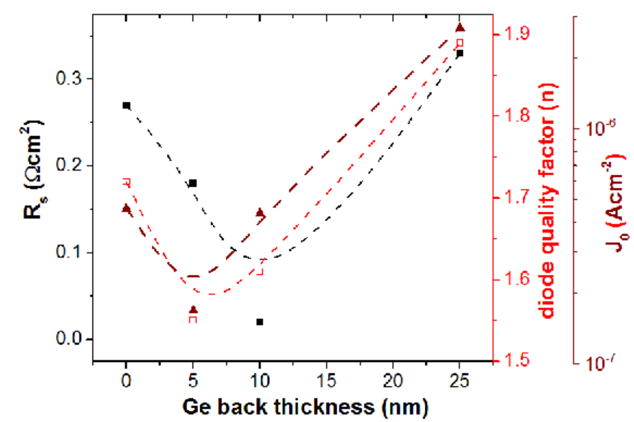
- Solar cells fabrication **varying Ge** content **at the bottom** of the precursor stack.







- **EQE** confirms the J_{SC} increase

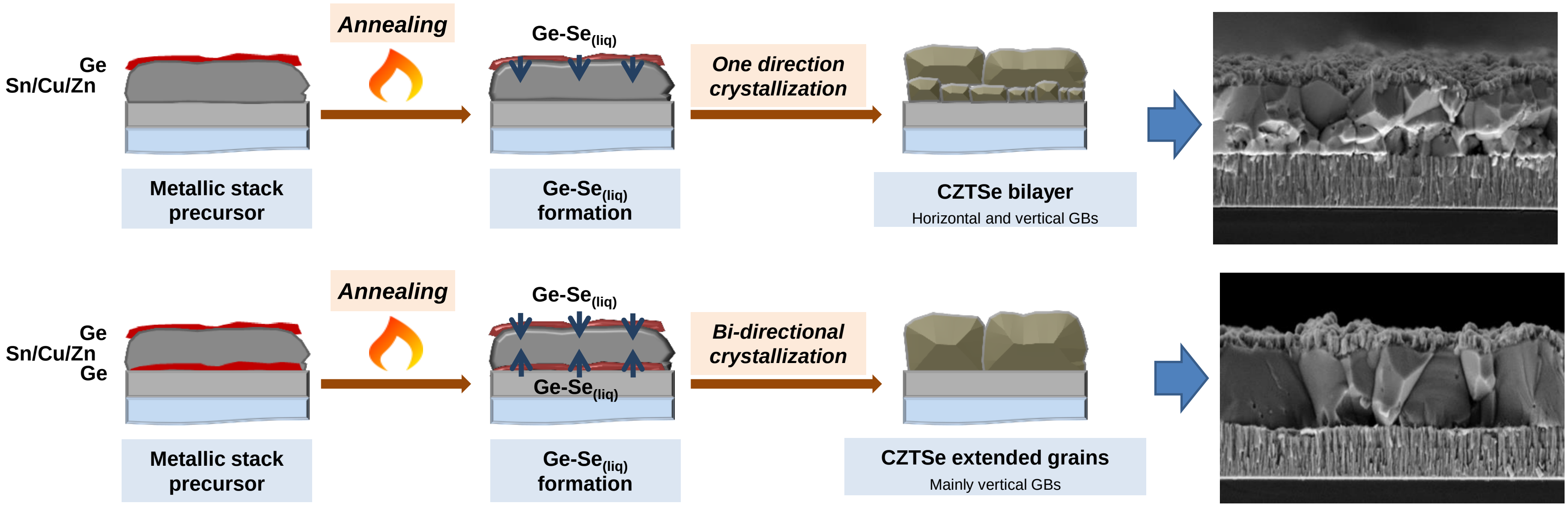


When **Ge** is introduced **at the bottom**:

- Remarkable **improvement** of **efficiency,** firstly due to a **FF increase**, and then owing to a **J_{SC} rise**.
- **R_S decreases** for the optimum Ge configuration, probably due to the **removal** of **meandering GBs** that could be adding additional resistance.

[1] S. Giraldo et al., under preparation.

Ge boost: Conclusions



- We believe that liquid Ge-Se acts as a flux assisting the crystallisation.
- Existence of **two types** of **grain boundaries** with different composition: “meandering” and “straight” GBs. Meandering GBs are surpressed by the bi-directional approach.
- A remarkable **increase** of the **grain size** is achieved, demonstrating that the presence of Ge at the bottom allows the formation of **CZTSe** at **early selenization stages**, **preventing** the **Sn loss** due to the **modification** of the **reaction** mechanism.
- Strong interaction with Na is also observed

➔ Routinely cell efficiencies around 10% are achieved

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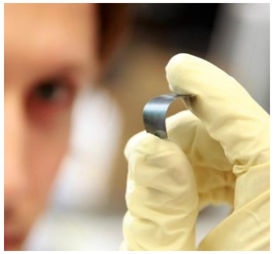
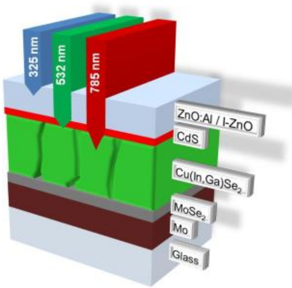
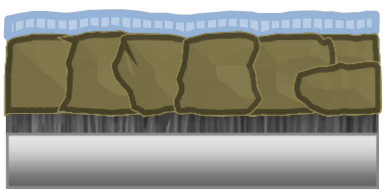
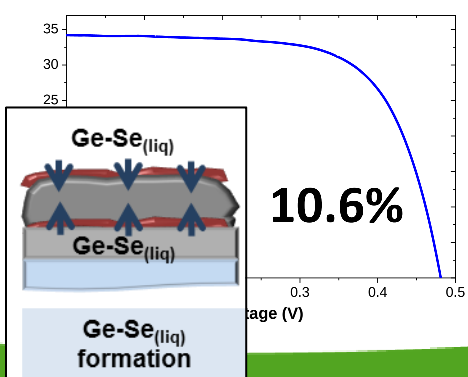
[1] S. Giraldo et al., under preparation.

Conclusions









- **Thin Film Photovoltaics**

My vision of the potential of Thin Film PV and the wide variety of applications for thin film PV, including BIPV, flexible applications.2-stage approach for CZTS absorber preparation

- **The SEMS group at IREC**

Main research lines include high-efficiency CZTS solar cells, alternative approaches including flexible and ceramic substrates and advanced process and quality control by Raman-based methodologies

- **The CZTS solar cell**

The CZTS material and the specific problems related to these solar cells, (high voltages deficits), solar cell processing and architecture.

- **Ge nanolayers boost device performanc**

Optimum for nanometric Ge layers enhancing all cell parameters, especially VOC (PCE=10.6%).

Ge-Se liquid phases enhances crystallinity in bi-directional growth.

Acknowledgements

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Former members: *Mirjana Dimitrievska , Andrew Fairbrother (NREL-NIST)*

University of Barcelona: *Lorenzo Calvo-Barrio, Tariq Jawhari, Xavier Alcobé*

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IMRA: *Gilles Denler, Gerardo Larramona*

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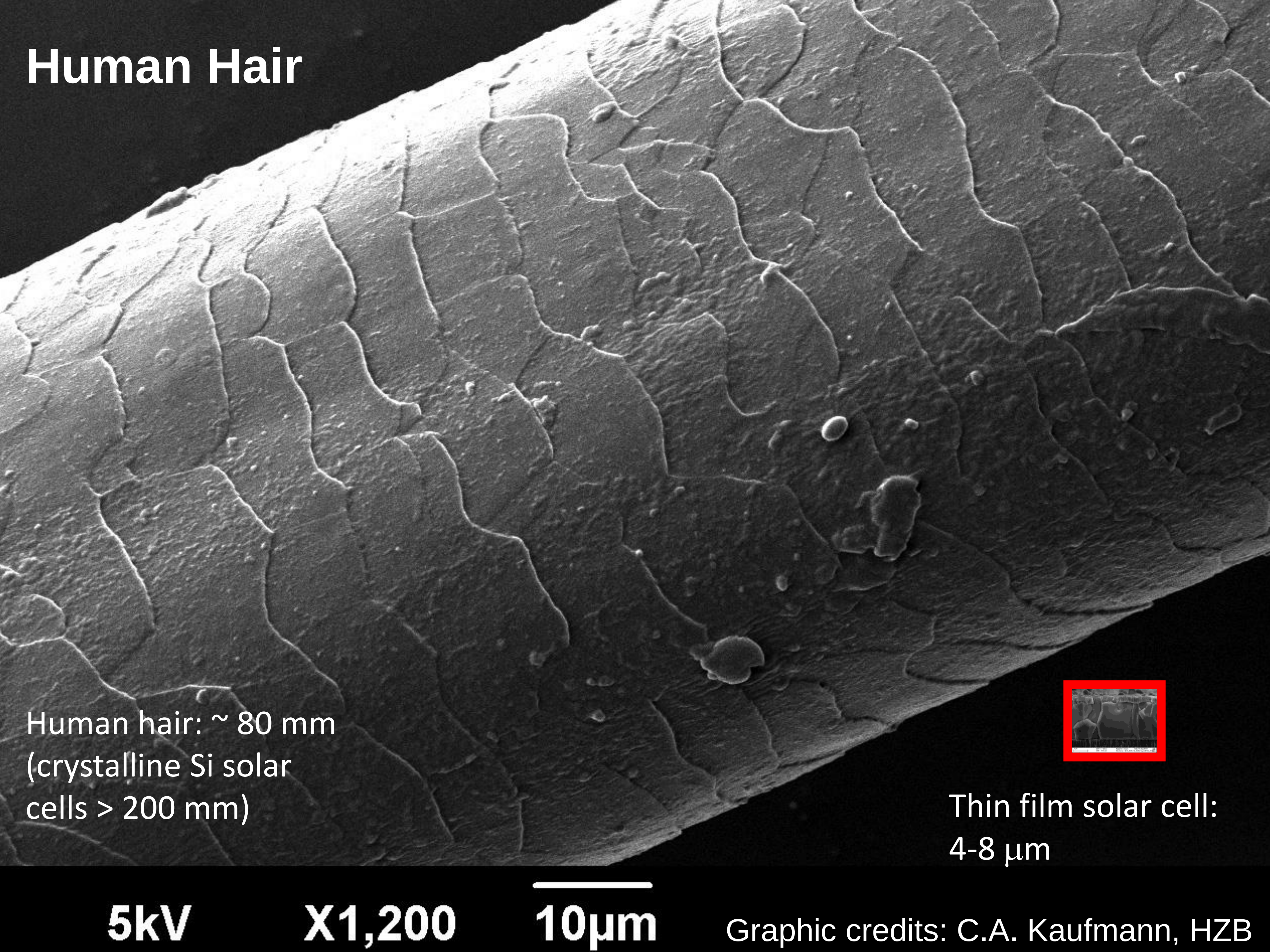

Human Hair
Human hair: ~ 80 mm
(crystalline Si solar
cells > 200 mm)
Thin film solar cell:
4-8 μm
5kV
X1,200
10μm
Graphic credits: C.A. Kaufmann, HZB

Crystal structure of CZTS

Synthesis

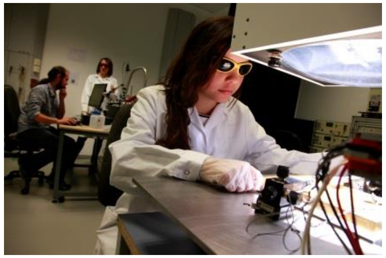
- ✓ Electrochemical workshop
- ✓ Spray pyrolysis reactor with controlled atmospheres
- ✓ Screen and ink-jet printing workshops
- ✓ Chemical Lab
- ✓ Furnaces for thermal treatments under controlled atmospheres

Device

- ✓3 Sputtering deposition systems for back contact & windows
- ✓CBD for synthesis of buffer layers
- ✓ Thermal evaporator

Optoelectronic Device/cell characterization

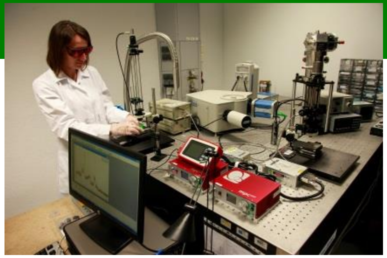
- ✓Scriber for delineation of cells
- ✓Solar simulator (AAA, 6” x 6”)
- ✓ Spectral response & EQE / IQE measurements (Bentham PVE300)

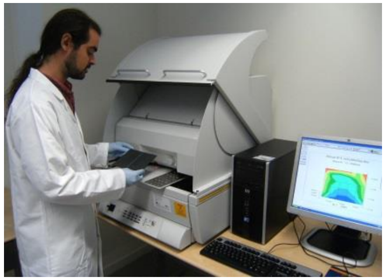


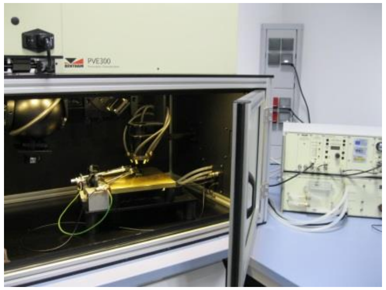
Characterisation Infrastructure

Physico-chemical characterization

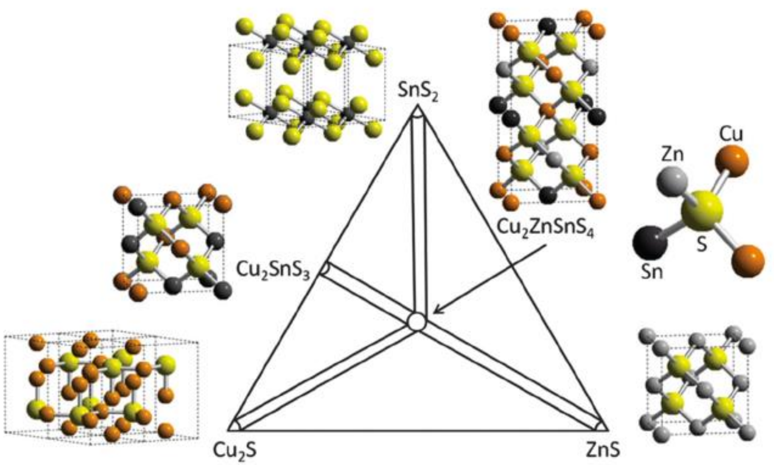
- ✓XRF (Fisherscope XDV-SDD)
- ✓4-points probe system & I(V) equipments for electrical and photoelectrical analysis
- ✓ Raman portable setups for process monitoring with several excitation sources
- ✓ Raman spectrometers:T64000 and LabRam systems
- ✓ Auger electron spectroscopy
- ✓ XRD, TEM, SEM, AFM
- ✓ UV-Vis-IR spectroscopy
- ✓ Confocal/interferometric microscope, electrical test
- ✓ XPS, TOF-SIMS, FTIR







A well known structure, but with a complex phase diagram[1,2]….



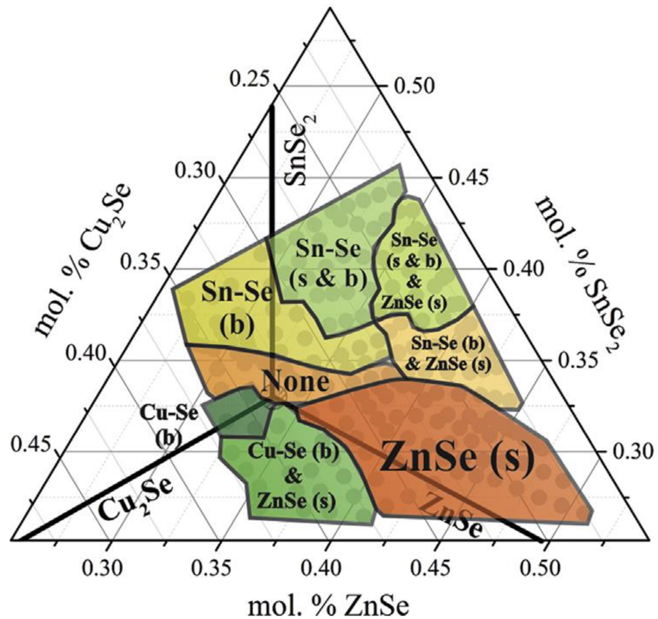


Table 1 Various properties of secondary phases observed in CZTS materials

Properties	Cu_2ZnSnS_4	ZnS	Cu_2S	SnS_2	Cu_2SnS_3
Band gap	~1.45 eV	3.54–3.68 eV	1.21 eV	2.2 eV	0.98–1.35 eV
Electrical properties	Semiconductor, p-type	Insulator	p-Type, metal like, and highly defective	n-Type	p-Type
Structural properties	Kesterite	Sphalerite and wurtzite	Chalcocite	Rhombohedral	Cubic and tetragonal
Impact on solar cell performance	Essential absorbing material	Insulating, reduces device active area	Metallic and short solar cell	n-type, forms diodes and barriers for carrier collection	Affects carrier collection efficiency

- Small single existence region
- Several secondary phases are possible depending on composition
- Presence of secondary phases is in general highly detrimental for devices performance

[1] H. Du et al. J. Appl. Phys. 115, 20015, 173502, [2] M. Dimitrievska et al., Solar Ener. Mater. Solar Cells 149, 2016, 304,

Defects in CZTS

- Intrinsic p-type conductivity thanks to the formation of V_{Cu}[1]
- Charge carrier concentration of the order of 10^{15}-10^{16} cm^{-3}[2]

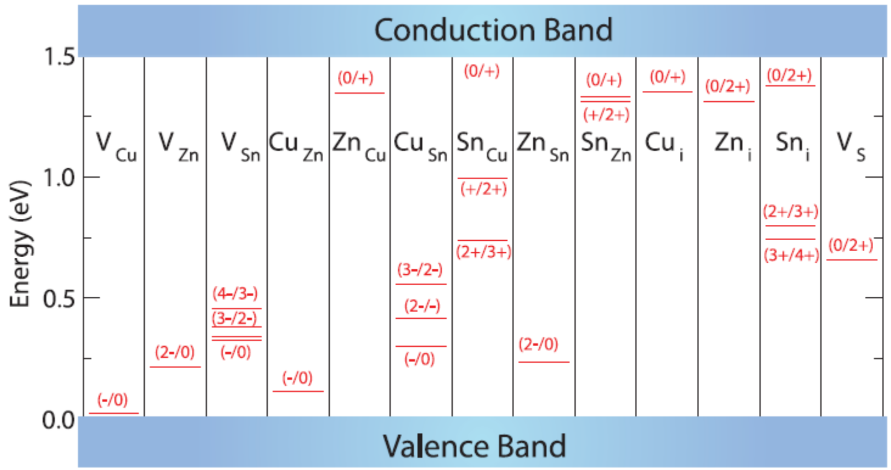


Figure 7. The ionization levels of intrinsic defects in the bandgap of Cu_2ZnSnS_4 (adapted from Ref. [68]). The copper vacancy results in a shallow acceptor level just above the valence band, while the Cu-on-Zn antisite results in a level 0.12 eV higher in energy.

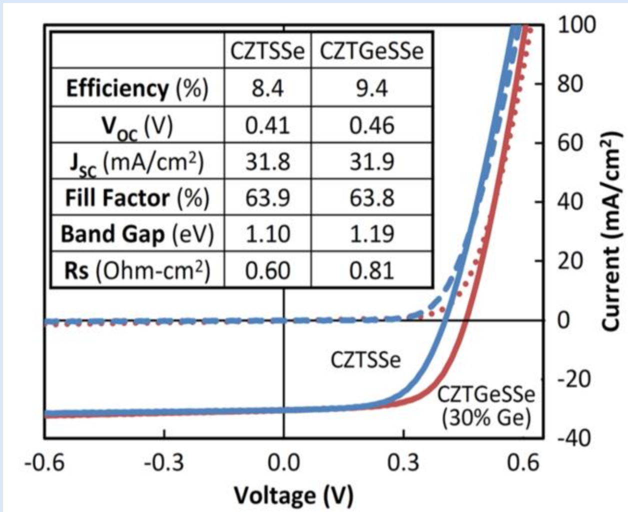
TABLE I. Cu/(Zn + Sn) and Zn/Sn compositional ratios, hole concentration, resistivity, and band gap energy of as-grown and annealed samples chosen for TSC study.

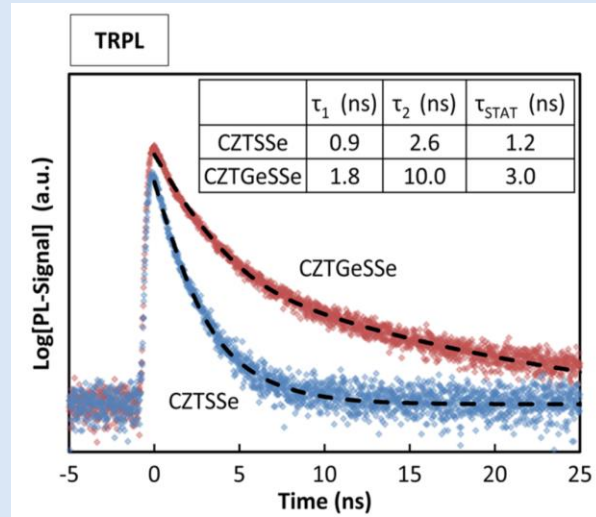
Sample	Cu/(Zn + Sn) (±0.04)	Zn/Sn (±0.03)	Hole concentration (cm^{-3}) (±0.5 × 10^{15})	Resistivity (Ω cm) (±0.3 × 10^2)	Band gap energy (eV) (±0.03)
As-grown (sample 1)	0.84	1.10	4.9 × 10^{15}	3.0 × 10^2	1.45
As-grown (sample 2)	0.87	1.21	6.2 × 10^{15}	2.5 × 10^2	1.49
Annealed (sample 3)	0.89	1.25	5.6 × 10^{15}	2.4 × 10^2	1.41
Annealed (sample 4)	0.87	1.18	6.9 × 10^{15}	1.3 × 10^2	1.43

- Cu vacancy the shallower and with the lowest formation energy together with Cu_{Zn} antisite (under stoichiometric conditions)
- Main deep defects are related to Sn

Ge in CZTSSe: Alloying based strategies

Purdue Univ. (in collab. with HZB and Cottbus Univ.)
C.J. Hages et al, Prog. Photovoltaics Res. Appl. 23 (2015) 376–384. DOI:10.1002/pip.2442.





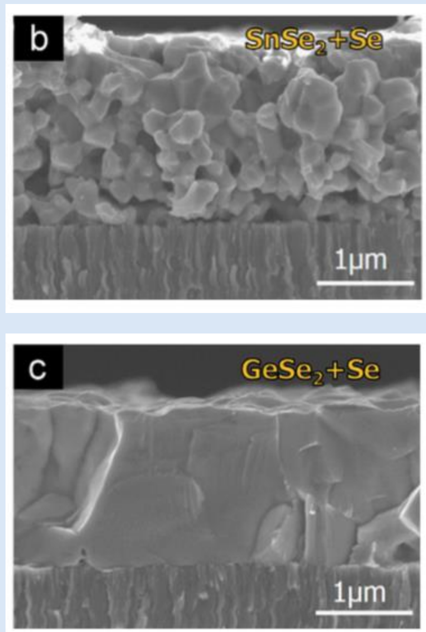
Nanocrystal-based CZTGeSSe absorbers with tunable band gap (first approach combining Sn/Ge and S/Se alloying):

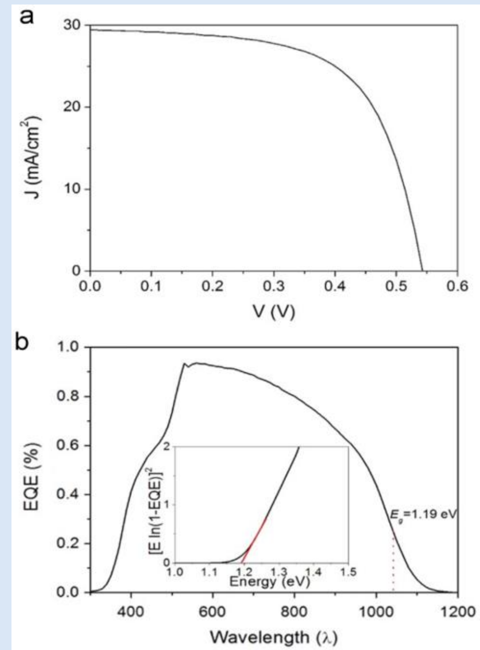
- Maximum solar-conversion **efficiencies** of **up to 9.4%** are achieved with a **Ge content of 30 at.%**, while for CZTSSe (without Ge), efficiencies remain at 8.4%
- Ge alloying leads to enhanced performance due to **increased minority charge carrier lifetimes** as well as **reduced voltage-dependent charge carrier collection**

➔ ***Potential impact of Ge on annihilation of deep levels (likely related to Sn)***.

Introduction

AIST (Japan)
S. Kim et al, Sol. Energy Mater. Sol. Cells. 144 (2016) 488. DOI:10.1016/j.solmat.2015.09.039.



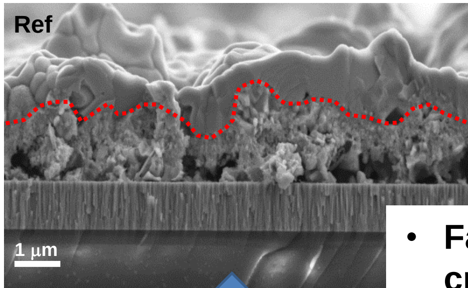


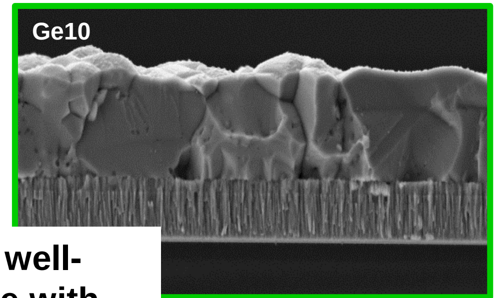
Sequential process involving coevaporation of Cu/Zn/Sn/Ge/Se followed by thermal annealing: **First group reporting pure Ge alloyed selenides with efficiencies > 10%**:

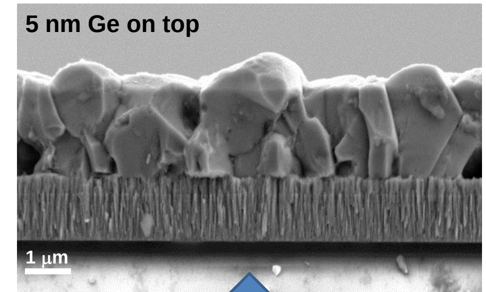
- Annealing in **environment containing $GeSe_2$** led to **improved morphological properties**: flat surfaces, dense morphologies, and large grains
- Highest **efficiency** of **10.03%**, with an **open circuit voltage (V_{OC})** of **0.54 V**, as well as an **improved V_{OC} deficit** of 0.647 V

Surface/back Ge nanolayers: Study of bi-directional crystallisation mechanisms

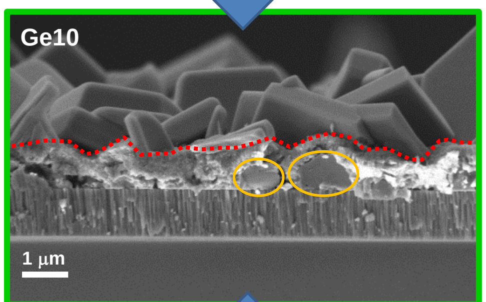
- Experiment stopping the annealing process at different points

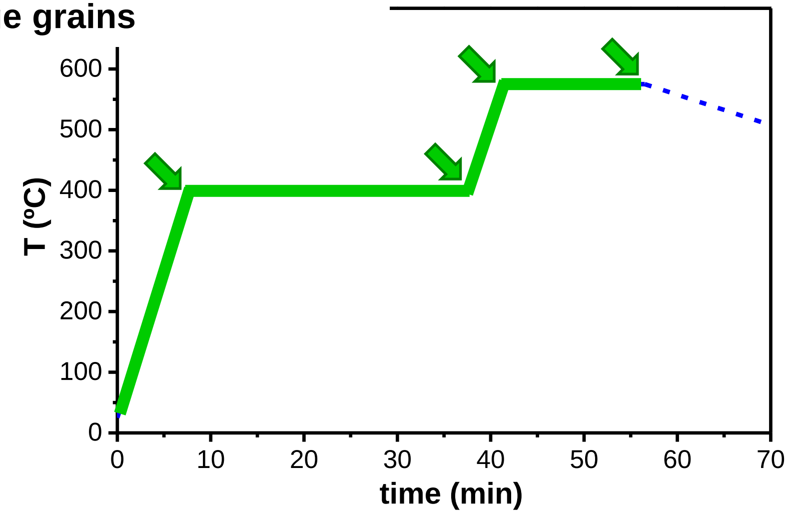


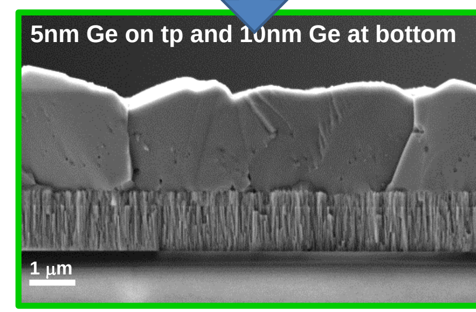




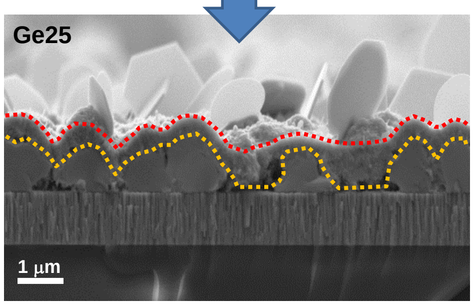
- **Fast formation of well-crystallized CZTSe with large grains**

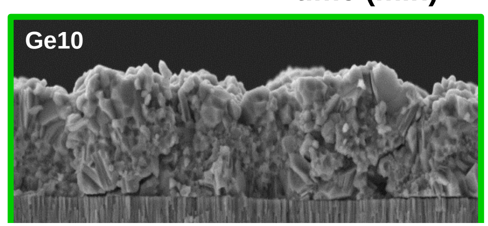






- **At the end of the complete selenization process, big crystals extend over the whole thickness**





- By using Ge at the bottom **large crystals** start to be observed at **early selenization stages**

´.

- **Uniform microcrystalline kesterite**

[1] S. Giraldo et al., under preparation.