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

Denver, Colorado

April 17-19, 2007

Processing, Materials, Devices and Diagnostics for Thin-Film Photovoltaics: Fundamental and Manufacturability Issues

NREL Subcontract #ADJ-1-30630-12

Institute of Energy Conversion
University of Delaware

Designated DOE/NREL Center of Excellence in 1992

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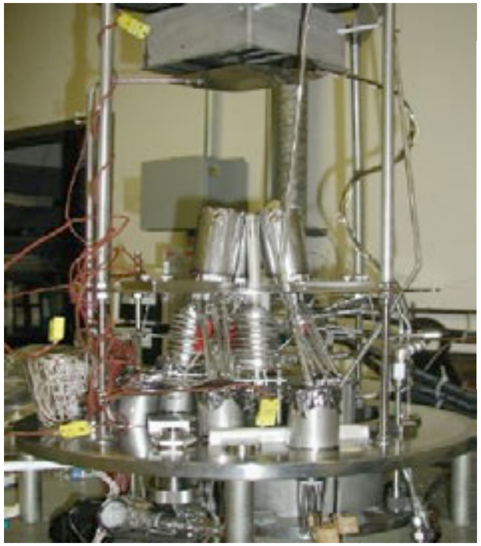
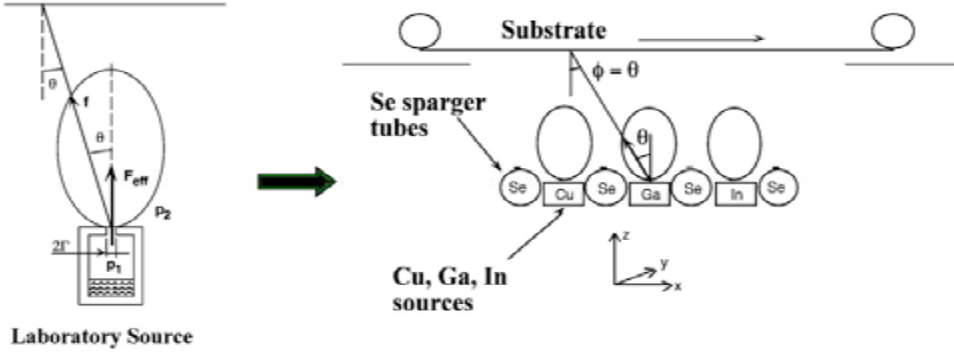
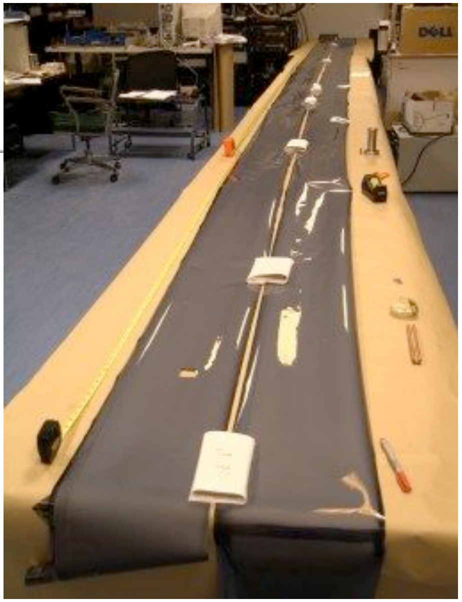
Overall Program Goal

Expand the fundamental science and engineering base for thin film photovoltaics needed to improve module performance and manufacturing technology and effectively transfer these technologies to large-scale manufacturing, supporting DOE's long term goal of 15% thin film module production.







Laboratory scale ⟺ Manufacturing scale

Focus on issues which impact manufacturing cost, such as film thickness, processing throughput and yield, and diagnostic methods for process monitoring.

Technical Program Objectives

- ☐ **Determine the relationships between film composition, structure and opto-electronic properties and solar cell performance emphasizing through-film uniformity, surface reactions, and interface chemistry**
- ☐ **Develop methods or modified material structures to increase V_{OC}**
- ☐ **Characterize the stability of devices and develop alternative processing steps to improve the stability of junction and contacts**
- ☐ **Develop in-situ and/or post-deposition methods to control film structure and electrical properties**
- ☐ **Develop the fundamental understanding needed for high-throughput manufacturing on moving rigid and flexible substrates**
- ☐ **Develop quantitative process models that relate sensor output to process parameters and film properties for use in model-based process control**

Summary of Activities

Technical focus:

- **Thin film PV technologies based on CdTe, $CuInSe_2$ and Si**
- **Low cost processing alternatives for crystalline Si**

Collaborations with:

- **Industry (27 since 2002)**
- **Universities (13) and National Laboratories (3)**

Methods:

- **Multidisciplinary interaction with integrated R&D facility**
- **Maintain baseline processes, perform scale-up engineering**
- **Verify models with pilot-scale systems**

Outcomes:

- **Development and licensing of new technologies to industry**
- **Training of qualified professionals**
- **Promote and support DOE program goals**

Summary of Activities

Five year contract encompassing broad R&D spectrum, from fundamentals to process engineering, provides stable support for an integrated PV laboratory serving as resource for industry, national laboratories and universities by:

- ☐ **Sharing over 34 years of know-how and expertise**
- ☐ **Training people needed for an emerging PV industry**
- ☐ **Access to a well defined baseline process for fabrication of thin film PV cells and a set of material and device characterization techniques that are referenced to an extensive data base**
  - ➢ **Allows individual companies, national laboratories or universities to develop/validate individual processing steps**
- ☐ **Leveraging DOE funding through direct industrial support which accelerates the development of the basic science and engineering required to effectively transfer laboratory results to manufacturing**

Accomplishments

Education / Training past 5 years

- ☐ 25 graduate students
  - ➢ 6 Ph.D. completed
  - ➢ 4 M.S. completed
- ☐ 31 Undergraduate students
- ☐ 17 Postdoctoral Fellows
- ☐ 5 Visiting Scholars

Professional Activities Past 5 Years

- ☐ Publications: over 100
- ☐ Invited talks: 15
- ☐ Patents: 6 issued, 1 provisional
- ☐ Book chapters: 4
- ☐ Conference committees, symposia organization, tutorials: 12

Accomplishments

Task 1. CdTe

- **Successfully designed, developed and implemented high throughput deposition (>10 µm/minute) and processing (1 plate per minute) on 4" x 4" commercial glass/TCO using vapor transport deposition and vapor chloride processing**
- **Achieved cells with V_{OC} > 800 mV and η >13% on commercial soda lime glass**
- **Developed transparent cells and analyzed junction operation of devices with different CdTe thickness**
- **Determined fundamental V_{OC} limit in present-generation CdTe/CdS cells to be ~950 mV**
- **Developed Chemical Surface Deposition (CSD) of CdS and transferred to $CuInSe_2$ based devices.**

See Supplemental Information for Details

Task 2. CuInSe$_2$

- **Developed continuous, roll-to-roll, high-throughput Cu(InGa)Se$_2$ deposition process on polyimide web: deposited over 100 ft with $\eta > 10\%$ on diagnostic cells**
- **Demonstrated cells with Cu(InGa)Se$_2$ thicknesses ≤ 0.5 µm that have no loss in V_{OC} and FF and analyzed device losses for thin absorbers**
- **Evaluated reaction pathways for Cu-Ga-In precursor reacted in H_2Se/H_2S: developed process for uniform Ga distribution to achieve device having $V_{OC} > 640$mV, $\eta = 13.5\%$**
- **Determined relative reaction preferences for formation of $MoSe_2$ and MoS_2 at the Cu(InGa)(SeS)$_2$ back contact**
- **Determined optical constants of Cu(InGa)Se$_2$ relative to Ga and Cu concentrations and in CdS as deposited on Cu(InGa)Se$_2$**

See Supplemental Information for Details

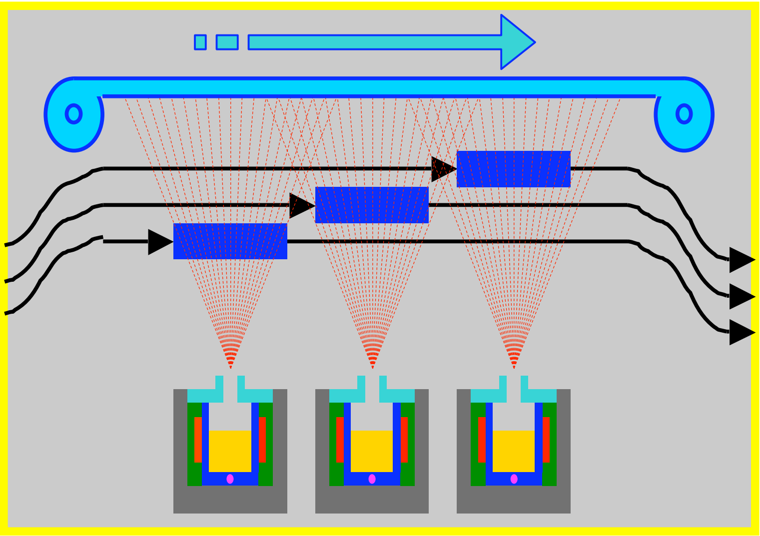
Task 3. Si

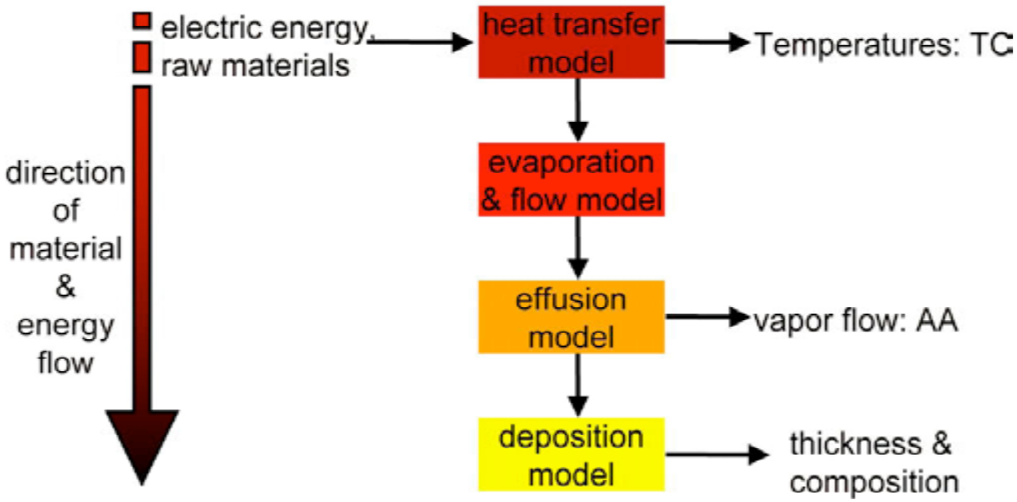
- ❑ **Developed process for aluminum induced crystallization to produce uniform Si film with micron-size grains that could be employed as seed layer for Si film growth**
- ❑ **Developed Si heterojunction solar cells with high performance due to excellent surface passivation: V_{OC} > 700 mV on FZ and > 690 mV on textured Cz material, with peak efficiency of ~19%**
- ❑ **Performed characterization and modeling to determine the effect of interface defects on cell V_{OC} and FF**
- ❑ **Developed all back contact c-Si devices using a-Si technology and fabricated device with $\eta = 11.8\%$ and have also made device with Voc> 0.680 V**

See Supplemental Information for Details

Task 4. Process Diagnostics

- **Developed fundamental heat & mass transfer model and 2d-deposition model for Cu(InGa)Se_2 film deposition**
- **Developed contact wetting angle technique to determine the surface chemical structure of CdTe and predict the effectiveness of the subsequent process treatments**





electric energy
raw materials

direction of material & energy flow

heat transfer model → Temperatures: TC

evaporation & flow model

effusion model → vapor flow: AA

deposition model → thickness & composition

See Supplemental Information for Details

Schedule of Major Events/Milestones

Successful expansion of fundamental science and engineering base needed for:

- **low cost manufacturing and implementation of CdTe and CuInSe$_2$ based thin film photovoltaics**
- **diagnostic tools for process control and product testing**

Transitioned a-Si program to develop hybrid crystalline silicon devices incorporating a-Si junction and contacts

Transferred science and engineering tools to photovoltaic industry through direct contracts, collaboration under NREL teams, and licensing agreements. On-going effort directed at SAI and other synergistic activities:

Solar America Initiative: Technology Pathway Partnerships

- **Team member on nine partnership programs**
  ⇒ four awarded contracts: Dow Chemical, GE Energy, Konarka & Miasole

Solar America Initiative: Future Programs

- **PV Incubator**
- **University Research & Development Support for SAI Technology Pathway Partnerships**
- **Applied Research for Future Generation Solar Electric Technologies**

Future Work: Critical R&D Issues

CdTe-based solar cell technology

- **Develop pathway to increase module performance from ~9% to 15%**
- **Reduce CdTe thickness**

$CuInSe_2$-based solar cell technology

- **Pathway to 15% module known but need to develop engineering base to transfer laboratory results to manufacturing environment**
- **Develop high V_{OC} $CuInSe_2$-based materials for improved module performance and potential for multi-junction structures**

Future Work: Critical R&D Issues

Si-based solar cell technology

- ☐ Increase efficiency in heterojunction device to >20% using low temperature processing
- ☐ Identify new heterostructures for higher efficiency and low cost

Process diagnostics and on-line sensors

- ☐ Identify and develop predictive sensors that can be used for process and product quality control needed for high throughput manufacturing

Future Work: Critical R&D Issues

Basic research for PV technologies

- ☐ **Fundamental science and engineering needed to underpin manufacturing needs to be continued:**
  - ➢ **c-Si has largest science base but significant advances over the past 5 to 10 years have resulted from R&D efforts**
  - ➢ **a-Si has reasonable science base but significant advance are being made in high rate manufacturing and stability based on R&D**
  - ➢ **CdTe & $CuInSe_2$ based thin film materials have a limited scientific base since the primary use is for PV so there is no complimentary R&D to augment the development ⇒ R&D critical to long term success**

IEC: Resource to the PV Community

Providing over 34 years of know-how and technology developed under government and industrial R&D support through: (past 5 years)

- ☐ **Joint research programs: SBIR, lower tier subcontracts, other**
  - **Foster Miller, Inc., ITN Energy Systems, Triton Systems, Inc., Unisun, AstroPower, Ultrafine Technologies**
  - **Georgia Institute of Technology, Hawaii Natural Energy Institute, University of Toledo**
- ☐ **Direct industrial funding: contracts, PO's**
  - **Global Solar Energy, BP Solar, Davis, Joseph & Negley, Shell Solar, Engelhard Corp., DuPont, Nanosolar, Miasolé, DayStar Technologies, Solyndra, SoloPower, Ascent Solar, GE Solar, ITN Energy Systems, ISET, Applied Materials, Stellaris, Foster Miller, Q1 Nanosystems, Ultrafine Technologies, Cermat, Gronet Technologies, Ceramem, AstroPower, Unisun, NPC America, Schafer**

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IEC: Resource to the PV Community

Providing over 34 years of know-how and technology developed under government and industrial R&D support through: (past 5 years)

- ☐ **Collaborative research efforts: universities, industry, national labs**
  - **National Thin Film Teams, National Renewable Energy Lab, Los Alamos National Lab, Idaho National Lab (BES proposal)**
  - **Florida Solar Energy Center, Colorado State University, Ohio State University, University of Florida, University of Illinois, University of Oregon, University of Nebraska, Oregon State University, University of Nevada Las Vegas, University of Syracuse, Washington State University, University of Hawaii, University of Texas (BES proposal)**
  - **First Solar, Miasole, Energy Photovoltaics, ISET, Solar Fields, Canrom, AFG Glass, Ceramem**
- ☐ **Solar America Initiative /Technology Pathway Partnership:**
  - **Partner on 4 programs**

Designated DOE/NREL Center of Excellence in 1992

IEC: Resource to the PV Community

Integrated laboratory for materials processing and characterization; device fabrication and analysis; process engineering ⇒ accessible to PV industries, national laboratories and universities

- **Over 20 deposition systems: PVD, Vapor Transport, CSVT, HWCVD, PECVD, sputtering, H_2S/H_2Se reaction, chemical bath**
- **Materials characterization: XRD, GIXRD, VASE, EDS, SEM, AFM, AAS, XPS, optical transmission and reflection, Hall effect**
  - **TEM, HRTEM, Raman at U. of Delaware, supported by IEC**
- **Film processing: controlled ambient furnaces, vapor halide, photolithography**
- **Device fabrication: complete capability for high efficiency a-Si, CdTe, and $Cu(InGa)Se_2$ solar cells**
- **Device characterization: J-V-T, QE, C-V, OBIC, controlled ambient stress**

IEC over past 10 years expanded its deposition and analytic capabilities through the acquisition of over $4M of equipment obtained through direct purchase or donations.

Designated DOE/NREL Center of Excellence in 1992

Supplemental Information

Institute of Energy Conversion

Who we are: **A multidisciplinary R&D team of scientists, engineers, faculty, post doctoral fellows, visiting scholars, and graduate and undergraduate students from physics, chemistry, materials science and electrical and chemical engineering. Entire staff and operation is supported by contracts.**

What we do: **Integrated research supported by U.S. Government, the photovoltaic industry, and University of Delaware consisting of:**

- **Deposition of semiconductor, metallic and oxide thin films**
- **Electrical, optical and structural characterization of thin films and devices**
- **Development and optimization of device fabrication processes**
- **Design, construction and operation of experimental systems**
- **Chemical reaction and reactor analysis as it applies to thin film processing**
- **Process diagnostics and on-line sensors**
- **Flexible solar cells, hybrid designs and tandem solar cells**
- **Solar Cell Materials: CdTe-alloys, $CuInSe_2$-alloys, Silicon (cryst. & a-Si)**

IEC: Resource to the PV Community

Providing direct technical support to the US PV Industry for 34 years. Selected examples over past five years and ongoing include:

Chevron (Cu_2S/CdS) Historic:

- IEC developed first commercial-scale roll-to-roll semiconductor thin film deposition system (1980)

First Solar (CdTe):

- Evaluated effect of contacts, surface chemistry and morphology on CdTe stability

BP Solar (CdTe):

- Optimized post-deposition CdTe process achieving higher efficiency and stability
- Chemical and mechanical failure analysis of completed CdTe modules

BP Solar (Si):

- Improved SnO_2/a-SiC interface for higher module FF
- Investigated passivation and low temperature processing for mc-Si wafers

IEC: Resource to the PV Community

Providing direct technical support to the US PV Industry for 34 years. Selected examples over past five years and ongoing include:

Global Solar Energy- GSE [$Cu(InGa)Se_2$]:

- **Provided the fundamental $Cu(InGa)Se_2$ technology for a DARPA consortium that formed the basis for founding Global Solar Energy**
- **Source design, evaluation of flexible substrates, and device characterization**
- **Transferred technology for high utilization CdS deposition**

Miasolé [$Cu(InGa)Se_2$]:

- **Fabricated and characterized devices to validate sputtered $Cu(InGa)Se_2$ process ⇒ lead to private funding for company**
- **Ongoing characterization of materials and devices**

Daystar, EPV, Nanosolar, SoloPower, Solyndra, Unisun [$Cu(InGa)Se_2$]:

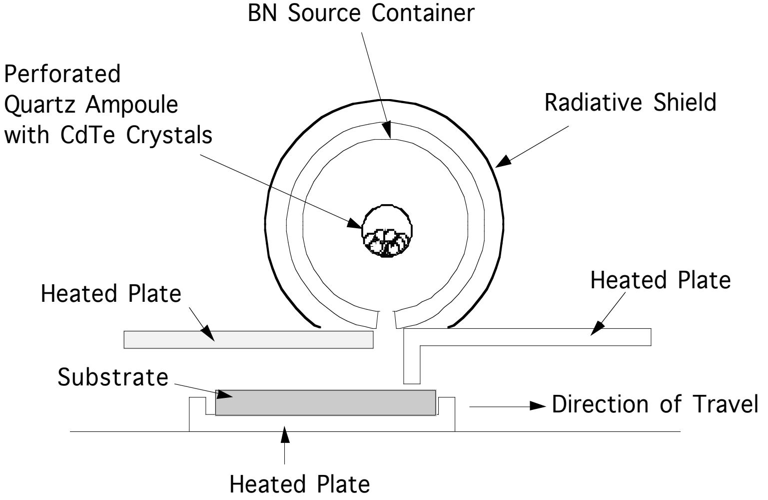
- **Utilize IEC's baseline process to develop and validate their cell fabrication processes**
- **Analysis of materials and devices supplied by company**

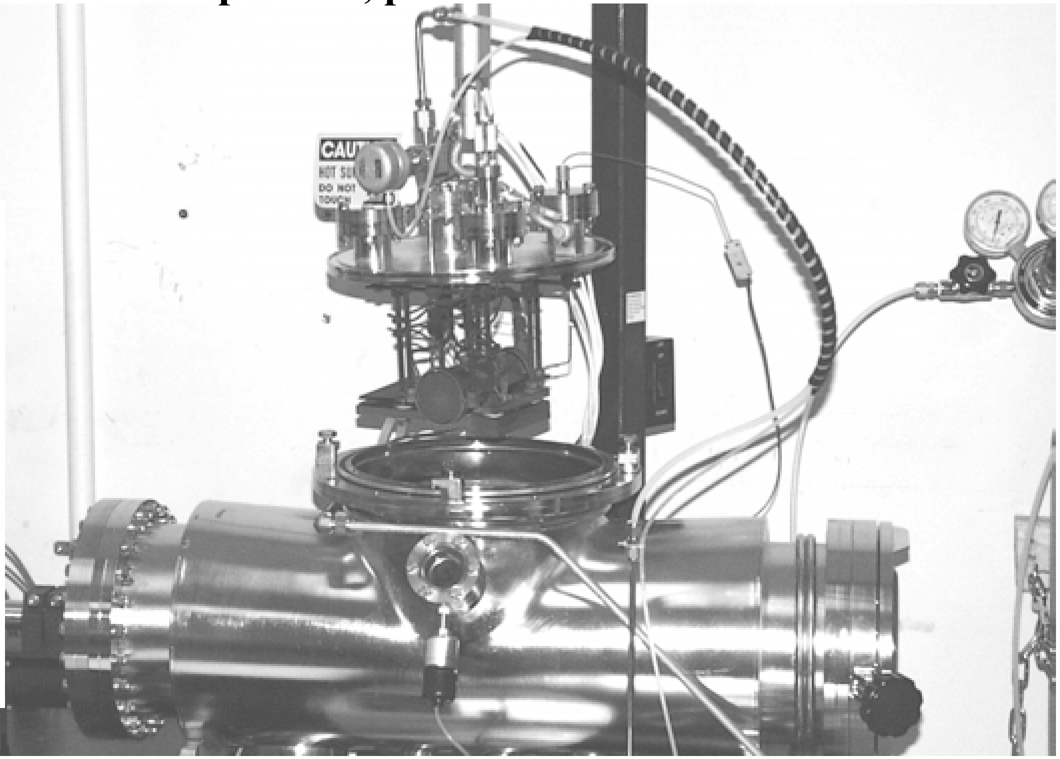
Task 1. CdTe

CdTe: High Throughput CdTe Deposition

Designed[1] and implemented[2] VT system for manufacturing-relevant R&D:

- **deposition rate from 1 to >80 µm/min at 500-700C**
- **controllable carrier gas and ambient composition, pressure and flow rates**





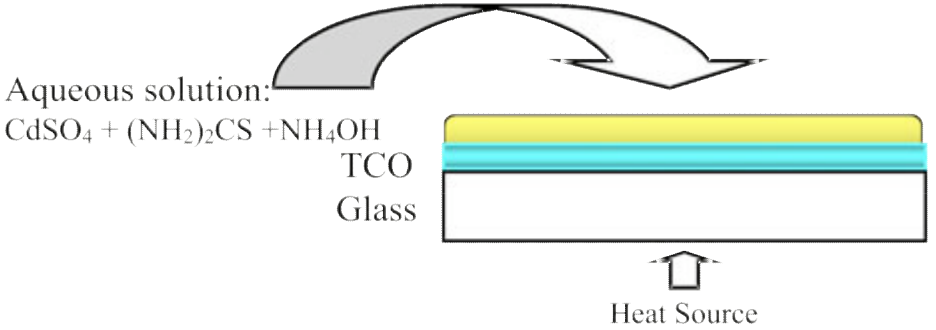
[1] R.Birkmire, E. Eser, G. Hanket, B. McCandless, *U.S. Patent* 6,676,994 (2004)

[2] G. Hanket, B. McCandless, W. Buchanan, S. Fields, R. Birkmire, *J.V.S.T.* A24(5) (2006) 1695-1701

CdTe: High Throughput CdS

Developed Chemical Surface Deposition[1] (CSD) process:

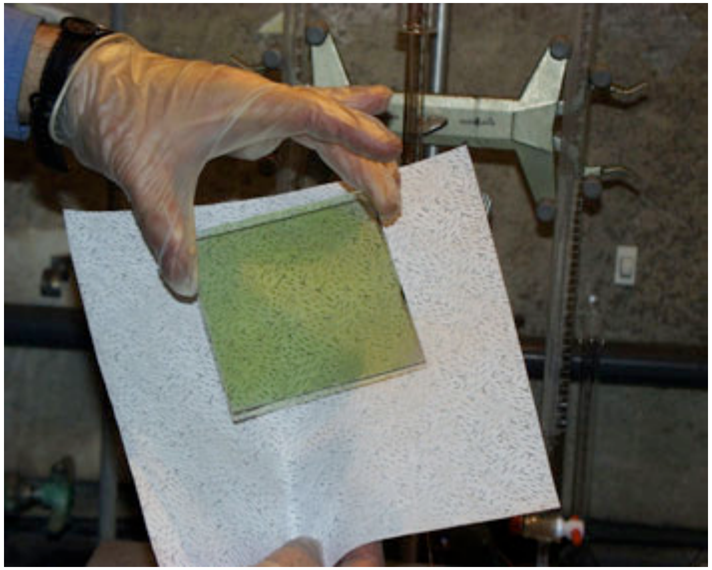
- **highly conformal, pinhole-free CdS and CdZnS films[2]**
- **high Cd utilization and deposition rate**



Aqueous solution:
$CdSO_4 + (NH_2)_2CS + NH_4OH$

$$Cd(NH_3)_4^{++} + (NH_2)_2CS + 2OH^- \rightarrow CdS + 4NH_3 + H_2CN_2 + 2H_2O$$

$$\Delta G_{rxn}(25°C) = -20.7\ \mathrm{kcal/mol}\ \text{and}\ \Delta G_{rxn}(100°C) = -24.4\ \mathrm{kcal/mol}$$



[1] B. McCandless and W. Shafarman, *U.S. Patent* 6,537,845 (2003)
[2] B. McCandless and W. Shafarman, *Conf. Rec. 3rd WCPEC* (2003) 562-565

CdTe: High Throughput Processing

Cell performance on moving substrate with commercial glass/TCO:

- ☐ **VT CdTe cells with high resistance buffer (Ga_2O_3, Al_2O_3) on low-cost SL glass substrate have same electrical performance as those on borosilicate glass**
- ☐ **Eff > 13% w/ 5 µm CdTe @ 8-10 µm/min and 1-2 min per post-dep step**
- ☐ **Eff > 11% w/5 µm CdTe @ 81 µm/min**
- ☐ **Eff > 10% w/1.5 µm CdTe @ 2 µm/min**

Reduced vapor $CdCl_2$ treatment time

- ☐ **1-2 minutes by thermal separation of film and $CdCl_2$ source[1,2]**
- ☐ **CdTe-CdS interdiffusion controlled by temperature-time**
- ☐ **Based on CdTe-CdS-$CdCl_2$-O_2 thermochemistry and polycrystalline diffusion model**

Developed vapor $ZnCl_2$ treatment as low temperature, safe alternative

Reduced contact etch time

- ☐ **Aqueous aniline etchant**
- ☐ **2 min @ RT and 80 mW/cm² illumination intensity**

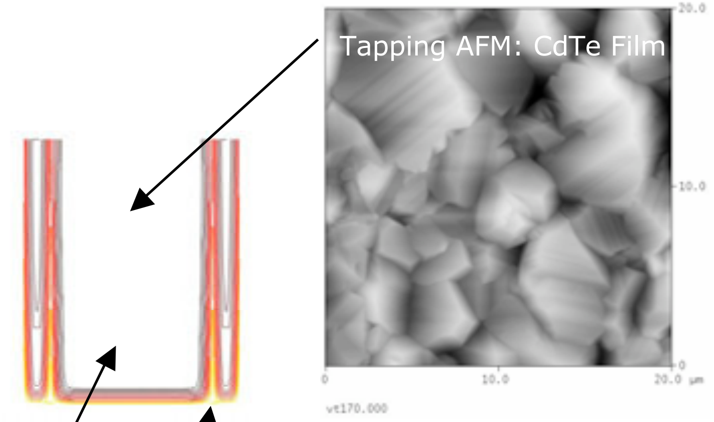
[1] B. McCandless, *U.S. Patent* 6,251,701 (6/26/01)

[2] B. McCandless and K. Dobson, *Solar Energy* **77** (2004) 839-856

CdTe: Thin Film Chemical Fundamentals

Determined chemical state versus post-deposition processing conditions [p($CdCl_2$), p(O_2), T, t]:

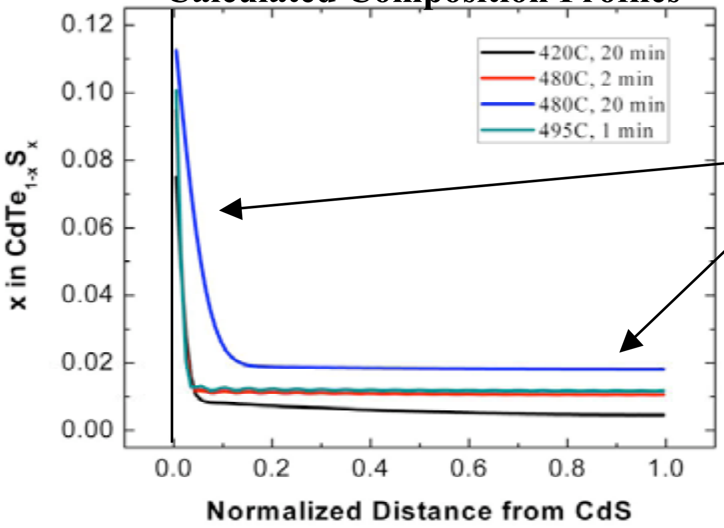
- ☐ **CdTe-CdS thin film phase diagram[1]**
- ☐ **CdTe oxidation rate[2,3]**
- ☐ **Bulk/grain boundary diffusion coefficients and activation energies[4]**



bulk

grain boundary

Calculated Composition Profiles



d_{eq}(CdS)
100 nm
40 nm
20 nm

CdS consumed determined by integration of composition profile

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[1] B. McCandless, G. Hanket, D. Jensen, R. Birkmire, *J.V.S.T.* A 20(4) (2002) 1462-1467
[2] B. McCandless, *Proc. Mat. Res, Soc. Symp*. 865 (2005) 75-83
[3] B. McCandless, S. Hegedus, R. Birkmire, D. Cunningham, *Thin Solid Films* 431-432 (2003) 249-256
[4] B. McCandless, M. Engelmann, R. Birkmire, *J. Appl. Phys.* **89**(2), 988 (2001) 988-994

CdTe: Fundamental V_{OC} Limit

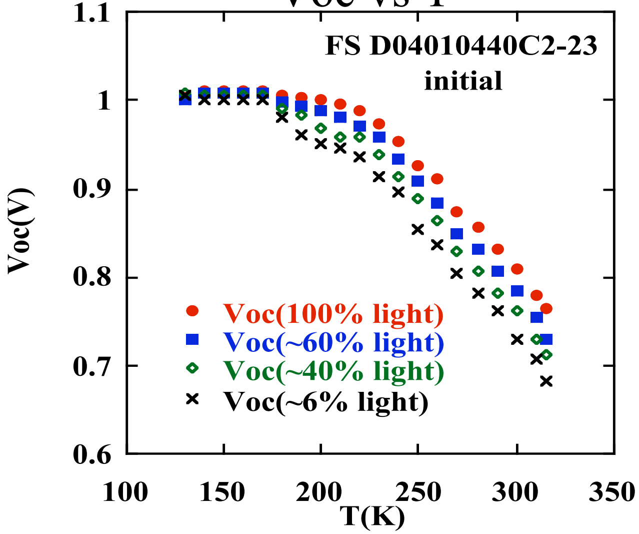
IEC VT cells:

- V_{OC} = 800 mV, best = 840 mV
- Comparable to record CdTe cell[1].

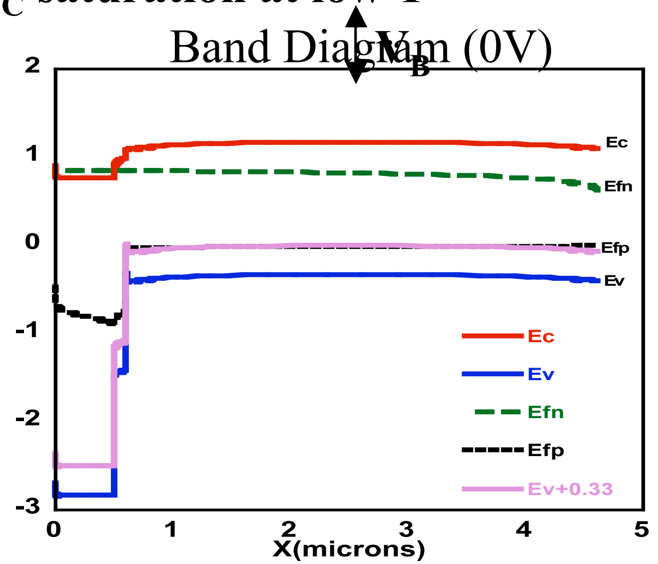
All CdTe thin-film solar cells:

- V_{OC} upper limit fixed by built-in voltage V_B
- Maximum RT V_{OC} = 0.95 V
- Verified by V_{OC} saturation at low T[2]

Voc vs T



Band Diagram (0V)



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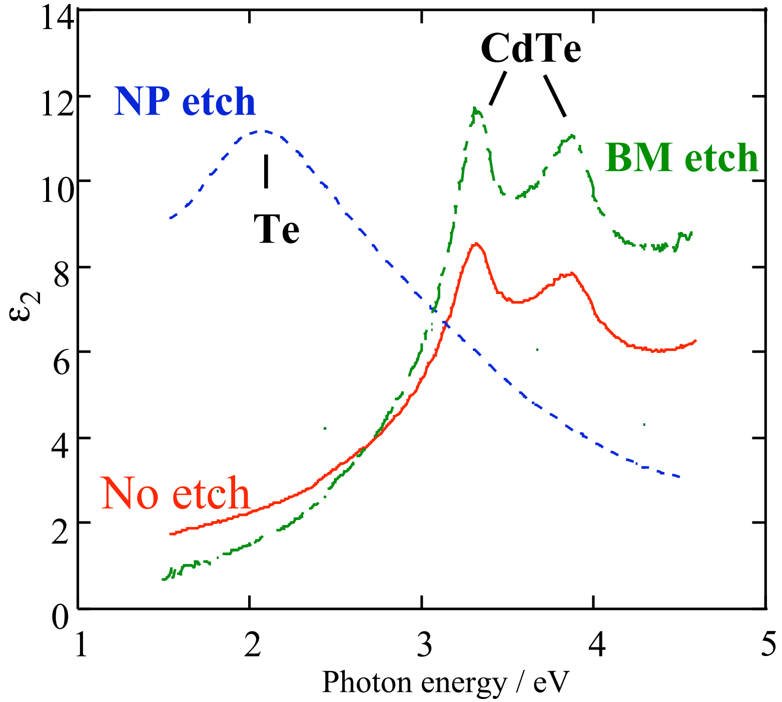
[1] B McCandless, K Dobson, S Hegedus, W Buchanan, D Desai, S Rykov, R Birkmire, *Solar Review* (2004)

[2] D Desai, *Ph. D. Dissertation*, University of Delaware (2006)

CdTe : Back Contact Surface Chemistry

Developed Variable Angle Spectroscopic Ellipsometry (VASE) for real-time analysis of CdTe surface during processing[1,2]

VASE before and after NP and BM etches



- ☐ **Potential value as process diagnostic tool to monitor chemical state of CdTe surface**
- ☐ **Analyzed Te formation and oxidation with various etchants:**
  - ➢ **Nitric/phosphoric acid (NP) etch: monitor real time crystallization of amorphous Te, ~10 nm thick**
  - ➢ **Bromine-methanol (BM) etch : enhanced signal due to surface polishing + thin 7-8 Å Te film**

[1] K. Dobson, P. Paulson, B. McCandless and R. Birkmire, *Mat. Res. Soc. Symp. Proc*. 763 (2003) 107-110

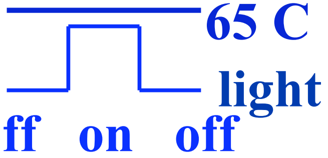
[2] B. McCandless, K. Dobson, *Solar Energy* **77** (2004) 839-856

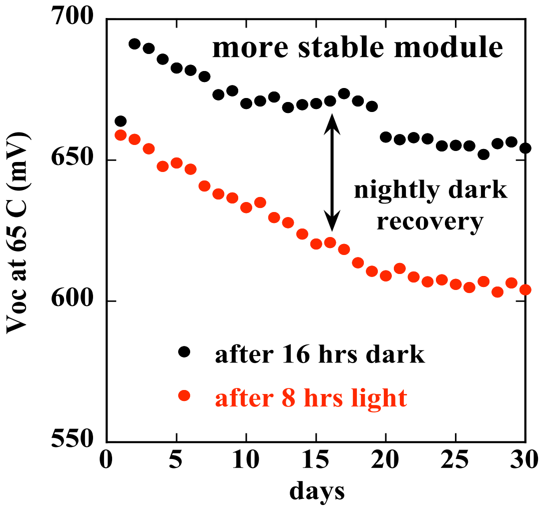
CdTe: Stability

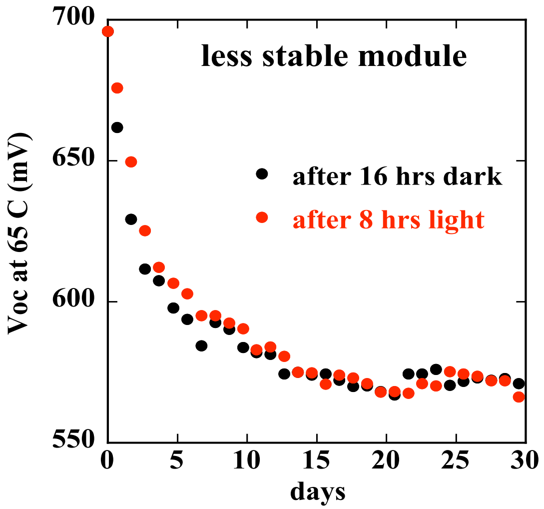
Evaluated cells from modules with good and poor stability provided by industry (TFP Team effort):

- **Effect of day/night cycle vs constant conditions**
- **Cells from stable module ~50 mV nightly dark recovery, smaller V_{OC} loss**
- **Correlated to field data from manufacturer**
  - **3.5 V module recovery seen every morning**
- **Less stable modules have irreversible changes[1], contacts implicated[2]**

“Day-night” light cycle
Constant T=65°C







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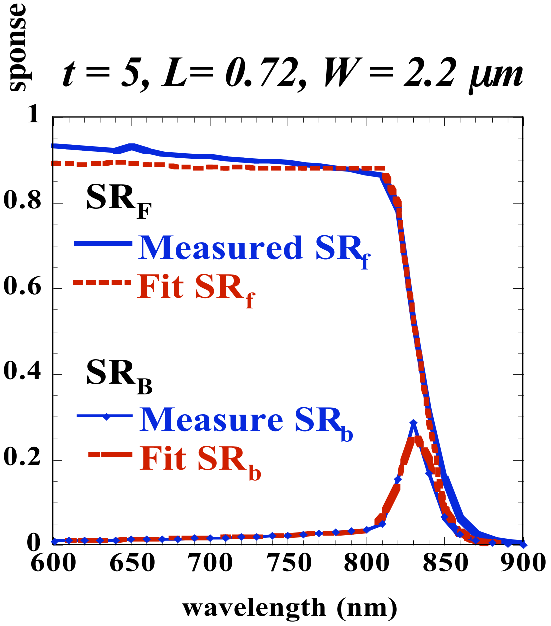
[1] S. Hegedus, D. Desai, D. Ryan, B. McCandless, *Conf. Rec. 31st IEEE PVSC*, 319-322

[2] S. Hegedus and B. McCandless, *Solar Energy Materials and Solar Cells*, **88** (2005) 75-95

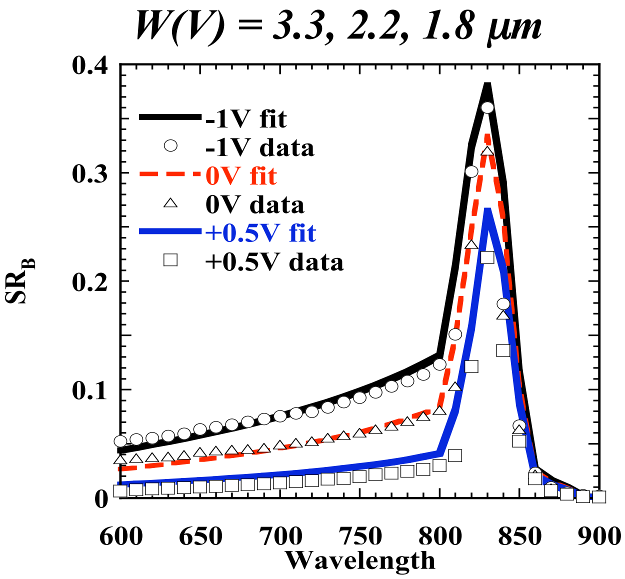
CdTe: Diffusion Length & Depletion Width

Bifacial spectral response (SR) used to determine diffusion length L and depletion width W(V) on cells with transparent ZnTe:Cu contact[1]:

- **Input: absorption (α (E)), thickness (t), optical correction (external SR)**
- **Fitting parameters: L,W; fitting data at multiple V bias: W(V)**
- **Front light: absorption in depletion region (drift)**
- **Back light: absorption in bulk CdTe (diffuse across bulk to depletion)**



t = 5, L= 0.72, W = 2.2 µm



W(V) = 3.3, 2.2, 1.8 µm

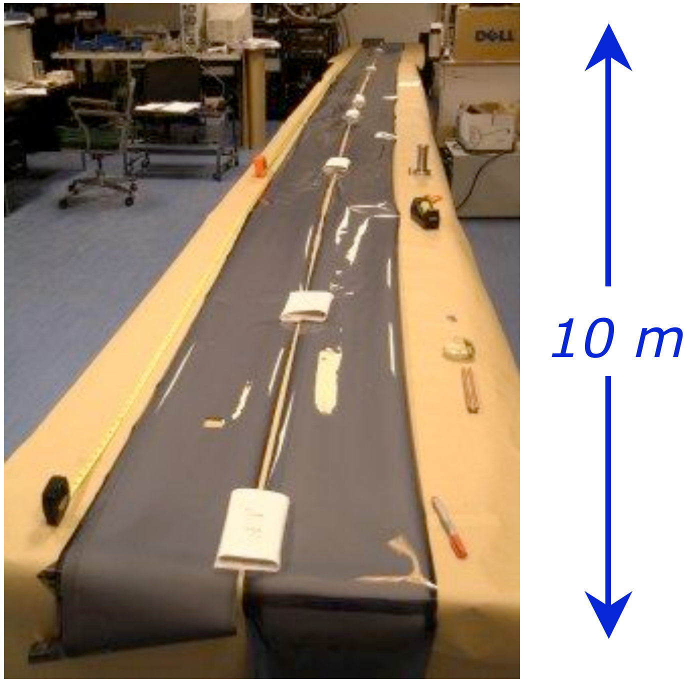
- **Fitted W(V) good agreement with C(V)**
- **L=0.6 - 0.8 µm for t=1.5 - 8 µm**

[1] D. Desai, S. Hegedus, B. McCandless, R. Birkmire, K. Dobson, D. Ryan, *Conf. Rec. 4th WCPEC* (2006)

Task 2. $CuInSe_2$

$Cu(InGa)Se_2$ Deposition on Polymer Web

- **Continuous, roll-to-roll, high-throughput process**
- **Flexible, lightweight modules: potential for building integrated applications**
- **Simplified and reduced handling during processing and deployment**



Multiple patents: US 6,310,281, 6,372,538, & 6,562,405
R. Birkmire, E. Eser, S. Fields and W. Shafarman., *Prog. Photovolt:Res. Appl.* **13**, 141 (2005).

$Cu(InGa)Se_2$ Deposition on Polymer Web

Device performance uniformity demonstrated

- **9.2% average device efficiency over 5 ft web**
- **Best device performance on web centerline**
- **Cross-web uniformity and average efficiency improve down the web**

Location	20”	30”	40”	50”	60”	Cumulative
-1.5”	9.0 ± 0.4		8.2 ± 1.6		9.1 ± 0.3	8.8 ± 1.0
0	9.4 ± 1.1*	9.8 ± 0.2	10.2 ± 0.1	10.0 ± 0.3	10.0 ± 0.2	10.0 ± 0.4
+1.5”	8.2 ± 0.4		8.2 ± 1.5		9.0 ± 0.2	8.4 ± 0.9
Cumulative	8.7 ± 2.1		8.8 ± 1.5		9.4 ± 0.5	9.2 ± 1.0

Structure: polyimide/Mo/Cu(InGa)Se_2/CdS/ZnO/ITO/Ni-Al, 0.56 cm^2 area

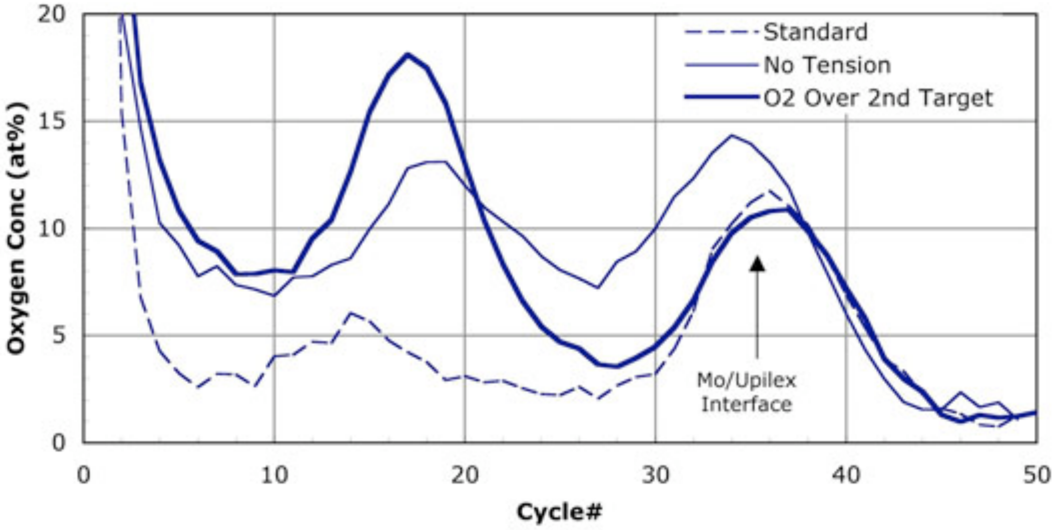
- **Best cell to date: η = 12.1 % (without benefit of Na)**

G. Hanket, U. Singh, E. Eser, W. Shafarman, R. Birkmire, *Proc. 29th IEEE PVSC*, 567 (2002).

Cu(InGa)Se_2 Deposition on Polymer Web

Critical problems identified and solved

- **Film cracking problem prevented current collection**
  - **Solved with oxygen in Mo back contact**
  - **Auger depth profile confirms two processes for O_2 incorporation**



- **Spitting of Cu source ⇒ defects in Cu(InGa)Se_2 films**
  - **Solved by improved effusion source design based on detailed thermal modeling**

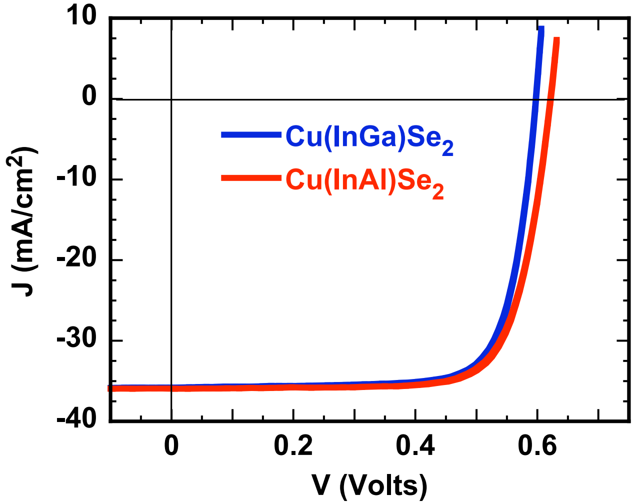
E. Eser, S. Fields *provisional pat. SN 60/620,352*

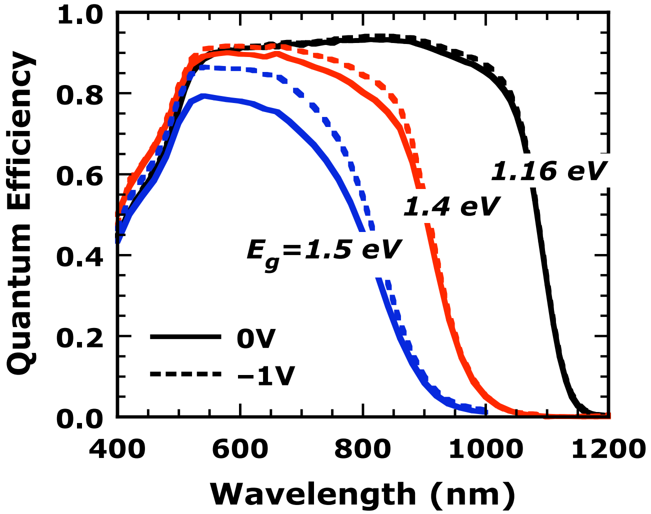
E. Eser, S. Fields, G. Hanket, R. Birkmire, J. Doody, *Proc. 31st IEEE PVSC*, 567 (2005).

$CuInSe_2$ Increased V_{OC}: $Cu(InAl)Se_2$

Evaluate $Cu(InAl)Se_2$ alloys for improved wide bandgap devices

- ☐ **Demonstrated comparable performance with $Cu(InAl)Se_2$ and $Cu(InGa)Se_2$ ⇒ $\eta = 17\%$ with $E_g = 1.16$ eV[1]**
  - ➢ **Ga at $Cu(InAl)Se_2$/Mo interface ⇒ improved adhesion**
- ☐ **Decreasing performance with increasing E_g, similar to $Cu(InGa)Se_2$[2]**
  - ➢ **Losses identified: SRH recombination and poor current collection**
- ☐ **Conclusion: no improvement over $Cu(InGa)Se_2$ in device performance, greater difficulties due to handling and poor adhesion**





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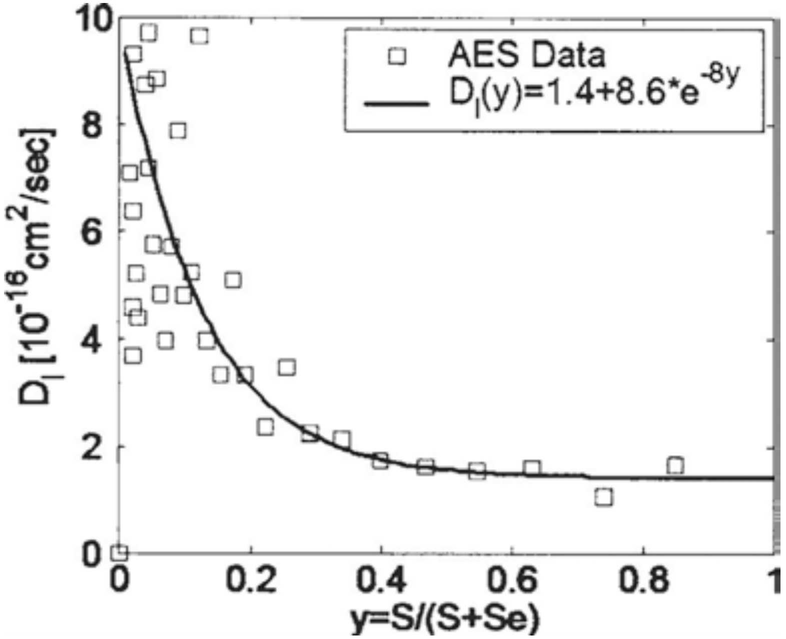
[1] S Marsillac, P Paulson, M Haimbodi, R Birkmire, W Shafarman, *Appl. Phys. Lett.* **81**, 1350 (2002)

[2] W Shafarman, S Marsillac, T Minemoto, P Paulson, R Birkmire. *Proc. 3rd World Conf PVEC* 2869 (2003).

$CuInSe_2$ Increased V_{OC}: Sulfur diffusion

S diffusion into $Cu(InGa)Se_2$ for increased E_g ⇒ higher V_{OC}

- ☐ **Diffusion coefficients for S determined in single crystals and polycrystalline films to separate bulk and grain boundary diffusion**
- ☐ **Cu-rich films: rapid S incorporation**
- ☐ **Single-phase films: slow S incorporation**

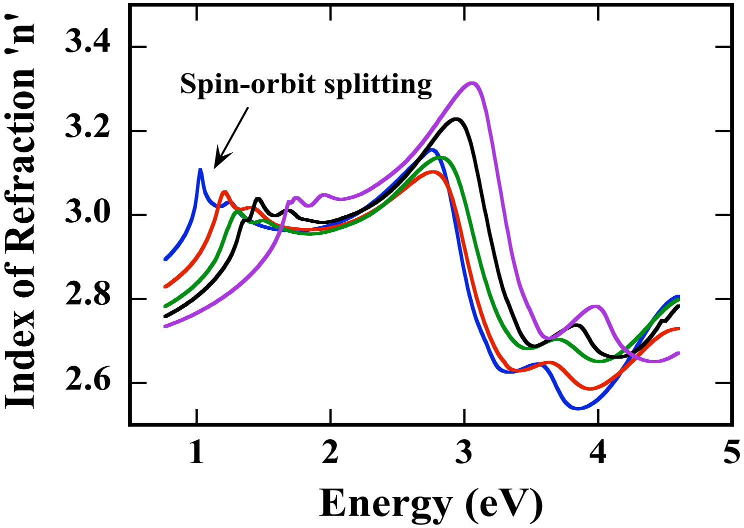


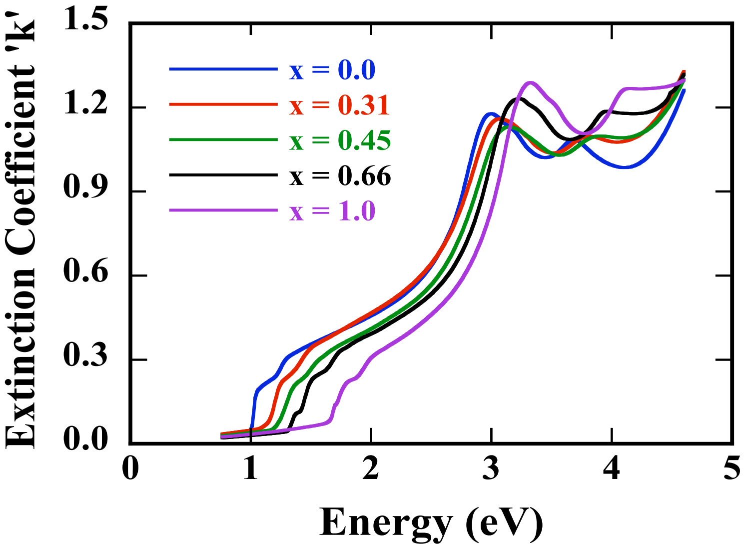
J Titus, R Birkmire, C Hack, G Muller, P. McKeown, *J. Appl Physics* **99**, 043502 (2006)

Cu(InGa)Se$_2$ Fundamentals: Ellipsometry

Determine fundamental optical properties of thin film Cu(InGa)Se$_2$

- **Determine optical constants vs. Ga/(In+Ga)[1]**
  - **critical point energies ⇒ optical transitions**
- **Effect of Cu off-stoichiometry: shift in Eg with decreasing Cu[2]**
  - **Use effective medium approximation to model data as mixture of α-Cu(InGa)Se$_2$ and β-Cu(InGa)$_3$Se$_5$**





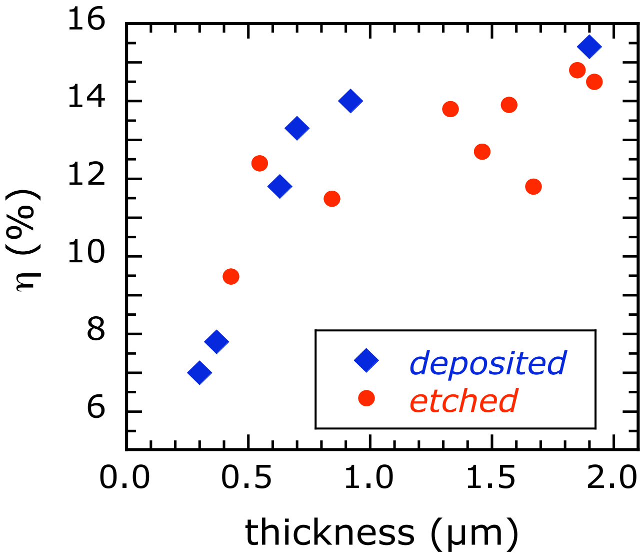
[1] P. Paulson, R. Birkmire, W. Shafarman, *J. Appl. Phys.* **94**, 879 (2003)

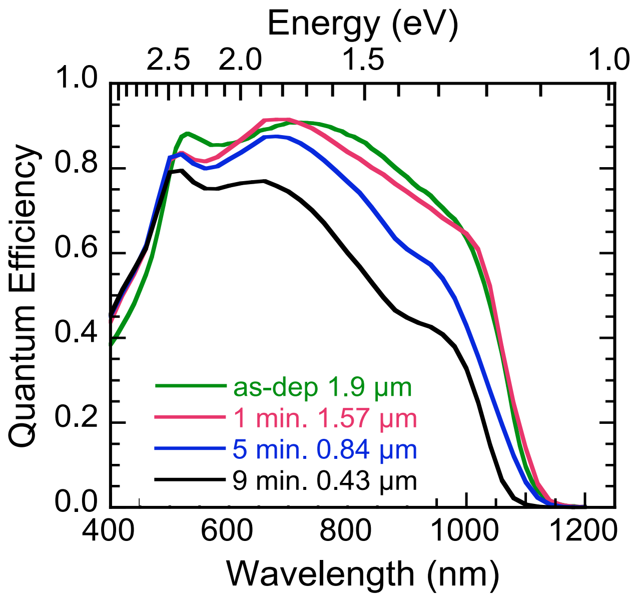
[2] P Paulson, S Stephens, and W Shafarman, *Mat. Res. Soc. Symp. Proc. 865*, 21 (2005).

$Cu(InGa)Se_2$ Device Processing: Thickness

Reduce $Cu(InGa)Se_2$ thickness to reduce process time and materials

- ☐ **Analyze losses for d < 1 µm by comparing films deposited with different time and chemical-etched films**
- ☐ **Losses with thin $Cu(InGa)Se_2$ characterized**
  - ➢ **J_{SC} loss not due to light scattering or voltage-dependent collection**
  - ➢ **Smooth (etched) cells ⇒ no loss in FF, V_{OC} with d = 0.4 µm**



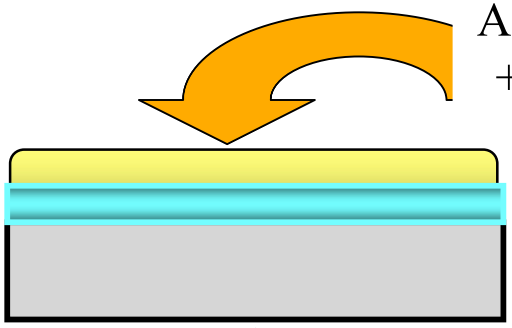


W Shafarman, R Huang, S Stephens , *Proc. 4th WCPVEC*, (2006).

$Cu(InGa)Se_2$ Device Processing: CdS Deposition

Chemical surface deposition (CSD)

- ❑ **High material utilization**
- ❑ **Potential for continuous processing**
- ❑ **Demonstrated comparable performance using CBD and CSD on $Cu(InGa)Se_2$**



Aqueous sol'n: $CdSO_4 + (NH_2)_2CS + NH_4OH$

$Cu(InGa)Se_2$

Substrate

Heat

CdS deposition		Eff (%)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)
CBD	Best cell	15.3	0.618	32.7	75.6
	Average	14.3	0.618	31.5	73.5
CSD	Best cell	14.5	0.620	32.2	72.6
	Average	13.9	0.615	31.3	72.0

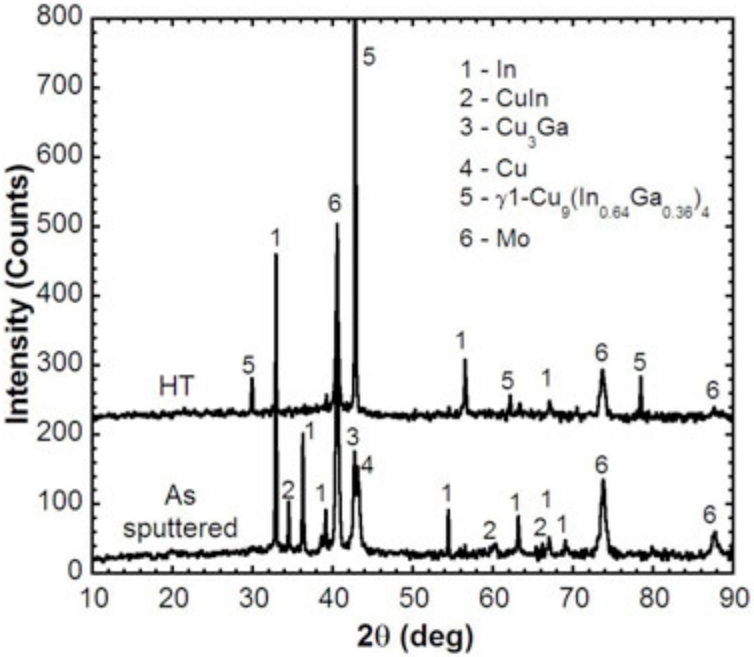
US Patent (#6,637,845) licensed to PV industry

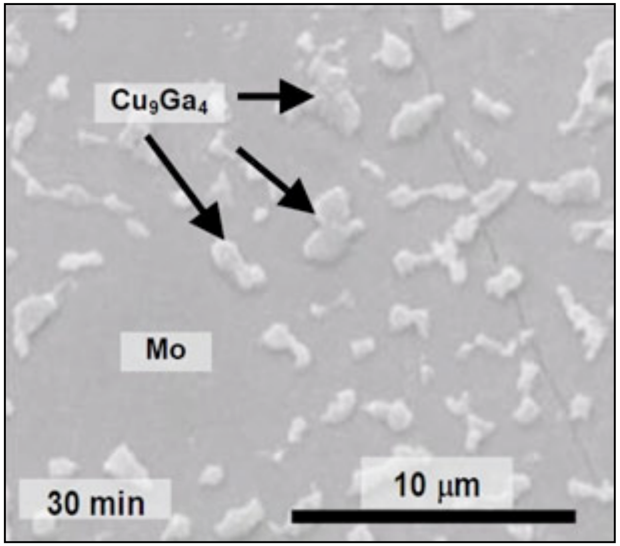
B.E. McCandless, W.N. Shafarman, *Proc. 3rd World Conf. on PVEC*, 562 (2003).

$Cu(InGa)Se_2$: H_2Se Reaction

Reaction of Cu-Ga-In precursor in H_2Se to form $Cu(InGa)Se_2$: segregation of Ga to back causes low V_{OC}

- ☐ **Characterization of precursor films ⇒ intermetallic $Cu_9(In_{1-x}Ga_x)_4$**
- ☐ **Reacted films contain stable Cu_9Ga_4 phase at back of film - revealed by peeling $Cu(InGa)Se_2$**





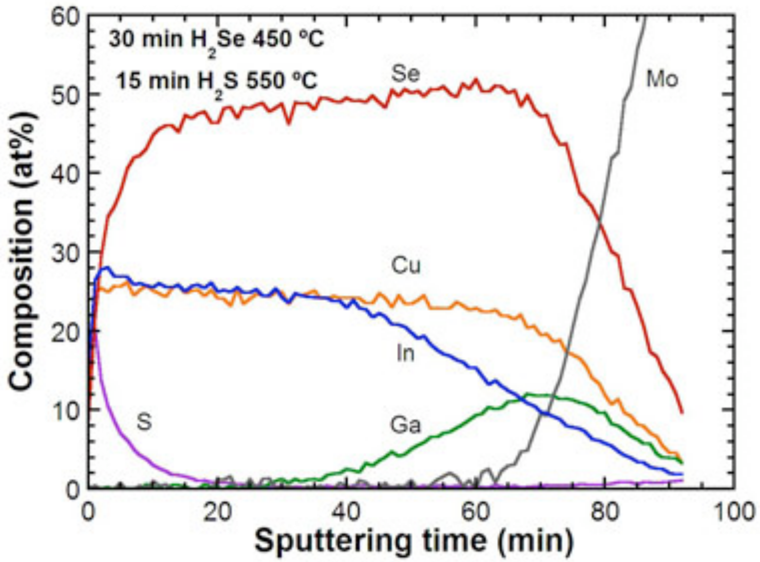
G Hanket, W Shafarman, R Birkmire, *Proc. 4th WCPVEC*, (2006).

$Cu(InGa)(SeS)_2$: H_2Se/H_2S Reaction

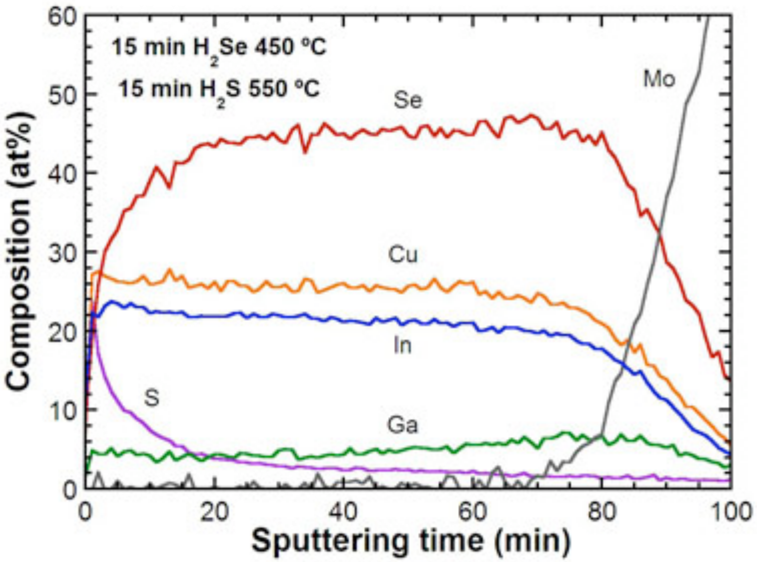
Uniform Ga distribution by controlling time-temperature-concentration profile

- ☐ **Partial reaction in H_2Se at 400 - 450 °C**
- ☐ **Complete reaction in H_2S at 550°C**
- ☐ **Solar cells with V_{OC} > 640 mV and $\eta = 13.5\%$**

Complete H_2Se reaction prior to H_2S
Ga segregated to back ⇒, low V_{OC}



Partial H_2Se reaction prior to H_2S
Ga distributed through film ⇒ high V_{OC}



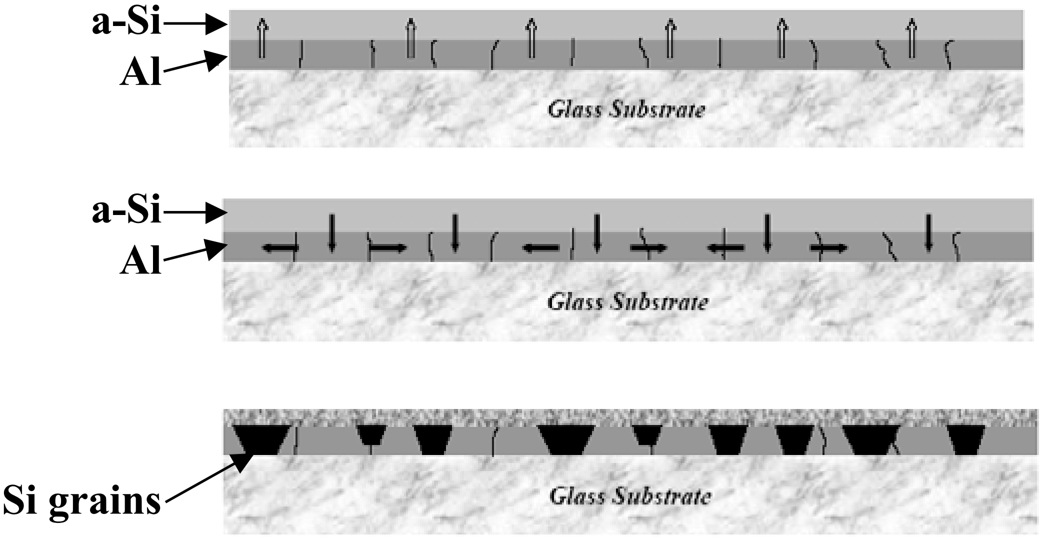
G Hanket, W Shafarman, R Birkmire. , *Proc. 4th World Conf. on PVEC*, (2006).

Task 3. Silicon

Poly-Si: Al Induced Crystallization

Al induced crystallization of a-Si

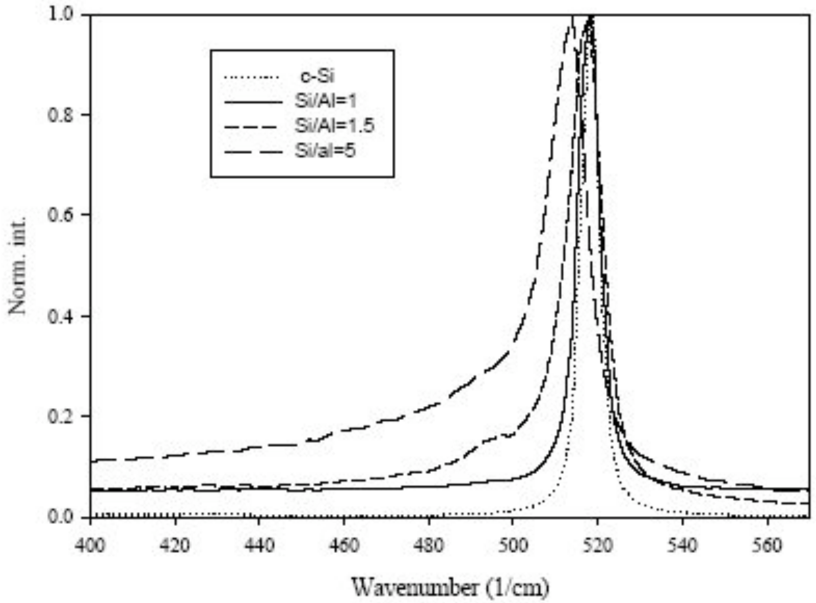
- **Solubility of a-Si with Al is greater than c-Si in Al**
- **Al becomes supersaturated with Si and c-Si grains nucleate at Al grain boundaries**
- **An oxide/hydroxide interfacial layer between the Al and Si regulates the transport**



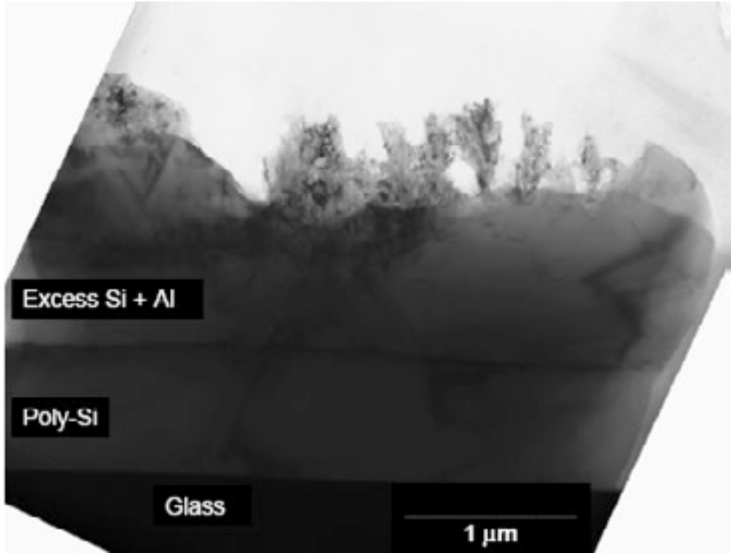
Poly-Si: Al Induced Crystallization

In-Situ AIC Below Eutectic: Effect of Si/Al Ratio

Raman profiles



TEM cross-section after Al etch, Si/Al=2



- ☐ **Increasing Si/Al ratio does not improve grain size or the thickness of poly-Si film**
- ☐ **Excess Si accumulates on top and contain nano-crystalline and amorphous phases**
- ☐ **Poly-Si film thickness limited to ~ 1 µm**

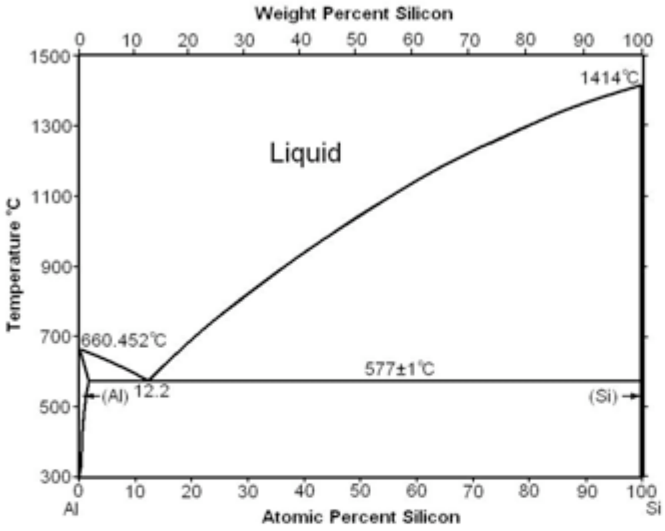
O. Ebil, R. Aparicio, S. Hazra, R.W. Birkmire and E. Sutter, *Thin Solid Films* ***430****, 120(2003).*

Poly-Si: Al Induced Crystallization

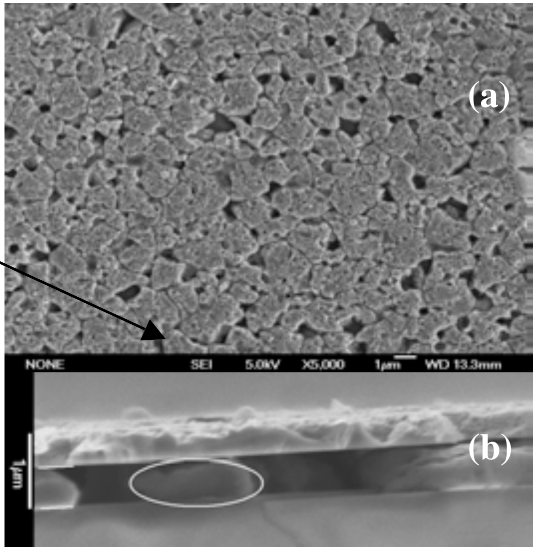
Si crystallization above eutectic temperature

- ❑ Above T(Eutectic) ⇒ Al/Si interface is melted ⇒ liquid phase
- ❑ Could we form larger grain and better continuous polycrystalline silicon under this condition?

Glass/Si/Al annealed at 600°C



Excess a-Si after Al etch



Nearly continuous, > 5 µm, poly- Si film

Ozgenc Ebil, Roger Aparicio and Robert Birkmire, *Mater. Res. Soc. Symp. Proc.* ***808****, A4.24 (2004).*

Back Contact c-Si HJ Solar Cells

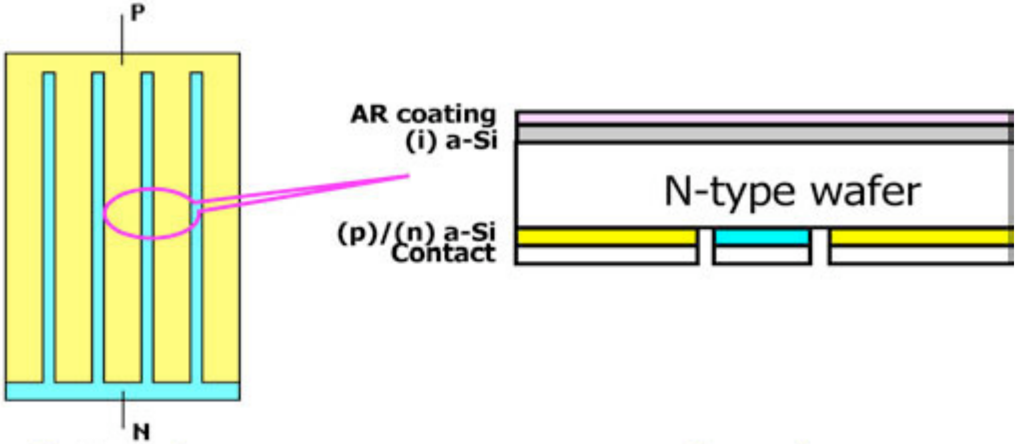
Develop all back contact c-Si using a-Si thin film technology

Comparing with front surface emitter/back contact heterojunction cell (Sanyo HIT cell)

- **No shading and area loss due to metal grids**
- **No absorption losses by electrode and emitter layer**
- **Easy to optimize front surface passivation and AR coating**

Comparing with conventional back-junction cell (SunPower)

- **a-Si based emitter and contact layers**
- **All low temperature processing ⇒ compatible with thin c-Si**
- **Simpler fabrication process**



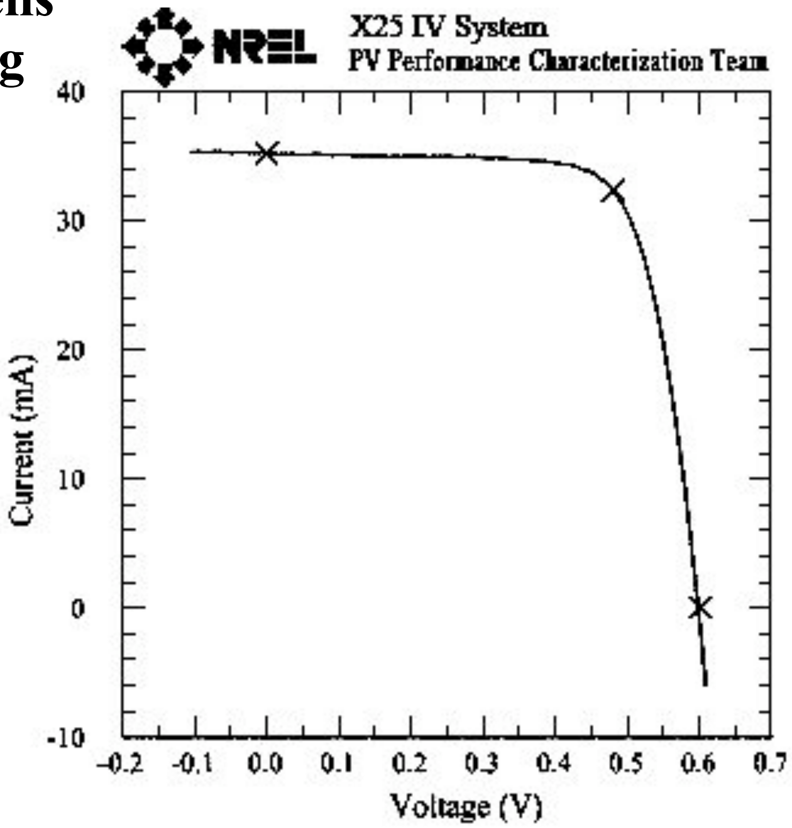
Bottom view **Cross view**

Back Contact c-Si HJ Solar Cells

Potential to reduce cost of c-Si cells

- **⇒ low temperature processing**
- **⇒ thin Si wafers**
- **⇒ reduced processing steps**

Voc = 0.602 V
Jsc = 26.7 mA/cm2
FF= 73.3%
η = 11.8%



Task 4. Diagnostics

Process Diagnostics and On-line Sensors

Determine process and product specification, and develop diagnostic and control tools needed:

- **to reduce ‘floor optimization’ time**
- **for robust manufacturing**
- **with high yield**

Identify materials properties that predict product quality using ‘bench level’ measurement tools and develop process model for simulation and process control

Process Diagnostics and On-Line Sensors

Optical: Variable Angle Spectroscopic Ellipsometry

- **Alloy composition, e.g., $CuInSe_2$-based materials**
- **Real-time surface and interface chemistry, e.g., Te on CdTe**[1]
- **TCO properties, e.g., SnO_2**[2]

X-Ray: Symmetric & Asymmetric Diffraction[3]

- **Compositional profile, e.g., $Cu(InGa)Se_2$**
- **Surface phases and properties, e.g., oxide growth, mechanical stress**

Contact wetting: Zisman method to determine surface energy[4]

- **Surface state before/after chemical reaction, e.g., film oxidation**

[1] K. Dobson, P. Paulson, B. McCandless, R. Birkmire, *Proc. Mat. Res. Soc. Symp*. 763 (2003) 107-118.

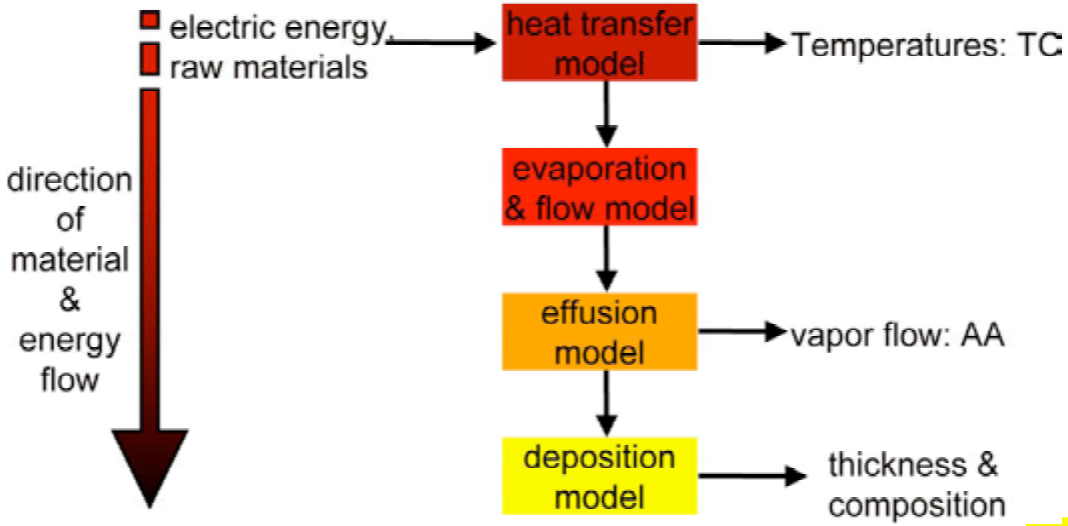
[2] P. Paulson and S. Hegedus, *J. Appl. Phys*. 96 (2004) 5469-5477

[3] B. McCandless, *Proc. Mat. Res, Soc. Symp*. 865 (2005) 75-83

[4] B.E. McCandless, R.W. Birkmire, S.A. Rykov and J.G. Chen, *Prog. in Photov* **14** (2006) 1-19.

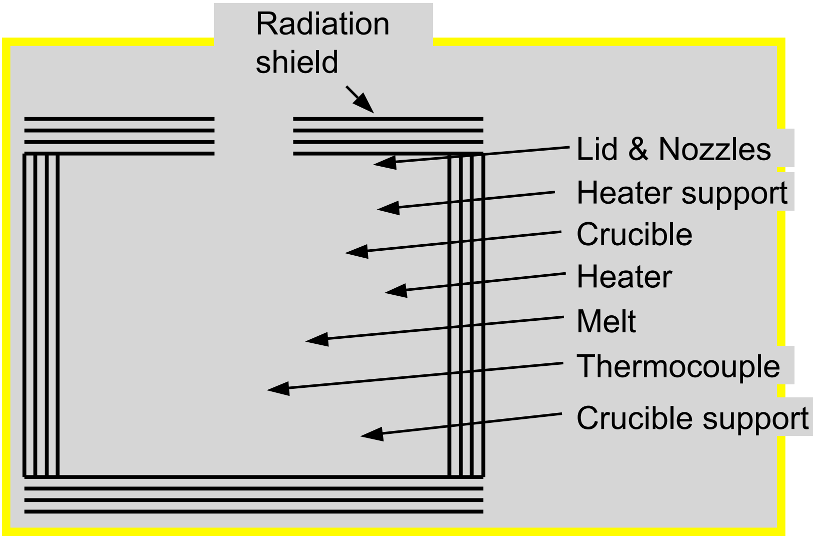
Process Modeling & Control

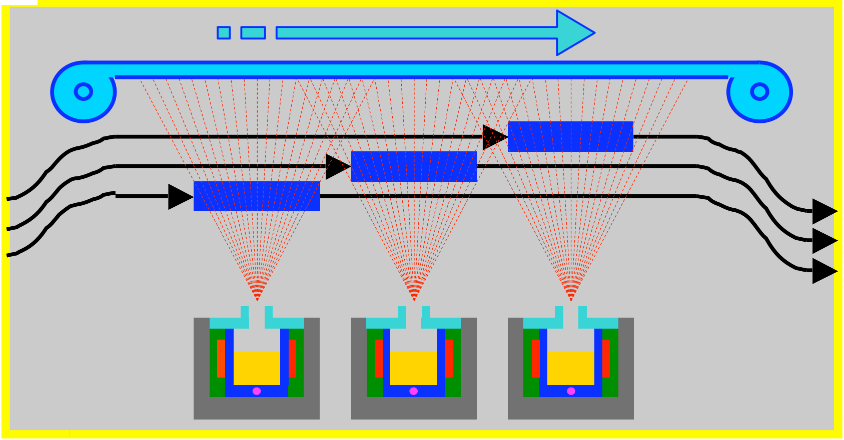
Model based process control



electric energy
raw materials
→ heat transfer model → Temperatures: TC
↓
evaporation & flow model
↓
effusion model → vapor flow: AA
↓
deposition model → thickness & composition

direction of material & energy flow





Developed fundamental heat & mass transfer model and 2d-deposition model

Evaluated different control scheme incorporating AA and XRF sensors

S Junker, R Birkmire, F Doyle III, *AIChE Journal 51(3), 878 (2005).*