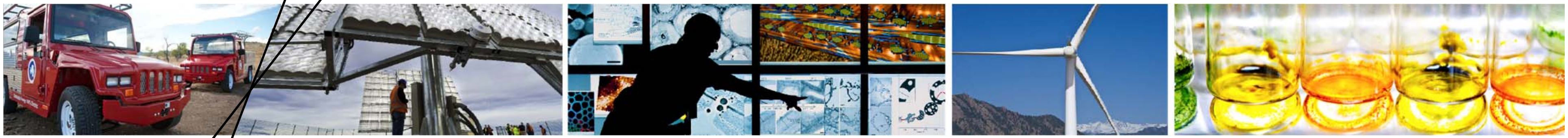
CIGS Material and Device Stability: A Processing Perspective



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 $MoSe_2$.
  - 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!

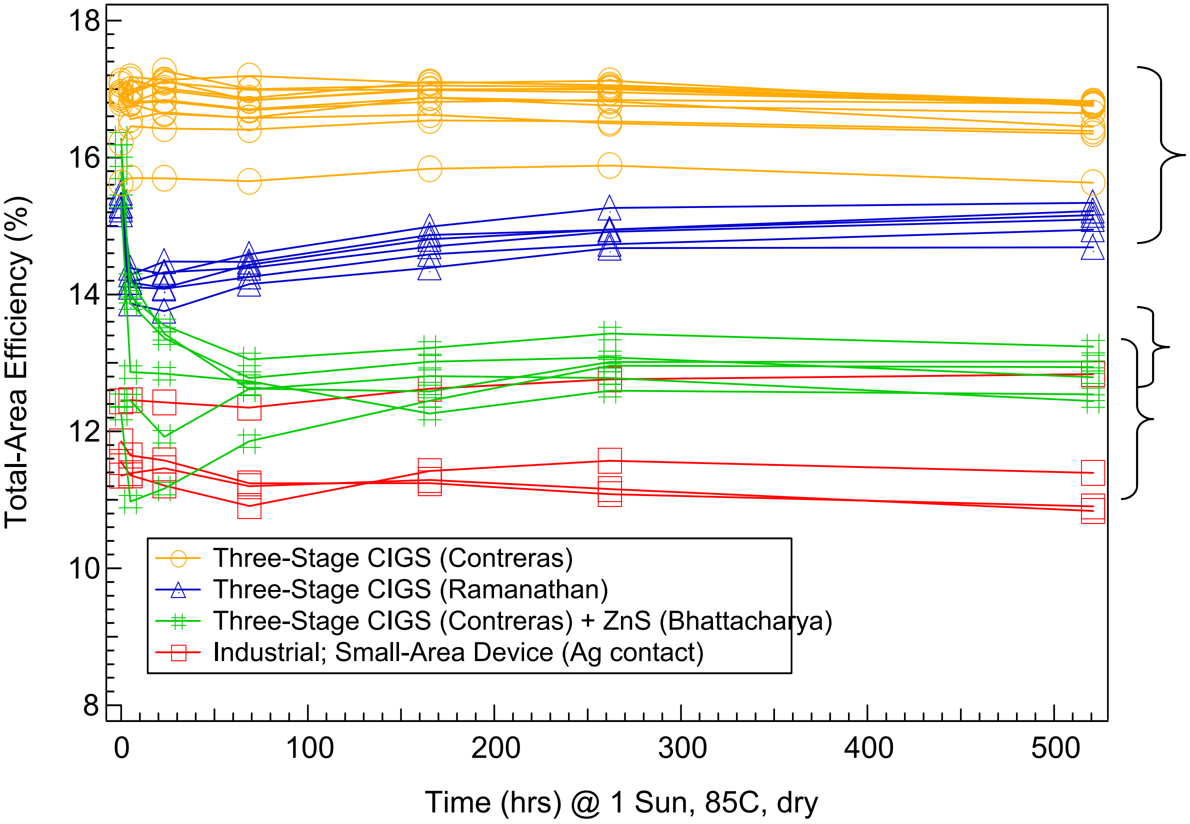
Junction

- 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_2S_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



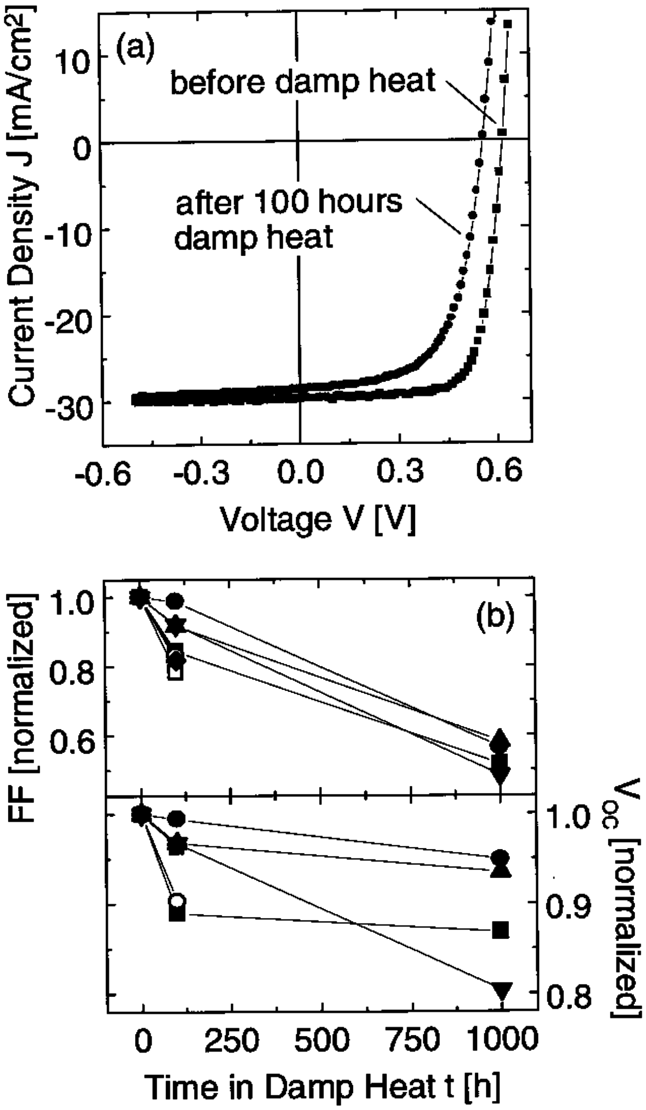
identical 3-stage process; yet very different transient recovery behavior; distinguishing difference = Mo

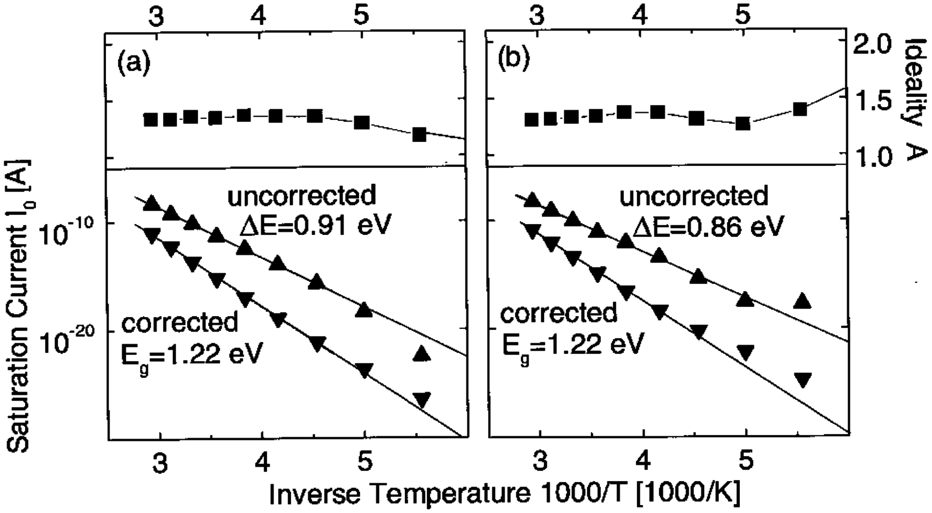
Modified “ZnS” junction; different characteristics on the same substrate

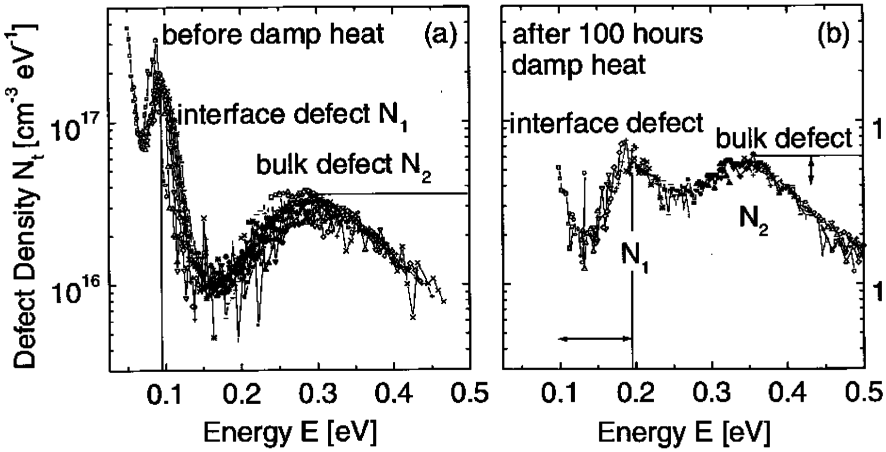
“industrial” samples showed biggest spread in light-soak behavior

All devices show attainment of a “stabilized” level

Cell in DH; no encapsulation







M. Schmidt et al. / Thin Solid Films 361±362 (2000) 283±287

PL of cells after damp heat exposure

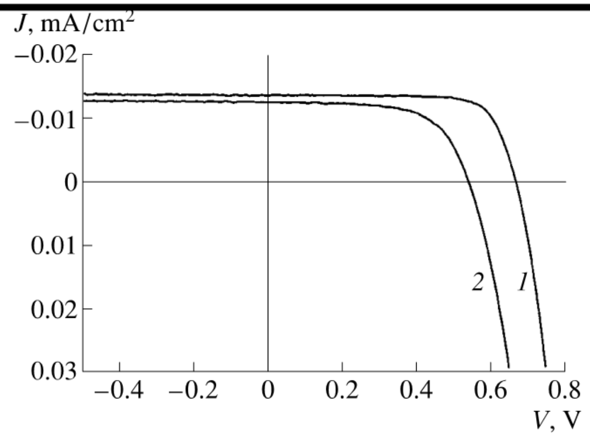


Fig. 1. Load characteristic of solar cells (*1*) prior to and (*2*) after treatment in a humid atmosphere at an elevated temperature. The measurement temperature $T = 25°C$.

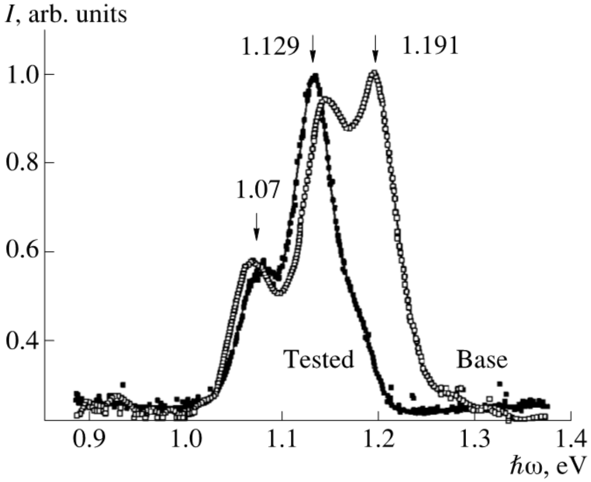


Fig. 2. PL spectra of CIGS solar cells prior to and after heating in humid atmosphere. The measurement temperature $T = 20$ K, the excitation wavelength $\lambda = 532$ nm, and the excitation power is 50 mW. Characteristic energies are given in eV.

DH effects:

- Decrease in absorber doping

(increase in defect level density)

- Increase in junction recombination

Light soaking: early Siemens cells

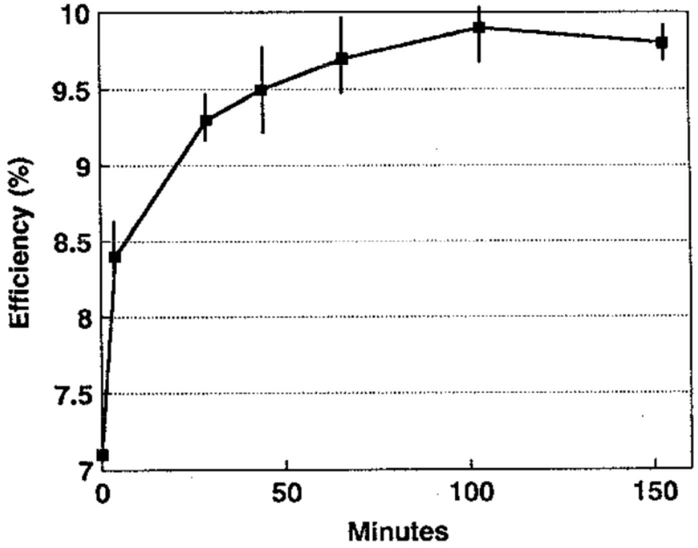


Fig. 6. Efficiency gains during light soaking by eight relatively poor CIS cells.

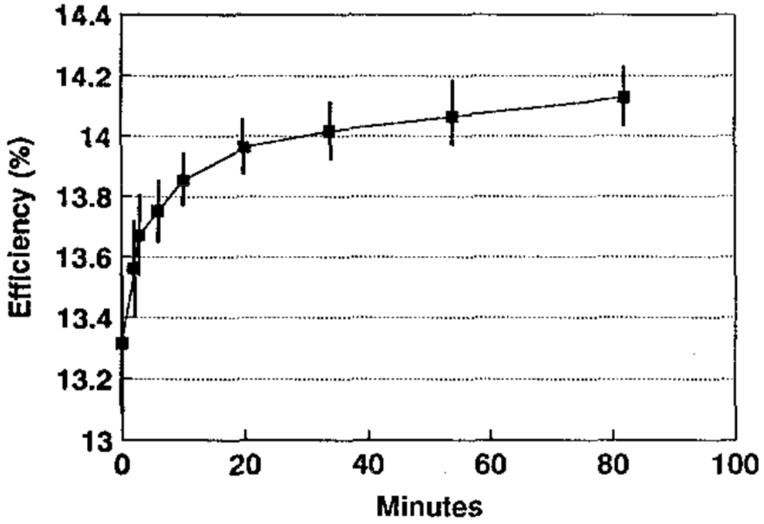
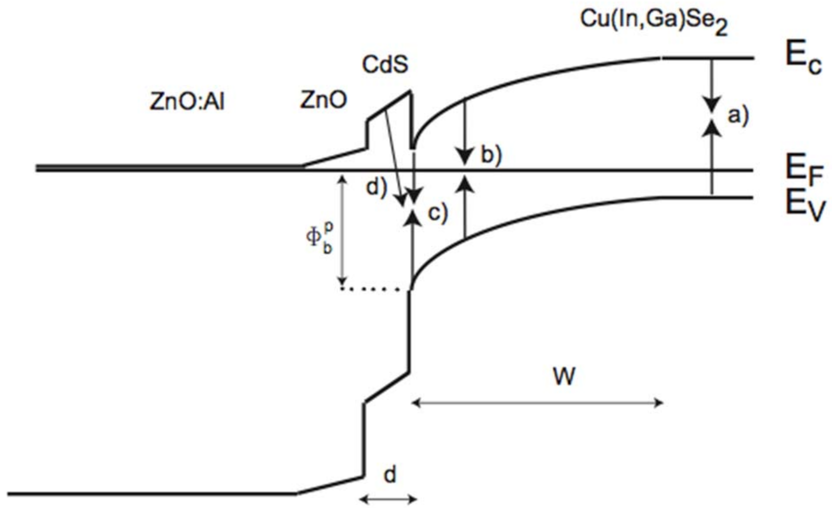
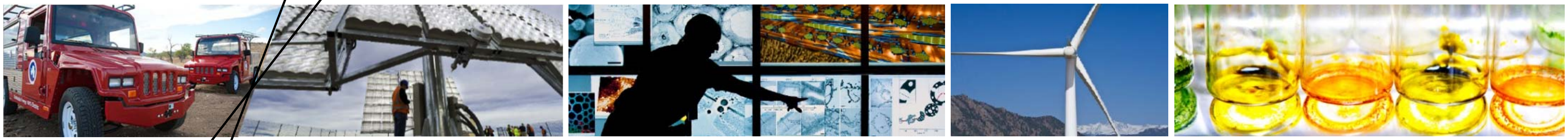


Fig. 7. Efficiency as a function of light soaking of 16 cells of high efficiency $CuInSe_2$ based materials.

D. Willett, IEEE PVSC, 1993

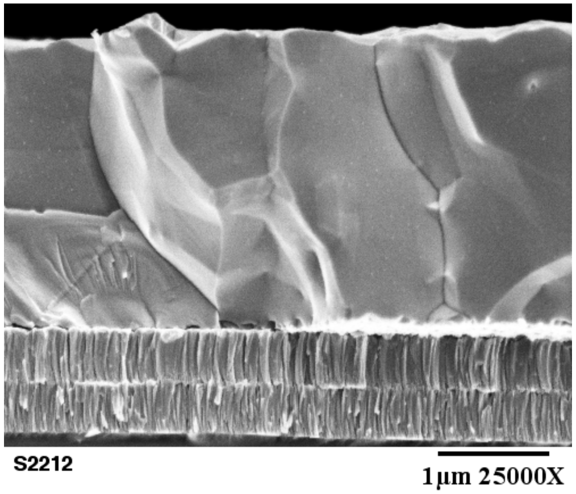


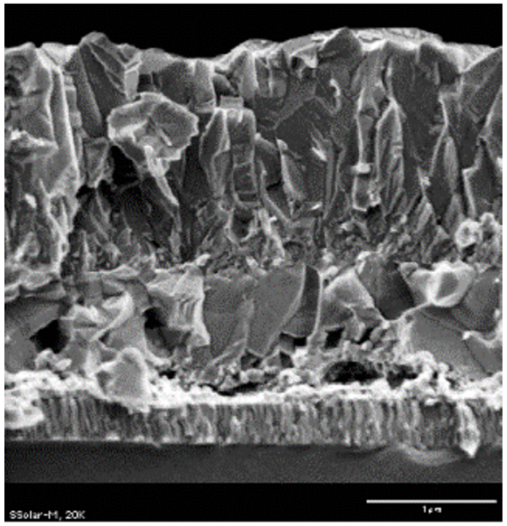


Process understanding/ quality improvement:

Case studies from past NREL work

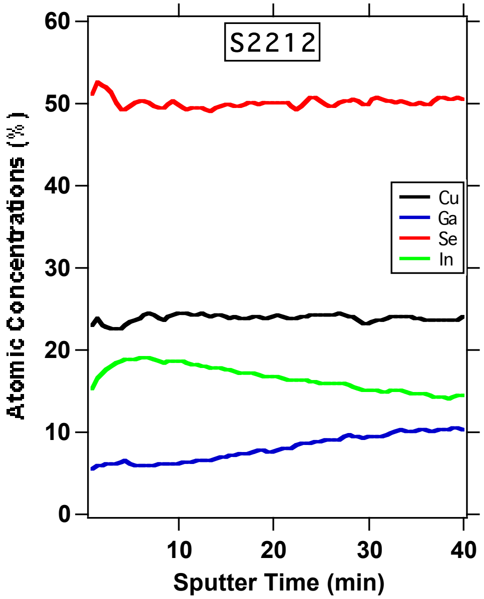
Comparison of NREL and SSI absorbers

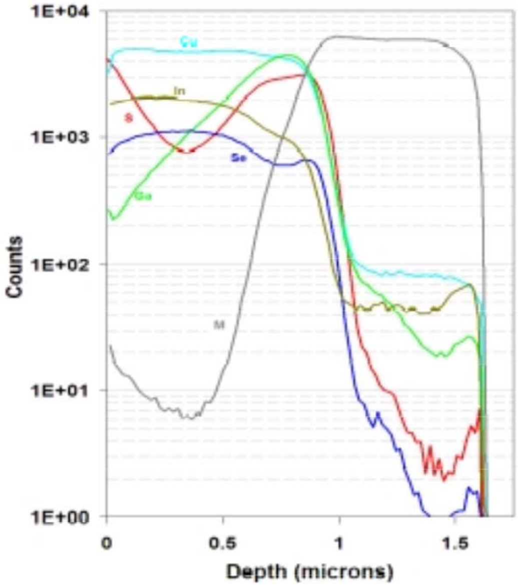




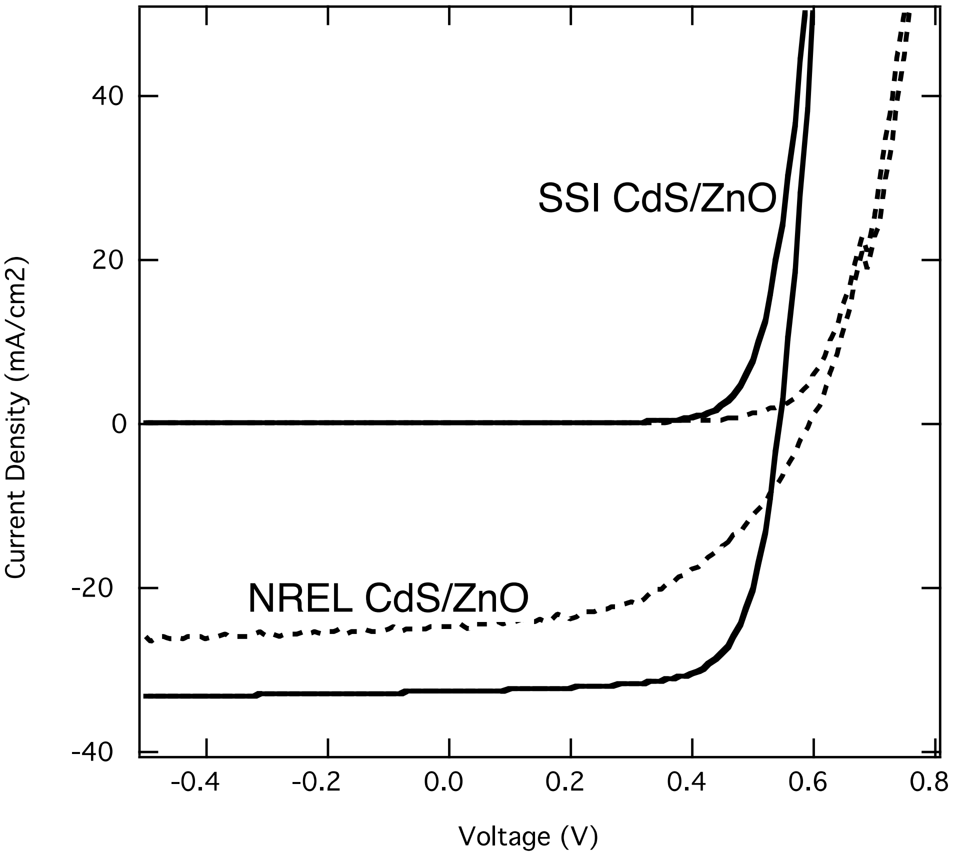
ZnO

CIGSS



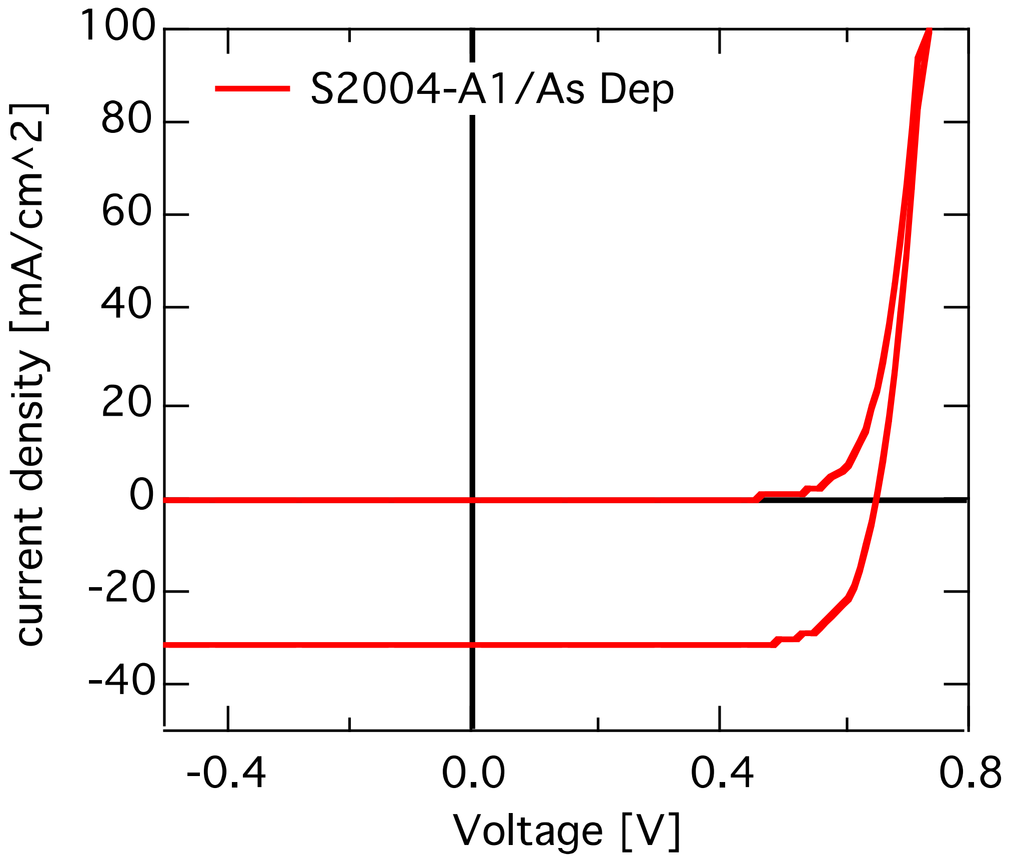


Example 1: SSI Absorber deviation



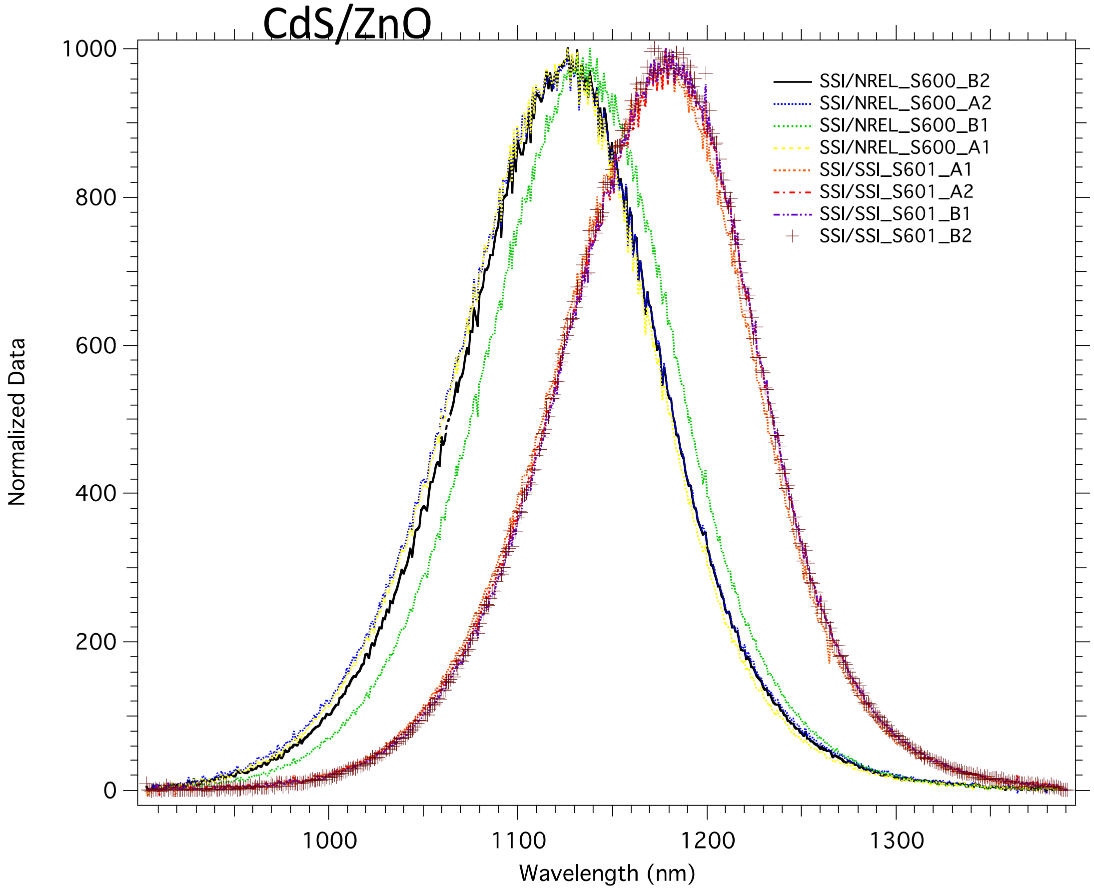
Common absorber
Lower performance with NREL CdS/ZnO
(not typical)

K. Ramanathan, CIS National Team, 2002



NREL absorber/ windows OK!

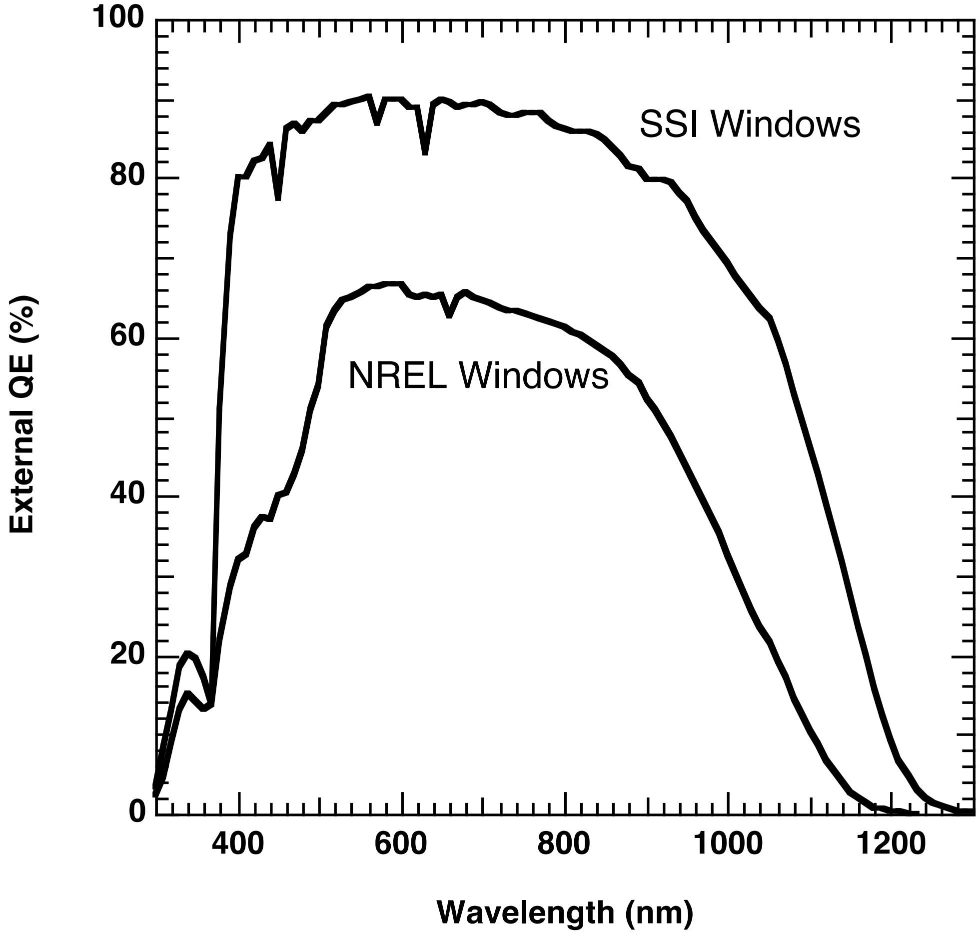
PL Spectra



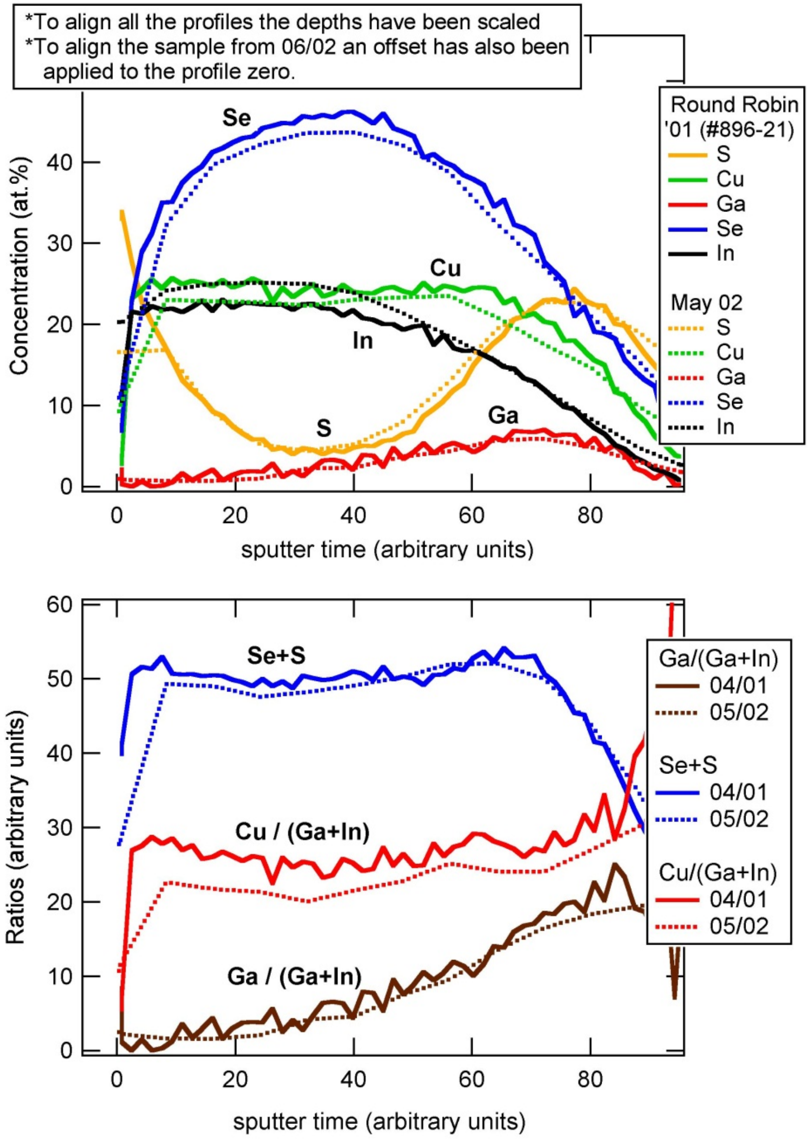
NREL CdS/ZnO

SSI CdS/ZnO

Quantum efficiency

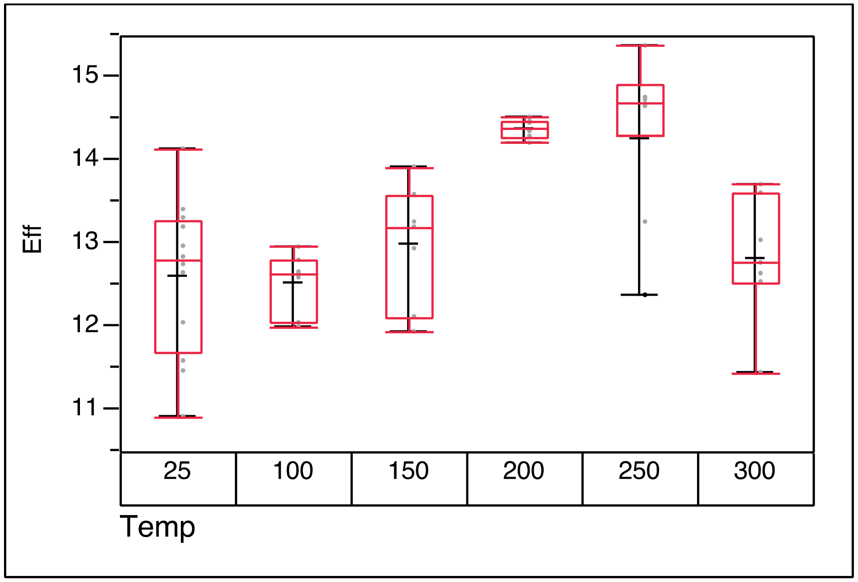


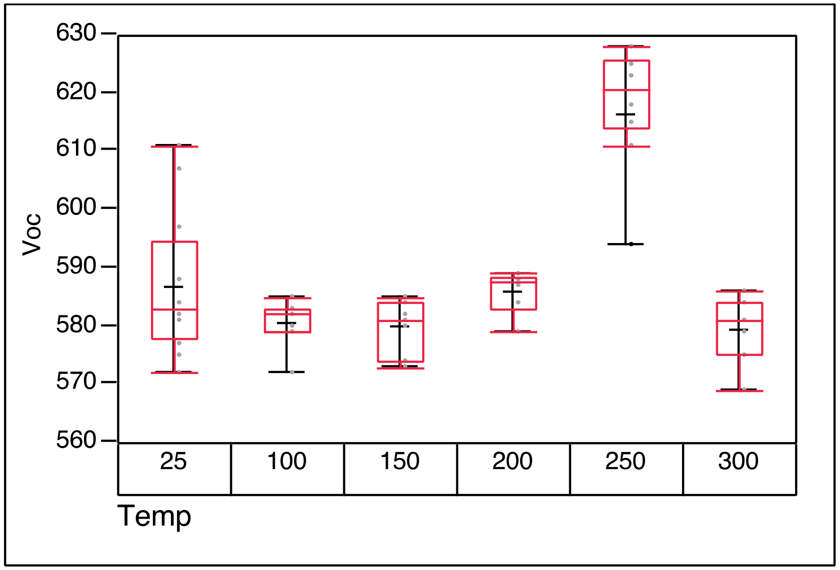
Compositional analysis

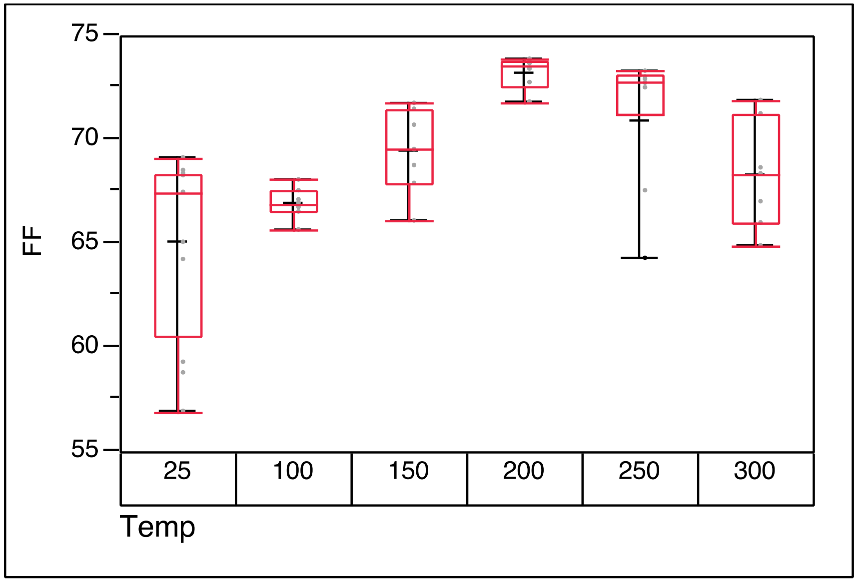

*To align all the profiles the depths have been scaled
*To align the sample from 06/02 an offset has also been applied to the profile zero.

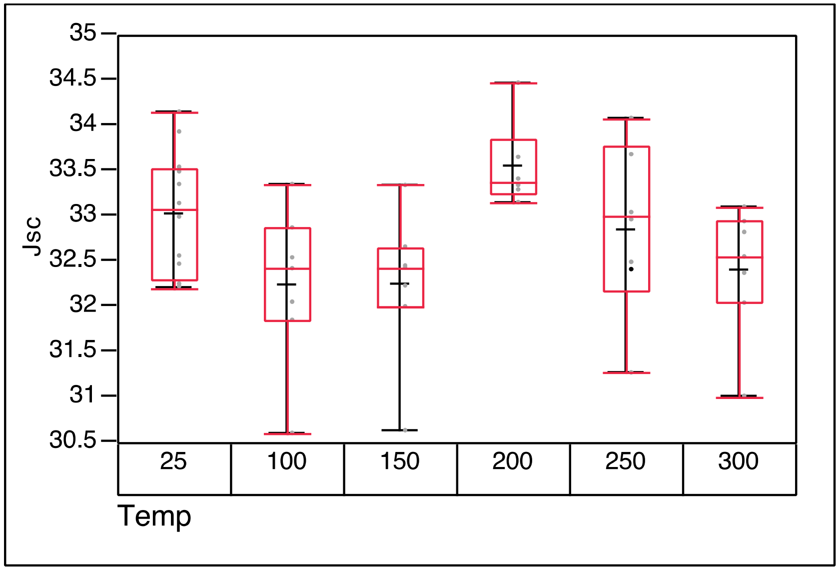
Revealed a large drop in the Cu ratio for the batch of absorbers.

Example 2: Junction anneal to improve performance



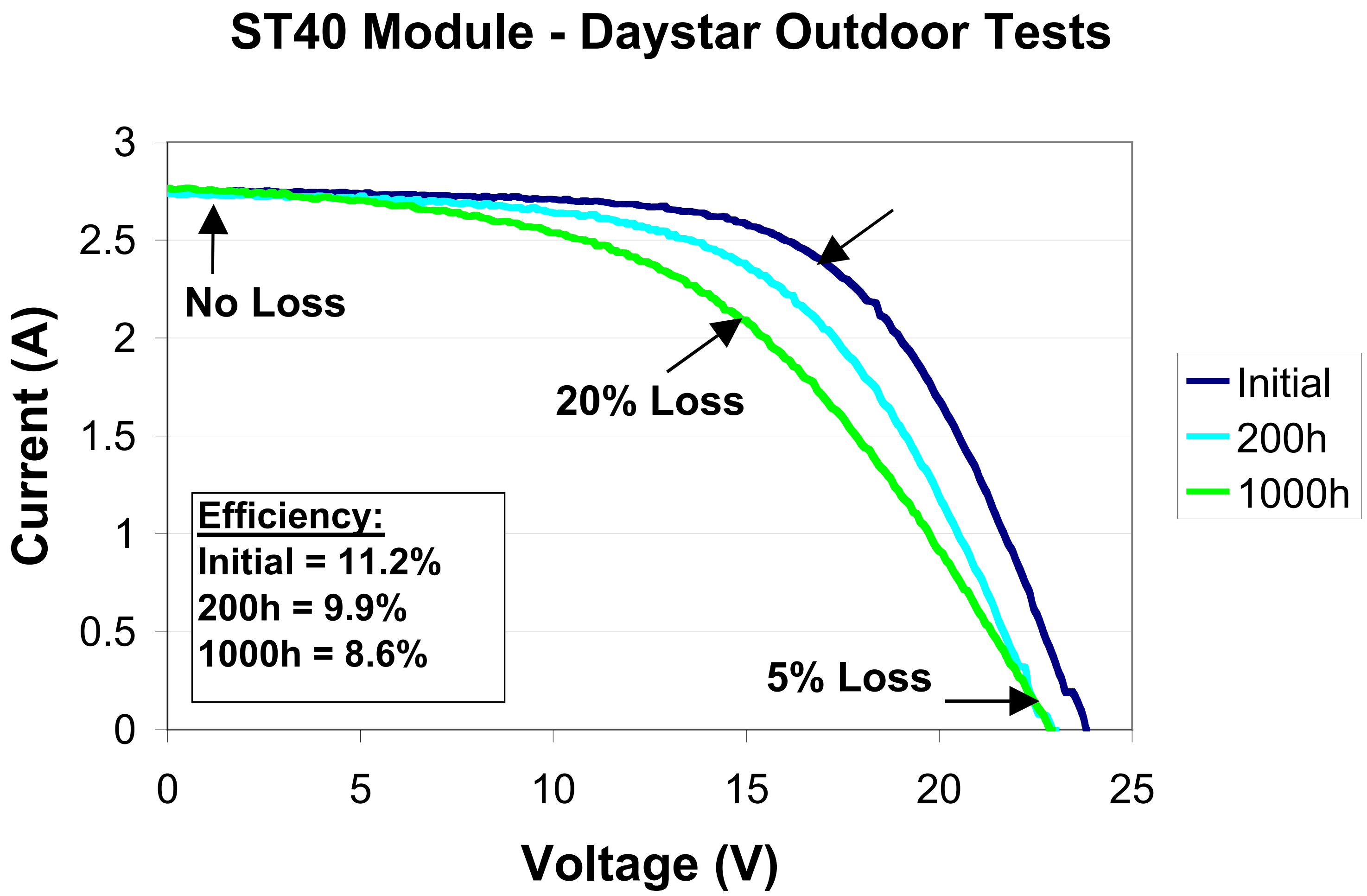






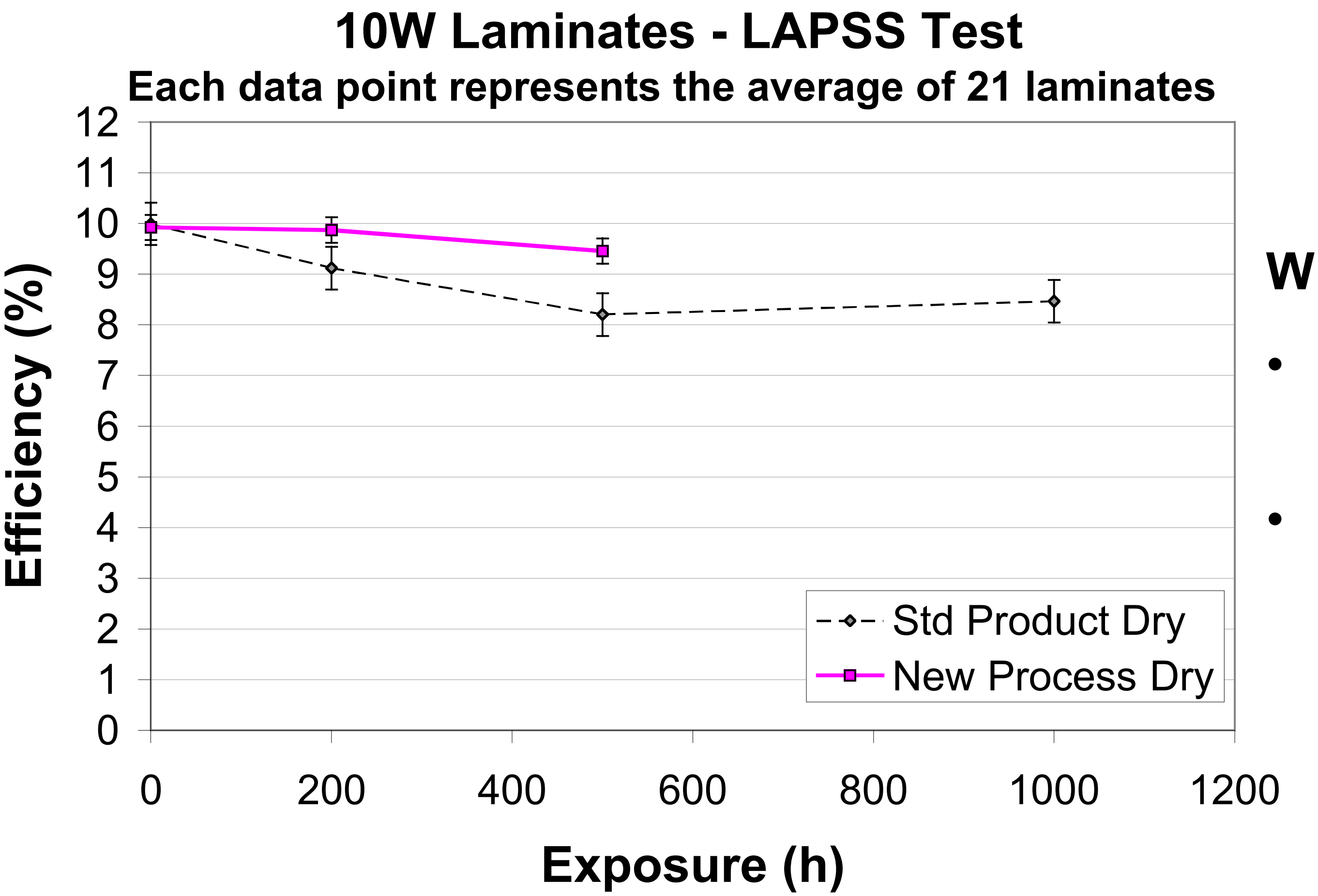
K. Ramanathan, NREL, 2002, unpublished

Thermal Degradation Characteristics



Modified Processing for Thermal Stability

Dry Heat Test Only



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.**
- **A recent NREL study of Shell's Eclipse 80 modules showed excellent stability and negligible effect of moisture because of improved packaging and edge seals. A paper that just appeared [Solar Energy Materials & Solar Cells 98 (2012) 398–403] showed that a new edge seal design enabled stable performance for 3000 h in damp heat.**
- **It is not possible to draw definitive conclusions about the moisture sensitivity of CIGS based on the available reports on unencapsulated cells.**