Influence of the rear interface on composition and photoluminescence of CZTSSe absorber

Antonio Cabas-Vidani[1], Leo Choubrac[2], José A. Márquez[2], Thomas Unold[2], Matthias Maiberg[3], Roland Scheer[3], Hu Li[4], Klaus Leifer[4], Robin Pauer[1], Evgeniia Gilshtein [1], Ayodhya N. Tiwari[1] and Yaroslav E. Romanyuk[1]

[1]Laboratory for Thin Films and Photovoltaics, Empa – Swiss Federal Laboratories for Materials Science and Technology, Dübendorf

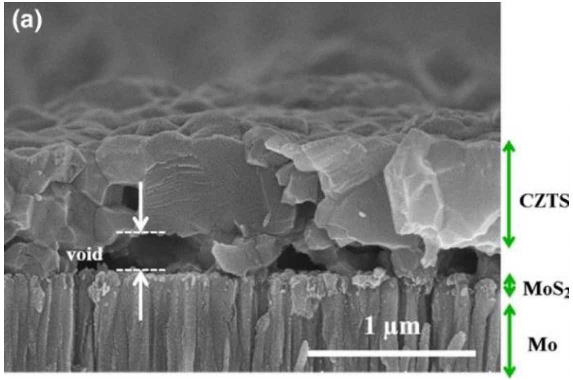
[2]Dept. Structure and Dynamics of Energy Materials Helmholtz-Zentrum für Materialien und Energie GmbH Hahn-Meitner-Platz 1, D-14109 Berlin, Germany

[3]Institute of Physics, Martin-Luther-University Halle-Wittenberg, Halle 06120, Germany

[4]The Ångström Laboratory, Department of Engineering Sciences, Uppsala University, Box 534, 75121 Uppsala, Sweden

Motivation

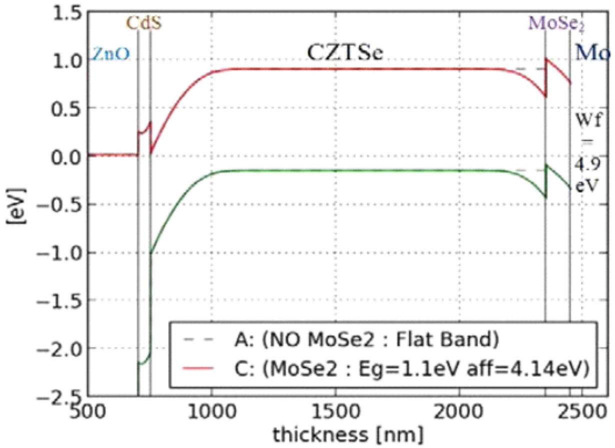
Problems of Mo back contact:



Chen et al., *J. Am. Ceram. Soc.*, *99*(5), 2016.

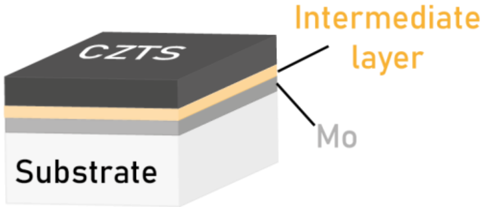
$$2CuZnSnS(e)_4 \rightarrow$$
$$2Cu_2S(e) + 2ZnS(e) + 2SnS(e) + MoS(e)_2$$

Scragg et al., *J. Am. Chem. Soc.*, *134*(47), 2012.

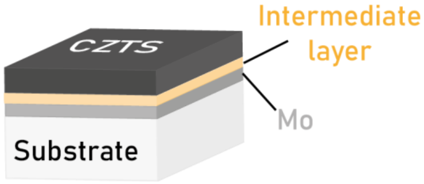


Cozza et al., *IEEE J. Photovolt.*,1-6, 2016.

Possible solution: insertion of an intermediate layer (IL)



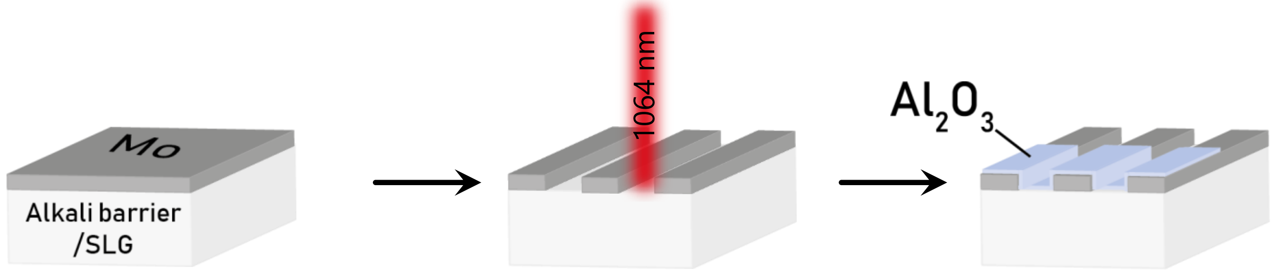
Intermediate layer (IL)



Ref	IL	Thinned $Mo(S,Se)_2$	Alkalis diffusion		Additional notes
Park et al., Thin solid films, 2017	MoO_3	✖	Na ↓	K ↑	Improved crystallization
Liu et al., Sol. RRL, 2018	MoO_3	✔	K ↑		Reduced voids at the back
Englund et al., Phys. Status Solidi A, 2018	TiN	✔	Na ↑		Improved crystallization
Liu et al., NPG Asia Materials, 2017	Al_2O_3	✔	Na ↑		Reduced phase segregation
Liu et al., Appl. Phys. Lett., 2014	TiB_2	✔	—		Smaller grains
S. López-Marino et al., J. Mater. Chem., 2013	ZnO	✖	—		Bilayer formation + less secondary phases
Colina et al., IEEE J. Photovoltaics, 2016	a-SiC	✖	—		Increase in grain size

Can we decouple the influence of the IL from growth variables?

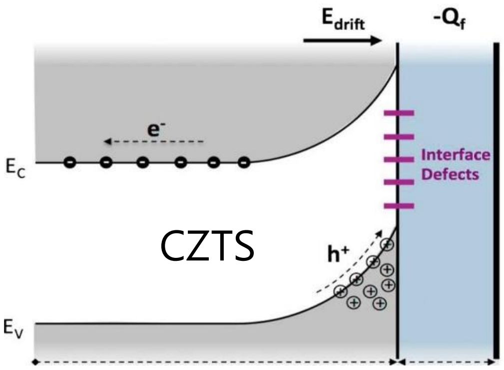
Design of the bottom surface



Controlled Na out-diffusion

Mo scribing

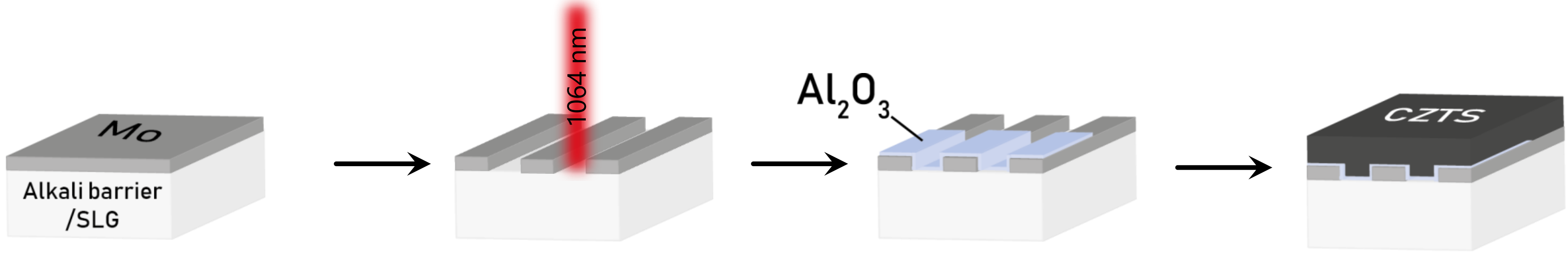
ALD-Al_2O_3 (20nm)



Kotipalli et al., *Solar Energy*, 157, 2017

- ALD allows for conformal deposition
- Fixed negative charges repel minority charge carriers
- Low interfacial defect density

Design of the bottom surface



Controlled Na out-diffusion

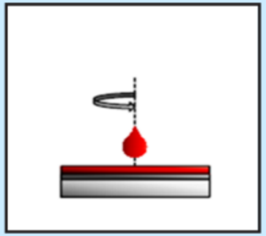
Mo scribing

ALD-Al_2O_3 (20nm)

Na-doped precursor

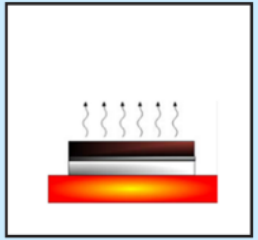
1. Spin coating

12 layers
1500 rpm

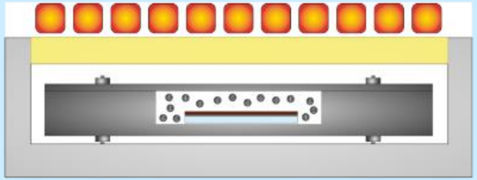


2. Drying

320°C on hotplate

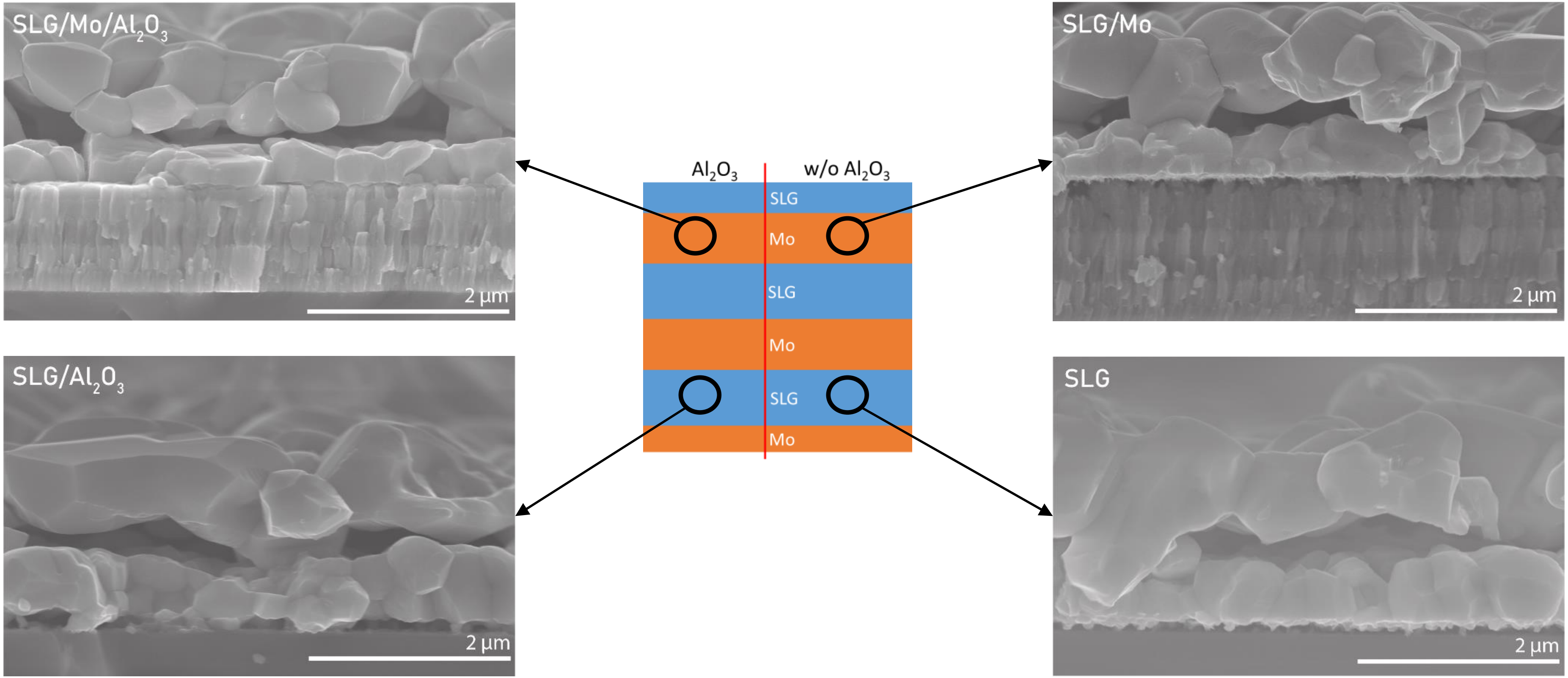


3. Annealing



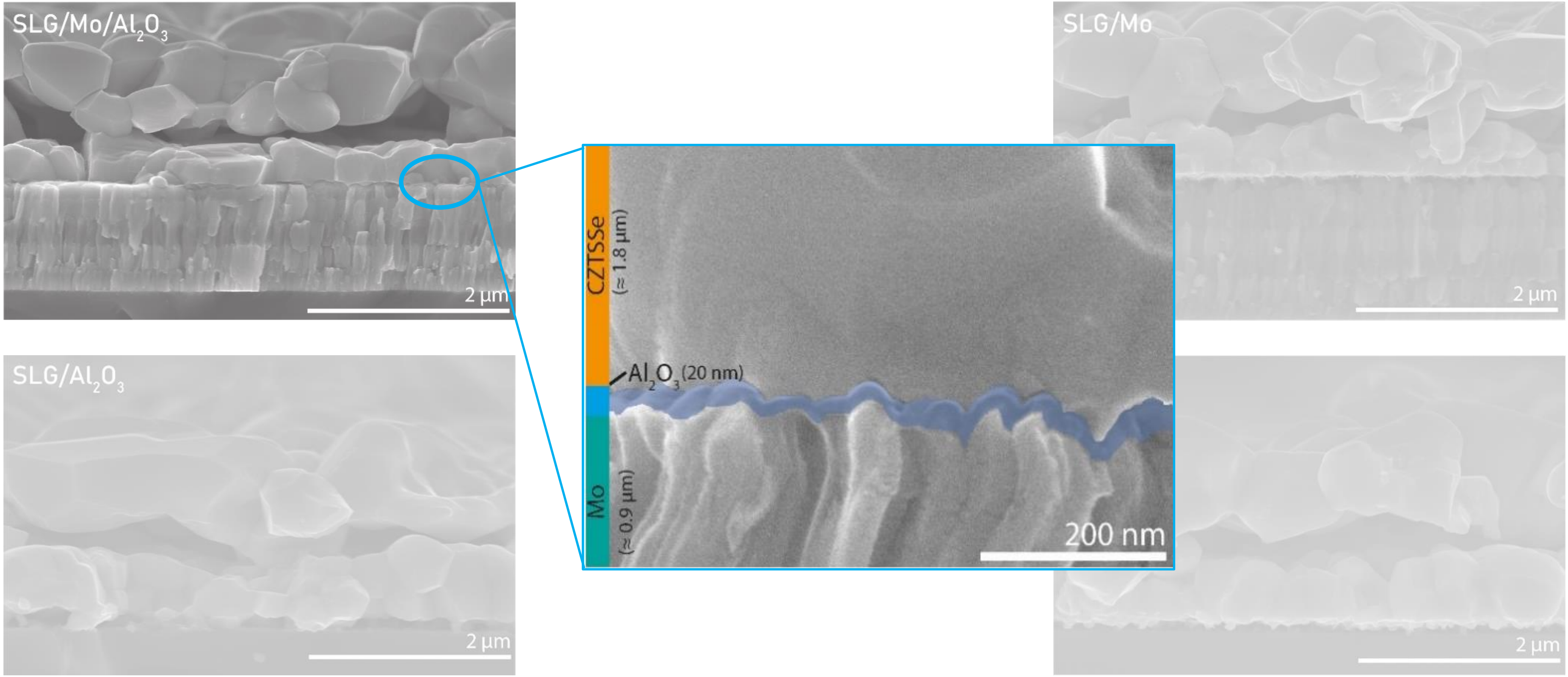
SEM (cross-section)

Empa
Materials Science and Technology



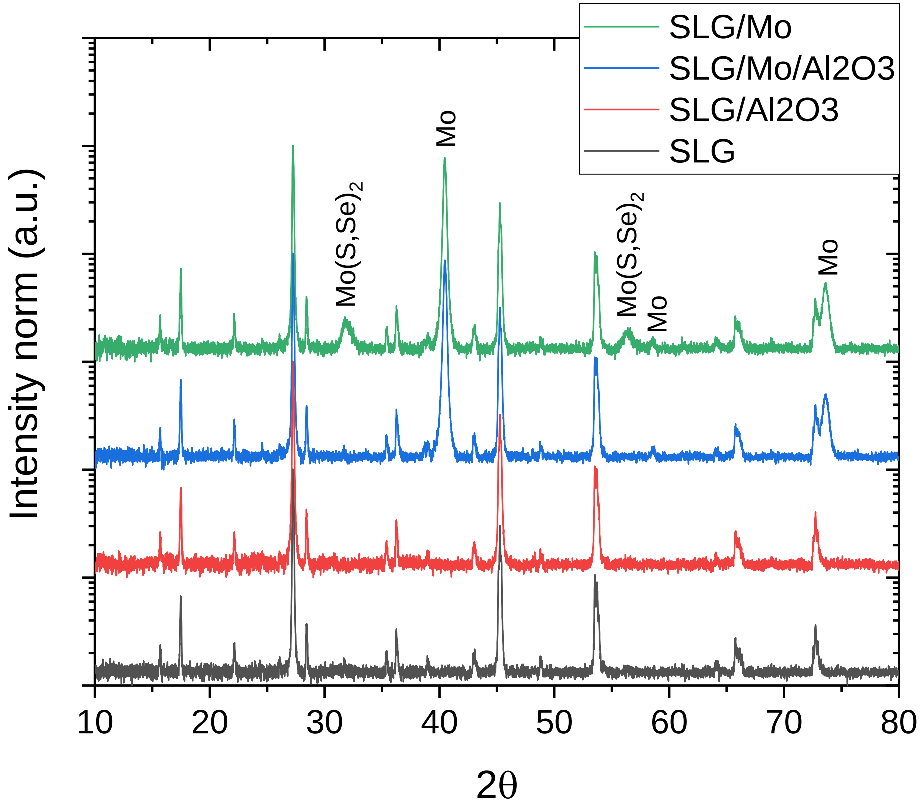
- Comparable growth for each section

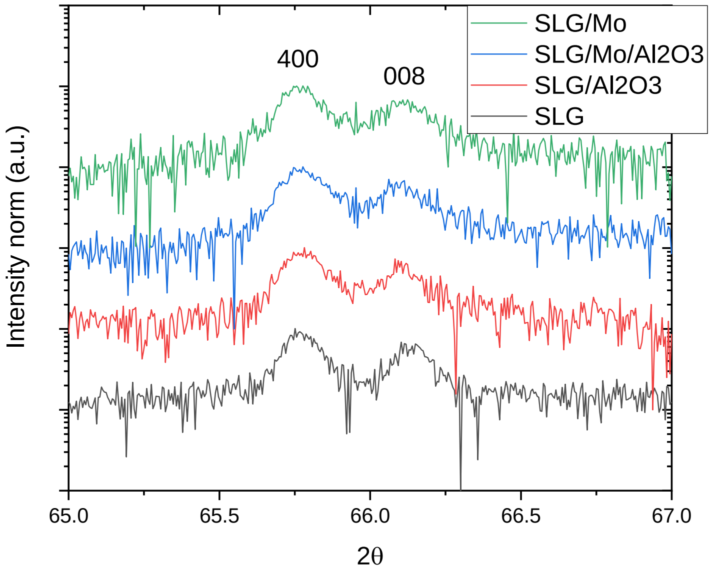
SEM (cross-section)



- Comparable growth for each section

XRD

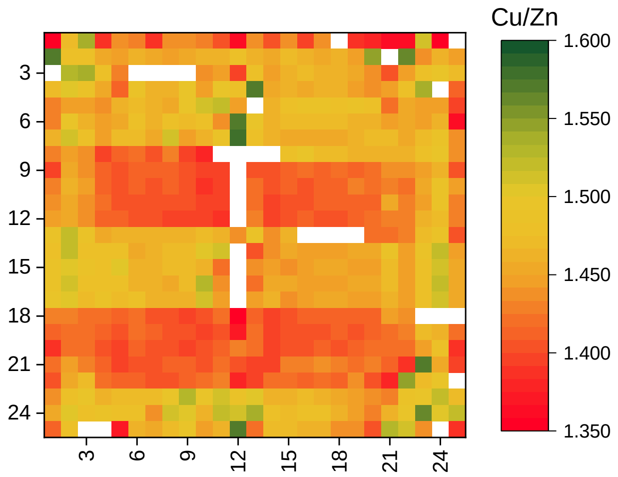


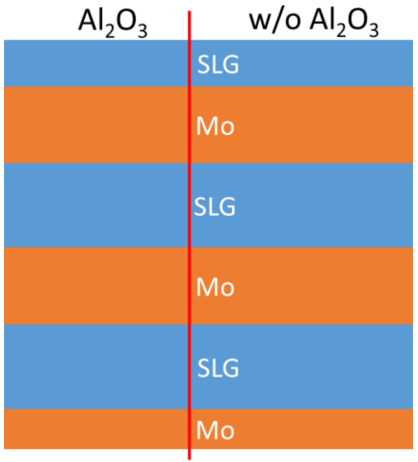


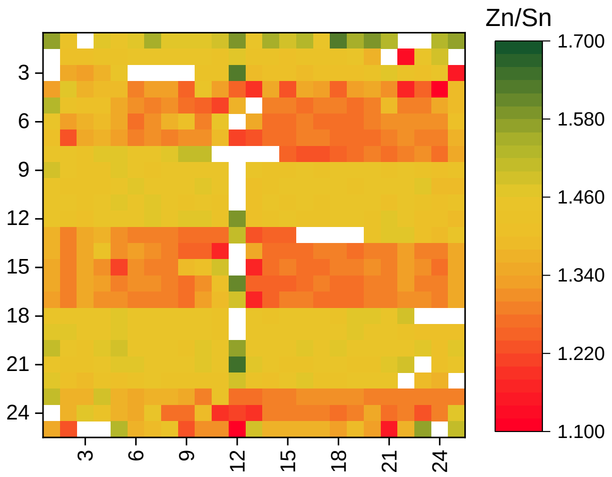
- Same cristallinity among the four parts of the absorber

XRF mapping

Empa
Materials Science and Technology





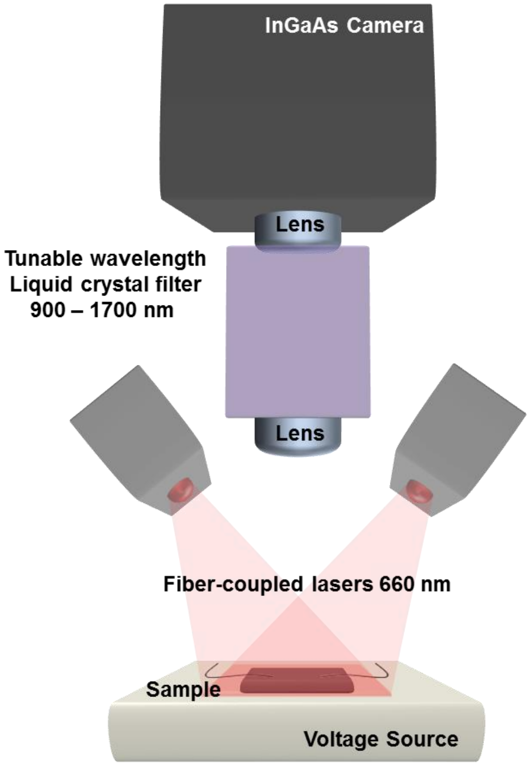


- Al_2O_3 layer does not influence composition
- Zn-richer and Sn-poorer on SLG

Empa
Materials Science and Technology

What about the opto-electronic properties of the absorber?

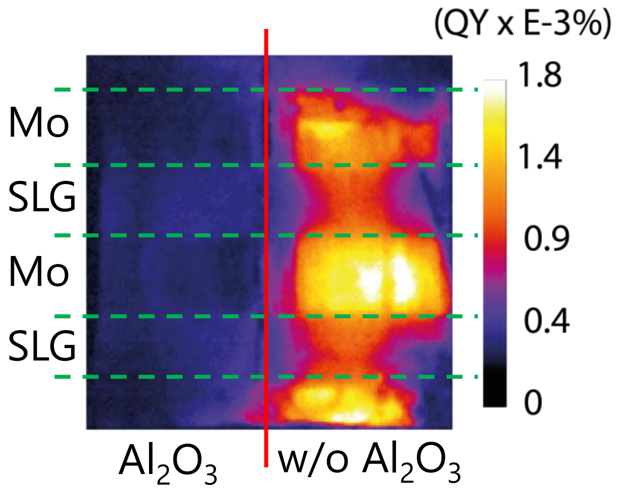
PL quantum yield (PLQY)

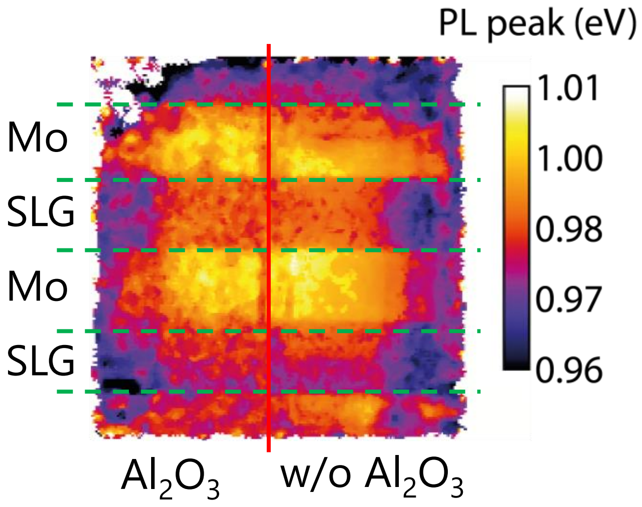


Quantitative PL allows to directly extract non-rad recombination losses:

$$\boxed{V_{oc,nrad} = -{}^{kT}/_{q}\, ln(PLQY)}$$

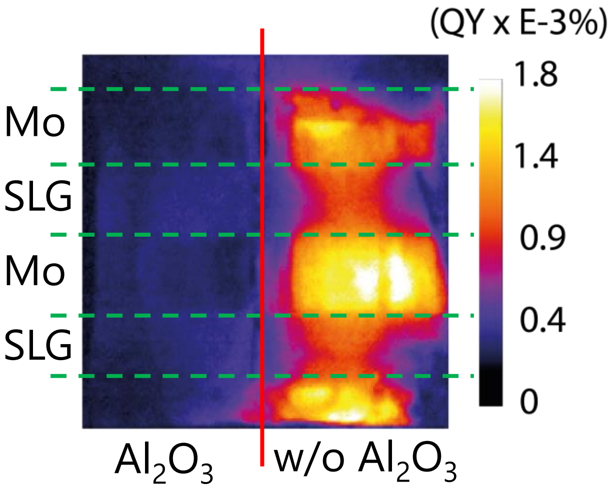
PL quantum yield (PLQY)

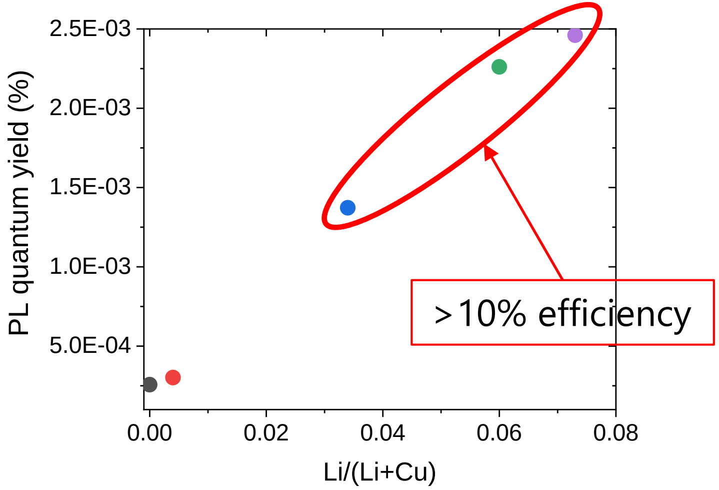




- Lower PL intensity on Al_2O_3
- PL peak shift agrees with composition change from XRF

PL quantum yield (PLQY)



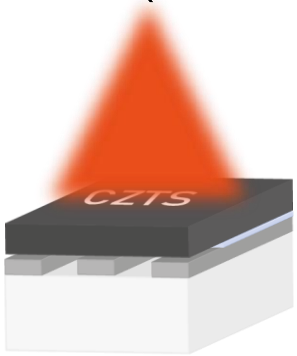


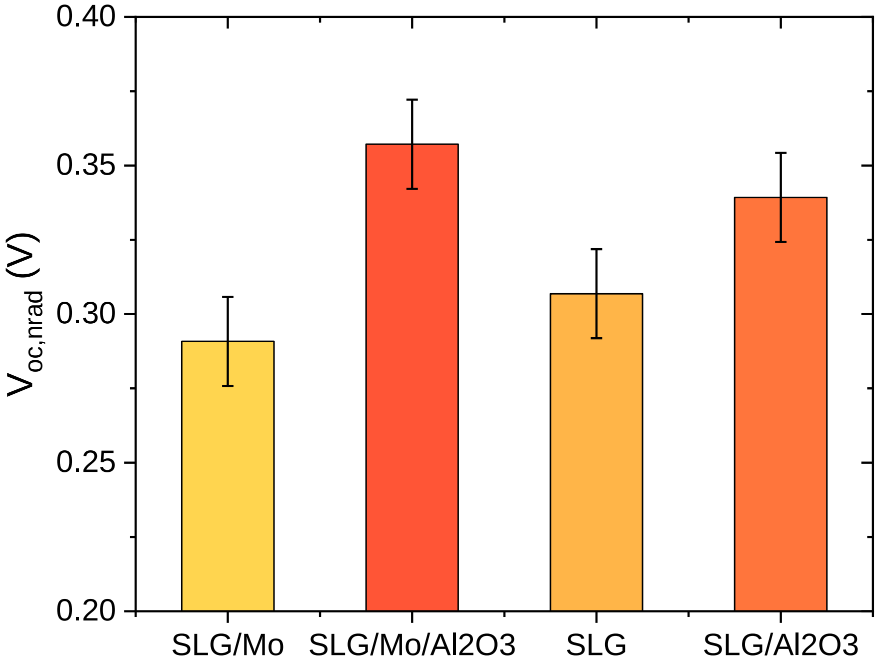
Cabas-Vidani et al., *Adv. En. Mater.*, *8*(34), 2018.

- PL intensity on Mo is comparable to devices with >10% device efficiency

PL quantum yield (PLQY)

PL laser (660 nm)





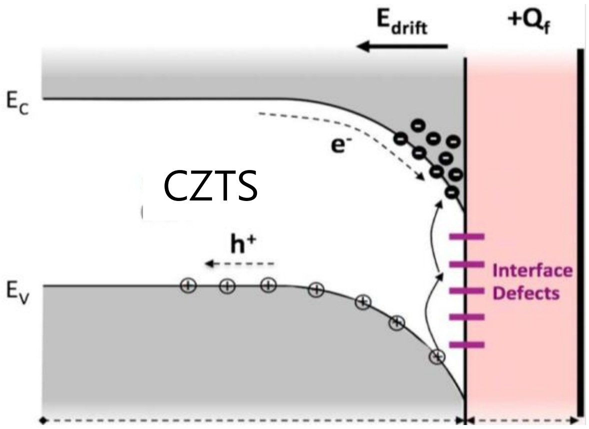
- Al_2O_3 increases non-rad losses

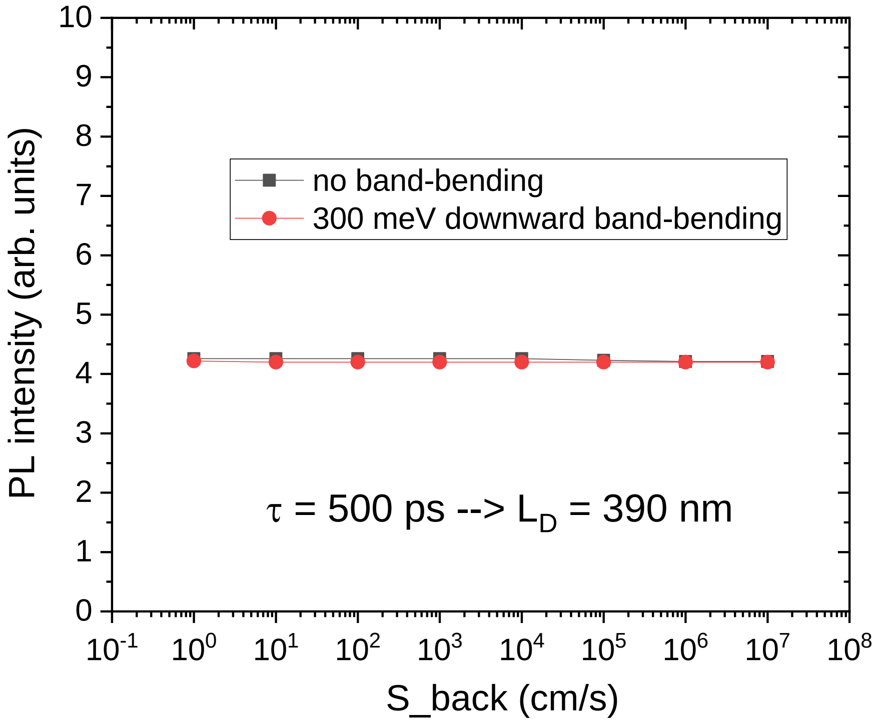
Can the rear interface influence PL from the top-surface?

Simulated PL (SCAPS)

Empa
Materials Science and Technology

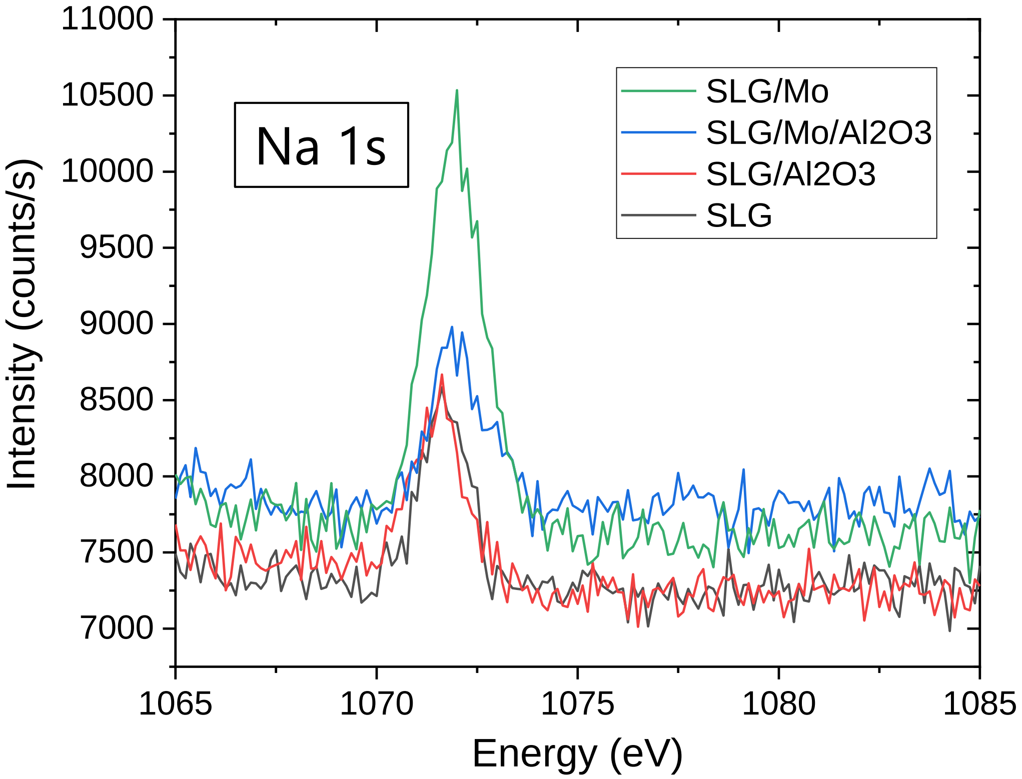
Worst case scenario:
downward band-bending





- PL from the top-surface should not be affected!
  – so there must be another reason!

XPS (front surface, ≈6nm)



- Higher Na intensity for CZTSSe on Mo

Conclusions

Empa
Materials Science and Technology

- Different rear interfaces can influence CZTSSe metal ratios
  (despite identical processing!)
- Al_2O_3 intermediate layer has (surprisingly) negative impact on the front PL
- Lowest non-rad recombination is still for Mo back contact

[manuscript in preparation]

Empa
Materials Science and Technology

Thank you for your attention!

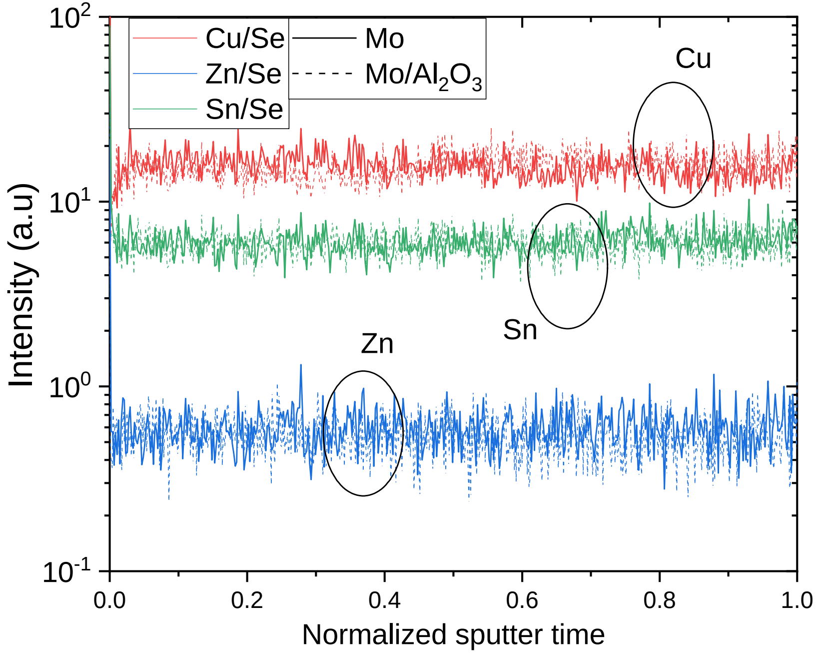
STARCELL

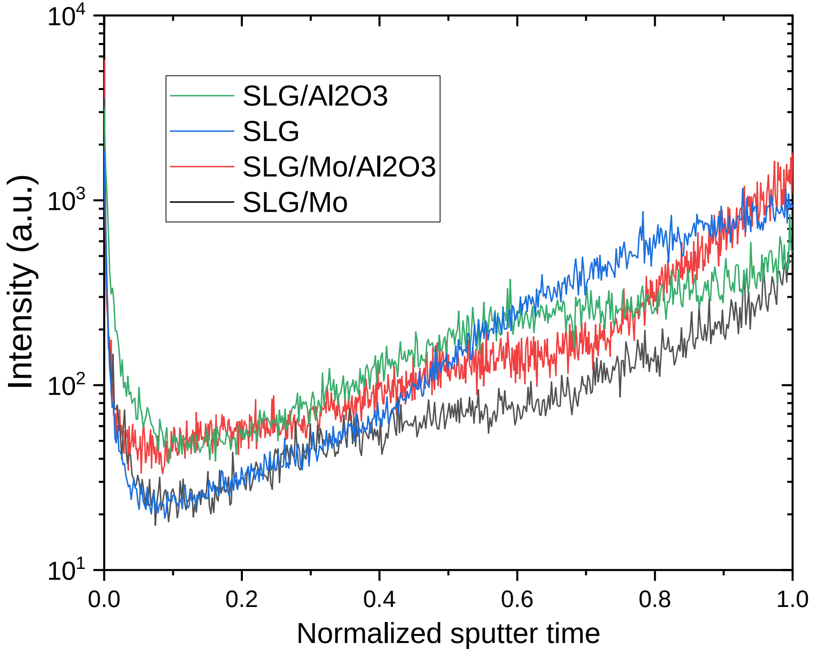
This research was supported by STARCELLS (H2020-NMBP-03-2016-720907)

Empa
Materials Science and Technology

BACK-UP SLIDES

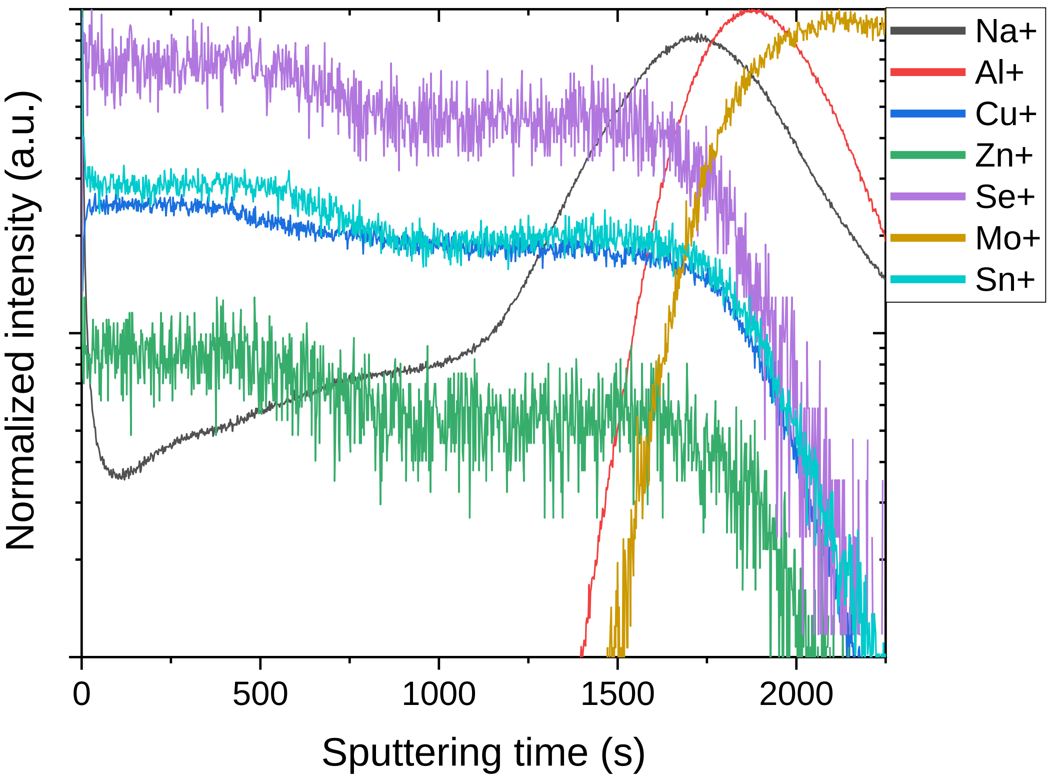
TOF-SIMS





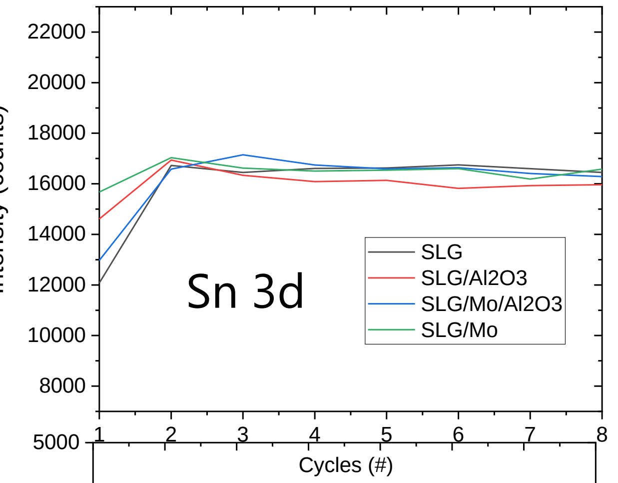
- Matrix elements are unaffected by back interface
- Na distribution is comparable

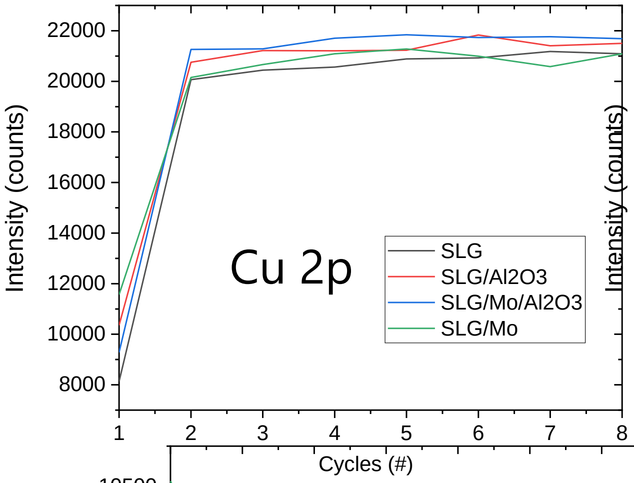
TOF-SIMS

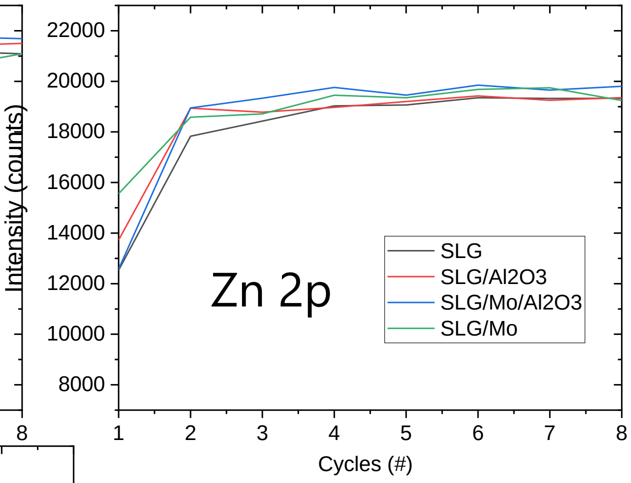


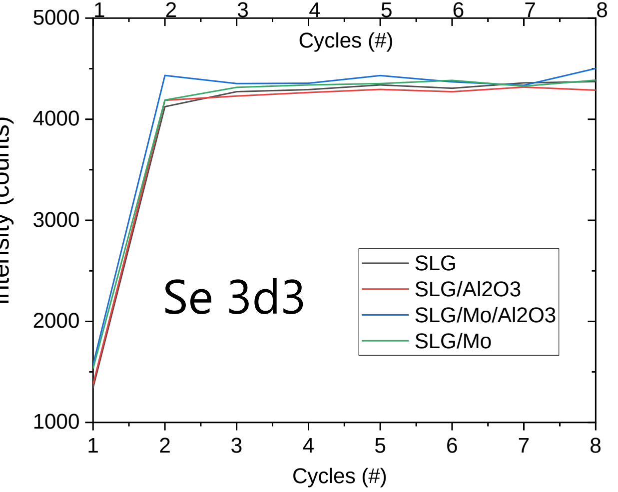
Empa
Materials Science and Technology

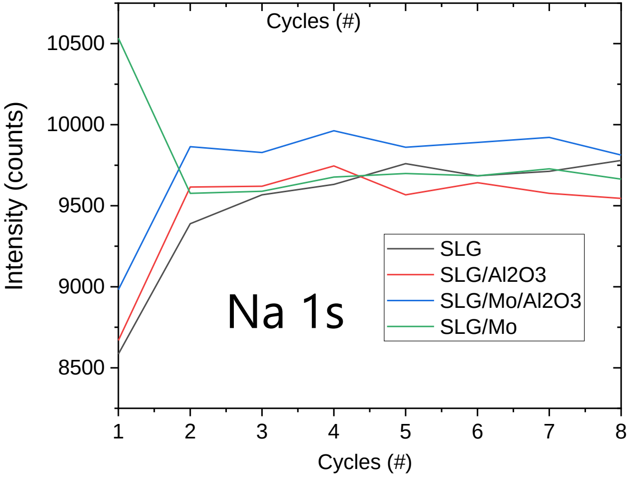
XPS (20-30 nm total depth)



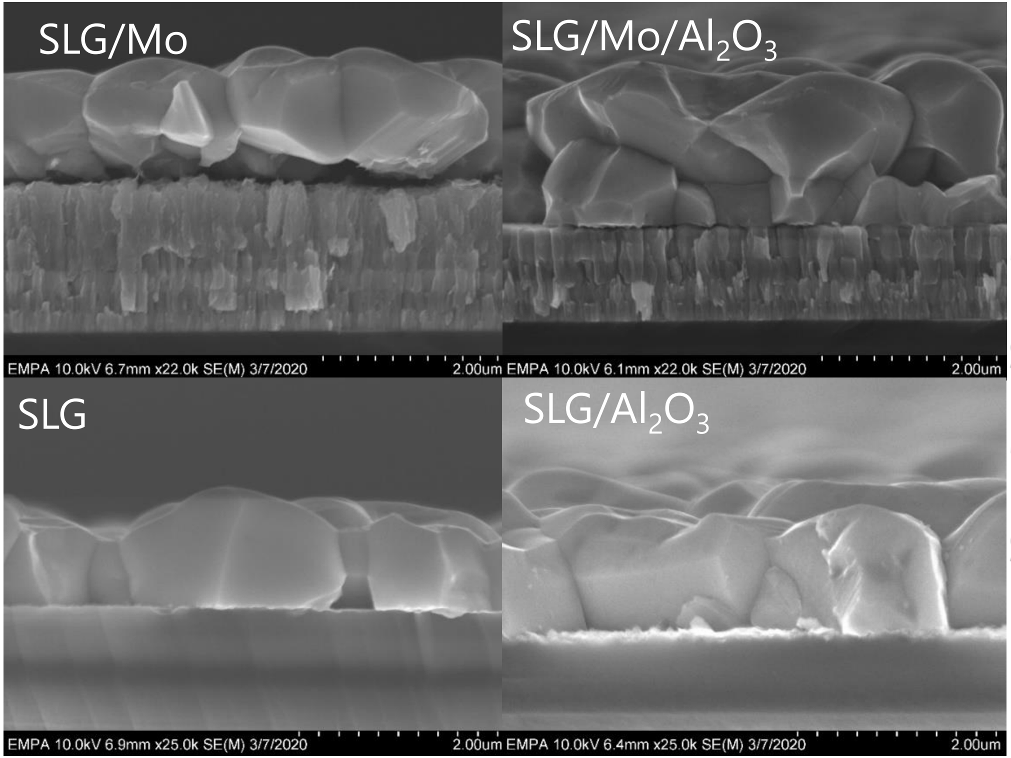


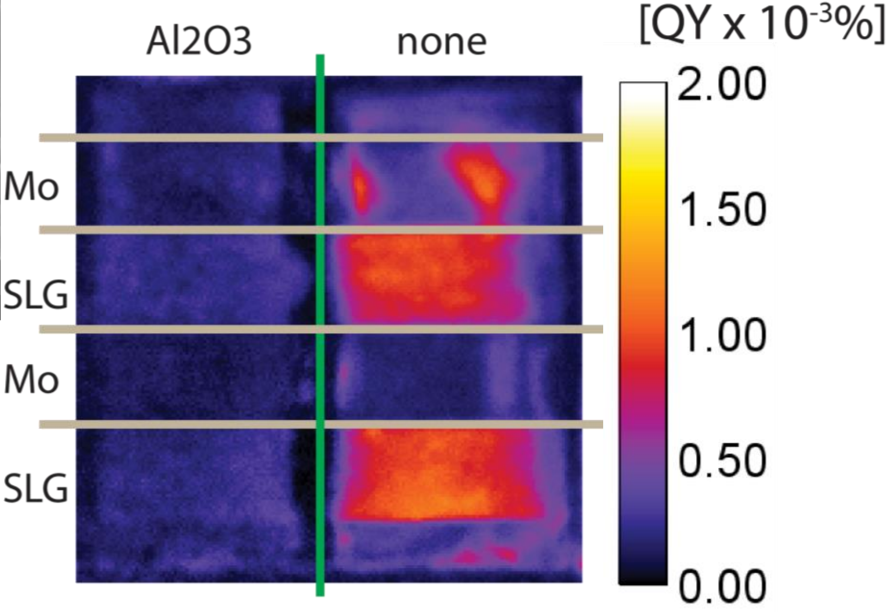




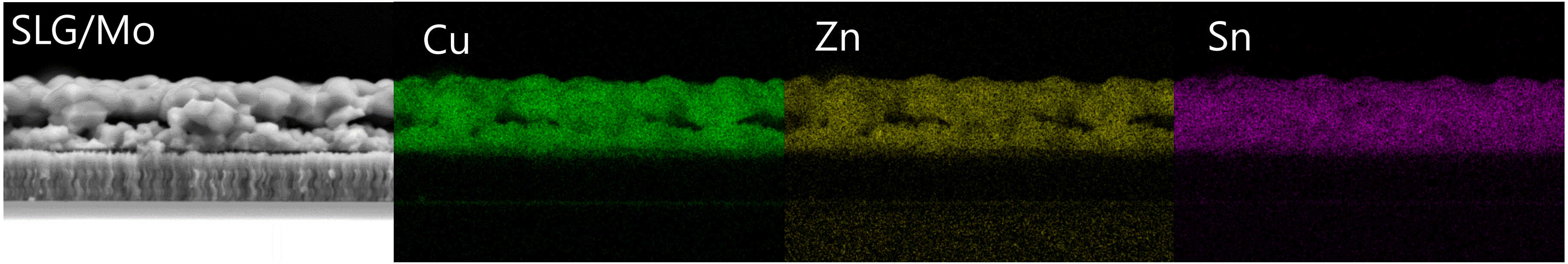


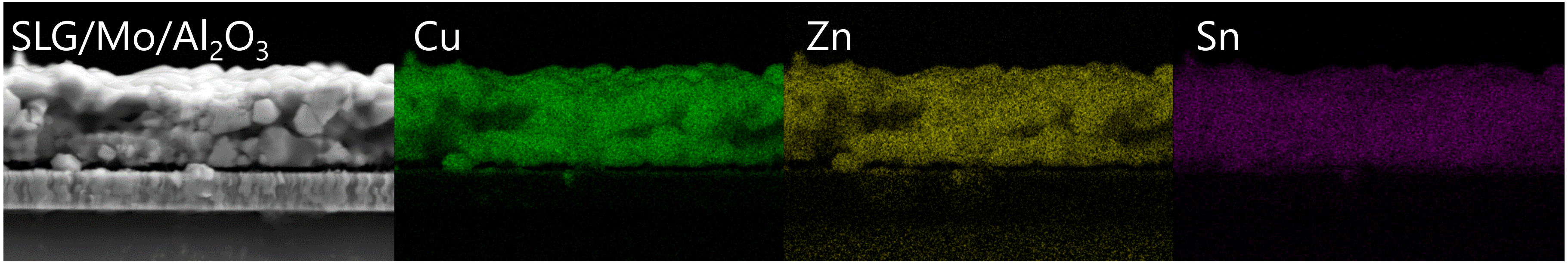
SEM Li-doped CZTSSe



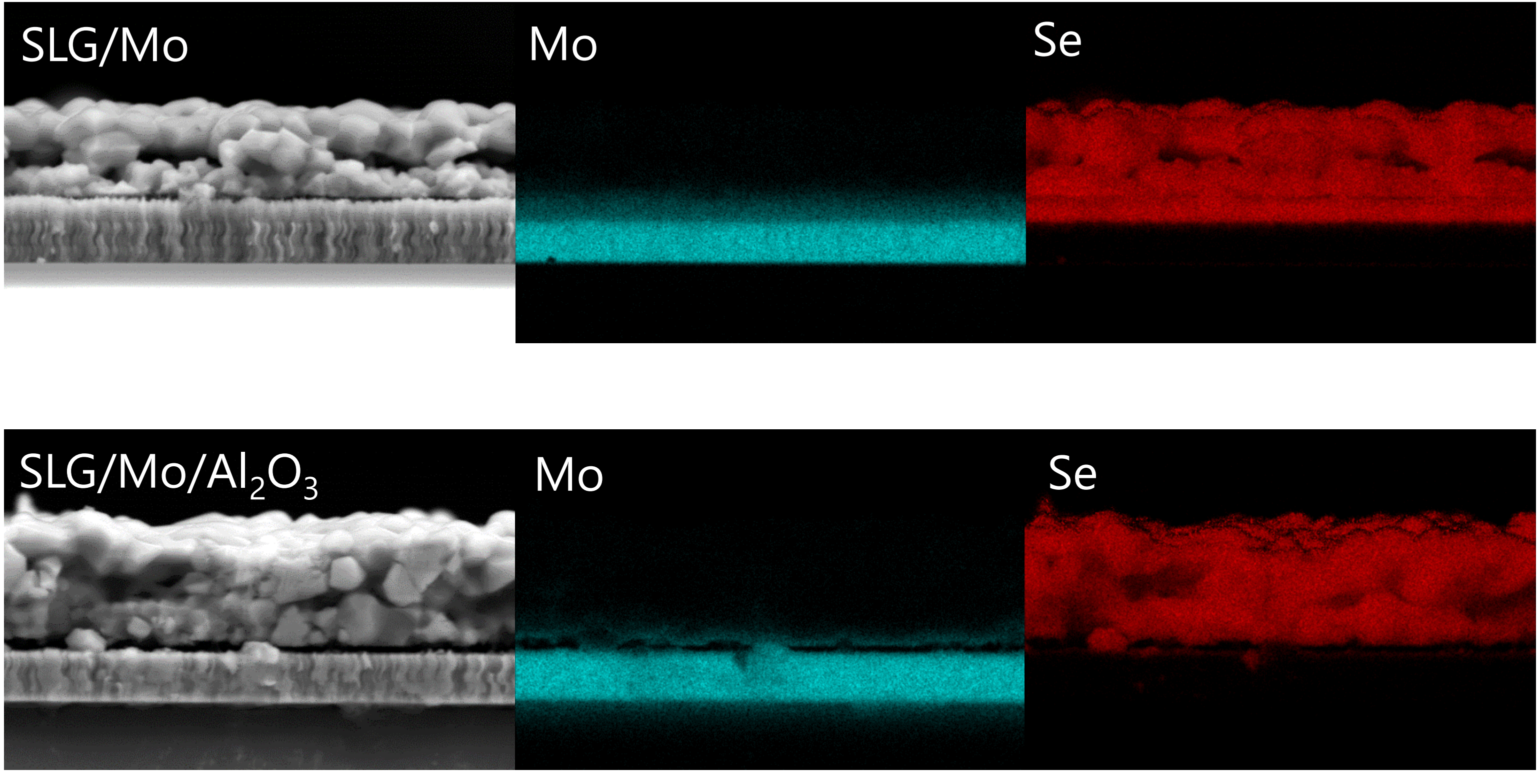


EDX



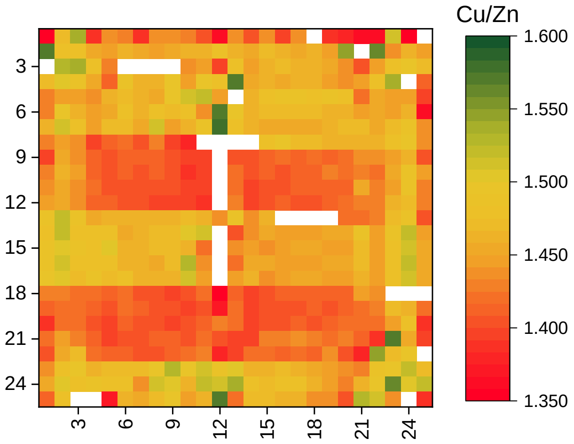


EDX

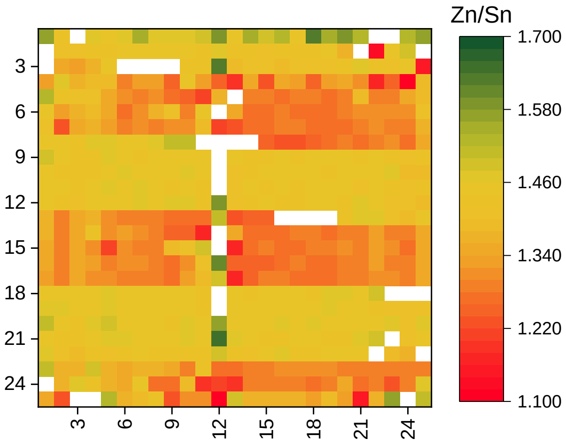


- Al_2O_3 acts as Se diffusion barrier

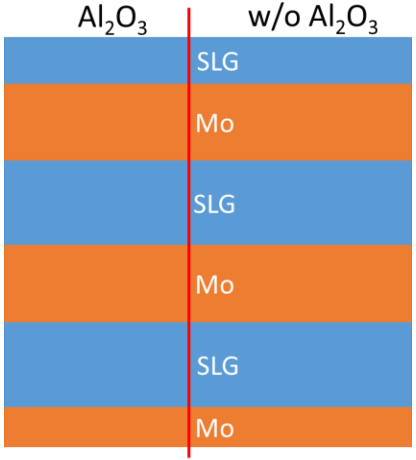
XRF



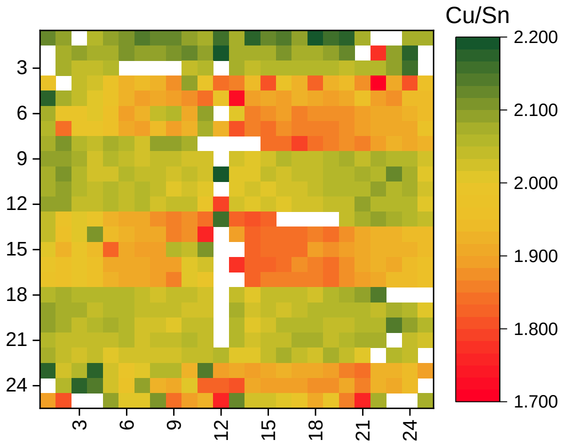
Cu/Zn
1.600
1.550
1.500
1.450
1.400
1.350
3
6
9
12
15
18
21
24



Zn/Sn
1.700
1.580
1.460
1.340
1.220
1.100
3
6
9
12
15
18
21
24

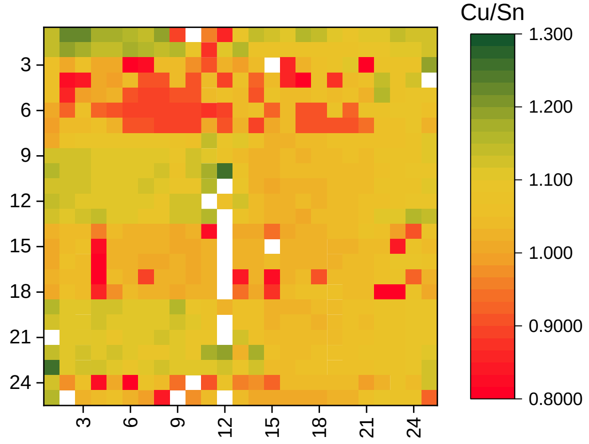


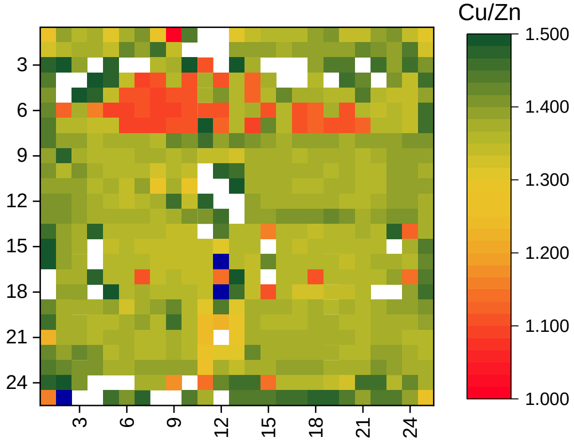
Al_2O_3
w/o Al_2O_3
SLG
Mo
SLG
Mo
SLG
Mo

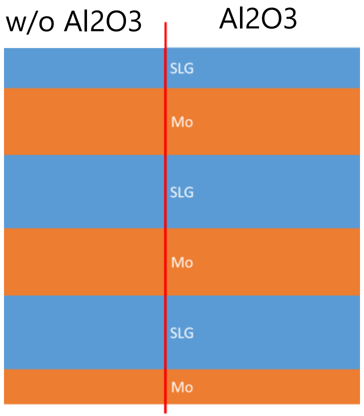


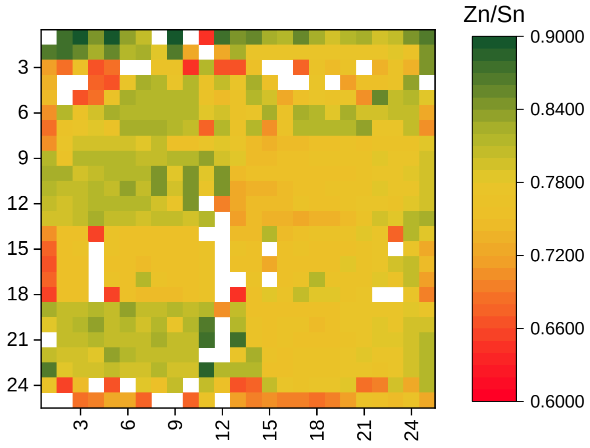
Cu/Sn
2.200
2.100
2.000
1.900
1.800
1.700
3
6
9
12
15
18
21
24

XRF vs EDX









EDX

	Cu/Zn	Cu/Sn	Zn/Sn
SLG	1.41	1.66	1.16
SLG/Mo	1.42	1.64	1.15
SLG/Mo/Al_2O_3	1.42	1.64	1.15
SLG/Al_2O_3	1.41	1.65	1.16

nrad losses (front vs back)

Empa
Materials Science and Technology