

High Efficiency CdTe and CIGS Thin Film Solar Cells: Highlights of the Technologies Challenges

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Outline

Introduction

Highlights

- summary of device performance
- how devices are structured
- properties of thin film layers
- summary of module performance

Key Challenges

Acknowledgements

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Dennis Hollars – MIASOLE

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Tim Anderson – U. of Florida

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Introduction

- CdTe and CIGS PV modules have the potential to reach cost effective PV-generated electricity.
- They have transitioned from the laboratory to the market place.
- Pilot production/first-time manufacturing (US) ~ 25 MW.
- CdTe technology ramping to 75 MW.
- Enjoying a flux of venture capital funding.
- Transitioning from the lab to manufacturing has been much more difficult than anticipated.

CIS and CdTe PV Companies

CIS

Shell Solar, CA
Global Solar Energy, AZ
Energy Photovoltaics, NJ
ISET, CA
ITN/ES, CO
NanoSolar Inc., CA
DayStar Technologies, NY/CA
MiaSole, CA
HelioVolt, Tx
Solyndra, CA
SoloPower, CA

Wurth Solar, Germany
SULFURCELL, Germany
CIS Solartech, Germany
Solarion, Germany
Solibro, Sweden
CISEL, France
Showa Shell, Japan
Honda, Japan

CdTe

First Solar, OH
Solar Fields, OH
AVA TECH, CO

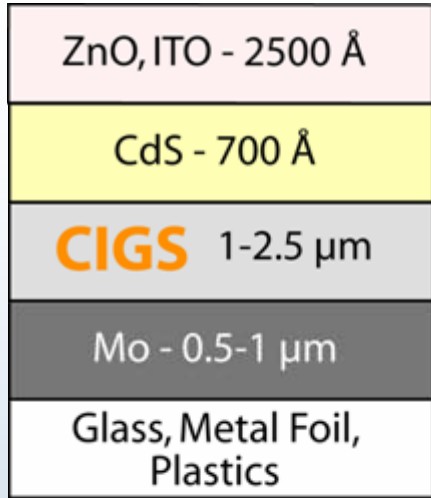
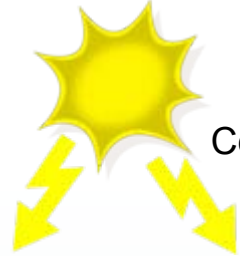
CANRON, NY
Antec Solar, Germany

Laboratory Solar Cells

Thin Film CIGS Solar Cells

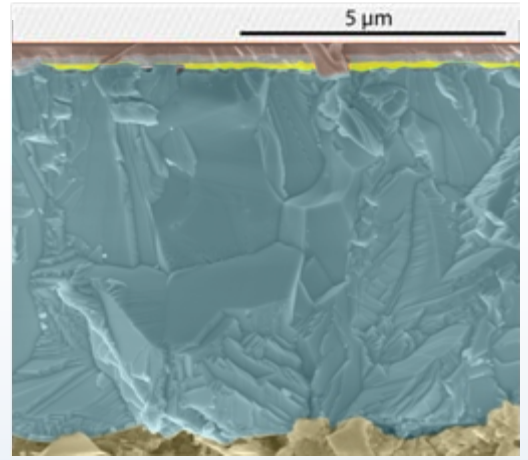
Efficiency

	Area (cm ²)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	Efficiency (%)	Comments
CIGSe	0.410	0.697	35.1	79.52	19.5	CIGSe/CdS/Cell NREL, 3-stage process
CIGSe	0.402	0.67	35.1	78.78	18.5	CIGSe/ZnS (O,OH) NREL, Nakada et al
CIGS	0.409	0.83	20.9	69.13	12.0	Cu(In,Ga) ₂ S ₂ /CdS Dhere, FSEC
CIAS	–	0.621	36.0	75.50	16.9	Cu(In,Al)Se ₂ /CdS IEC, E _g = 1.15eV
CdTe	1.03	0.845	25.9	75.51	16.5	CTO/ZTO/CdS/CdTe NREL, CSS
CdTe	–	0.840	24.4	65.00	13.3	SnO ₂ /Ga ₂ O ₃ /CdS/CdTe IEC, VTD
CdTe	0.16	0.814	23.56	73.25	14.0	ZnO/CdS/CdTe/Metal U. of Toledo, sputtered



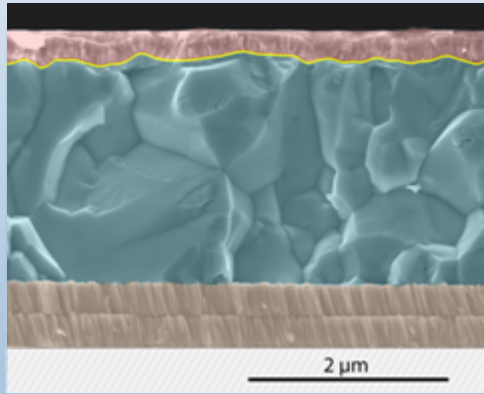
CIGS

Glass
Cd₂SnO₄/ZnSnO_x
CdS



CdTe

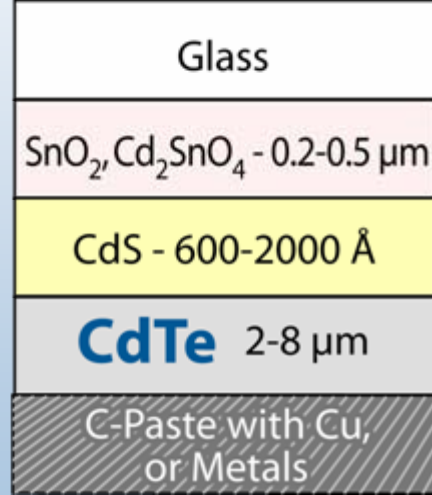
C-Paste/Cu



ZnO/CdS

CIGS

Mo
Glass



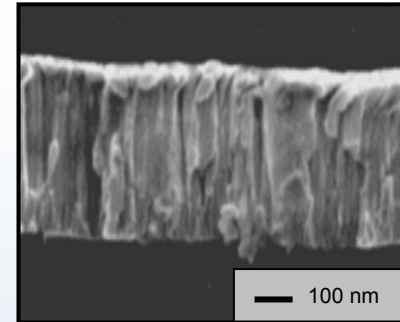
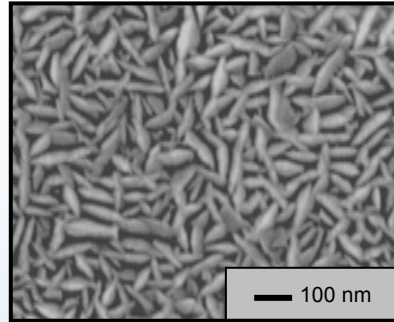
CdTe

CdTe and CIGS Device Structure

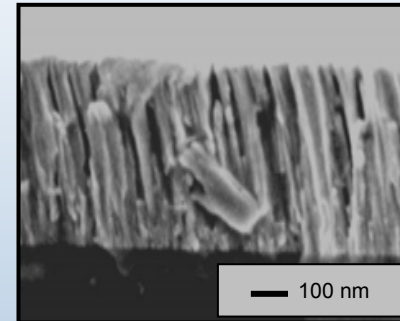
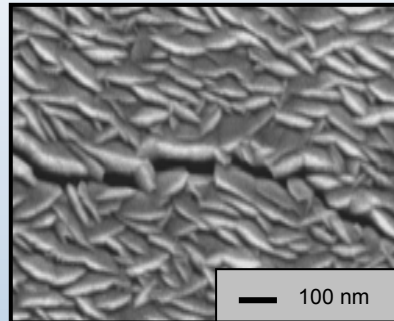
SEM Micrographs - Sputtered Mo Thin Films

Rate: 25Å/sec.

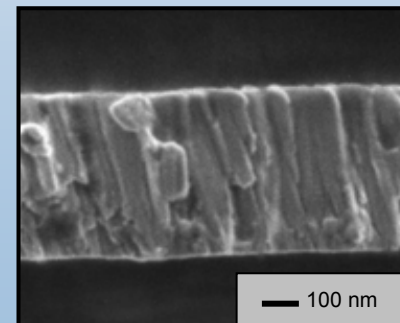
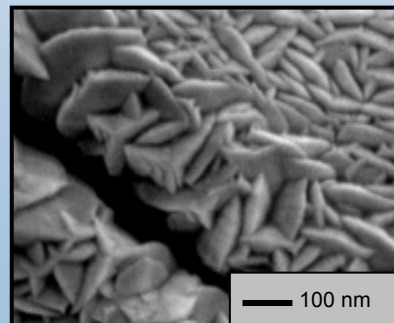
ZnO, ITO - 2500Å
CdS - 700Å
CIGS 1-2.5µm
Mo - 0.5-1µm
Glass, Metal Foil, Plastics



Pressure
5 mTorr



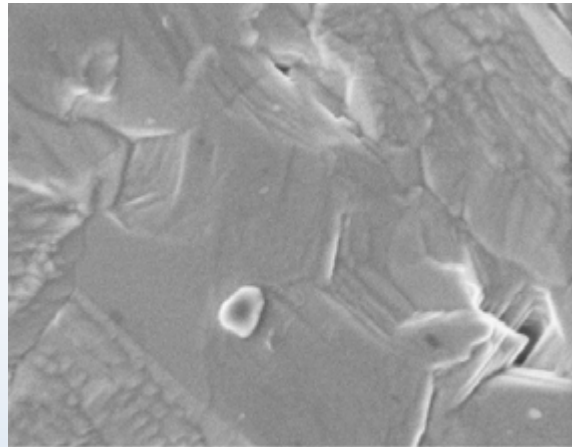
8 mTorr



12 mTorr

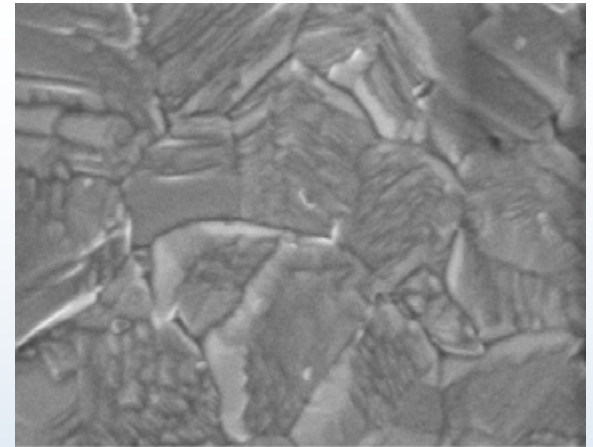
CIGS Thin Film with $E_g=1.1-1.2$ eV

ZnO, ITO - 2500Å
CdS - 700Å
CIGS 1-2.5μm
Mo - 0.5-1μm
Glass, Metal Foil, Plastics



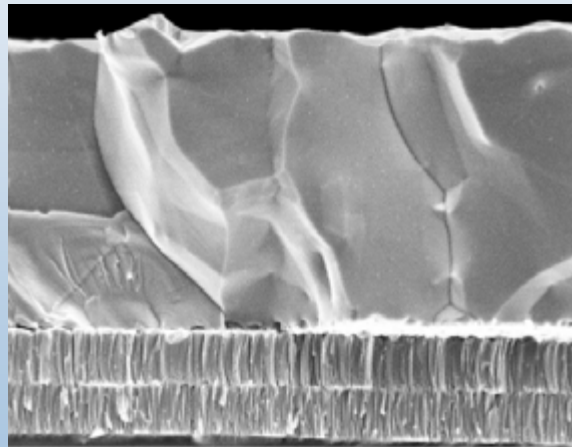
S2212

600nm 40000X



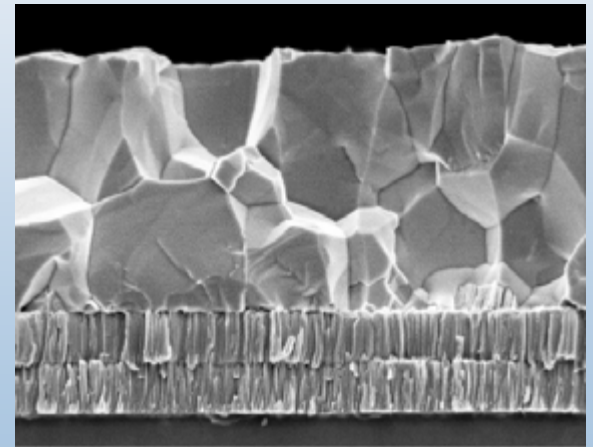
S2213

600nm 40000X



S2212

1μm 25000X



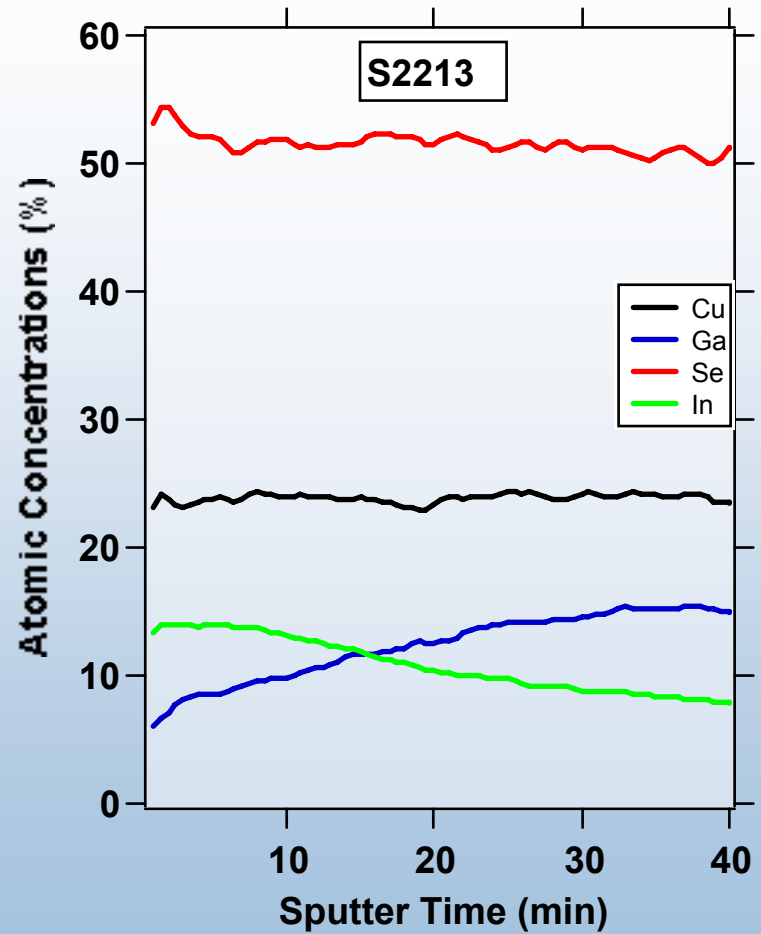
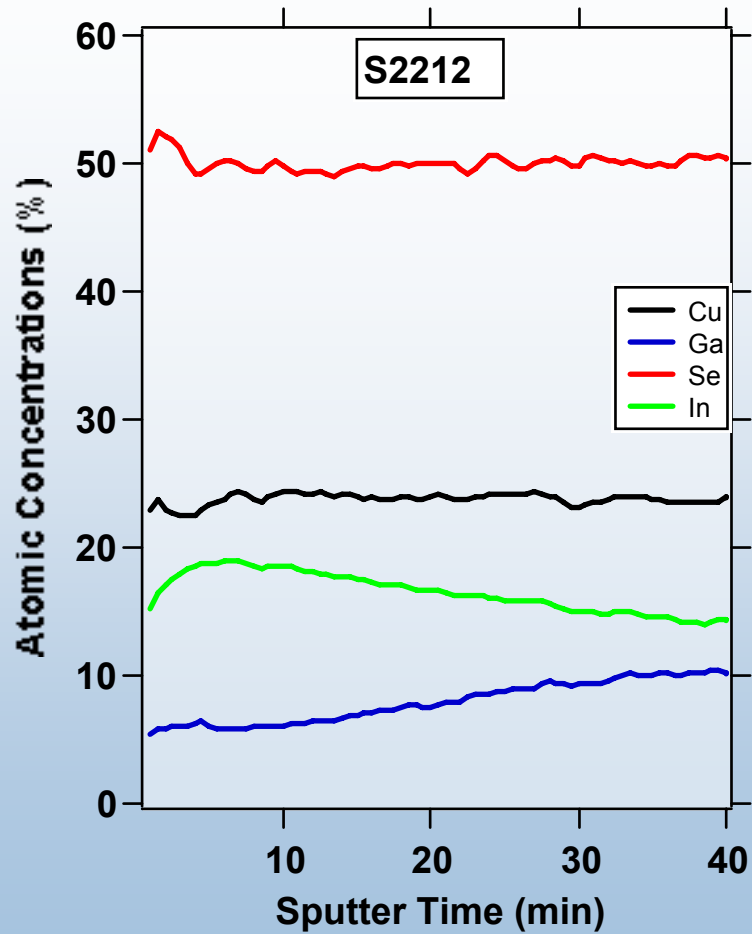
S2213

1μm 25000X

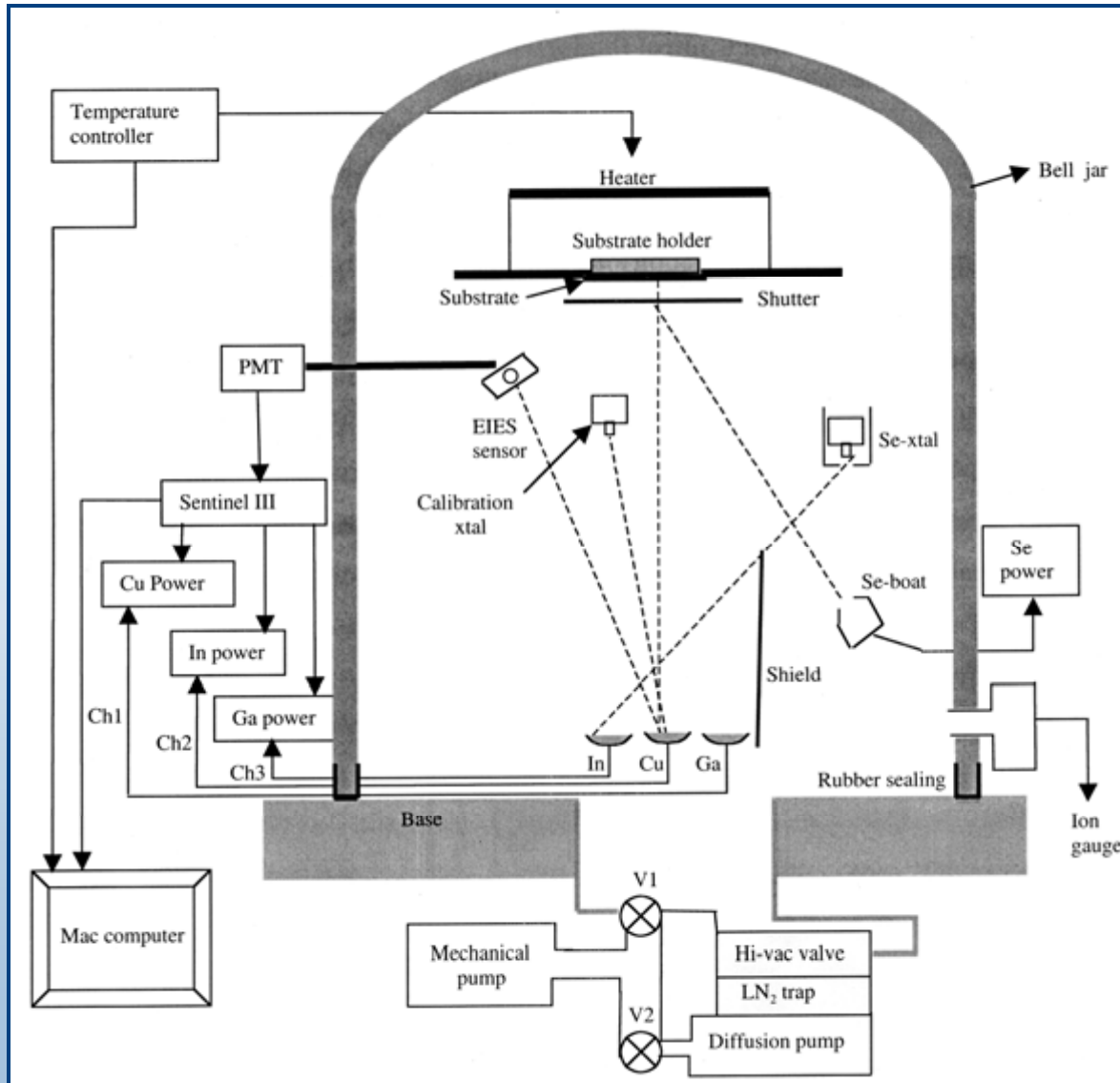
26% Ga/(In+Ga)

31% Ga/(In+Ga)

AES Depth Profiles



CIGS Deposition System



CIGS Formation Pathways

1. $\text{Cu} + \text{In} + \text{Ga} \longrightarrow \text{Cu:In:Ga intermetallic}$

$\text{Cu:In:Ga intermetallic} + \text{H}_2\text{Se (or Se)} \longrightarrow \text{Cu(In,Ga)Se}_2$

2. $\text{Cu}_2\text{Se} + (\text{In,Ga})_2\text{Se}_3 \longrightarrow \text{Cu(In,Ga)Se}_2$

3. $\text{Cu} + \text{In} + \text{Ga} + \text{Se} \longrightarrow \text{Cu(In,Ga)Se}_2$

Deposition Methods

Evaporation of the Elements

Vacuum

Sputtering of the Elements

Vacuum

Nanotechnology/Nano-particles-(Inks)

Printing

CVD-based (lab. R&D)

Low Vacuum

Deposition of CdS

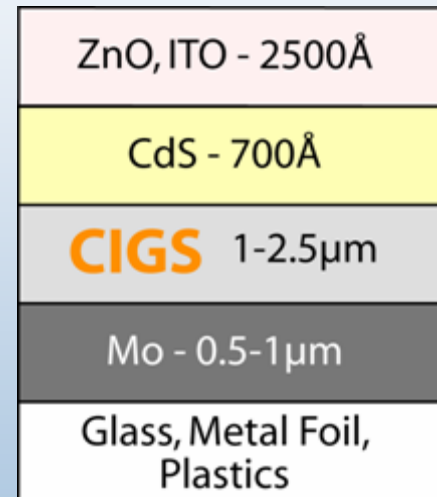
Solution (CBD): CdSO_4 , NH_4OH , $\text{N}_2\text{H}_4\text{CS}$ (Thiourea), H_2O

Temperature: 60°C to 85°C

Time: 4 to 20 min.

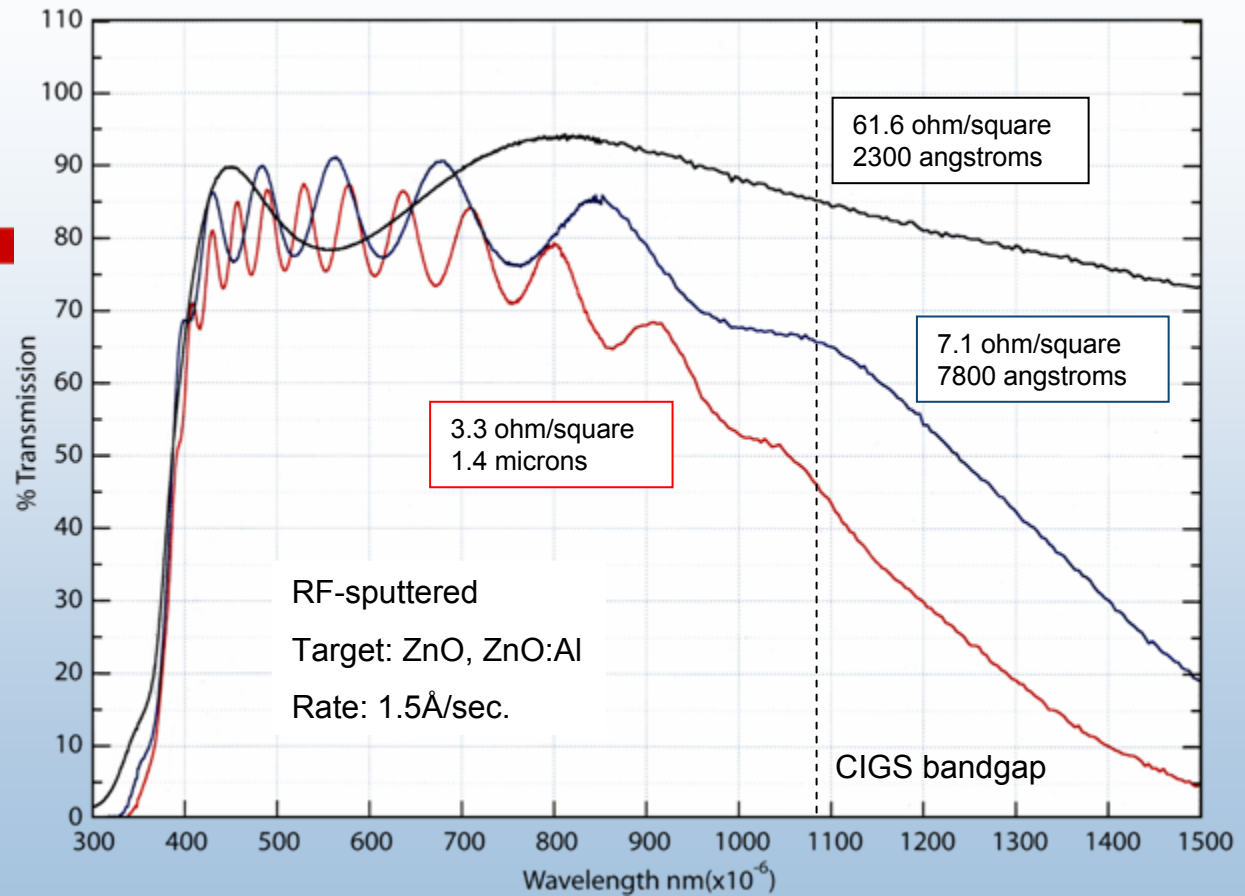
Sputtered CdS

T_s $150\text{-}200^\circ\text{C}$



Optical Transmission - ZnO

ZnO, ITO - 2500Å
CdS - 700Å
CIGS 1-2.5μm
Mo - 0.5-1μm
Glass, Metal Foil, Plastics



Parameters of High Efficiency CIGS Solar Cells

Sample Number	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill factor (%)	Efficiency (%)
C1812-11	0.692	35.22	79.87	19.5 (World Record)
S2212-B1-4	0.704	34.33	79.48	19.2
S2232B1-3	0.713	33.38	79.54	18.9
S2232B1-2	0.717	33.58	79.41	19.1
S2229A1-3	0.720	32.86	80.27	19.0
S2229A1-5	0.724	32.68	80.37	19.0
S2229B1-2	0.731	31.84	80.33	18.7
S2213-A1-3	0.740	31.72	78.47	18.4

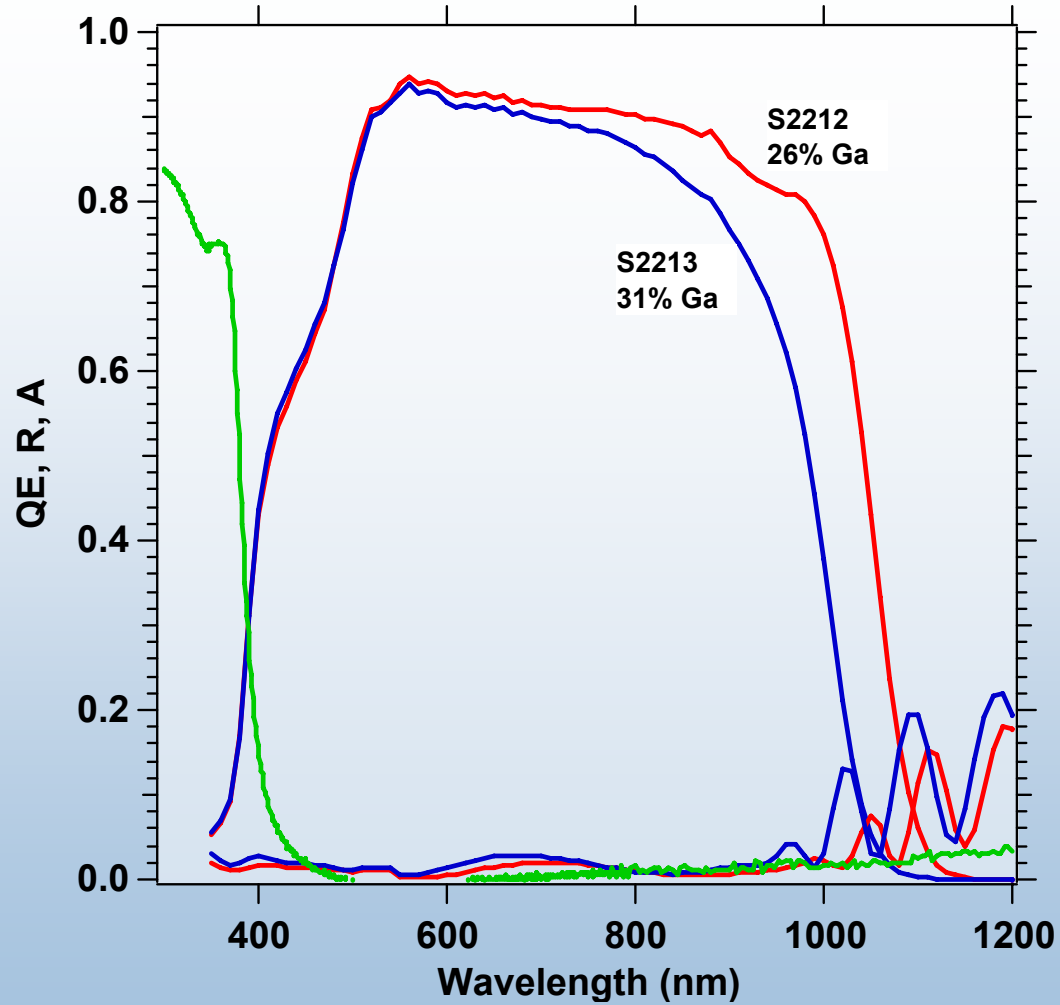
Tolerance to wide range of molecularity

$Cu/(In+Ga)$ 0.95 to 0.82

$Ga/(In+Ga)$ 0.26 to 0.31

Yields device efficiency of 17.5% to 19.5%

Quantum Efficiency



Diode Quality

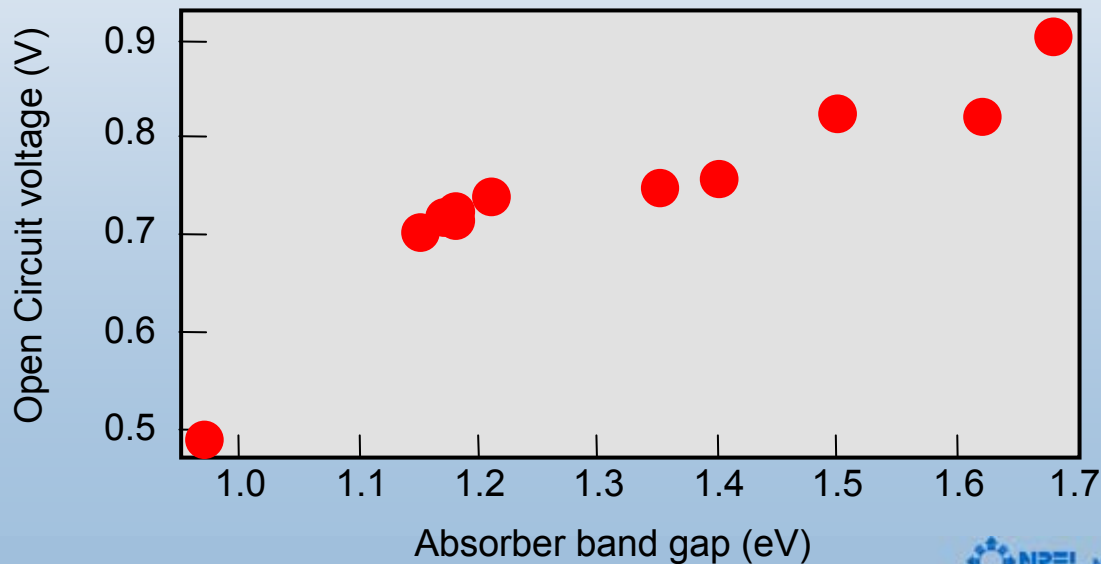
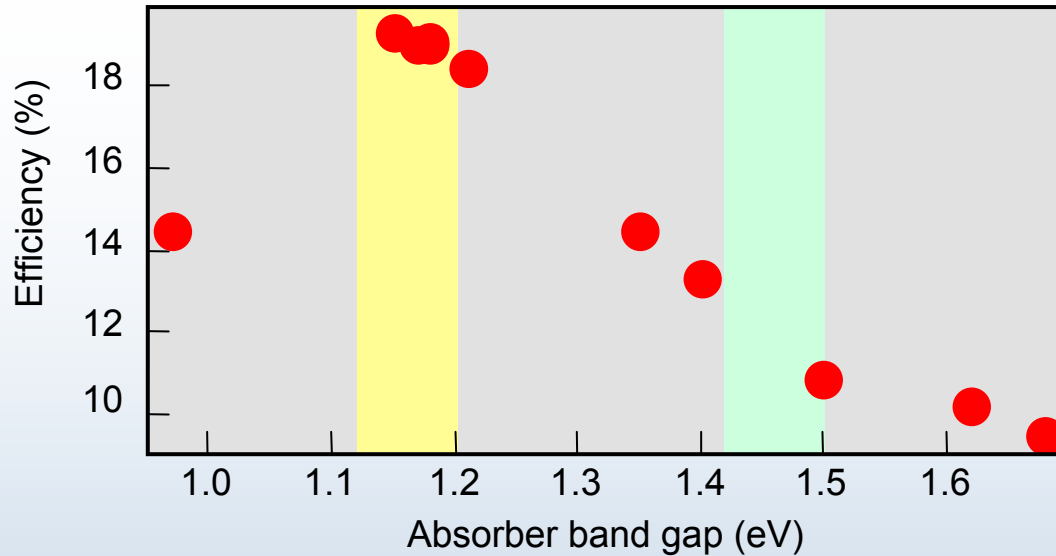
J_0 and n (light curves)

Bandgap (eV)	J_0 (A/cm ²)	n (Diode Quality Factor)
1.10	5×10^{-11}	1.35
1.12	6×10^{-11}	1.36
1.12	6×10^{-11}	1.35
1.21	4×10^{-10}	1.57
1.22	5×10^{-10}	1.62

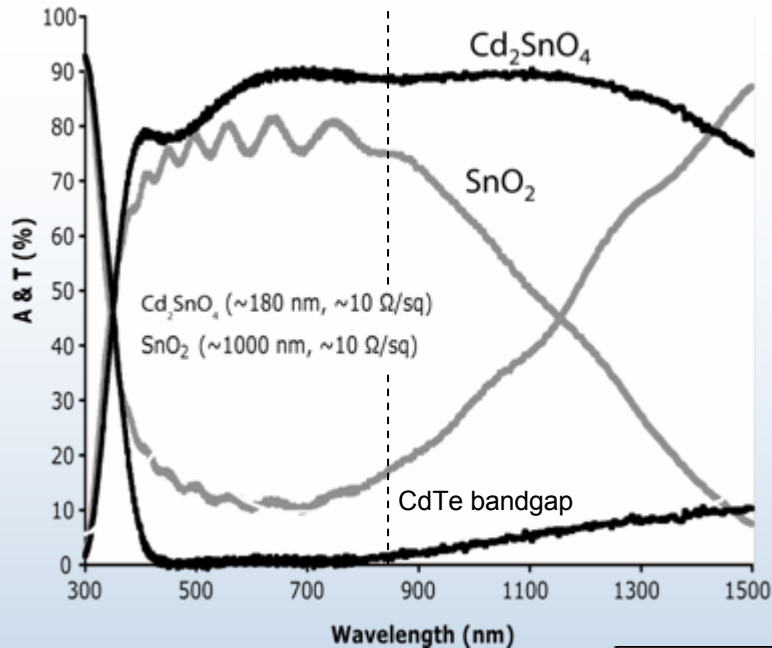
$$R = 0.25 \, \Omega \, \text{cm}^2$$

$$G = 0.10 \, \text{mS} \, \text{cm}^{-2} \text{ (or } R_{\text{sh}} = 10 \, \text{k}\Omega \, \text{cm}^2\text{)}$$

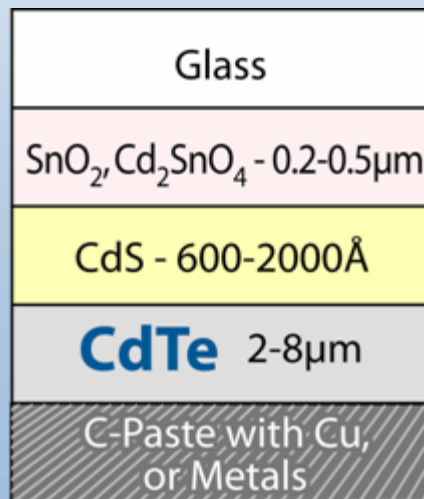
Efficiency and V_{oc} vs E_g



High Quality TCO – Cd_2SnO_4 (CTO)



Sample	Cd_2SnO_4	SnO_2 (SnCl_4)	SnO_2 (TMT)
t (nm)	510	~1000	~1000
n (cm^{-3})	8.94×10^{20}	4.95×10^{20}	4.52×10^{20}
μ (cm^2/Vs)	54.5	15.4	42.-0
Resistivity ($\Omega \text{ cm}$)	1.28×10^{-4}	8.18×10^{-4}	3.29×10^{-4}
R_s (Ω/sq)	2.6	8.6	3.3



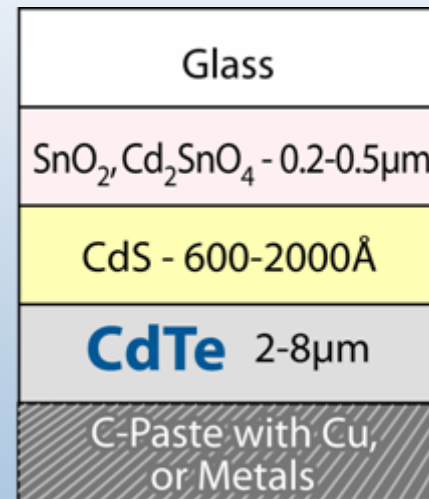
Deposition of CdS

Solution (CBD): CdSO_4 , NH_4OH , $\text{N}_2\text{H}_4\text{CS}$ (Thiourea), H_2O

Temperature: 60°C to 85°C

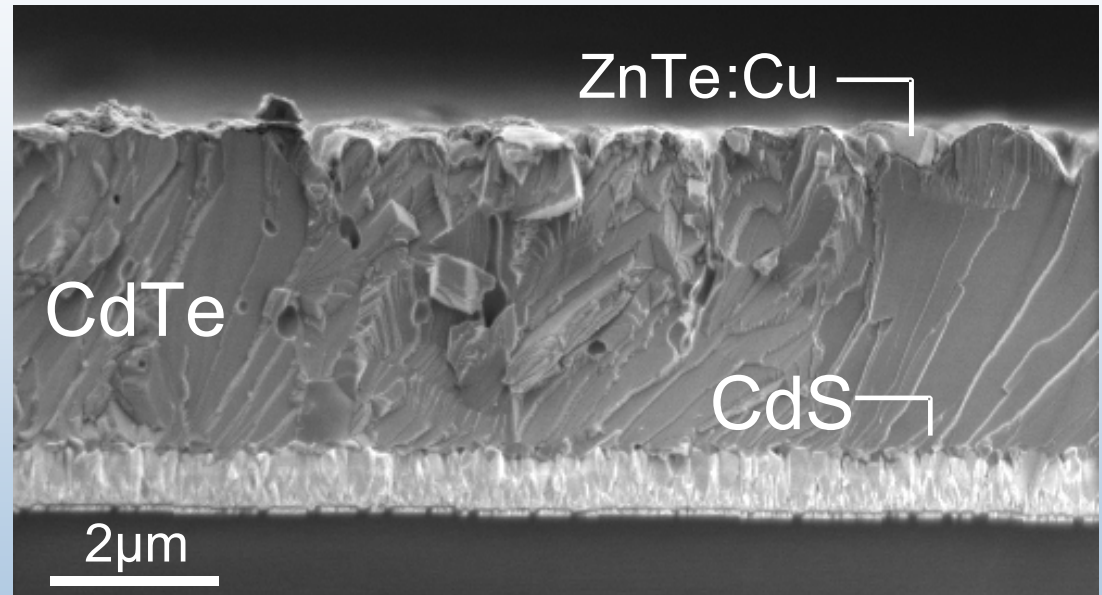
Time: 15 to 30 min.

Vapor Transport
Deposition of CdS

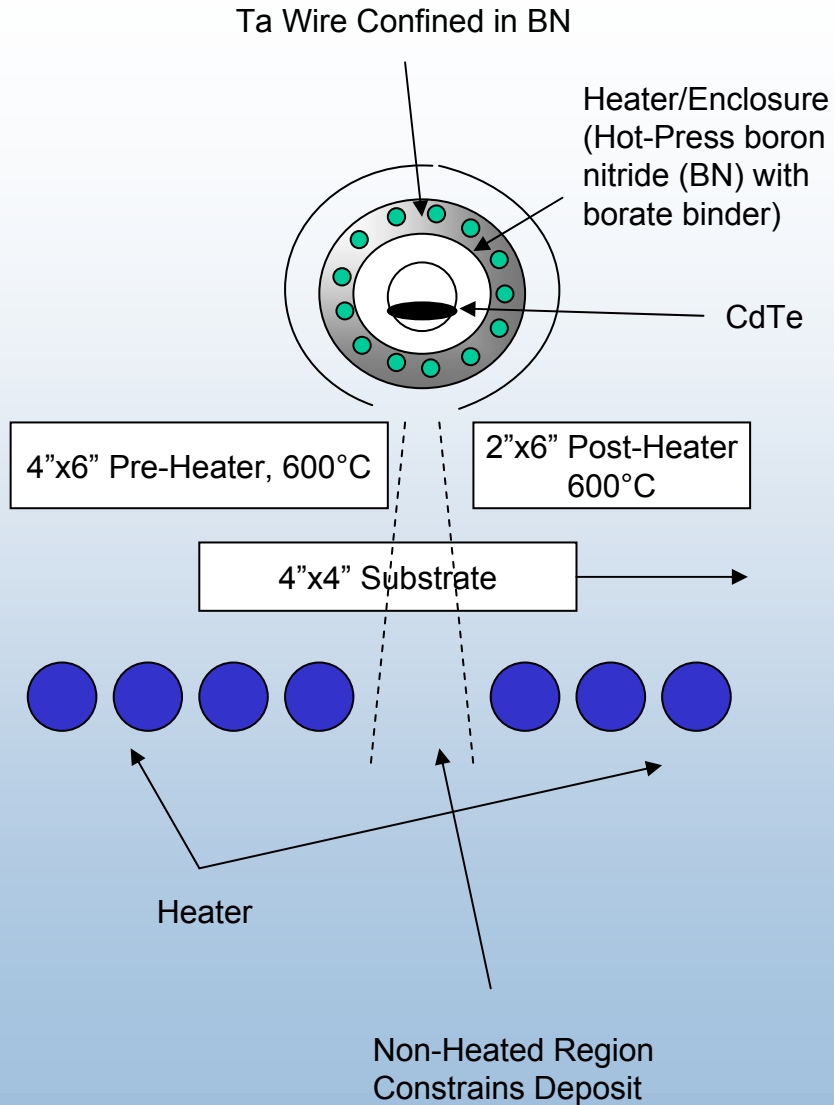


CdTe Thin Film Morphology

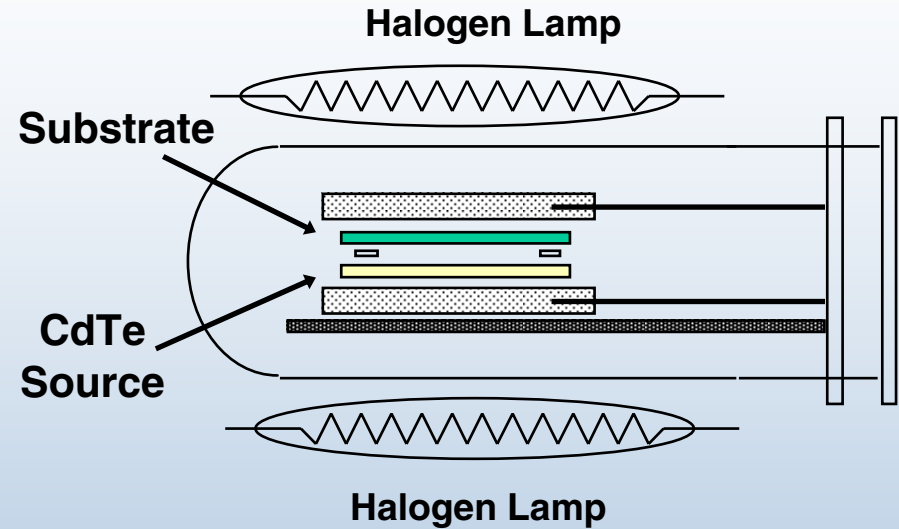
Glass
$\text{SnO}_2, \text{Cd}_2\text{SnO}_4$ - 0.2-0.5 μm
CdS - 600-2000 \AA
CdTe 2-8 μm
C-Paste with Cu, or Metals



IEC VTD



Close Space Sublimation (CSS) Schematic



High-Efficiency CTO/ZTO/CdS/CdTe Cells

Cell #	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	η (%)	Area (cm ²)
W547-A	847.5	25.86	74.45	16.4	1.131
W553-A	849.9	25.50	74.07	16.1	1.029
W566-A	842.7	25.24	76.04	16.2	1.116
W567-A	845.0	25.88	75.51	16.5	1.032
W597-B	835.6	25.25	76.52	16.1	0.961
W608-B	846.3	25.43	74.24	16.0	1.130
W614-B	842.2	25.65	74.67	16.1	0.948

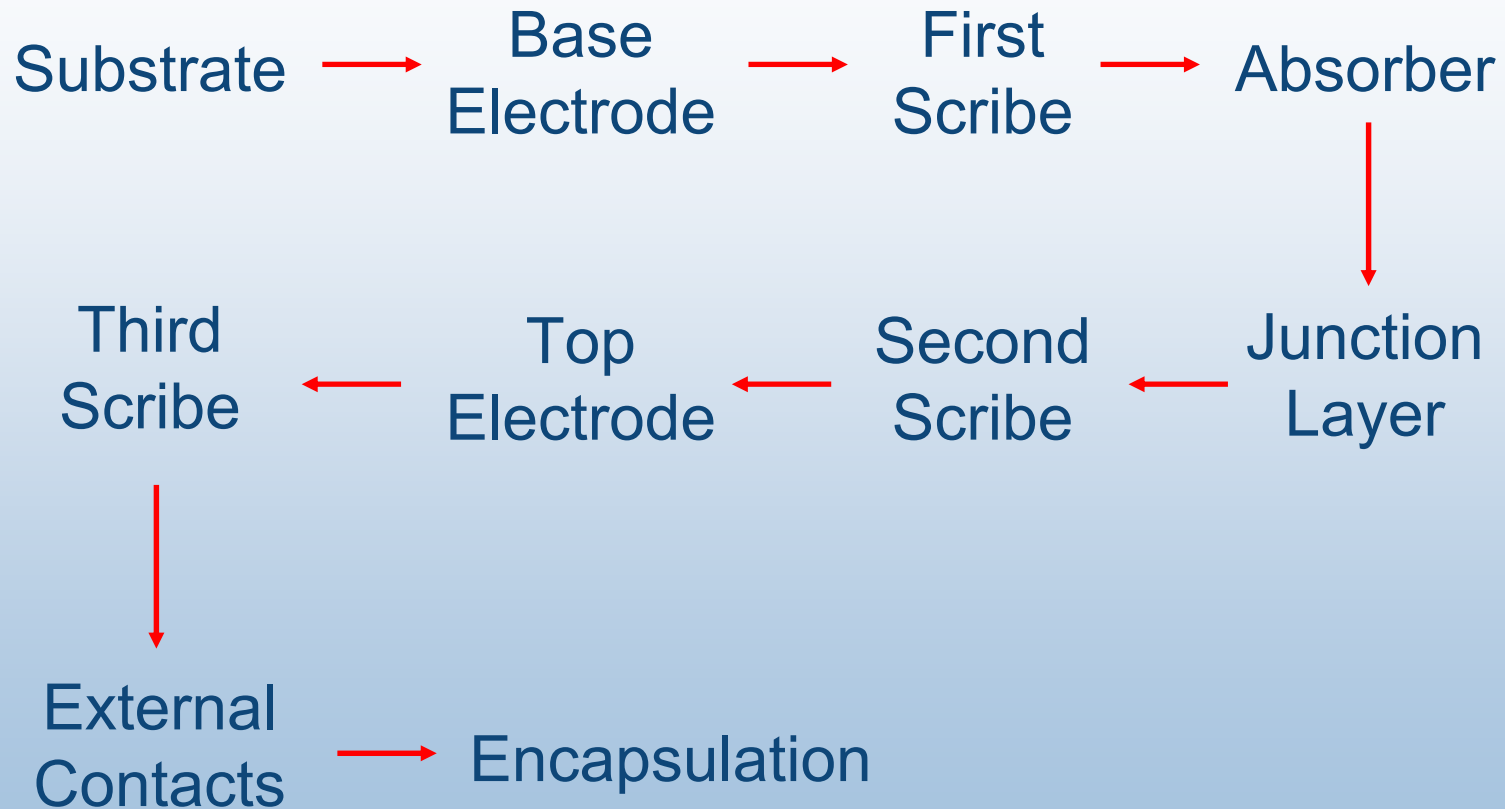
Thin Film Modules

Polycrystalline Thin Film PV Modules (standard conditions, aperture-area) Ranked by Power

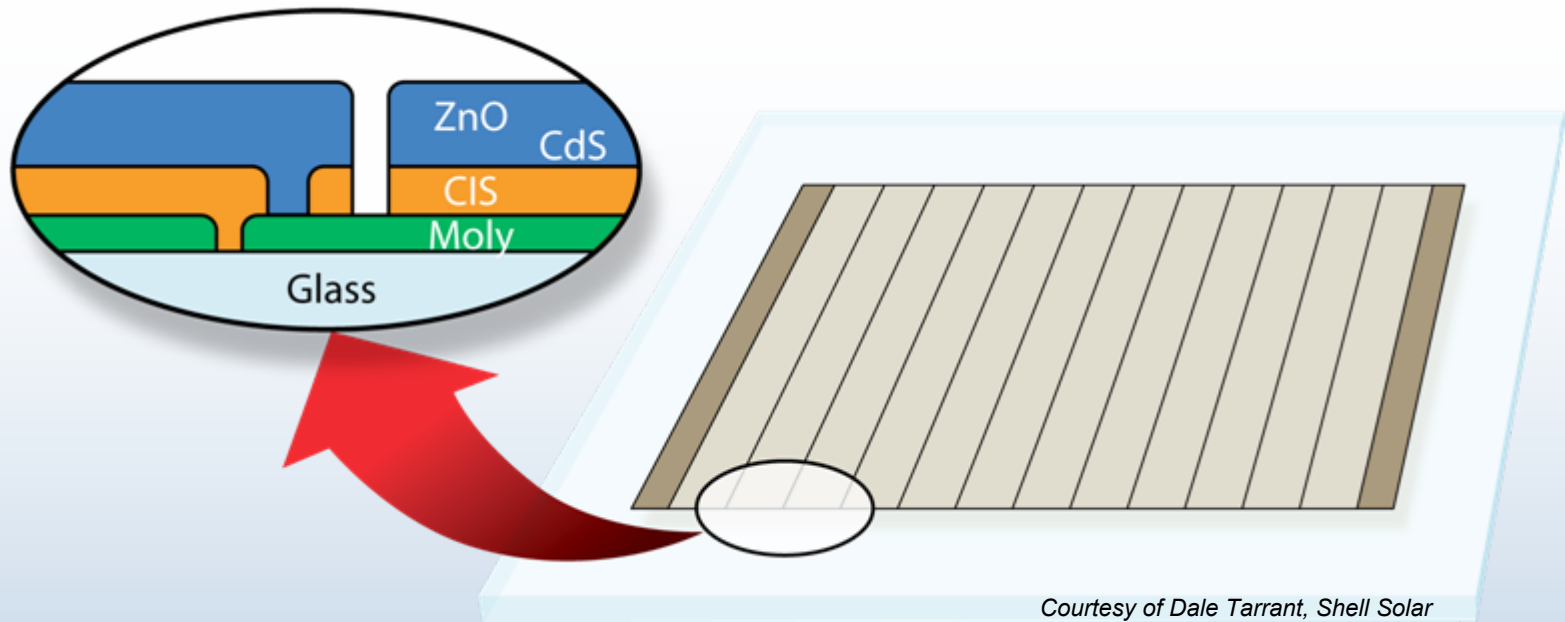
Company	Device	Aperture Area (cm ²)	Efficiency (%)	Power (W)	Date
Global Solar	CIGS	8390	10.2*	88.9*	05/05
Shell Solar	CIGSS	7376	11.7*	86.1*	10/05
Worth Solar	CIGS	6500	13.0	84.6	06/04
First Solar	CdTe	6623	10.2*	67.5*	02/04
Shell Solar GmbH	CIGSS	4938	13.1	64.8	05/03
Antec Solar	CdTe	6633	7.3	52.3	06/04
Shell Solar	CIGSS	3626	12.8*	46.5*	03/03
Showa Shell	CIGS	3600	12.8	44.15	05/03

* NREL Confirmed

CIGS and CdTe Devices and Modules Have Similar Structure and Process Sequence



Module Monolithic Interconnect Scheme



Monolithic integration of TF solar cells can lead to significant manufacturing cost reduction; e.g., fewer processing steps, easier automation, lower consumption of materials.

Shared characteristics lead to similar cost per unit area: $\$/\text{m}^2$.

Efficiency \Rightarrow discriminating factor for cost per watt: $\$/\text{watt}$.

Challenges

Lack of adequate science and engineering knowledge base

- Measurable material properties that are predictive of device and module performance
- Relationship between materials delivery and film growth
- Develop control and diagnostics based on material properties and film growth
- Coupling of this knowledge to industrial processes

Benefits:

- High throughput and high yield at every step of the process
- High degree of reliability and reproducibility
- Higher Performance

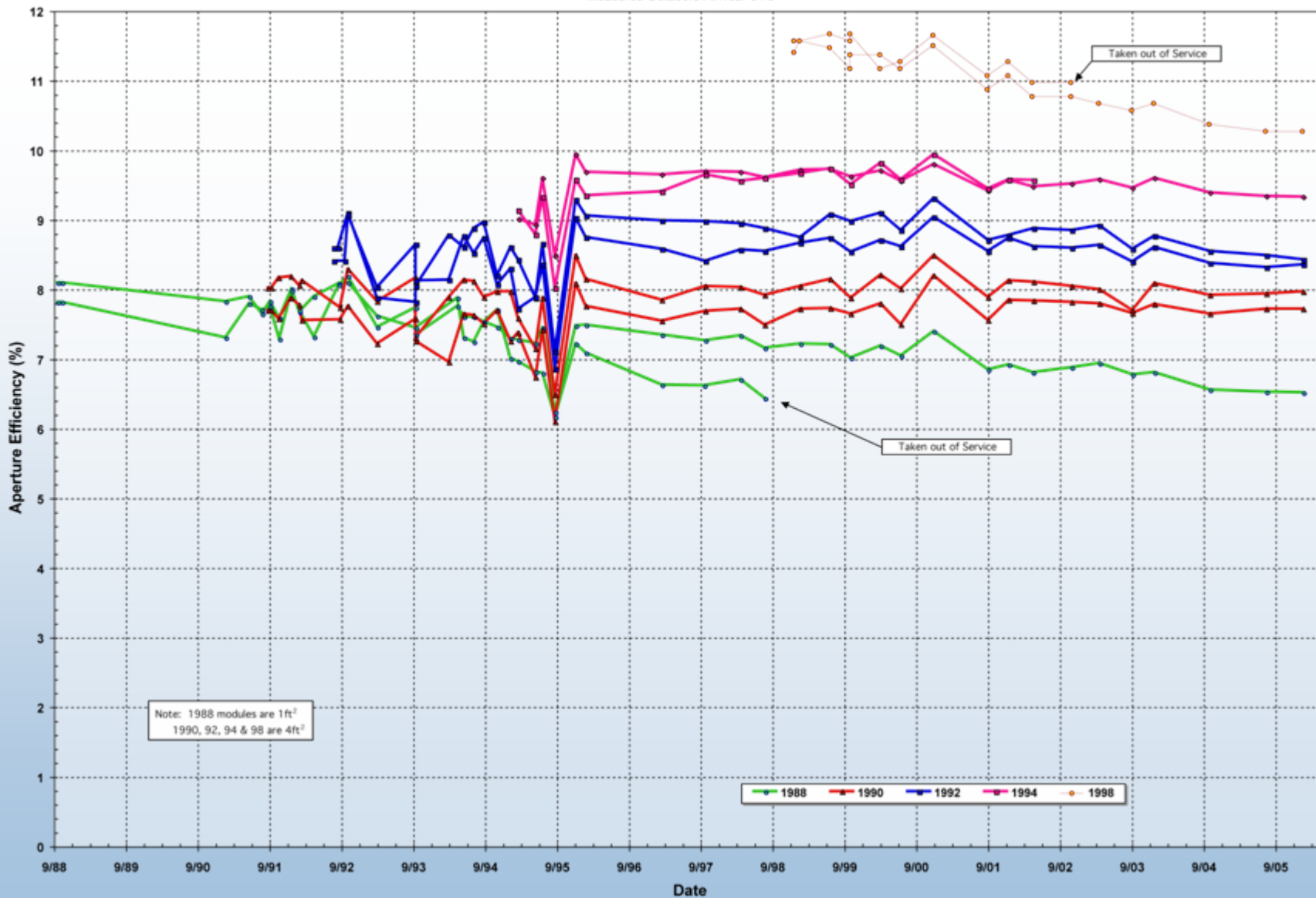
Challenges *(cont.)*

Long-Term Stability (Durability)

- Both technologies have shown long-term stability. However, performance degradation has also been observed.
- CdTe and CIGS devices have different sensitivity to water vapor; e.g., oxidation of metal contact, change in properties of ZnO.
 - Thin Film Barrier to Water Vapor
 - New encapsulants and less aggressive application process
- Need for better understanding degradation mechanisms at the device level and prototype module level.

Siemens Solar Industries CIS Modules

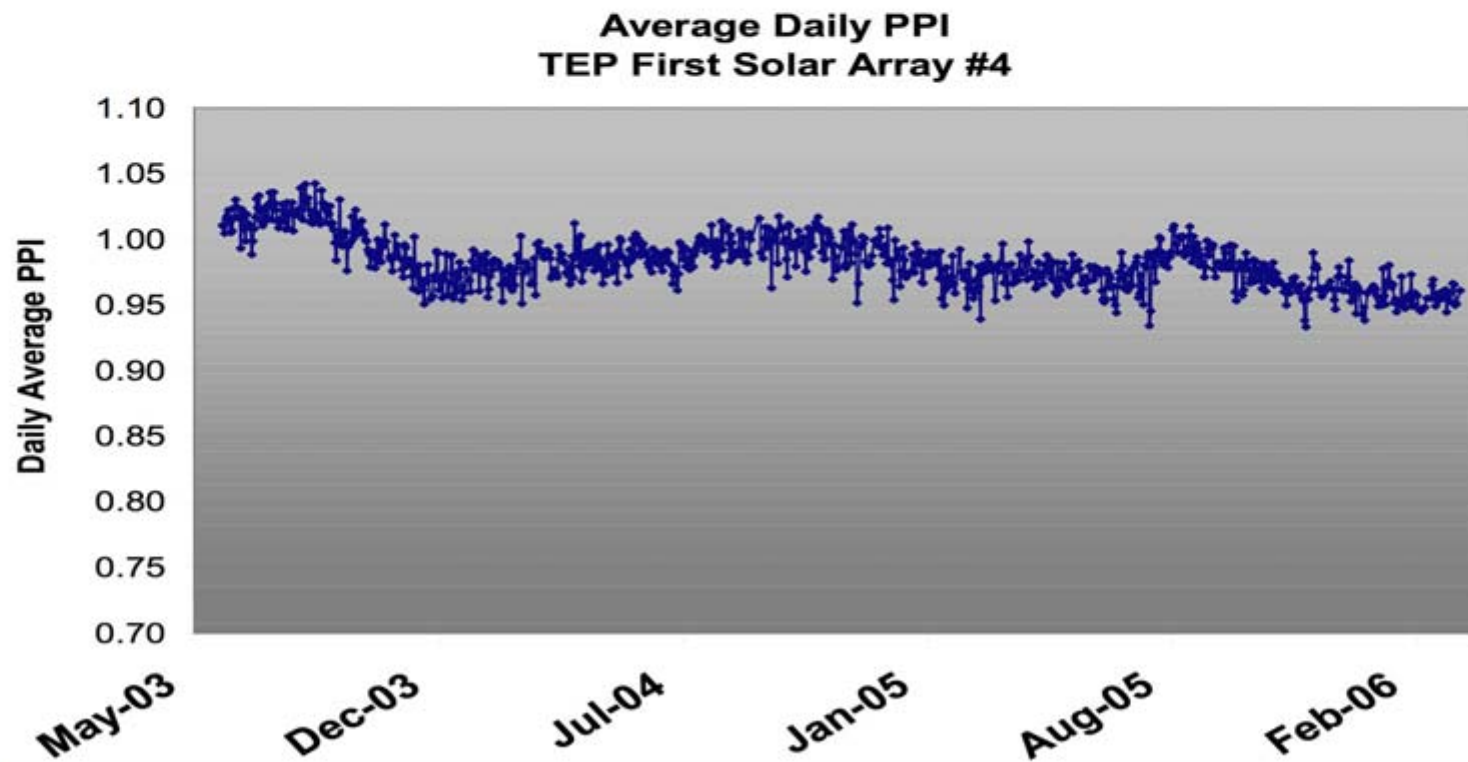
Measured Outdoors At Near STC



Stable Long Term Performance

TEP Array 4 – Tucson Electric Power - Springerville, Arizona

- Longest running, commercial array (commissioned May 2003)
- After the anticipated 3-5% initial stabilization period, the array has maintained a degradation rate of approximately -0.6%/year.



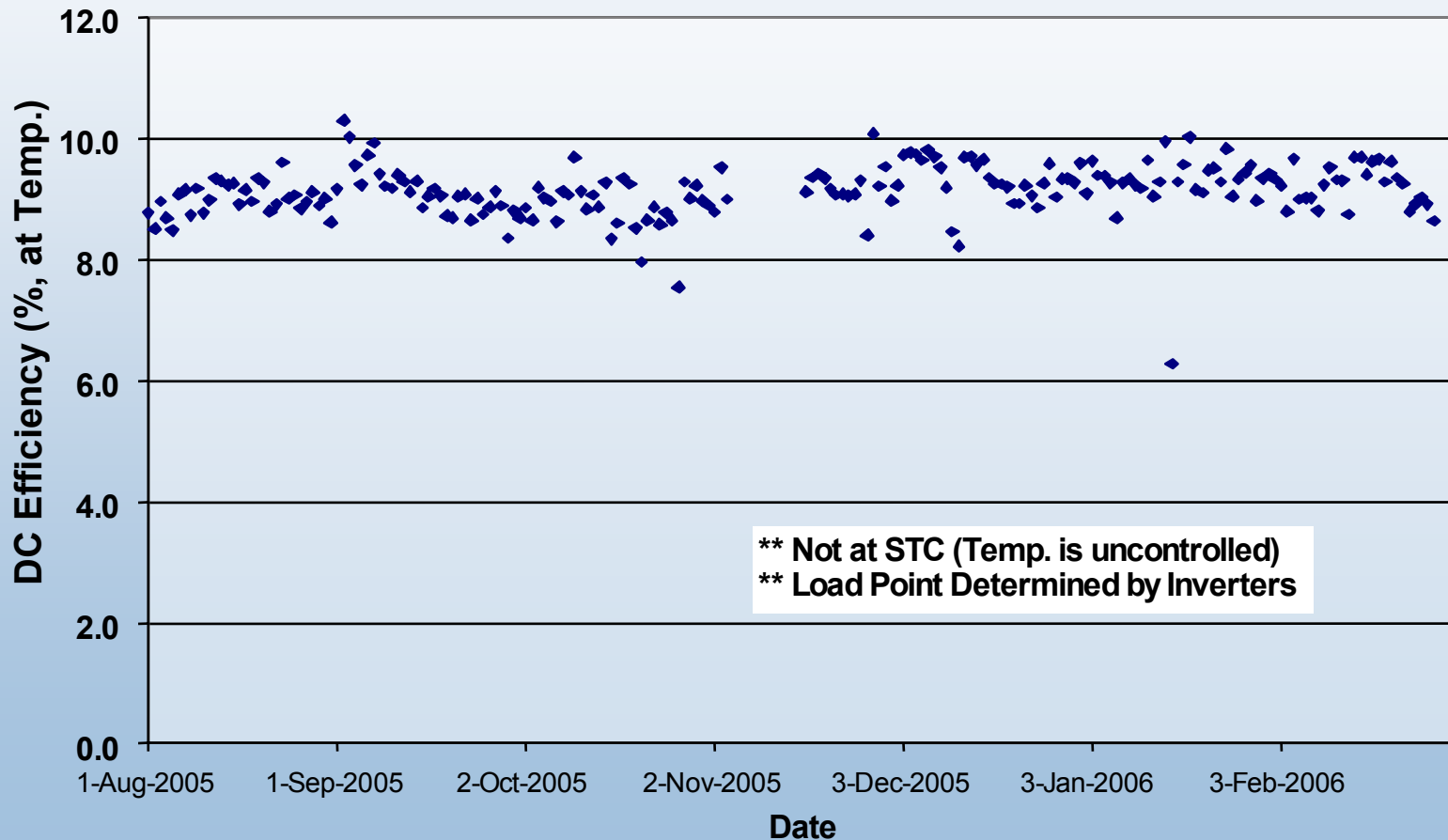
Recent Effort at GSE



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- Product Durability:
Environmental, Lifetime Tests

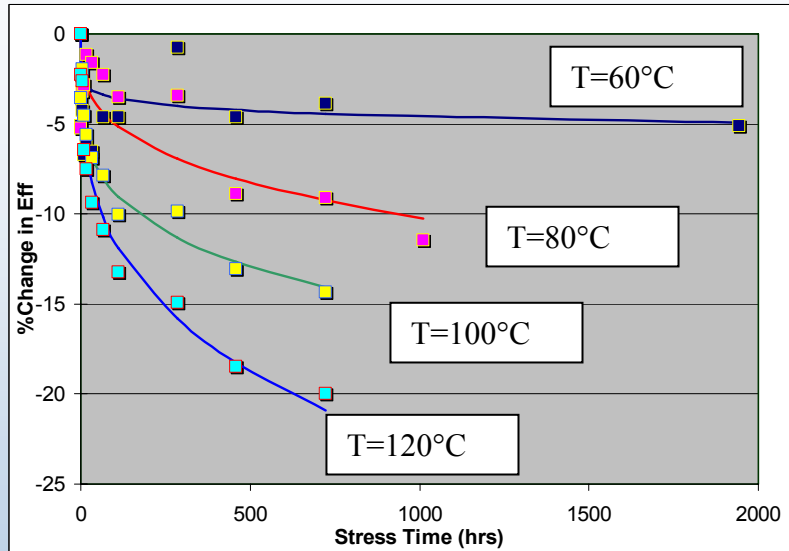
GSE CIGS-Glass (2.3 kW at Springerville, AZ)



Temperature Dependent Degradation

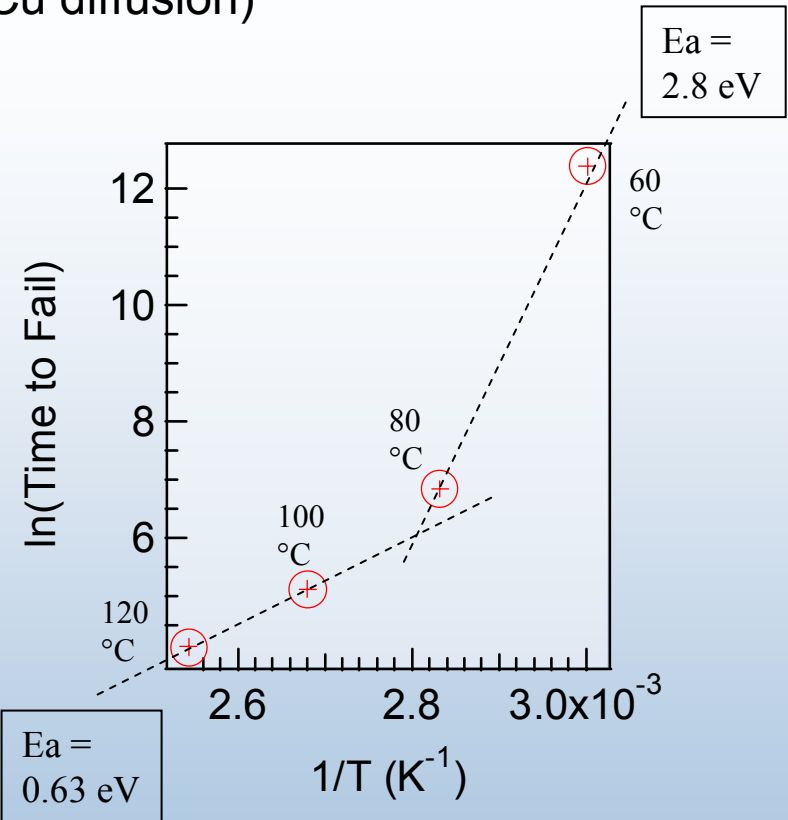
Different mechanisms dominate degradation at different temperatures (~90-120°C associated with Cu diffusion)

Stress Data Fit: $y = b \cdot x^a$



arb. assign 10% as "time to fail"

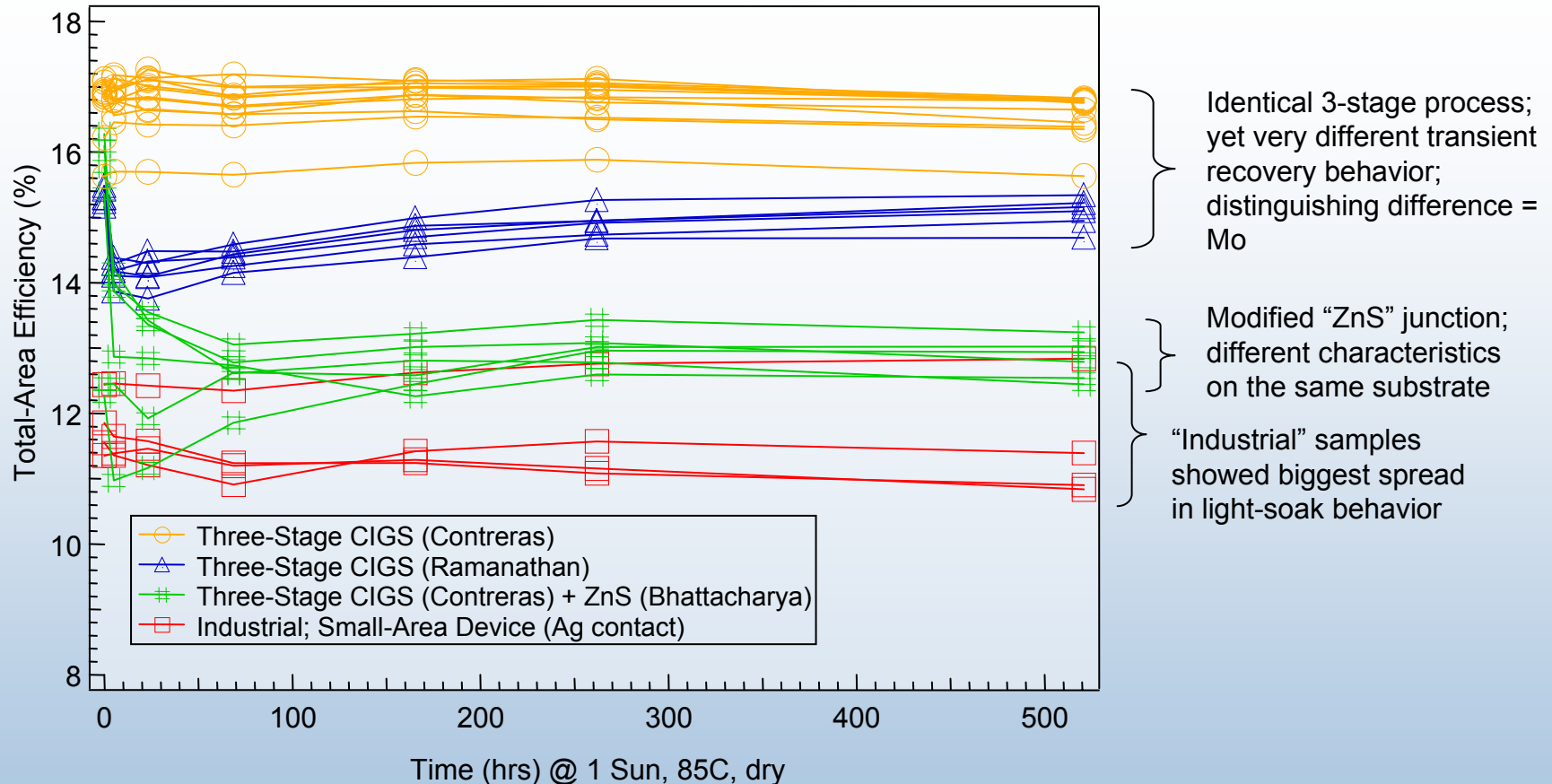
Temp	Time to Failure
60	240000
80	940
100	168
120	62



Cu diffusivity in CdTe:

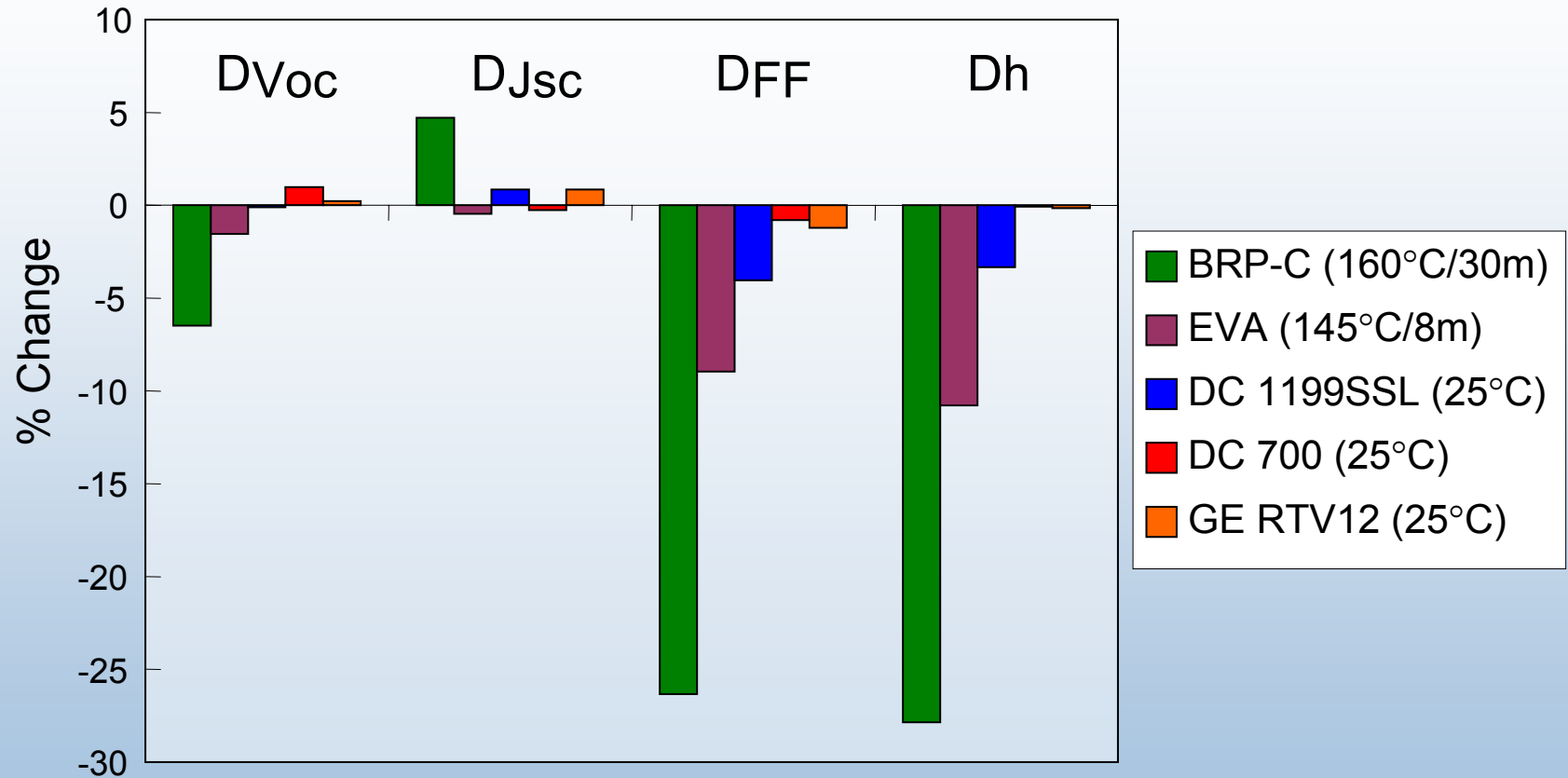
$$D = 3.7 \times 10^{-4} \exp(-0.67 \text{ eV}/kT)$$

CIGS Stability Dry/1-Sun/85° C/ V_{oc} Bias



After some initial “equilibration”, CIGS devices show excellent stability (dry/1-Sun/85°C/ V_{oc} bias)

Lamination Losses with Different Encapsulants



Challenges *(cont.)*

Thinner CIS and CdTe layers

- Current thickness is 1.3 to 8 μm
- Target $<0.5\mu\text{m}$ thick layers
- Maintain state-of-the-art performance
- Requires modification of deposition parameters regime
- Need for models that relate film growth to material delivery
- Device structure that maximizes photon absorption

Benefits:

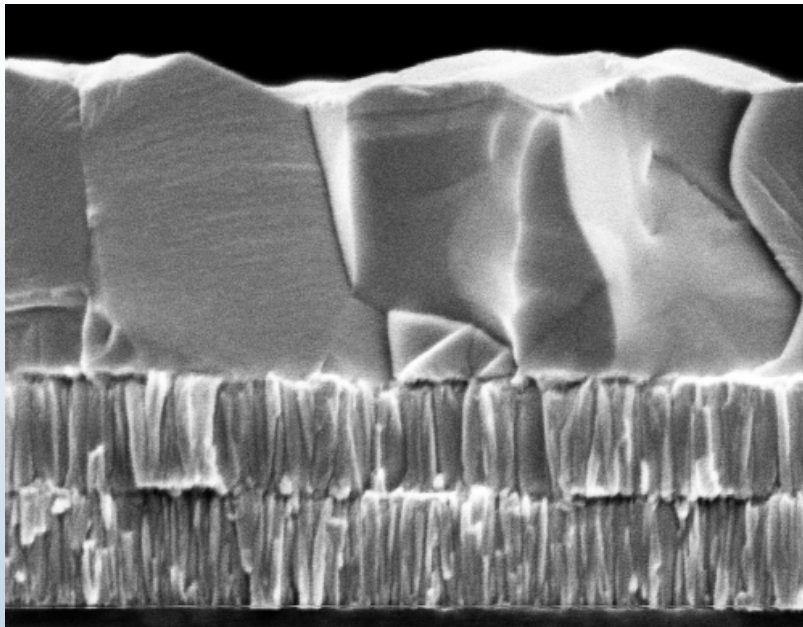
- Addresses the issue of In and Te availability
- Higher throughput
- Less material usage
- Cost??

Risks:

- potential for lower performance
- changes in device physics and structure
- Non-uniformity
- lower yield?

Thinner Absorbers

1 μm



S2264

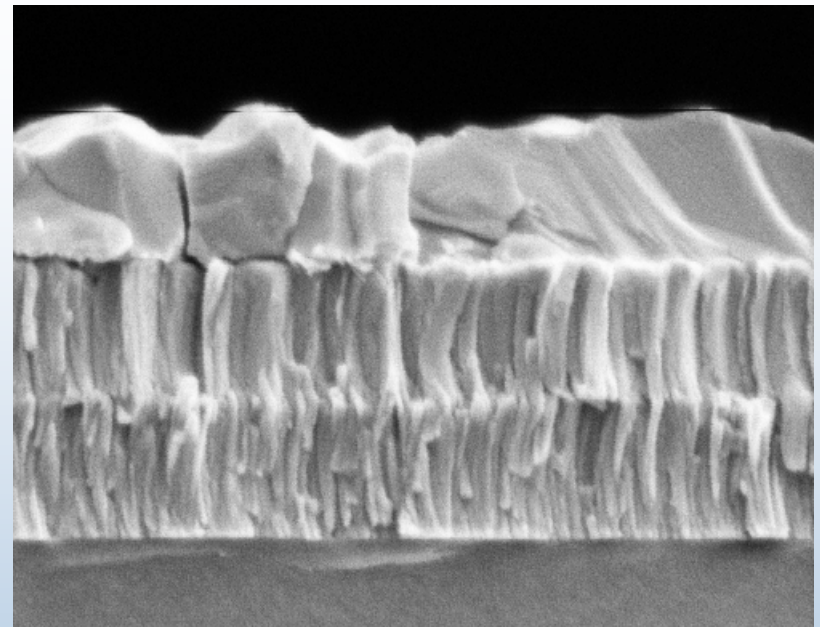
600nm 40000X

$$V_{oc} = 0.676 \text{ V}$$

$$J_{sc} = 32 \text{ mA/cm}^2$$

$$FF = 79.5\%; \text{ Eff} = 17.2\%$$

0.4 μm



S2372

600nm 50000X

$$V_{oc} = 0.565 \text{ V}$$

$$J_{sc} = 21.3 \text{ mA/cm}^2$$

$$FF = 75.7\%; \text{ Eff} = 9.1\%$$

Thin Cells Summary

t (μm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	Eff (%)
1.0 CIGS	0.676	31.96	79.47	17.16 NREL
0.75 CIGS	0.652	26.0	74.0	12.5
0.40 CIGS	0.565	21.3	75.7	9.1
0.47 CIGS	0.576	26.8	64.2	9.9 EPV
1.3 CIGSS Module	25.26	2.66	69.2	12.8 Shell Solar
0.87 CdTe	0.772	22.0	69.7	11.8 U. of Toledo

Challenges *(cont.)*

Need for Low-cost processes

- More relevant to CIGS technology
- Relatively slow throughput and poor material utilization because of complex processes
- High cost of In; ~\$1000/kg
- High rate co-sputtering from the elements (in the presence of Se)
- Non-vacuum or low vacuum, simple equipment
- Innovative processes:
 - CVD-based
 - Nanotechnology utilizing nano-components to make CIGS, e.g. printable CIGS

480-kW Thin Film CdTe Solar Field



Tucson Electric/First Solar

245-kW Thin Film CIGSS Rooftop Array



Wales CIGS - 84 kW





San Diego CIGS - 4 kW

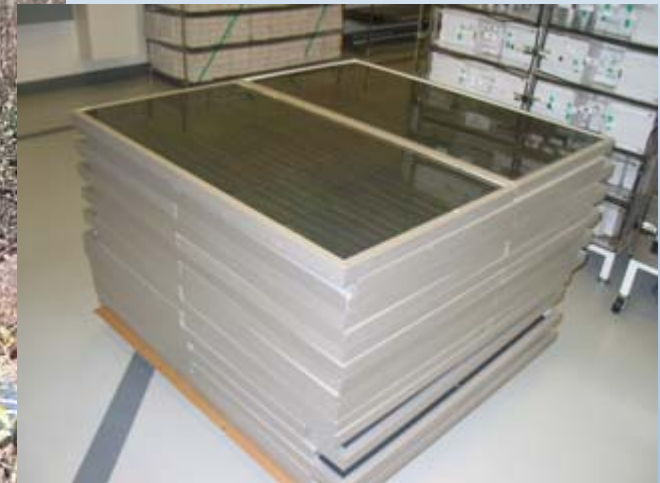




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Flexible PV Technology

- Roll-Roll production of CIGS PV
- Web-based processes for all Mat'l Deposition
 - Stainless Foil or Polyimide Film
 - 1000-ft x 1-ft Process lots



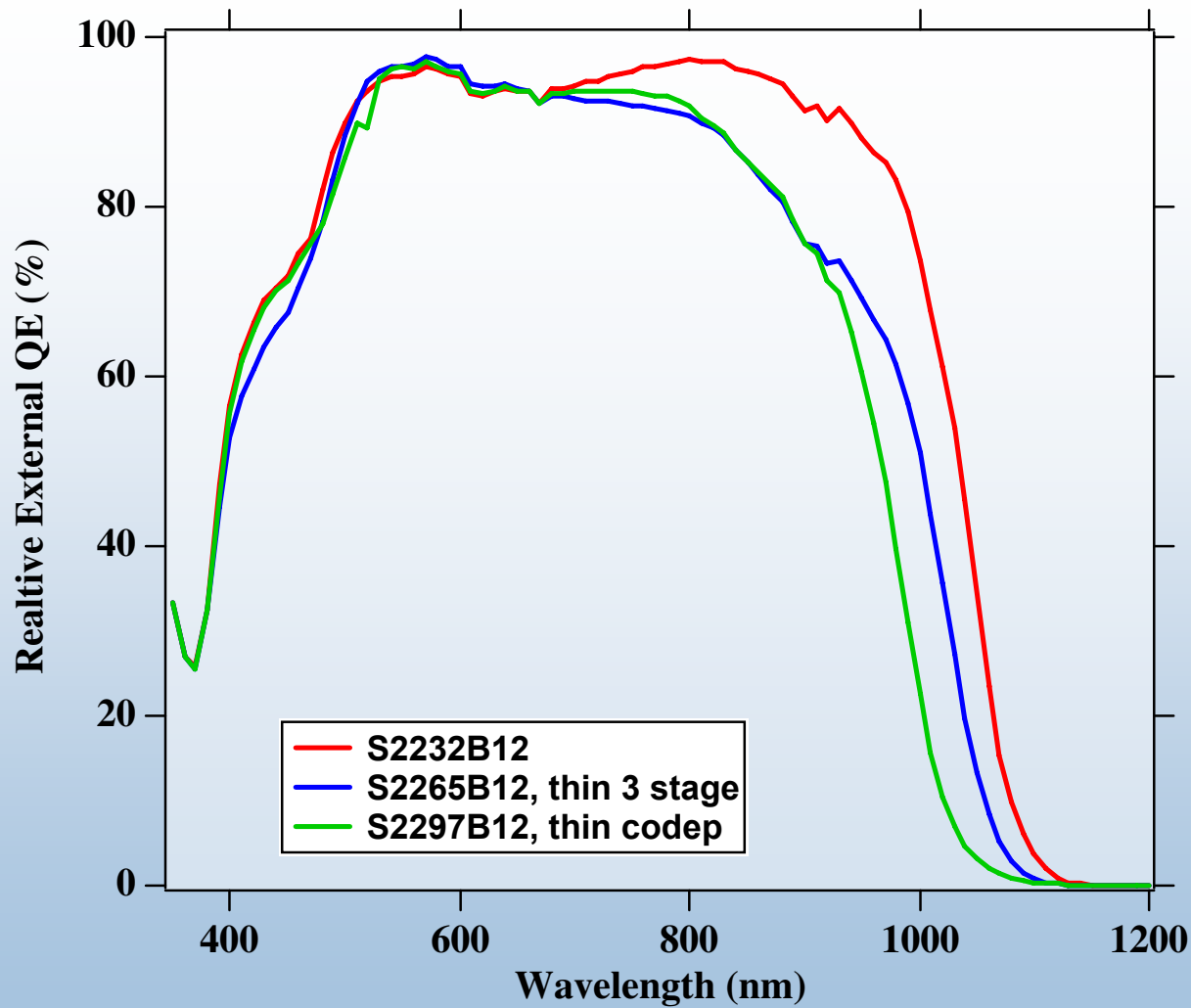
Finally

Thin Film CIGS and CdTe technologies will become cost competitive with Si.

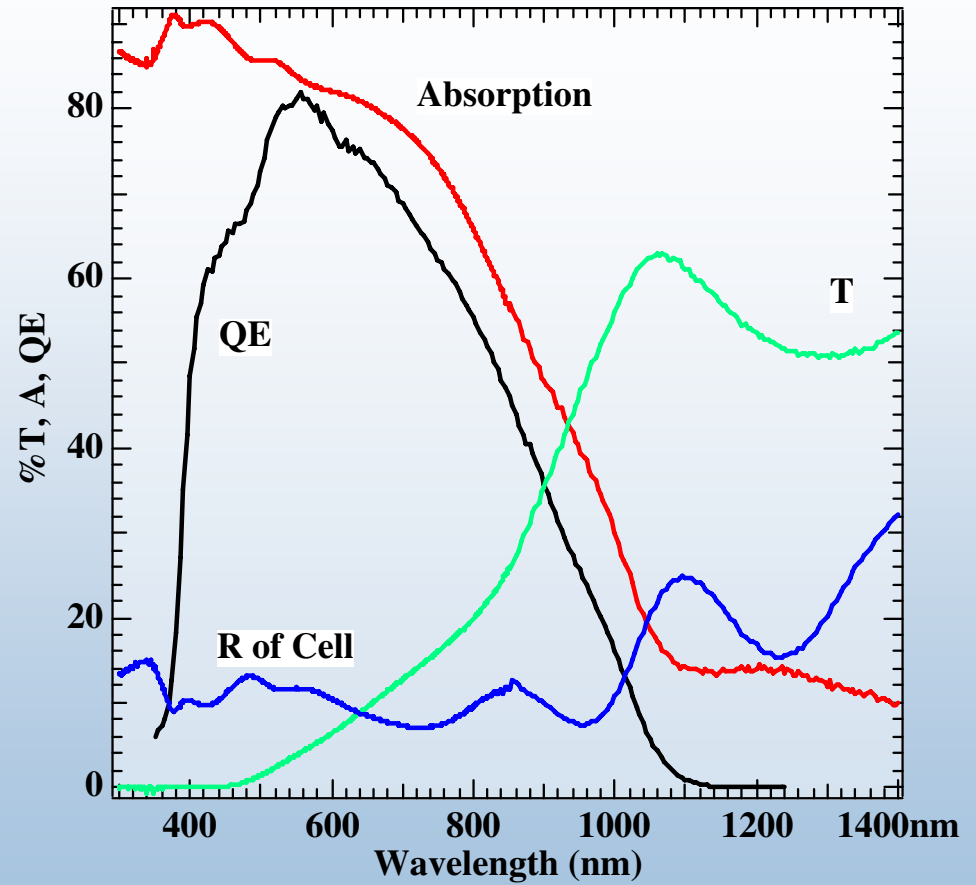
Challenge: obtain large investment for large facility/equipment to take advantage of high throughput and simplified manufacturing.

End

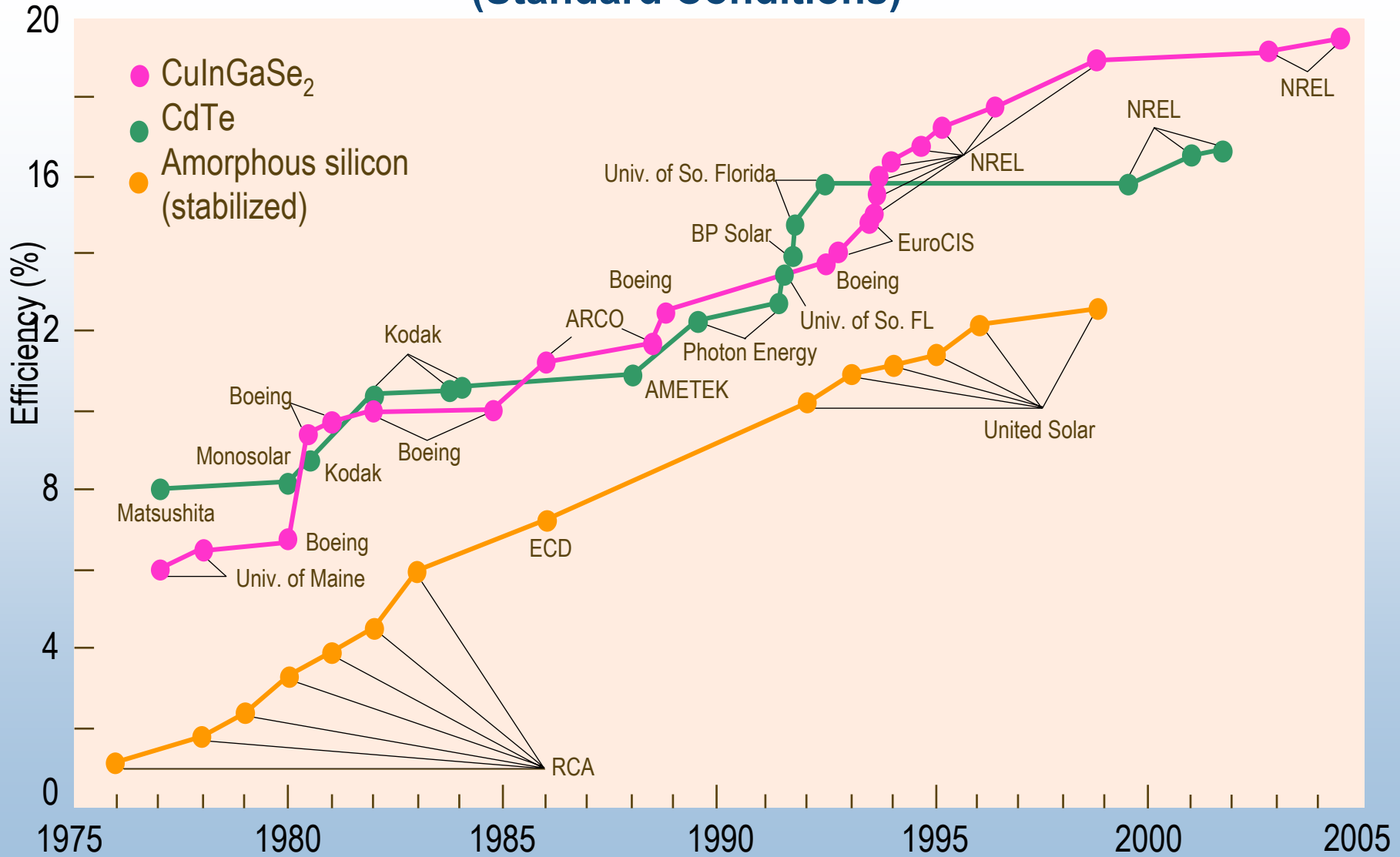
QE



0.4 μm Cell - Optical

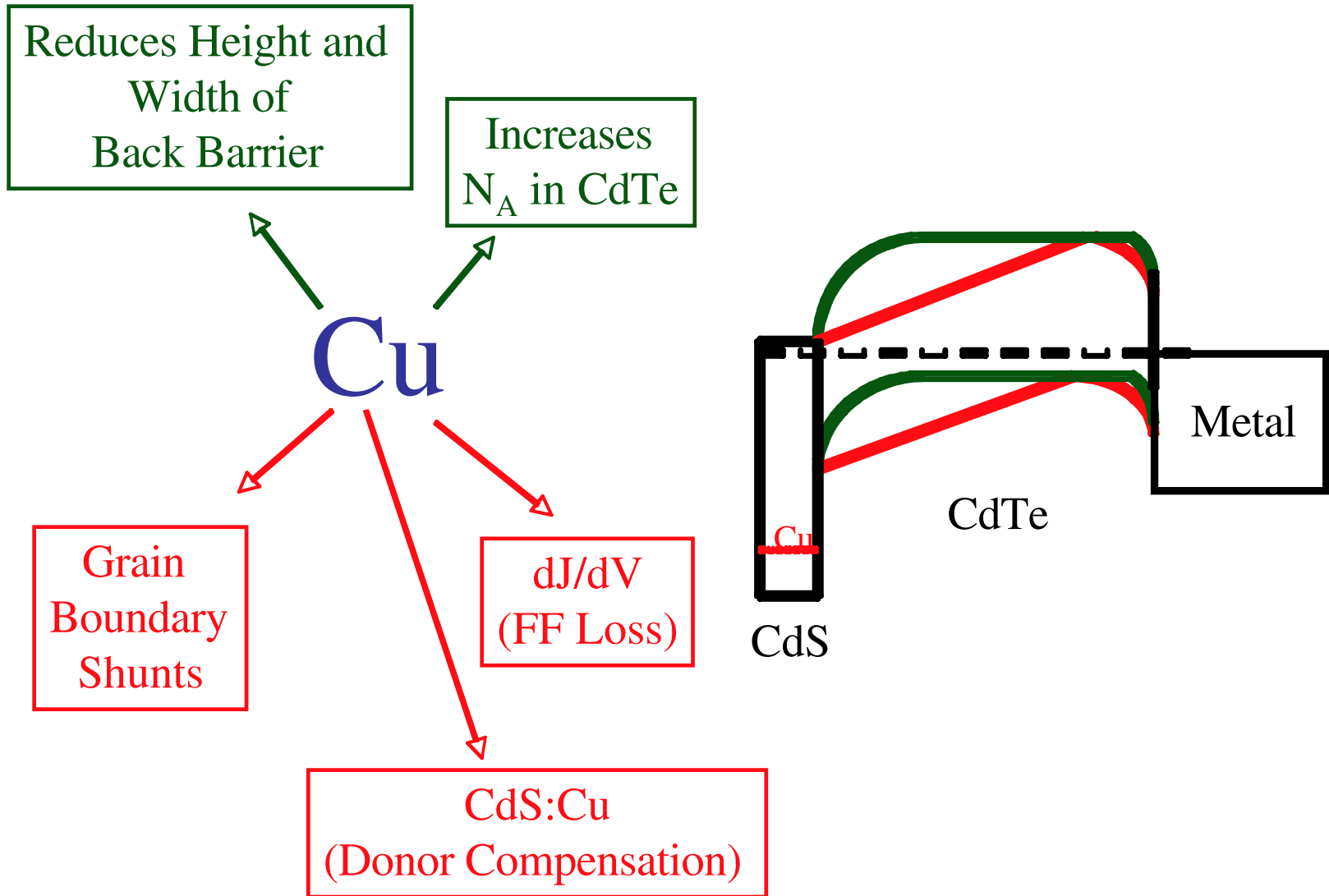


The Best One-of-a-Kind Laboratory Cell Efficiencies for Thin Films (Standard Conditions)



Cu in CdTe PV Devices

The Good, Bad, and the Ugly



High Efficiency CdTe Cells

Replaced SnO_2
with Cd_2SnO_4 in
CdTe cells,
yielding improved
 J_{sc} and FF

High-efficiency CdTe cells with high J_{sc}

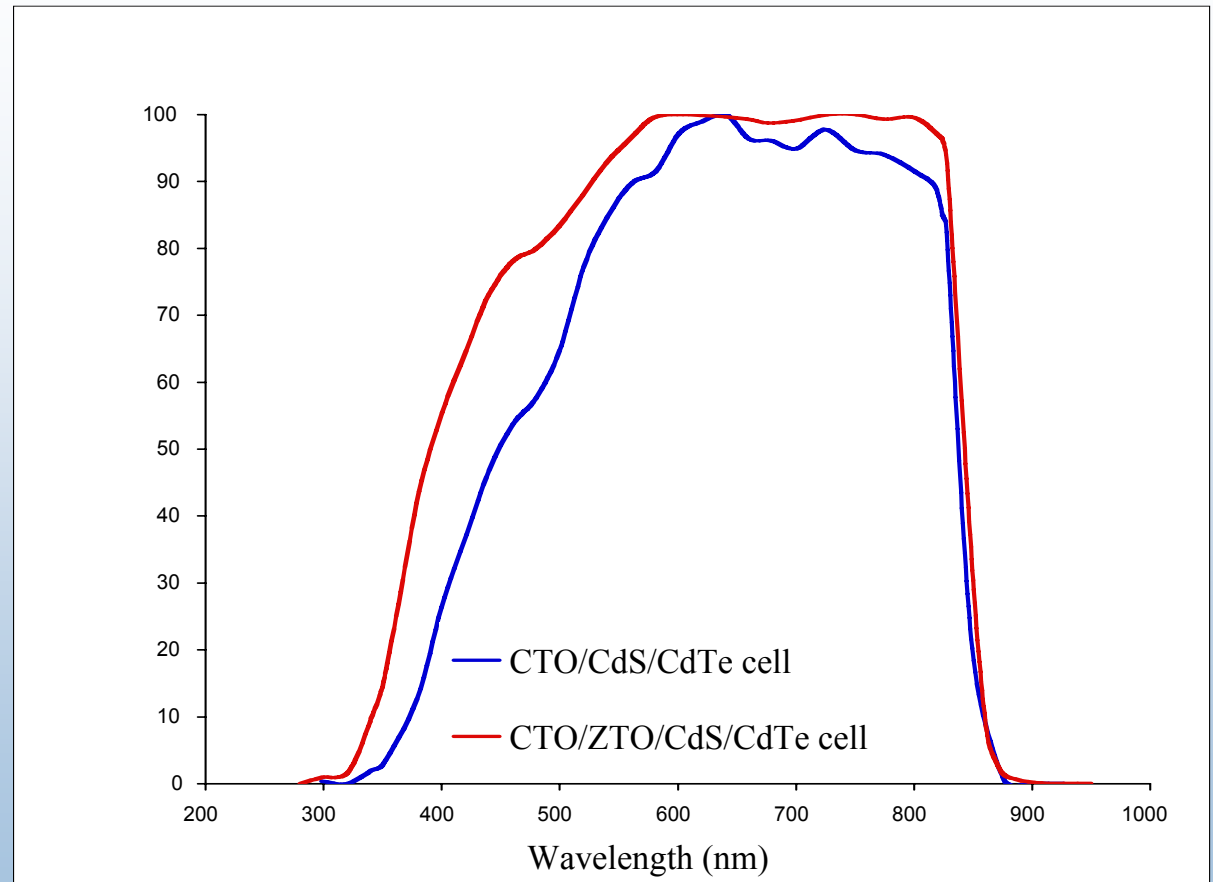
Cell #	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	η (%)	Area (cm ²)
1	847.5	25.86	74.45	16.4	1.131
2	845.0	25.88	75.51	16.5	1.032

High-efficiency CdTe cells with high fill factor

Cell #	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	η (%)	Area (cm ²)
1	842.1	24.12	77.26	15.7	1.001
2	848.1	23.97	77.34	15.7	0.976

Effect of Zn_2SnO_4 Buffer Layer

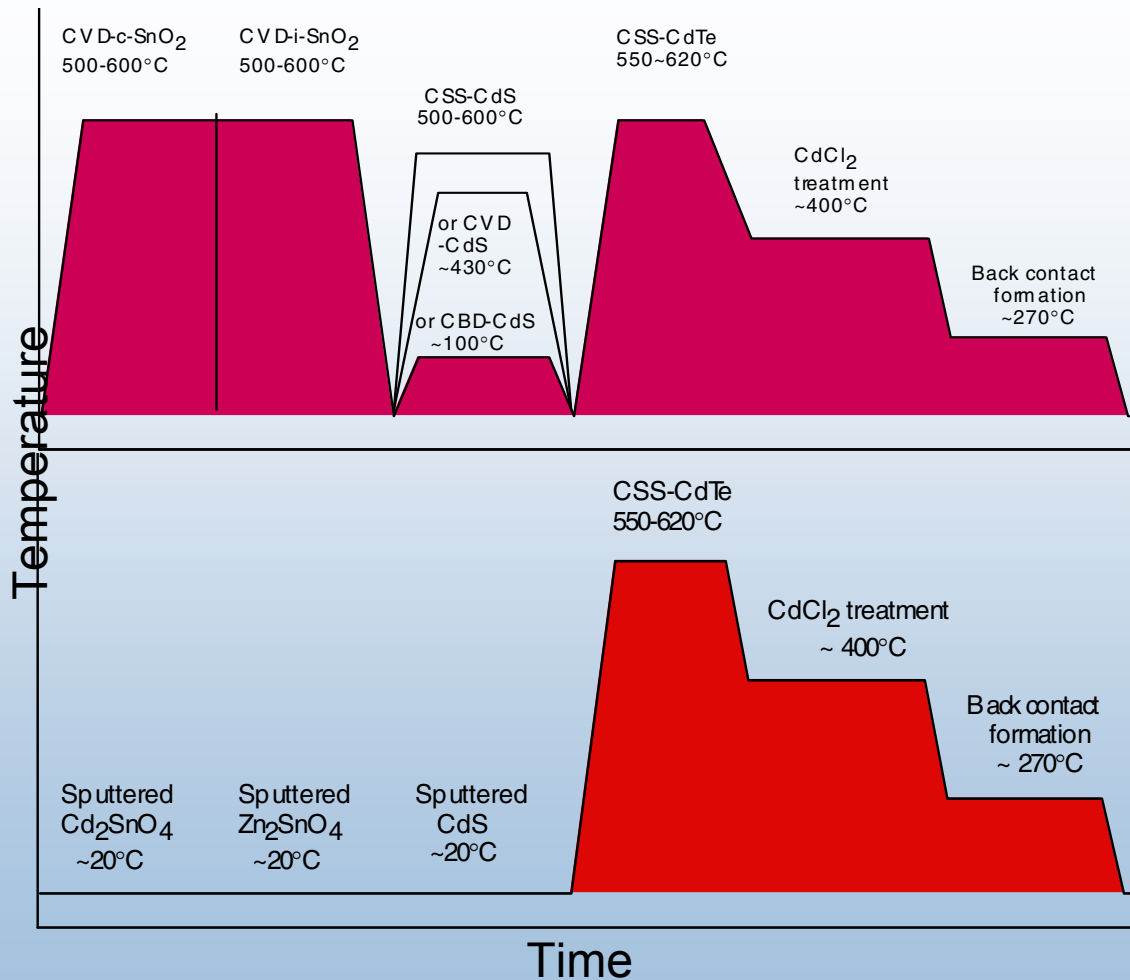
Integrated high-resistivity Zn_2SnO_4 (ZTO) buffer layer, yielding improved device performance and reproducibility



V_{oc} Improvement

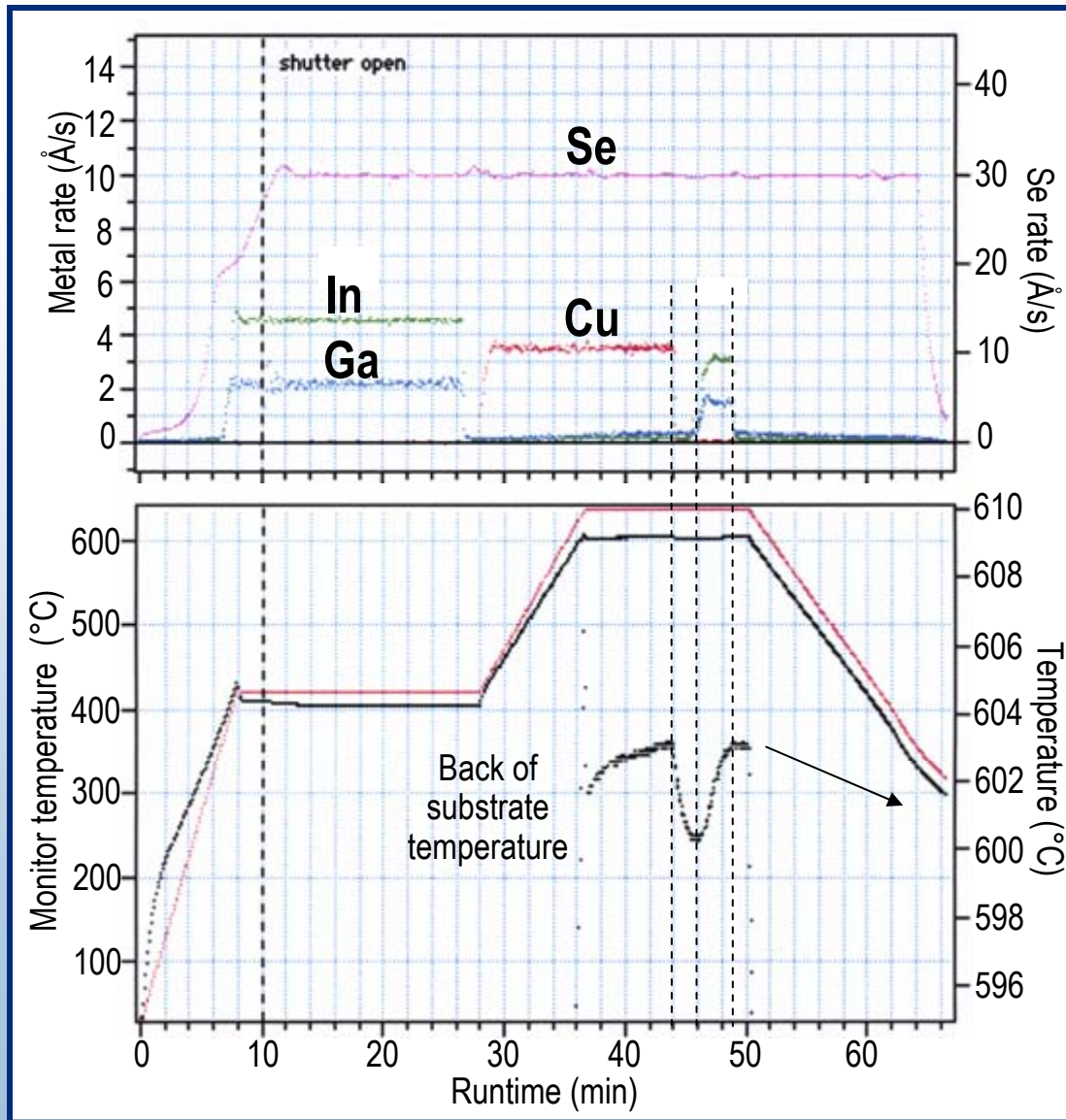
- To achieve CdTe cell with efficiency higher than 16.5%, needs V_{oc} improvement
- V_{oc} improvement :
 - (1) Optimize device process to improve junction quality (reduce A & J_0) and reduce back barrier height;
 - (2) Study defects that limit doping and lifetime in CdTe device
- Achieved an NREL-confirmed V_{oc} of 858 mV in a CdTe cell with an efficiency of 15.6%

Improvement to the Deposition Processes



- Conventional SnO₂/CdS/CdTe device structure (requiring a thicker CdS layer)
- Mix “wet” and “dry” processes
- Several heat-up and cool-down process segments (consuming time and increasing thermal budget)
- CTO, ZTO and CdS are deposited on substrate at RT by RF sputtering
- Single heat-up segment
- Crystallization of CTO, ZTO, and CdS, and interdiffusion occurs during the CdTe deposition step

CIGS Deposition Profile



Global Solar

