Investigating the role of Copper in Arsenic doped CdSeTe Photovoltaic Devices

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We still need to improve Voc

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

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

Why?

As-only  As+Cu

Data taken by Eric Colegrove at NREL
**Introduction: Fabrication**

**As deposited**
- VTD
  - CdTe:As (~3um)
  - CdCl₂
- Evaporation
  - CdTe (250nm)
  - CdSe (150nm)
  - MZO (60nm)
  - TO (~100nm)
  - FTO (~400nm)
- Sputtering
  - Glass (3mm)

**As-only**
- HCl or DI
- OR
- Anneal
  - CdTe:As (~2um)

**As+Cu**
- CuCl₂
- Evaporation
  - CdSeTe:As (~1um)
- Anneal
  - CdTe:As (~3um)

**Variety of VTD conditions and source materials**
- WSU – High Pressure Bridgman (HPB)
- Mixed powder (Cd₃As₂:CdTe)

*Data taken by Eric Colegrove at NREL*
JV and CV trends

As-only

550-650mV (high CC)

350-500mV (low CC)

5-10% (high CC)

0-2% (low CC)

Highly compensated?
High recombination reduced with high doping/activation

As+Cu

750-800mV (low CC)

650-750mV (high CC)

15-18% (low CC)

10-14% (high CC)

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

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
As+Cu – High-CC (10-20% Cd₃As₂)

As-only – High-CC (10-20% Cd₃As₂)

As+Cu – Low-CC (1% Cd₃As₂)

As-only – Low-CC (1% Cd₃As₂)
As deposited VTD material shows long columnar grains (low-T and rapid quenching).

1-2 um grains after CdCl₂ 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: $1-2 \times 10^{16} \text{ cm}^{-3}$
- As+Cu: $1 \times 10^{18} \text{ cm}^{-3}$ (1x10^{19} at the interface)

**Arsenic**
- Low CC: $2-3 \times 10^{17} \text{ cm}^{-3}$
- High CC: $1 \times 10^{18} \text{ cm}^{-3}$

Higher at the interface (recently confirmed using LN2 cleave)

Data taken at Eurofins EAG
Electro-optical : EQE

Back contact could still use improvement

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
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
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
- No clear distinction with Cu

Deeper defects present for higher CC
- Large capacitance changes between from 300K to 200K trend also trend with higher CC (not shown)

Data taken by Steve Johnston at NREL

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
“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?

SCAPS model
Graded doping in CdSeTe layer introduced near front interface – thickness “d” varied
Low (1e14) and high (1e18) MZO doping considered

Modelling performed by Brian Good at NREL
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
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
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
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?)

<table>
<thead>
<tr>
<th></th>
<th>CdSeTe VBM (eV)</th>
<th>ZMO VBM (eV)</th>
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</thead>
<tbody>
<tr>
<td>As-only – low-CC</td>
<td>0.92</td>
<td>2.71</td>
</tr>
<tr>
<td>As+Cu – low-CC</td>
<td>0.66</td>
<td>2.70</td>
</tr>
<tr>
<td>As only – high-CC</td>
<td>1.11</td>
<td>2.86</td>
</tr>
<tr>
<td>As+Cu – high-CC</td>
<td>0.71</td>
<td>2.86</td>
</tr>
</tbody>
</table>

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

As-only

Back Surface

As+Cu

Interface

No clear differences with vs without Cu

Data taken by John Moseley at NREL
What is holding Voc back? (Eff. ?)

$S_i = 10^5 \text{ cm/s}$

**Poor band alignment**

- Better Emitter doping
  
**Better Absorber doping**

$750 \text{ mV} \leftrightarrow 650 \text{ mV}$

- Better Emitter doping
  - Poor band alignment

**Good band alignment**

$>900 \text{ mV}$

- Better Absorber doping
  - Better Emitter doping

$650 \text{ mV} \rightarrow 750 \text{ mV}$

- Better Absorber doping
  - Better Emitter doping

Ablekim, et al.
Goals

![Graph showing Goals](image-url)