CIGS Material and Device Stability: A Processing Perspective

Kannan Ramanathan, NCPV

PV Module Reliability Workshop, March 1, 2012
Golden, Colorado

NREL/PR-5200-54569
CIGS landscape

- Multiple companies trying to get to high volume, low-cost manufacturing. Challenged to increase efficiency, control variability and ensure reliability. Efficiency bar is rising.
- Diverse approaches, cell designs. Different stages of maturity. Process details largely proprietary.
- Process control and understanding of ‘cause and effect’ still needed, desired.
- Precursor selenization/sulfurization and co-evaporation based processes have an edge.
Connecting the pieces

- Solar cell fabrication method, tool, process details
- Process to property correlation
- Cause and effect analysis of variability
- Performance improvement
- Device level changes and mitigation
- Packaging/ Protection of circuits
- Above pieces are connected, must work together to address stability issues.
Stability Topics

• Light soaking
• Post lamination loss
• Changes due to moisture ingress
• Reverse bias leakage
• Shunts
• Hot spots
• Weak diodes
Outline

• CIGS Material Properties: Basics
• CIGS Devices: Basic features
• Cell level changes
• Examples of previous work
• What do we need to measure? Interpret? Improve?
CIGS(S) Absorber

- Quaternary and pentenary alloys derived from base compound CuInSe$_2$. Band gap is increased by alloying with Ga and/or S.
- Band gap may not be uniform across the depth of the film, often graded.
- Phase purity and stoichiometry are important to control.
- Single crystal/epi knowledge base is weak.
- Adequate working knowledge of physical and electronic properties, bear great resemblance to II-VI ‘parents’.
Absorber: desired properties, process

- **Durable metal contact to the p-side (Mo)**
  - Minimally reactive, ohmic contact stabilized by \( \text{MoSe}_2 \).
  - Needs proper process conditions to be the best

- **P-type absorber**
  - Doping by native defects (close compensation)
  - Some elements enhance p-type doping (Na, Sb)
  - Higher temperature growth preferred
  - Chalcogen rich growth preferred
  - Crystal quality = efficiency (stability?)
Absorber: Electrical

- CuInSe$_2$ can be n- or p-type
- Thin films are p-type when grown Cu-poor in Se-rich conditions.
- With Ga and Na included, p-type is likely stabilized.
- If grown in Se-poor conditions, material can be high resistivity p-type or even n-type (more compensation, low lifetime).
- Electrical properties are a sensitive function of the growth method, tool, recipe.
- No direct measure of absorber’s electrical properties!
Junction

- Chemically grown CdS layers form the n-type emitter. Preferred junction partner.
- CBD bath induces change in electronic properties in addition to the growth of a compatible “buffer layer”
- Alternative emitter layers (ZnOS, In$_2$S$_3$) promising, come with unique characteristics.
- ZnO conductivity can degrade upon carrier compensation.
Device stability/ Metastability

• **1992:** Siemens Solar asked for help in understanding “transient effects”
  - Device properties changed dramatically when exposed to light, voltage bias etc.

• **2012:** Similar products in vogue, exhibit similar characteristics.

• Device characteristics are a function of how they are made. NREL ≠ Miasole ≠ Stion. Specifics of each device to be taken into account when solving cell/module optimization.
Prior NREL work: D. Albin

All devices show attainment of a “stabilized” level
Cell in DH; no encapsulation

PL of cells after damp heat exposure

DH effects:
• Decrease in absorber doping (increase in defect level density)
• Increase in junction recombination
Light soaking: early Siemens cells

Fig. 6. Efficiency gains during light soaking by eight relatively poor CIS cells.

Fig. 7. Efficiency as a function of light soaking of 16 cells of high efficiency CuInSe₂ based materials.

D. Willett, IEEE PVSC, 1993
Process understanding/ quality improvement:
Case studies from past NREL work
Comparison of NREL and SSI absorbers

S2212

1 µm 25000X

ZnO

CIGSS

Atomic Concentrations (%) vs Sputter Time (min)

Counts vs Depth (microns)
Example 1: SSI Absorber deviation

Common absorber
Lower performance with NREL CdS/ZnO
(not typical)

K. Ramanathan, CIS National Team, 2002
J-V curve: NREL absorber
CdS and ZnO processed in same runs as SSI

NREL absorber/ windows OK!
PL Spectra

Left most 2 curves: NREL CdS, no air anneal. Green: 5°/200°C/air anneal after CdS.

Right most 3 curves: PL from 3 cells with SSI windows. NREL CdS/ZnO.
Quantum efficiency

External QE Comparison

- Long wave edge influenced by:
  - Poor Diffusion Length
  - Drift assisted collection
  - ZnO reflectance
  - Band gap grading

Extracting band gap not straightforward in SSI cells.

There appears to be a shift! Same direction as PL peak shift.
Compositional analysis

Revealed a large drop in the Cu ratio for the batch of absorbers.
Example 2: Junction anneal to improve performance

K. Ramanathan, NREL, 2002, unpublished
Thermal Degradation Characteristics

ST40 Module - Daystar Outdoor Tests

Voltage (V)

Current (A)

Efficiency:
- Initial = 11.2%
- 200h = 9.9%
- 1000h = 8.6%

No Loss

20% Loss

5% Loss
Modified Processing for Thermal Stability
Dry Heat Test Only

10W Laminates - LAPSS Test
Each data point represents the average of 21 laminates

What was changed?
• Increased CdS thickness
• Low CIG ratio
Summary

• Proper encapsulation of CIGS devices can alleviate much of the moisture driven performance degradation.

• It is possible the high efficiency devices exhibit fewer metastable effects. Efficiency improvement efforts may pay off in stability.

• A case by case approach is needed to optimize devices for performance and long term stability.
Note added March 5, 2012

• Important questions were raised in the afternoon discussion session that call for clarifications and further work on how CIGS devices are affected by moisture.
• Siemens/ Shell Gen II arrays have demonstrated stable operation at the OTF.
• It is not possible to draw definitive conclusions about the moisture sensitivity of CIGS based on the available reports on unencapsulated cells.