Vacuum deposited Copper zinc tin sulfide (CZTS) thin film solar cells

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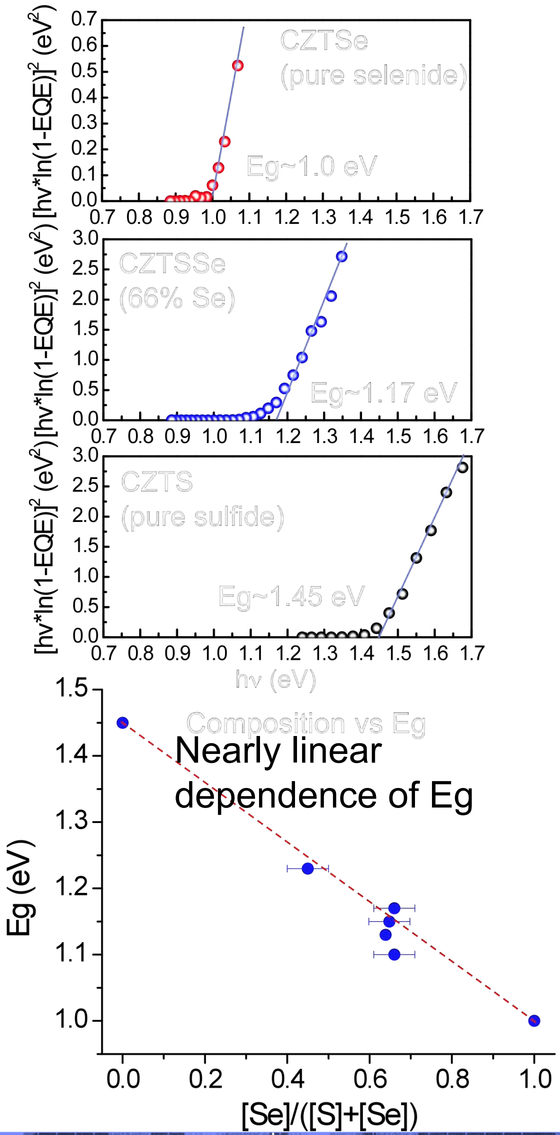
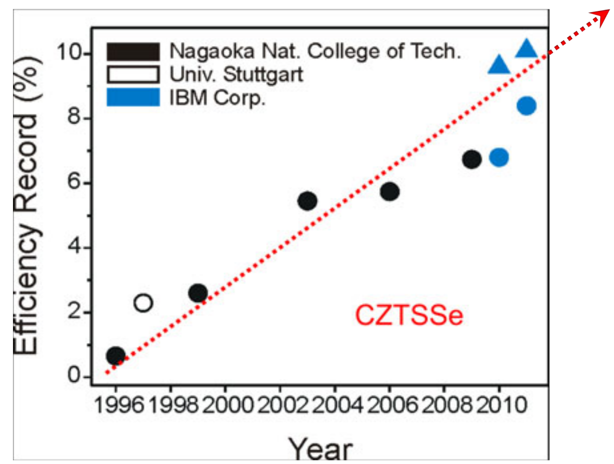
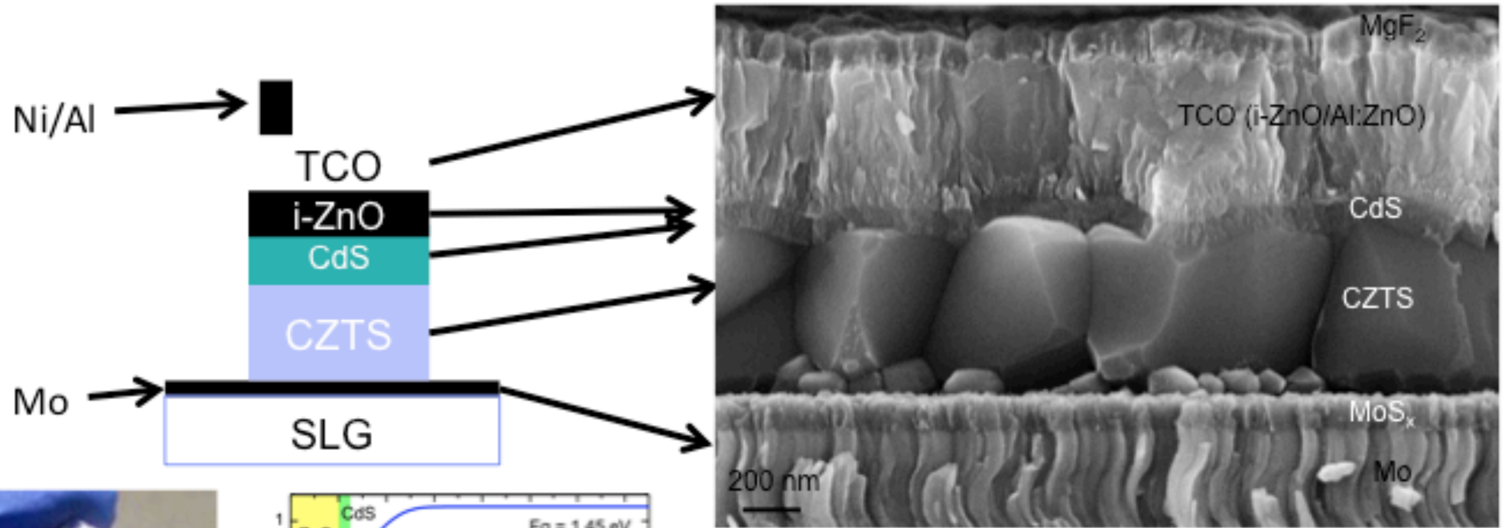
Tunable band gap of CZTSSe

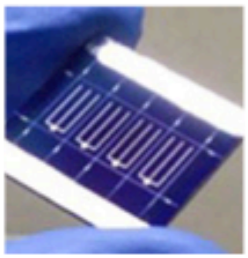


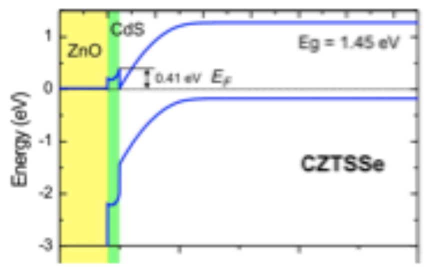
Only truly earth abundant non-Si absorber with efficiencies >10%

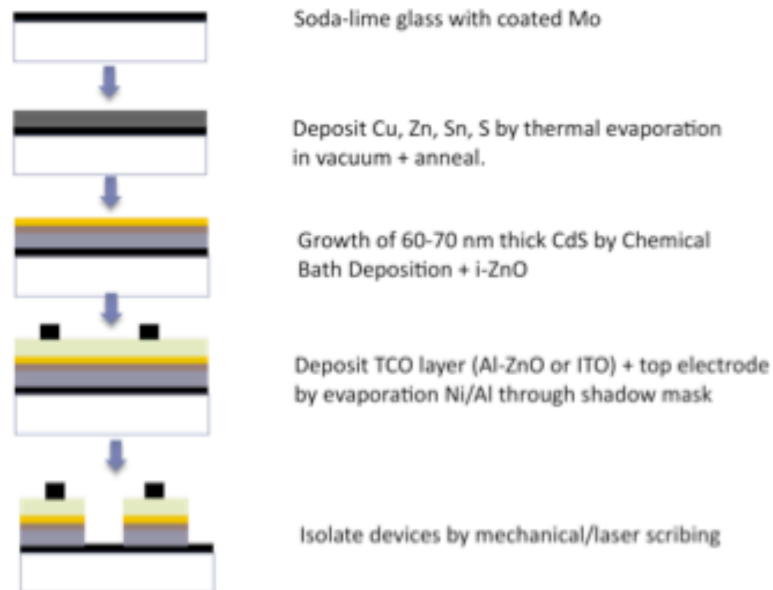


- *Solution processed →highest efficiency, ~ 11% (CZTSSe)*
- *Thermal evaporation→ highest efficiency, 8.4% (CZTS), 9.15% (CZTSe)*
- *Electroplating → 7.4% (CZTS)*
- *Need → >15%, eventually >18%*









Rest of device structure uses components similar to CIGS

Is this optimal?

35

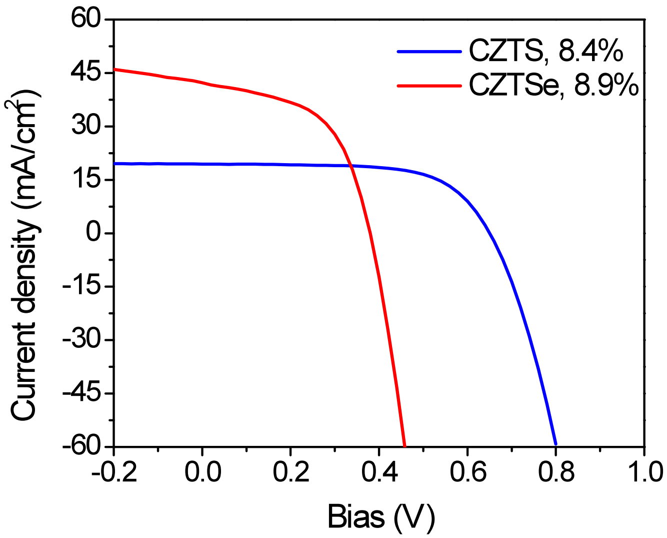
Vacuum deposited CZTSSe

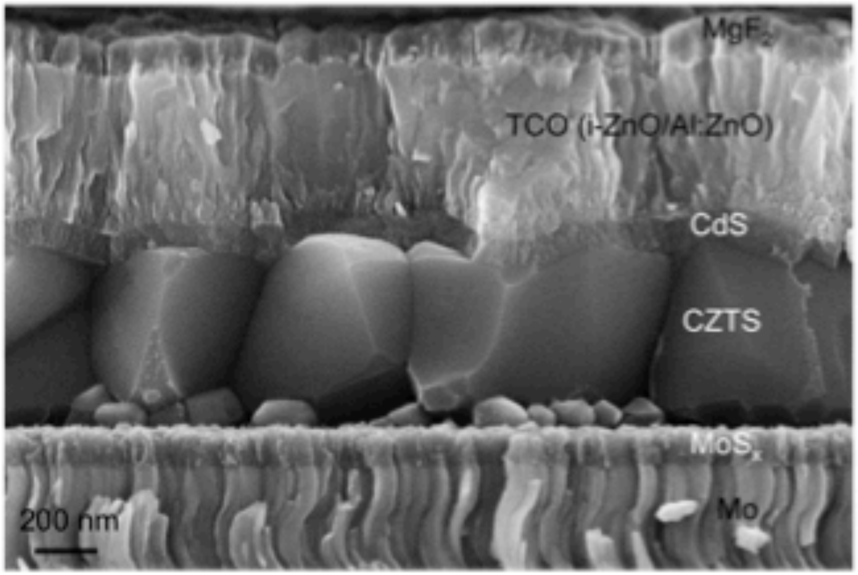
8.4% (FF~65%) Cu_2ZnSnS_4 solar cell

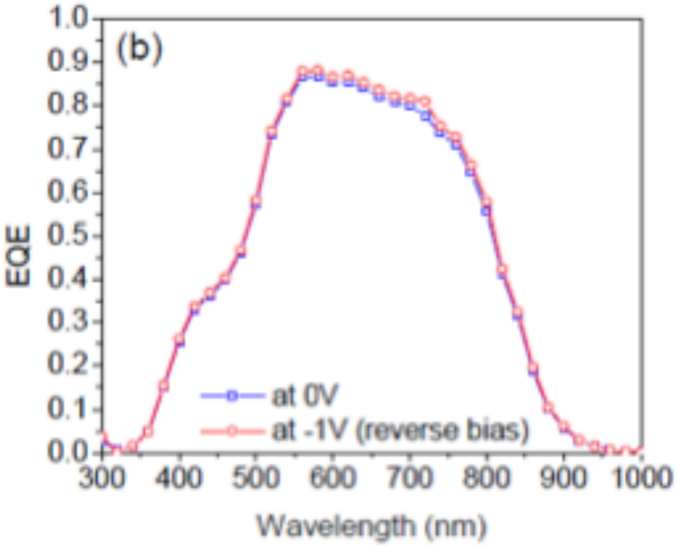
8.9% (FF~54%) $Cu_2ZnSnSe_4$ solar cell

100% sulfur preferable

Cu:Sn→ 1.8-1.9; Zn:Sn→ 1.3-1.4

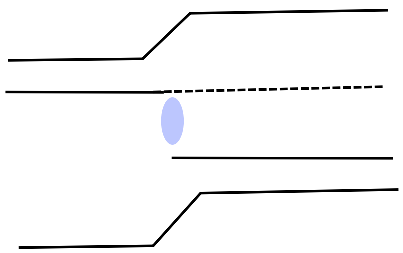




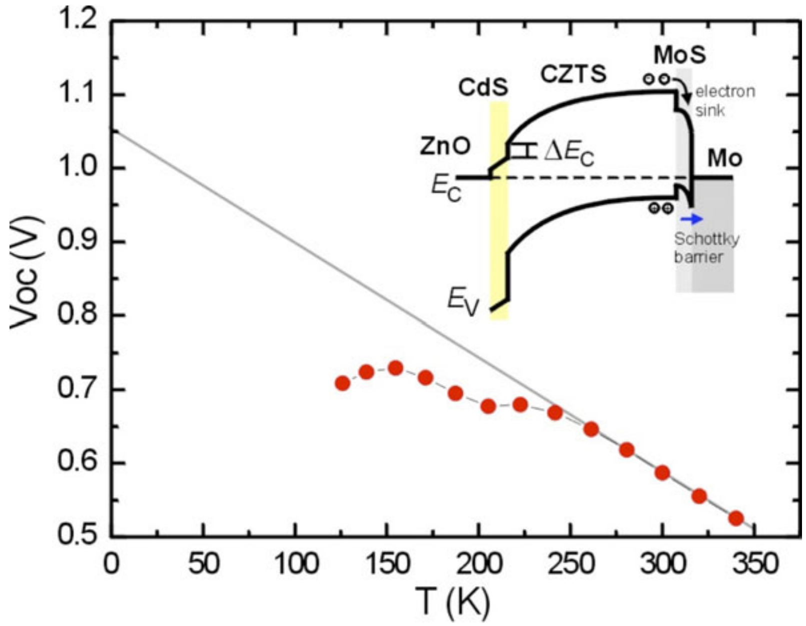


Shin, Zhu, Gunawan, Chey, Bojarczuk, Guha, Prog. Photovolt. DOI: 10.1002/pip.1174

Major problems in CZTS where TSM can help
1) Why is the Voc low?



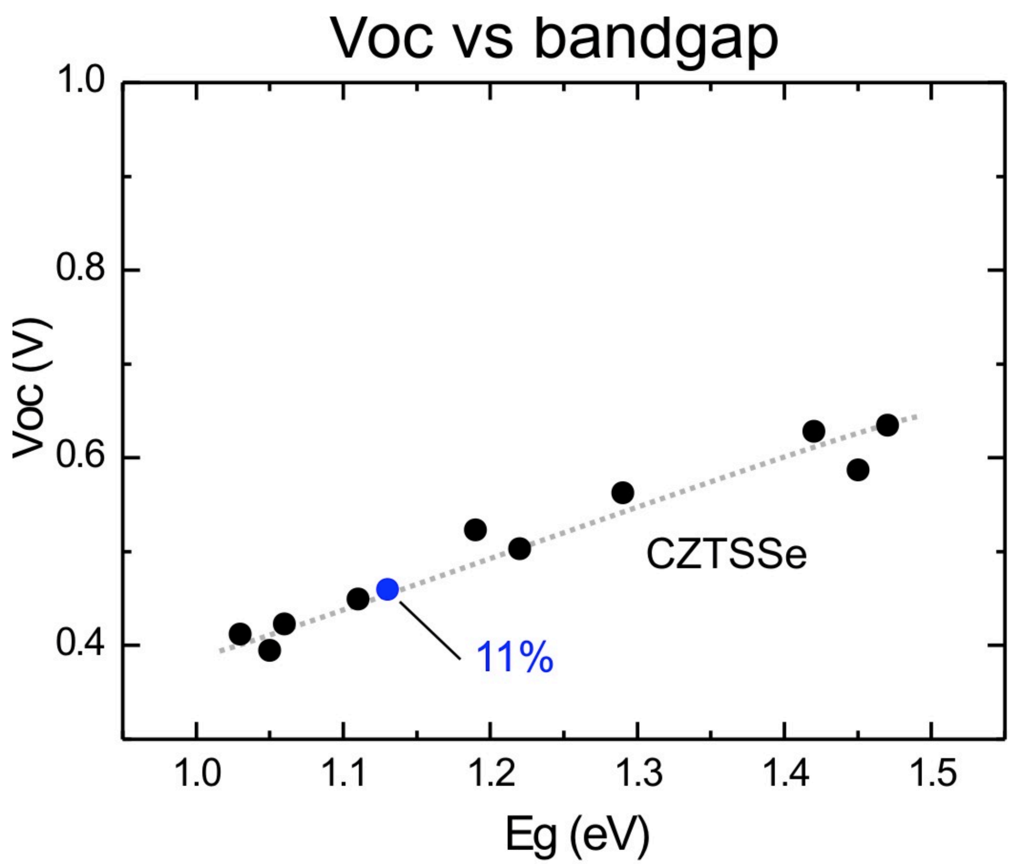
$$Voc = \frac{E_A}{q} - \frac{AkT}{q}\ln\frac{J_{00}}{J_L}$$



Temperature dependence of the open circuit voltage (Voc)

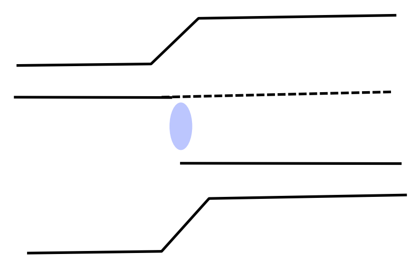
- Dominant carrier recombination mechanism can be obtained from the open circuit voltage vs. temperature data [1]

[1] U. Rau, Cu(In,Ga)Se2 solar cells, Chap. 7 Clean energy from photovoltaics, Imperial College Press, London (2000).
[2] M. Gloeckler, J.R. Sites, Efficiency limitations for wide-bandgap chalcopyrite solar cell, Thin Solid films 4801, 241 (2005).



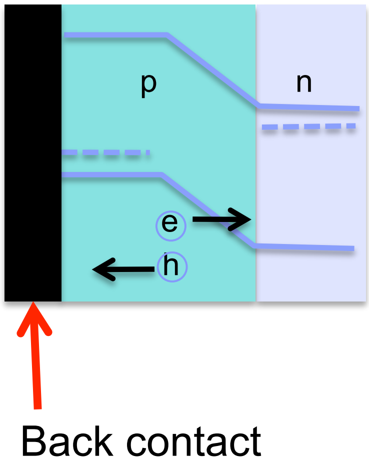
0 $x = \frac{[S]}{[S]+[Se]}$ 1

- •Low carrier lifetimes—not likely
- •Voltage barrier at interface
- •Fermi level deep in gap
- •Alloy composition fluctuations

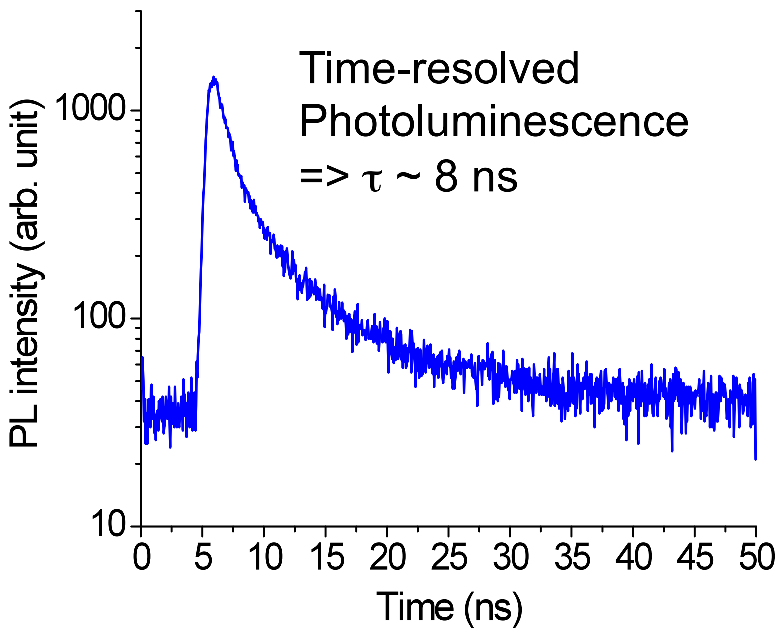


From Gunawan and Mitzi

Problem #2: poor carrier lifetimes



Thickness dependent efficiencies

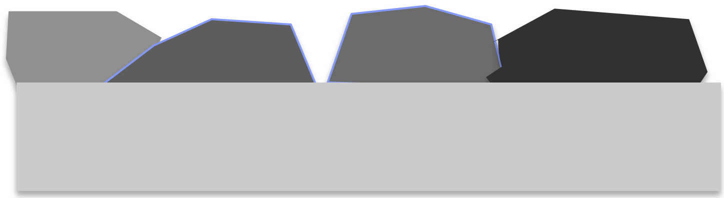


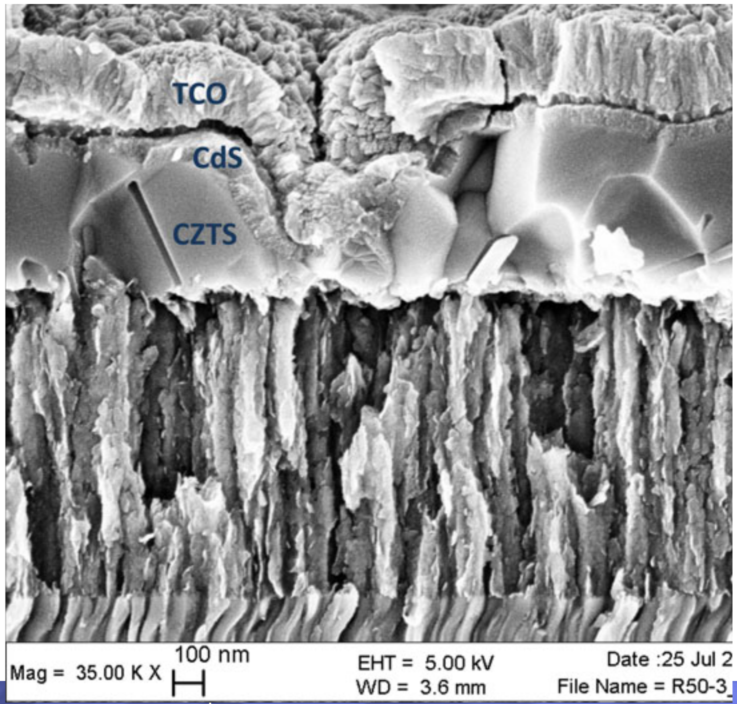
Need an accurate model for the device
Where does recombination occur?

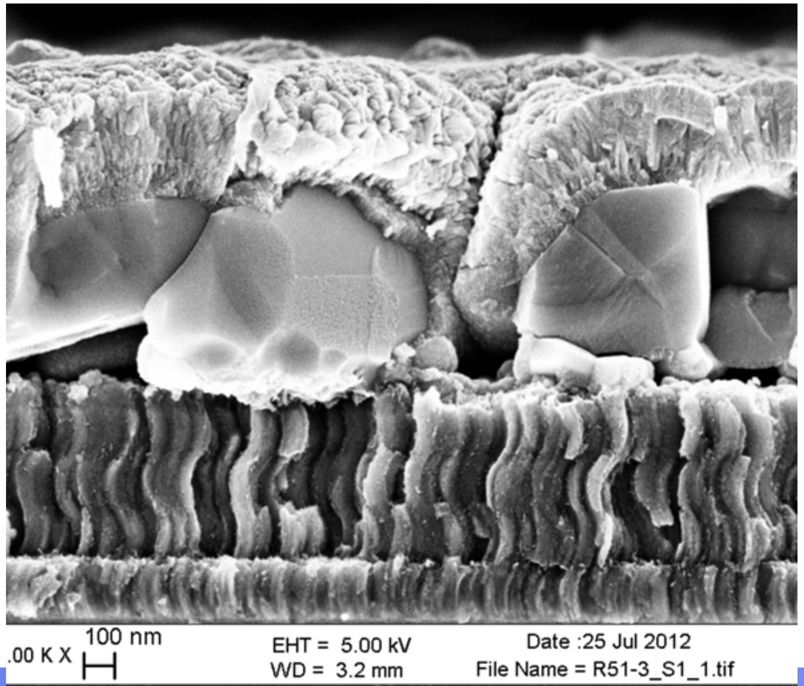
CZTS: Jsc typically ~20 mA/cm2
theoretically ~ low 30s mA/cm2

Problem #3: thin film microstructure—grain boundaries

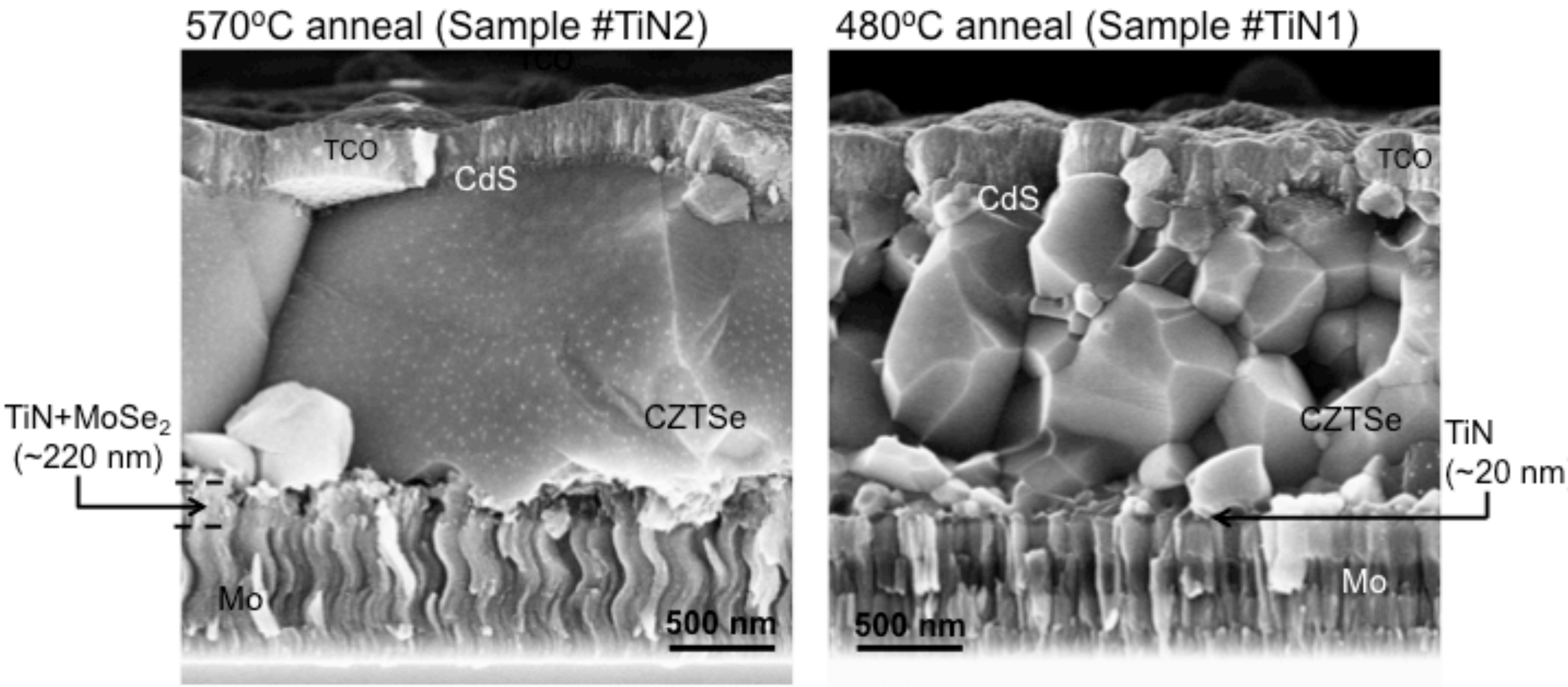
Re-entrant grain boundaries—good or bad?
gb conductivity
gb diffusion







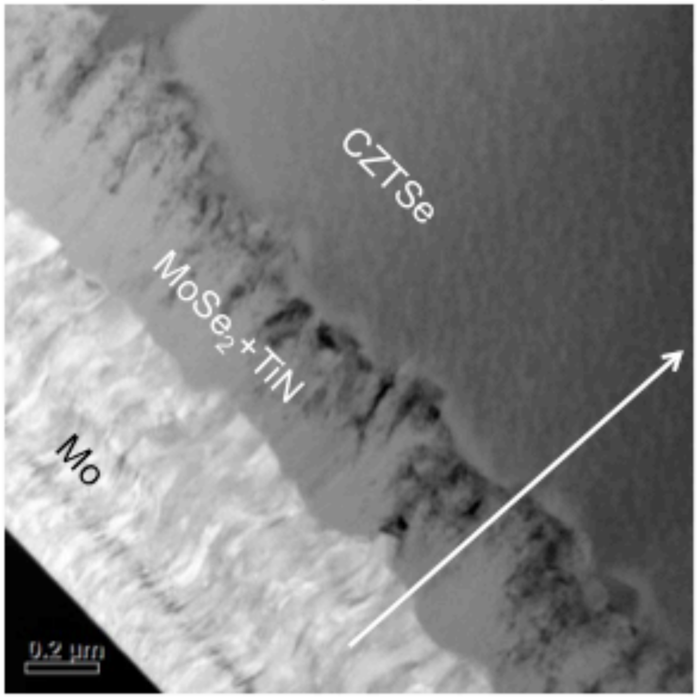
TiN diffusion barrier between CZTSe and Mo: SEM

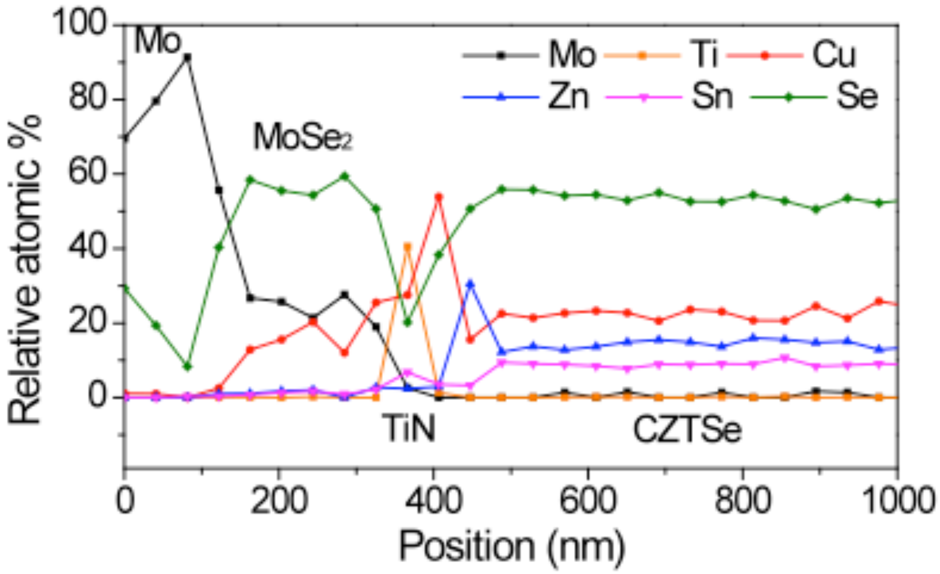


- With 20 nm TiN, $MoSe_2$ formation completely suppressed at 480°C
- At 570°C, $MoSe_2$ still formed but its thickness (~220 nm) is much smaller without TiN (~1300 nm)

TiN diffusion barrier between CZTSe and Mo: TEM

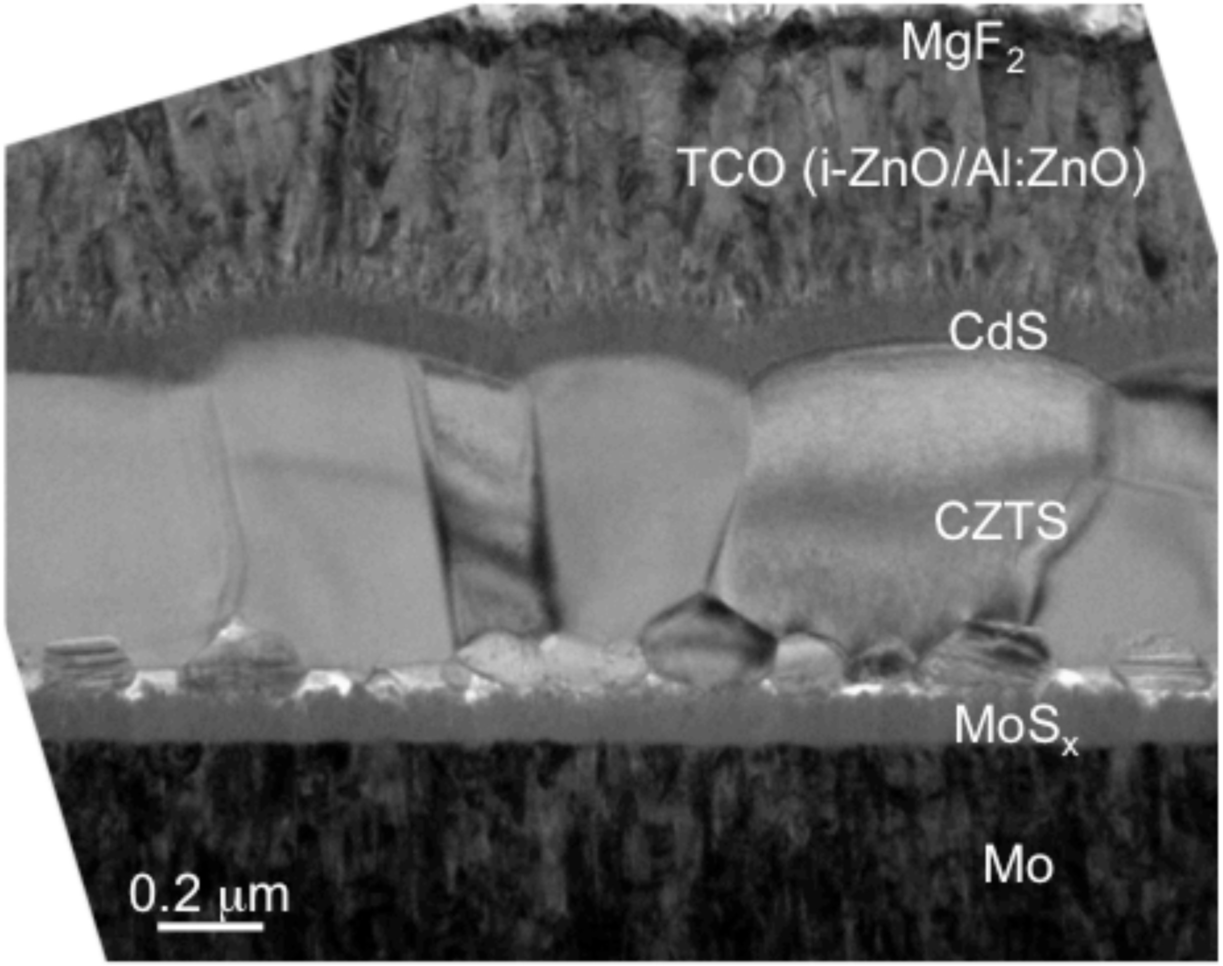
570°C anneal (Sample #TiN2)



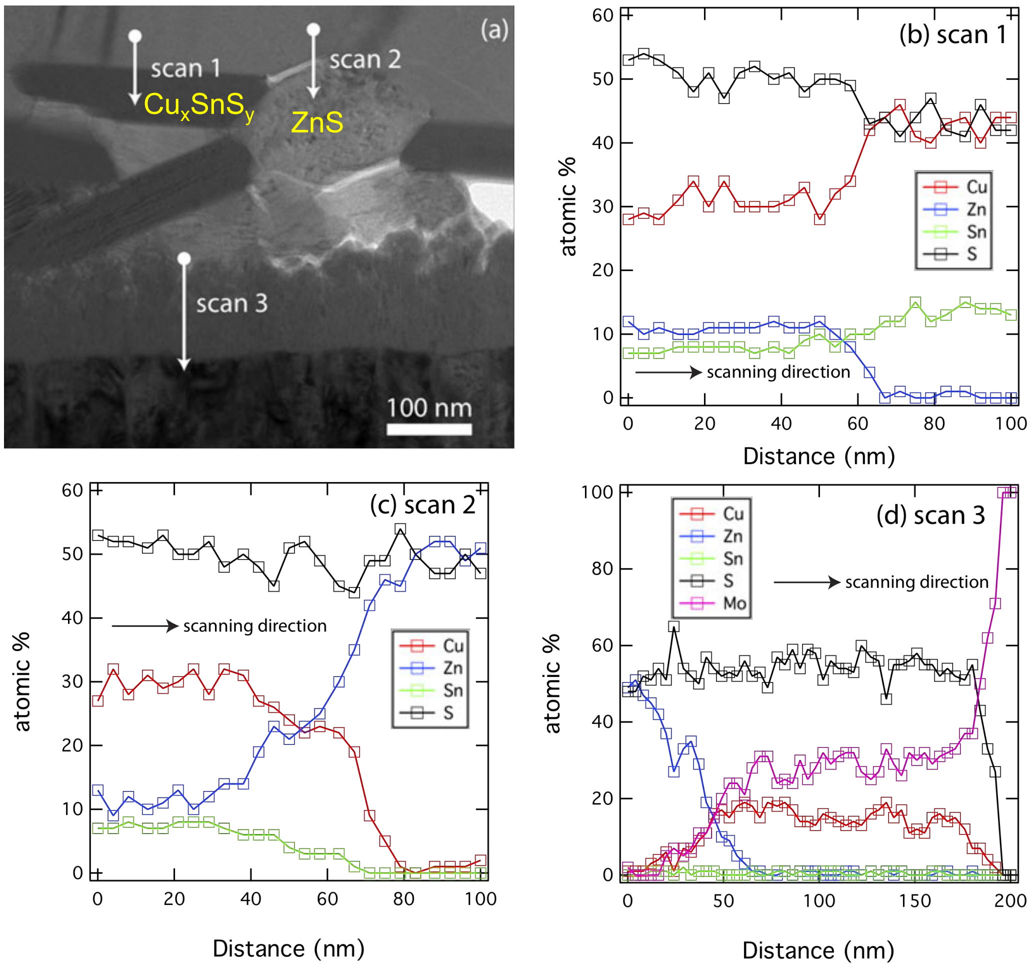


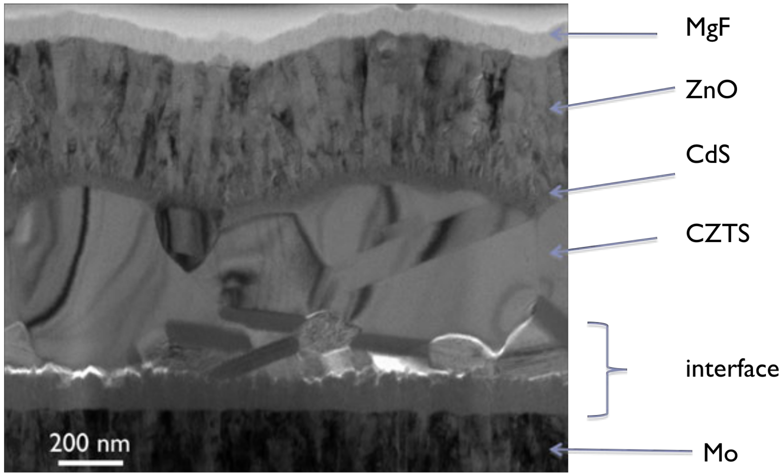
- ~220 nm $MoSe_2$ underneath TiN
- Some out-diffusion of Cu into $MoSe_2$ from CZTSe

Phase separation and interdiffusion



- Bimodal grain size distribution



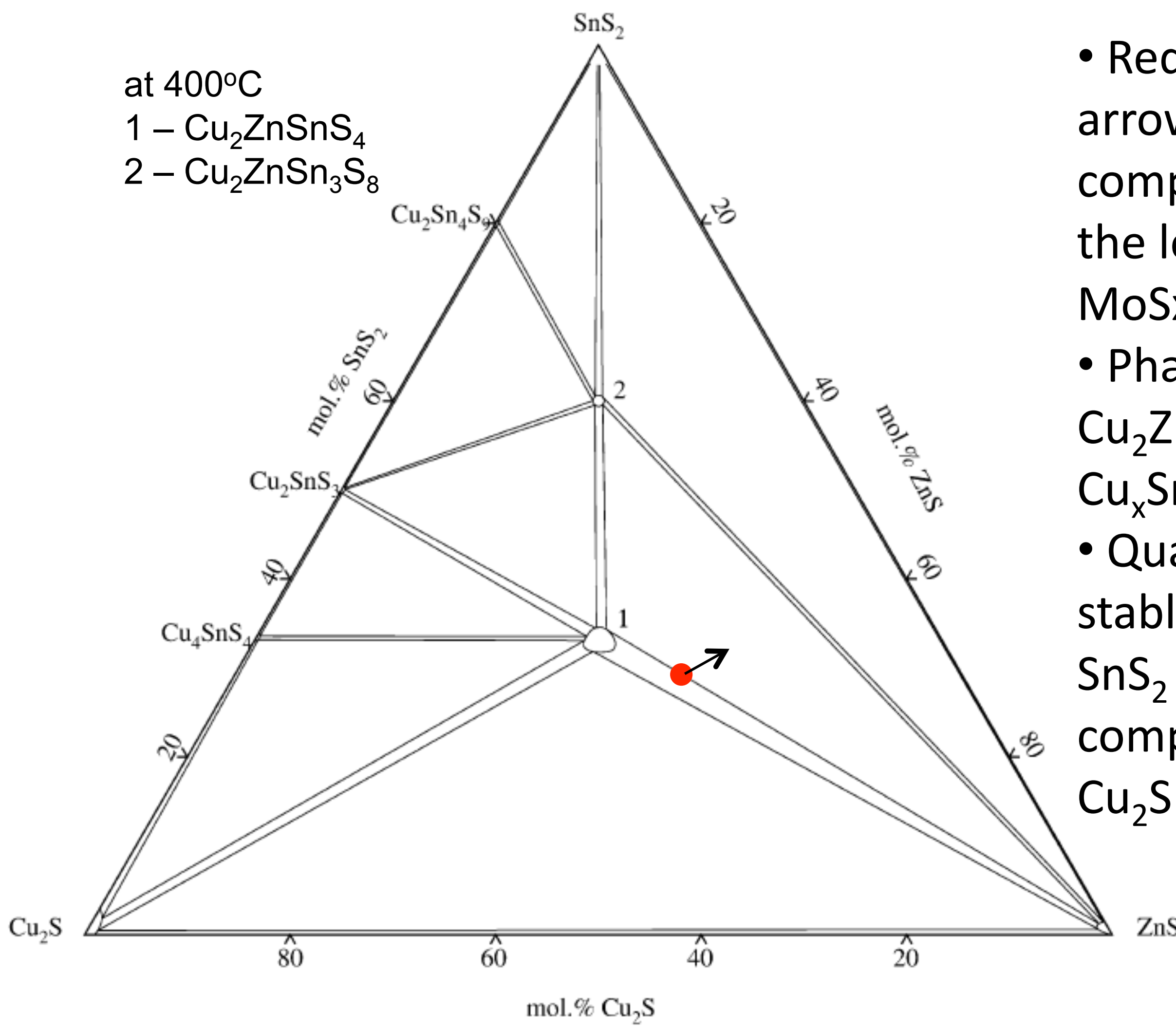


Observation:

1)Phase separation of CZTS into ZnS and Cu_xSnS_y near back contact

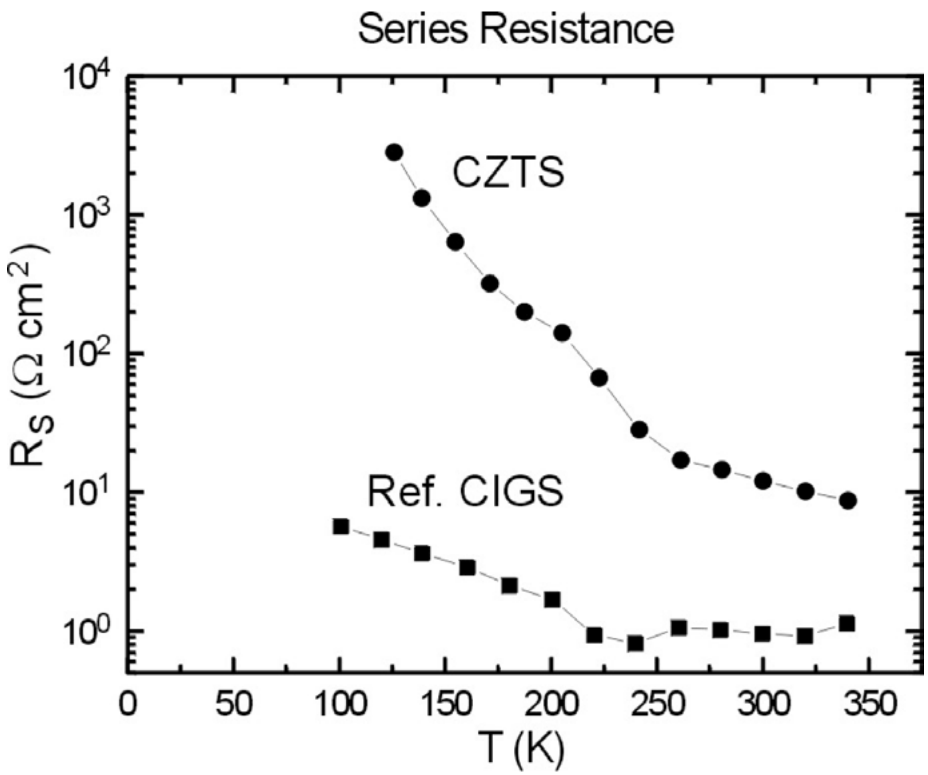
2)Cu diffuse in the MoS amorphous layer

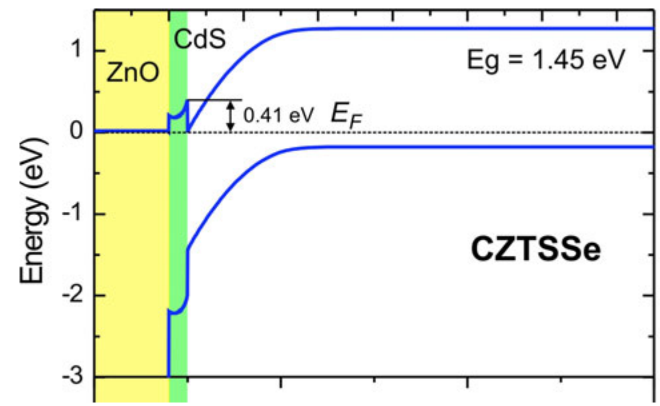
Microstructure issues increase with higher number of components



- Red dot: initial composition / arrow: direction of compositional change due to the loss of Cu from CZTS into MoSx
- Phase diagram: CZTS => ZnS + $Cu_2ZnSn_3S_8$; TEM: CZTS => ZnS + Cu_xSnS_y
- Qualitative agreement: several stable solid solutions between SnS_2 and Cu_2S, while no stable compound between ZnS and Cu_2S or ZnS and SnS_2

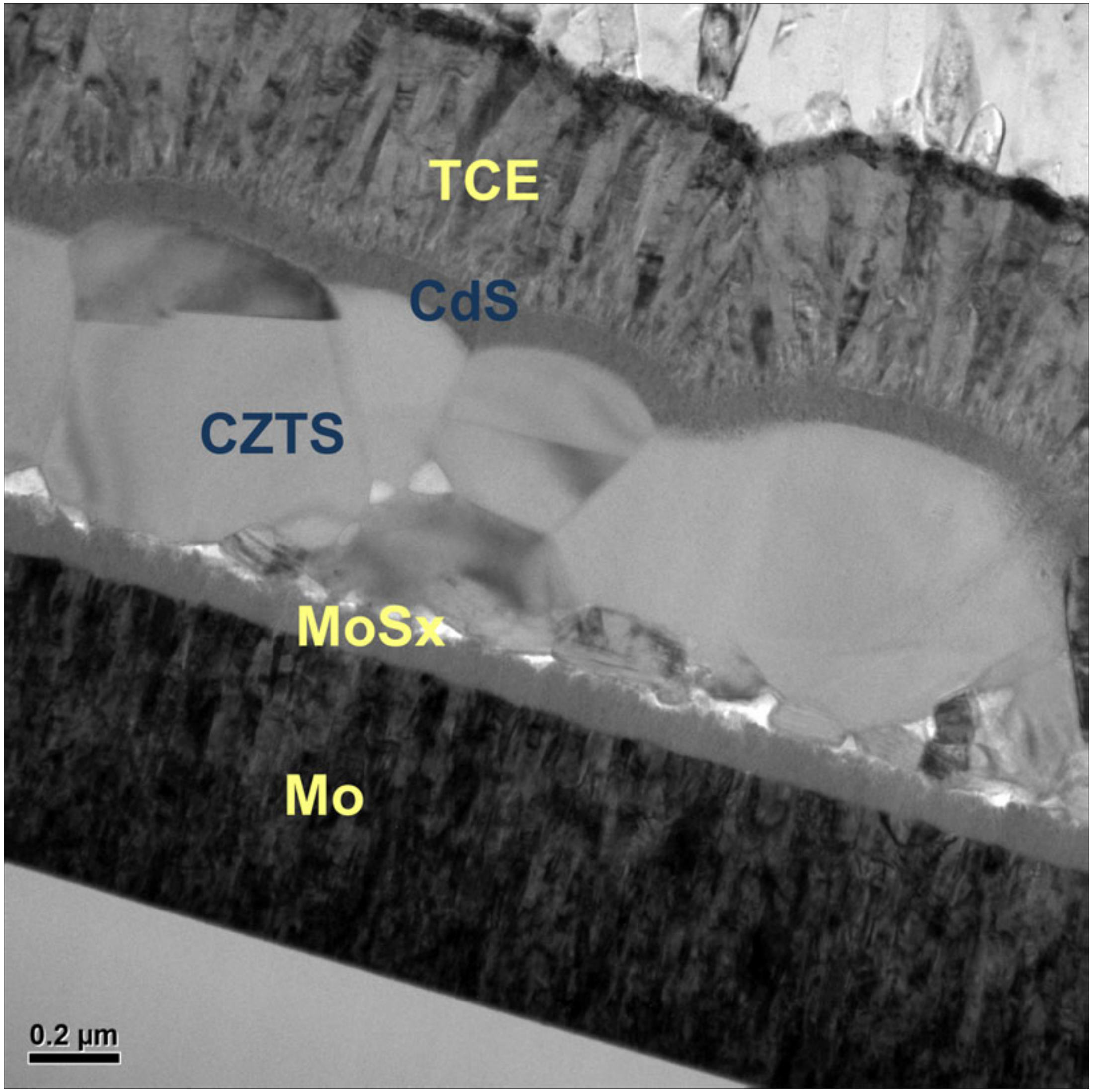
Problem # 4: high series resistance





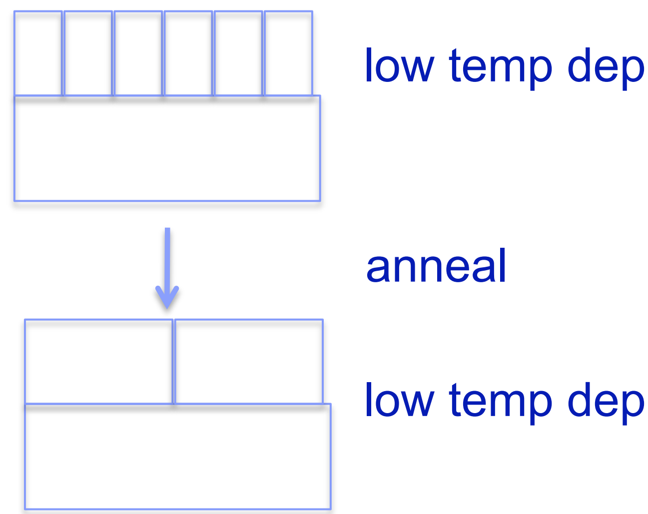
- Potential barriers
- Physical integrity of the interface

Problem # 5: Interfacial voiding and adhesision

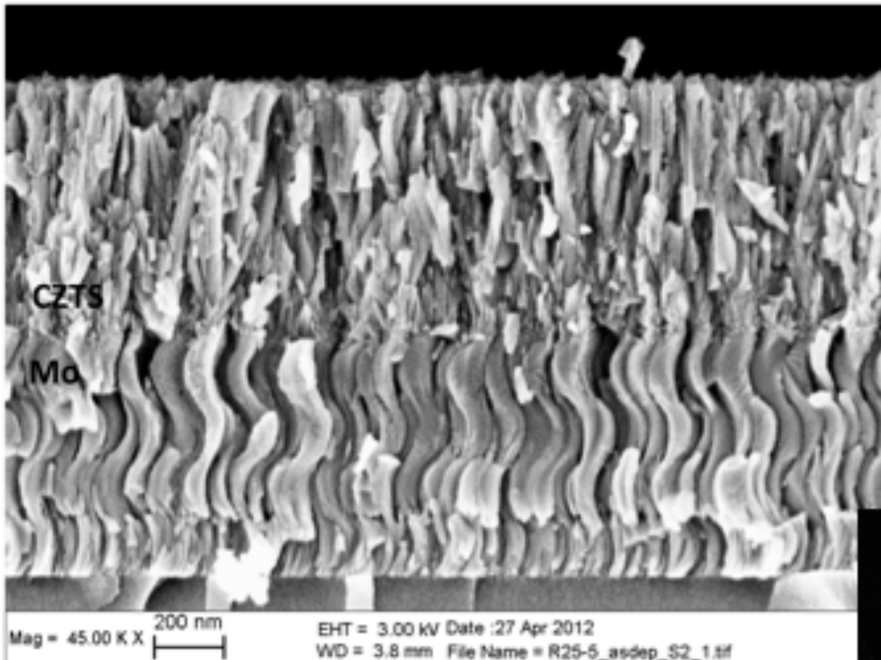


Interfacial energies—wetting layer

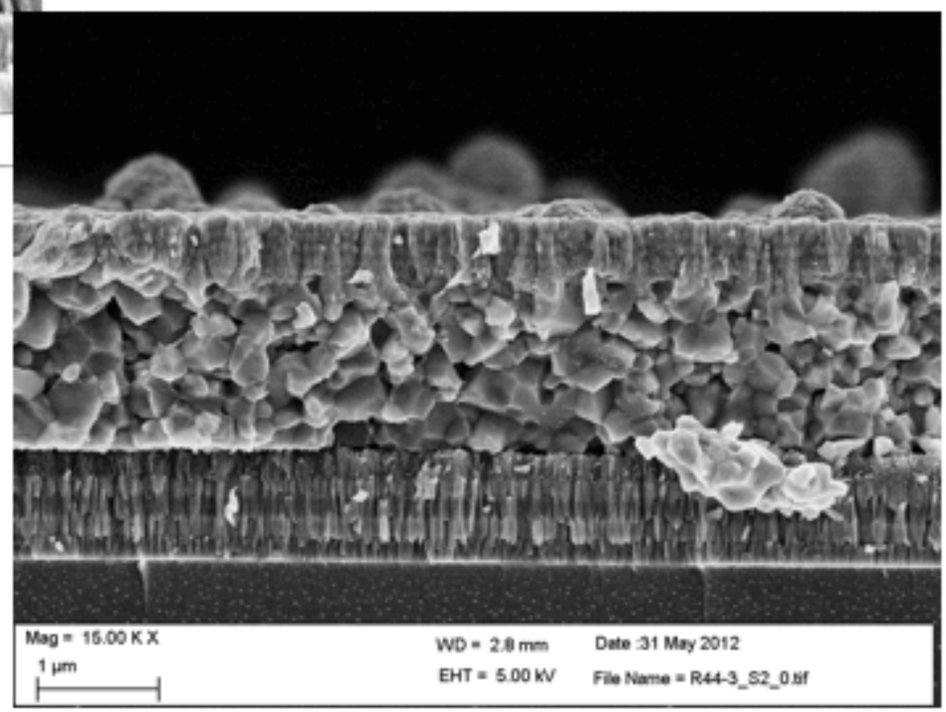
Voiding from gb growth and densification

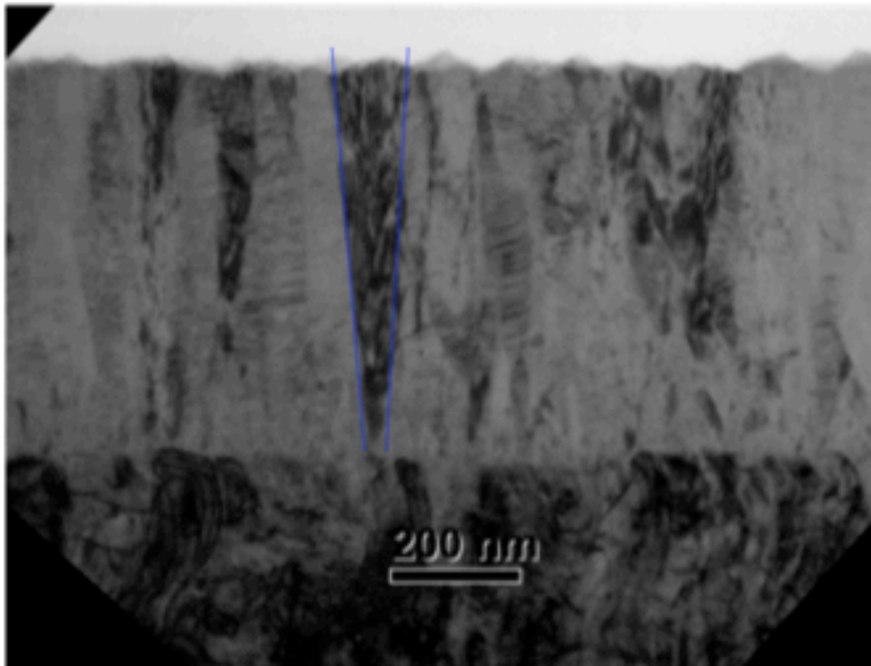


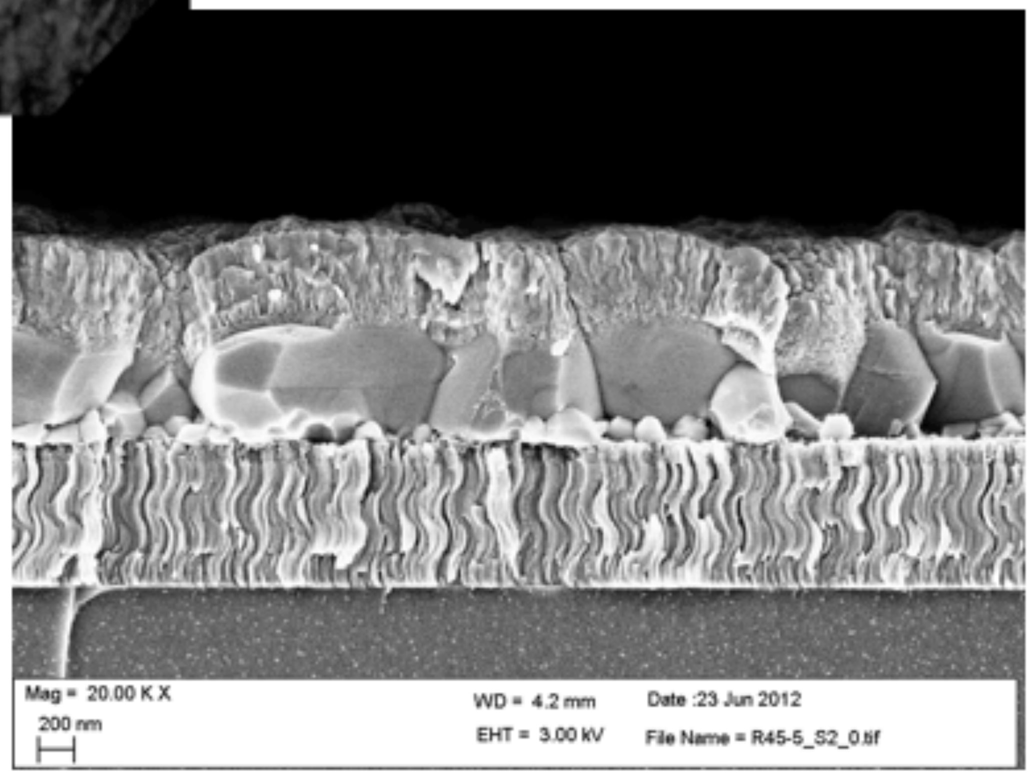
Grain growth



50 C deposition
580 C anneal







150 C deposition
580 C anneal

Challenge #6: New earth abundant materials

Absorber material	Band Gap(eV)	Device Structure	Highest efficiency	Remarks
Cu2S	1.2	p Cu2S/CdS	10-12%	Compound decomposes under own electric field, Cu++ ion motion; active work in early 80s.
FeS2	1		3%	Voc~200 mV; formation of other phases?
Zn3P2	1.5	p Zn3P2/Mg/ITO	6%	6% reached in 1980*; Voc of 550 mV reached by Caltech group
Cu2O	2	p Cu2O/ZnO	3.80%**	formation of other phases? Exciton binding energy high
Mo & W sulfides and selenides	1-1.5		few %	

Bhushan & Catalano, APL 1981
***Minami Appl Phys Express 2011*

Things to do for earth abundant thin film solar cells

1. Modelling of the device with candidate bottom electrodes, emitters etc.
2. Role of the grain boundary
3. Phase and microstructure stability
4. New materials discovery