



U.S. Department of Energy
Energy Efficiency
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DOE Solar Energy Technologies Program Peer Review

Technical Track: Thin Films

Project Name: CIGS Conversion Devices

Principal Investigator: Miguel A. Contreras

Denver, Colorado

March 9-10, 2009

This presentation does not contain any proprietary or confidential information.



- **ClGS Group members:**

Miguel Contreras (Group Supervisor/Senior Scientist): 18 years of R&D experience in thin-film materials for electronic applications and particularly for PV applications.

Ingrid Repins (Senior Scientist): 10+ years of industrial experience in production/manufacturing environments (ITN, MRG, Global Solar). Received an R&D 100 award in '04.

John Pern (Senior Scientist): : 23 years of PV R&D at NREL including CIS, module encapsulants and encapsulation, and performance reliability.

Xiaonan Li (Senior Scientist): 18 years of R&D experience in thin film PV materials (ITO and other noble TCO's, InP, CdTe and ClGS absorber materials).

Clay DeHart (Process Engineer): >22 years of experience in thin film PV

John Scharf (Process Engineer): 9+ years in electronics and engineering

Stephen Glynn (Technician): 2 years experience

- **Special Recognition Received:**

Dr. M. Contreras authored the most cited paper (for the 1999-2008 decade) in the area of Energy and Fuels and was ranked as one of the top 10 most cited scientists/physicists by ScienceWatch for the same period. He also received the 2008 HENAAC award for Outstanding Technical Achievement for his contributions to the field of Solar and Renewable Energy. Similarly, for his contributions to science and technology he is a member elect of the World Technology Network and a board member of Energy Research News.

Dr. Xiaonan Li achieved a world record in energy conversion efficiency for ITO/InP solar cells for space applications in 1994.



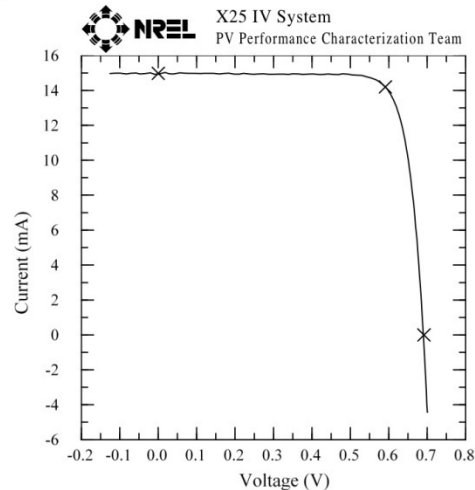
- **Group's major accomplishments:**
 - The group is a world class leader in CIGS technology as demonstrated by awards and recognition given to the group and individual members of the group, number of citations, invited talks and seminars, etc., and by establishing the state-of-the-art for CIGS technology and the world-record energy conversion efficiency for these type of solar cells (currently at 20%). Because the figure of merit for PV cost effectiveness is the \$/watt ratio, it is clear that this result points out a realistic means for attaining additional cost reductions of CIGS PV modules. Additionally, this unique NREL result implies that thin-film CIGS PV products can be made of a quality that can compete directly with the most common wafer solar cell in the market today: the polycrystalline silicon cell.
 - Provided (and continues to provide) expertise and tech transfer efforts to industrial partners via formal mechanisms such as CRADA, WFO, TSA, etc. Previous industrial partners include Lockheed-Martin Corp., the U.S. Air Force, OCLI, EPV, Siemens, Solyndra, Global Solar, Daystar, ISET.
 - Developed IP for the fabrication of high efficiency CIGS solar cells. Example of companies that have licensed the group's patents include: Global Solar, Daystar, and JLN Solar.
 - Designed the CIGS cluster tool (currently being built) for the PDIL which will allow further scientific studies and more industrial collaborations.



- Group's major accomplishments:

NREL
CdS/Cu(In,Ga)Se₂ Cell

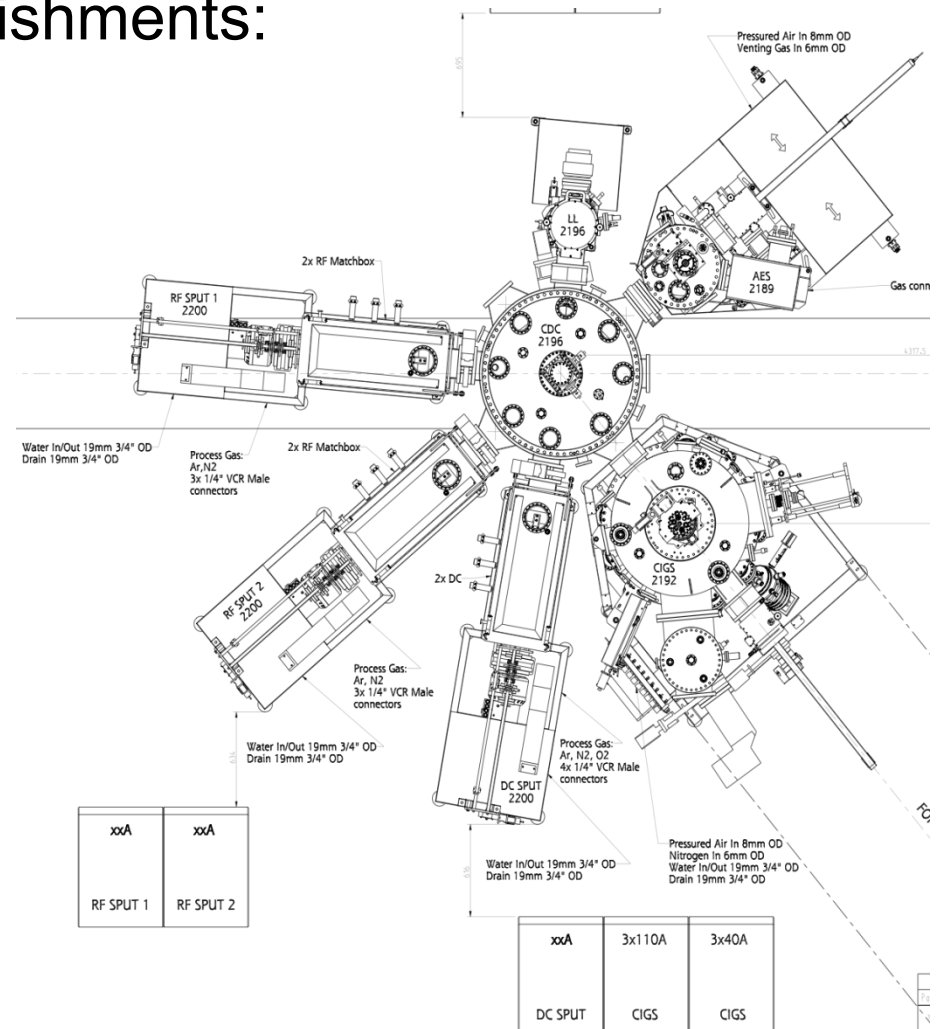
Device ID: M2992-11 #5 Device Temperature: 25.0 ± 1.0 °C
Oct 16, 2007 11:53 Device Area: 0.419 cm^2
Spectrum: ASTM G173 Global Irradiance: 1000.0 W/m^2



$V_{oc} = 0.6918 \text{ V}$
 $I_{sc} = 14.97 \text{ mA}$
 $J_{sc} = 35.74 \text{ mA/cm}^2$
Fill Factor = 81.03 %

$I_{max} = 14.20 \text{ mA}$
 $V_{max} = 0.5911 \text{ V}$
 $P_{max} = 8.393 \text{ mW}$
Efficiency = 20.0 ± 0.8 %

After 10 minute soak at P_{max} , 5 minute cool.
IEC 60904-3 edition, ASTM G173 global



State-of-the-art in
CIGS

Future CIGS cluster tool to be operational by 3Q
2009



- Current sub-projects funded (*or to be funded*) by DOE

CIGS project	Funding level in k\$
1.-Installation to Baseline-Readiness	900
<i>Installation to Baseline-Readiness Enhanced</i>	200
2.-Front Contact ZnO Alternatives	250
<i>Front Contact ZnO Alt Enhanced</i>	50
3.-Sensors: Deposit & Char NREL films	500
<i>Sensors: Deposit & Char NREL Enhanced</i>	50
4.-Cell Level Reliability	185
<i>Cell Level Reliability Enhanced</i>	115
<i>5.-Alternative CIGS Growth Process</i>	145
<i>6.-Large Area CIGS Studies</i>	140



- Current sub-projects funded by non-DOE

CIGS project	Funding level in k\$
1.-Optony: CRADA--Development of low concentration solar cells based on thin-film CIGS	600
2.- JLN Solar: WFO--Development of the monolithic interconnection for CIGS minimodules	100
3.-Dupont: WFO--Development of substrates for CIGS	180
4.- Solopower: TSA	35
5.-Dow Chemical: WFO	21
6.- Applied Quantum technologies: WFO	50



Technical Approach

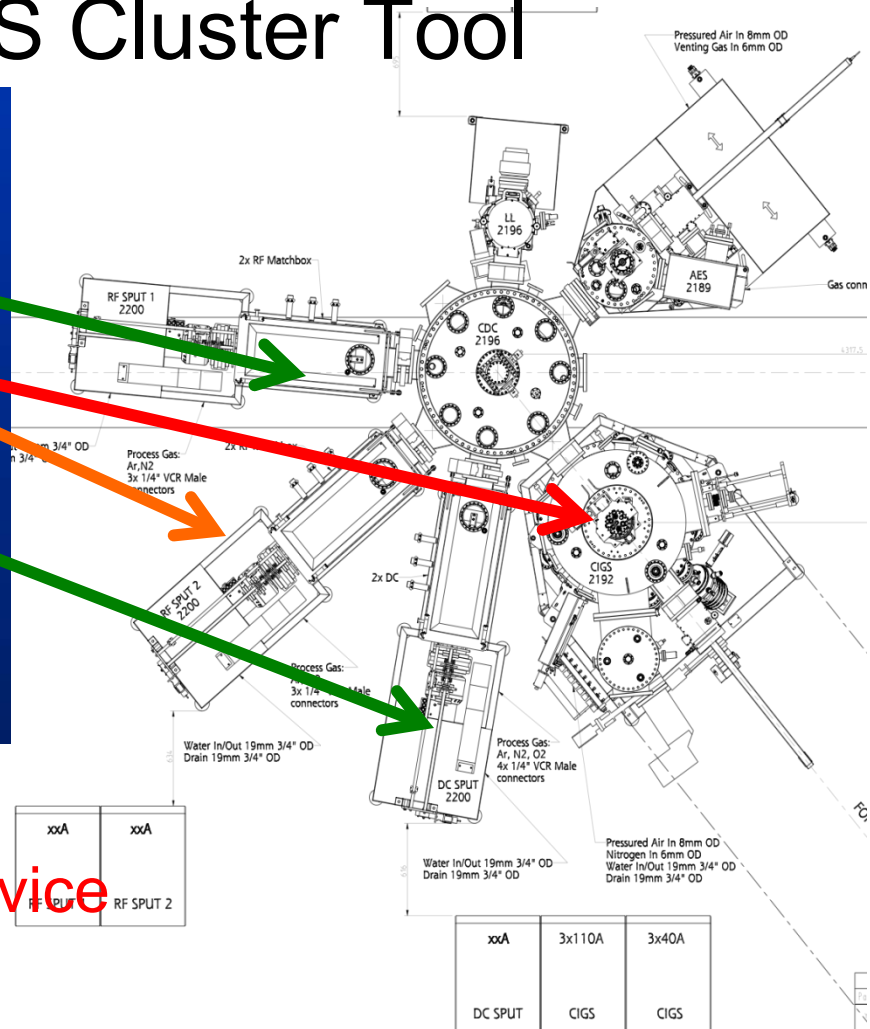
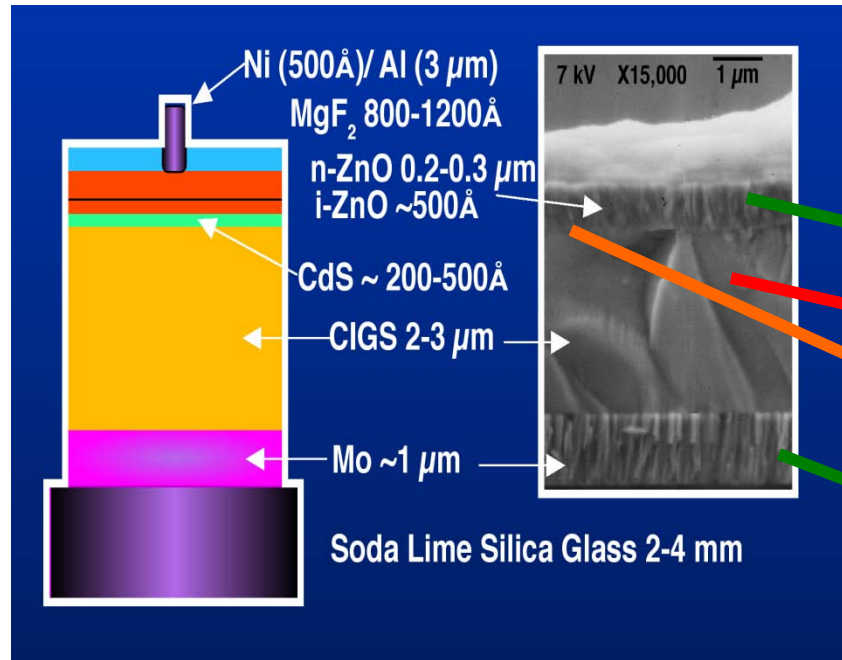
- Installation to baseline-readiness: *the CIGS cluster tool in the Process Development and Integration Laboratory*

(Project leader: M. Contreras)

- Design of the tool based on input from (1) researchers in the CIGS group, (2) the Materials and Characterization Group at NREL, (3) industrial collaborators/partners
- Incorporate concepts to enhance capabilities to carry out fundamental studies in materials and devices previously unavailable (UHV, in-situ monitoring, accurate control of growth environment for studies of impurities, contaminants and other)
- Incorporate concepts that permit studies relevant to industrial issues (fast deposition rates; development of sensors for industrial processes, techniques and hardware for quality control, process control, prototyping, etc)
- Incorporate flexibility in the design for future expansion (adaptability for future needs).



The CIGS Cluster Tool



- 1) Fully integrated CIGS device fabrication
- 2) Analytical (AES) and other
- 3) Expansion/collaborations



Technical Approach

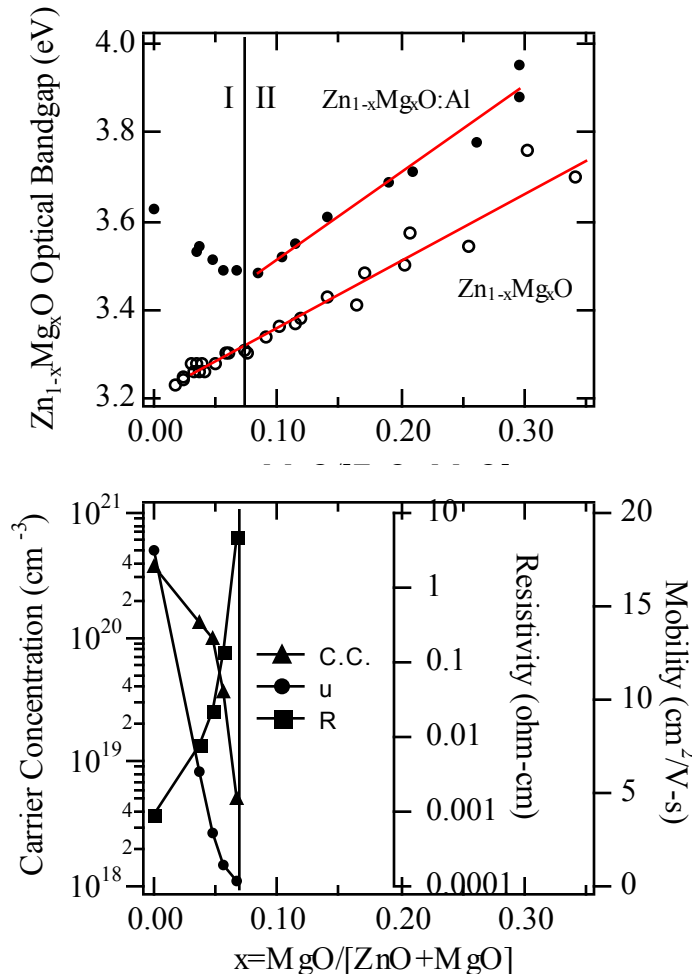
- Front Contact ZnO Alternative: *Assess the development of alternative TCOs to ZnO and demonstrate their performance and enhancement to device stability and reliability.*

(Project leader: X. Li)

- Evaluate the front contact materials (ZnO and other TCO's) for durability by subjecting these materials to rigorous (environmental and accelerated) tests, particularly at std. 85/85 (85°C/85% RH) conditions.
- Select promising front contact materials for testing in device structures (if any)
- Develop, test and evaluate protective thin-films for ZnO. These protective layers will be selected based upon the criteria of high optical transmission and tolerance to temperature and humidity exposure (hydrophobic materials)
- Select promising protective layers and a test in actual device structures.



Alternative TCOs: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

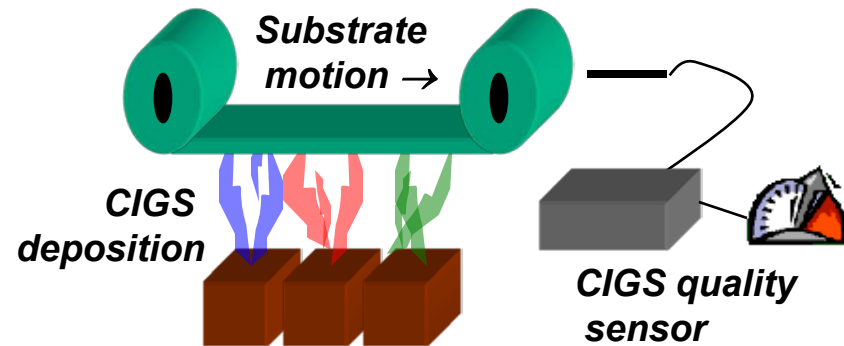


- Al-doped $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ is not conductive enough for front contact TCO.
- The increased bandgap would make undoped $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ a useful material for the window layer in wide band gap CIGS Solar cell.
- It is too early to conclude whether the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ has the potential with appreciable stability compared with ZnO.
- The order of degradation rate is determined to be $\text{ZnO} \gg \text{ITO} > \text{SnO}_2:\text{F}$.¹
- Sputtering deposited SnO_2 based oxide could be used for protective layers.

¹"Damp-Heat Induced Degradation of Transparent Conducting Oxides for Thin-Film Solar Cells" F.J. Pern, R. Noufi, X. Li, C. DeHart, and B. To, Presented at the 33rd IEEE Photovoltaic Specialists Conference San Diego



Technical Approach



- Sensors: *Development of sensors for CIGS industrial fabrication processes and/or material quality control*

(Project leader: I. Repins)

- Develop (non-destructive) techniques and tools that can provide information on CIGS absorber quality (*electronic defect content*) and are amenable for incorporation into manufacturing lines typically operating at high speed for high throughput
- Select promising technique/tool for testing in-house CIGS materials and devices
- Extend the study to CIGS materials manufactured by industrial partner
- Build prototype tool for application to manufacturing line at industrial partner site.



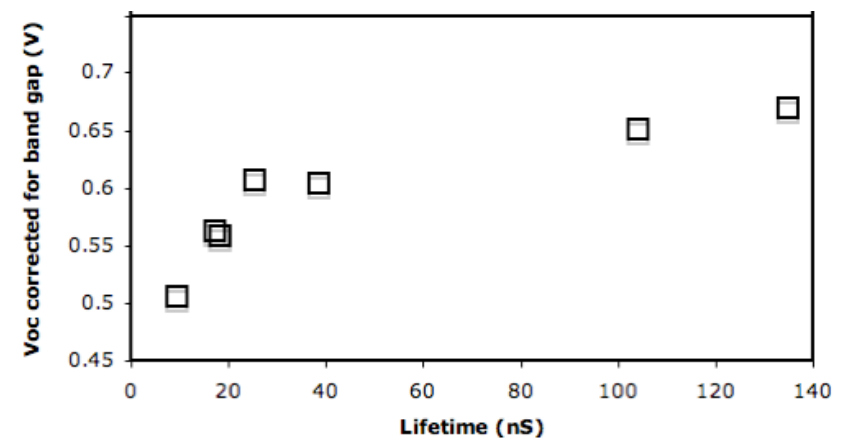
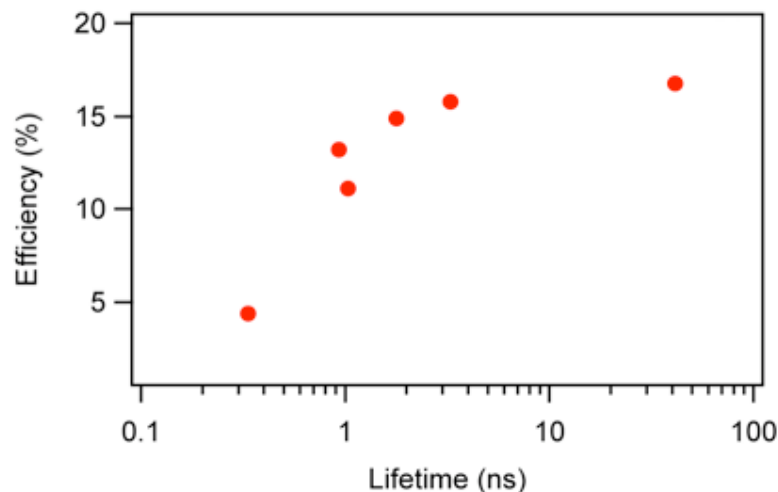
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Scientific/Technical Approach

- Strong correlation found between carrier lifetimes measured by TRPL and device performance (see graph below left); same Ga profile and deposition T for each sample
- Correlation was extended to a diverse sample set—thin, varying Ga gradings, low T, contaminated back contact (see graph below right)
- Commitment from Solopower to provide a samples extending the study to industrial electrodeposited CIGS
- Also currently extending study to other industrially-relevant conditions—low thermal budget, high Ga content, lower efficiencies.
- The CIGS community recognizes the importance of the problem and the promise of results to date—invited presentations at IEEE and SPIE upcoming, two refereed journal papers

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Technical Approach

- CIGS cell level reliability : *establish experimental procedures and tests to evaluate the reliability of the various CIGS solar cell constituent layers to improve the cell reliability*

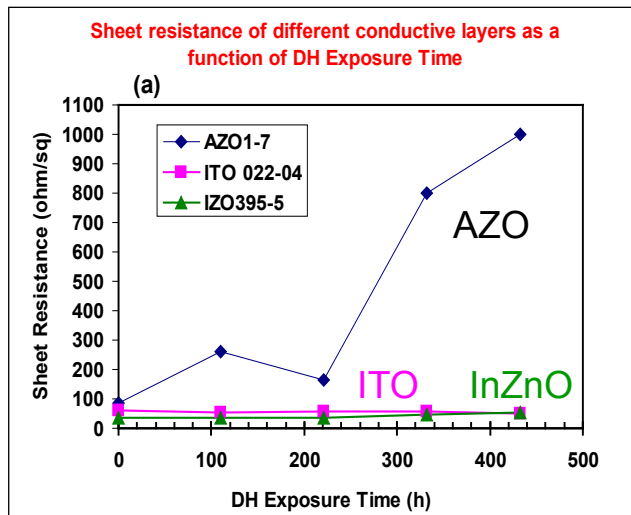
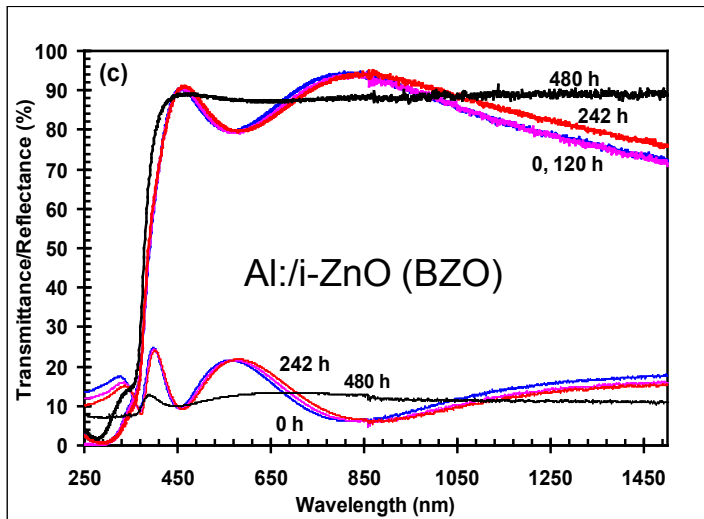
(Project leader: John Pern)

- Build/acquire instrumentation and equipment for accelerated stress and weathering exposures at elevated temperature and moisture to evaluate the optical, electrical, structural, and/or mechanical properties of the constituent layers of the CIGS solar cell
- Identify the degradation mechanism and quantify degradation rates for the CIGS solar cell
- Identify more stable materials, and seek chemical and/or physical mitigation methods to improve their reliability.



Stability of Various TCO's on Glass substrates (on-going):

- Single-/Bi-layer Al-/i-ZnO (**AZO & BZO**), Al:Zn_{1-x}Mg_xO (**ZMO**), **ITO** (commercial & in-house), **F:SnO₂** (commercial & in-house), B:ZnO, **InZnO**, single-layer AZO (thickness effect), sputtered TCO on AZO and BZO, InZnO/i-ZnO, and chemical surface treatment.



Damp Heat (85/85) Stability:
F:SnO₂ > In-house ITO ≥ InZnO >> Al:ZnO-based AZO, BZO, and ZMO.

Table 1. Sample Data and Degradation Rates upon Accelerated Exposures

Sample ID	BZO-1A	BZO-1B	BZO-1C	BZO-2A	BZO-2B	IZO-11	AZO-21	BZO-31	ZMO-383	ZMO-471	ZMO-501	ZMO-681
Composition	i-/Al:ZnO	i-/Al:ZnO	i-/Al:ZnO	i-/Al:ZnO	i-/Al:ZnO	int.-ZnO	Al:ZnO	i-/Al:ZnO	Al:ZnO	Al:ZnO	Al:ZnO	Al:ZnO
MgO (wt%)									0	1	10	0
Dep. Tsub (oC)	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient	100	100	100
Thickness (μm)	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.2	0.3	0.5	0.5	0.6
Chem. Mitigation			PDMS	PDMS								
AET Type	DH	DH	DH	DH	WOM	DH	DH	DH	DH	DH	DH	DH
Degrad. Rate [(ohm/sq)/h]	5.42	6.38	2.27	0.16	0.08	HR* at 0 h	62.08	1.84	0.69	0.82	HR* at 0 h	0.09

* HR: highly resistive



Stability of Alternative TCOs for CdS/CIGS/Mo/SLG Device (Ongoing):

- **As part of device structure** – both resistive and conductive layers window layer:
 - Al:Zn_{1-x}Mg_xO, ITO and InZnO to replace “standard” Bilayer Al:/i-ZnO (BZO)
- **As protective layer for the BZO:**
 - ITO, InZnO, sputtered undoped TCOs

Cell ID	Window layer	Thickness (μm)	Voc (V)	Jsc (mA/cm ²)	FF (%)	Eff (%)	R _{shunt} (ohm)	R _{series} (ohm)
M3047-11	ZnO	.12	0.67	-31.67	75.72	15.96	1.19	4562.07
M3047-21	Optimized* IZO	.127	0.69	-30.90	77.49	16.45	1.59	3678.93
M2991-13	ZnO	.12	0.62	-34.42	74.09	15.8	1.37	3438.49
M2991-11	ZnO	.12	0.66	-33.14	75.78	16.6	1.44	3708.68
M2991-21	unoptimized IZO	.148	0.64	-23.07	74.34	10.9	2.06	2728.54

* optimized for sheet resistance of current contact electrode grid pattern.

- InZnO, as part of device structure, performs similarly to standard Al:ZnO
- ITO and InZnO are promising as protective and conductive window layers
- Accelerated damp heat (85°C/85%RH) and dry heat (85°C/~4%RH) tests of devices and various TCOs/glass are on-going.



• Humidity Susceptibility of Thin-Film CIGS Absorber

Table 2. Cell Parameters for CIGS Samples with or without Exposure to Ambient or Damp Heat

Sample ID	Exposure	Cell #	Voc (V)	Jsc (mA/cm ²)	FF (%)	Eff (%)	Rs (ohm-cm)	Rsh (ohm-cm)
A	ambient	1	0.42	10.30	34.31	1.47	16.76	58.28
		3	0.44	6.44	31.62	0.89	33.25	77.68
B	ambient	1	0.41	22.89	40.46	3.81	6.85	43.63
		4	0.39	25.67	44.91	4.44	4.52	54.56
C-1A	DH 15 min	2	0.54	30.84	65.57	11.01	2.50	412.76
		4	0.56	32.04	65.97	11.84	2.36	628.01
C-1B	DH 30 min	1	0.51	30.20	64.40	9.96	2.76	504.29
		3	0.51	30.91	63.69	10.09	2.80	375.83
C-0A	No (N2 dry box)	1	0.65	30.28	71.06	14.06	1.66	4490.60
		7	0.65	31.39	76.91	15.73	1.39	14126.49
C-0B	No (N2 dry box)	1	0.67	29.78	71.16	14.15	2.06	4228.40
		5	0.67	31.10	77.22	16.14	1.41	20536.12

➤ **CIGS gradually degraded by ambient humidity, but rapidly at DH 85/85.**

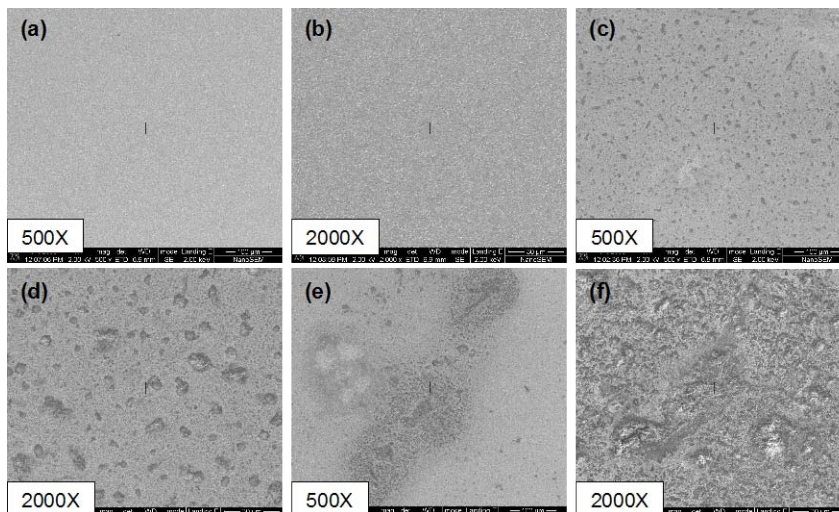


Fig. 1. SEM micro-images showing the morphological changes for an ambient-degraded sample (#A) over several months. (a, b): A still "smooth" area, (c, d): an area with a large number of small pits, and (e, f): a large pitting spot, which was also visible visually and corresponding to the images seen under optical and interference microscopes. The magnification factors are indicated.

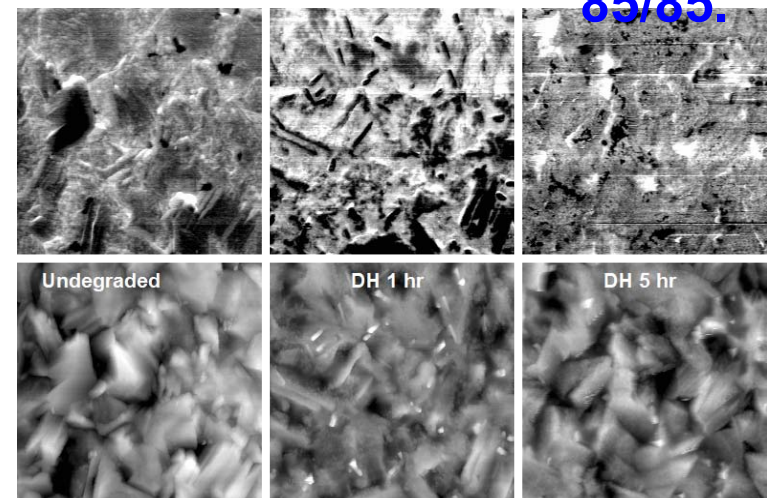


Fig. 2. Corresponding scanning Kelvin probe (SKP) and AFM images for DH-degraded CIGS on Mo/SLG. Exposure time was indicated in the photographs.



Installation to Baseline-Readiness: *The CIGS cluster tool in the Process Development and Integration Laboratory*

- This sub-project will impact costs by addressing relevant issues to large-scale production efforts via direct collaborative work with CIGS manufacturing partners (qualification of materials, comparative studies, specific industrial problems and limitations)
- We expect to develop and improve techniques and instrumentation for film deposition and process controls in collaboration with commercial/industrial partners who specialize in this area (new deposition sources, new in-situ monitoring and control instruments, quality control, feedback controls, etc)
- We expect to impact the technology at a larger scale/size than we have done in the past (large area cells and mini module development, improvements to interconnect schemes, etc.)
- The new capability of improved controls and environment for film growth could also impact the performance of devices and provide a new state-of-the art for this technology.



Front Contact ZnO Alternative: *Assess the development of alternative TCOs to ZnO and demonstrate their performance and enhancement to device stability and reliability*

- Thin-film and wafer-based PV technologies have a common problem: long term environmental exposure deteriorates performance and diminishes the reliability of the devices and modules.
- The problem arises from current encapsulation methods and materials employed in the manufacturing of all PV modules; water vapor eventually penetrates the module and deteriorates the cells.
- This problem can be mitigated by (a) developing alternative TCO's that are tolerant to water vapor exposure; (b) improving the water vapor resistance by chemically modifying existing TCO's; and/or (c) developing protective layers that will repel water vapor from the cell.
- The net impact of a successful completion of this research is that PV product warranties could be extended beyond today's standard 25-year warranty.



Sensors: *Development of sensors for CIGS industrial fabrication processes and/or material quality control*

- Current successful thin-film production efforts typically rely on high-throughput approaches to mass produce PV products (roll to roll coating, in-line glass coating).
- A big limitation of these industrial deposition methods is the low yield of quality/performance materials due to the lack of process and quality controls.
- There is a clear need to develop sensors and techniques that can be applied to these industrial manufacturing environments to either provide feedback for process control or for quality control in between the processing of each layer composing the CIGS device
- The net impact of a successful completion of this research is that production yields and product quality could be dramatically improved, thus having a direct effect on the final cost of the CIGS product.



CIGS Cell-Level Reliability : *Establish experimental procedures and tests to evaluate the reliability of the various CIGS solar cell constituent layers to improve the cell reliability*

- There is a need to establish the long term stability and reliability of thin-film products in general. Current available reliability data for these PV products are limited and additional studies in this area will provide the necessary information to investors, end-users, and manufacturers in their decision making process.
- The study of each layer composing the CIGS solar cell for long term stability and reliability will provide the necessary data to improve the reliability of thin-film PV products based on CIGS.
- We have begun studying in-house materials and cells but eventually these studies could be further expanded to include commercially produced materials and devices.



- **Alternative Low-Cost CIGS Growth Processes:** One issue with bringing down the cost of CIGS PV products is the high cost of the capital equipment (vacuum chambers) used in manufacturing. Alternative growth processes (for CIGS and all layers that make up the cell) based on non-vacuum approaches are ideal due to their intrinsic low-cost nature (wet chemistry of solutions, inks and pastes based on nano and micro material precursors for screen printing, dip coating, spin coating, electroless deposition, ink jet printing, etc).
- **Large-Area Studies:** There is a big gap between the energy conversion efficiency attained at the lab scale (20%) and commercial CIGS modules (~11-12%). Much of this gap is due to non-uniformities encountered in the process of scaling up and to deficiencies in the interconnect scheme currently used in thin-film modules (monolithic interconnection). Tackling this issue could have a significant impact across the board with all manufactures of CIGS products because it is a common problem to all manufacturers and a significant limitation in today's state-of-the-art commercial CIGS modules.