Three ways to grow faster and better CIGSe:

In-Ga co-electrodeposition, 1 second laser annealing, and Cu-rich growth

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Acknowledgements

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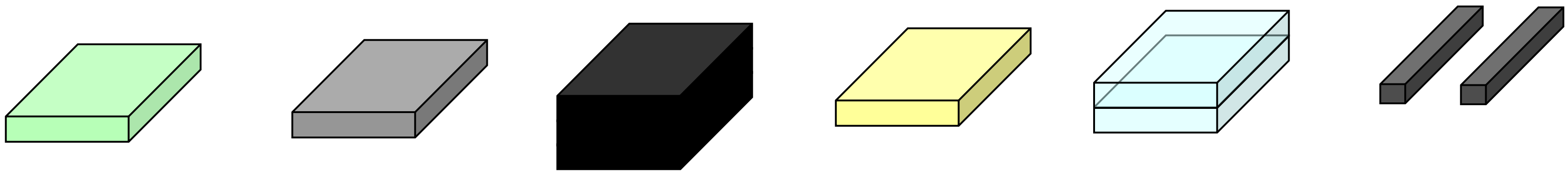
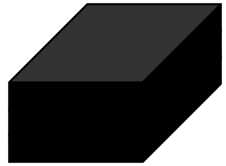
Luxembourg baseline process



Soda Lime Glass	Mo	$Cu(In,Ga)Se_2$ $Cu_2ZnSnSe_4$	CdS	i-ZnO Al:ZnO	Ni/Al
	DC sputter	Co-evaporation / Electrodeposition and annealing	CBD	Rf – sputter	E-beam evaporation
25 x 25 x 2 mm	500 nm	1 – 3 µm	50 nm	80 nm 500 nm	10 nm 2000 nm

Luxembourg $Cu(In,Ga)Se_2$ processes



	Electrodeposition	Annealing	Advantage
1	Cu; In-Ga / Cu →	Elemental selenium Tube furnace / RTP	Good control of Ga / III
2	Cu_2Se + In_2Se_3 + $CuInSe_2$ →	1064 nm Nd:Yag Laser	Very fast annealing
	Co-evaporation		
3	Cu rich $CuInSe_2$ →	In_2Se_3 / Cu rich $CuInSe_2$	Less defects

Talk outline

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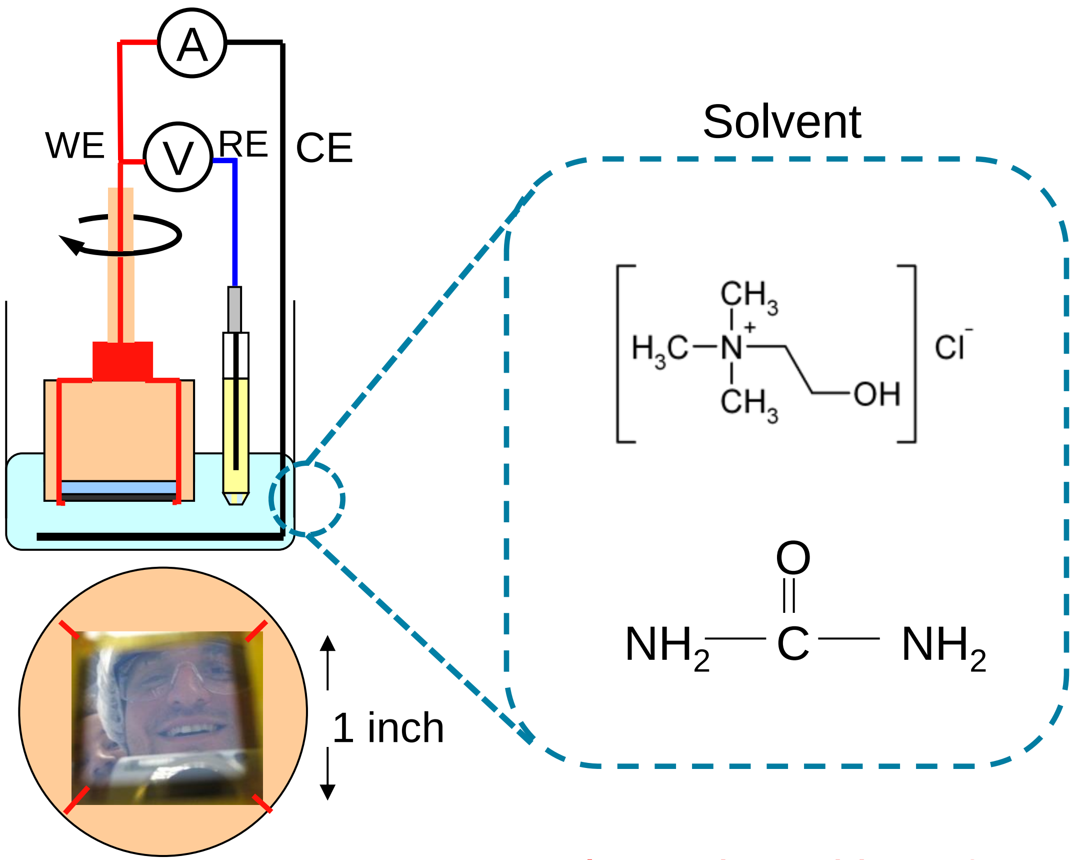
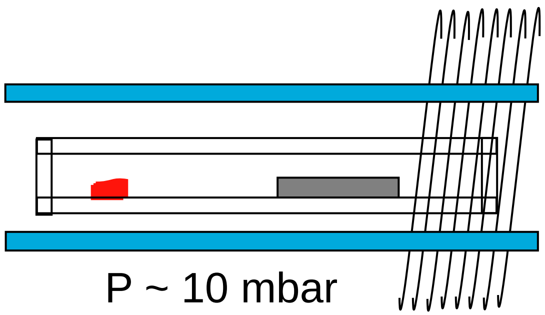
Electrodeposition and annealing

Electrodeposition of metals



Mo/Cu/In:Ga

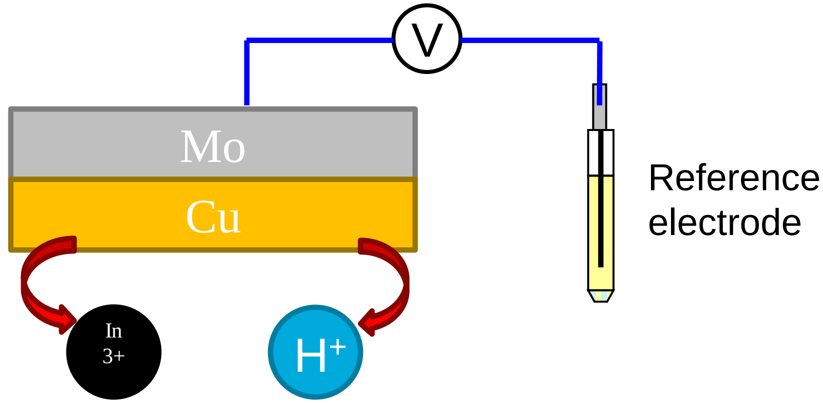
Tube furnace
$\Delta T \sim 33\ °C\ min^{-1}$

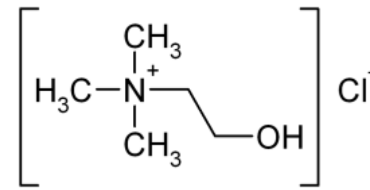


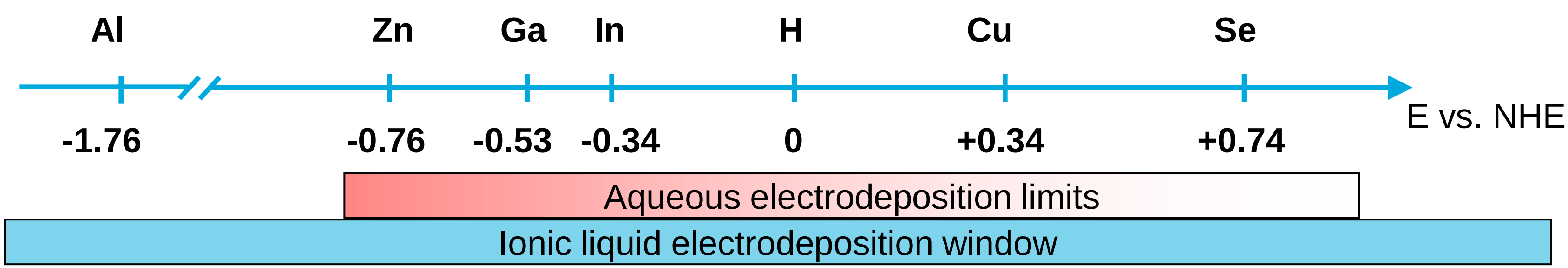
N_2,H_2

1.Co-electrodeposition of In and Ga could lead to more uniform electrodeposits on the microscale?
2. Could lead to faster deposition times.

Advantages of electrodeposition from ionic liquids



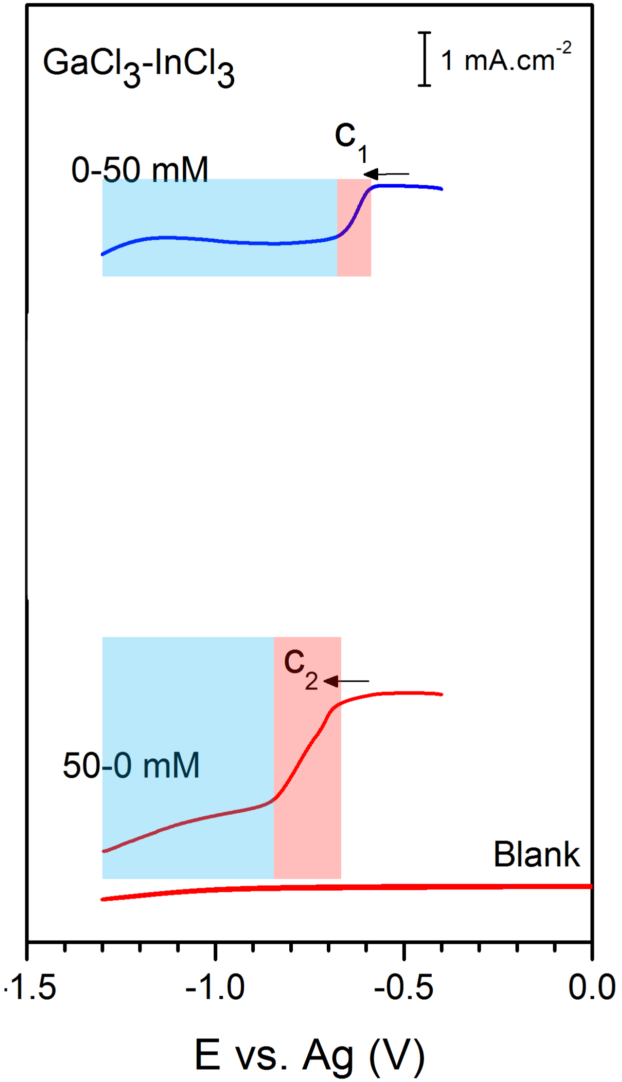


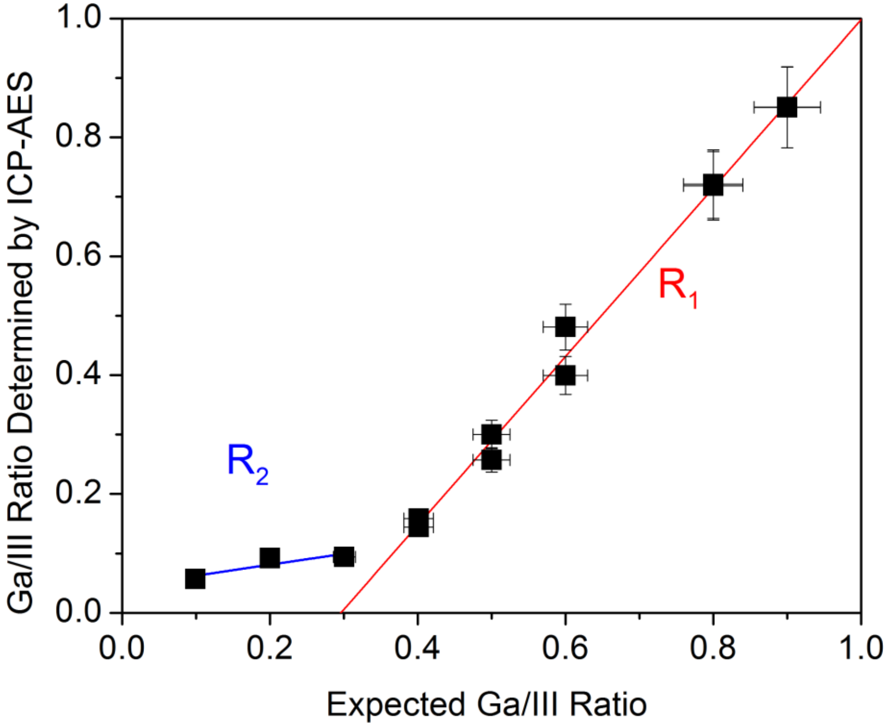


Wider electrochemical window enables facile deposition of low reduction potential elements like Ga

Steichen, Thomassey, Siebentritt, Dale . *Phys. Chem. Chem. Phys.* **13** 4292-302

Co-electrodeposition of In and Ga

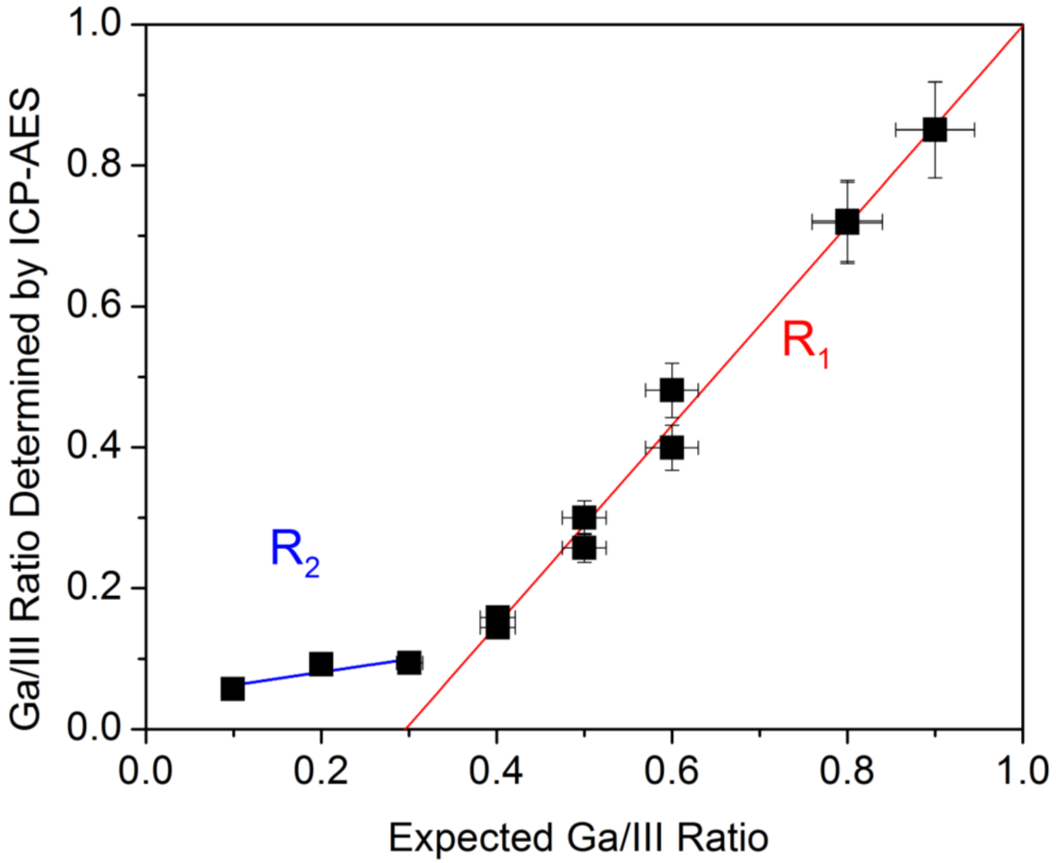


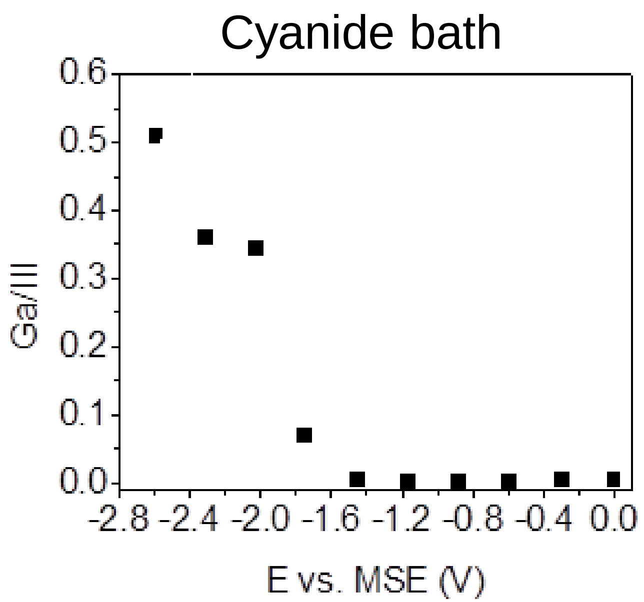


Malaquias et al. Manuscript in preparation

Ga / III ratio controllable over the whole range

Comparison to academic literature





Adapted from Zank et al., ***Thin Solid Films***, 1996 , **286**, 259

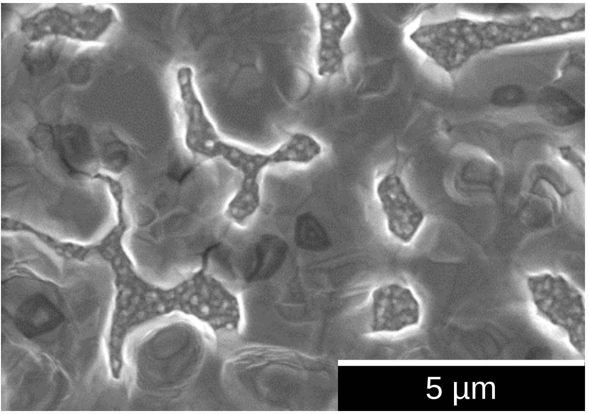
Ga / III ratio controllable over the whole range

Coelectrodeposition of In-Ga on Cu

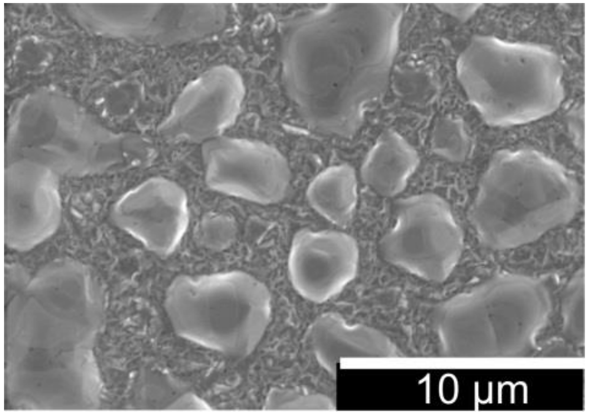
→ Depositions at E_d = -1.2 V ; constant Q; $Ga/III_{obtained}$ = 0.1; 0.4; 0.7 ; T = 60 °C

- SEM/EDX

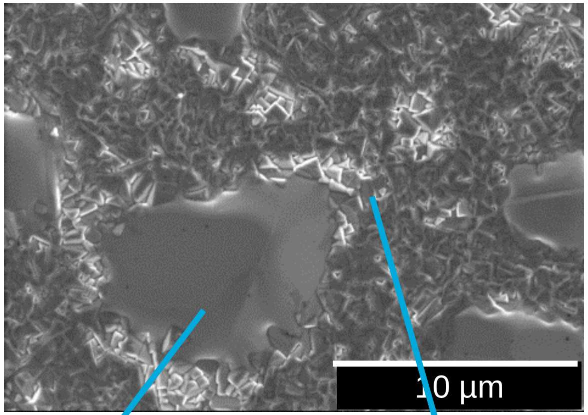
Ga/III = 0.1

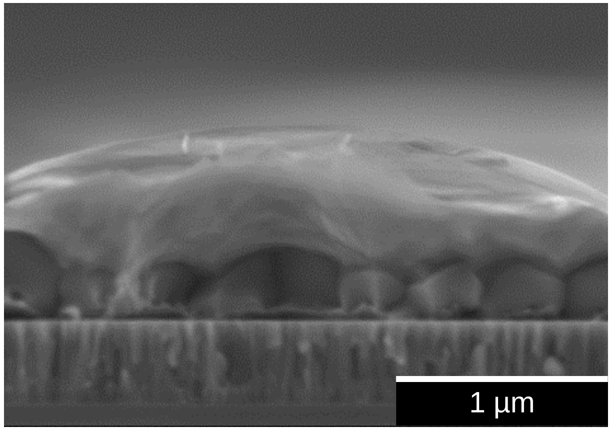


Ga/III = 0.4



Ga/III = 0.7





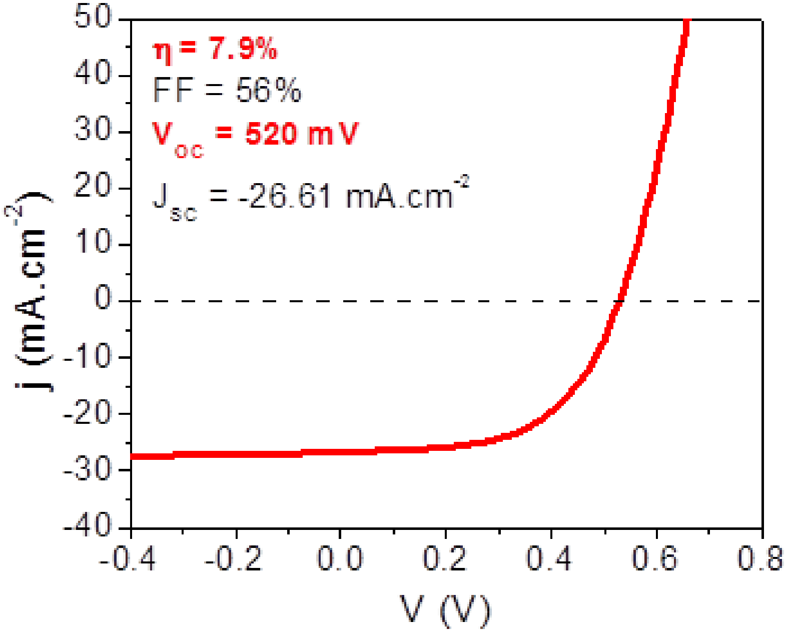
EDX:

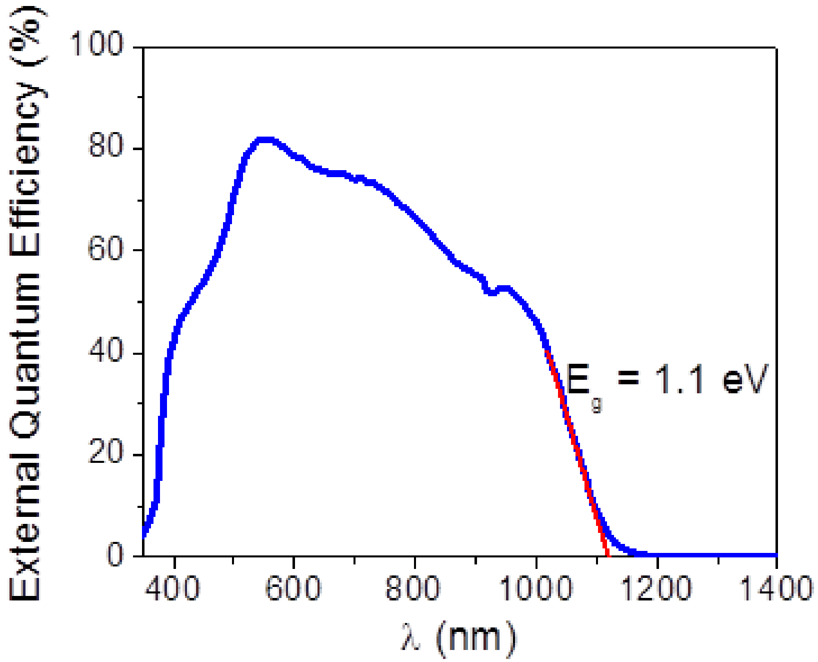
Element	Atomic %
Cu	4.6
In	88.5
Ga	4.8

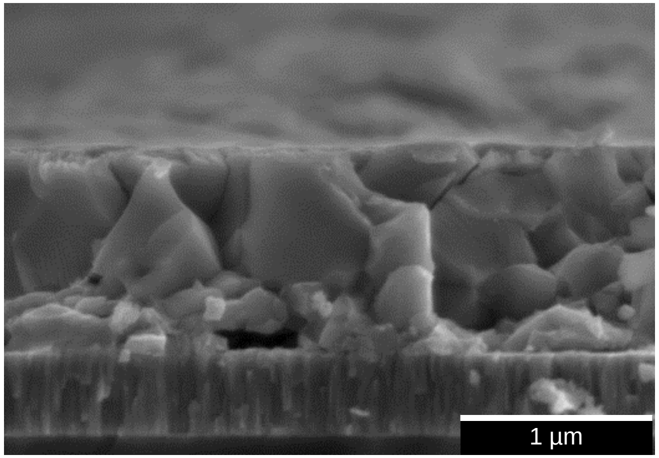
Element	Atomic %
Cu	42.6
In	0.5
Ga	26.5

Morphology changes with Ga content

Best Preliminary Device Results
Ga/III = 0.4

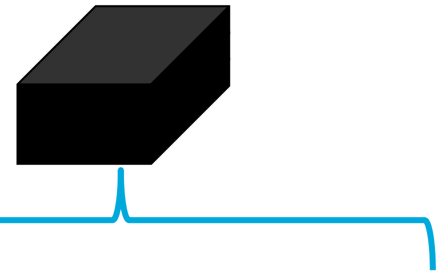






Malaquias et al. Manuscript in preparation

Talk outline



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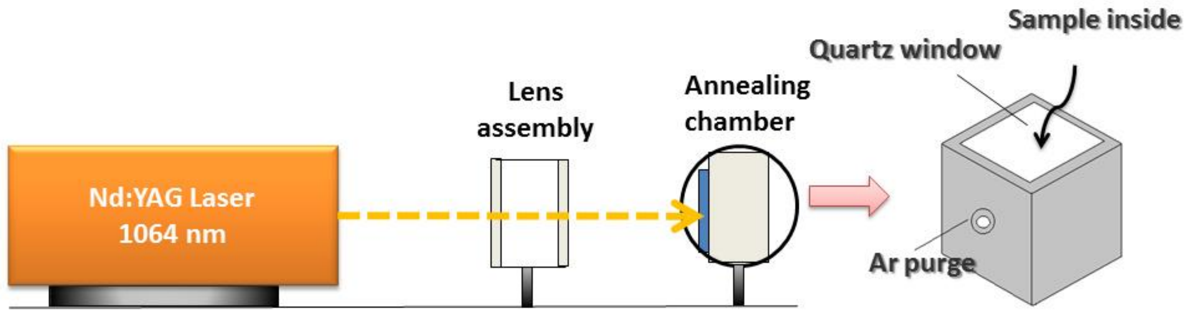
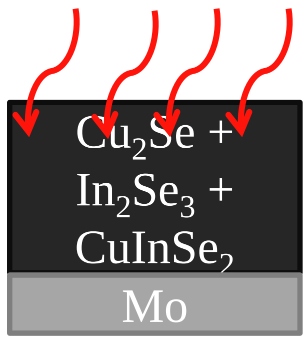
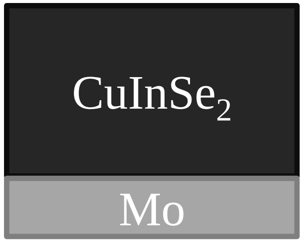
Electrodeposition and Laser Annealing



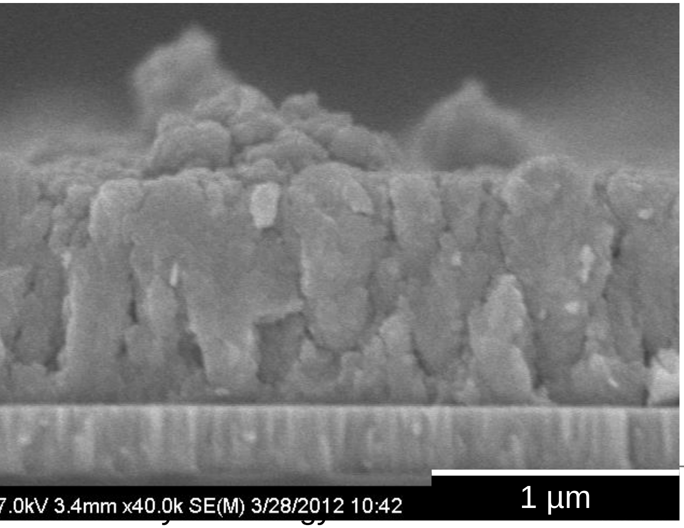
Room temperature deposited precursor



Energy + Se?



Absorber layer



Advantages of Laser Annealing?

1. heat just the local environment
2. absorber layer temperature can exceed glass softening temperature on sub milli-second timescales

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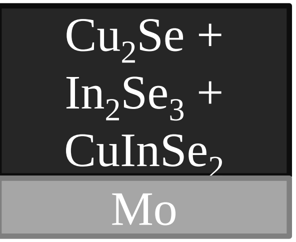


Is it possible to anneal an absorber in 1 s?
What does annealing do?

Energy side

1. diffuse atoms to remove concentration gradients (Cu, In, Se) → chemical depth profiles

2. grow grains

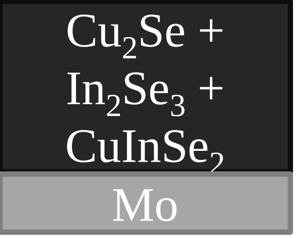
3. drive chemical reactions

(2, 3) → x-ray diffraction

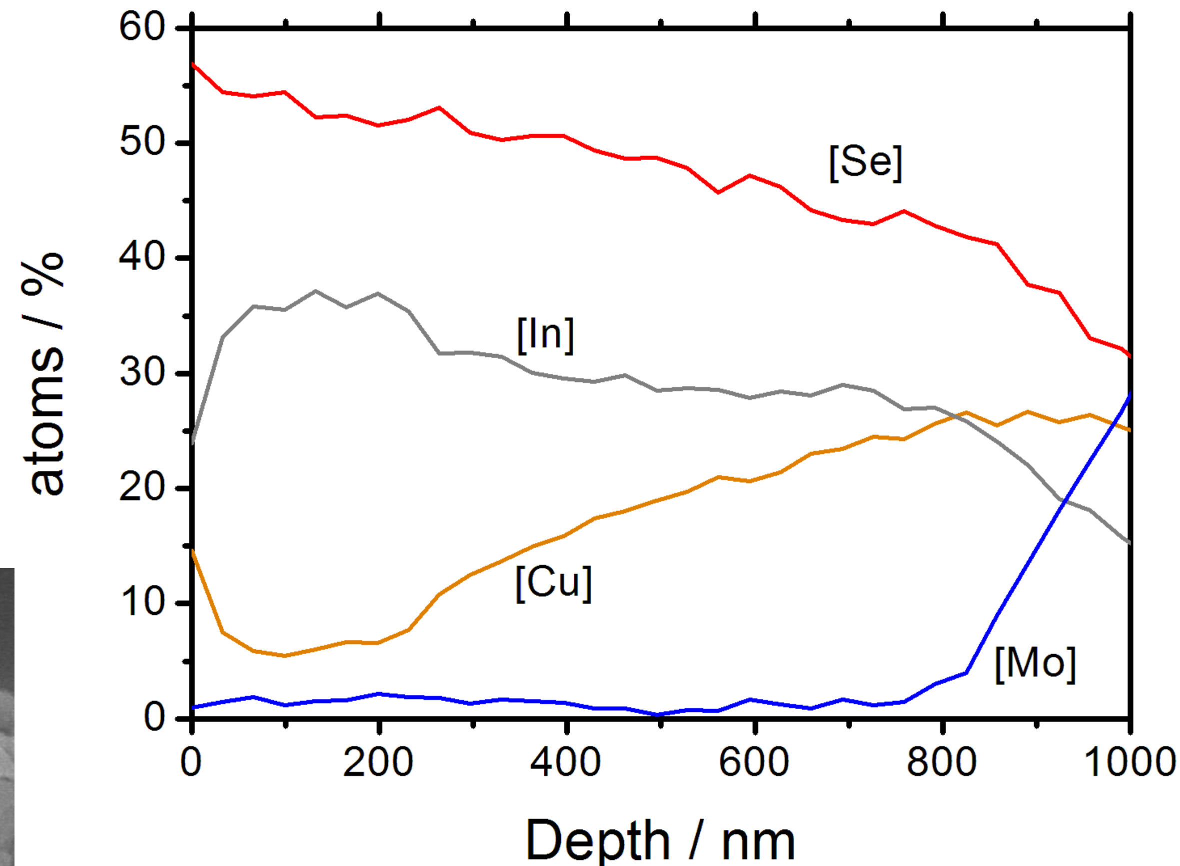
4. move defects to grain boundaries

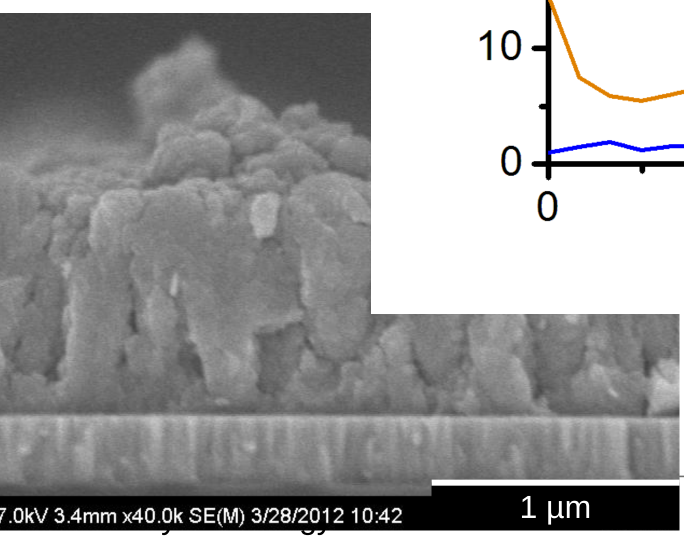
5. move Na or O to pacify defects at grain boundaries

(4, 5) ? opto-electronic properties



Precursor





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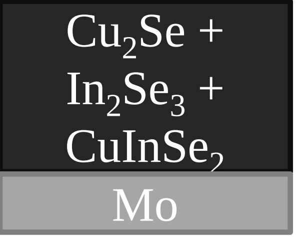
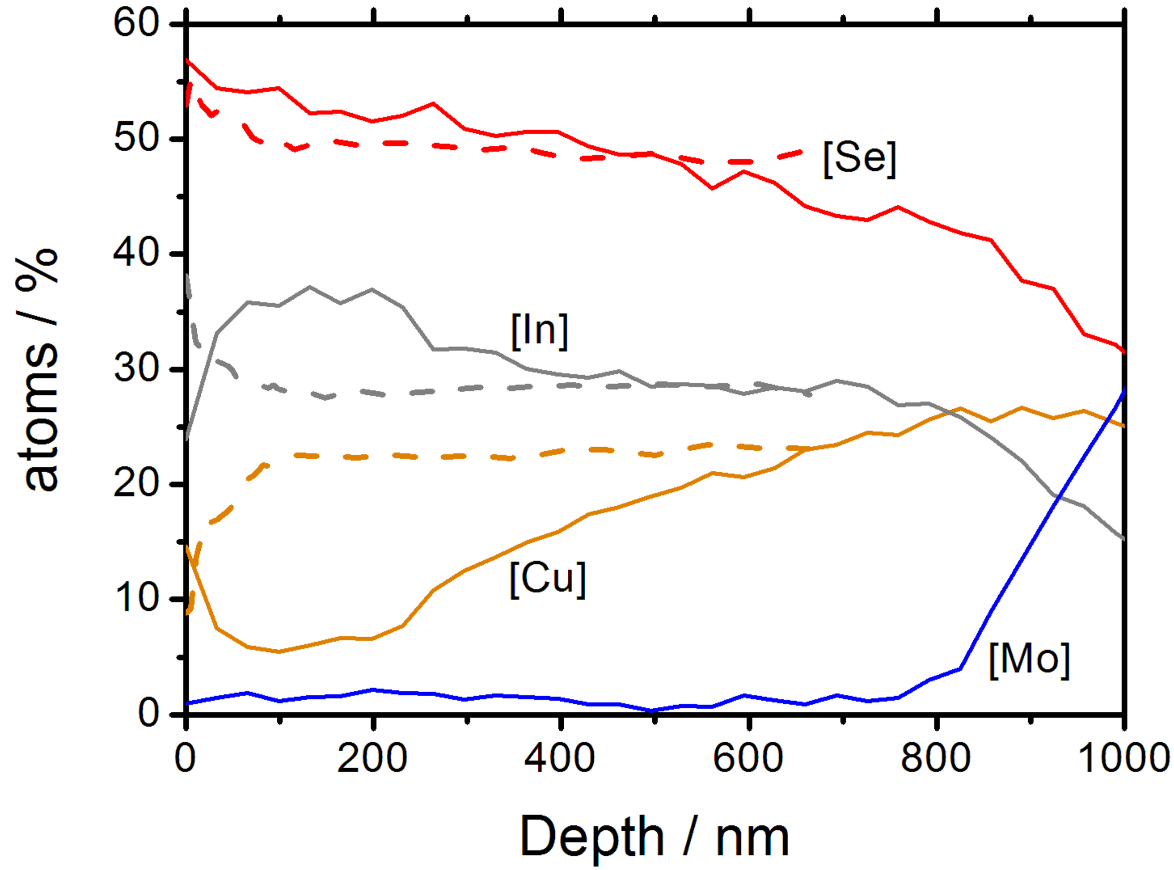
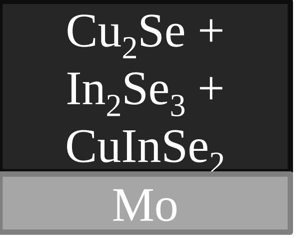


Laser Annealing for 1s at 945 W.cm^{-2}



No large concentration gradients of Cu, In, and Se in the bulk



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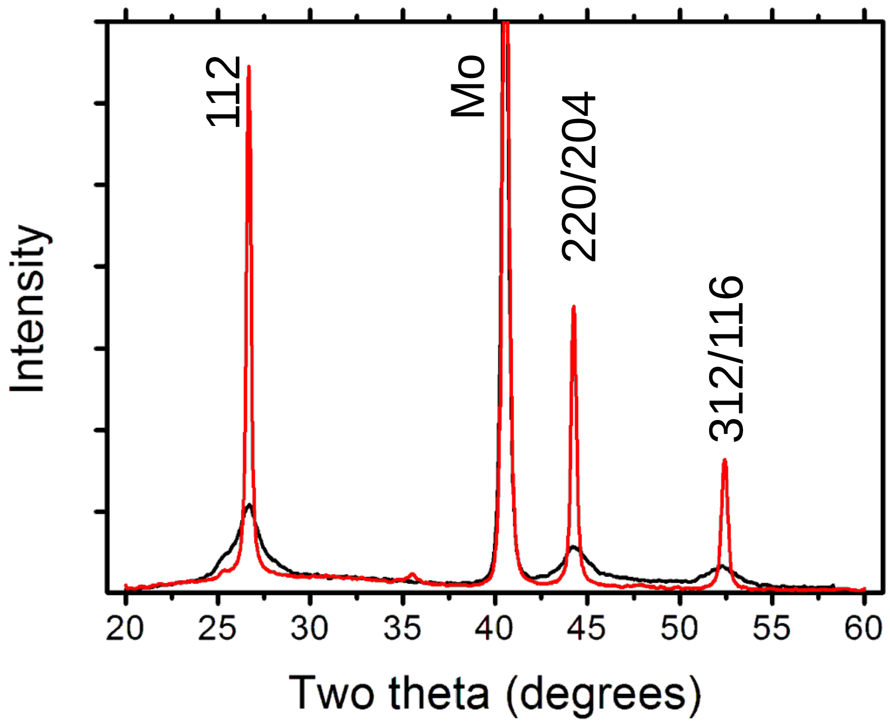
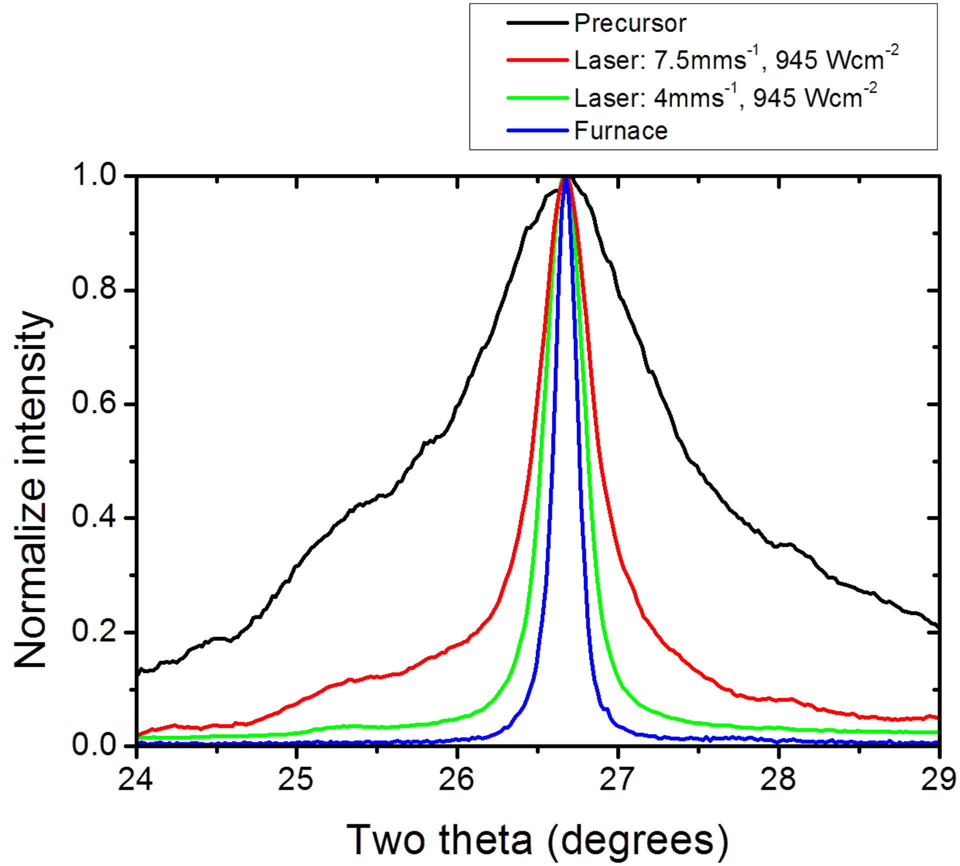
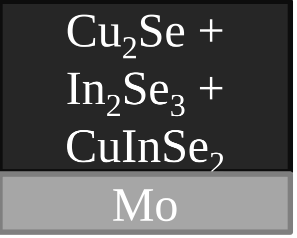
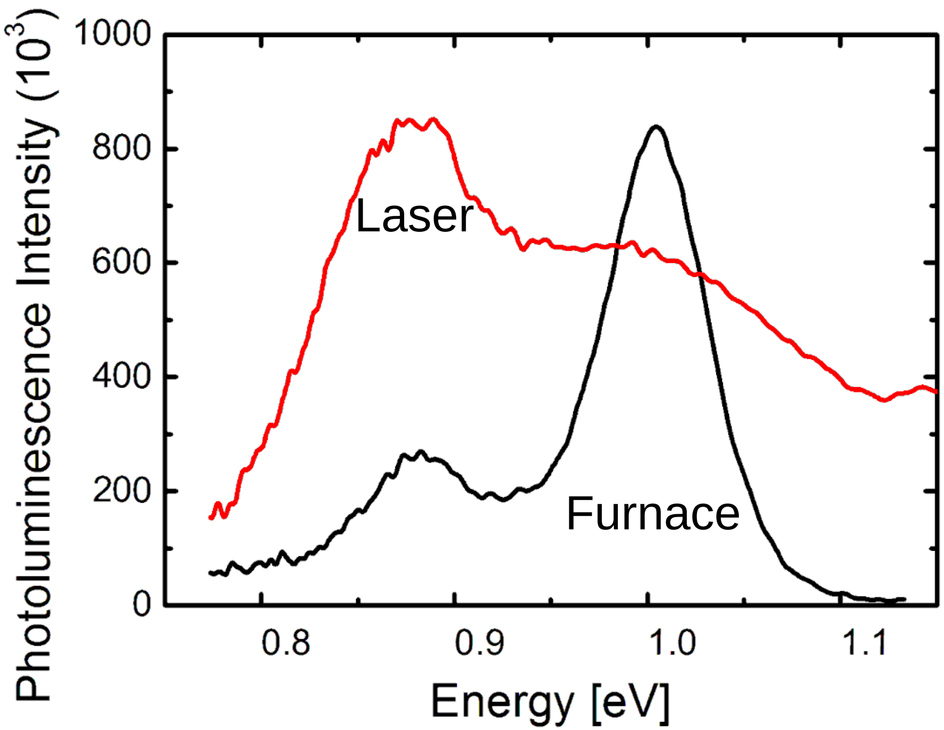


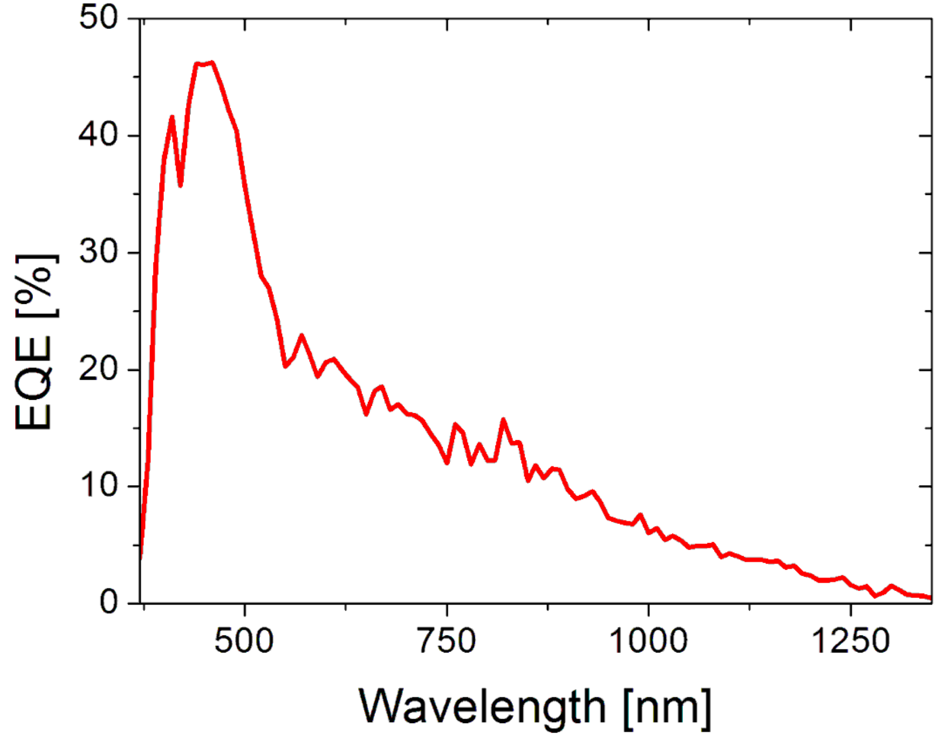


FWHM of main peaks decreased after laser annealing indicating increased crystal coherence length



Opto – electronic properties

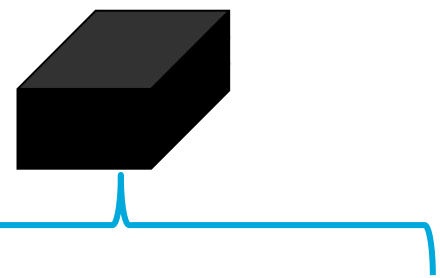




Meadows et al. manuscript in preparation

Laser annealed absorber layer shows PL properties
When completed to full device, shows rectification…

Talk outline



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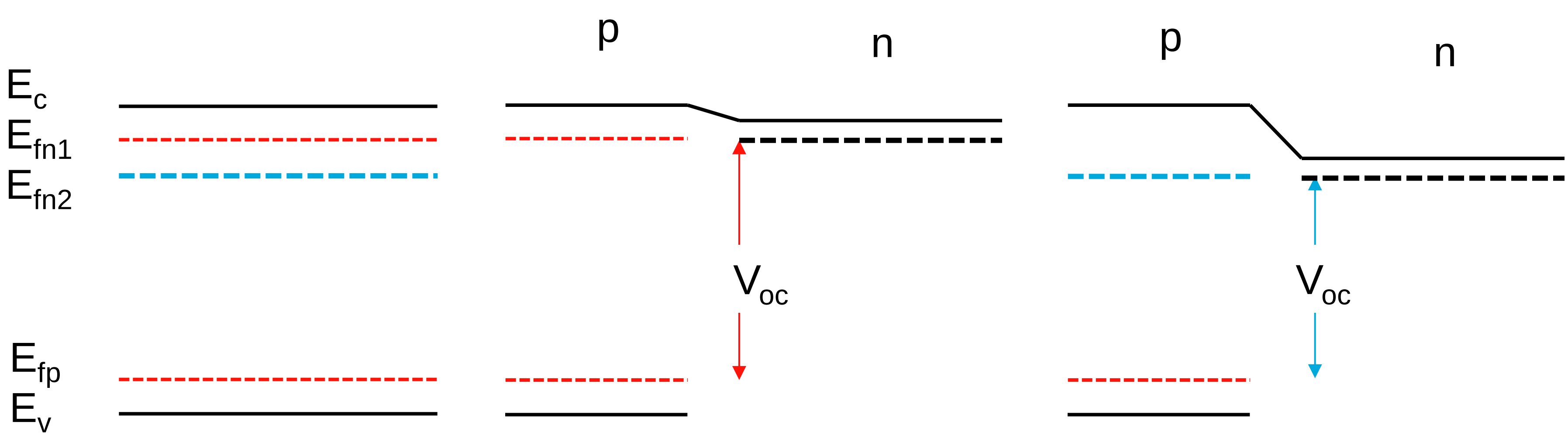
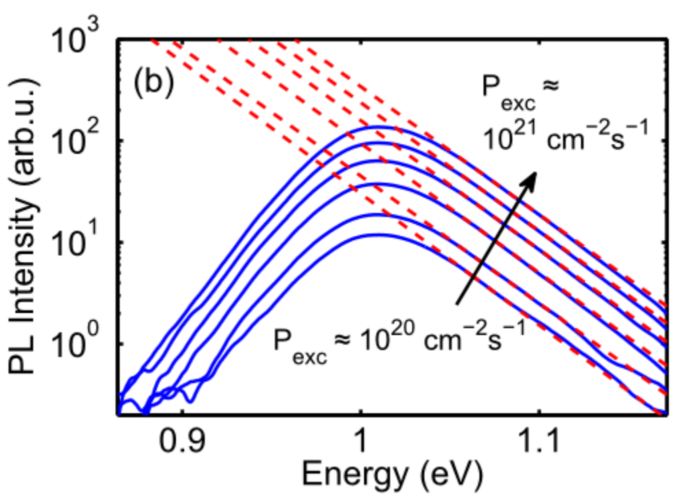
Quasi fermi level splitting in absorber indicates maximal V_{oc} of device

PL

Device, large E_{fn}-E_{fp}

smaller E_{fn}-E_{fp}

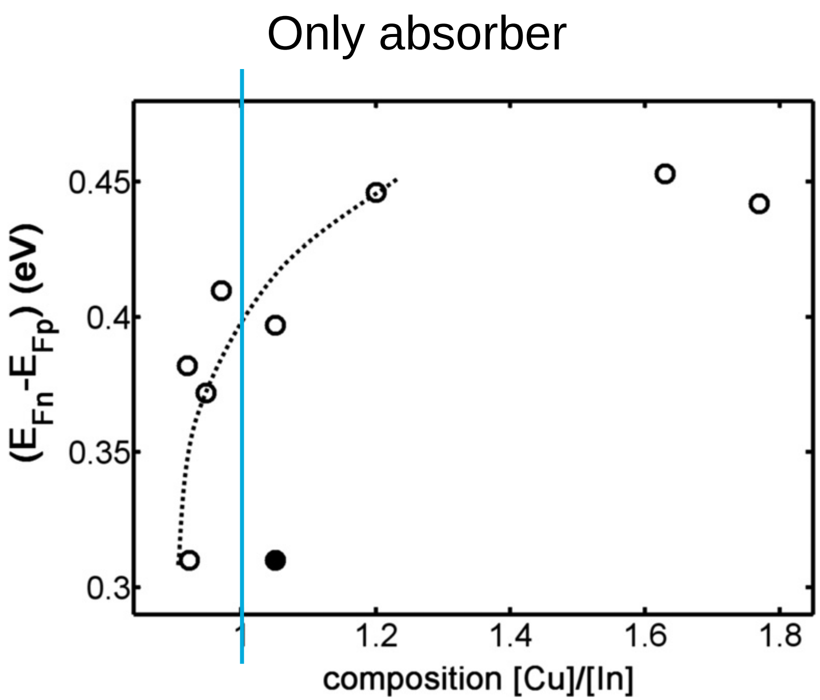


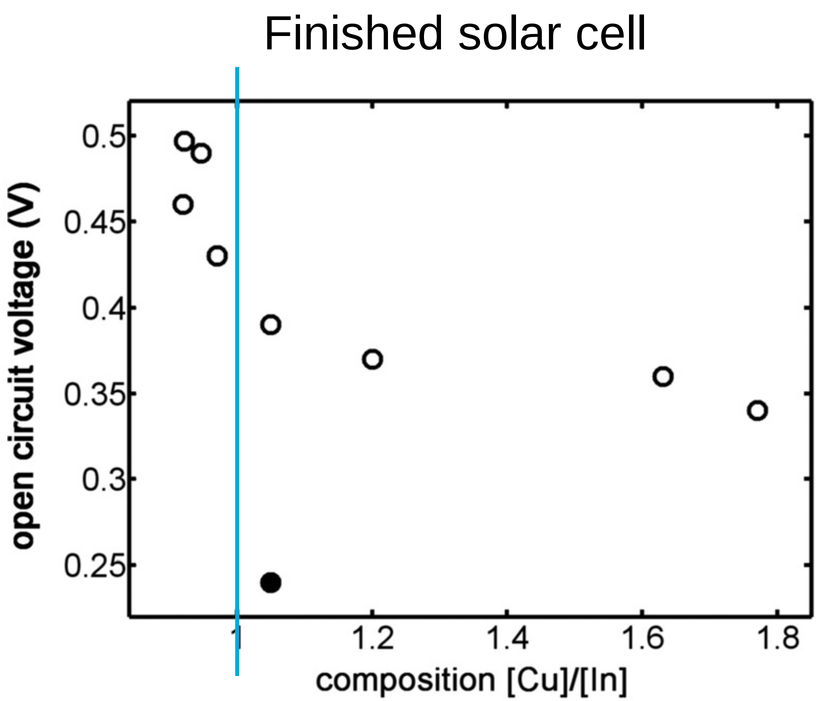


higher V_{oc}

lower V_{oc}

Quasi-Fermi level splitting in polycrystalline layers





"Cu-rich": larger splitting of quasi-Fermi levels → higher V_{oc} potential

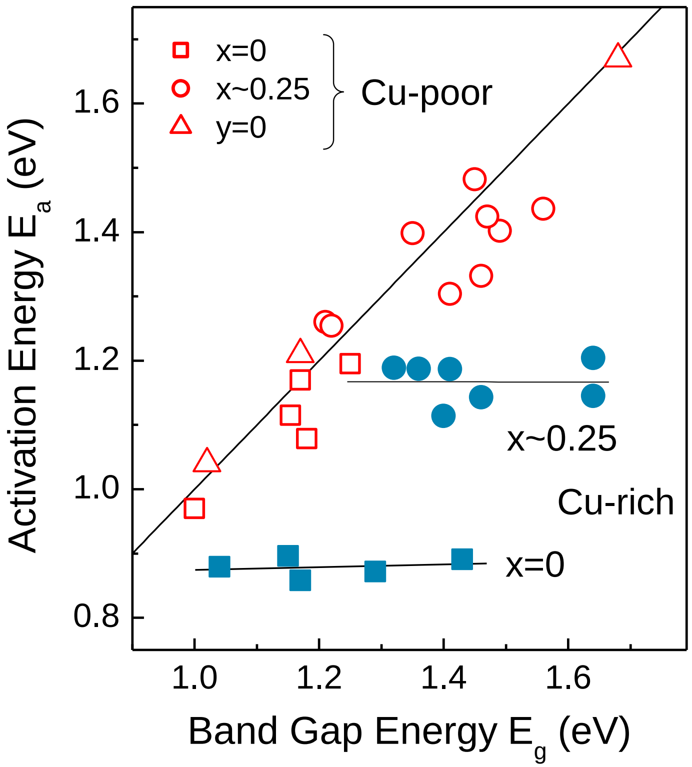
Finished cells: actual resulting V_{oc} drops at higher Cu-contents

⇒ splitting of quasi-Fermi levels not fully exploited for high Cu-contents

Gütay, Regesch, Larsen, Aida, Siebentritt, Appl. Phys. Lett, 99, 151912, 2011

Recombination path in Cu-poor and "Cu-rich"

$Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)$



⇒
Cu-poor cells dominated by SCR recombination
"Cu-rich" by interface recombination

Turcu, Pakma, Rau, Appl. Phys. Lett., 80 (2002) 2598

A new process for "Cu-rich" solar cells

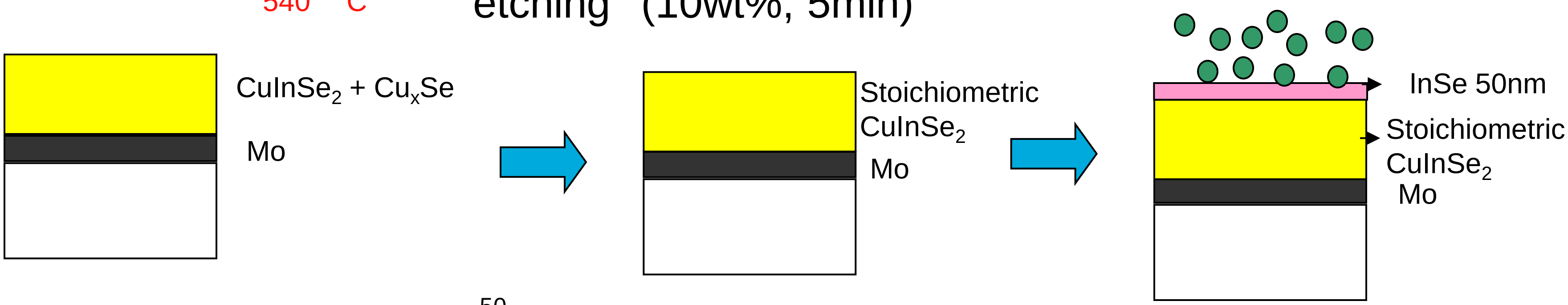
→ "Cu-rich" bulk with Cu-poor surface:

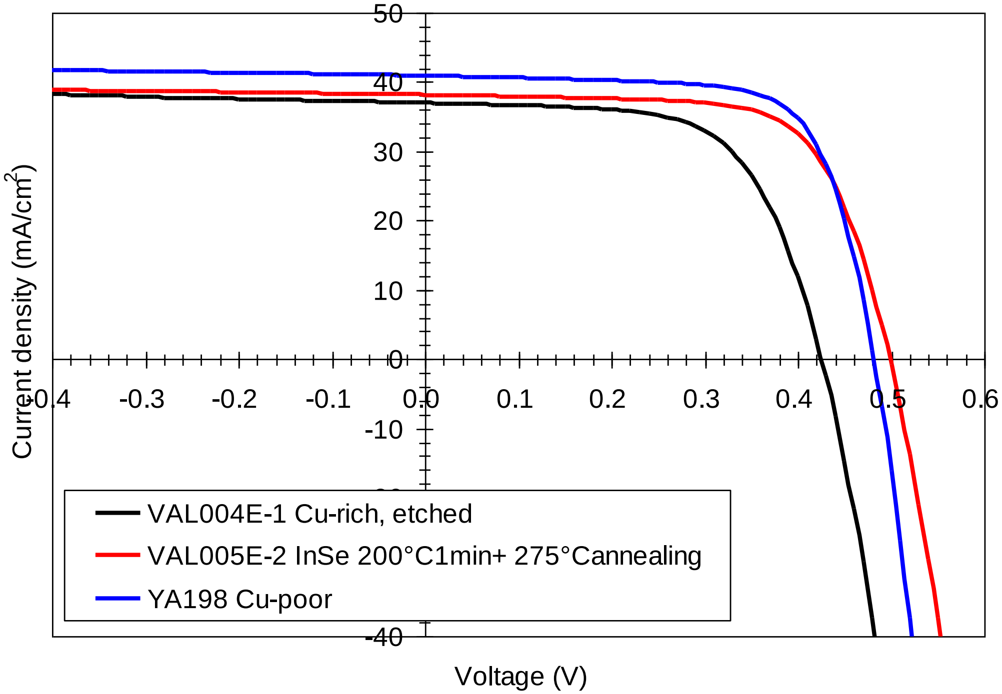
Cu, In, Se
co-deposition

540 ° C

KCN
etching (10wt%, 5min)

In-Se deposition
200 °C 1min + annealing





currently best result:
13.1% efficiency

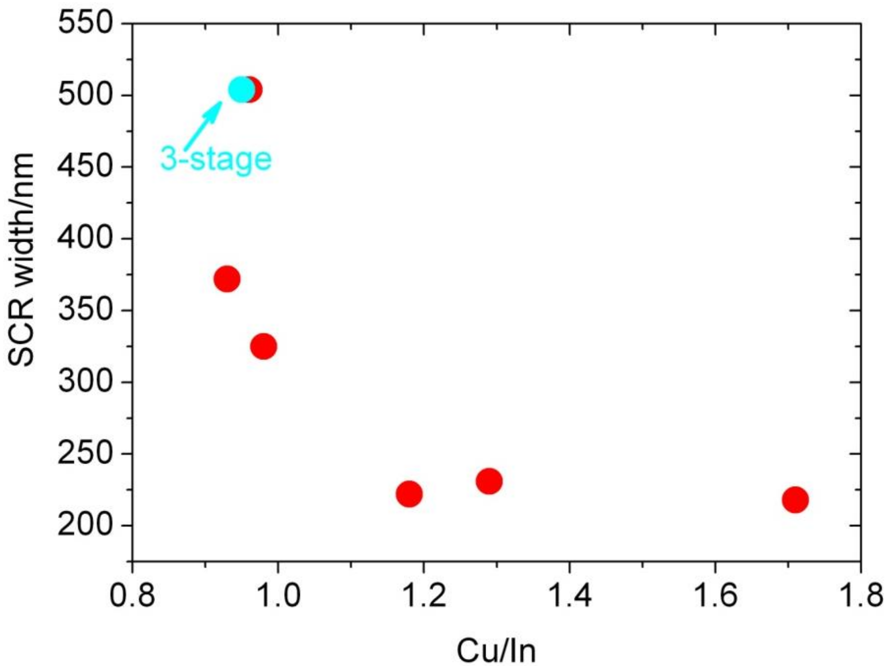
compare with
14.0% from Cu-poor

Depredurand, Aida, Siebentritt,
IEEE PVSC, Seattle, 337, 2011

Why is the current low?

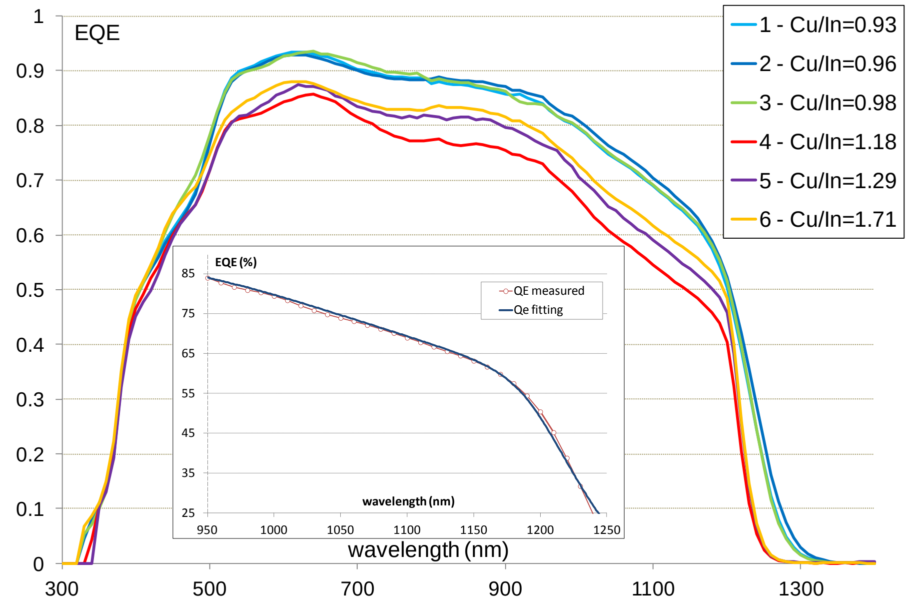
one reason:
space charge width is too short

from capacitance measurements:



BUT: from QE ⇒ collection length

$$L_{eff} = W_{SCR} + L_{diff}$$



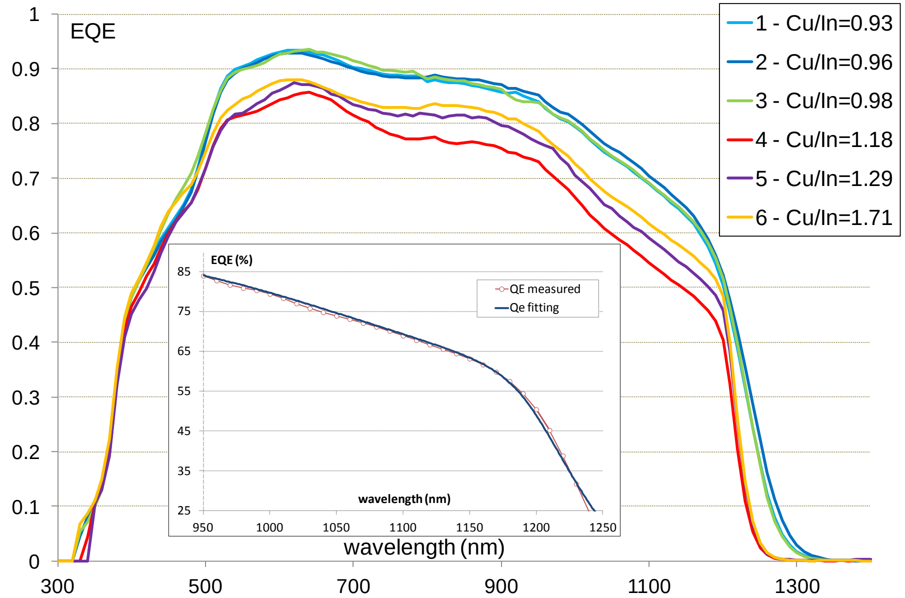
⇒ space charge width is smaller
⇒ the doping is too high!

⇒ L_{eff} (Cu-rich) ≈ 3μm
L_{eff} (Cu-poor) ≈ 2μm

⇒ collection length is better, in spite of shorter SCR width

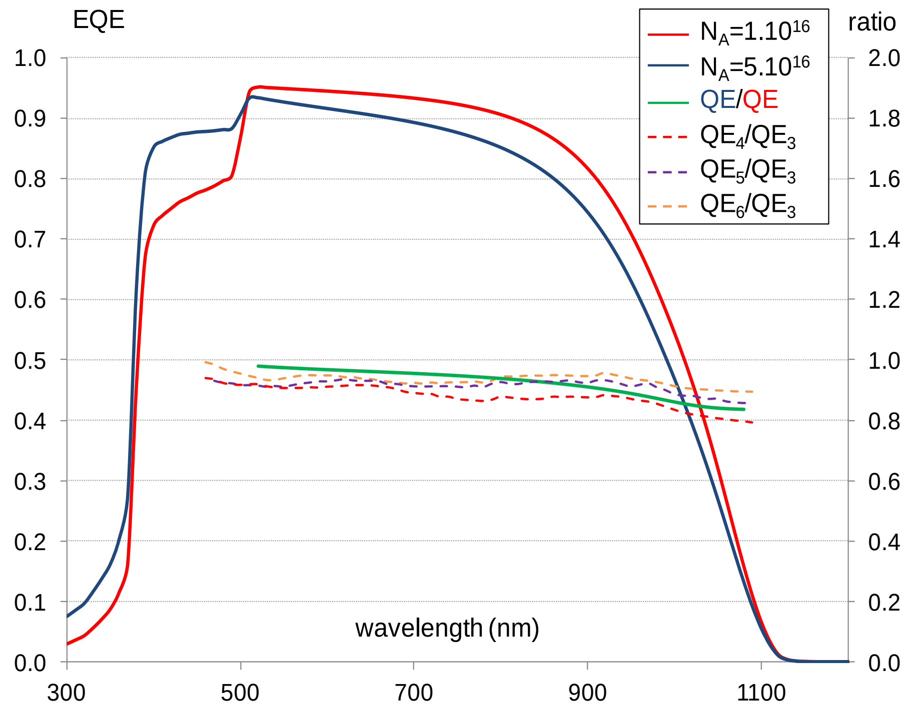
Depredurand, Tanaka, Aida, Fevre, Siebentritt, submitted

Then why is the current lower?



⇒ QE lower by constant factor

SCAPS modelling:



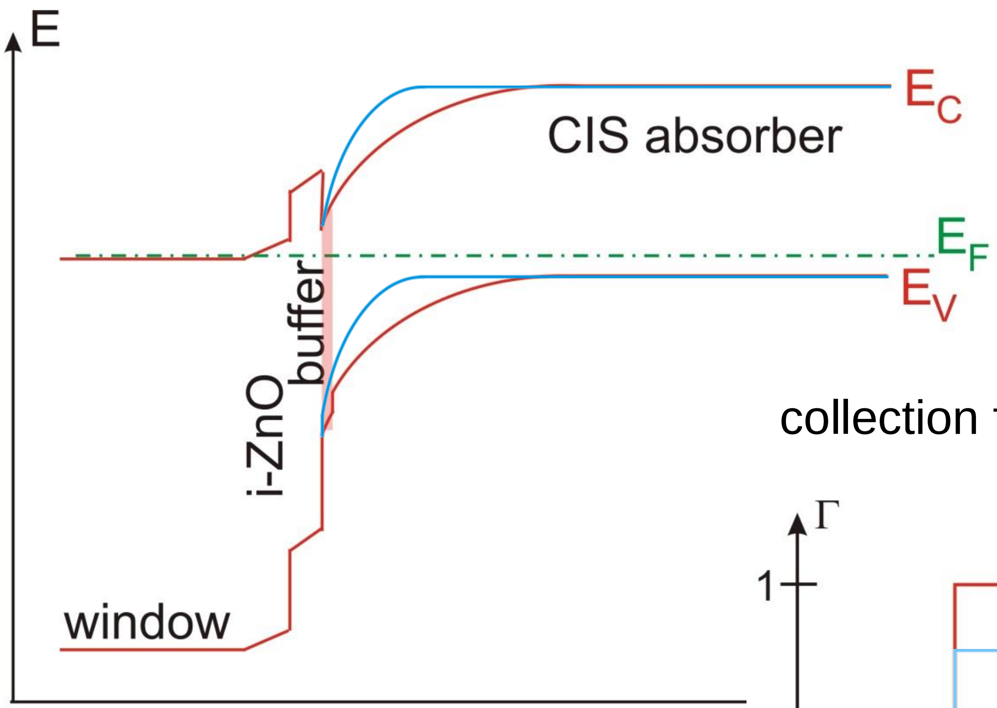
⇒ reduced collection probability

⇐ high recombination in SCR due to tunneling

Depredurand, Tanaka, Siebentritt et al., submitted

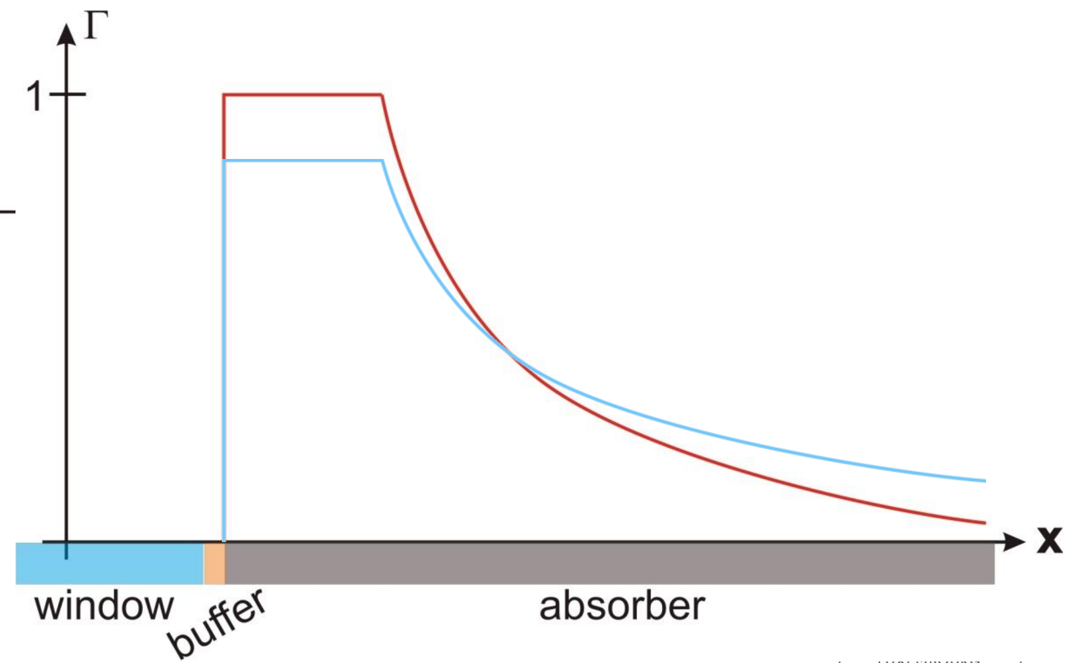
Cu-poor vs. Cu-rich

band diagram:



Cu-poor or
Cu-rich

collection function:



Summary

- Indium and Gallium can be simultaneously electrodeposited with good compositional control over a large potential range.

- Laser annealing of nanocrystalline $CuInSe_2$ precursors for one second is sufficient to diffuse elements, grow grains, and develop semiconductor properties.

- Cu rich grown absorbers contain fewer defects and have a potential to produce higher V_{oc} devices than Cu poor grown absorbers.

Summary and Acknowledgements

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Fonds National de la Recherche Luxembourg

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Thank you for your attention. Questions?

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