

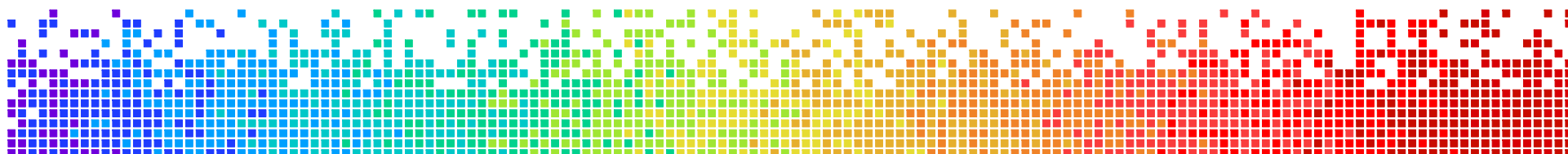


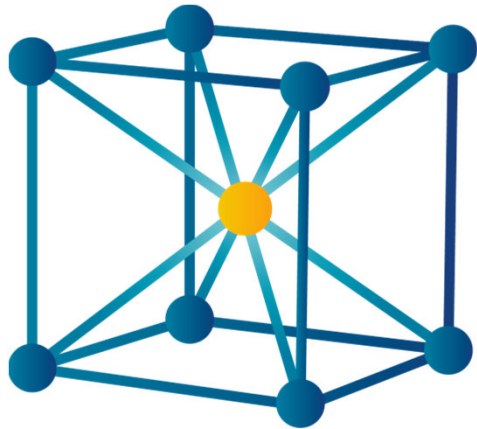
Molecular Beam Epitaxy Application in Chalcogenide Based Solar Cell Technologies

Mirjana Dimitrievska

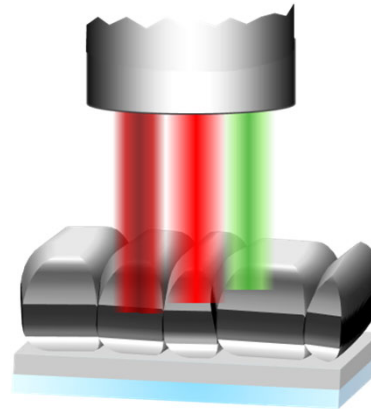
Laboratory of Semiconductor Materials
Lausanne Federal Institute of Technology (EPFL)
Lausanne, Switzerland

26. August 2020

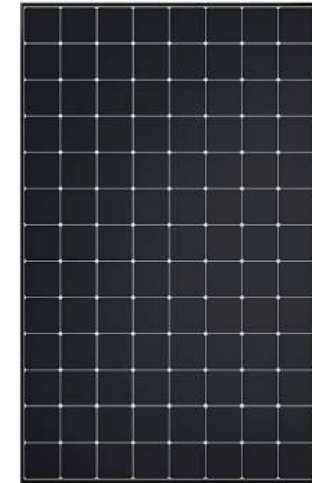




Advancing the knowledge of materials engineering (epitaxial growth)

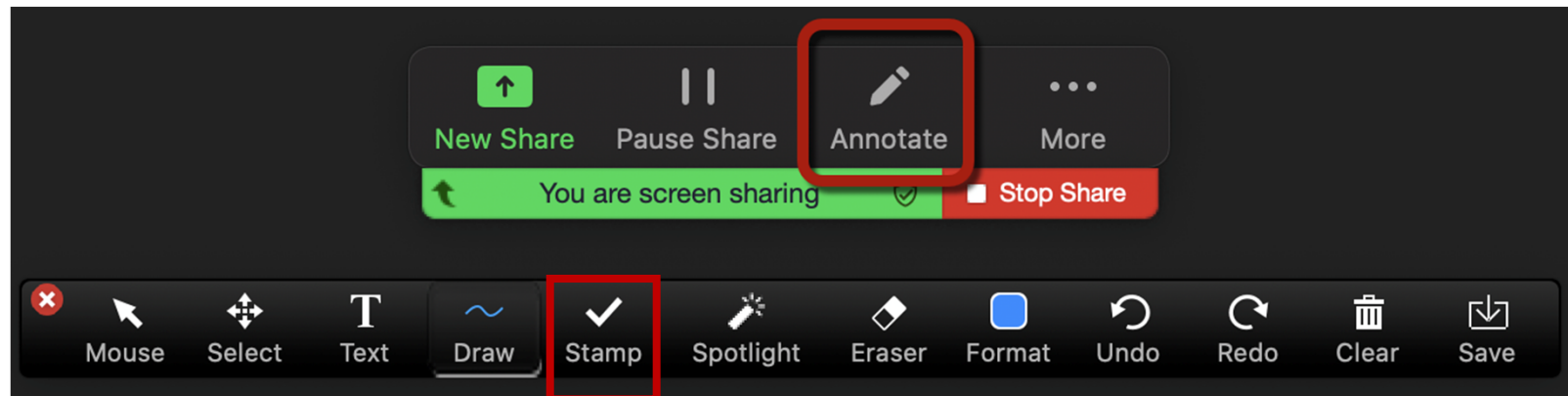


Overview and introduction of new characterization techniques



Expanding the knowledge of solar cells

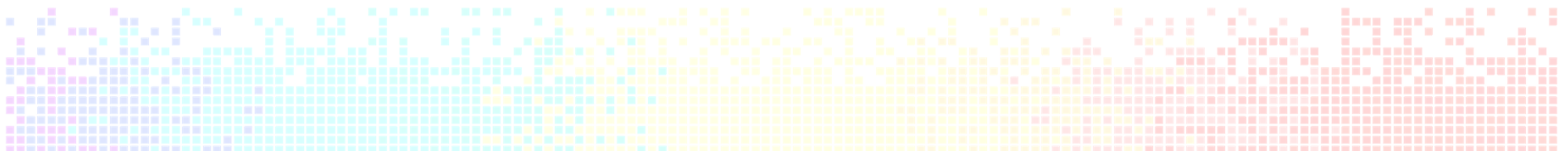
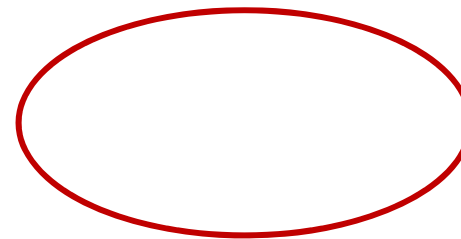
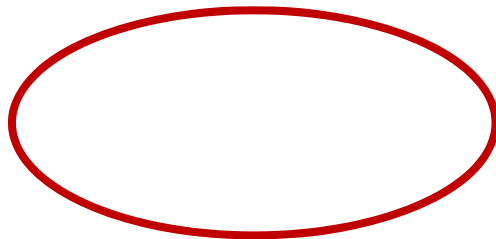
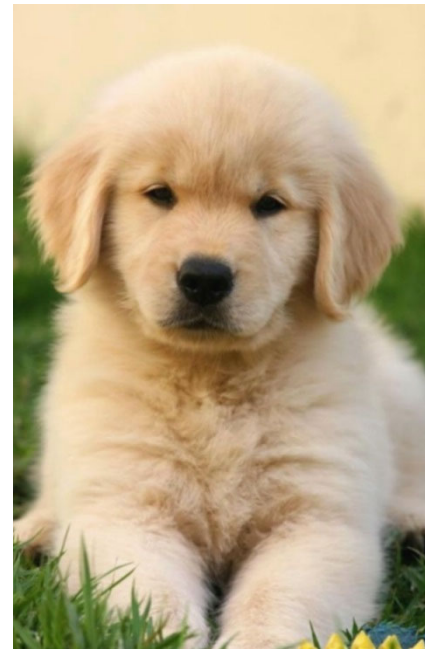
Zoom > View Options > Annotate



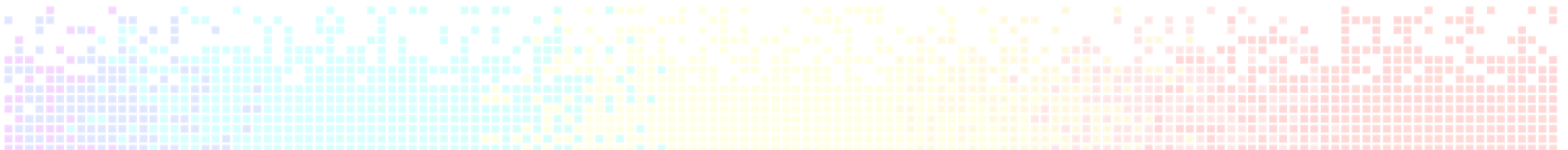
Let's interact! (technical notes)

Example:

Q1: Are you a cat or dog person?

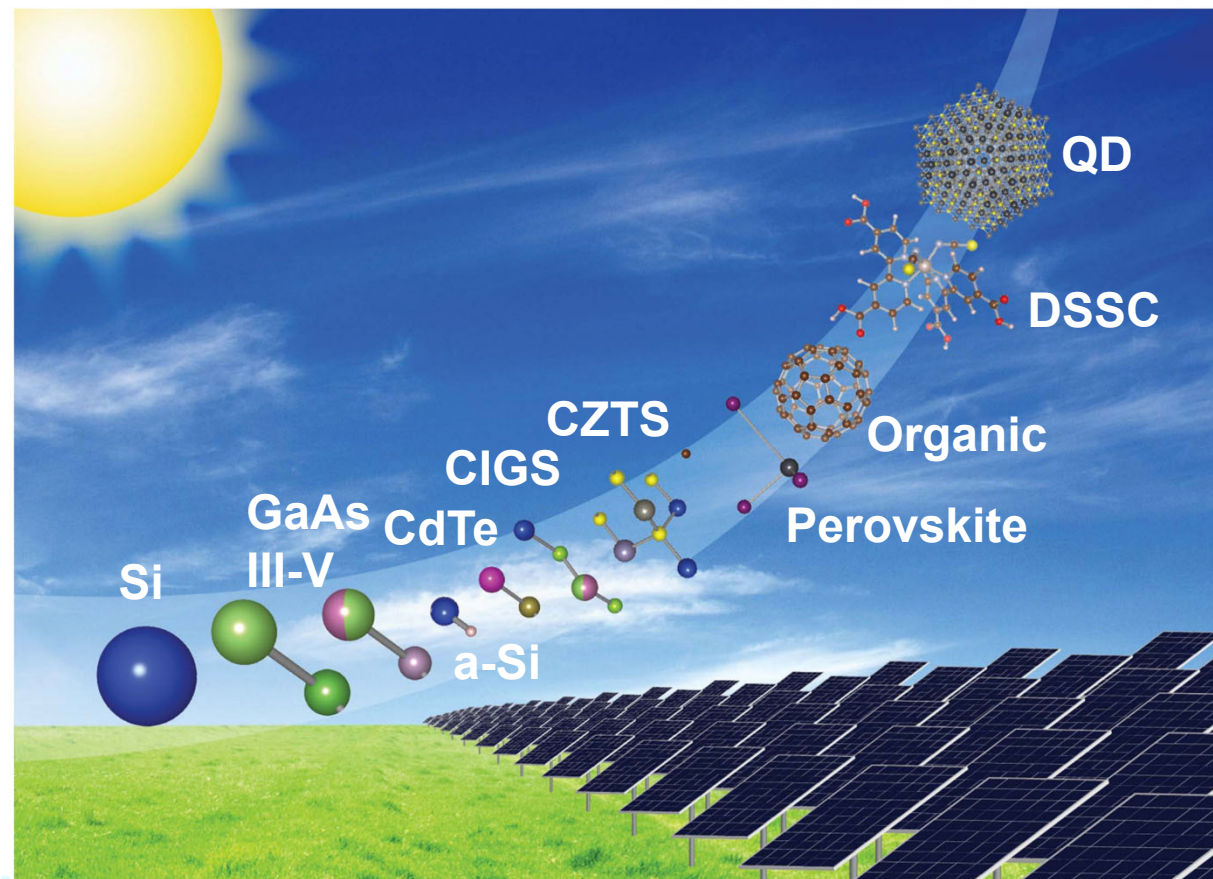


- Introduction into solar cells
- Application of epitaxial growth in chalcopyrites
- Application of epitaxial growth in kesterites



Solar photovoltaics (PV):

- ✓ renewable, sustainable and carbon-free electricity generation technology
- ✓ fastest-growing energy technology in the world today
- ✓ a leading candidate for terawatt-scale deployment

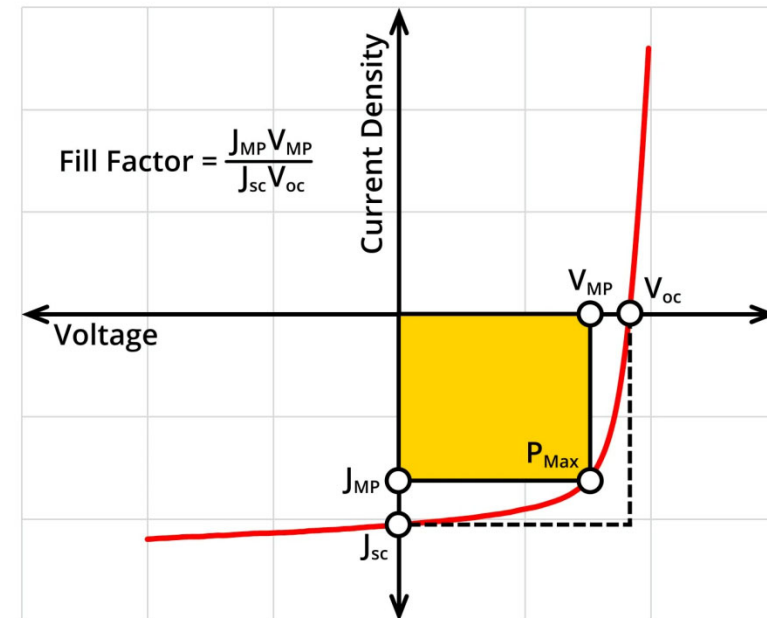
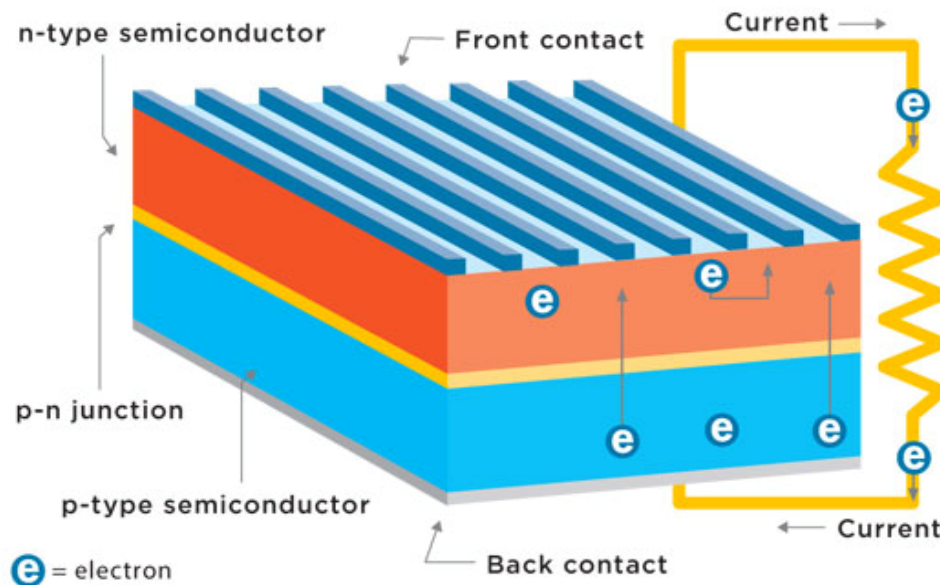


Wide span of materials used as absorbers (the heart of the solar cell).

Solar cells: short overview

Working principle of a solar cell

7/31



Two main characterization techniques:
J-V and external quantum efficiency (EQE)

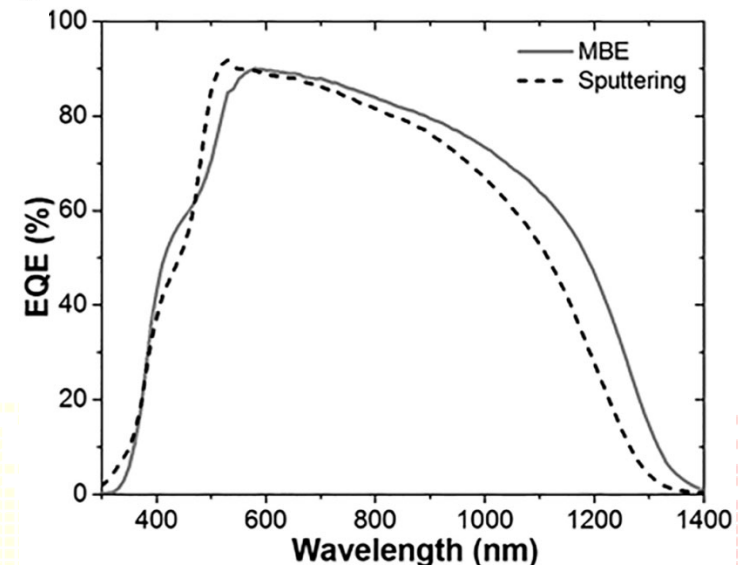
Main parameters:

V_{oc} – open circuit voltage

J_{sc} – short circuit current

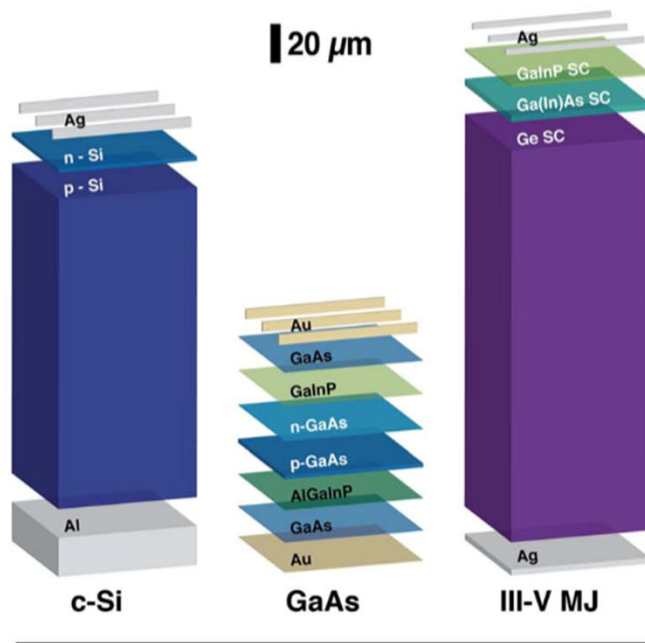
FF – fill factor

η - efficiency



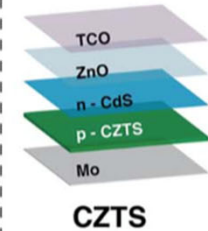
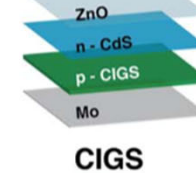
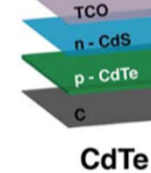
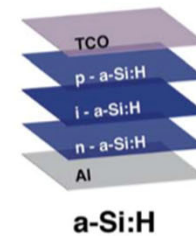
Solar cell structure in various technologies:

8/31

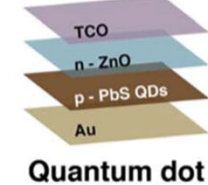
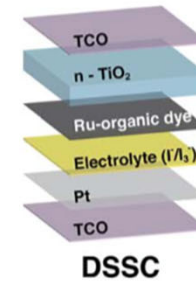
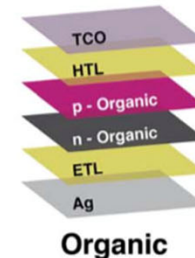


Wafer

**Commercial
Thin film**

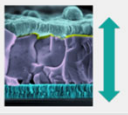
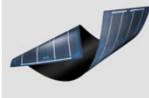
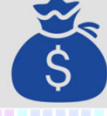


**Emerging
Thin film**



Thin film

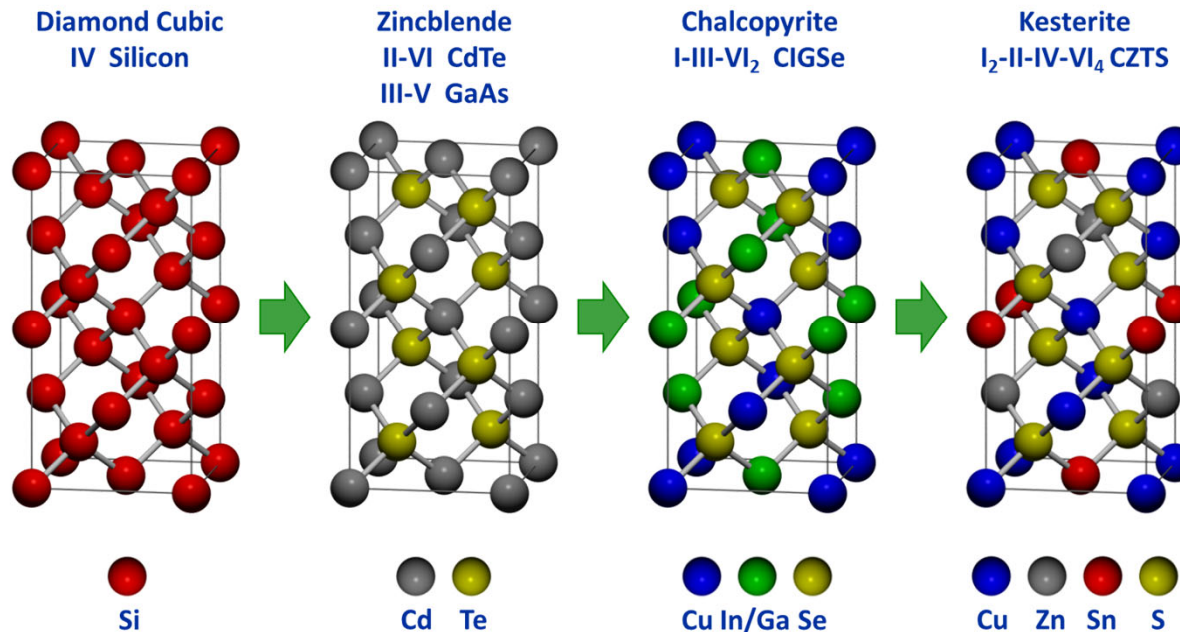
J. Jean et al. Energy Environ. Sci., 2015, 8, 1200

Property		State of the art				
		Si	GaAs	CIGS	CZTSSe	Perovskite
	Bandgap (eV)	1.1	1.5	1-1.5	1-1.5	1.5
	Record efficiency (%)	26	29	23	12	22
	Thickness (μm)	100 - 200	1	1	1	0.5
	Mechanical properties (flexibility)	✗	✓	✓	✓	✓
	Abundance	✓	✗ CRM: Ga	✗ CRM: In, Ga	✓	✗ CRM: Pb, and other
	Toxicity	✓	✗ (As)	✓	✓	✗ (Pb)
	Recyclability	✓	✗ Difficult	✓	✓	✗ Difficult
	Cost	\$	\$\$\$\$	\$\$	\$	\$

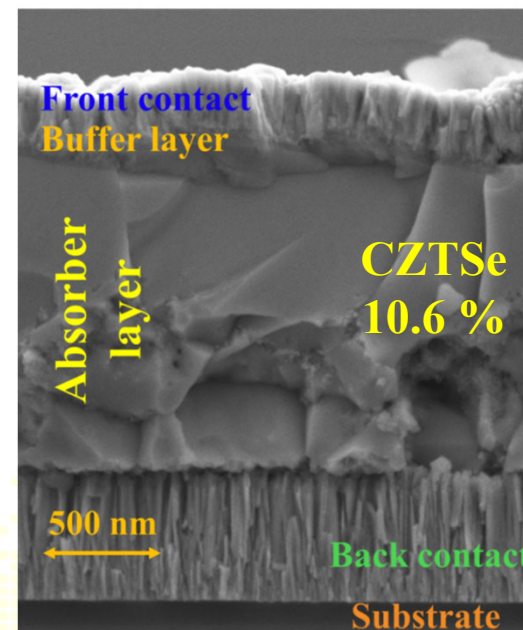
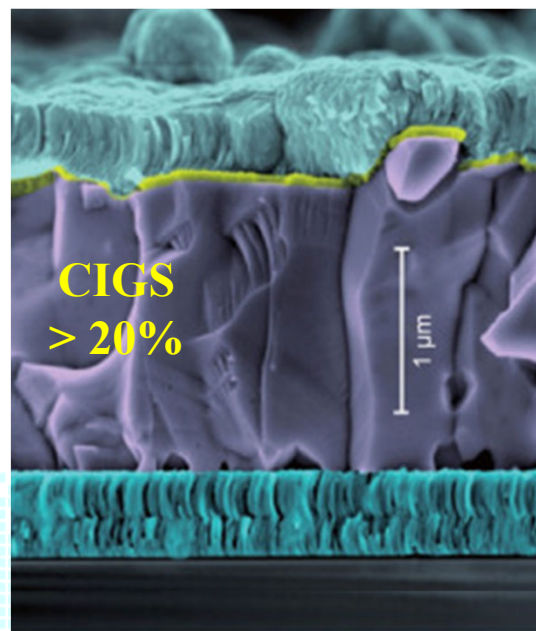
Objectives:

- 1) What is the role of epitaxial growth techniques in CIGS and CZTS solar cell?
- 2) Does epitaxial growth advance the technological development?
- 3) Does it increase efficiency of the cells?

CIGS vs CZTS: structure and devices



Polycrystalline
thin films



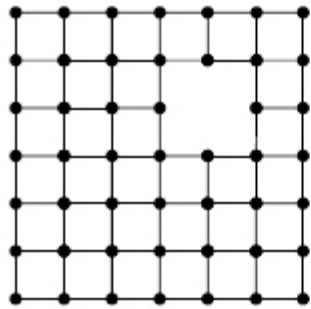
ZnO
CdS

CIGS/CZTS

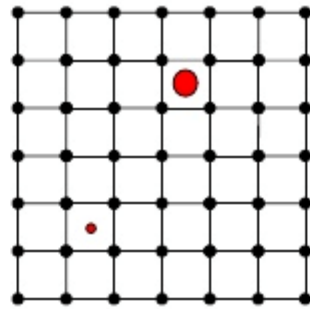
Mo
Glass

Point defects

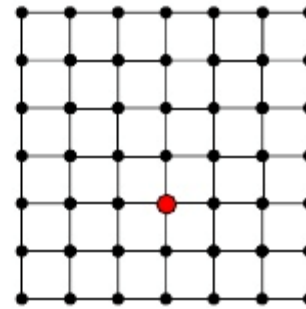
11/31



Vacancy



Interstitial

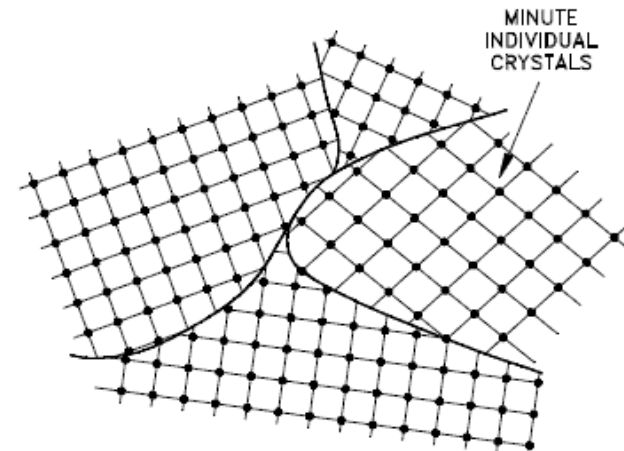
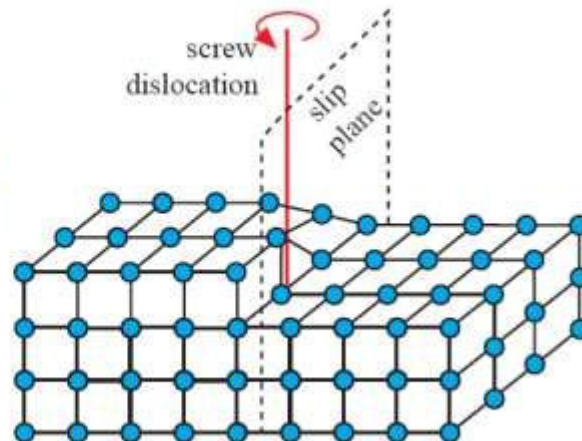
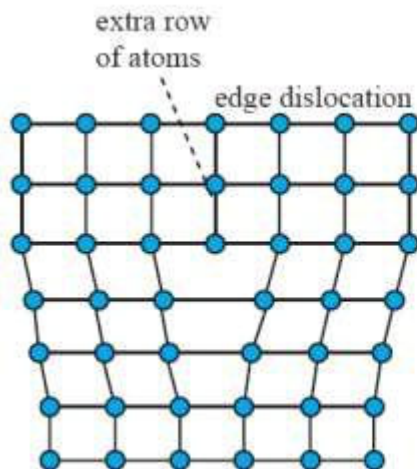


Substitutional

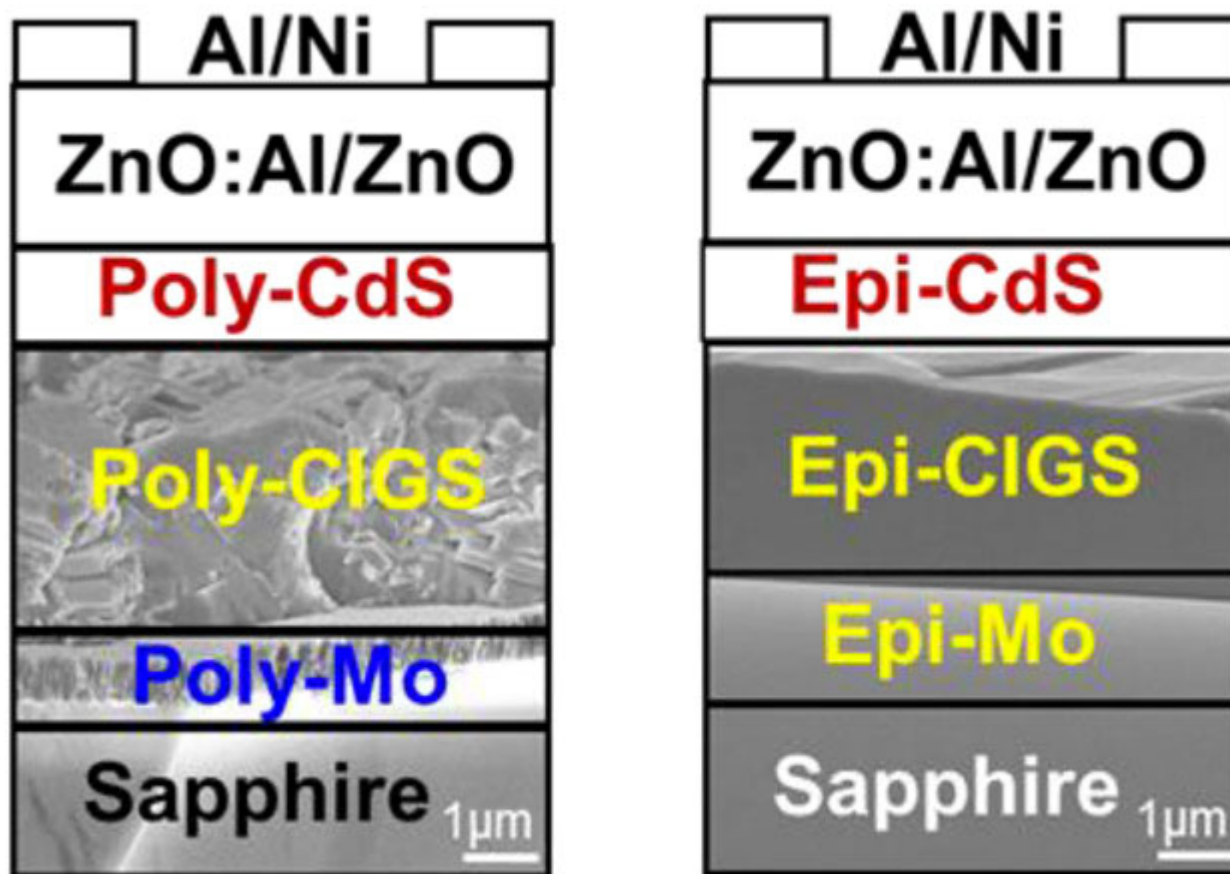
Beneficial or not?

Dislocations

Grain boundaries



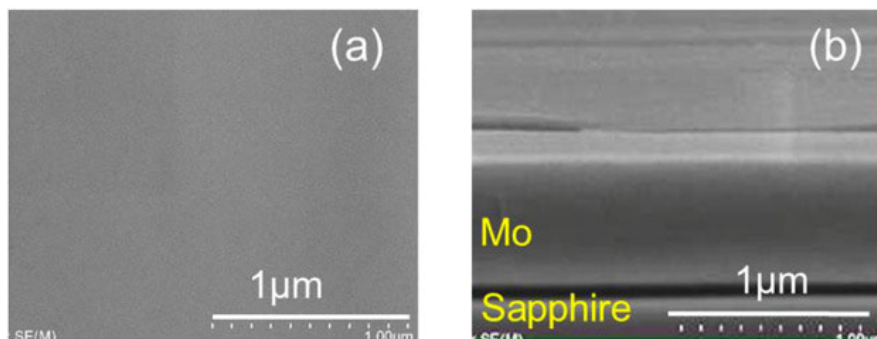
To understand the effect of grain boundaries and impurities, it is essential to compare the properties of epitaxial and polycrystalline CIGS films.



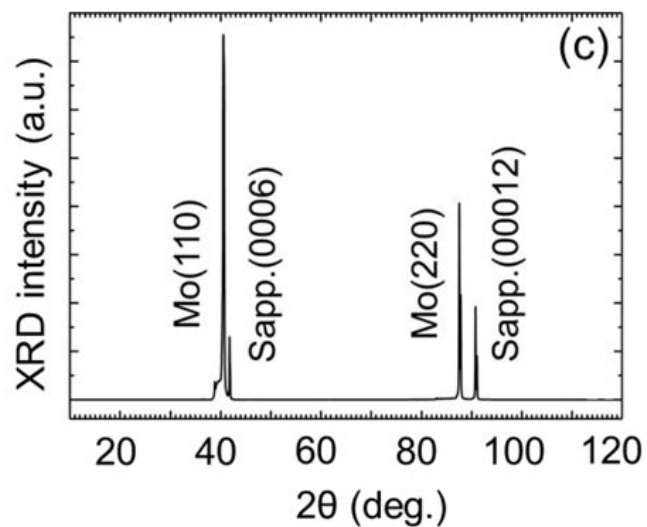
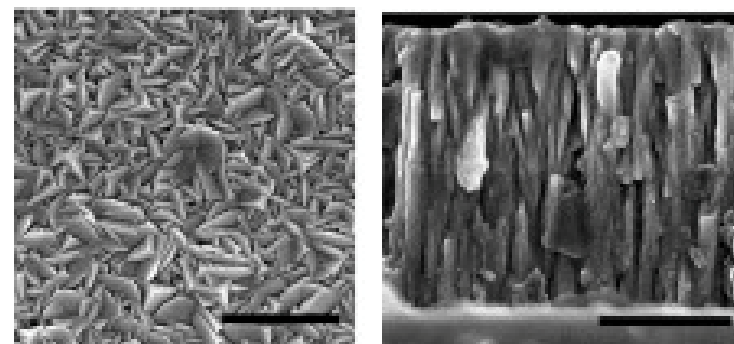
Growth of Mo back contact

13/31

Epitaxial growth

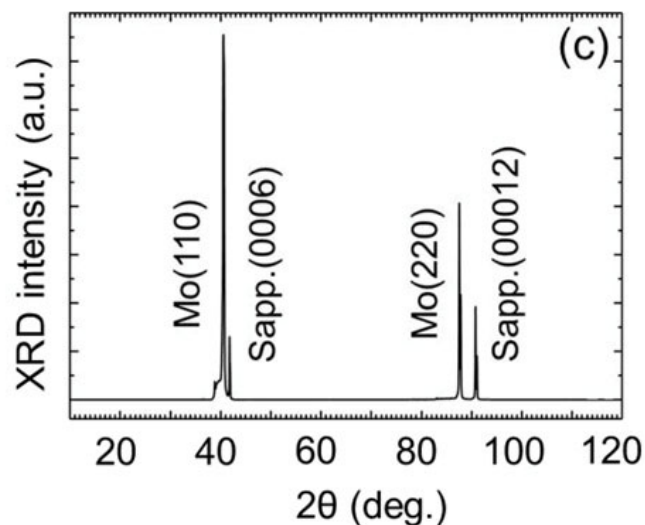
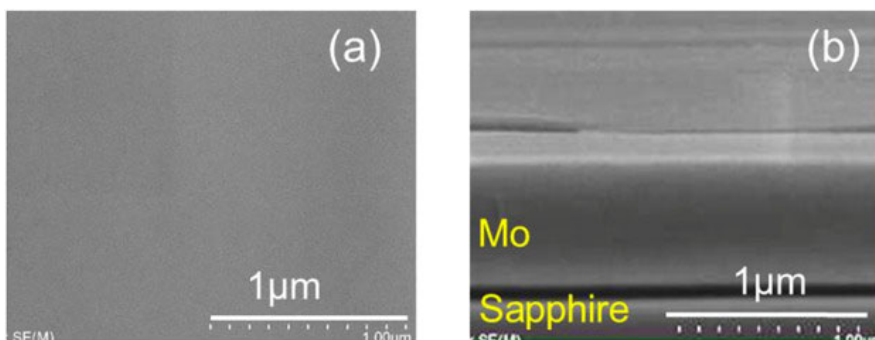


Magnetron sputtering



Growth of Mo back contact

14/31



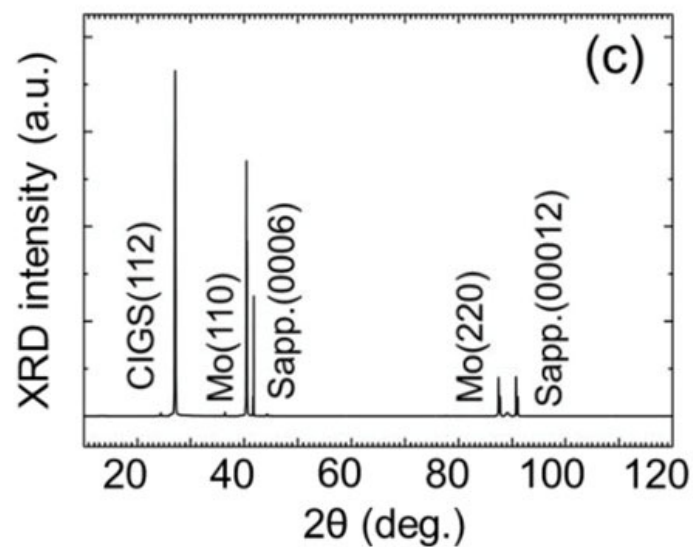
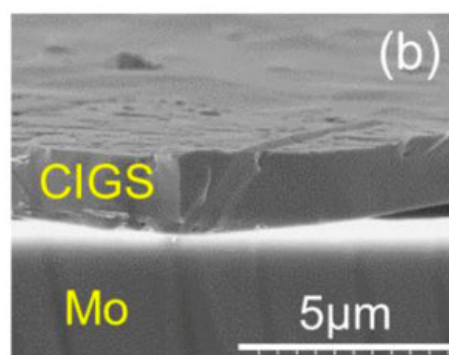
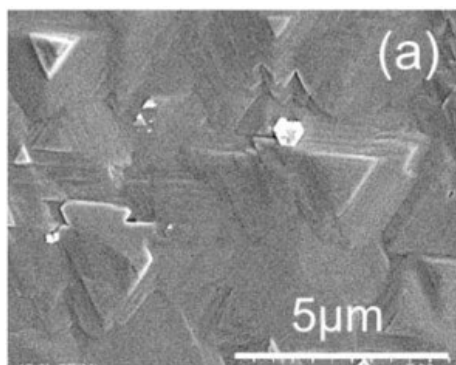
Q: Based on the given XRD pattern, in which orientation did Mo {110} plane grow on the sapphire {0001} substrate?

Parallel

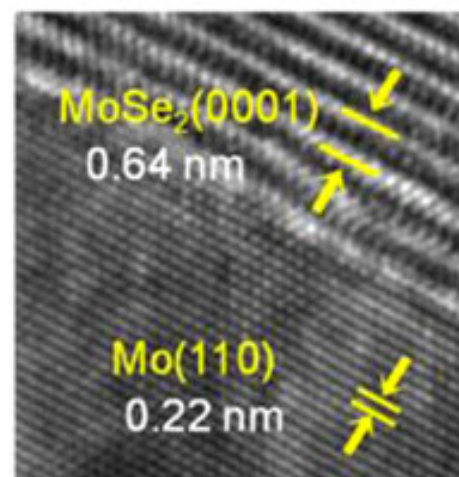
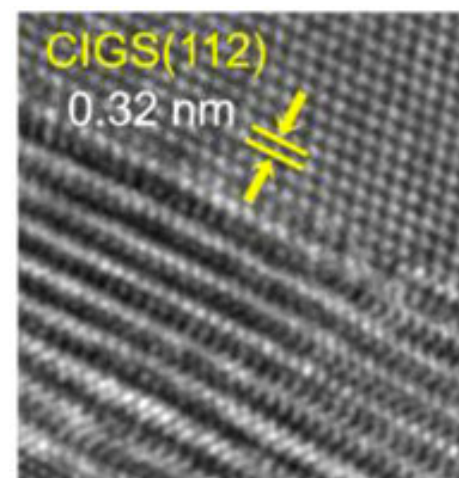
Perpendicular

Growth of CIGS absorber

15/31

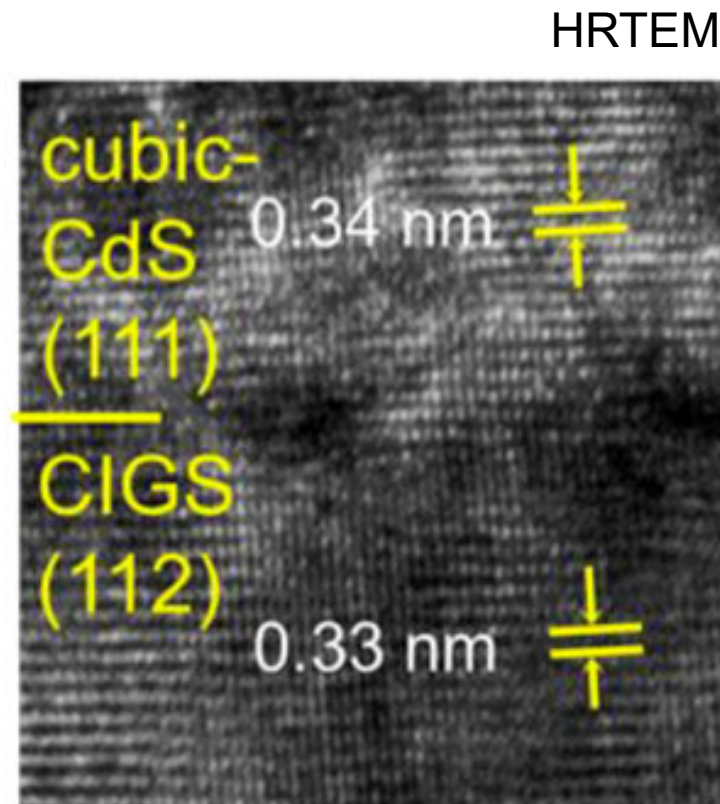
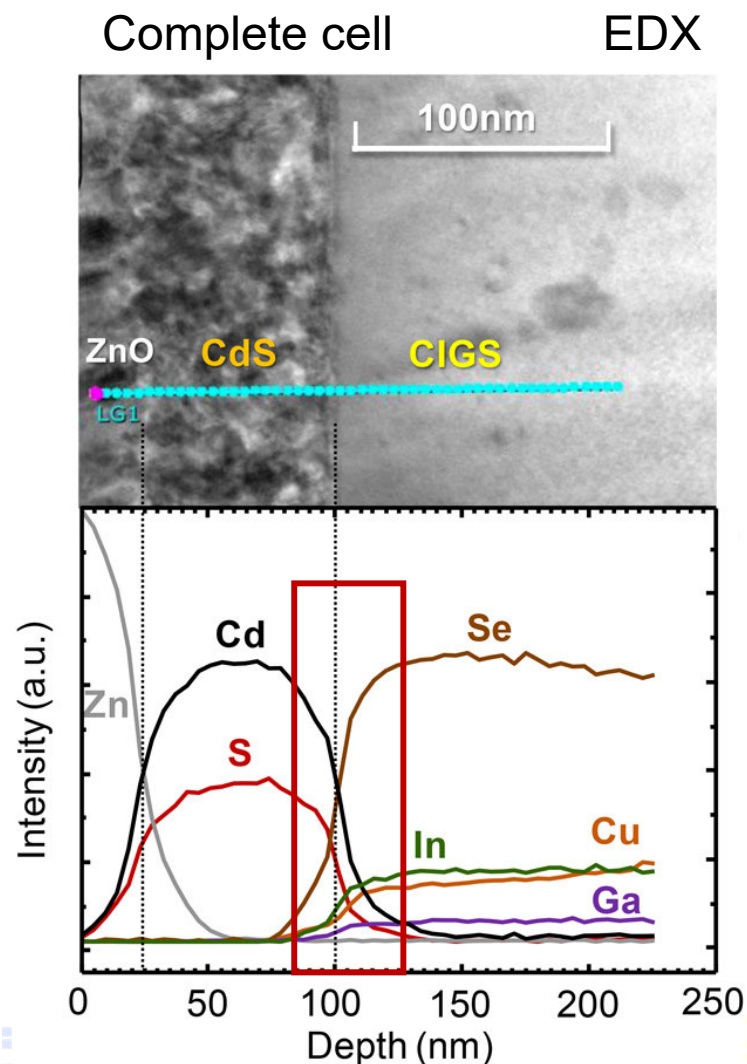


HRTEM



Growth of CdS buffer (CBD) and ZnO front contact

16/31



□ Mirjana.Dimitreivska@epfl.ch

Cd diffusion into CIGS layer

Y. Ando et al., Phys. Status Solidi A, 216, 1900164 (2019)

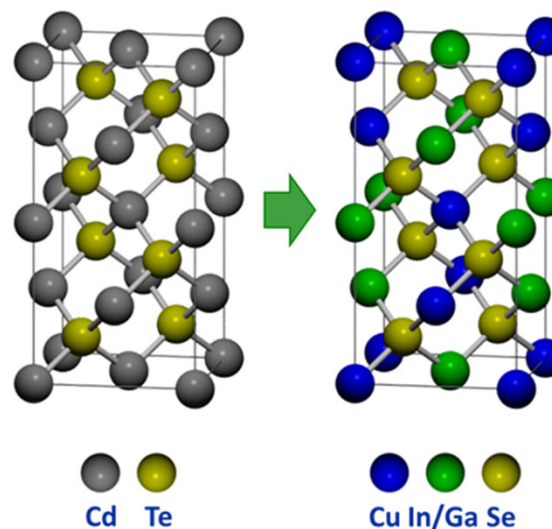
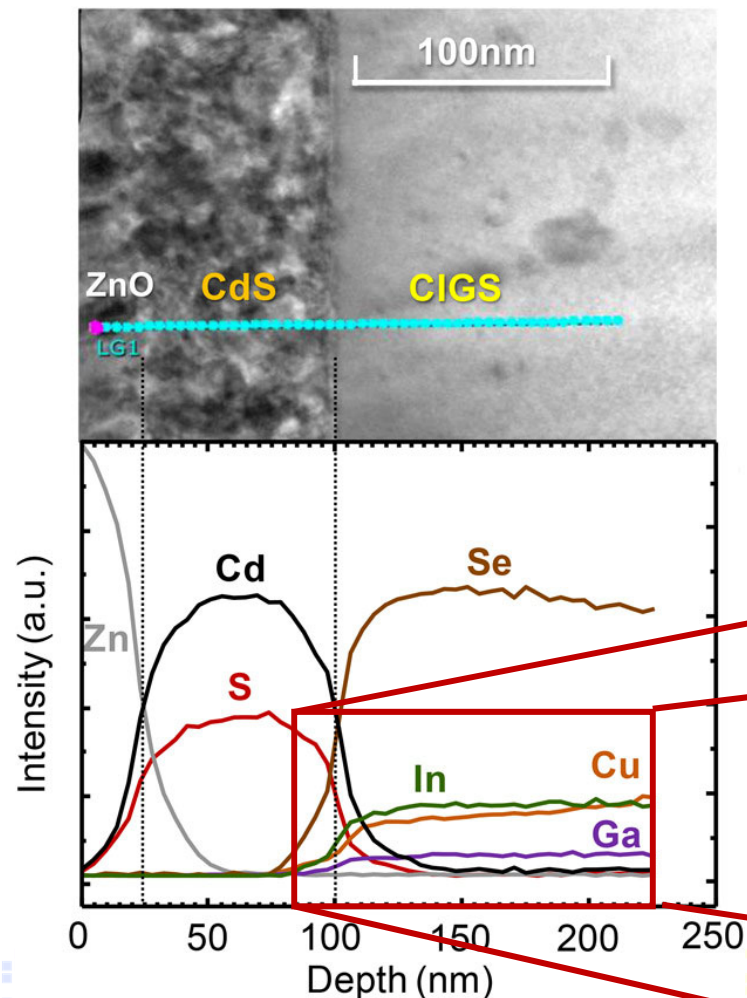
Growth of CdS buffer (CBD) and ZnO front contact

17/31

Complete cell

EDX

Q: Where is Cd integrated in CIGS?



Cu

In

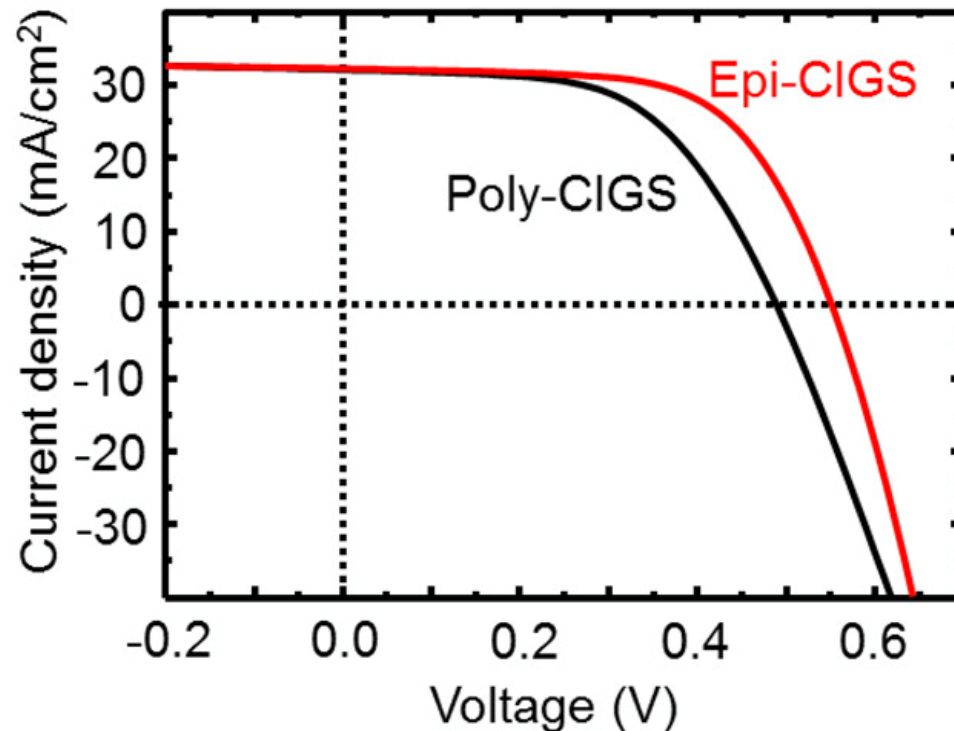
Ga

Se

□ Mirjana.Dimitrevska@epfl.ch

Cd diffusion into CIGS layer

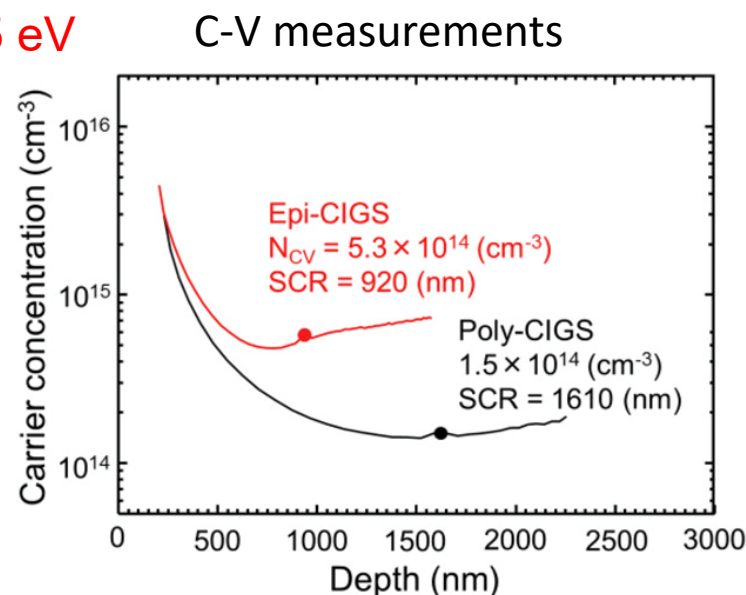
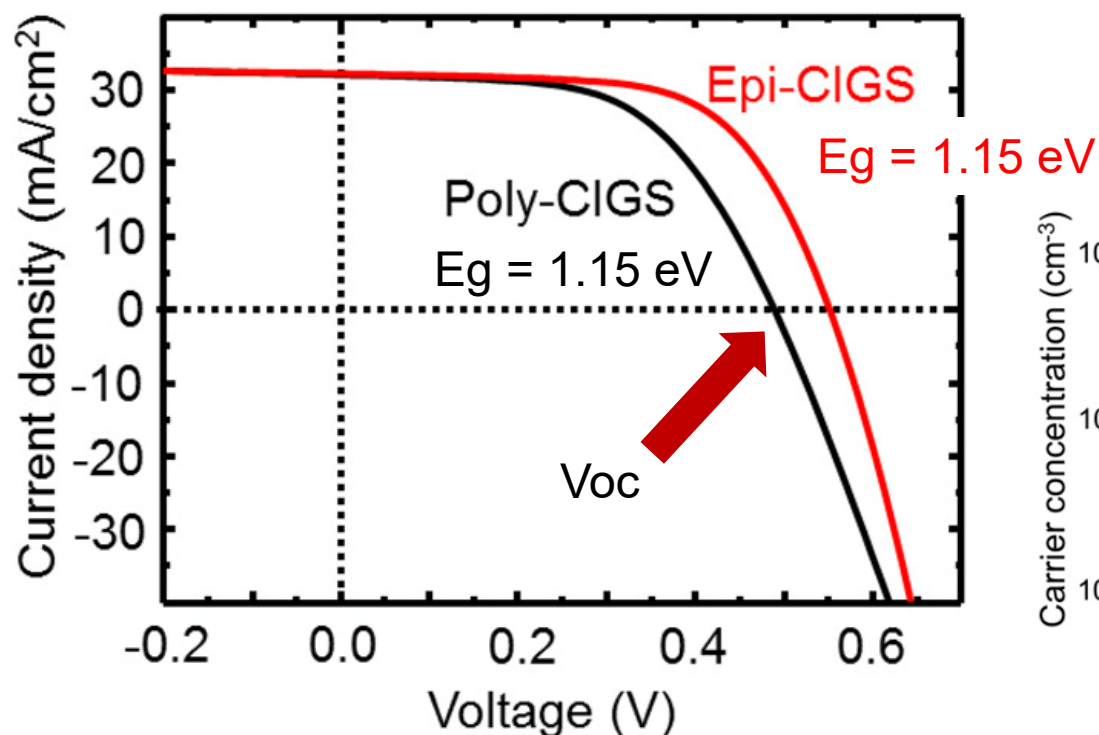
Y. Ando et al., Phys. Status Solidi A, 216, 1900164 (2019)



Q: Which cell is better performing?

**Epi-
CIGS**

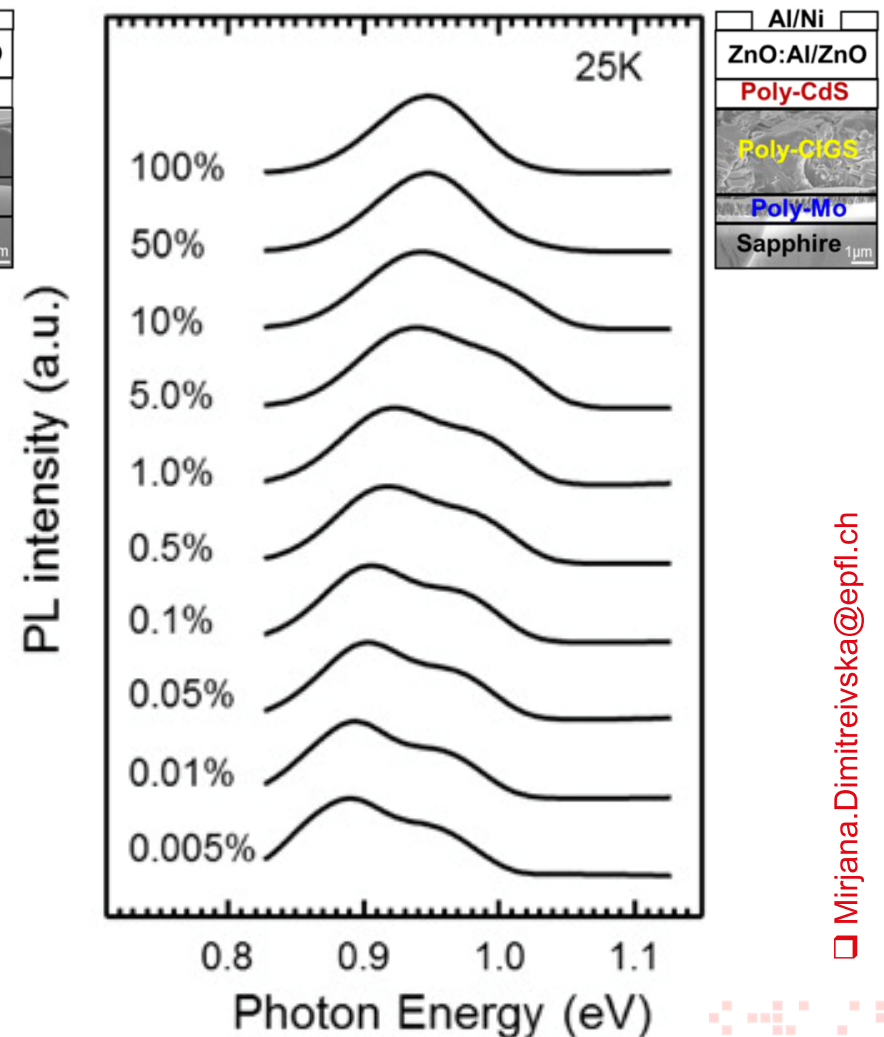
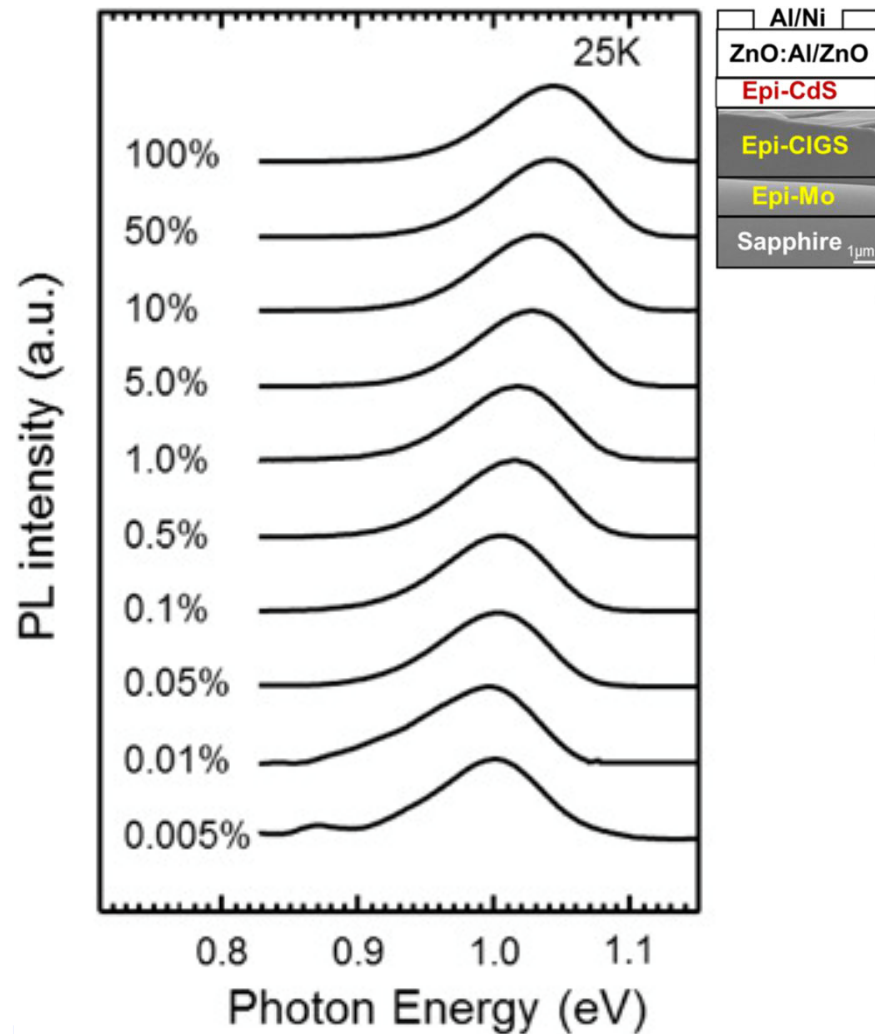
**Poly-
CIGS**



Epitaxial growth :
reduction in the density of
compensation defects
leading to better
performance

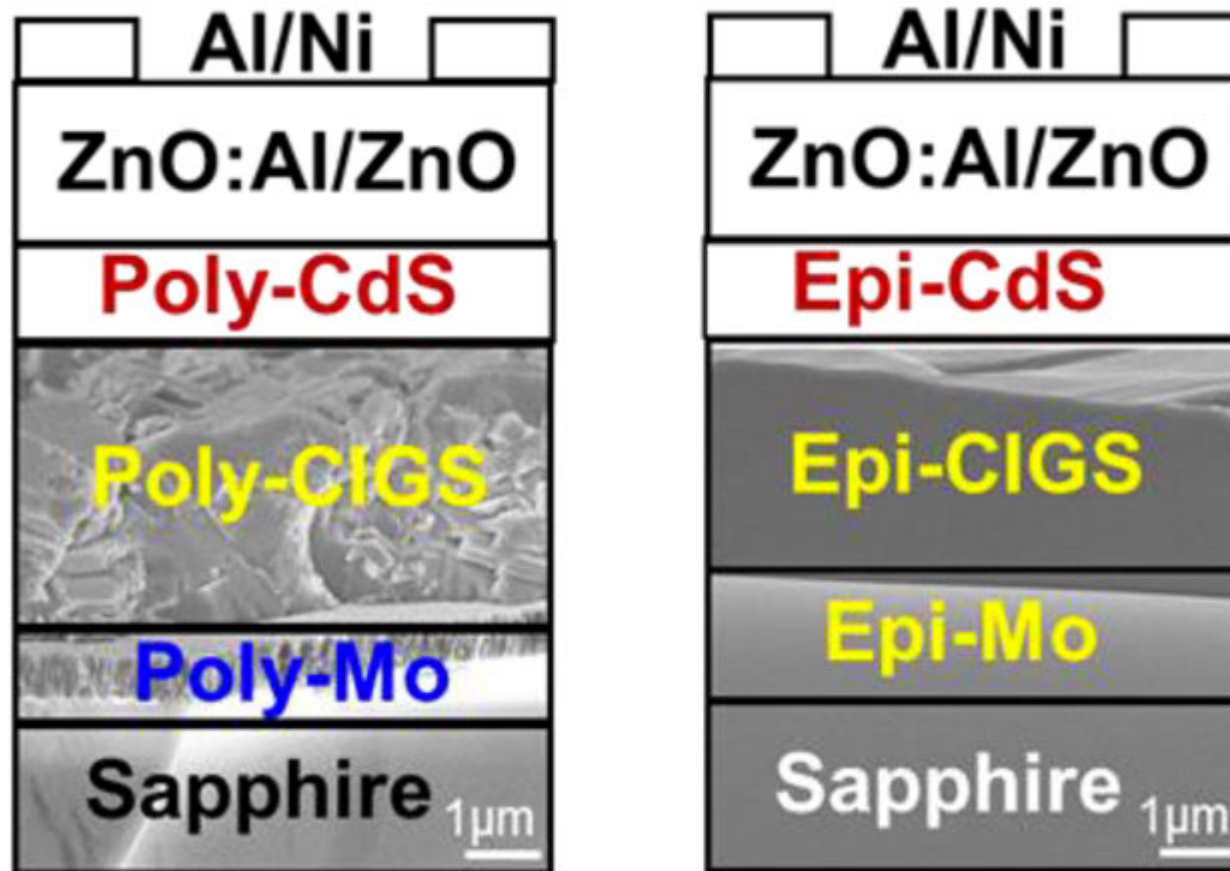
	$J_{sc} \text{ [mA cm}^{-2}\text{]}$	$V_{oc} \text{ [mV]}$	FF	Eff. [%]
Epi-CIGS	32.3	553	0.623	11.3
Poly-CIGS	32.2	489	0.570	8.95

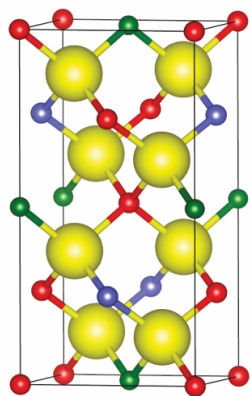
Photoluminescence measurements



Epitaxial growth improved solar cell performance

21/31

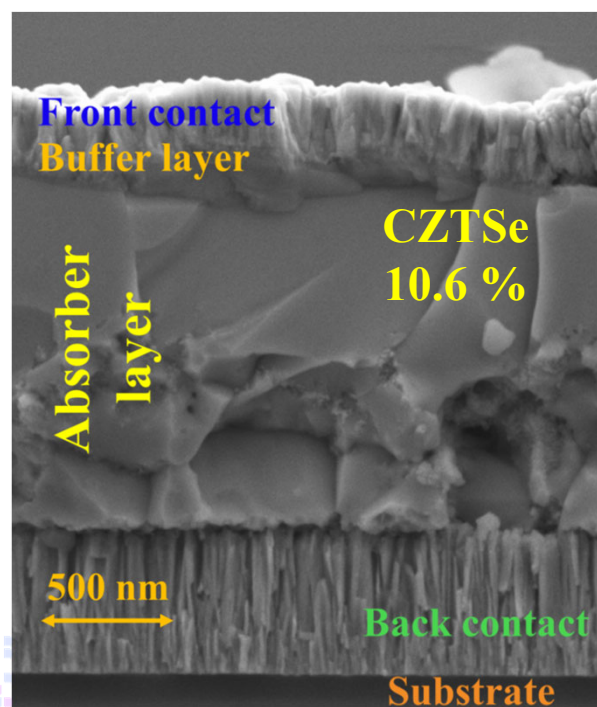




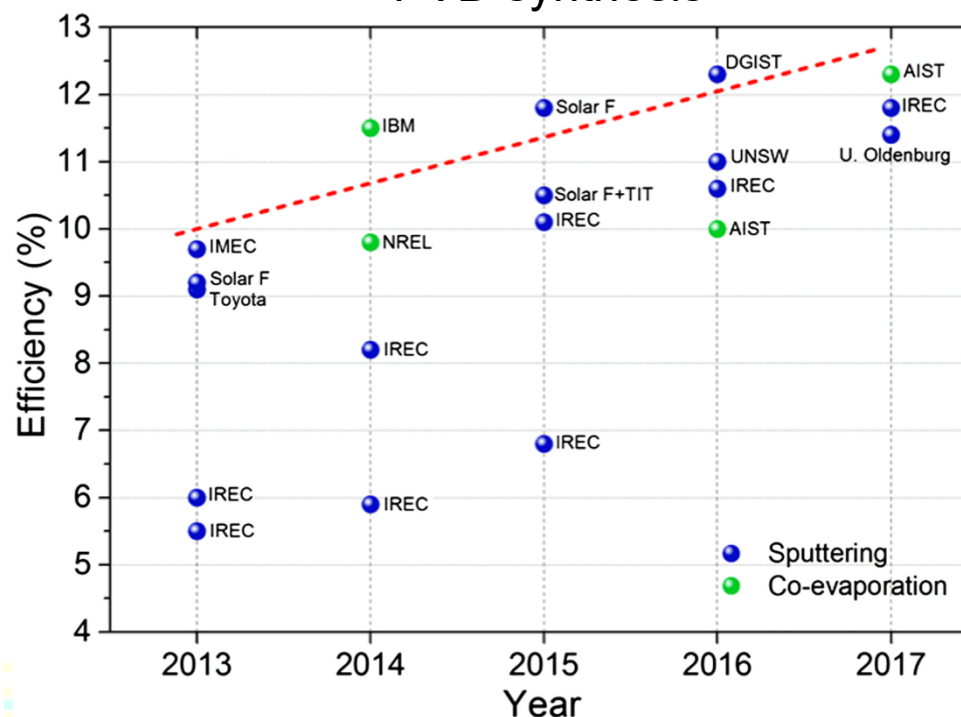
● Cu ● Zn ● Sn ● S or Se

Kesterite solar cells are significantly newer technology than CIGS (more problems):

- Secondary phases
 - Defect structure
 - Decomposition
 - Non-optimal device structure
- } Cu poor –Zn rich conditions



PVD synthesis



S. Giraldo et al., Prog Photovolt Res Appl. 27:779 (2019)

MBE technique is used for synthesis of metallic stack precursors: high control over the growth parameters compared to other techniques.

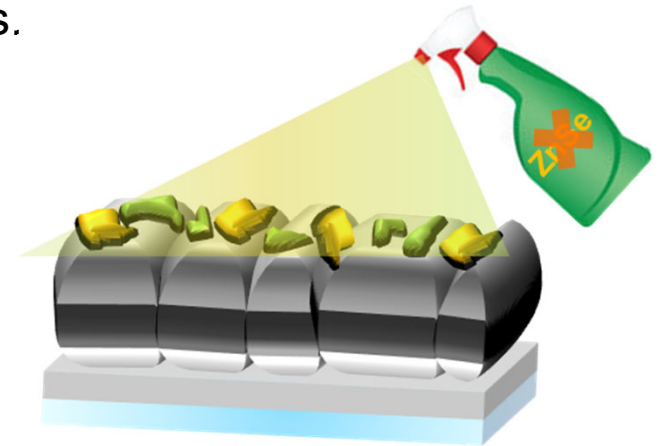
23/31



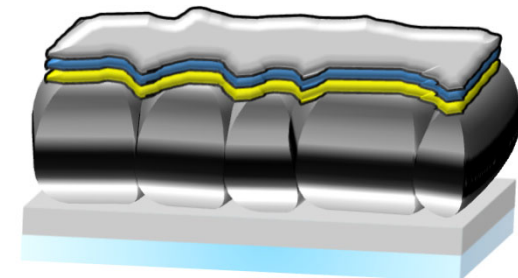
Metallic stack deposition



Annealing in Ge atmosphere
(changes in the amount and temperature)

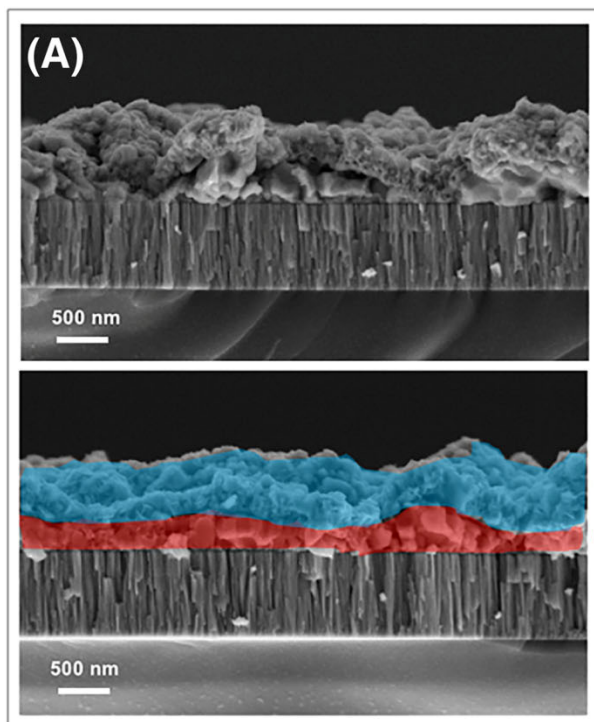


Chemical etching for removal of secondary phases

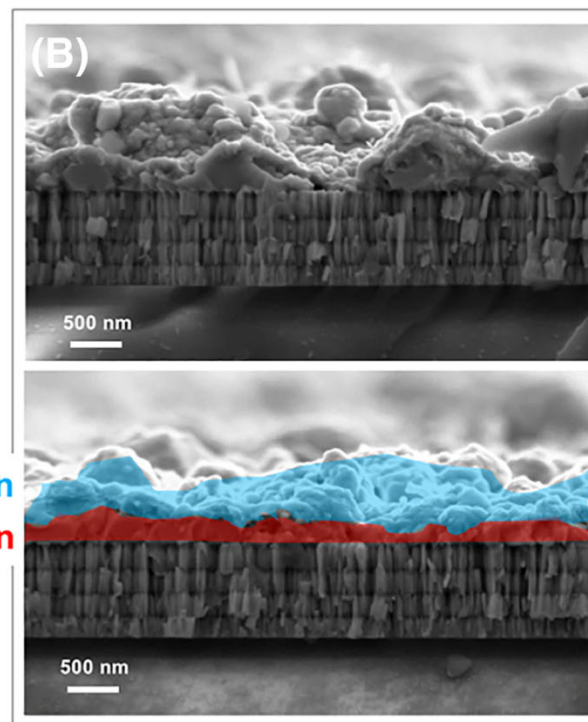


CdS/i-ZnO/ITO deposition

Magnetron sputtering



Epitaxial growth

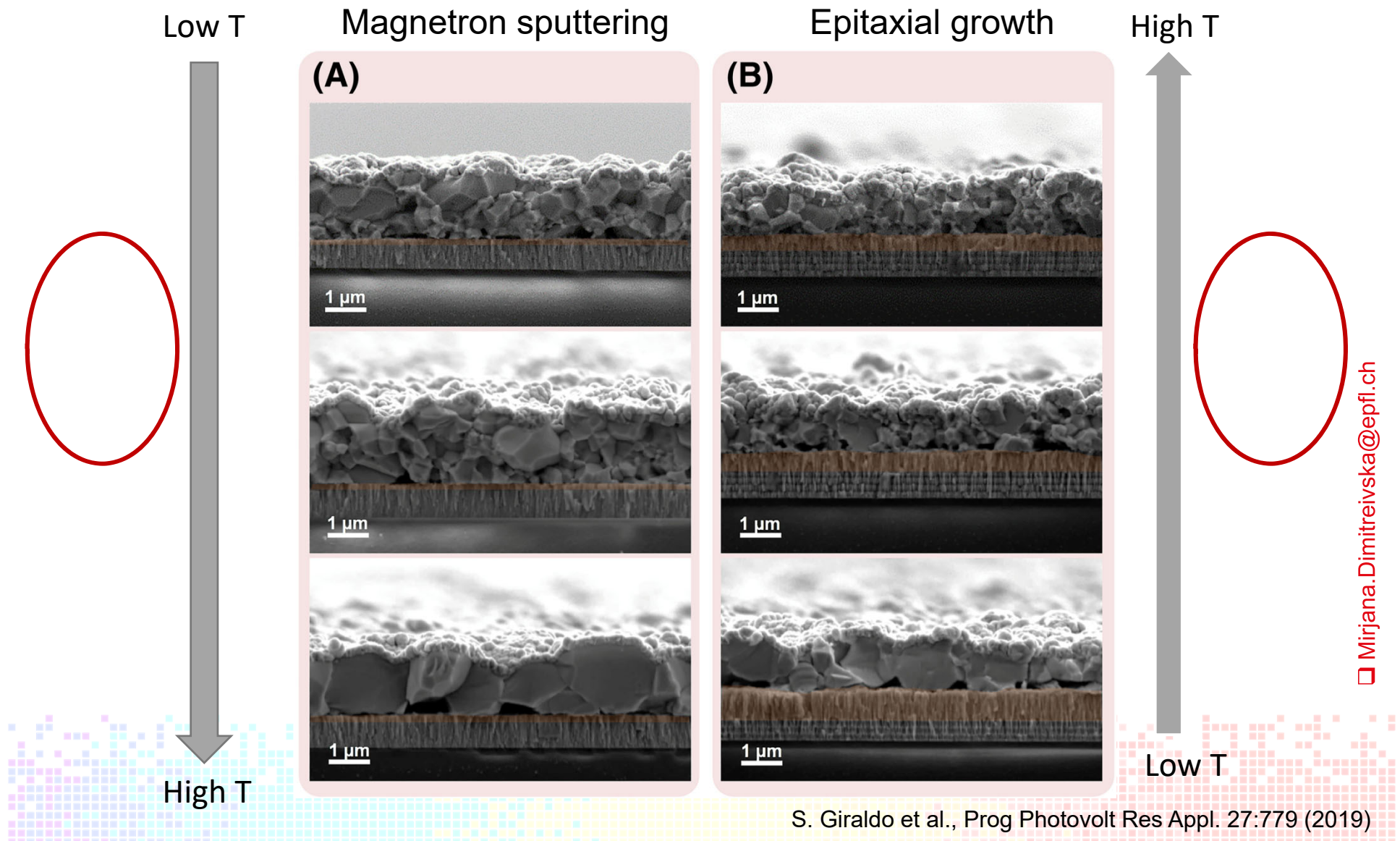


Cu-Zn
Cu-Sn

Annealing under different temperatures

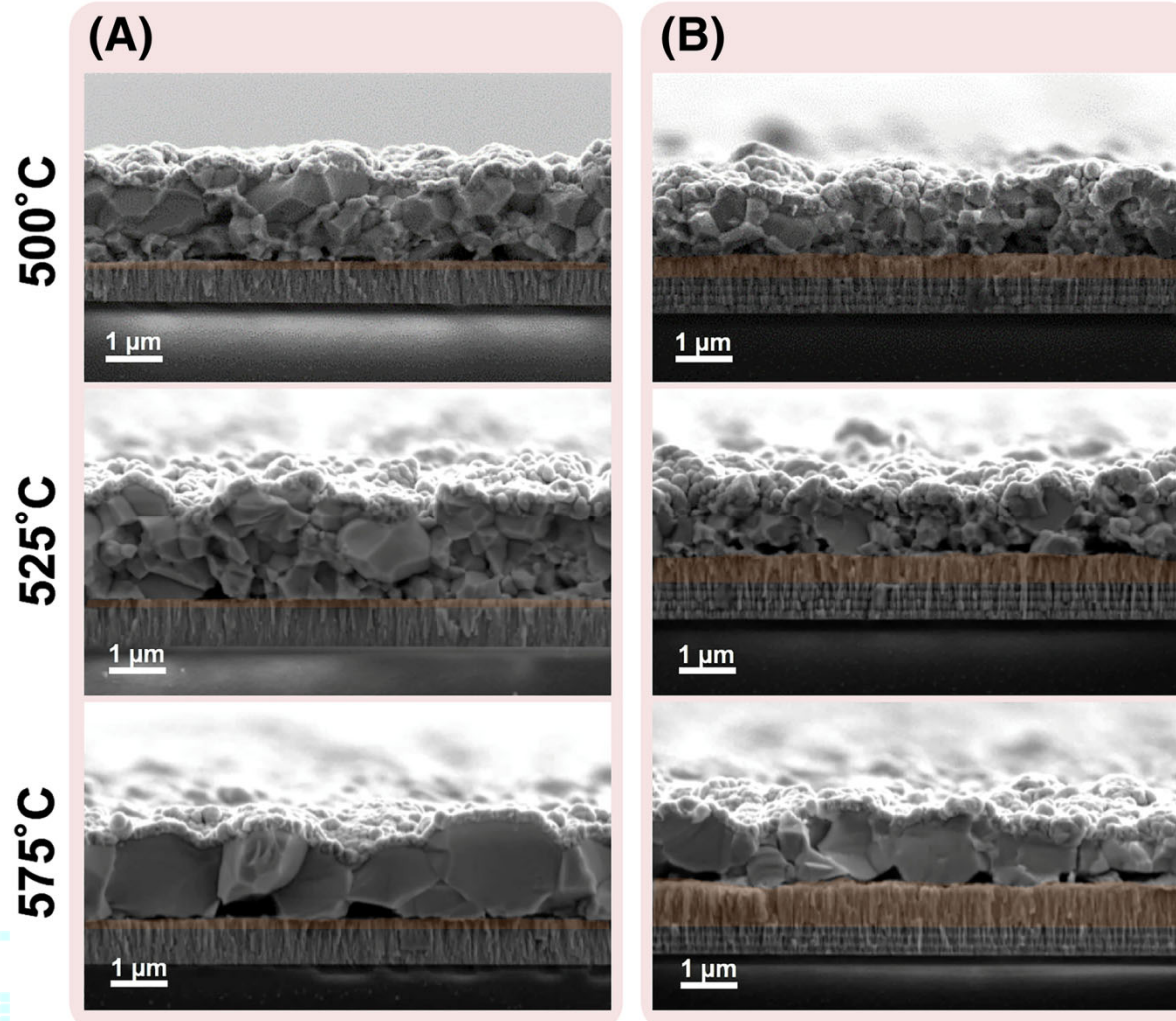
Q: How is the temperature changing?

25/31



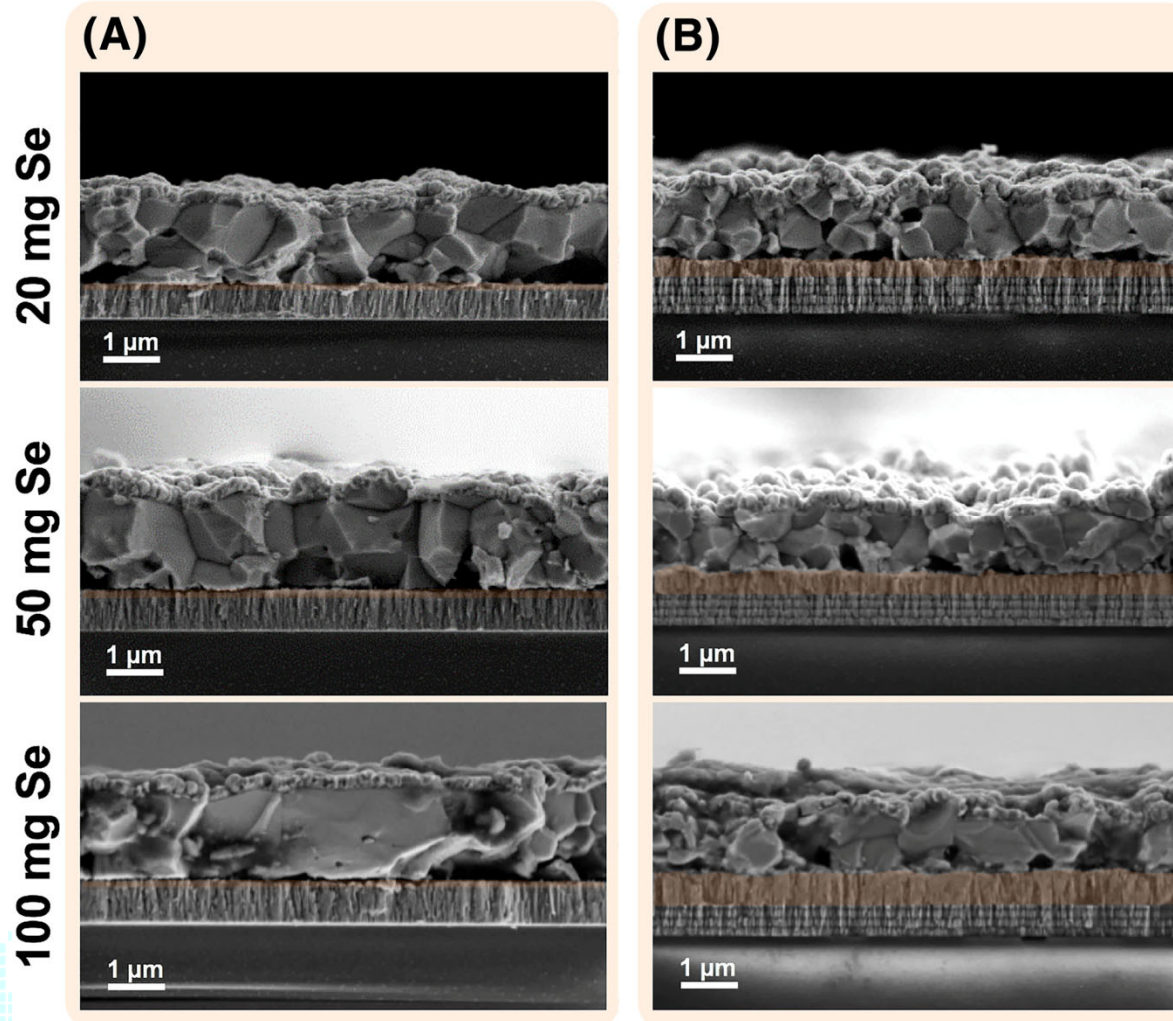
Magnetron sputtering

Epitaxial growth



Magnetron sputtering

Epitaxial growth

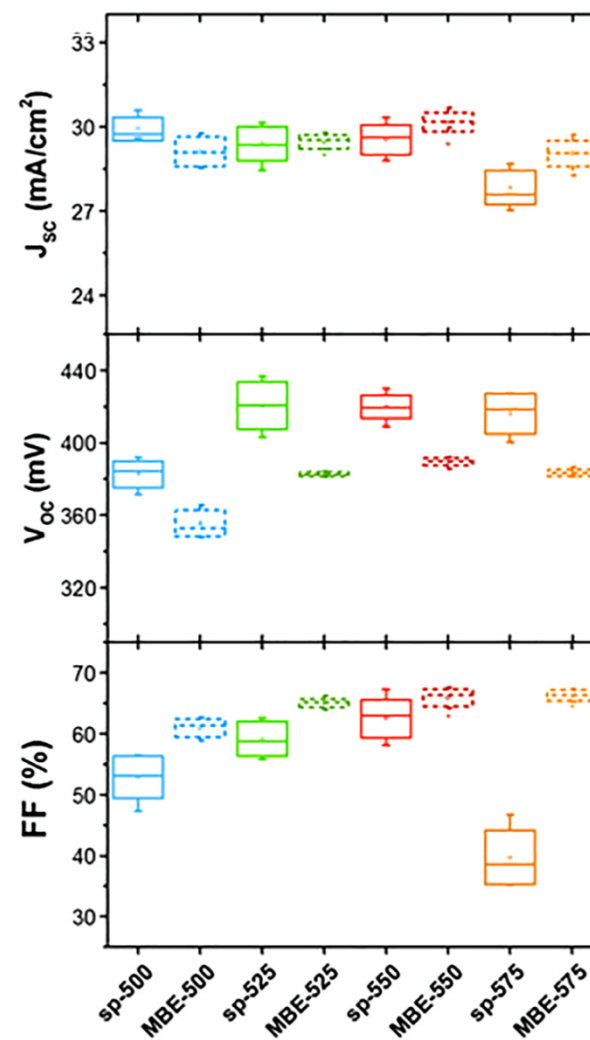
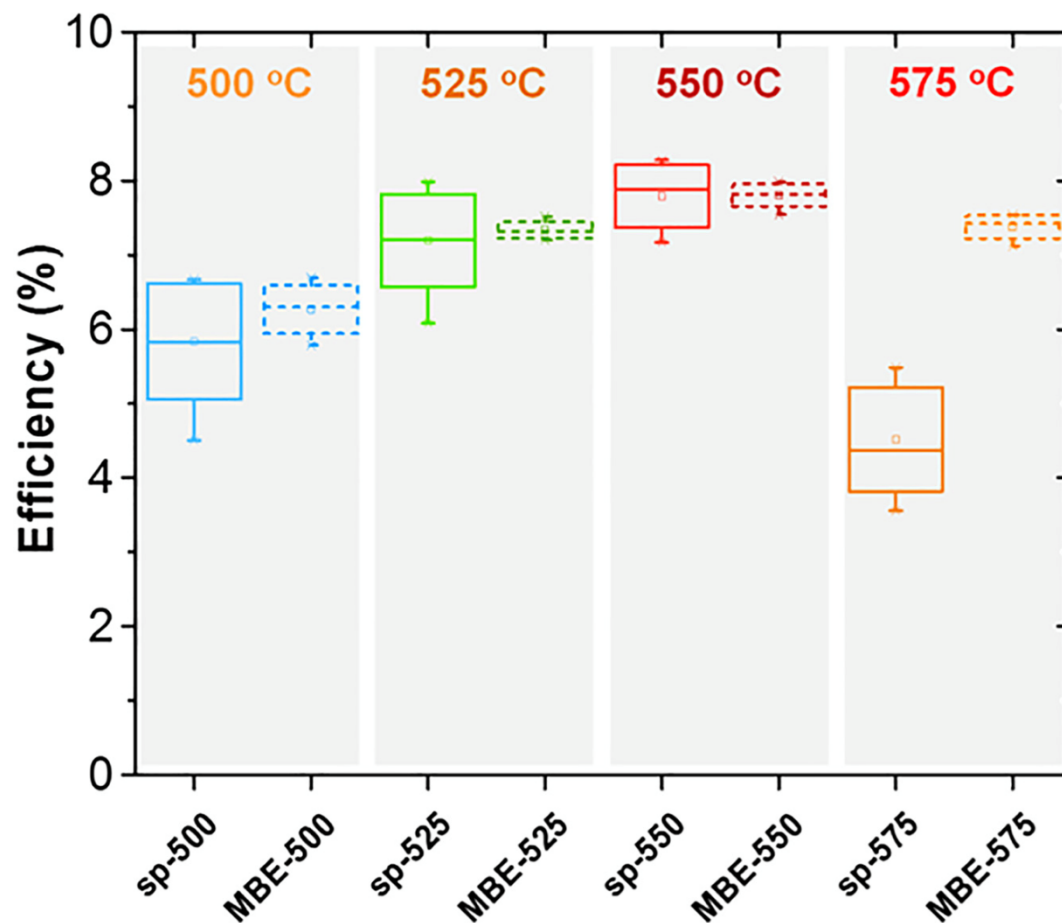


Annealing under different temperatures

28/31

(full line) Magnetron sputtering

(dotted line) Epitaxial growth



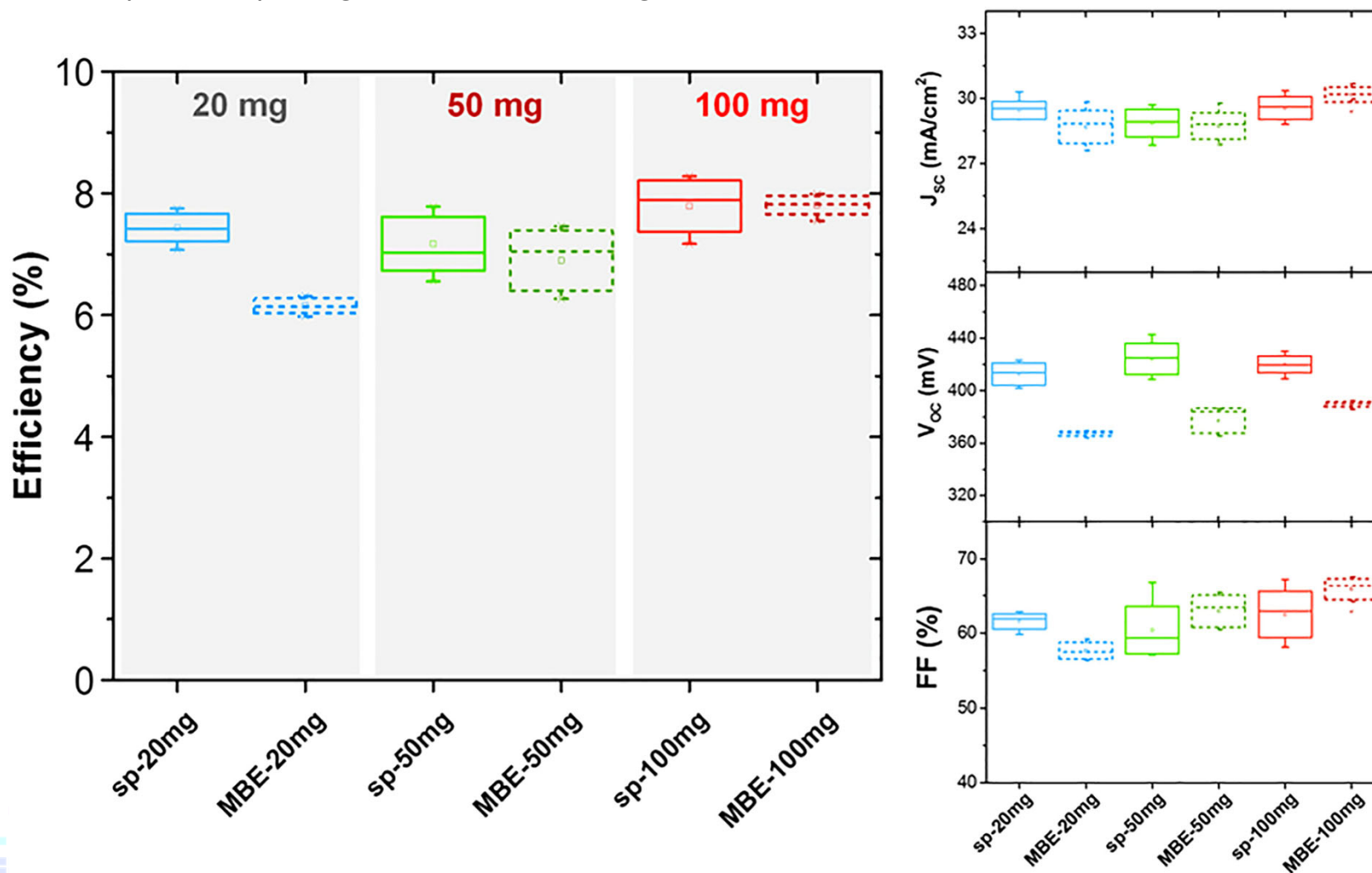
□ Mirjana.Dimitreivska@epfl.ch

Annealing with different amount of Se

29/31

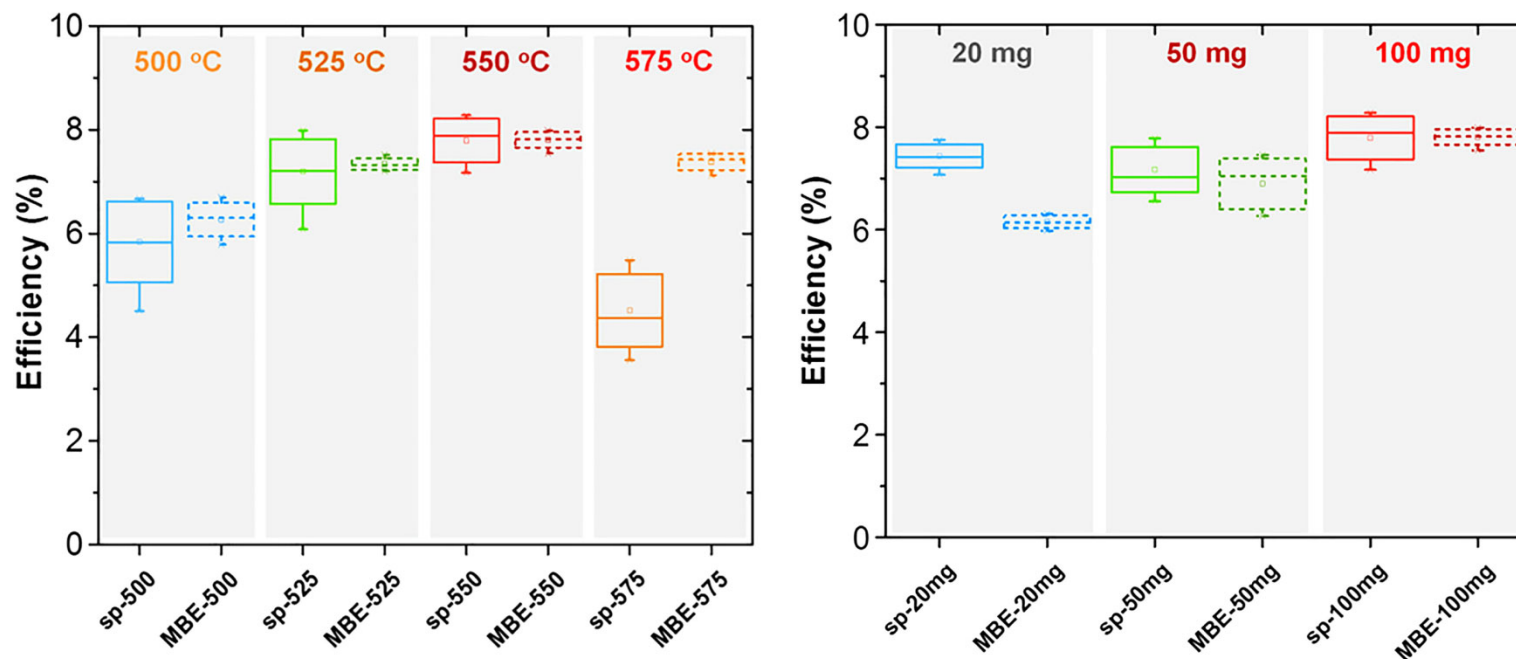
(full line) Magnetron sputtering

(dotted line) Epitaxial growth



□ Mirjana.Dimitreivska@epfl.ch

Q: Which annealing conditions would you choose for the growth of the absorber 30/31 for obtaining best performing solar cells?



T = 550 °C
m (Se) = 100 g

T = 525 °C
m (Se) = 50 g

T = 550 °C
m (Se) = 50 g

(full line) Magnetron sputtering

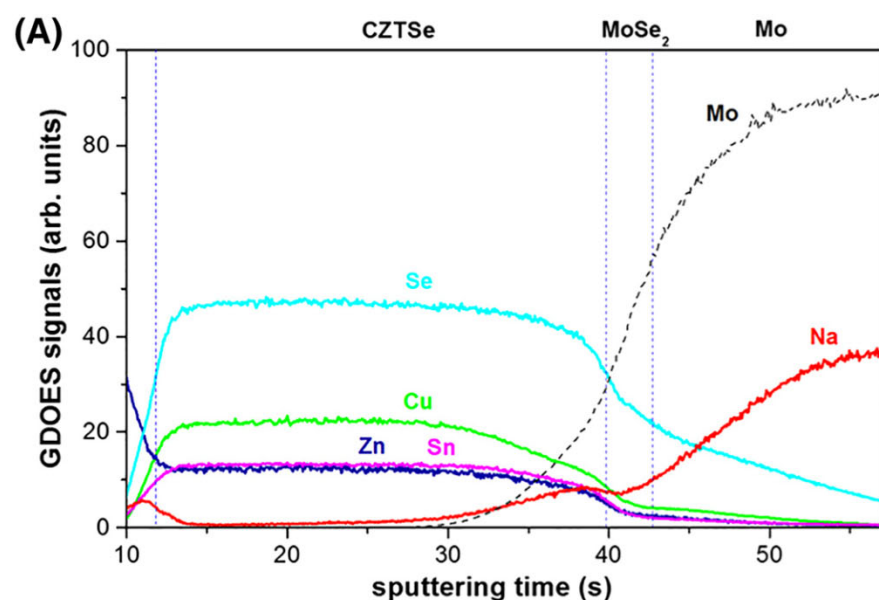
(dotted line) Epitaxial growth

Voc is always underperforming in case of epitaxial growth, related to substrate thickness?

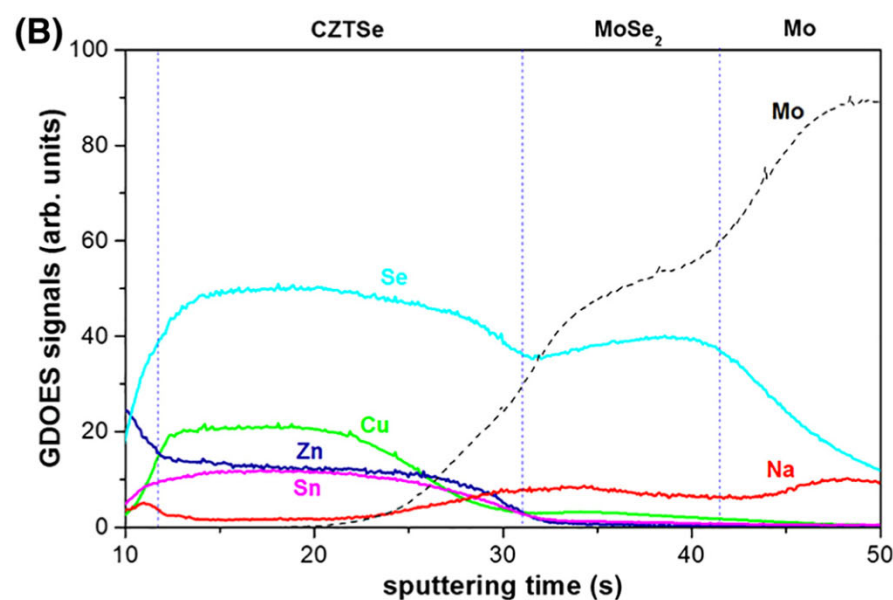
31/31

Compositional profiling

Magnetron sputtering

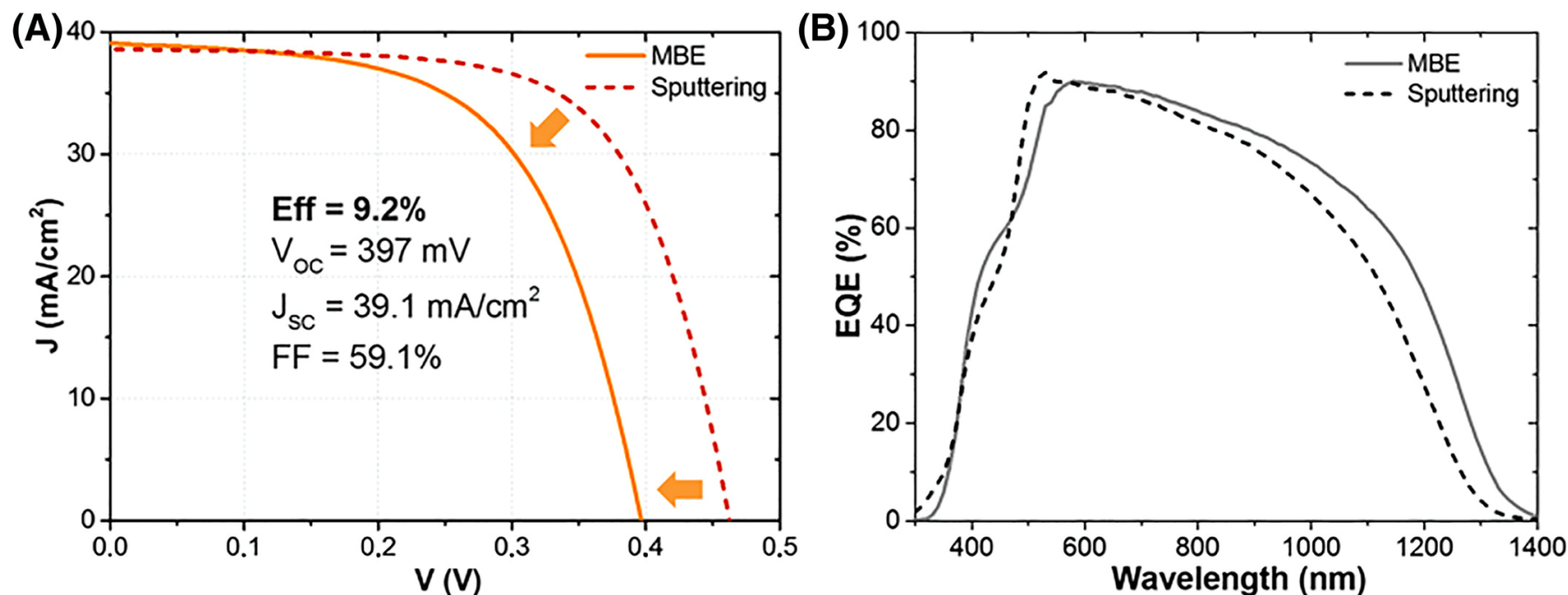


Epitaxial growth



□ Mirjana.Dimitreivska@epfl.ch

Champion solar cells



Epitaxial growth :

Did not improve the performance of solar cells, though there is still room for optimization.

- The effect of epitaxial growth was investigated on two solar cell technologies : CIGS and kesterites
- CIGS technology is more suitable for epitaxial growth, leading to improved solar cell performance
- Kesterite based solar cell underperformed when grown with MBE in comparison to conventional methods (mostly due to the difference in alkali metal incorporation)