History and prospects of the physical synthesis of kesterite for photovoltaic applications

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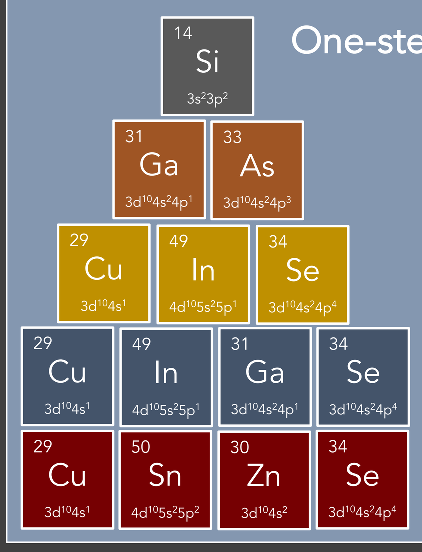
Overview of the physical routes for the synthesis of kesterite $Cu_2ZnSn(S,Se)_4$ as absorber layer for PV applications



One-step process: Vacuum deposition of elements onto heated substrate at high temperature ~$500°C$

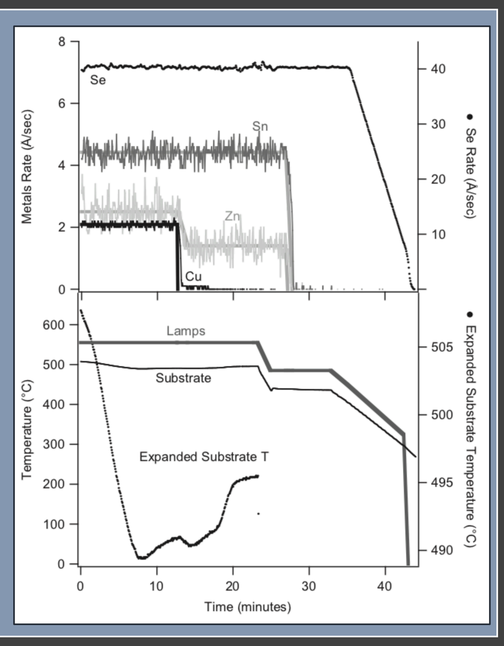
Single step synthesis and crystallization

- Low efficiencies $\eta < 5\%$
- Secondary phases
- Stoichiometry deviations
- Loss of volatile species: $Sn(S,Se)$ & Zn

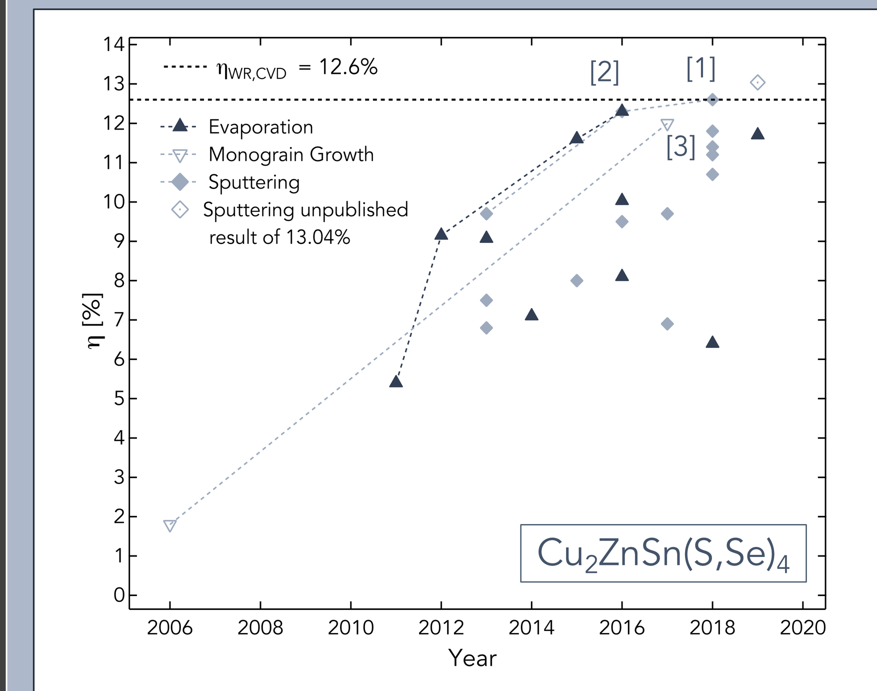
Increase background pressure to prevent losses within the deposition machine design

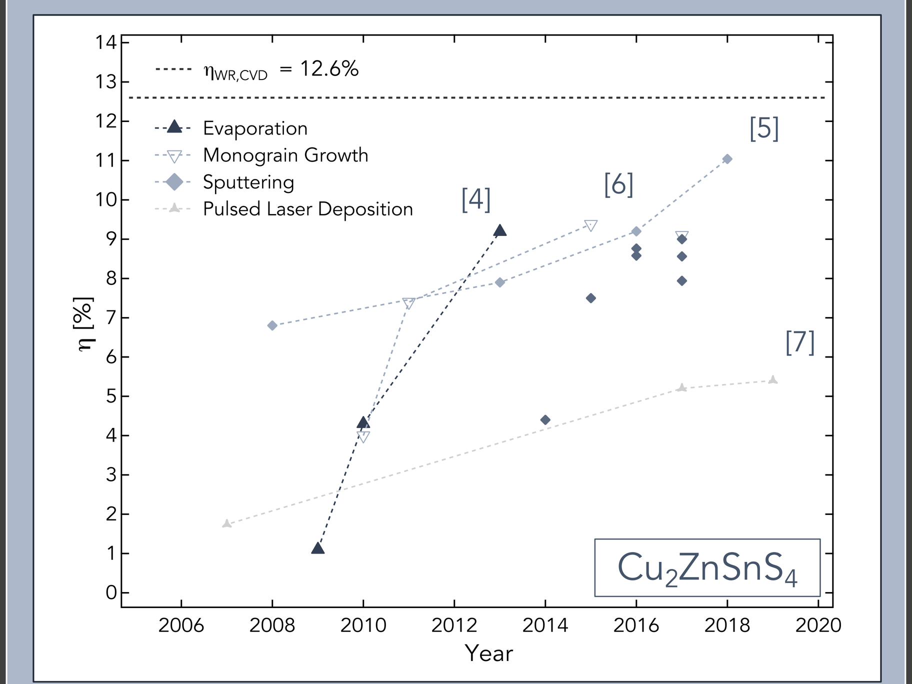
- $\eta \in [5;10]\%$
- Elemental losses & secondary phases
  - → Deep defects within the band gap
  - → V_{OC} deficit

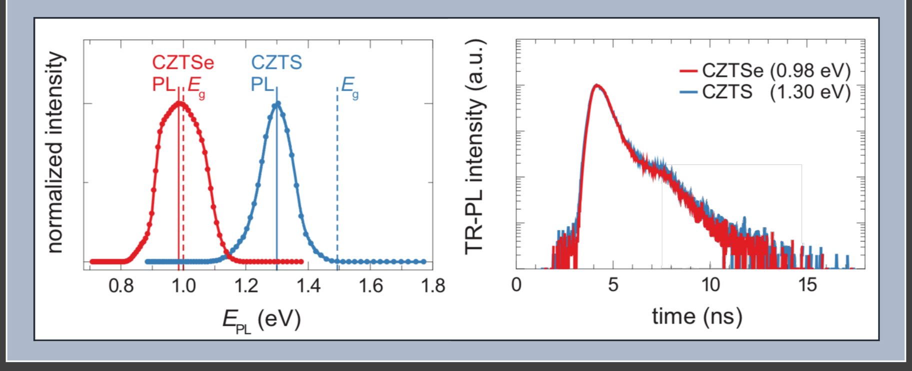
One-step processes limit the efficiency of kesterite-based solar cells



Kesterite-based cell efficiency through the years







From one-step to two-step processes

(i) Low temperature deposition of precursor film containing all (or part of) the elements for the kesterite formation
(ii) Crystallization induced by thermal annealing under S (sulfurization) or Se (selenization) atmosphere

❑ Sequential and co-evaporation

Elemental sources evaporation with/without chalcogen at low substrate temperature $[RT - 150]°C$:

$$Cu, Zn, Sn, Se$$
$$Cu, ZnSe, Sn \,\&\, Se$$
$$\ldots$$

High temperature annealing $[550 - 590]°C$ in various atmospheres:

$$N_2, Ar, S, Se, Sn$$

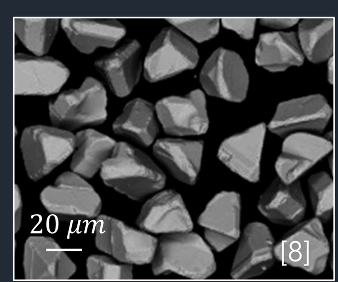
Achievement of high-efficiency kesterite-based solar cells:

$$CZTS: \eta \rightarrow 9.2\% \qquad CZTSe: \eta \rightarrow 12.3\%$$

Compare to CVD, safer and more reproducible processes

❑ Growth of monograins

- Chemical etching optimization
- Single crystal structure
- Max. working area of 80%

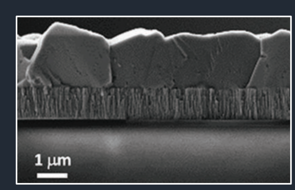


❑ Sequential and co-sputtering

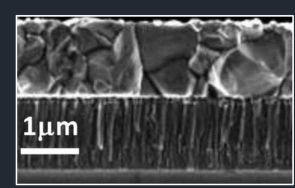
Routes involving $Cu_2Sn(S,Se)_3$ and $Zn(S,Se)$ phases limit elemental losses compared to binary compounds route

Pure metallic, metallic alloys or chalcogen containing targets with (i) sequential or (ii) co-sputtering process

(i) Stack structure optimization and compositional control (thicknesses, stacking order, …)



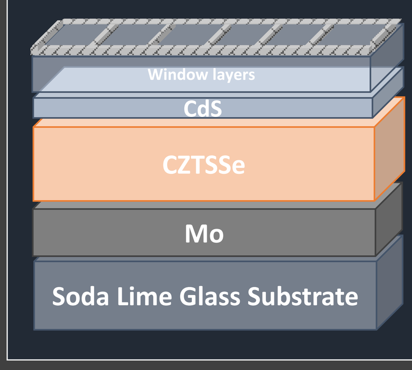
(ii) Homogeneous elemental distribution but target cross-contaminations



$$CZTS: \eta \rightarrow 11\% \qquad CZTSSe: \eta \rightarrow 12.6\%$$

❑ Pulsed Laser Deposition (PLD)

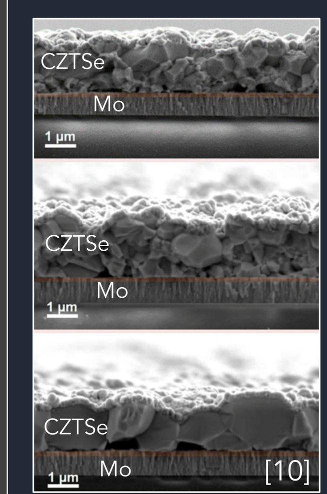
- Laser fluence → stoichiometry control
- Reproducibility issues
- High crystallinity and good adhesion

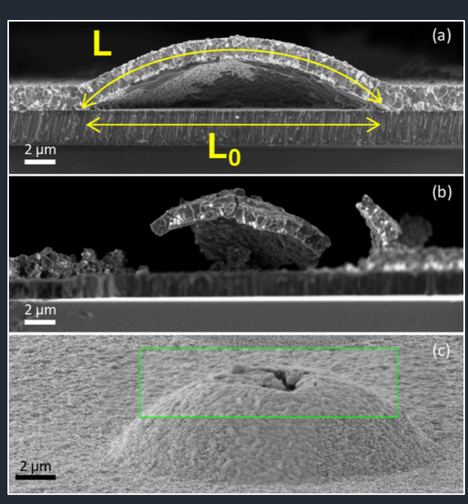


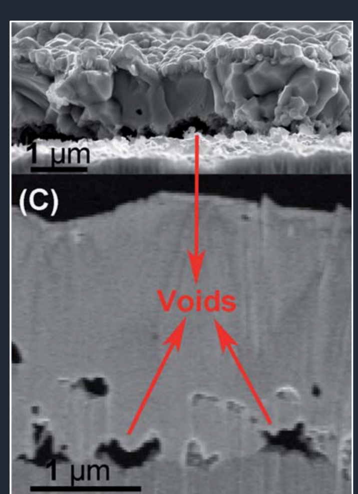
Efficiency improvements cannot only be ascribed to the absorber layer synthesis optimization

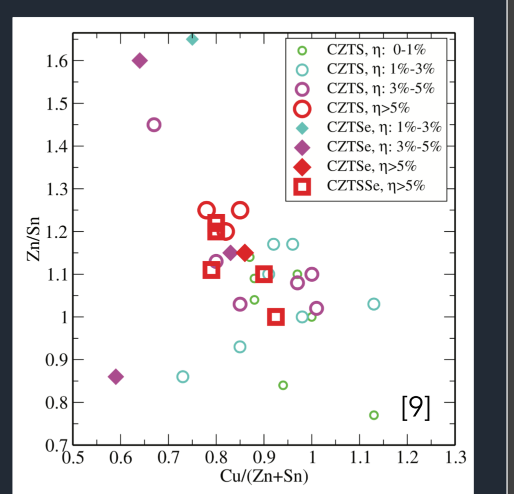
Composition	Physical Route	Annealing	Efficiency	Institution Reference
CZTSSe	Seq. Sputt.	H_2S,Se - 300;480°C	12.6%	DGIST [1]
CZTGSe	Co-Evap.	$GeSe_2$,$SnSe_2$,Se - 525°C	12.3%	AIST [2]
CZTSe	Monograin	740 °C	12.0% (EA)	Crystalsol [3]
CZTS	Co-Evap.	S_2, N_2 – 570°C	8.4%	IBM [4]
CZTS	Co-Sputt.	SnS,S - 560°C	11.0%	UNSW [5]
CZTS	Monograin	S – 740°C	9.4% (EA)	Taltech [6]
CZTS	PLD	N.A.	5.4%	DTU [7]

Key aspects of the kesterite thin films synthetised by physical routes









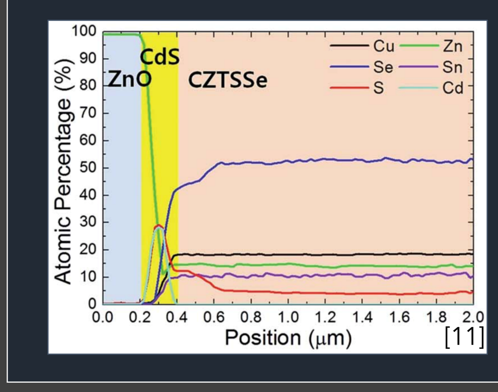
Grain growth: Control of the synthesis and annealing parameters. Grain size ~$1 - 2\ \mu m$

Blistering: Background pressure and smoothing of the annealing/cooling ramp

Voids - Adhesion: $Mo(S,Se)_2$ layer; Sn back layer; S-containing kesterite; Interlayers (oxides, …)

Volatility - stoichiometry: Annealing conditions control: → reduce the elemental losses → Prevent voids formation

→ Platzer-Björkman C., et al. "Back and front contacts in kesterite solar cells: state-of-the-art and open questions." *Journal of Physics: Energy* 1.4 (2019): 044005.



Alkali doping → Grain size and recrystallisation
→ Role not completely understood $\quad Na, Li, K, \ldots$

Alloying → Cationic substitution
→ Anionic substitution (S,Se) $\quad \binom{Cu}{Ag}_2 \binom{Zn}{Cd} \binom{Ge}{Sn} \binom{S}{Se}_4$

→ Romanyuk, Y., et al. "Doping and alloying of kesterites." *Journal of Physics: Energy* (2019).

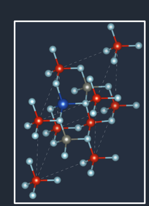
Personal approach

"From atomic-scale calculations to experimental synthesis of kesterite thin films"

Primitive cell – Ab initio calculation

GGA-PBE & HSE06 calculations using VASP

- Density of states
- Band dispersion: m^*, E_G (direct/indirect)
- Optical properties: ϵ, α, n

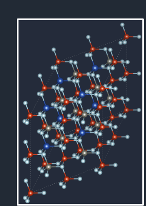


Primitive Cell

Supercell (64 atoms) – Ab initio calculation

GGA-PBE & HSE06 calculations using VASP

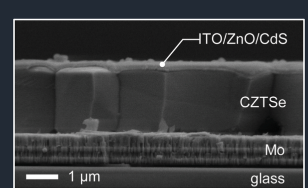
- Defects formations energies $\Delta H_{F,\alpha}(\mu_E, \mu_i)$
- Charge carriers concentration
- Link to growth conditions μ_i



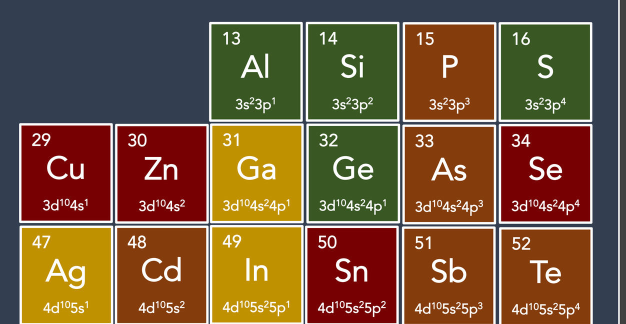
Supercell

Kesterite thin film – Electrical characterization

- Stoichiometry variation based on annealing conditions
- Electrical characterizations of defects



Kesterite thin film



→ Hood, Samantha N., et al. "Status of materials and device modelling for kesterite solar cells." *Journal of Physics: Energy* 1.4 (2019): 042004.

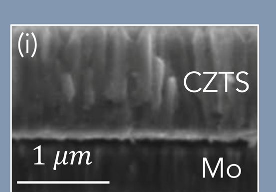
→ Grossberg, Maarja, et al. "The electrical and optical properties of kesterites." *Journal of Physics: Energy* (2019).

In a nutshell

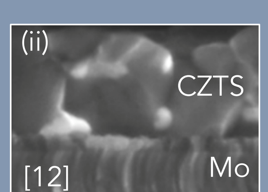
Efficiency enhancements thanks to the evolution of the physical deposition procedures

One-step to two-step process:
(i) Precursor deposition
(ii) Selenization/sulfurization

Strong dependency on the deposition and annealing parameters



Precursor



Kesterite

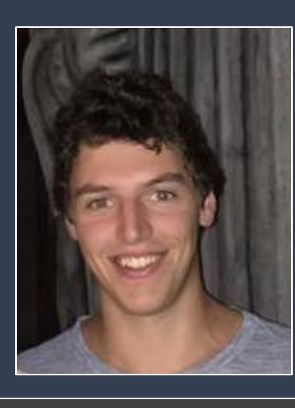
Grain growth control and of elemental loss limitation during the annealing lead to efficiency over 10%

η comparable to CVD kesterite-based cells with safer and more reproducible processes

Various perspectives:

- Sulfurization/selenization conditions
- Doping
- Alloying

Ratz, Thomas, *et al.* "Physical routes for the synthesis of kesterite." *Journal of Physics: Energy* 1.4 (2019): 042003.



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