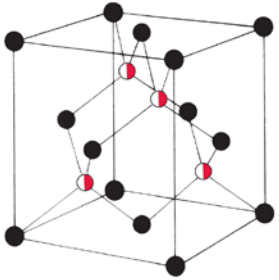
14.8

Investigating the role of Copper in Arsenic doped CdSeTe Photovoltaic Devices

Eric Colegrove

Oct. 28, 2021



2021 U.S. Workshop on the Physics and Chemistry of II-VI Materials

Outline

1. Introduction
2. JV and CV trends (As-only vs As+Cu)
3. Structure - EBSD, TEM (SEM) and Composition - SIMS (EDS)
4. Electro-optical - EQE, VocT, TRPL, KPFM, DLTS, (XPS, PL, CL)
5. Conclusions – “Cu benefit”
6. Modeling
7. Moving Forward

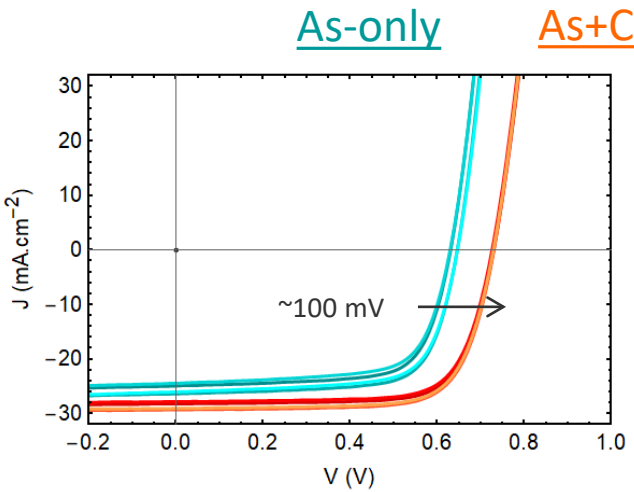
Introduction : Background

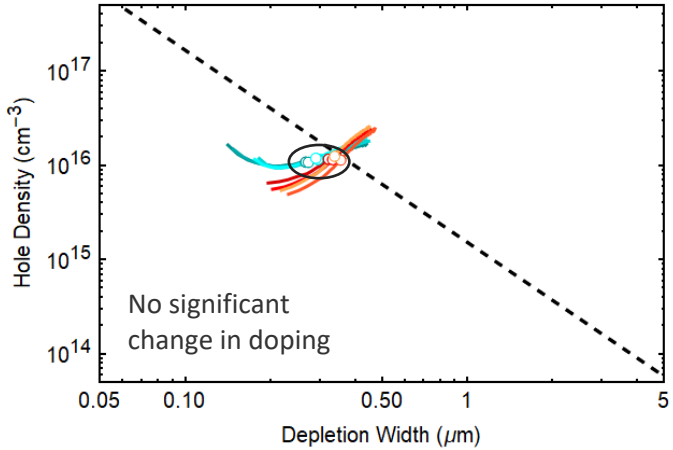
We still need to improve Voc

Arsenic has now widely enabled higher p-type absorber doping
→ record Voc's remain low (**why?**)

WHY?

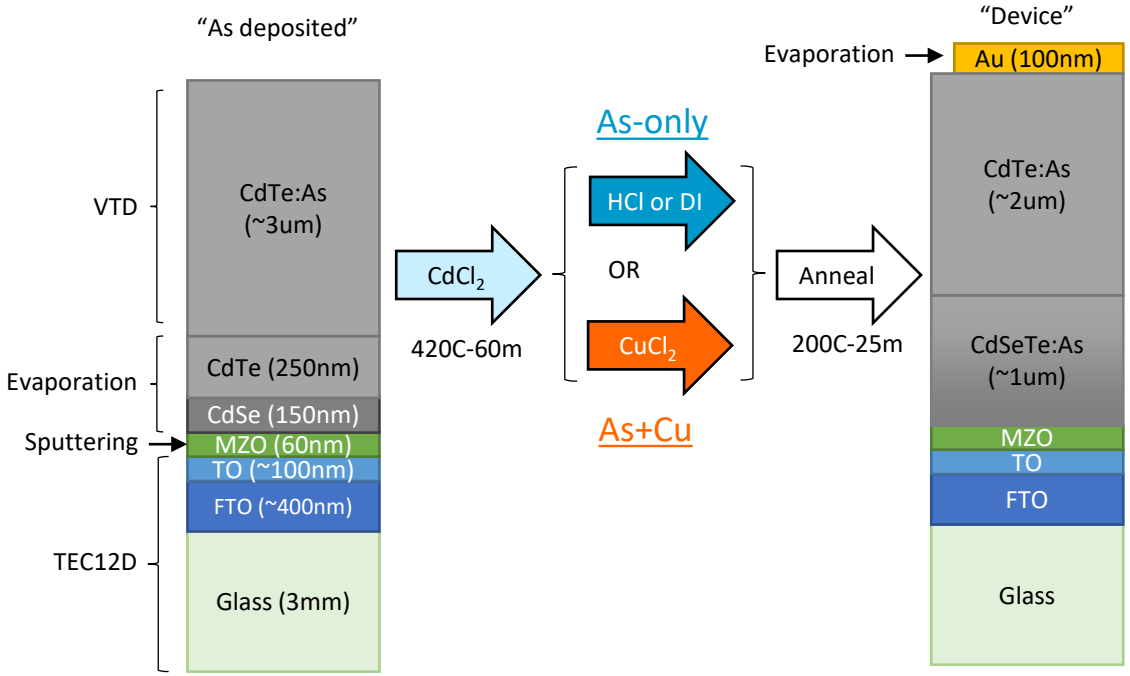
At NREL, co-doping with Cu enables improved Voc (**why?**),
but Voc is still (very) low relative to the band gap entitlement (**why?**)

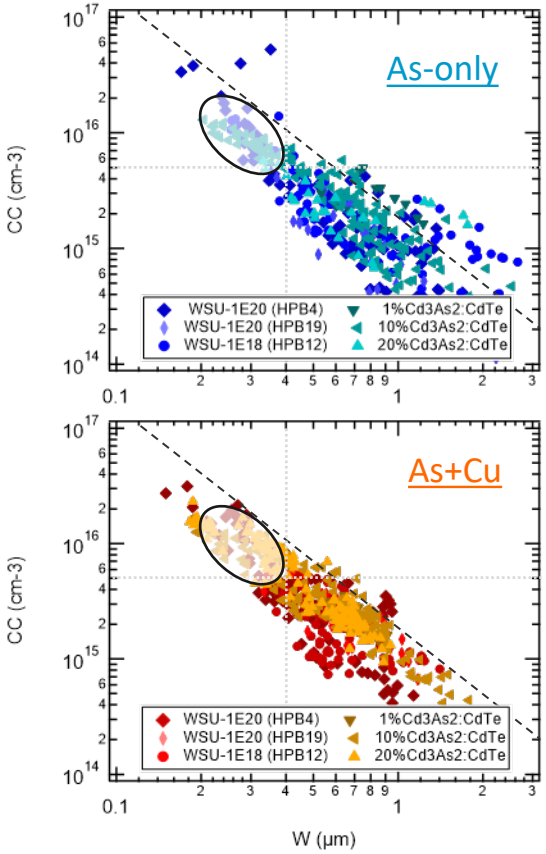




Data taken by Eric Colegrove at NREL

Introduction : Fabrication





Variety of VTD conditions and source materials

- WSU – High Pressure Bridgman (HPB)
- Mixed powder (Cd_3As_2:CdTe)

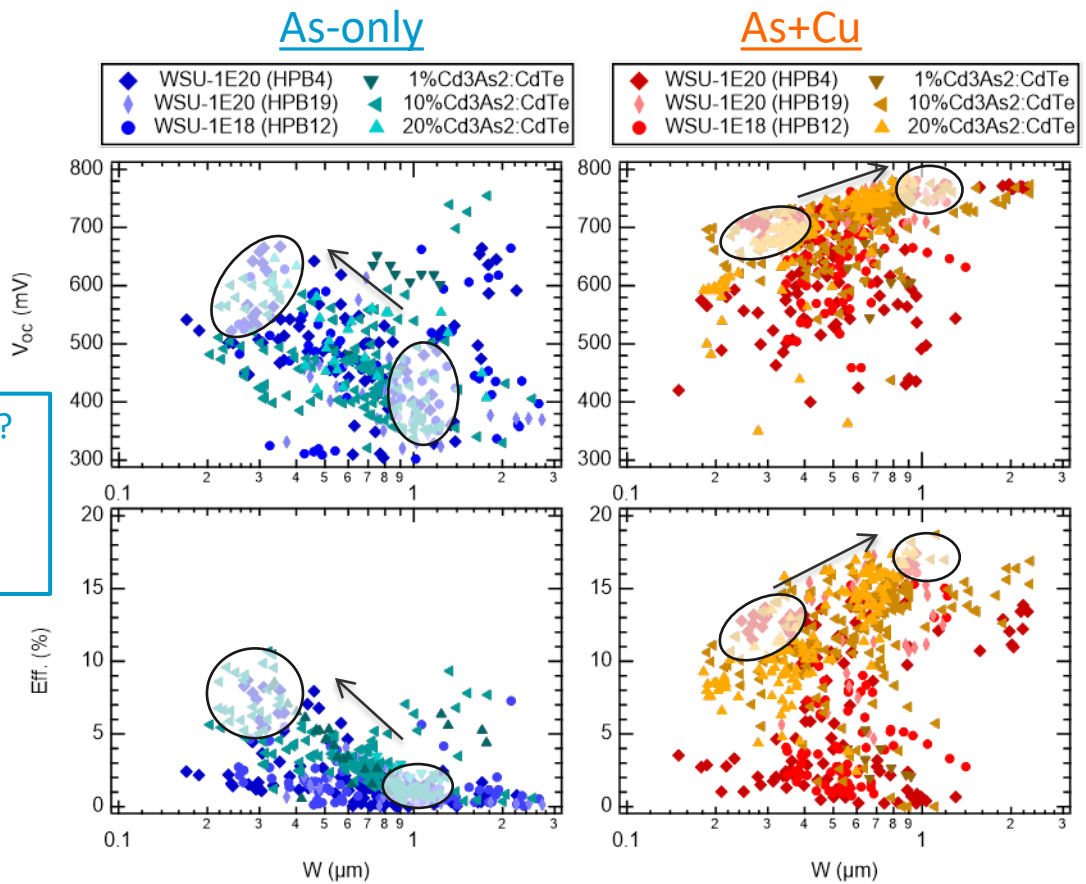
Data taken by Eric Colegrove at NREL

JV and CV trends

550-650mV (high CC)
↑
350-500mV (low CC)

Highly compensated?
High recombination reduced with high doping/activation

5-10% (high CC)
↑
0-2% (low CC)



750-800mV (low CC)
↑
650-750mV (high CC)

Interface/emitter limited?
interface recombination and/or poor emitter doping less important for low CC absorber

15-18% (low CC)
↑
10-14% (high CC)

Data taken by Eric Colegrove at NREL

Why is Cu helping?

Front interface/contact improvement?

- Cu at the interface promotes passivation (Cu directly, oxidation, other?)

Bulk absorber improvement?

- Cu process improves structure
- Cu passivates inter-grain defects (GBs)
- Cu passivates intra-grain defects
  (deep SRH defects, shallow compensating defects, …?)

Back contact/interface improvement?

- Cu diffuses from back resulting in more doping near the back
  → electron reflector
- Cu passivates the back contact/improves back interface recombination

Characterization Subset

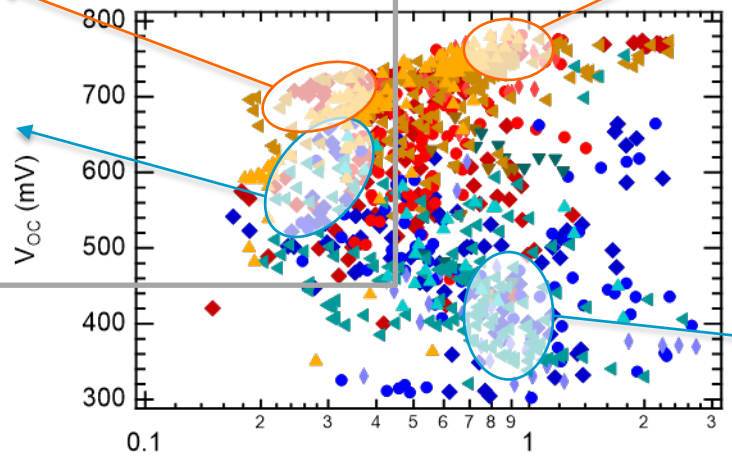
Focusing primarily on this

As+Cu – High-CC
(10-20% Cd_3As_2)

As-only – High-CC
(10-20% Cd_3As_2)

As+Cu – Low-CC
(1% Cd_3As_2)

As-only – Low-CC
(1% Cd_3As_2)



Data taken by Eric Colegrove at NREL

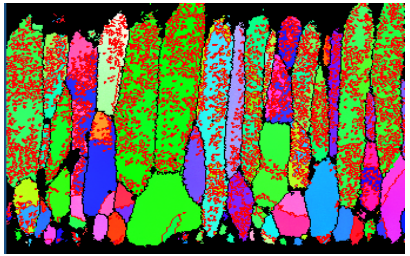
Structure : electron microscopy

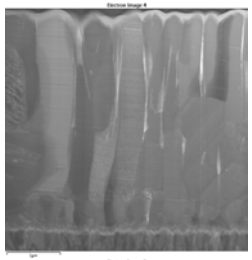
2 um

EBSD*

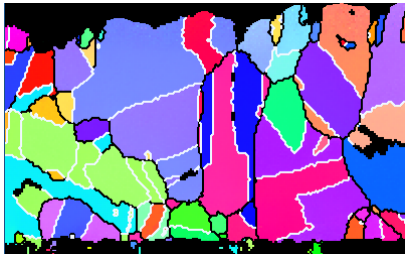
TEM**

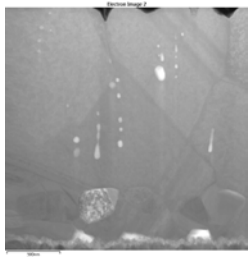
as deposited



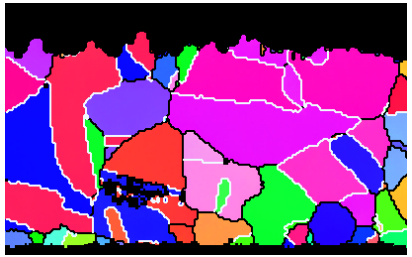


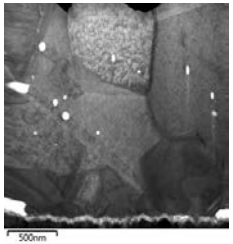
As-only





As+Cu





As deposited VTD material shows long columnar grains
(low-T and rapid quenching)

1-2 um grains after $CdCl_2$ treatment with some smaller grains near front interface

No obvious structural differences with vs without Cu (or low vs high doping)

*Data taken at *NREL-Helio Moutinho and **CREST-Ali Abbas*

Composition : SIMS

Composition largely identical with two exceptions:

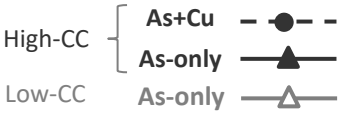
Copper

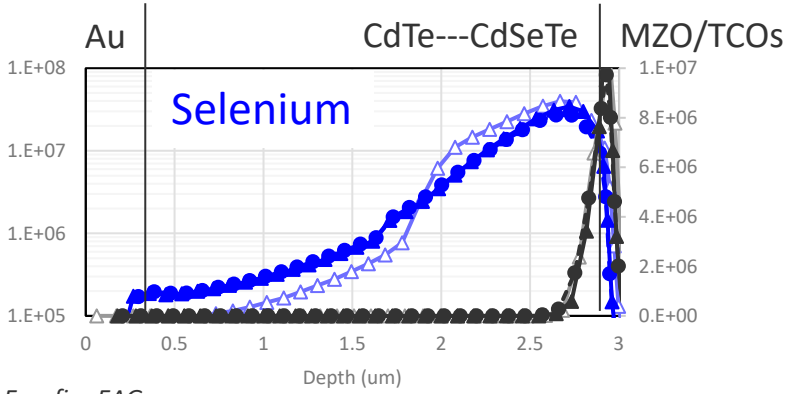
- As only — 1-2x10^{16} cm^{-3}
- As+Cu — 1x10^{18} cm^{-3} (1x10^{19} at the interface)

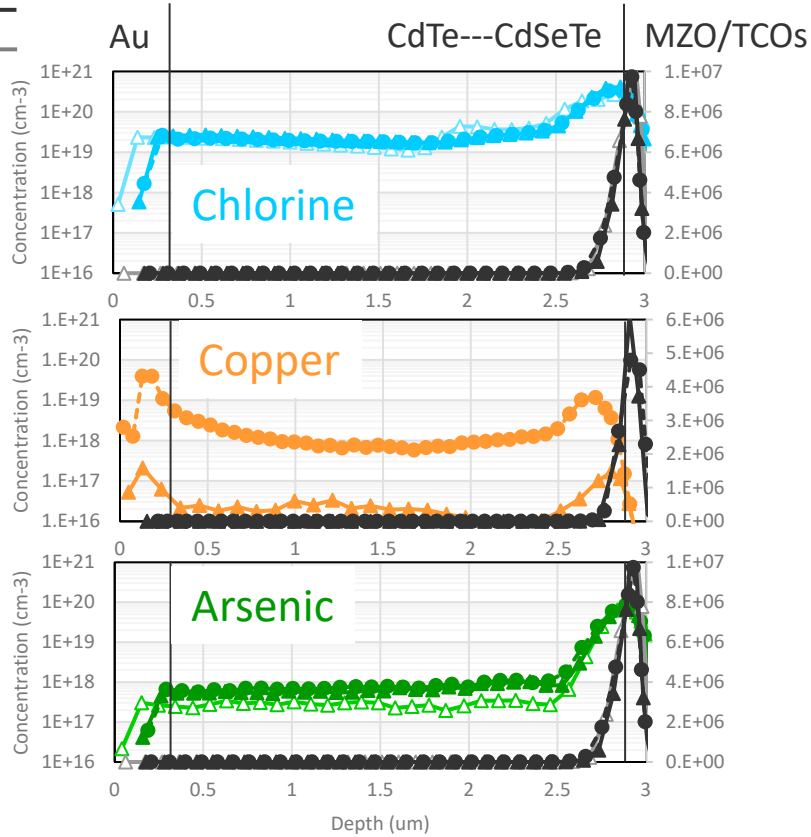
Arsenic

- Low CC — 2-3x10^{17} cm^{-3}
- High CC — 1x10^{18} cm^{-3}

Higher at the interface (recently confirmed using LN2 cleave)

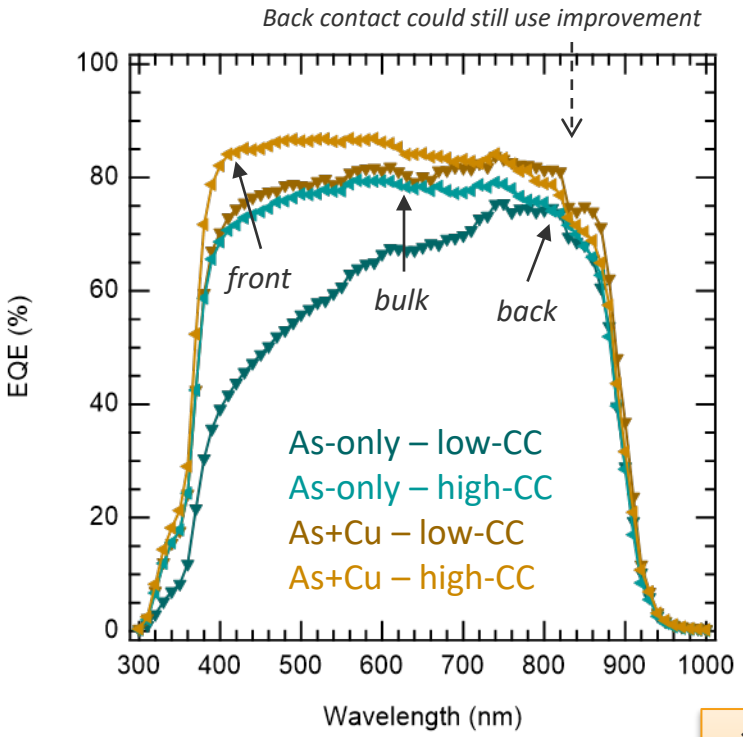






Data taken at Eurofins EAG

Electro-optical : EQE



Blue response improved with higher CC for As-only material

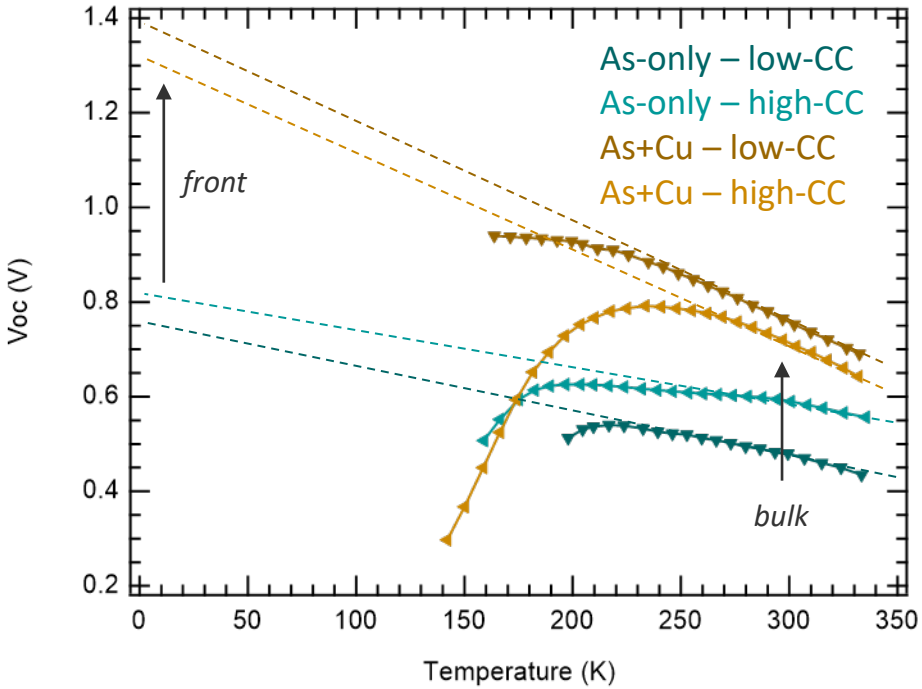
Best blue response for As+Cu - high CC (best interface?)

Improved green and red response with Cu suggests improved bulk and back contact

→ Front interface recombination reduced with Cu
→ Bulk recombination potentially improved
→ Back contact likely better with Cu

Data taken by Eric Colegrove at NREL

Electro-optical : VocT



Vastly improved 0K Voc indicates Cu significantly improves front interface

- Better for low CC

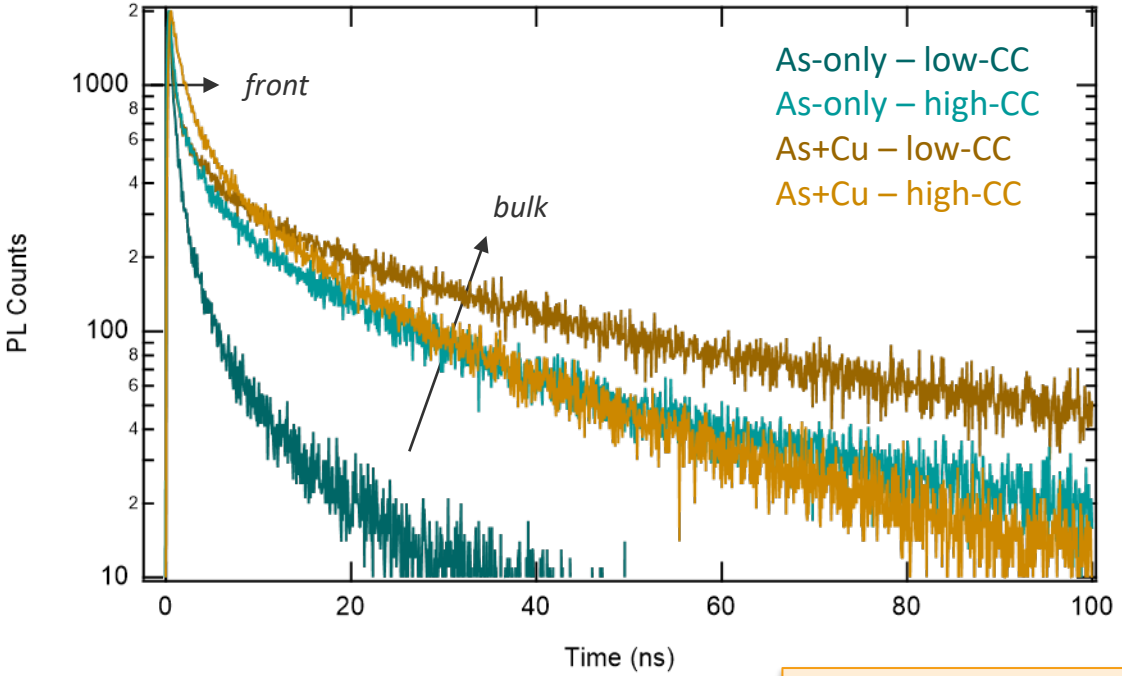
RT Voc indicates better bulk material properties with Cu

- Worst/Best when CC is low (Cu passivates bulk?)

→ Front interface recombination reduced with Cu
→ Bulk recombination potentially improved
→ Back contact likely better with Cu

Data taken by Steve Johnston at NREL

Electro-optical : TRPL



Worst lifetimes for As-only low-CC

Best tau1 for As+Cu high-CC
Best tau2 for As+Cu low-CC

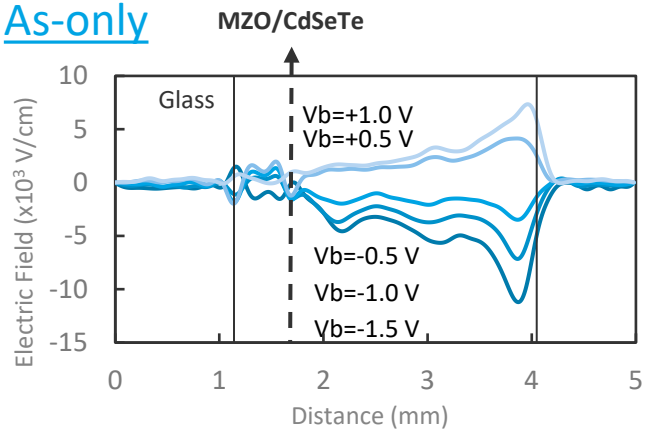
- High doping degrades bulk (compensated?)
- Cu helps with interface and bulk recombination

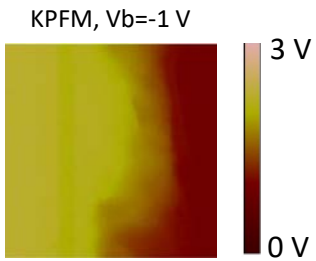
→ Front interface recombination reduced with Cu
→ Bulk recombination potentially improved
→ Back contact likely better with Cu

Data taken by Brian Good at NREL

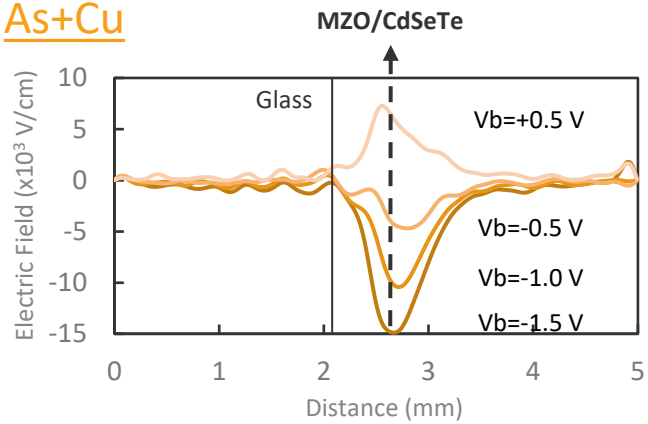
Electro-optical : KPFM

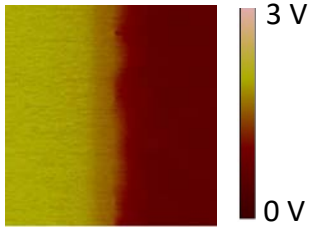
As-only





As+Cu





Non-uniform and buried junction consistent with EQE for As-only

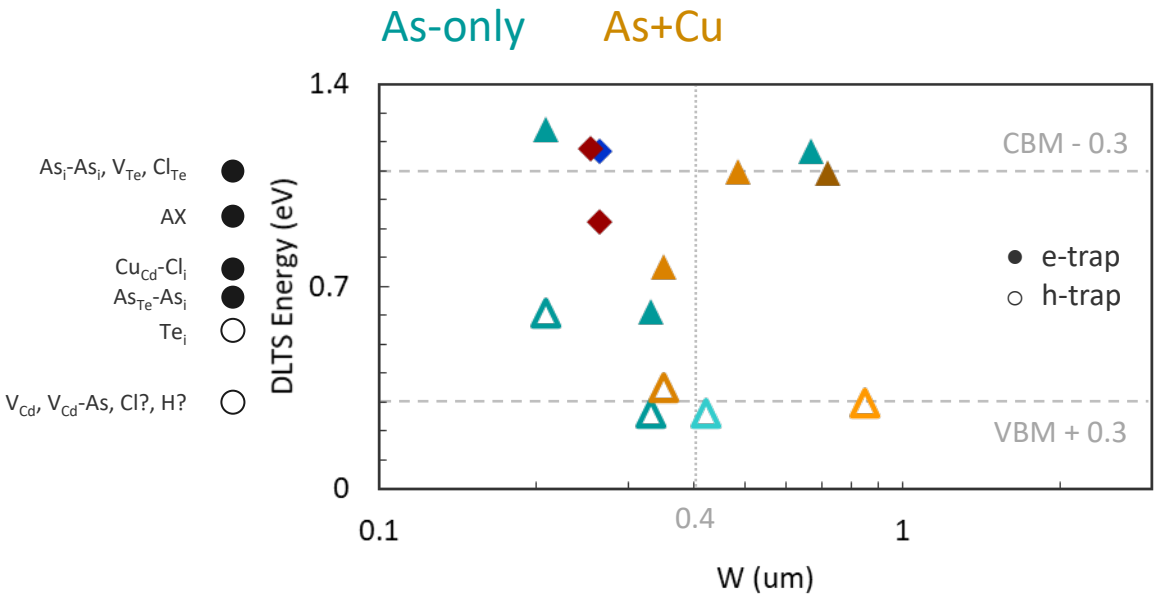
- Compensation leads to buried junction?

Expected field location/behavior for As+Cu

→ Front interface recombination reduced with Cu
→ Bulk recombination potentially improved
→ Back contact likely better with Cu

Data taken by CS Jiang at NREL

Electro-optical : DLTS



Defect chemistry is complex

Hole and electron traps at around 0.3eV relative to VBM and CBM respectively

- Independent of CC or Cu

Deeper defects present for higher CC

- No clear distinction with Cu

Large capacitance changes between from 300K to 200K trend also trend with higher CC (not shown)

D. Krasikov, et al., SEMSC **224**, 2021
G. Kartopu, SEMSC **194**, 2019
D. Krasikov, and I. Sankin, PRM **2,** 2018
T. Gessert, et al., SEMSC **119**, 2013
S-H. Wei et al., PRB **66**, 2002

Data taken by Steve Johnston at NREL

“Cu benefit”

Front interface/contact improvement? - Yes
- TRPL, EQE, JVT, XPS, and KPFM all point to improved interface quality with Cu

Bulk absorber improvement? - Probably
- TRPL, EQE, JVT, KPFM all show improved bulk type properties with Cu

Back contact/interface improvement? - Probably
- JV trends and EQE show indications of improved back contacts with Cu

→ Front interface recombination reduced with Cu
→ Bulk recombination potentially improved
→ Back contact likely better with Cu

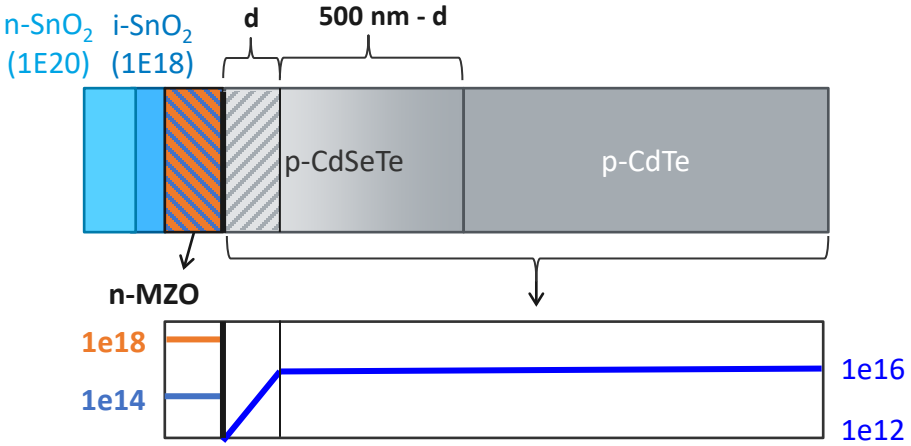
Modeling

- Do we need to dope the emitter?
  - Ablekim, et al. and Pandey, et al. modeling papers both suggest YES
- What if a thin layer in the absorber near the interface is compensated?
  - How thick/thin can compensated regions be?
  - Can poorly doped interface regions be “hidden” from CV?

<u>SCAPS model</u>

Graded doping in CdSeTe layer introduced near front interface – thickness “d” varied

Low (1e14) and high (1e18) MZO doping considered



Modelling preformed by Brian Good at NREL

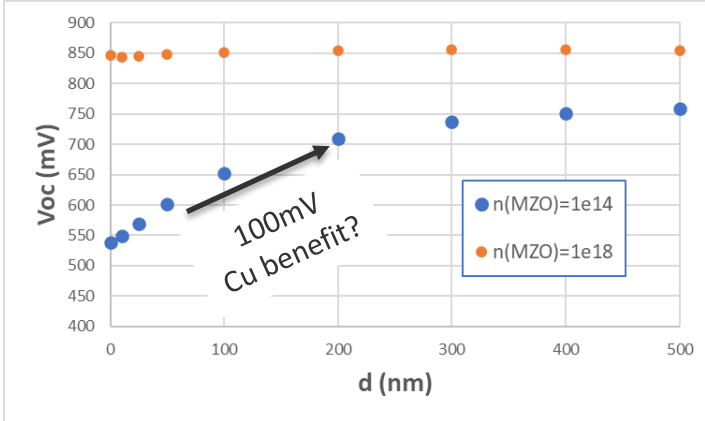
Modeling

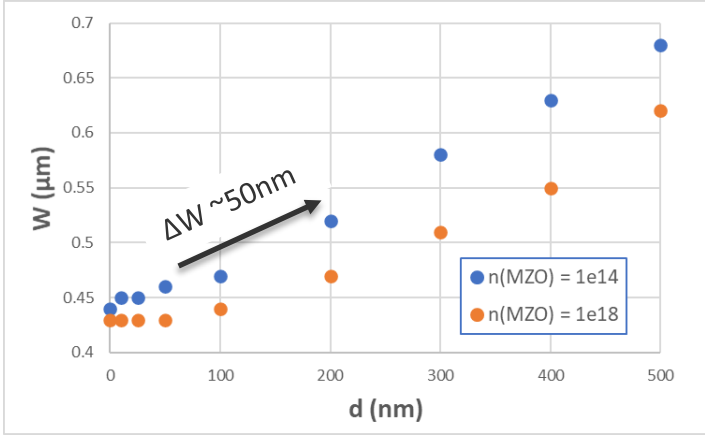
Near interface compensation (As, Cu, or ?) could be **improving performance** when MZO doping is low

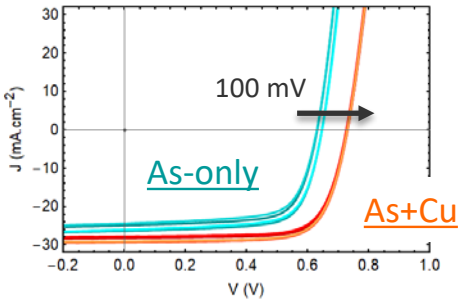
- Highly doped MZO (~1e18) enables higher Voc

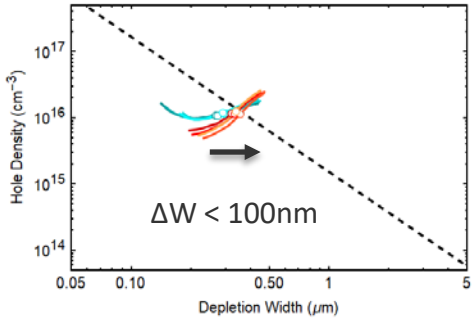
Depletion width increases slightly with thickness of graded CdSeTe

- It may be difficult to detect thin (<200nm) compensated layers near interface with CV









Modelling preformed by Brian Good at NREL

Moving Forward

- Detailed DFT work examining Cd-Se-Te-As-Cl-Cu-(others?) likely needed to determine specific defect mechanisms associated with “Cu benefit”

- **Higher emitter doping** still seems like a straightforward route to **improved Voc** (and efficiency) when absorber doping is high
  - Thin (10-20nm) intrinsic/buffer layers may enable best of both worlds
  - All window layers need to maintain performance through processing and operational life

Thank You!

Questions?

NREL
Matt Reese, David Albin, Joel Duenow,
Brian Good, Helio Moutinho, Steve Johnston,
CS Jiang, Darius Kuciauskas,
(Patrick O'Keefe, Xin Zheng, John Moseley)

CREST
Mike Walls, Ali Abbas, Tom Fiducia

www.nrel.gov

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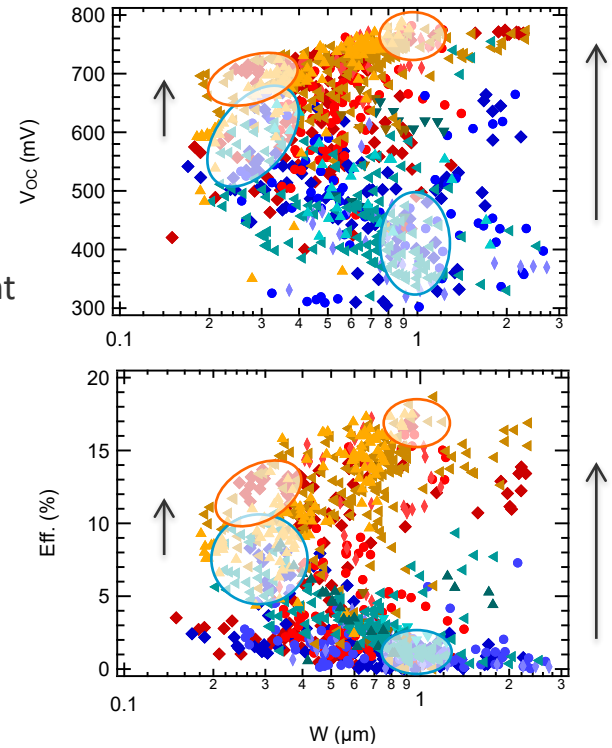
NREL
Transforming ENERGY

JV and CV trends : “Cu benefit”

As-only vs As+Cu

“Small” performance improvement
- Improved recombination?
- Improved contacts?

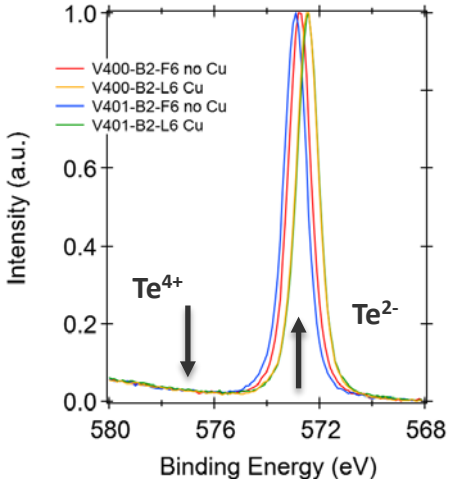


“Huge” improvement in performance for low CC devices
- Significant material quality improvement
- Reduced recombination throughout device (interfaces and bulk)

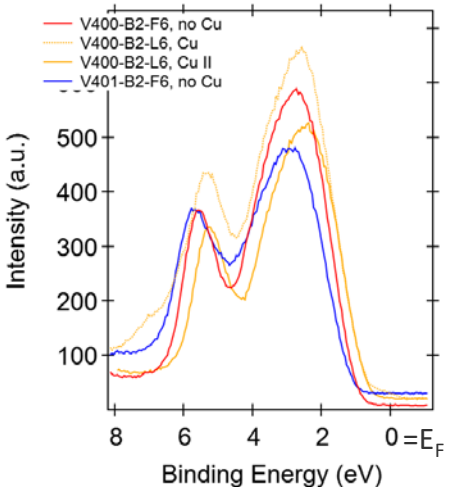
Data taken by Eric Colegrove at NREL

XPS

Te $3d_{5/2}$



CdSeTe side VB spectra



	CdSeTe VBM (eV)	ZMO VBM (eV)
As-only – low-CC	0.92	2.71
As+Cu – low-CC	0.66	2.70
As only – high-CC	1.11	2.86
As+Cu – high-CC	0.71	2.86

No oxidized Te observed (Te^{4+})

- Interface improvement with Cu not associated with oxidation

Valance bands closer to E_F with Cu

- Cu-containing films have less band bending at free surfaces
- Unique band alignment expected in each case

Emitter more n-type for high CC devices (As may be a donor in ZnO?)

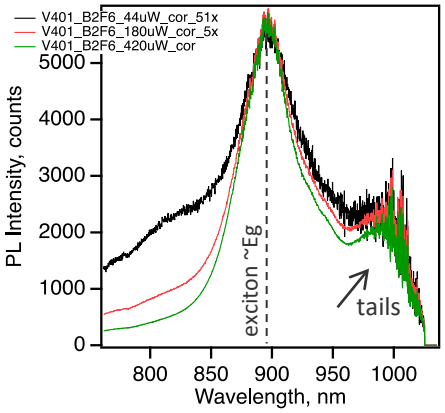
Data taken by Craig Perkins at NREL

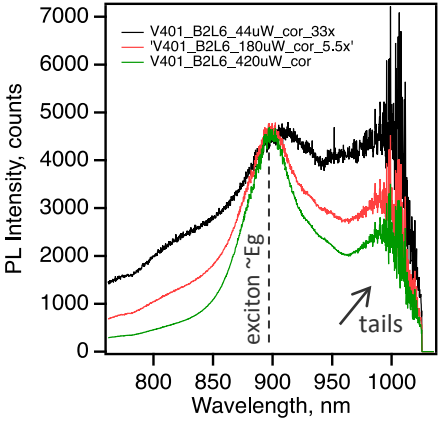
Photoluminescence

As-only – High-CC

As+Cu – High-CC

HeNe excitation= 632.8nm ; detector QE corrected





"Tails" best for As-only – high-CC

→ Best ERE

Data taken by Darius Kuciauskas at NREL

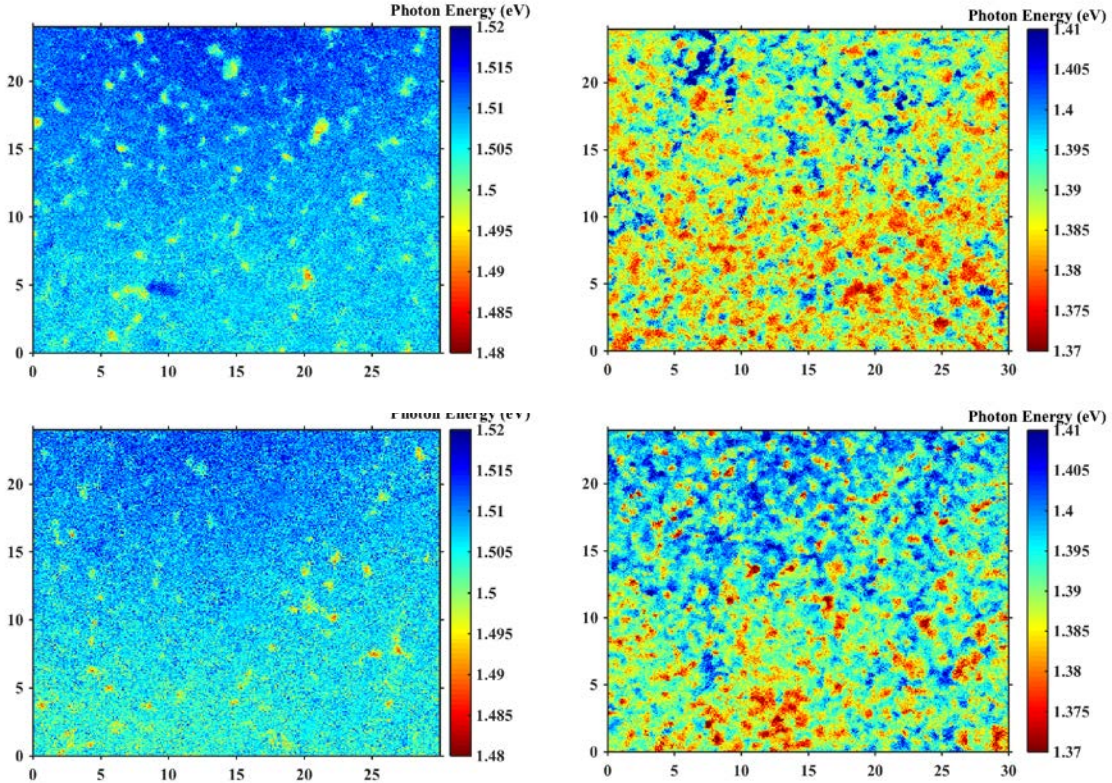
Cathodoluminescence

Back Surface

Interface

As-only

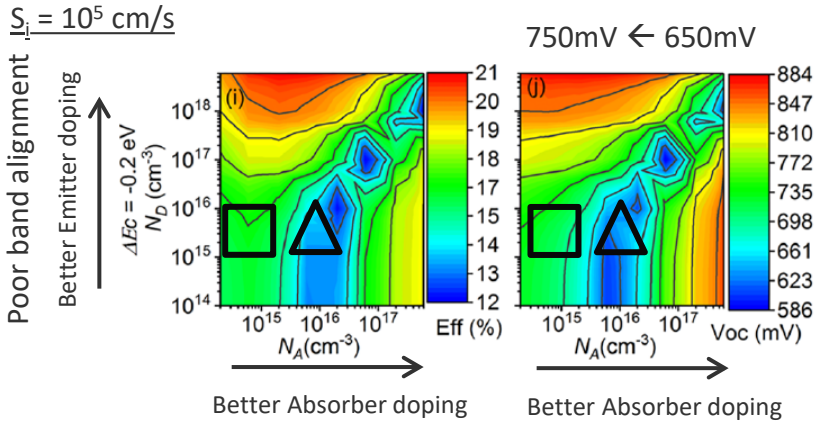
As+Cu

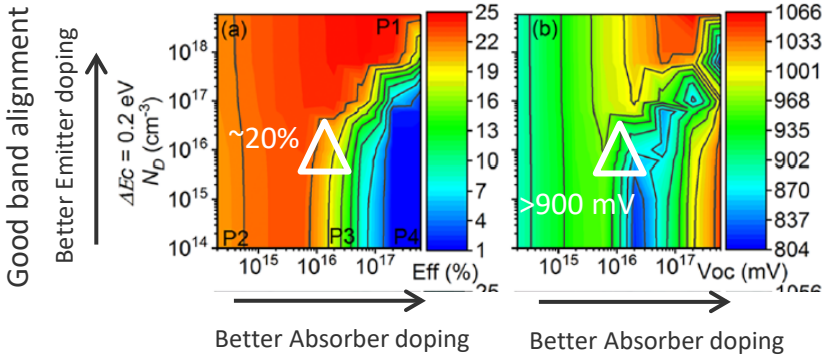


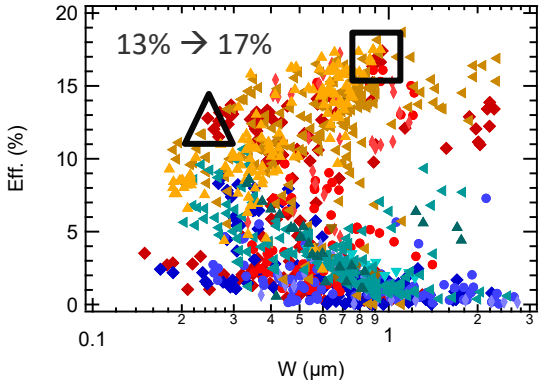
No clear differences with vs without Cu

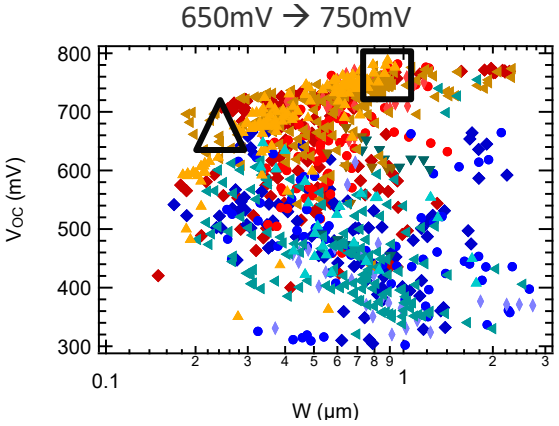
Data taken by John Moseley at NREL

What is holding Voc back? (Eff. ?)



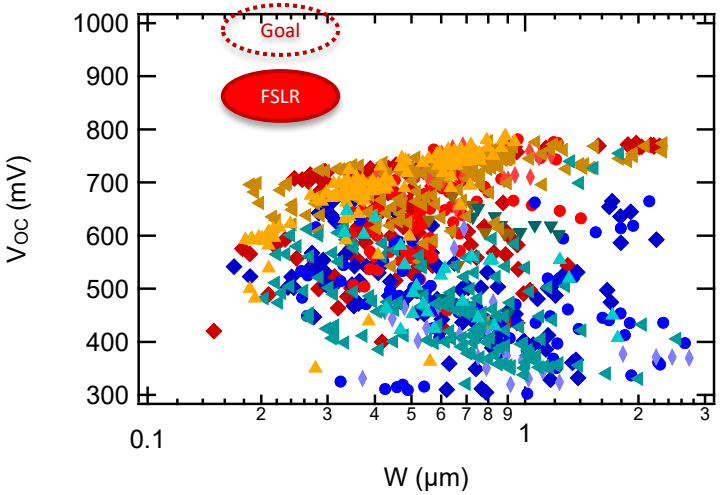


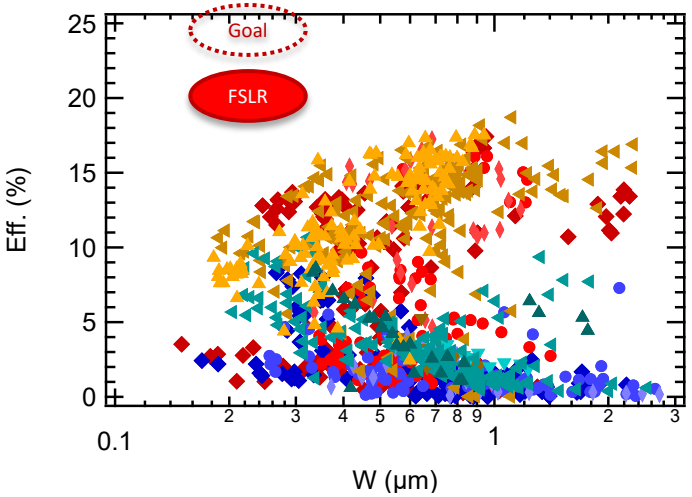




Ablekim, et al.

Goals


Goal
FSLR
1000
900
800
700
600
500
400
300
V_{OC} (mV)
0.1
1
W (μm)


Goal
FSLR
25
20
15
10
5
0
Eff. (%)
0.1
1
W (μm)