



# Polarized Wave Probes for Thin Film Photovoltaics: From the Lab to the Production Line

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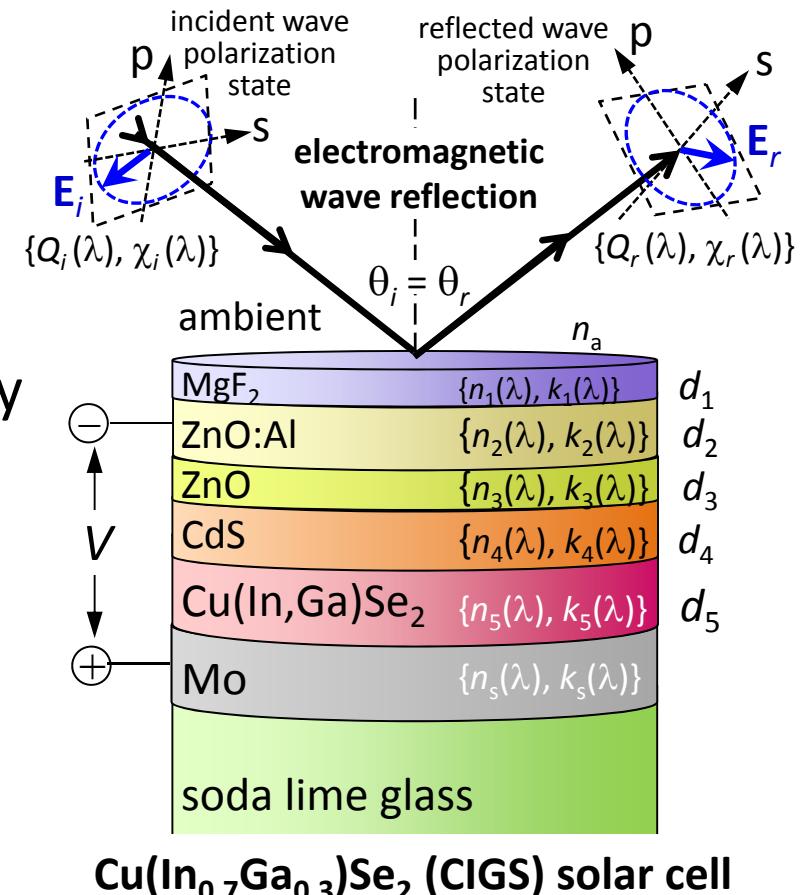
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Wright Center for Photovoltaics

Innovation and Commercialization  
**University of Toledo**

Special thanks to:

**Profs. Jian Li and Nikolas Podraza**

**Prakash Koirala**





## What is “Solar Energy”?

Useful forms of energy generated from the radiant energy emitted by the sun.

Examples:

Solar Energy  
Industries  
Association  
(SEIA);  
([www.seia.org](http://www.seia.org))

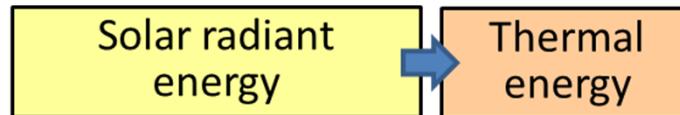
### 1. Solar Heating and Cooling



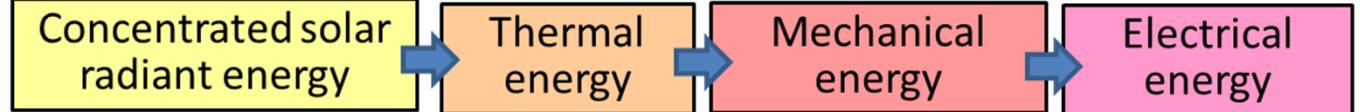
### 2. Concentrated Solar Power

Photos reproduced with permission of SEIA

### 1. Solar heating and cooling (SHC)



### 2. Concentrated solar power (CSP)



### 3. Solar photovoltaics (PV)



## What is “Solar Photovoltaics (PV)”?

Type of solar energy in which radiant energy from the sun is converted directly to electrical energy via absorption within the region of a semiconductor junction



# Outline of Major Topics

- **Photovoltaics (PV): Motivation, status, and goals** (5 slides: 3-7)
- **The first generation (Si) solar cell:** Semiconductor physics and operation (7 slides: 8-14)
- **Second generation (thin film) PV:** Advantages over 1<sup>st</sup> generation and its challenges (15 slides: 15-29)
- **Polarized light and its applications in PV:** Research on CdTe and CIGS thin film PV technology (15 slides: 30-44)



## Motivation: Why Photovoltaics? PV is a clean, sustainable energy technology that generates no emissions during its lifetime.

*“Observational determination of surface radiative forcing by CO<sub>2</sub> from 2000 to 2010”*

D. R. Feldman, W. D. Collins, P. J. Gero, M. S. Torn, E. J. Mlawer, & T. R. Shippert

Online Feb 26, 2015: *Nature* 000, 1-5 (2015); doi:10.1038/nature14240

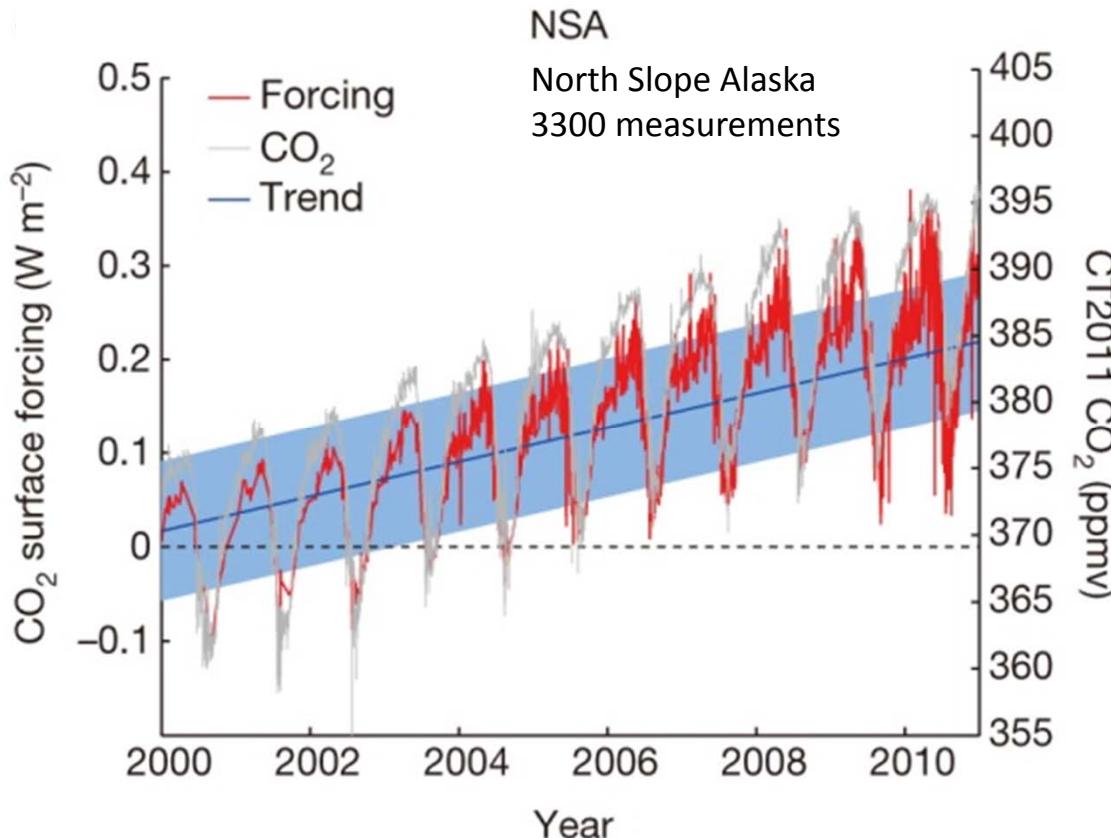


Figure reproduced with permission from Nature Publishing Group

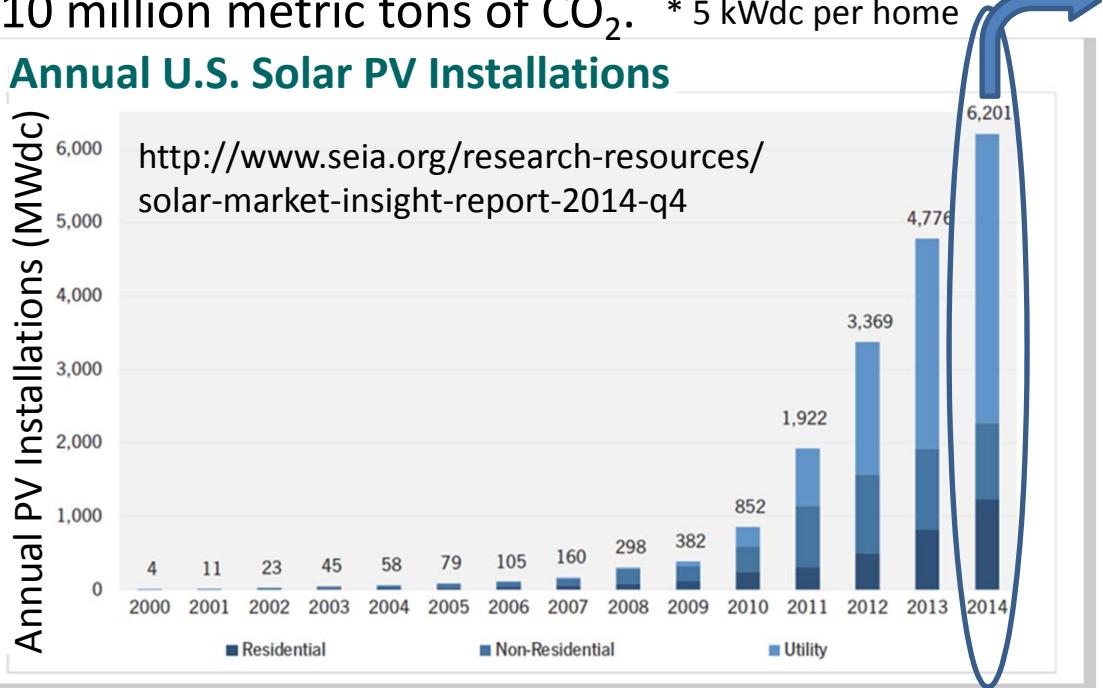
- Although many studies report increasing atmospheric CO<sub>2</sub> concentrations, this study has determined the “surface radiative forcing” due to the increasing CO<sub>2</sub> concentrations.
  - Radiative forcing is defined as a change in the difference between the solar irradiance incident on the Earth and the irradiance returning to space (in W/m<sup>2</sup>).
  - This study by Feldman *et al.* determined radiative forcing as 0.2 W/m<sup>2</sup> per decade.
- Earth's area:  $5 \times 10^{14} \text{ m}^2$



## Status: Where are we? *SEIA Solar Market Insight Report Q4 2014:* **32% OF ALL NEW U.S. ELECTRIC CAPACITY IN 2014 CAME FROM PV**

"The U.S. installed 6,201 MWdc of solar PV in 2014, up 30 percent over 2013, making 2014 the largest year ever in terms of PV installations." -- [www.seia.org](http://www.seia.org)  
The total U.S. PV capacity has surpassed 20,000 MWdc (or 20 GWdc), sufficient to power 4 million U.S. homes\* and avoid 10 million metric tons of CO<sub>2</sub>. \* 5 kWdc per home

### Annual U.S. Solar PV Installations



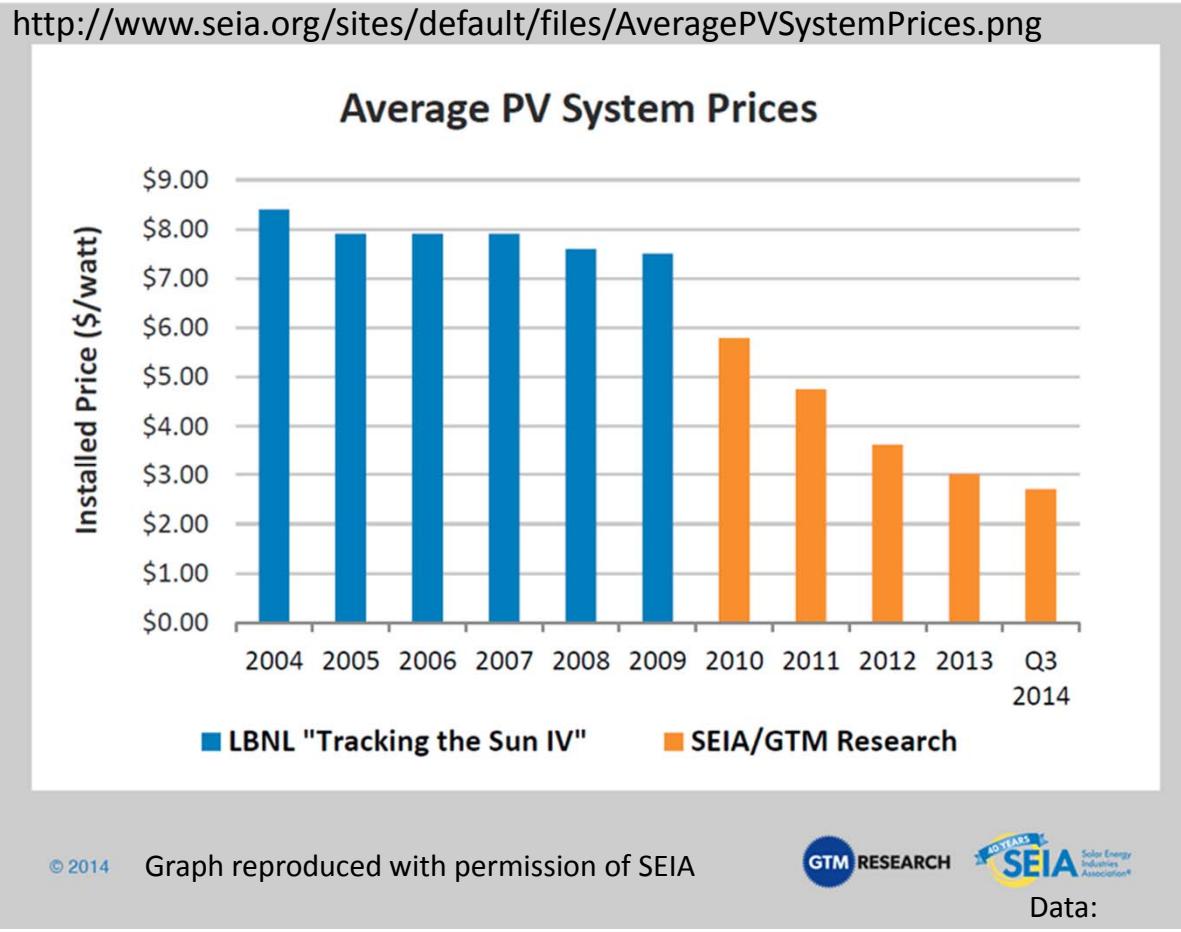
In 2014, energy sources and % share of electricity generation in the US were ([www.eia.gov](http://www.eia.gov)):

- Coal 38.7%
- Natural gas 27.4%
- Nuclear 19.5%
- Hydropower 6.3%
- Other renewable 6.9%
  - Biomass 1.57%
  - Geothermal 0.41%
  - Solar 0.45%
  - Wind 4.44%
- Petroleum 0.6%
- Other Gases 0.3%
- Other 0.3%



## Goal: Increased Adoption of PV by Reduction of the Installed Price (\$/W)

<http://www.seia.org/sites/default/files/AveragePVSystemPrices.png>



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Data:

[www.eia.gov](http://www.eia.gov)

[http://pvwatts.nrel.gov/version\\_5.php](http://pvwatts.nrel.gov/version_5.php)

- Year-over-year, the national average PV installed system price declined by 11% to \$2.71/W in 2014 Q3.
- Since the third quarter of 2010, the average price of a PV panel has dropped by 63%.

How many Watts are required to supply 100% of electricity requirements of an average home in Toledo?

$$\frac{29.7 \text{ kW h(ac)/day}}{4.37 \text{ avg. sun h/day}} \frac{1 \text{ (dc)}}{0.8 \text{ (ac)}} = 8.5 \text{ kW(dc)}$$

Average cost: \$23 K

30% tax credit reduces cost

Average monthly consumption in Ohio (2013): 892 kW h

Monthly bill: \$107

## Goal: Continuous Reduction of the Installed Price (\$/W) of PV

### Technology Approaches

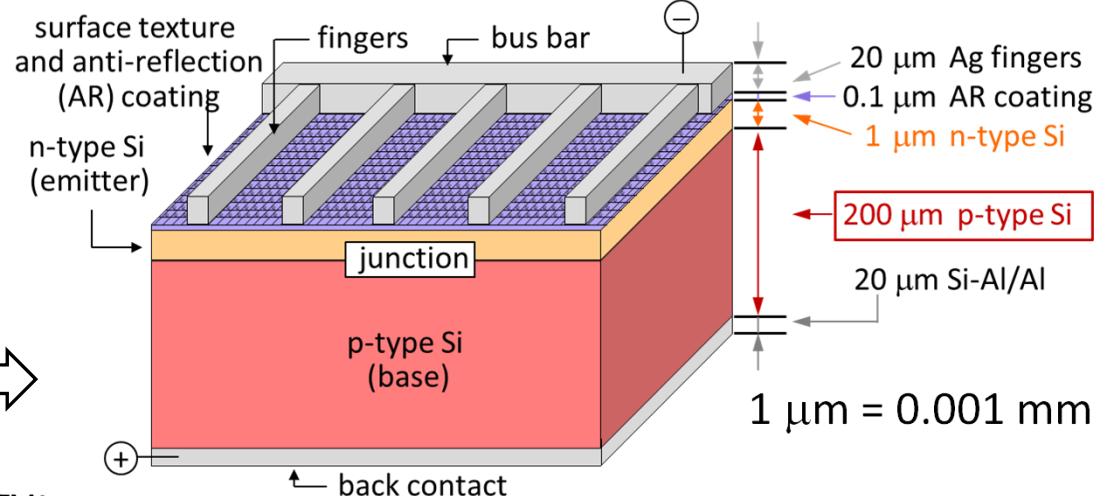
Solar radiant energy is converted directly to electrical energy via light absorption within the region of a semiconductor junction

#### **First Generation PV**

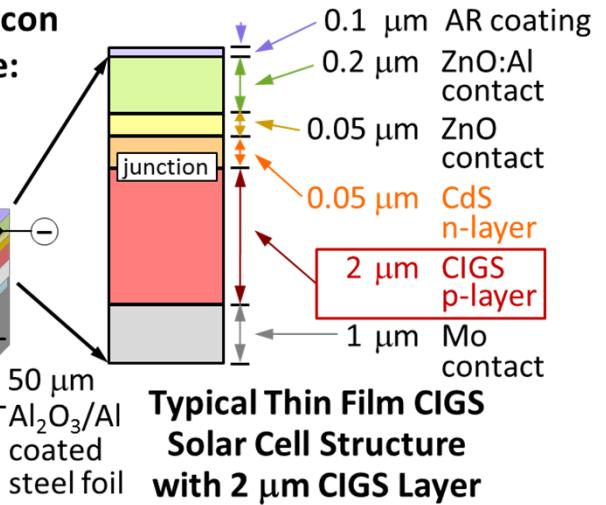
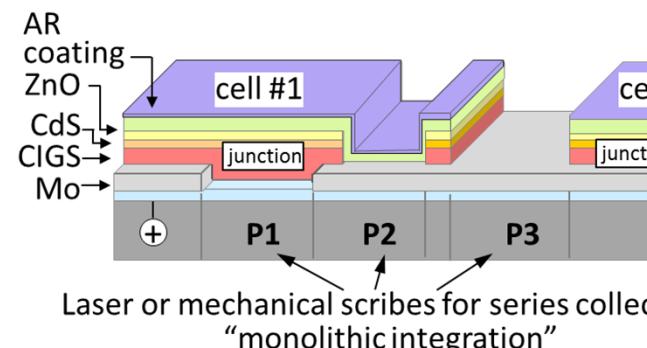
Based on crystalline silicon semiconductor wafer technology;  
90% of total PV production (2013)  
(Bell Labs: Chapin, Fuller, Pearson; 1954)

#### **Second Generation PV**

Based on thin film semiconductor coating technology on rigid glass and flexible polymer or steel foils (General Electric Labs: Cusano; 1963)



Typical Crystalline Silicon Solar Cell Structure:  
200 μm Wafer



Typical Thin Film CIGS Solar Cell Structure with 2 μm CIGS Layer

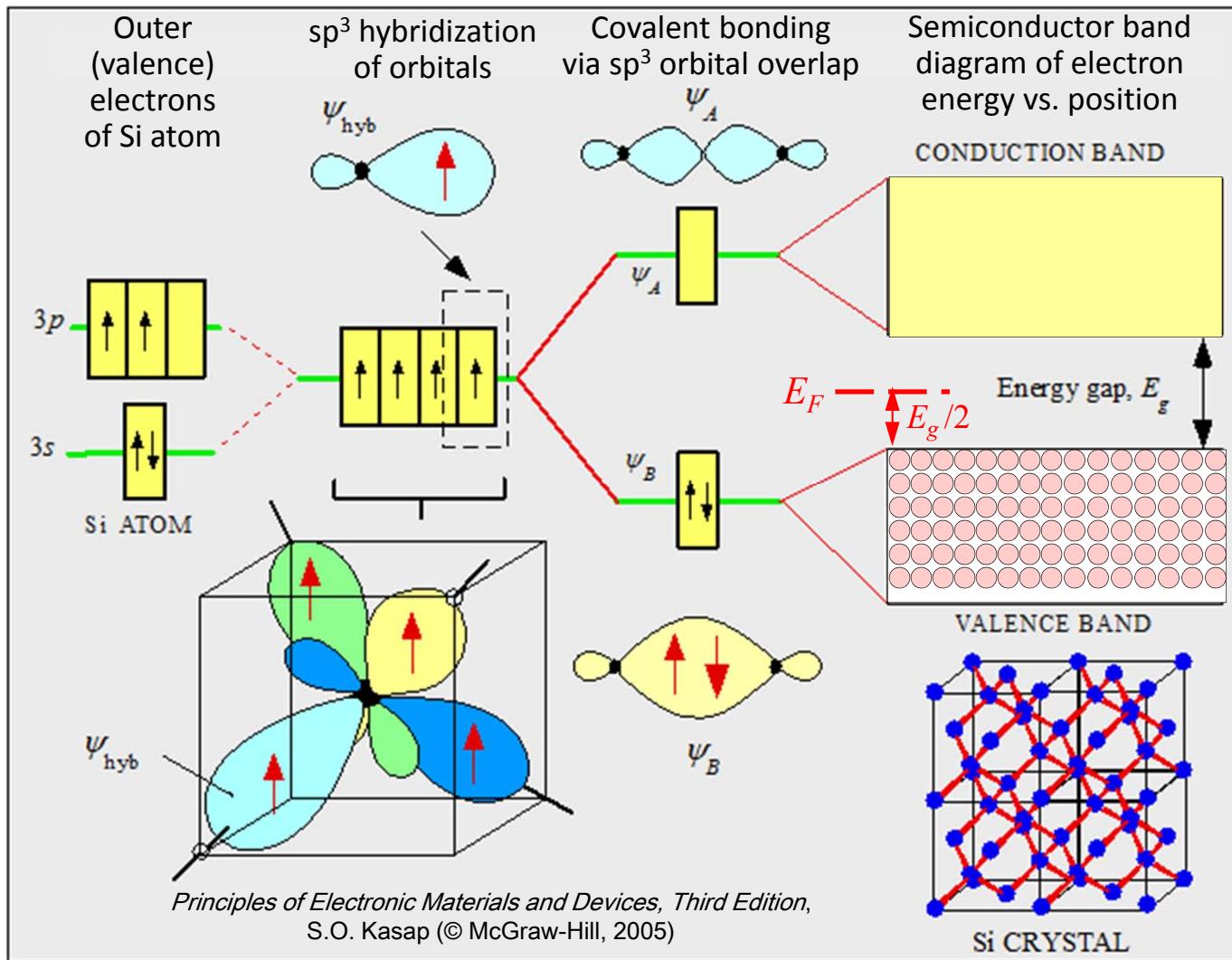
Schematics by P. Koirala, UT



# Outline of Topics

- Photovoltaics (PV): Motivation, status, and goals
- The first generation (Si) solar cell:  
Semiconductor physics and operation (7 slides: 8-14)
  - Bonding and bands in silicon
  - Illuminating silicon
  - Doping silicon *n* and *p* type
  - Forming a silicon *p/n* junction
  - Illuminating a silicon *p/n* junction
  - Generating electrical power from a solar cell
- Second generation (thin film) PV: Advantages and challenges
- Polarized light and its applications: Studies of thin film CdTe and CIGS PV

## “Intrinsic” Crystalline Silicon Semiconductor



In the limit of low temperature ( $T \rightarrow 0$  Kelvin), the valence band is completely filled with electrons and the conduction band is empty.

The fraction of electrons  $n/N$  in the conduction band follows “Boltzmann statistics”:

$$\frac{n}{N} = \exp\left(-\frac{E_g}{2kT}\right)$$

$k$  is Boltzmann’s constant.  
At  $T = 300$  K (room  $T$ )

$\frac{n}{N} \approx 10^{-9}$  hence  
“semiconductor”.

## Light Absorption in a Crystalline Silicon Semiconductor



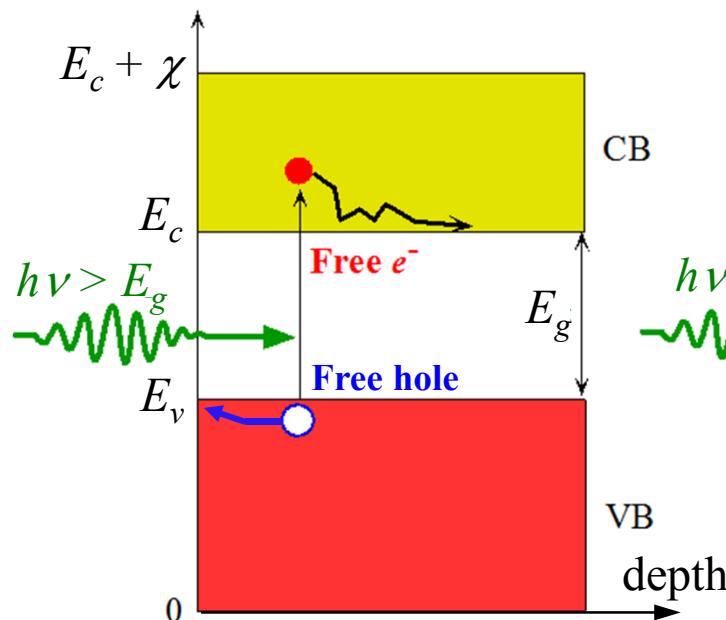
Light as electromagnetic waves or as photons?

**electromagnetic wave:** orthogonal electric and magnetic fields oscillating at frequency  $\nu$ ; wavelength  $\lambda = c/\nu$ ;  $c$  is speed of light

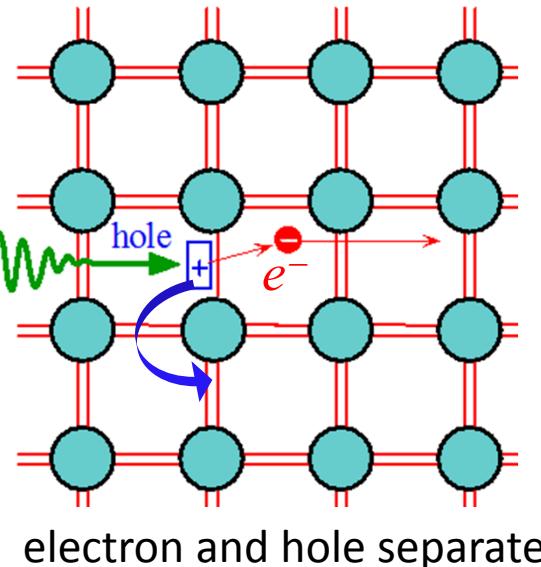
**photons:** each photon carries energy  $E = h\nu$  where  $h$  is Planck's constant ;  $E = hc/\lambda$

$$E \text{ (eV)} = 1240/\lambda \text{ (nm)}$$

Electron energy



Principles of Electronic Materials and Devices, Third Edition,  
S.O. Kasap (© McGraw-Hill, 2005)



Light absorption by a semiconductor is understood in terms of photons:

$h\nu < E_g$  no absorption

$h\nu > E_g$  absorption generates free electrons and holes ... and “photoconductivity”

## Doped Crystalline Silicon Semiconductors

Typical doping levels in solar cells: 0.1 – 100 impurity atoms per million Si atoms

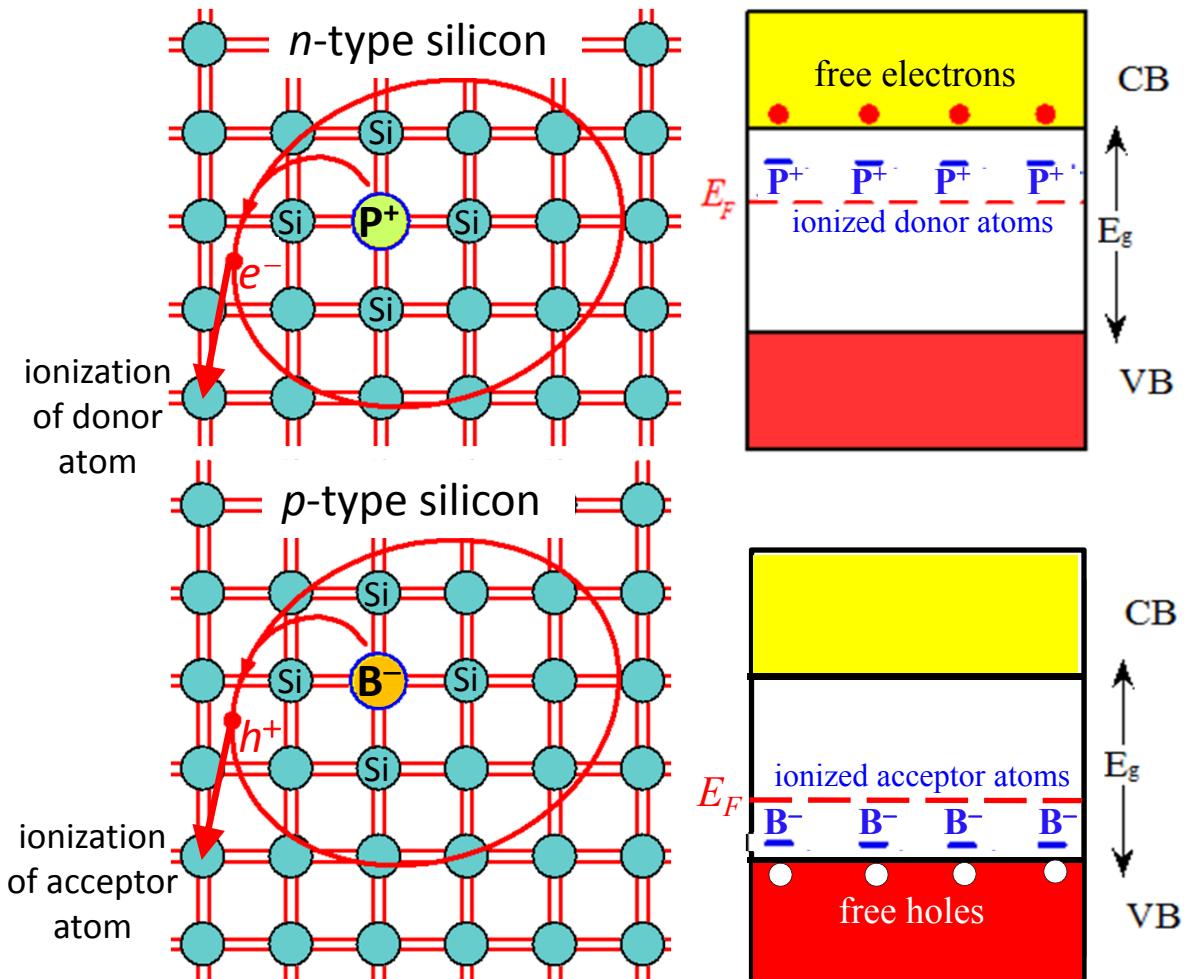
Group

III	IV	V
boron 5 <b>B</b> 10.811	carbon 6 <b>C</b> 12.011	nitrogen 7 <b>N</b> 14.007
aluminium 13 <b>Al</b> 26.982	silicon 14 <b>Si</b> 28.086	phosphorus 15 <b>P</b> 30.974
gallium 31 <b>Ga</b> 69.723	germanium 32 <b>Ge</b> 72.61	arsenic 33 <b>As</b> 74.922

3      4      5  
number of s and p  
valence electrons

↑  
p-type  
dopants

↑  
n-type  
dopants



## Junction between *n* and *p*-Type Silicon

A junction is shown between electrically neutral *n* and *p*-type silicon.

*This system is not in equilibrium.*

Electrons move to the left and annihilate holes.

Holes move to the right and annihilate electrons.

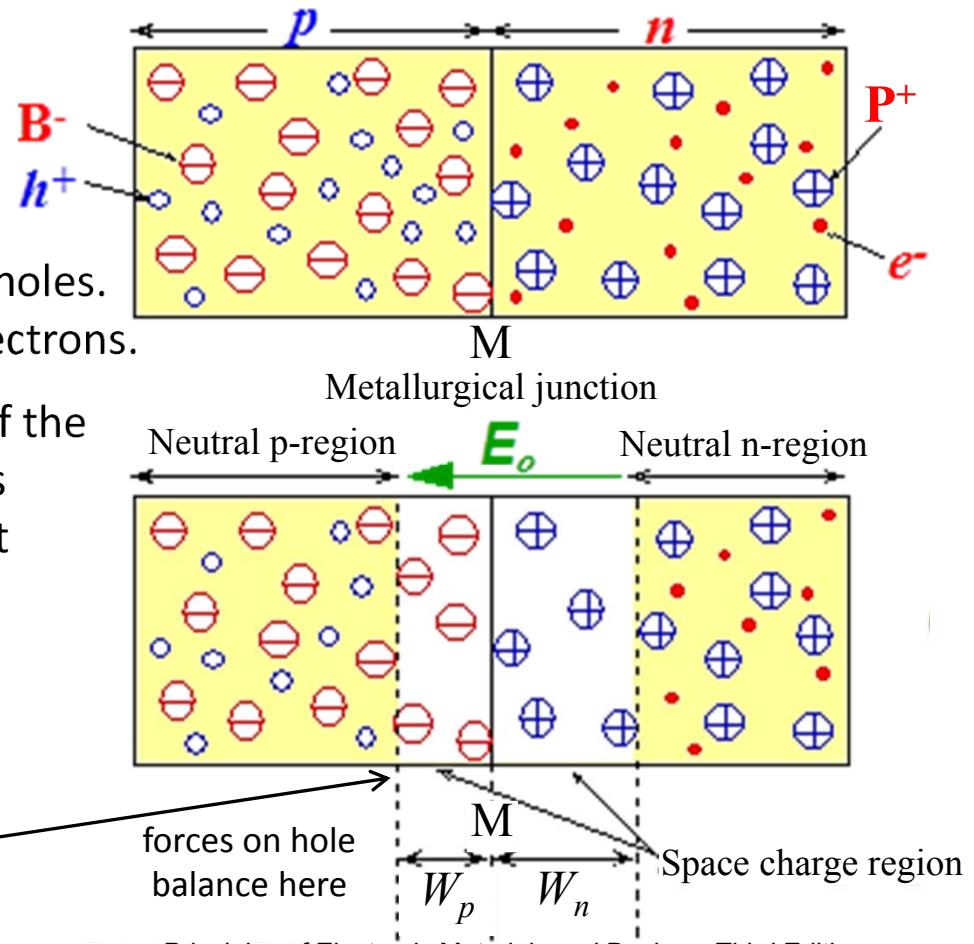
Equilibrium is achieved when the forces of the electric field  $E_o$  on the electrons and holes balance the “driving forces” of diffusion at the space charge boundaries.

An equation describes this equilibrium at the two space charge boundaries:

$$F_{net} = eE_o - kT \left( \frac{1}{n} \frac{\Delta n}{\Delta x} \right) = 0$$

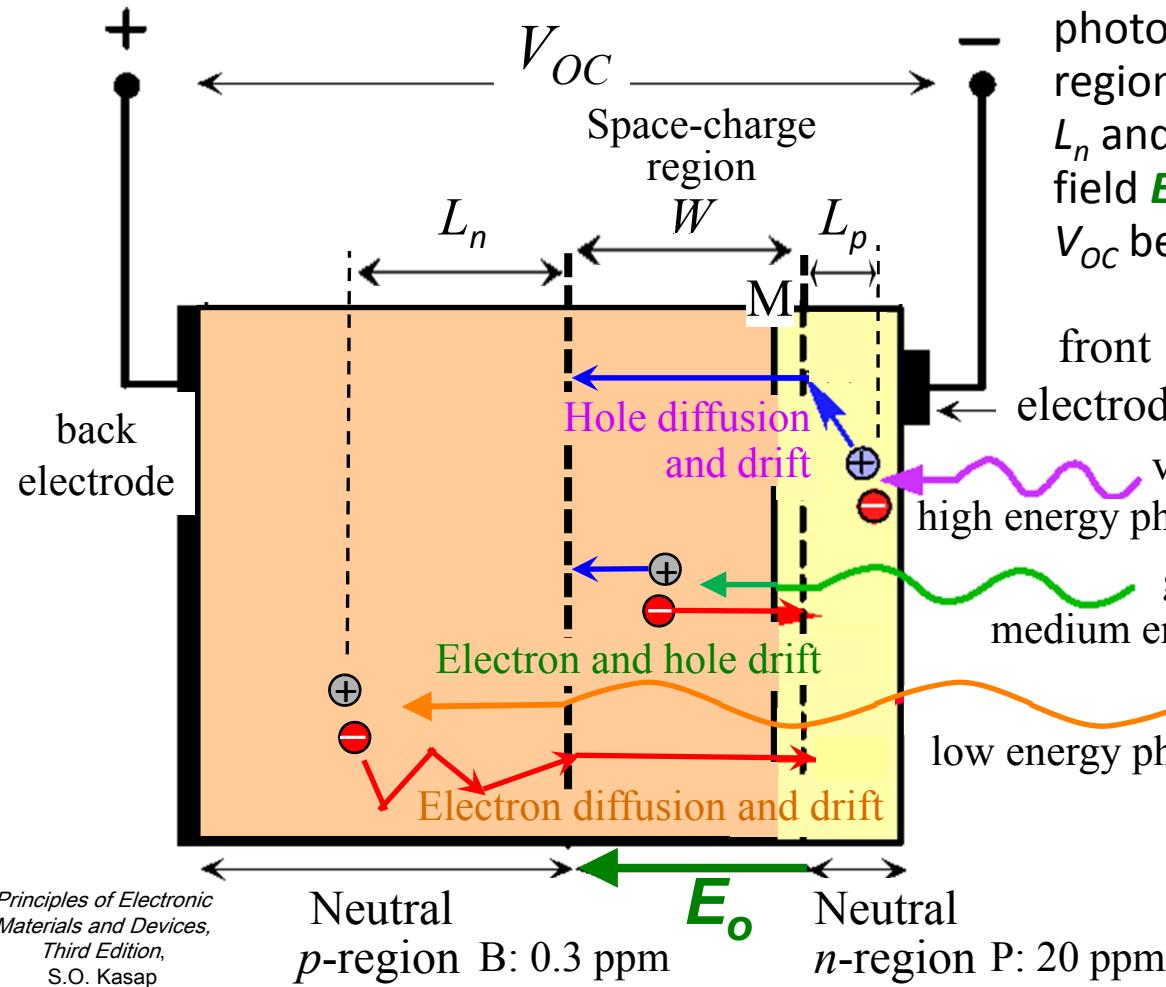
force holes  
by field (left-ward)

“force” on holes  
due to concentration gradient  $\Delta n / \Delta x$  (right-ward)



*Principles of Electronic Materials and Devices, Third Edition,*  
S.O. Kasap (© McGraw-Hill, 2005)

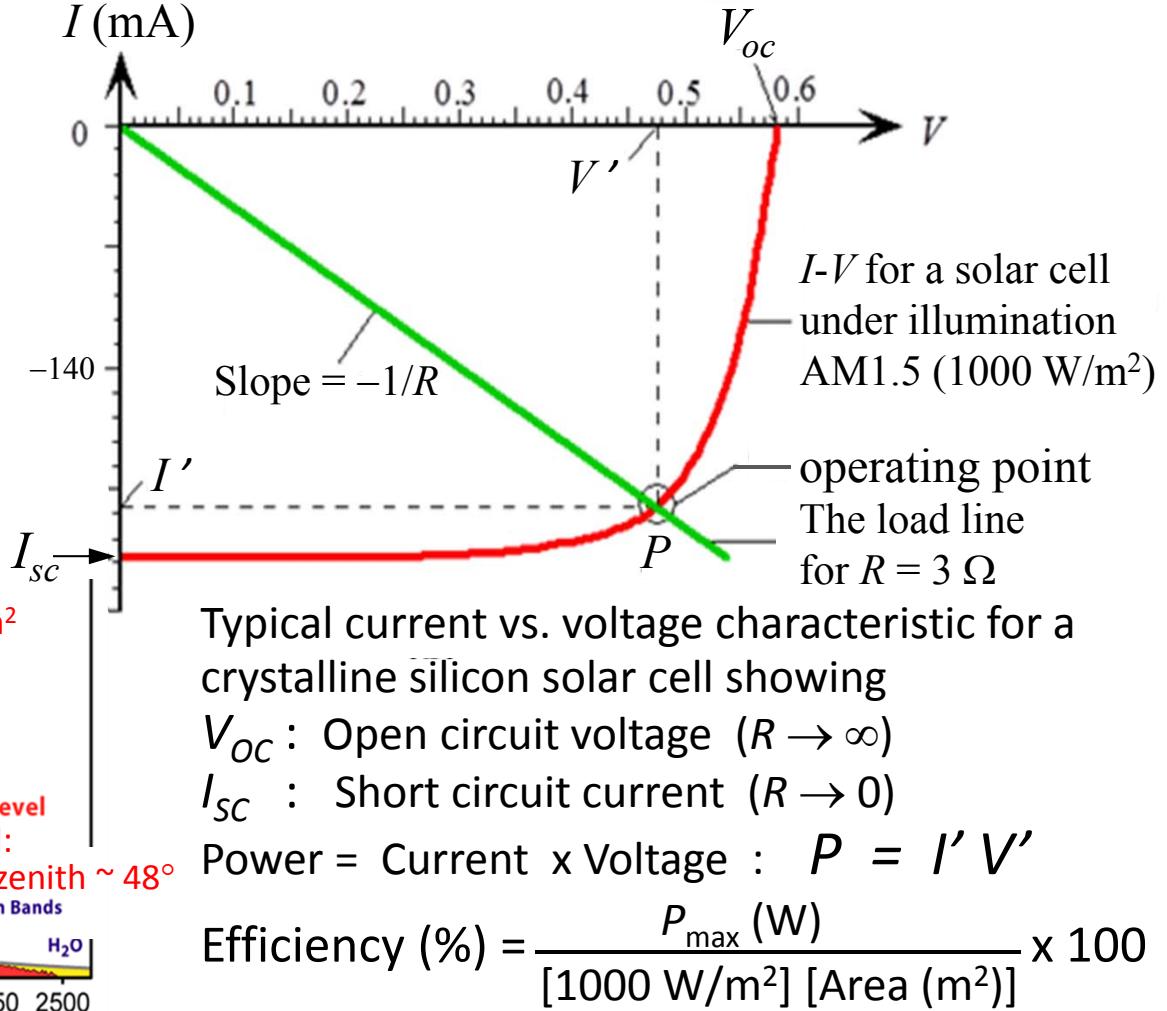
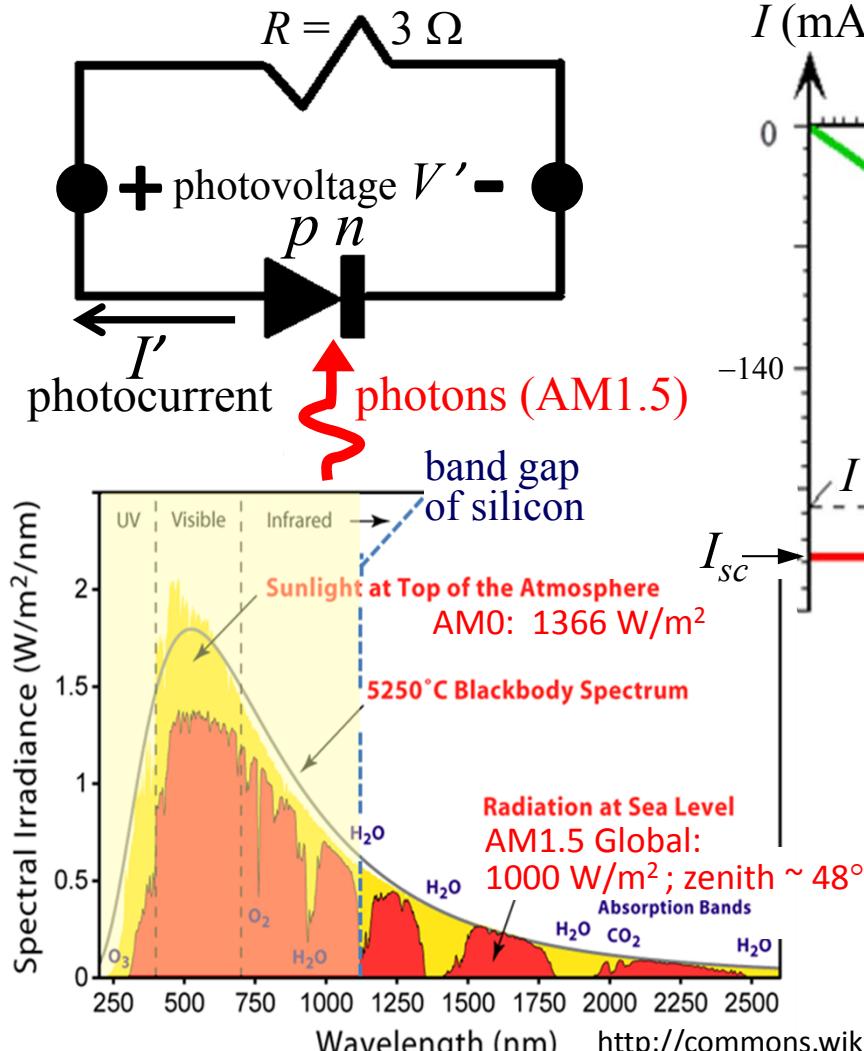
## Finally: The Crystalline Silicon *p-n* Junction Solar Cell under Light !



The electrons and holes generated by photons absorbed within the depletion region  $W$  and the two diffusion regions  $L_n$  and  $L_p$  are separated by the built-in field  $E_o$  and generate a photovoltage  $V_{OC}$  between the two electrodes.

$$E \text{ (eV)} = \frac{1240}{\lambda \text{ (nm)}}$$

## Photovoltaic Power from a Crystalline Silicon Solar Cell



[http://commons.wikimedia.org/  
wiki/File:Solar\\_spectrum\\_en.svg](http://commons.wikimedia.org/wiki/File:Solar_spectrum_en.svg)

Principles of Electronic Materials and Devices, 3<sup>rd</sup> Edition,  
S.O. Kasap (© McGraw-Hill, 2005)



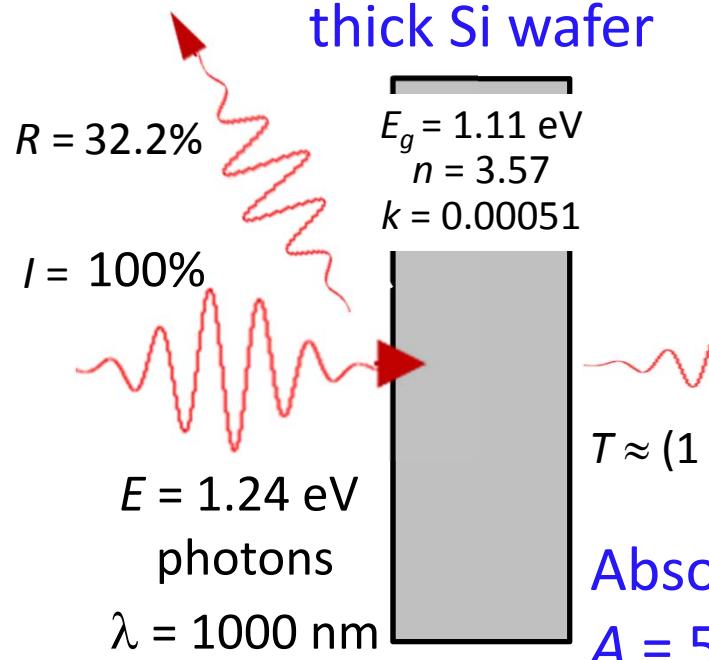
# Outline of Topics

- Photovoltaics (PV): Motivation, status, and goals
- The first generation (Si) solar cell: Semiconductor physics and operation
- **Second generation or thin film PV:  
Advantages over 1<sup>st</sup> generation and its challenges**
  - > Advantages of thin film technology 7 slides: 15-21
    - Much stronger absorption in thin films for lower materials usage
    - Low temperature processes for shorter energy payback time
    - Greater potential for scalability and in-line automation
  - > Challenges of thin film technology
- Polarized light and its applications: Studies of 2<sup>nd</sup> generation PV

## Silicon (Si): Indirect Bandgap    vs.    Copper Indium-Gallium Diselenide [Cu(In<sub>0.7</sub>Ga<sub>0.3</sub>)Se<sub>2</sub>; CIGS]: Direct Bandgap

For a given photon energy just above their bandgaps, the absorption strength (absorbance/volume) of CIGS is ~ 250 times higher than that of Si.

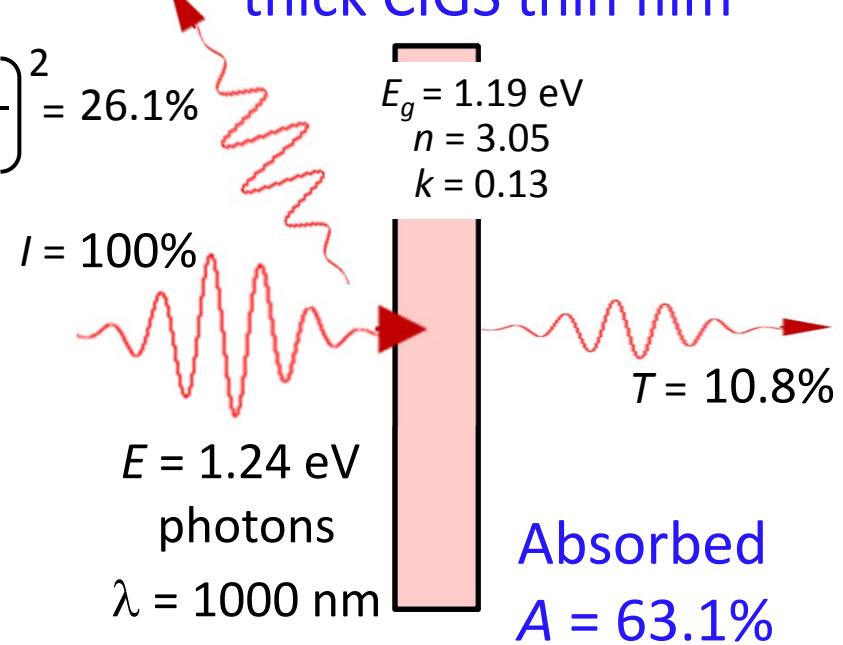
$d = 250 \text{ micron} = 0.25 \text{ mm}$   
thick Si wafer



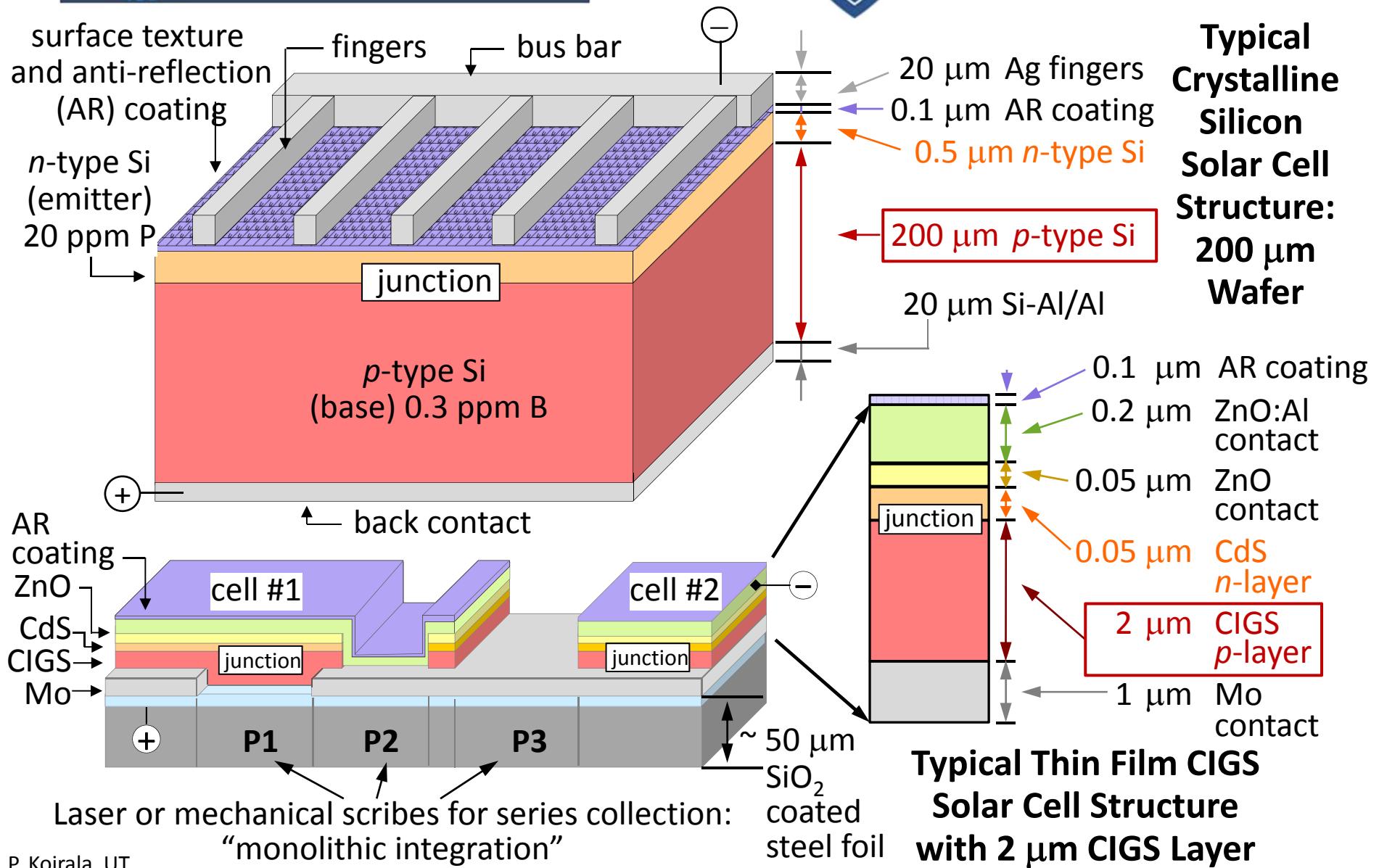
$$R \approx \left( \frac{n - 1}{n + 1} \right)^2 = 26.1\%$$

$$T \approx (1 - R)^2 e^{-\frac{4\pi kd}{\lambda}} = 9.5\%$$

$d = 1 \text{ micron} = 0.001 \text{ mm}$   
thick CIGS thin film



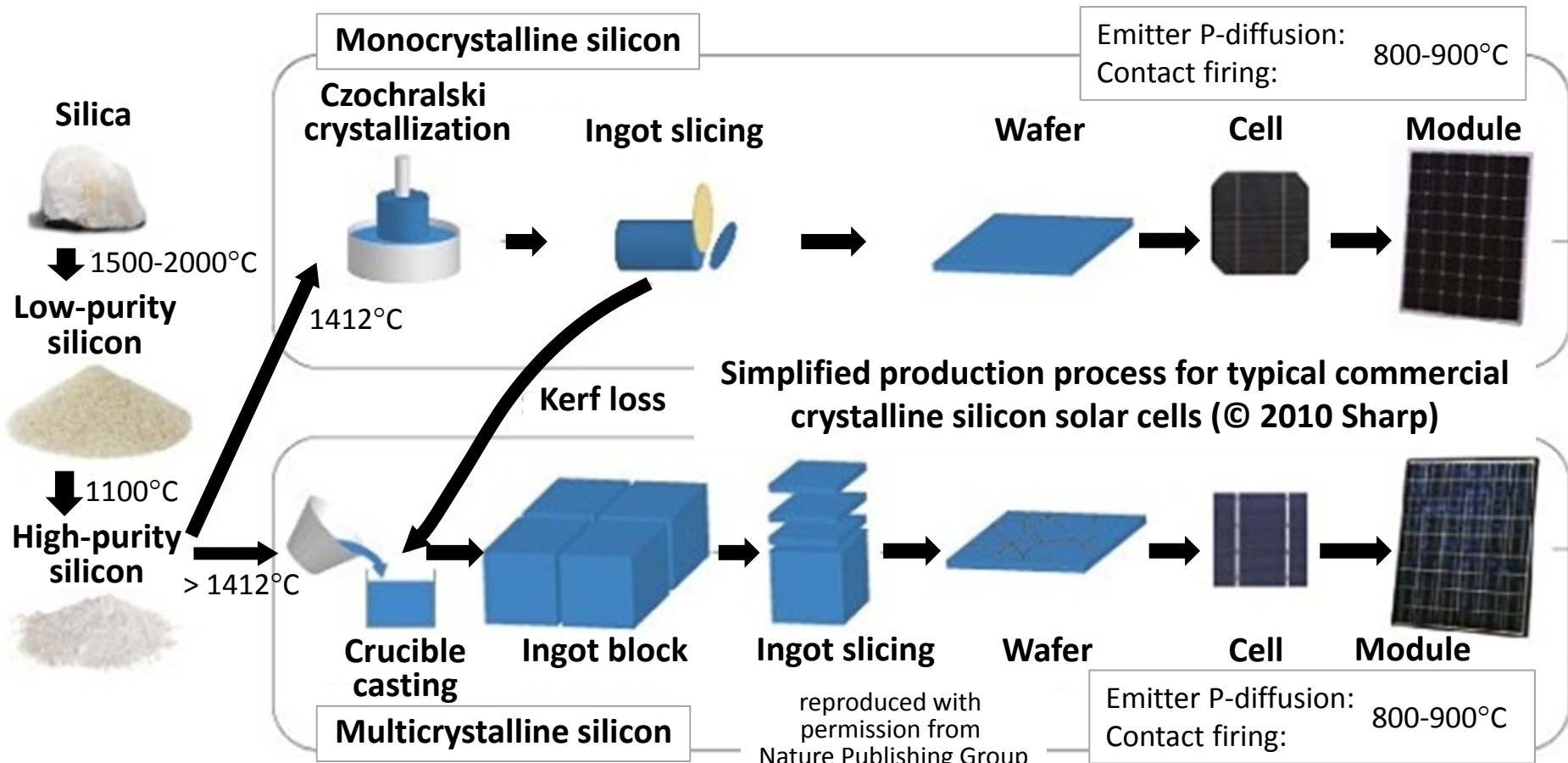
Reflectance  $R$ , transmittance  $T$ , and absorbance  $A$  of a material is controlled by its index of refraction  $n$ , and its extinction coefficient  $k$  which vary with wavelength  $\lambda$



## Drawbacks of Crystalline Silicon PV: Cost Related Issues

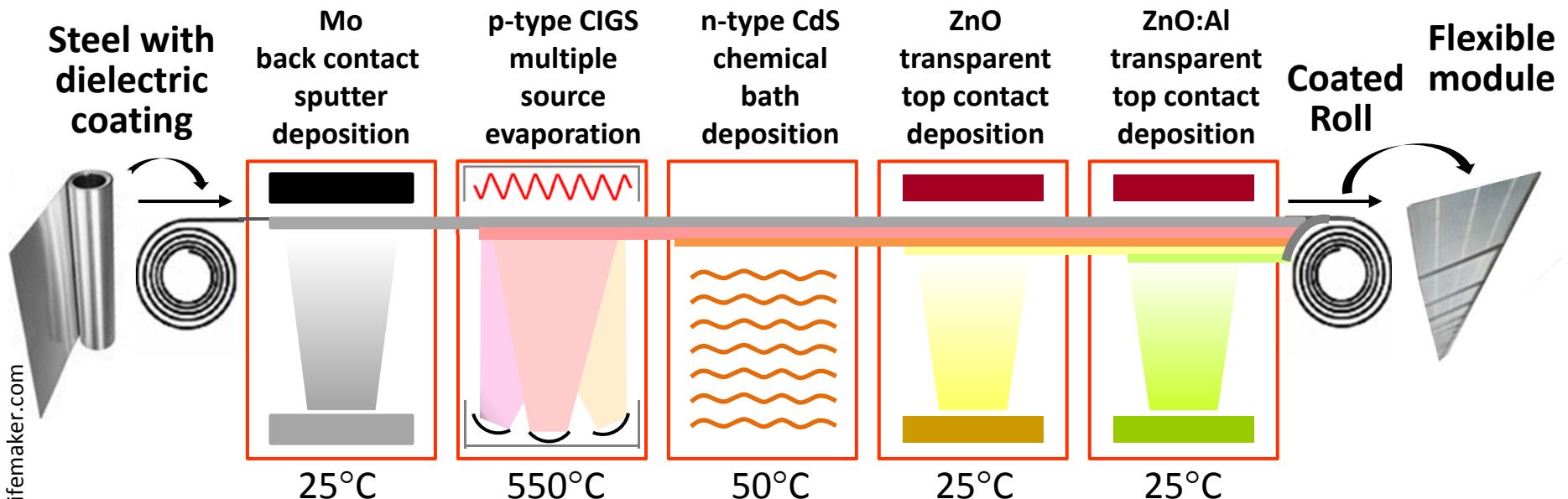
- Higher materials cost
- High temperature processes -- energy intensive
- Capital intensive processes with limited scalability
- Greater challenges in in-line automation due fragility of wafers

Tatsuo Saga,  
*NPG Asia Materials* (2010)  
2, 96–102;  
doi:10.1038/asiamat.2010.82



## Advantages of Thin Film Photovoltaics: Cost Related Issues

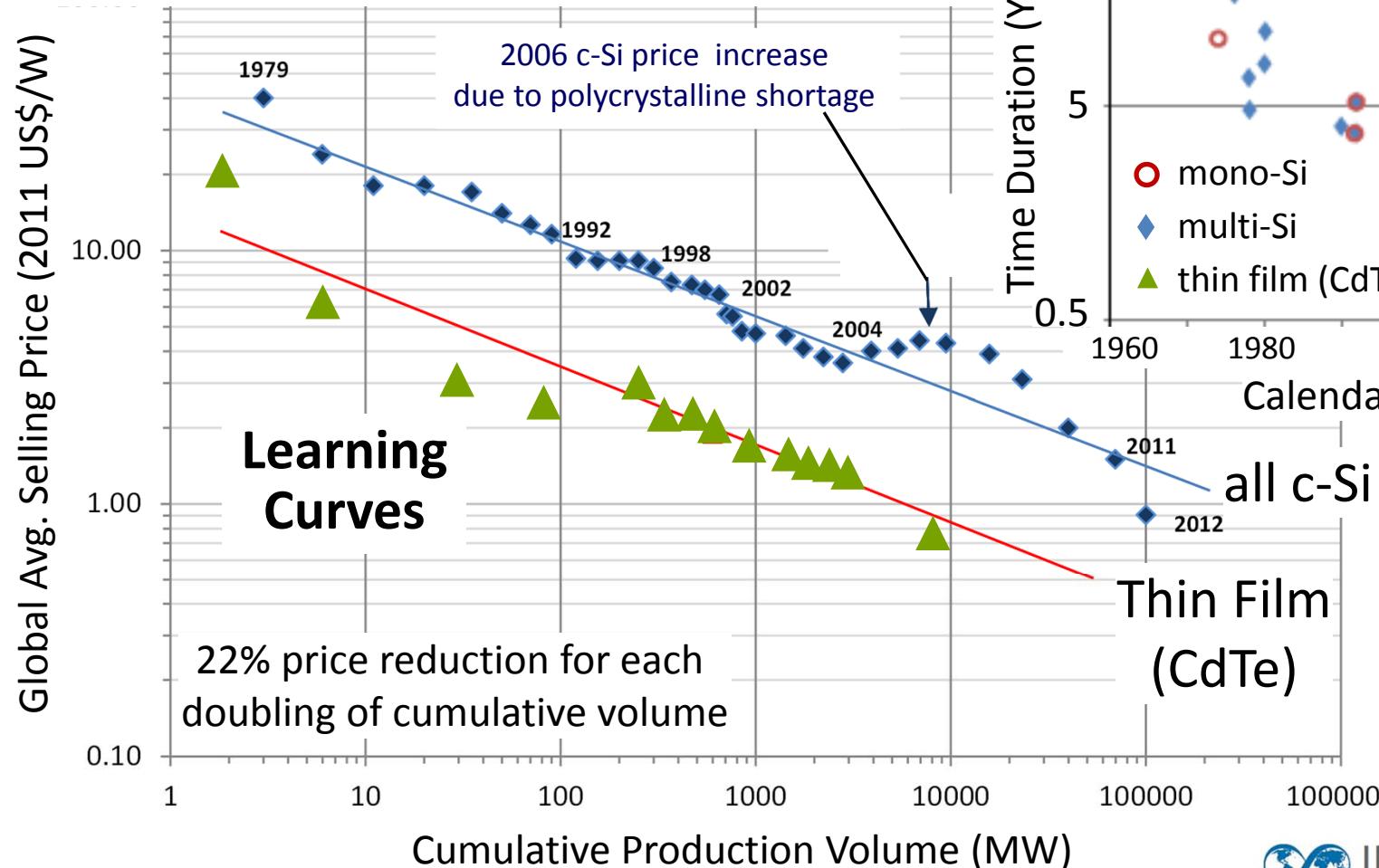
- Lower materials cost due to lower materials usage
- Lower temperature processes – lower thermal budget and shorter energy payback times
- Manufacturing scalability
- Continuous production line with greater automation



**Production line schematic for  $\text{Cu}(\text{In}_{0.7}\text{Ga}_{0.3})\text{Se}_2$  (CIGS) solar cells on flexible steel foil**

See for example: <http://www.flisom.ch> ; [www.nuvosun.com](http://www.nuvosun.com)

## Comparisons of Crystalline Silicon and Thin Film (CdTe) PV Manufacturing



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## Example Installations of Thin Film (CdTe, CIGS) Photovoltaics



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<http://www.calyxo.com/en/news-events/news/251-completed-anthony-wayne-solar-array-is-providing-power-for-the-toledo-zoo-and-new-life-to-brownfield-site.html>

**Utility scale  
power plants from  
CdTe on glass  
PV technology**

2.1 MW Anthony Wayne Solar Array provides power to The Toledo Zoo

World's largest plants are thin film: Topaz (2014, 550 MW); Desert Sunlight (2015, 550 MW)



thin film PV ⇒ solar anywhere

Reproduced with permission of Dow Solar

**Residential PV  
power from  
CIGS on steel foil  
PV Technology**

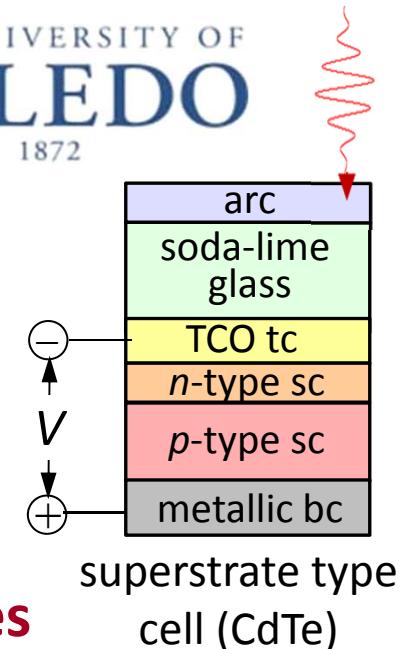
Solar shingles on a residence in Katy, Texas.

<http://www.dowpowerhouse.com/why-powerhouse/index.htm>

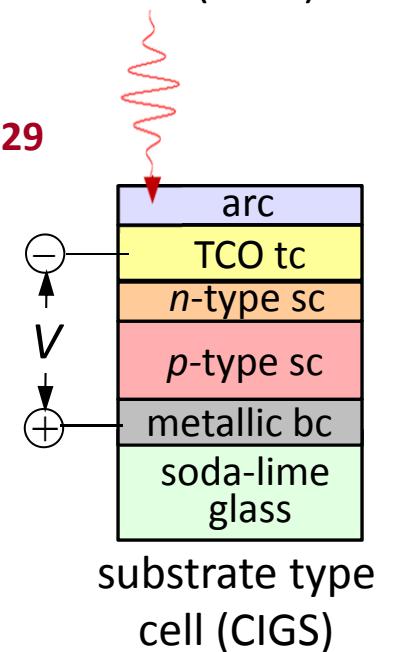


## Outline of Topics

- Photovoltaics (PV): Motivation, status, and goals
- The first generation (Si) solar cell: physics and operation
- **Second generation or thin film PV:**  
**Advantages over 1<sup>st</sup> generation and its challenges**
  - > Advantages of thin film technology
  - > Challenges of thin film technology
    - Materials development for:  
*p*-type and *n*-type semiconductors (sc's)  
Transparent conducting oxide (TCO) top contact (tc)  
Back contact (bc) and anti-reflection coating (arc)
    - Approaching the performance of 1<sup>st</sup> generation PV
    - Controlling the fabrication process
- Polarized light and applications: Studies of 2<sup>nd</sup> generation PV



8 slides: 22-29





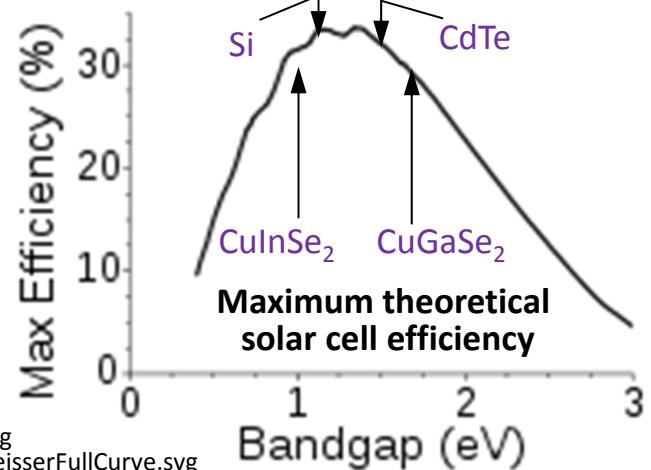
## Tetrahedrally-Bonded Semiconductor Materials Development

I-B Groups	II-B	III-A	IV-A	V-A	VI-A	VII-A
		boron 5 10.811 <b>B</b>	carbon 6 12.011 <b>C</b>	nitrogen 7 14.007 <b>N</b>	oxygen 8 15.999 <b>O</b>	fluorine 9 18.998 <b>F</b>
		aluminium 13 <b>Al</b>	silicon 14 <b>Si</b>	phosphorus 15 <b>P</b>	sulfur 16 32.065 <b>S</b>	chlorine 17 35.453 <b>Cl</b>
copper 29 <b>Cu</b> 63.546	zinc 30 <b>Zn</b> 65.39	gallium 31 <b>Ga</b> 69.723	germanium 32 <b>Ge</b> 72.61	arsenic 33 <b>As</b> 74.922	selenium 34 <b>Se</b> 78.96	bromine 35 <b>Br</b> 79.904
silver 47 <b>Ag</b> 107.87	cadmium 48 <b>Cd</b> 112.41	indium 49 <b>In</b> 114.82	tin 50 <b>Sn</b> 118.71	antimony 51 <b>Sb</b> 121.76	tellurium 52 <b>Te</b> 127.60	iodine 53 <b>I</b> 126.90
gold 79 <b>Au</b> 196.97	mercury 80 <b>Hg</b> 200.59	thallium 81 <b>Tl</b> 204.38	lead 82 <b>Pb</b> 207.2	bismuth 83 <b>Bi</b> 208.98	polonium 84 [209]	astatine 85 <b>At</b> [210]
1	2	3	4	5	6	7
number of s and p valence electrons						

Ternary and quaternary compound semiconductors: provide flexibility in tuning band gap and properties

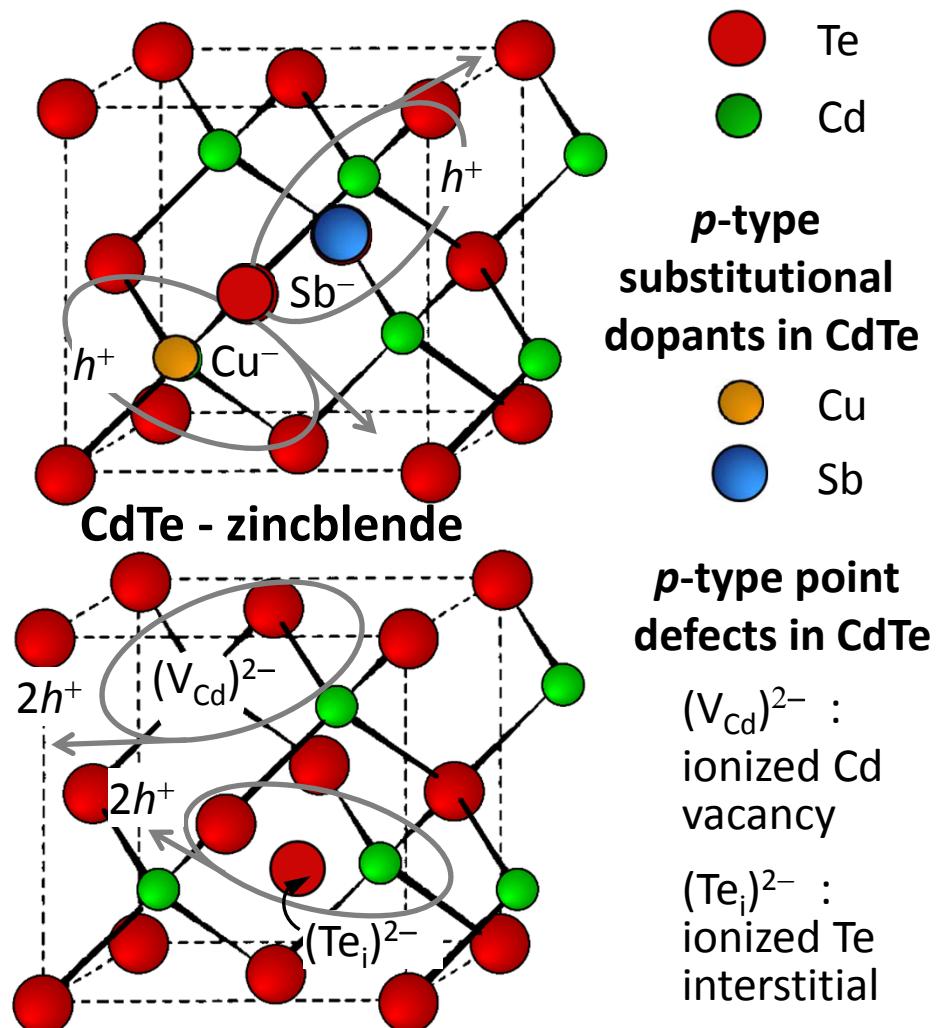
Type	Family	Examples	No. of Valence e <sup>-</sup>	No. of Valence e <sup>-</sup> per atom
Elemental	<b>IV</b>	<b>Si</b>	4	4
Binary	<b>II</b> <b>VI</b>	<b>CdTe</b> <b>CdS</b>	8	4
Ternary	<b>I</b> <b>III</b> <b>VI<sub>2</sub></b>	<b>CuInSe<sub>2</sub></b>	16	4
Quaternary	<b>I<sub>2</sub></b> <b>II</b> <b>IV</b> <b>VI<sub>4</sub></b>	<b>Cu<sub>2</sub>ZnSnS<sub>4</sub></b>	32	4

- Group I alloying:  $(Cu_{1-x}Ag_x)InSe_2$
- Group III alloying  $Cu(In_{1-x}Ga_x)Se_2$
- Group VI alloying  $CuIn(Se_{1-x}S_x)_2$

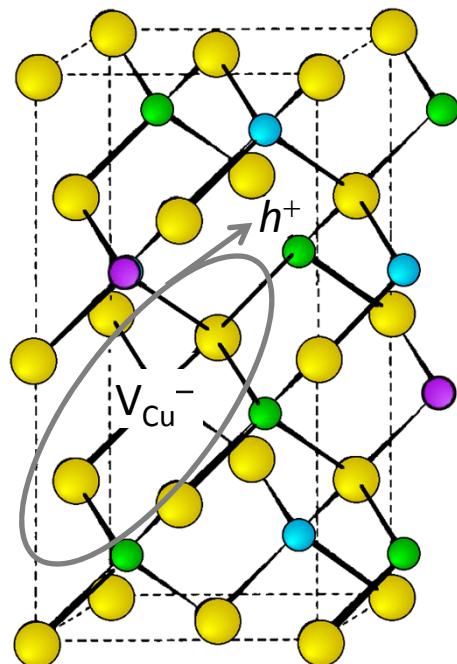


## (n,p)-Type Tetrahedrally-Bonded Semiconductor Materials

I-B Groups	II-B	III-A	IV-A	V-A	VI-A	VII-A
	boron 5 <b>B</b> 10.811	carbon 6 <b>C</b> 12.011	nitrogen 7 <b>N</b> 14.007	oxygen 8 <b>O</b> 15.999	fluorine 9 <b>F</b> 18.998	
	aluminum 13 <b>Al</b> 26.982	silicon 14 <b>Si</b> 28.086	phosphorus 15 <b>P</b> 30.974	sulfur 16 <b>S</b> 32.065	chlorine 17 <b>Cl</b> 35.453	
copper 29 <b>Cu</b> 63.546	zinc 30 <b>Zn</b> 65.39	gallium 31 <b>Ga</b> 69.723	germanium 32 <b>Ge</b> 72.61	arsenic 33 <b>As</b> 74.922	selenium 34 <b>Se</b> 78.96	bromine 35 <b>Br</b> 79.904
silver 47 <b>Ag</b> 107.87	cadmium 48 <b>Cd</b> 112.41	indium 49 <b>In</b> 114.82	tin 50 <b>Sn</b> 118.71	antimony 51 <b>Sb</b> 121.76	tellurium 52 <b>Te</b> 127.60	iodine 53 <b>I</b> 126.90
1	2	3	4	5	6	7
number of s and p valence electrons						
 p-type dopants substituting for Cd	 n-type dopants substituting for Cd	 p-type dopants substituting for Te	 n-type dopants substituting for Te			



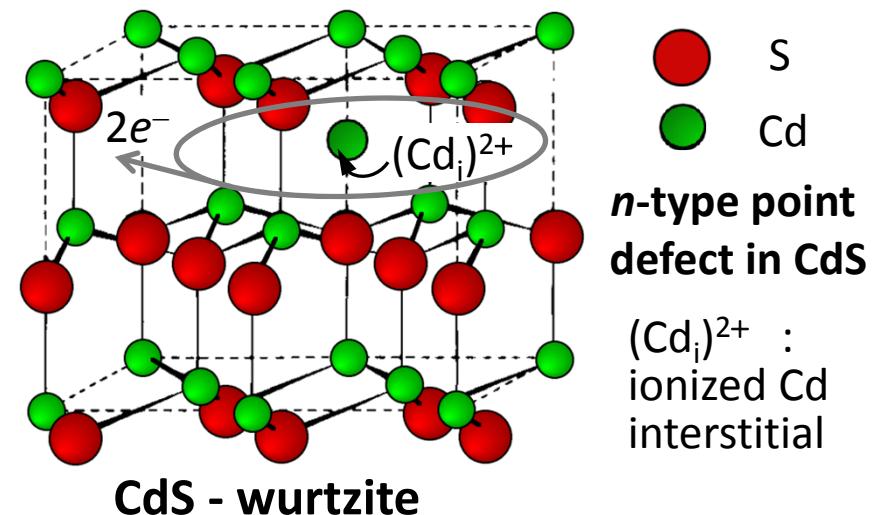
## (n,p)-Type Tetrahedrally-Bonded Semiconductor Materials



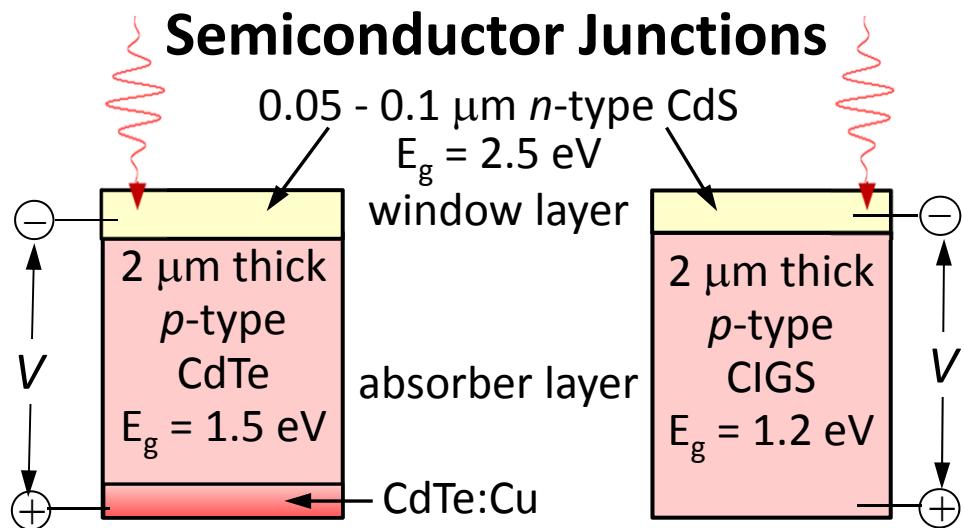
● Se  
 ● In  
 ● Cu  
 ● Ga  
**p-type point defect in  $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$**   
 $\text{V}_{\text{Cu}}^-$  : ionized Cu vacancy

### $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ - chalcopyrite

The most successful solar cell designs incorporate thin n-type CdS as an inactive window layer and a thick p-type CdTe or CIGS absorber. With the exception of a Cu-doped region at the back of the CdTe cell, materials rely on defects for doping.



### CdS - wurtzite Semiconductor Junctions





## Materials Development: Transparent Conducting Oxide Top Contacts

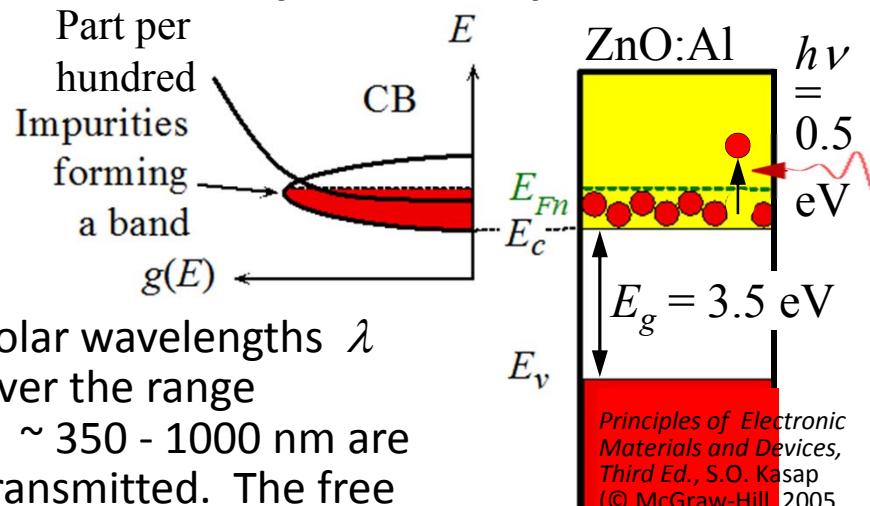
I-B	II-B	III-A	IV-A	V-A	VI-A	VII-A
Groups						
boron 5 <b>B</b> 10.811	carbon 6 <b>C</b> 12.011	nitrogen 7 <b>N</b> 14.007	oxygen 8 <b>O</b> 15.999	fluorine 9 <b>F</b> 18.999		
aluminum 13 <b>Al</b> 26.982	silicon 14 <b>Si</b> 28.086	phosphorus 15 <b>P</b> 30.974	sulfur 16 <b>S</b> 32.065	chlorine 17 <b>Cl</b> 35.453		
copper 29 <b>Cu</b> 63.546	zinc 30 <b>Zn</b> 65.39	gallium 31 <b>Ga</b> 69.723	germanium 32 <b>Ge</b> 72.61	arsenic 33 <b>As</b> 74.922	selenium 34 <b>Se</b> 78.96	bromine 35 <b>Br</b> 79.904
silver 47 <b>Ag</b> 107.87	cadmium 48 <b>Cd</b> 112.41	indium 49 <b>In</b> 114.82	tin 50 <b>Sn</b> 118.71	antimony 51 <b>Sb</b> 121.76	tellurium 52 <b>Te</b> 127.60	iodine 53 <b>I</b> 126.90
1	2	3	4	5	6	7
number of s and p valence electrons						

Most common solar cell TCOs (all *n*-type):

**In<sub>2</sub>O<sub>3</sub>:Sn** -- Sn substitutes for In  
**SnO<sub>2</sub>:F** -- F substitutes for O  
**ZnO:Al** -- Al substitutes for Zn

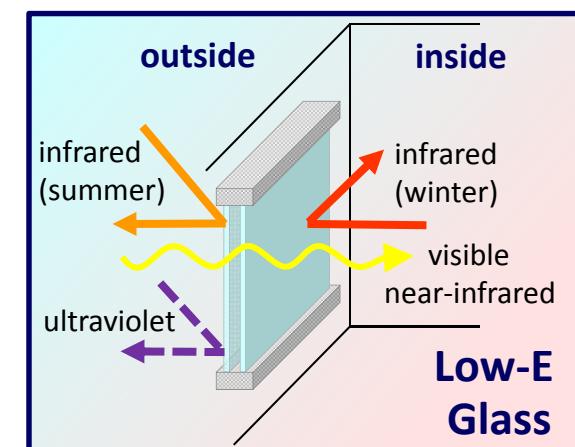
<http://commons.wikimedia.org/wiki/File:Periodic-table.jpg>

### Physical Principle of TCOs



Solar wavelengths  $\lambda$  over the range  $\lambda \sim 350 - 1000$  nm are transmitted. The free electrons reflect infrared light  $\lambda > 2000$  nm

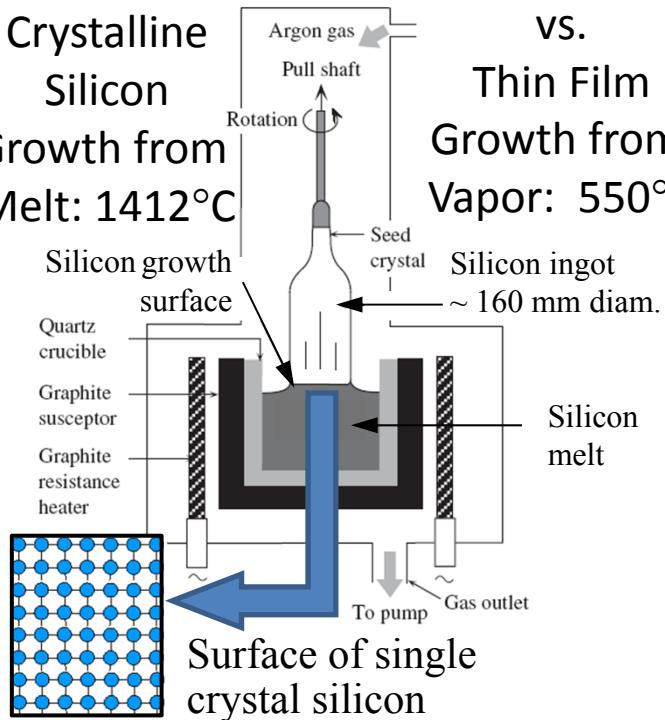
Low emissivity glass is coated with TCO layers



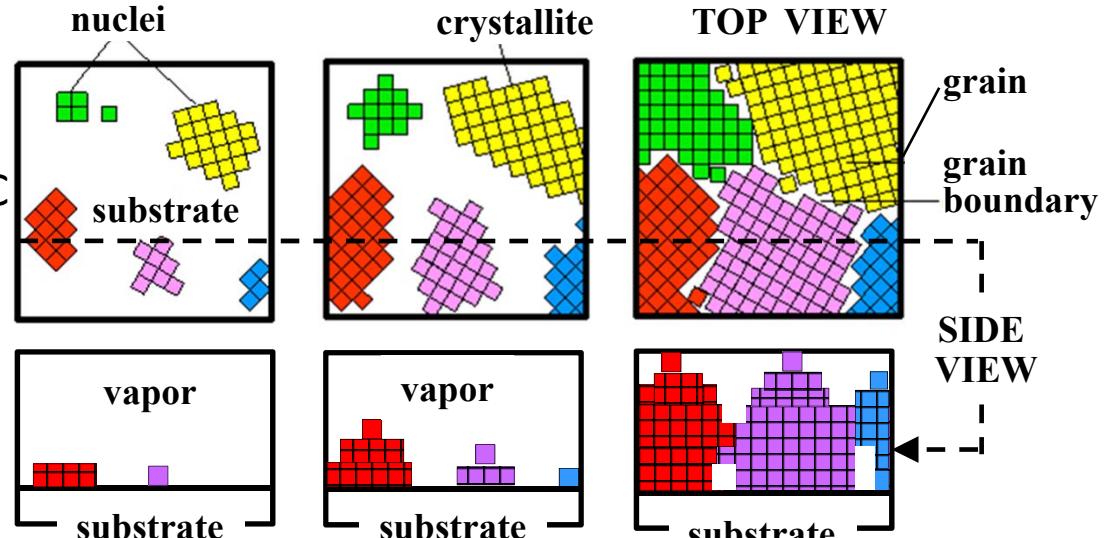


## Materials Development: Thin Film Structure and Grain Boundaries

Crystalline  
Silicon  
Growth from  
Melt:  $1412^{\circ}\text{C}$



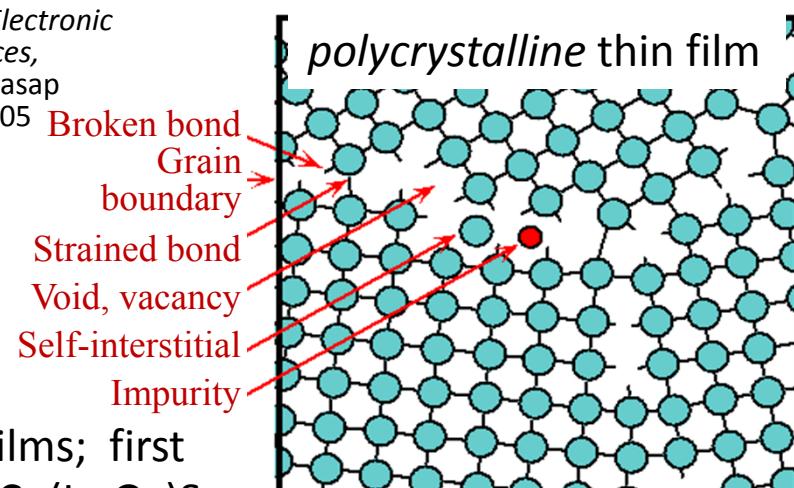
VS.  
Thin Film  
Growth from  
Vapor:  $550^{\circ}\text{C}$



**Goal in thin film PV: mitigate the role of grain boundaries and associated structural defects:**

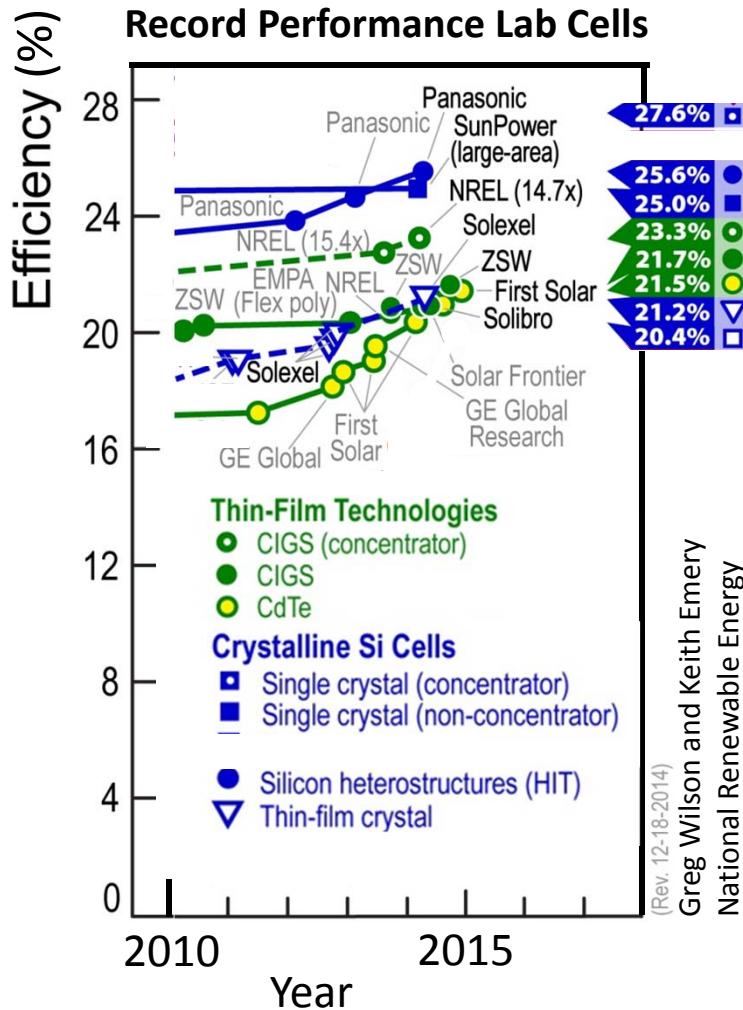
**CdTe:** After deposition coat with aqueous  $\text{CdCl}_2$  solution and anneal at  $\sim 400^{\circ}\text{C} \Rightarrow$  grain growth

**CIGS:** Diffuse Na and K atoms into the growing films; first grow  $(\text{In},\text{Ga})_2\text{Se}_3$ , then diffuse Cu into it to form  $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ .

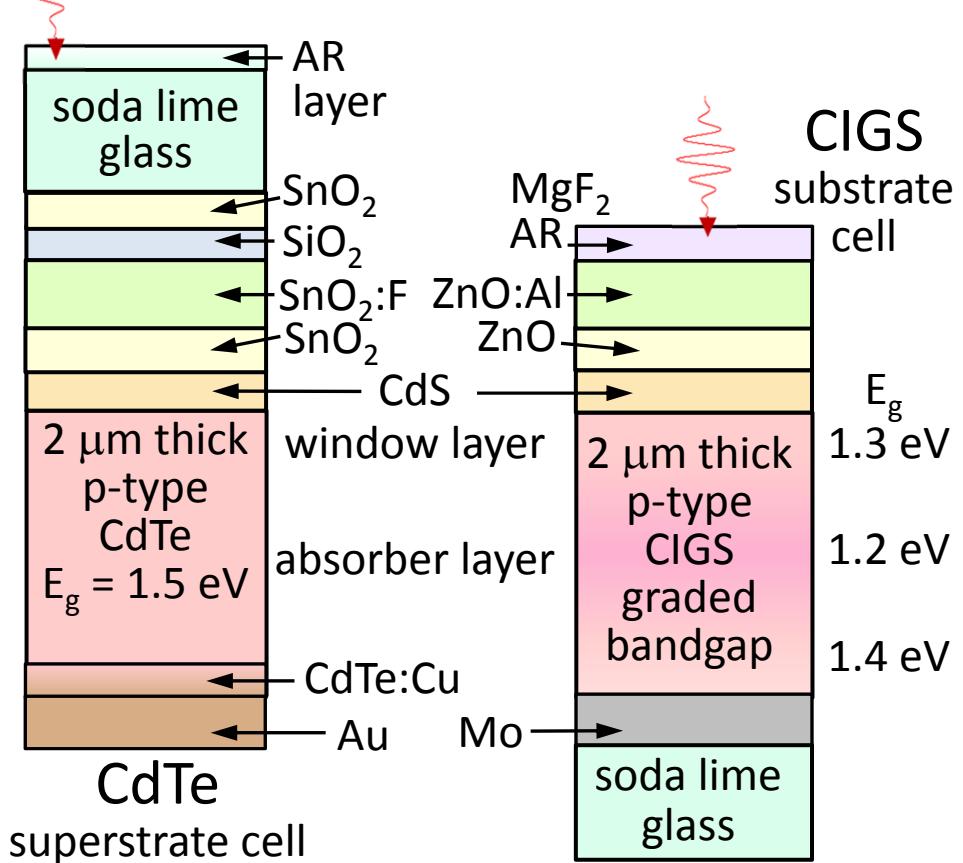




## Thin Film PV in the Laboratory: Approaching the Laboratory Performance of Single Crystal Silicon PV



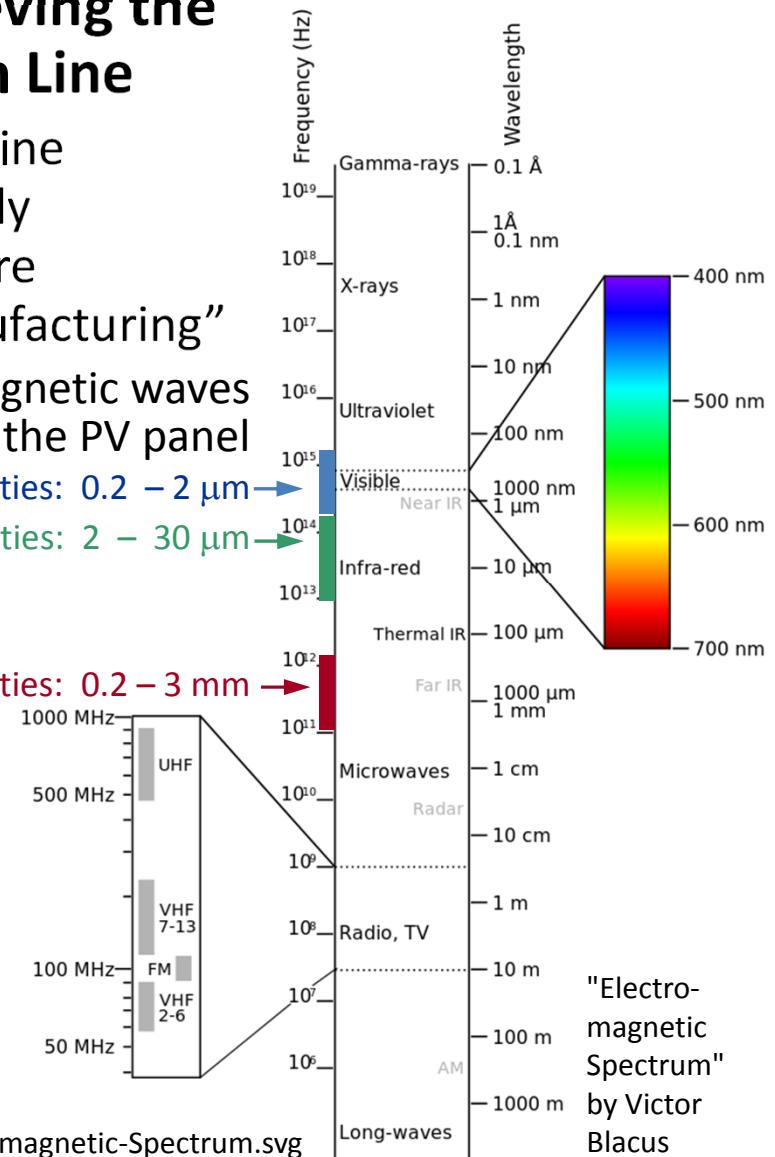
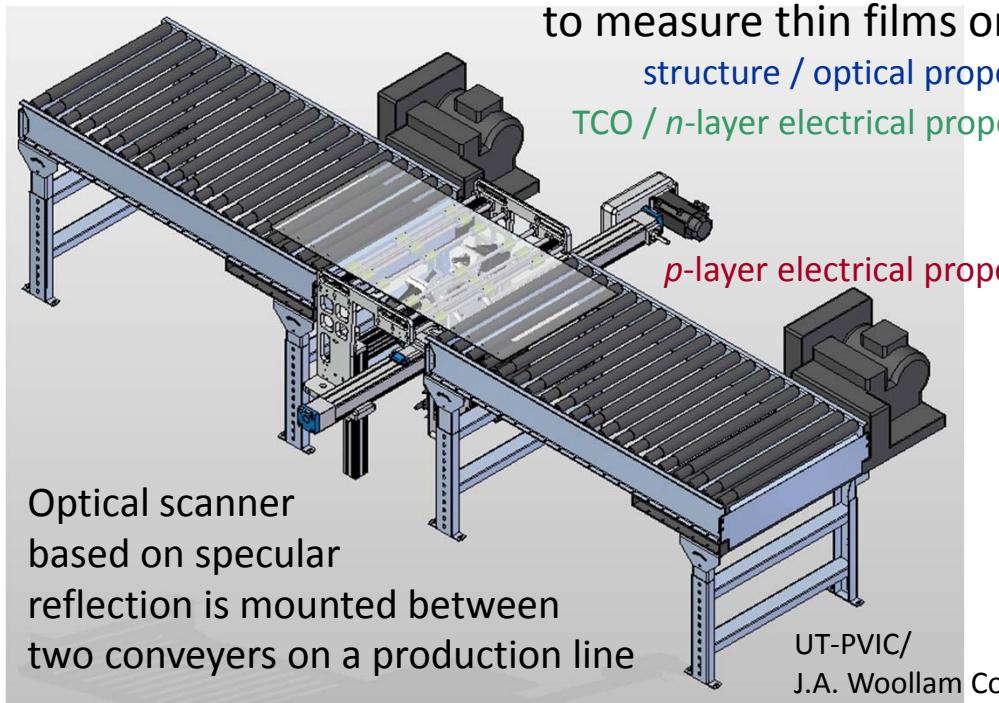
Compared to single crystal Si PV, a larger gap exists for thin film PV between best lab efficiency and best production line efficiency



## Controlling Module Fabrication: Achieving the Best Lab Efficiencies on the Production Line

- Rapid optimization and troubleshooting of line
- Enables tracking of fabrication steps for early detection of process deviations before failure
- Potential of on-line control: “adaptive manufacturing”

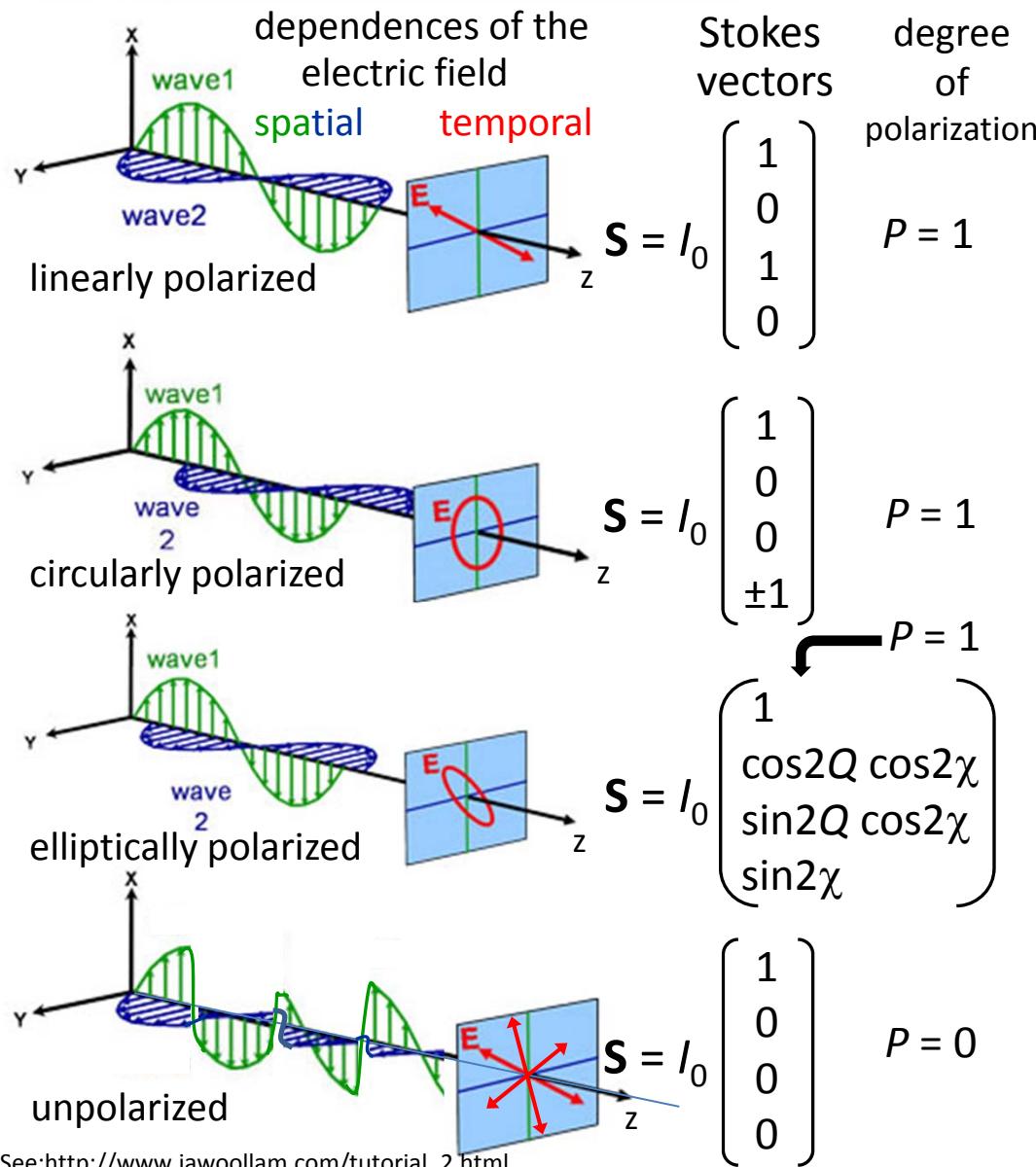
Non-invasive tools utilize electromagnetic waves to measure thin films on the PV panel





# Outline of Topics

- Photovoltaics (PV): Motivation, status, and goals
- The first generation (Si) solar cell: Semiconductor physics and operation
- Second generation or thin film PV:  
Advantages over 1<sup>st</sup> generation and its challenges
- Polarized light and its applications:  
Studies of second generation PV (15 slides: 30-44)
  - Polarized electromagnetic waves: Stokes vectors and Mueller matrices
  - Polarized light studies of CdTe PV
  - Polarized light studies of Cu(In,Ga)Se<sub>2</sub> PV



See:[http://www.jawoollam.com/tutorial\\_2.html](http://www.jawoollam.com/tutorial_2.html)

## Electromagnetic Waves

Electromagnetic waves consist of orthogonal electric and magnetic field vectors that are in turn orthogonal to the ray vector (along z).

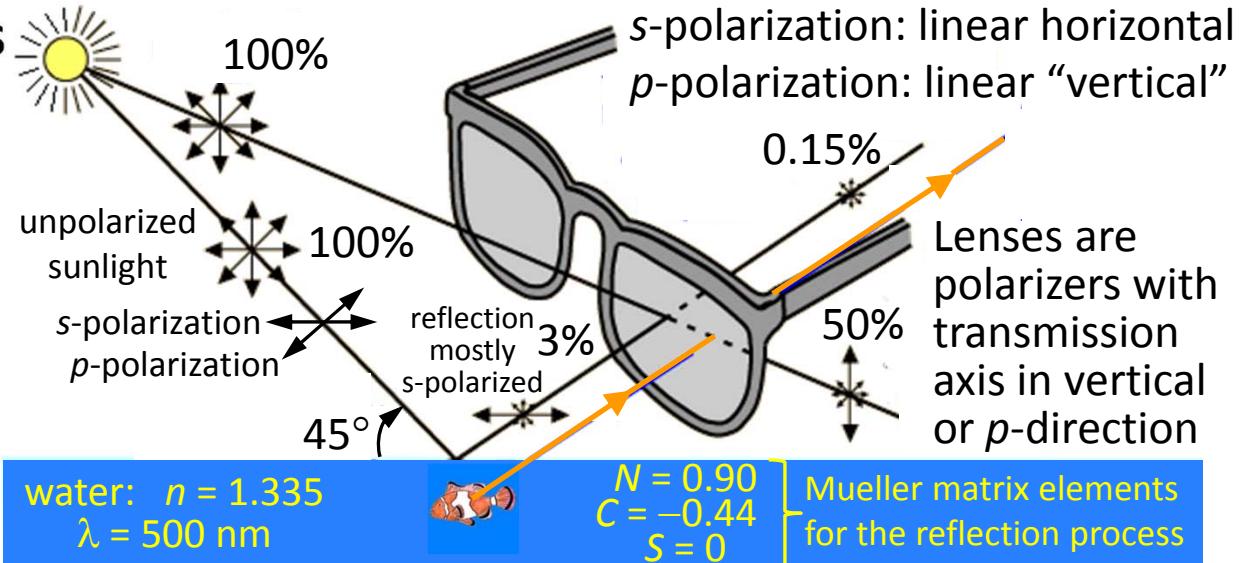
Polarization describes the **spatial** and **temporal** dependences of the electric field vector projected along x and y axes (waves 1 and 2).

The Stokes vector is a column of 4 numbers used to completely describe the polarization characteristic of the e-m wave. It includes information on:

- (1) irradiance [power/area] ( $I_0$ )
- (2) tilt angle of ellipse ( $Q$ )
- (3) ellipticity angle of ellipse ( $\chi$ )
- (4) degree of polarization ( $P$ ).

## Polarizing Sunglasses

Reflection of light from a surface at oblique incidence leads to a change in the polarization state of the light as described by the Stokes vector. The reflection and transmission processes can be described by Mueller matrices.



Reduction of Glare:	With sunglasses	Without sunglasses	Stokes vector for unpolarized sunlight
% reduction	$I_0 R$	$I_0 R$	$\begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}$
$= 100\% \left( 1 - \frac{\frac{1}{2}(1-N)}{1} \right)$	$\begin{bmatrix} \frac{1}{2}(1-N) \\ \frac{1}{2}(1-N) \\ 0 \\ 0 \end{bmatrix}$	$\begin{bmatrix} 1 \\ -N \\ 0 \\ 0 \end{bmatrix}$	$\begin{bmatrix} 1 & -N & 0 & 0 \\ -N & 1 & 0 & 0 \\ 0 & 0 & C & S \\ 0 & 0 & -S & C \end{bmatrix} \times \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}$
$= 95\%$	$\begin{bmatrix} 1 \\ -N \\ 0 \\ 0 \end{bmatrix}$	$\begin{bmatrix} 1 \\ -N \\ 0 \\ 0 \end{bmatrix}$	$\begin{bmatrix} 1 & -N & 0 & 0 \\ -N & 1 & 0 & 0 \\ 0 & 0 & C & S \\ 0 & 0 & -S & C \end{bmatrix} \times \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}$

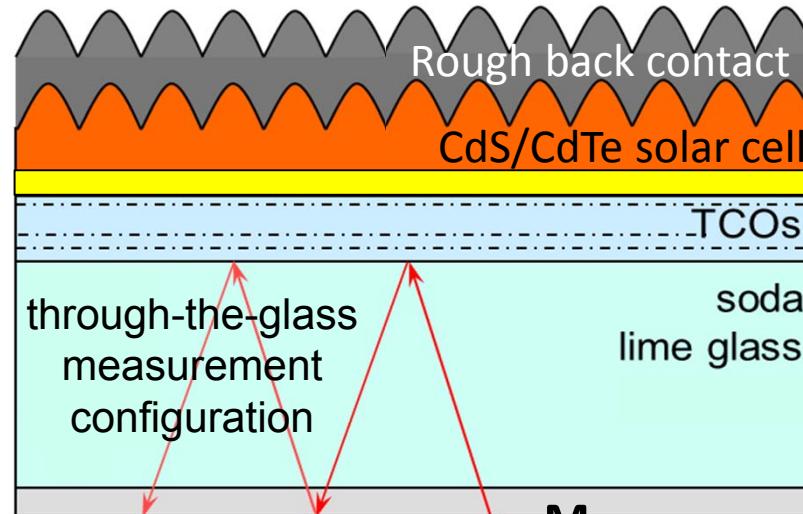
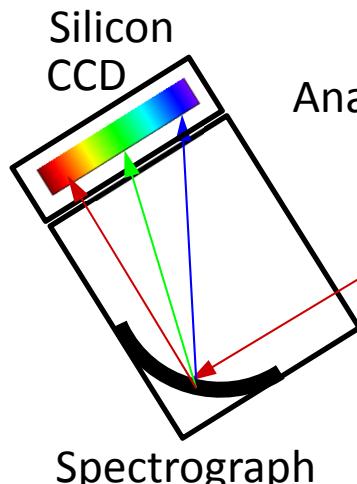
Stokes vector for light at the eye

Mueller matrix for sunglass lens

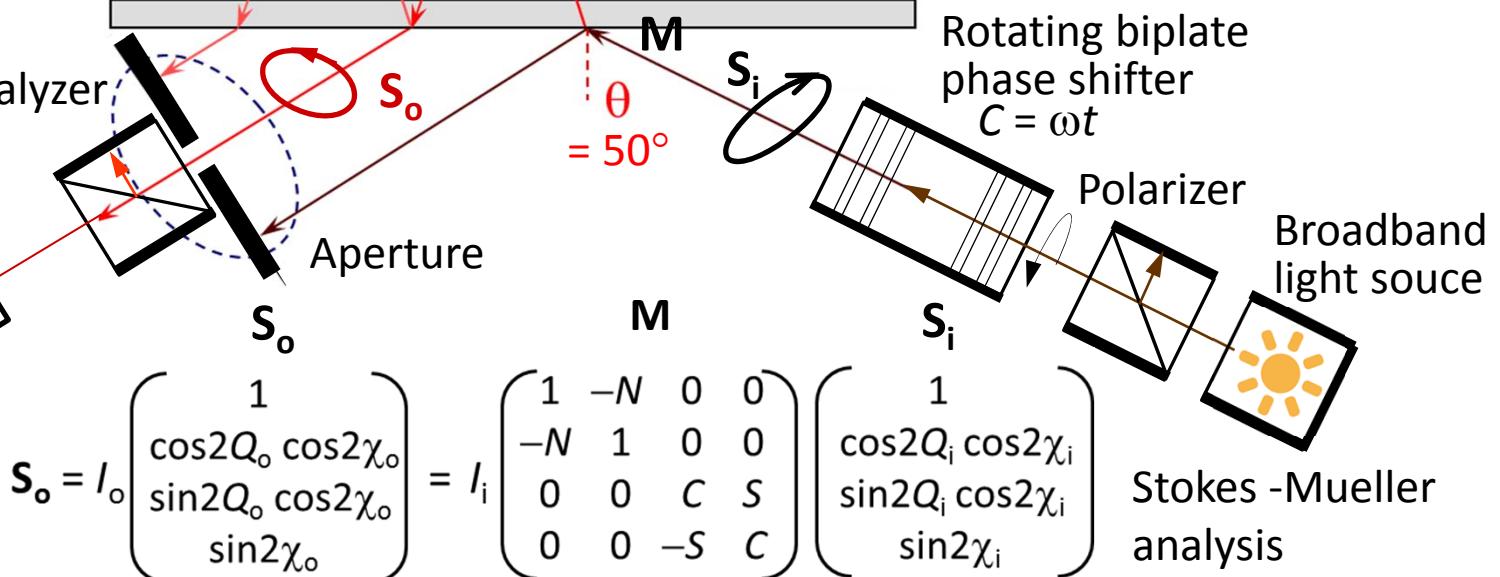
Mueller matrix for water reflection

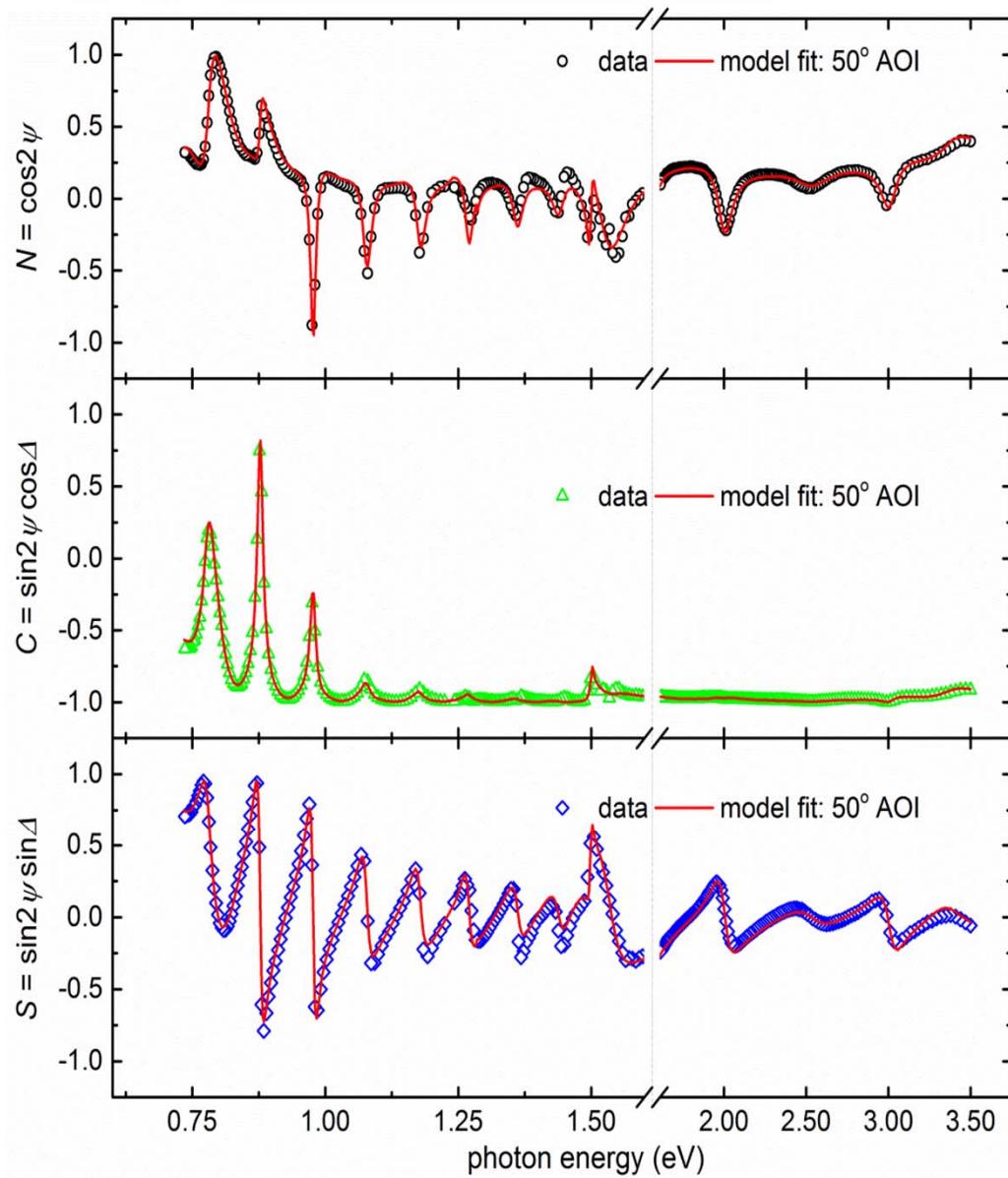
## “Spectroscopic Ellipsometry” Measurement of a CdTe Solar Cell

High speed  
spectroscopic  
(0.75 – 6.5 eV or  
1600 – 190 nm)  
polarization  
analysis  $\Rightarrow$   
50 millisecond  
measurement  
time possible



High sensitivity  
polarization analysis  
 $\delta Q \sim 0.1^\circ$  ]  
 $\delta \chi \sim 0.1^\circ$  ]  $\Rightarrow$   
Sensitivity to thickness  
differences of thin films  
at the level of 0.1 nm  
(10 billionths of cm).





## Mueller Matrix Analysis

- 6 bulk and 3 interface thicknesses
- 4 layer compositions
- 7 optical property parameters
- 2 parameters describing glass stress

Layer stack	SE
Au/CdTe layer ( $0.74 \pm 0.02 / 0.26 \pm 0.02$ )	opaque
CdTe/Au intf. ( $0.88 \pm 0.03 / 0.12 \pm 0.03$ )	$184 \pm 10$ nm
CdTe bulk layer	$1815 \pm 5$ nm
CdS/CdTe intf. ( $0.48 \pm 0.10 / 0.52 \pm 0.10$ )	$31 \pm 3$ nm
CdS bulk layer	$67 \pm 4$ nm
HRT/CdS intf. ( $0.45 \pm 0.08 / 0.55 \pm 0.08$ )	$33 \pm 2$ nm
HRT layer	$84 \pm 3$ nm
$\text{SnO}_2:\text{F}$ layer	$304 \pm 3$ nm
$\text{SiO}_2$ layer	$27 \pm 1$ nm
$\text{SnO}_2$ layer	$21 \pm 1$ nm
Soda lime glass	$3.16$ mm
Stress birefringence $c_1$	$4.5 \pm 1.2$ deg./eV
Stress birefringence $c_2$	$-2.4 \pm 1.0$ deg./eV <sup>3</sup>

Prakash Koirala, UT, 2014

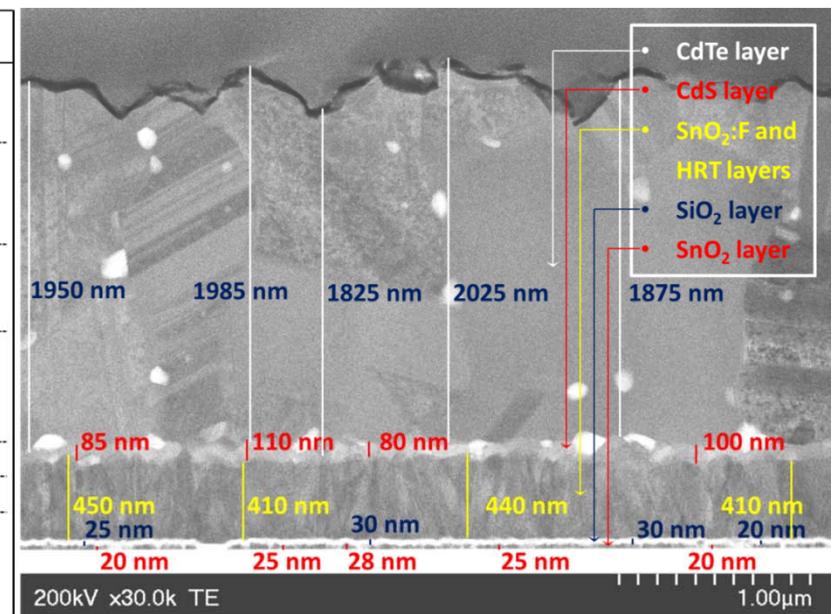


## Key TCO / CdTe Optical Parameters and Verification with Microscopy

Layer	Optical parameters from SE analysis		Physical/electrical properties from optical parameters	
CdTe	Bandgap, $E_0$ (eV)	Broadening, $\Gamma_0$ (eV)	Compressive stress (MPa)	Mean free path (nm)
	$1.496 \pm 0.004$	$0.044 \pm 0.002$	70	320
$\text{SnO}_2:\text{F}$	Resistivity, $\rho$ ( $10^{-4} \Omega\text{-cm}$ )	Broadening, $\Gamma_D$ (eV)	Sheet resistance ( $\Omega/\text{sq}$ )	Mean free path (nm)
	$3.5 \pm 0.3$	$0.093 \pm 0.007$	11.5	5.2

Layer stack	SE	Eff. SE	XTEM
Au/CdTe layer ( $0.74 \pm 0.02/0.26 \pm 0.02$ )	opaque		
CdTe/Au intf. ( $0.88 \pm 0.03/0.12 \pm 0.03$ )	$184 \pm 10$ nm		
CdTe bulk layer	$1815 \pm 5$ nm	$1997 \pm 15$ nm	$1932$ nm
CdS/CdTe intf. ( $0.48 \pm 0.10/0.52 \pm 0.10$ )	$31 \pm 3$ nm		
CdS bulk layer	$67 \pm 4$ nm	$100 \pm 6$ nm	$94$ nm
HRT/CdS intf. ( $0.45 \pm 0.08/0.55 \pm 0.08$ )	$33 \pm 2$ nm		
HRT layer	$84 \pm 3$ nm	$403 \pm 6$ nm	$428$ nm
$\text{SnO}_2:\text{F}$ layer	$304 \pm 3$ nm		
$\text{SiO}_2$ layer	$27 \pm 1$ nm		$26$ nm
$\text{SnO}_2$ layer	$21 \pm 1$ nm		$22$ nm
Soda lime glass	$3.16$ mm		
Stress birefringence $c_1$	$4.5 \pm 1.2$ deg./eV		
Stress birefringence $c_2$	$-2.4 \pm 1.0$ deg./eV <sup>3</sup>		

P. Koirala / J. Lawrence  
UT, 2014

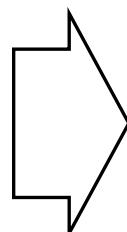


## Prediction of Performance from Optical Model

$$EQE(\lambda) = \frac{\text{Electrons collected from cell area / time}}{\text{Photons incident on cell area / time}}$$

- 6 bulk and 3 interface thicknesses
- 4 layer compositions
- 7 optical property parameters
- 2 parameters describing glass stress

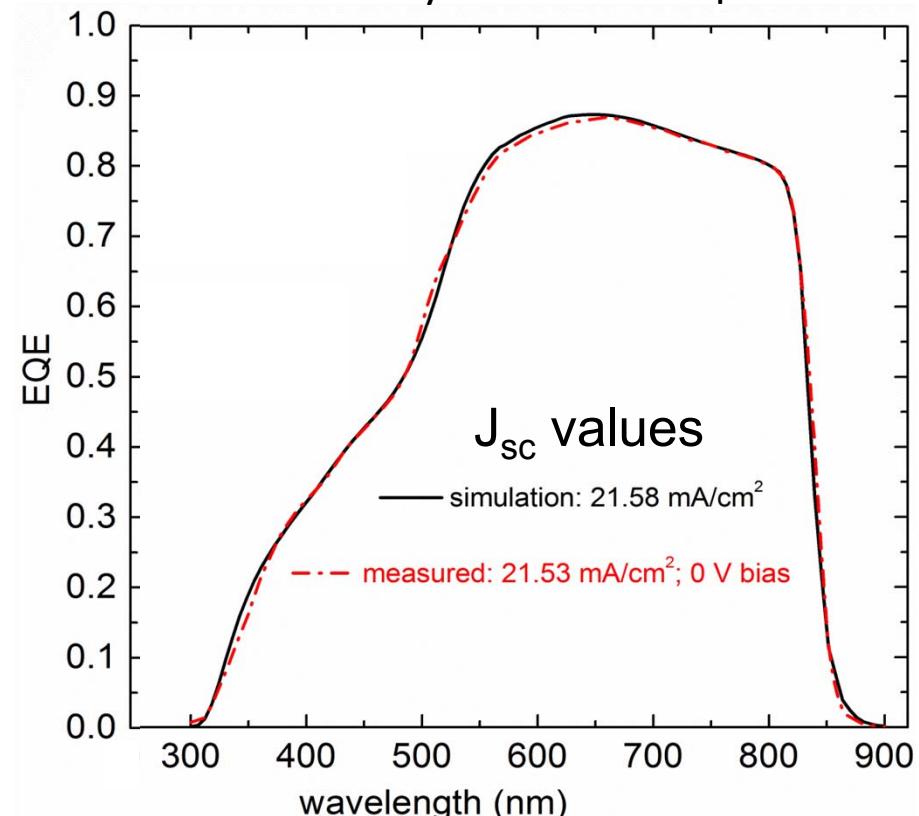
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CdTe bulk layer	1815±5 nm
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CdS bulk layer	67±4 nm
HRT/CdS intf. (0.45±0.08/0.55±0.08)	33±2 nm
HRT layer	84±3 nm
SnO <sub>2</sub> :F layer	304±3 nm
SiO <sub>2</sub> layer	27±1 nm
SnO <sub>2</sub> layer	21±1 nm
Soda lime glass	3.16 mm
Stress birefringence $c_1$	4.5±1.2 deg./eV
Stress birefringence $c_2$	-2.4±1.0 deg./eV <sup>3</sup>



$$J_{SC} = \sum_{\lambda} \Phi_{AM1.5G} \times EQE(\lambda) \Delta\lambda$$

Short circuit  
current density

AM 1.5  
solar spectral flux



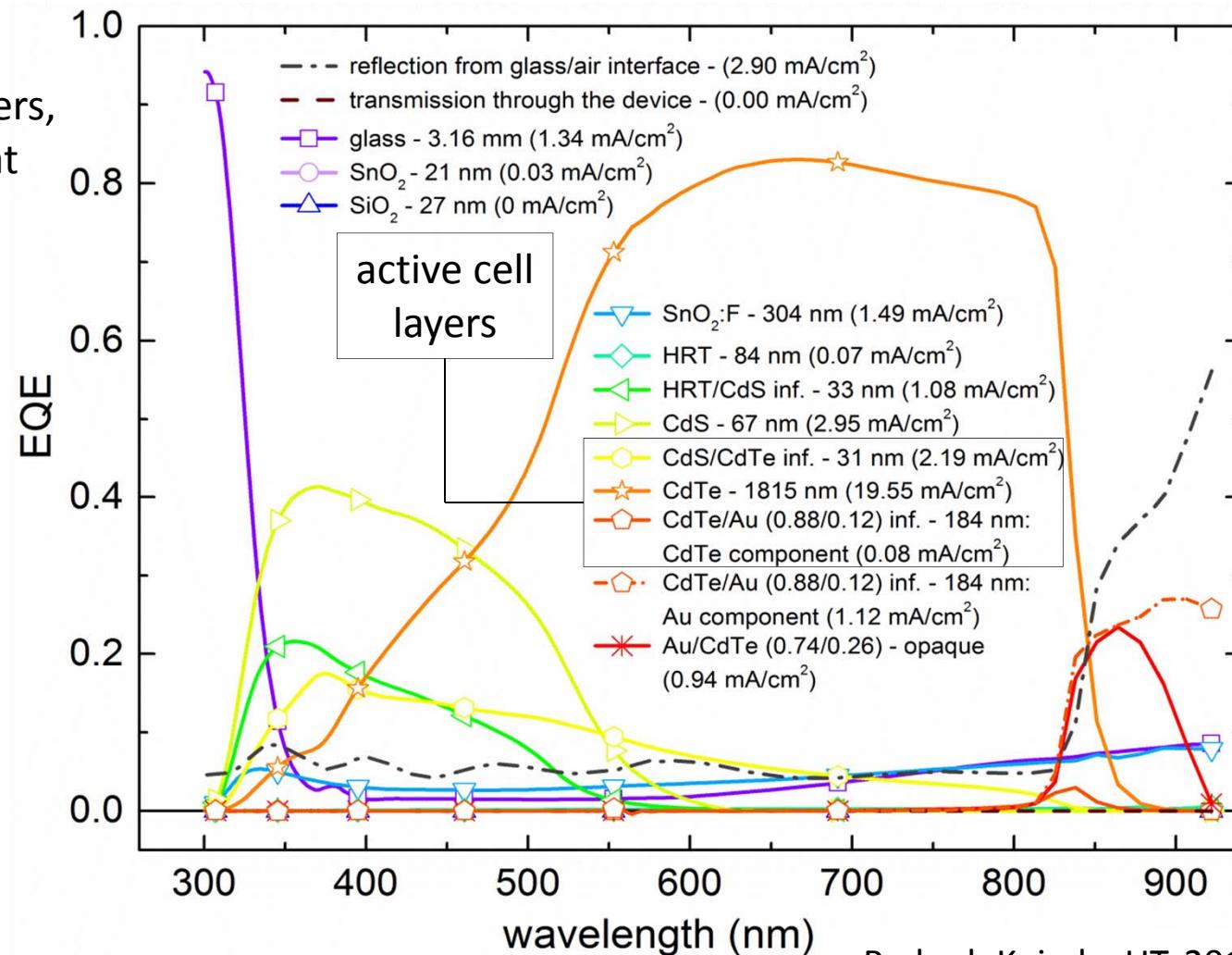
## Prediction of Losses from Optical Model

Useful current is collected by the active solar cell layers, i.e. those layers that include CdTe:

$$J_{sc} = 21.58 \text{ mA/cm}^2$$

The largest losses are due to ...

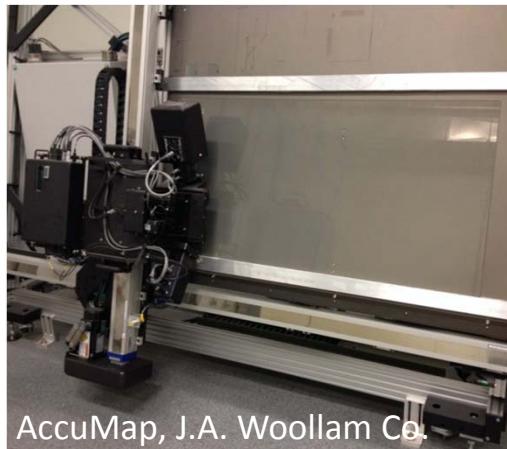
- absorption in CdS layer:  $2.95 \text{ mA/cm}^2$
- top surface reflection:  $2.90 \text{ mA/cm}^2$
- absorption in  $\text{SnO}_2:\text{F}$  layer:  $1.49 \text{ mA/cm}^2$





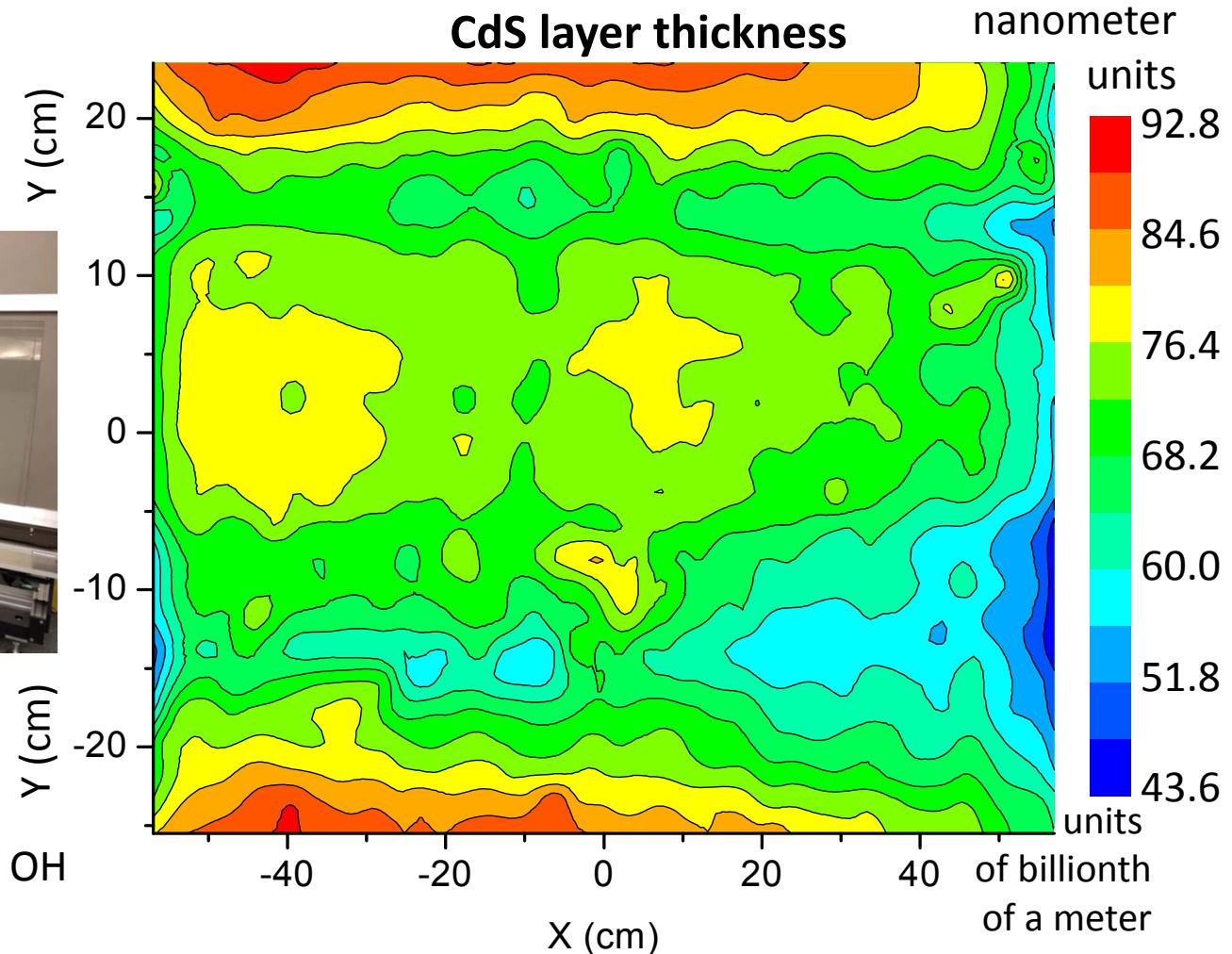
## Scaling Up the Spectroscopic Ellipsometry Measurement to PV Module Size: 60 cm x 120 cm: Fast Measurement Desired !

Map of CdS layer thickness, which is the major factor in controlling losses



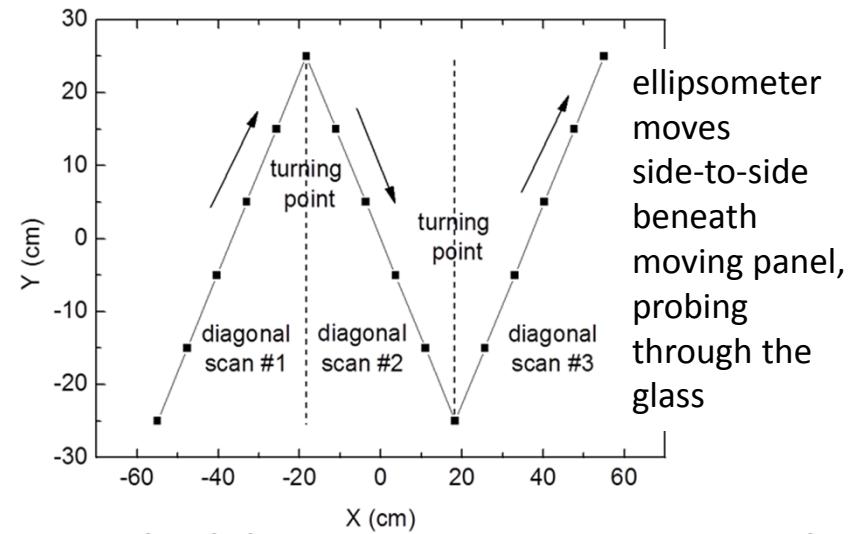
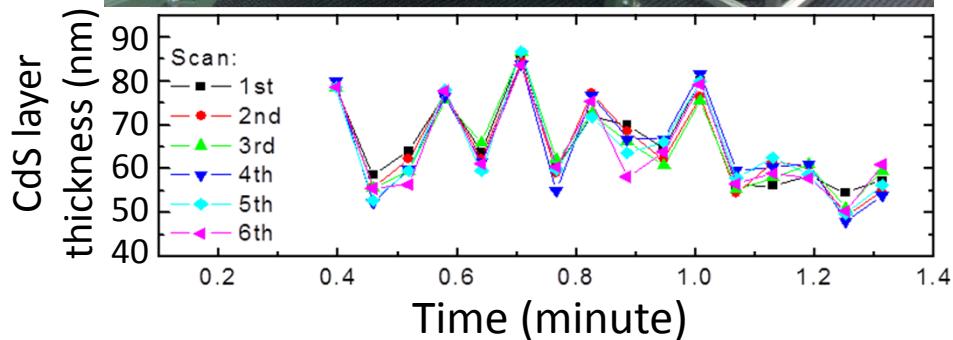
AccuMap, J.A. Woollam Co.

Non-optimized solar panel courtesy of Kenneth Kormanyos Calyxo USA, Perrysburg OH  
J. Chen, J. Li; UT 2013

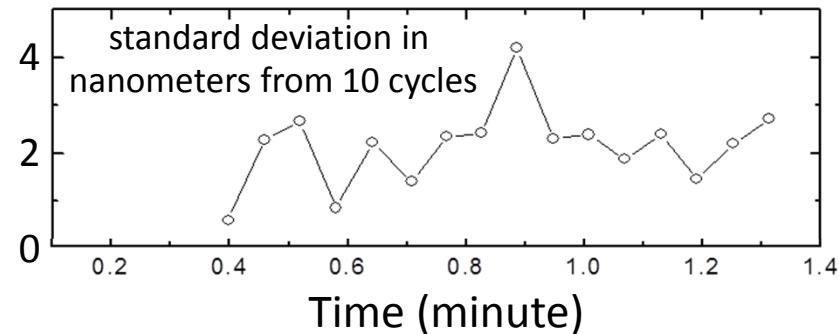




## Performing the Spectroscopic Ellipsometry Measurement In-Line on 60 cm x 120 cm PV Module: Fast Measurement a Necessity !

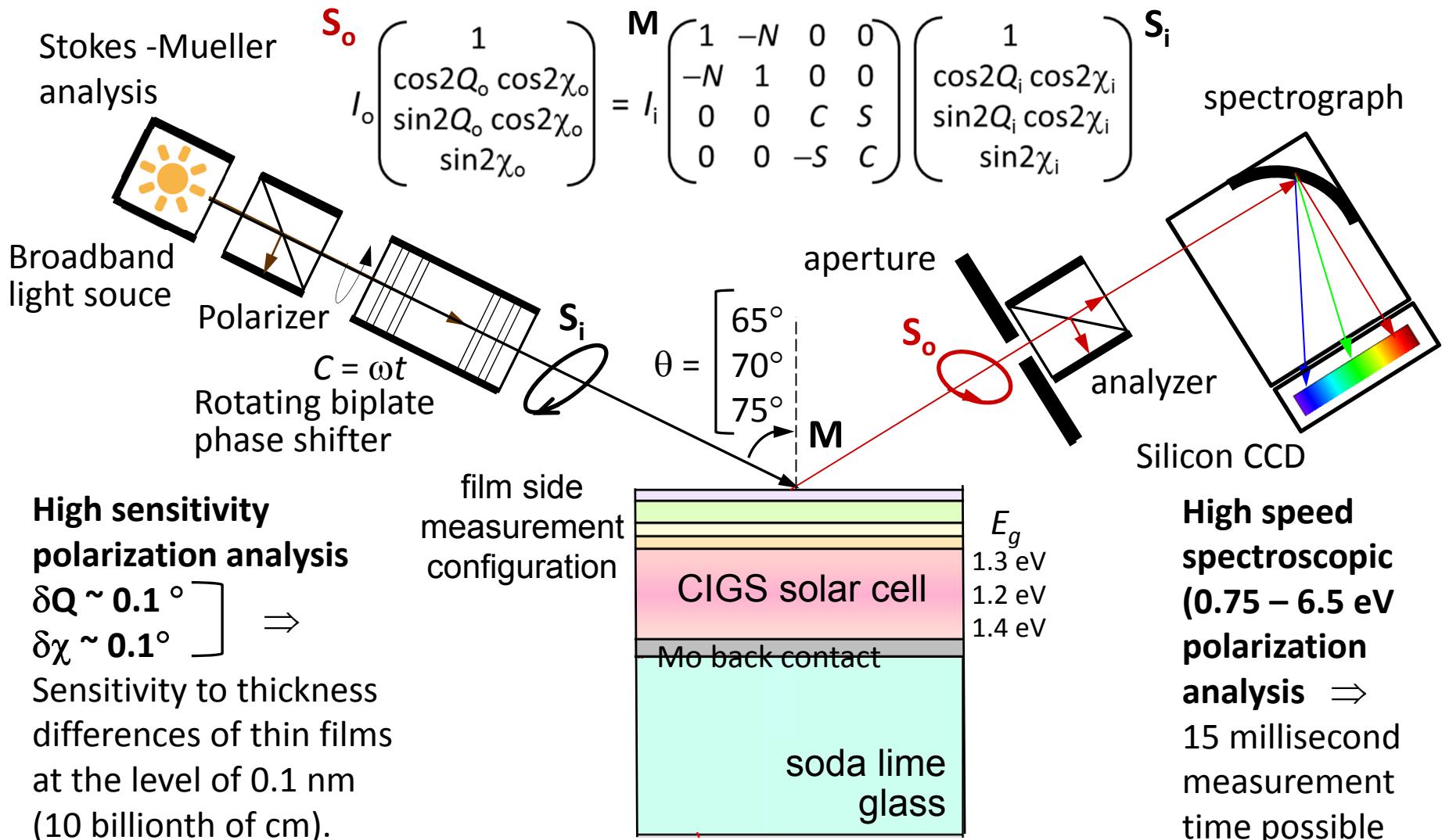


Standard deviation < 5 nm  $\Rightarrow$  success !

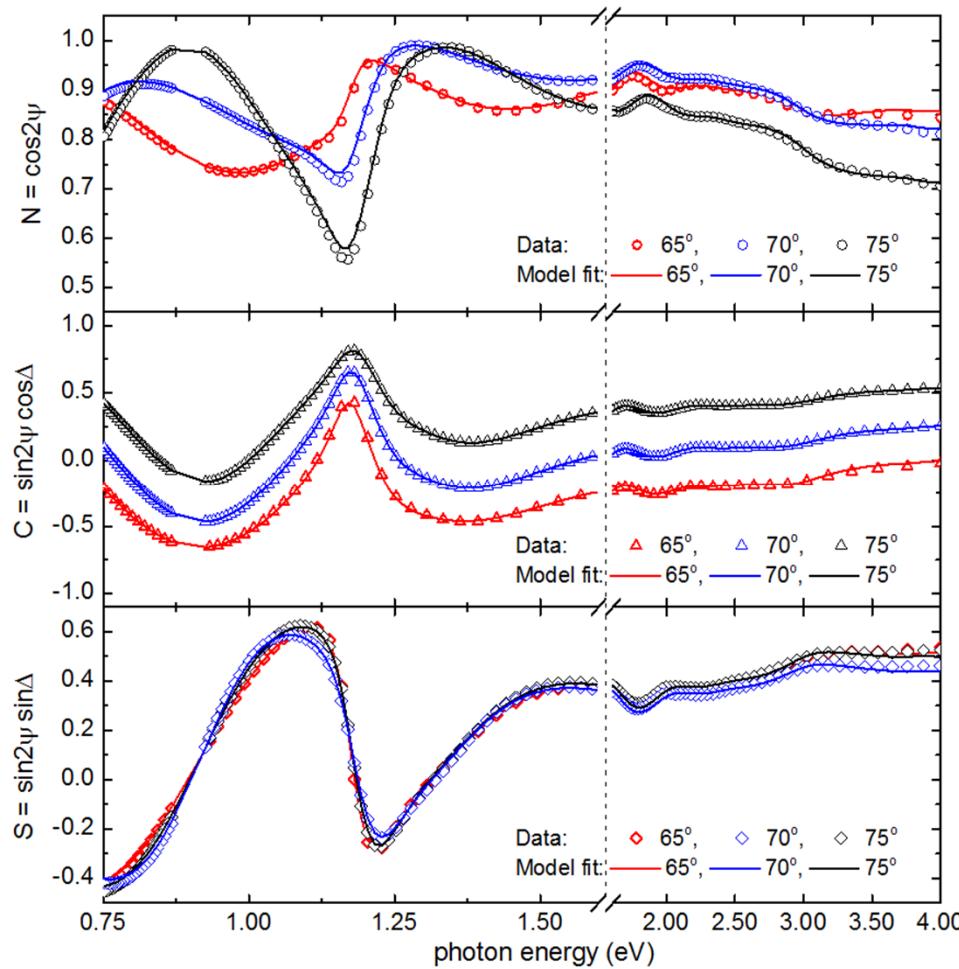


Non-optimized solar panel courtesy of Kenneth Kormanyos Calyxo USA, Perrysburg OH; J. Chen, J. Li; UT 2013  
Chen, J.; Koirala, P.; Salupo, C.; Collins, R. W.; Marsillac, S.; Kormanyos, K. R.; Johs, B. D.; Hale, J. S.; and Pfeiffer, G. L., *Conference Record of the 38th IEEE Photovoltaic Specialists Conference (PVSC)*, Austin, TX, June 3-8, 2012, (IEEE, New York, 2012) Article Number: 000377.

## “Spectroscopic Ellipsometry” Measurement of a CIGS Solar Cell



## Mueller Matrix Analysis of CIGS Cell at Multiple Angles of Incidence



- 4 bulk and 5 interface thicknesses
- 7 interface compositions
- 3 Ga compositions and
- 1 thickness describing the CIGS composition profile

Surface roughness ( $f_v=30.6\%$ )	34.29 nm
ZnO:Al ( $f_v=2.9\%$ )	111.97 nm
ZnO:Al / i-ZnO ( $f_{ZnO}=21.8\%, f_v=2.9\%$ )	140.08 nm
i-ZnO ( $f_v=0.0\%$ )	36.23 nm
i-ZnO / CdS ( $f_{CdS}=48.6\%, f_v=0.0\%$ )	44.47 nm
CdS ( $f_v=0.0\%$ )	48.67 nm
CdS / CIGS ( $f_{CIGS}=77.5\%, f_v=0.7\%$ )	59.12 nm
CIGS (Graded layer, $f_v = 0.0\%$ ) $x_{HF} = 0.304, x_L = 0.182, x_{HB} = 0.469$	2177.73 nm
CIGS / Mo ( $f_{Mo}=82.0\%$ )	19.89 nm
Mo (Opaque)	

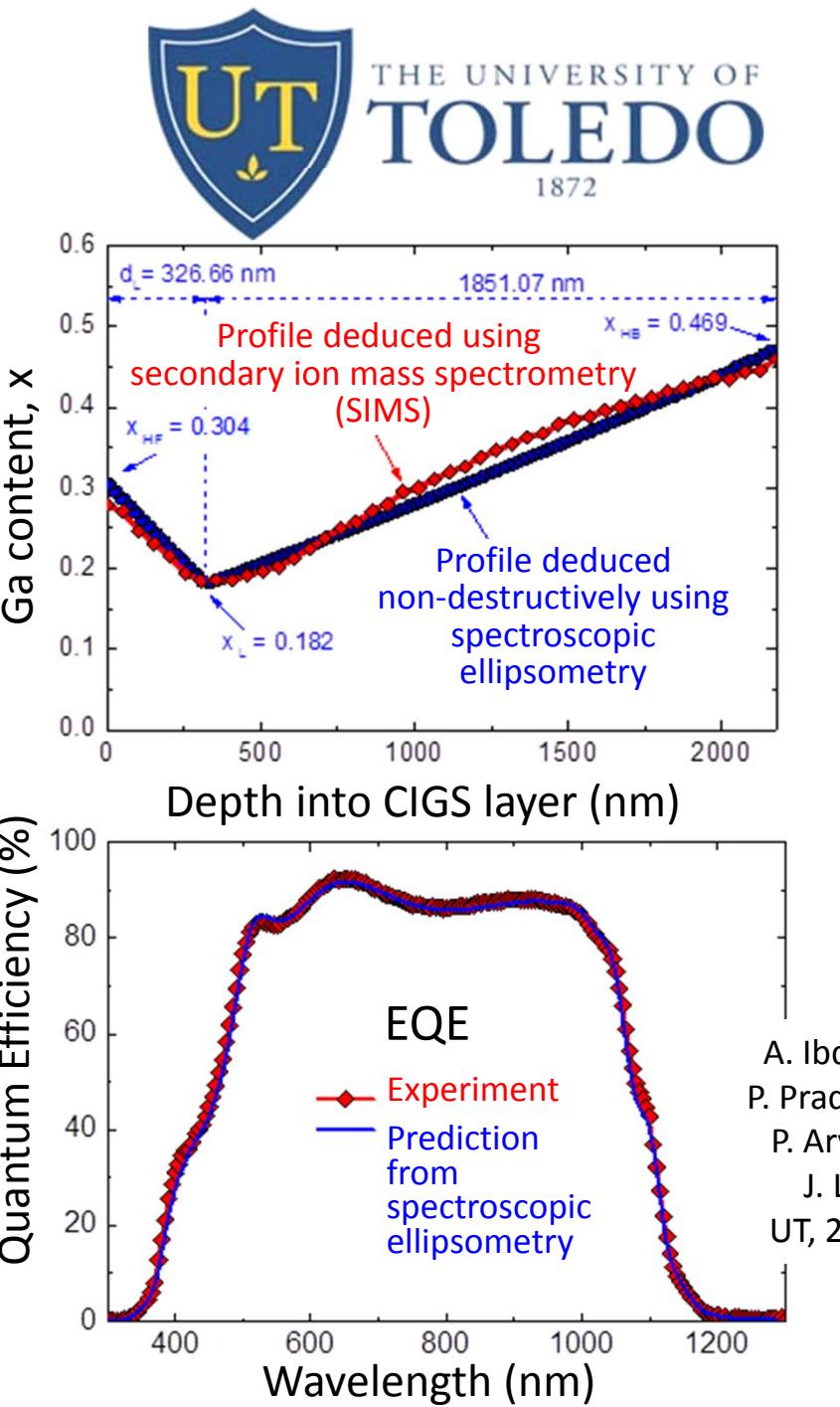
A. Ibdah, P. Pradhan, P. Aryal, J. Li  
UT, 2014



## Verification of Optical Model with Destructive Chemical Depth Profiling Method (Secondary Ion Mass Spectrometry)

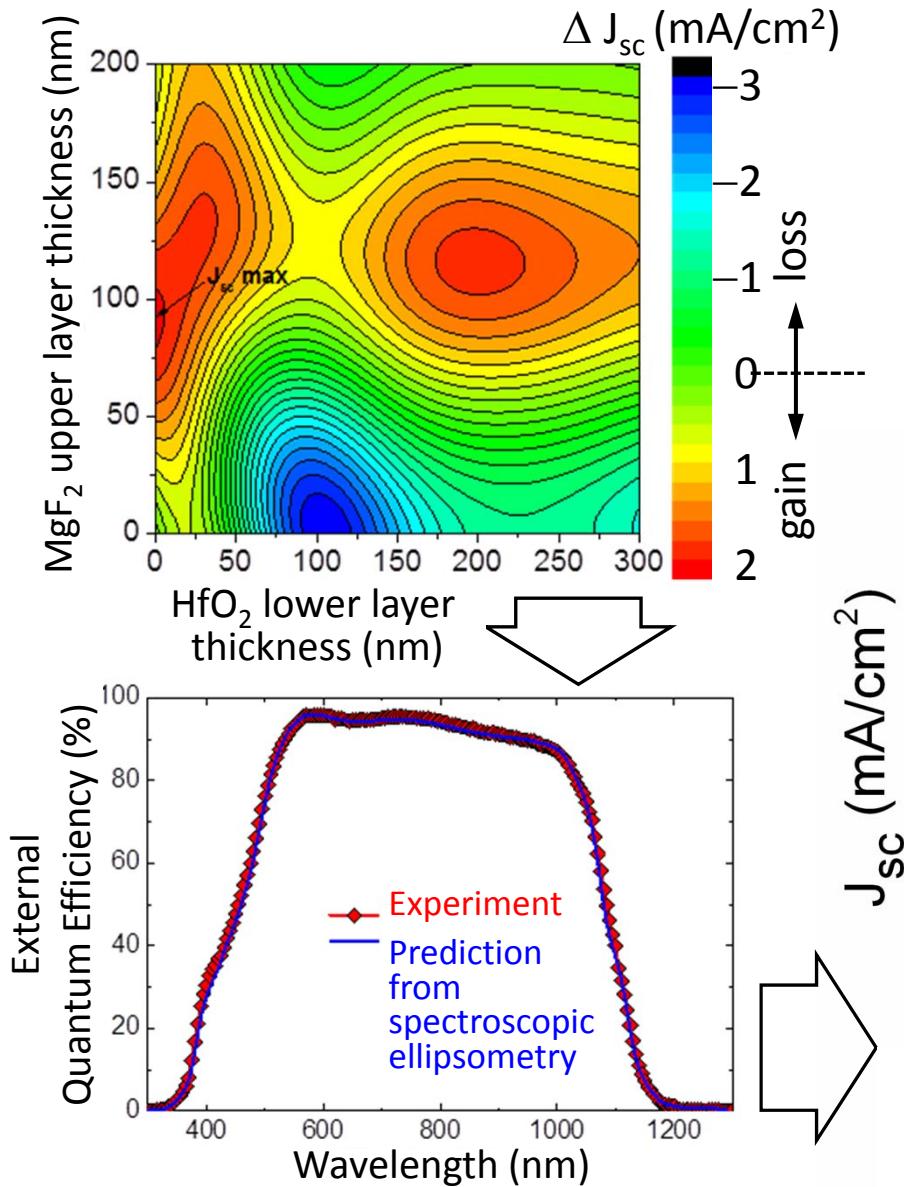
Surface roughness ( $f_v = 30.6\%$ )	34.29 nm
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Mo (Opaque)	

External





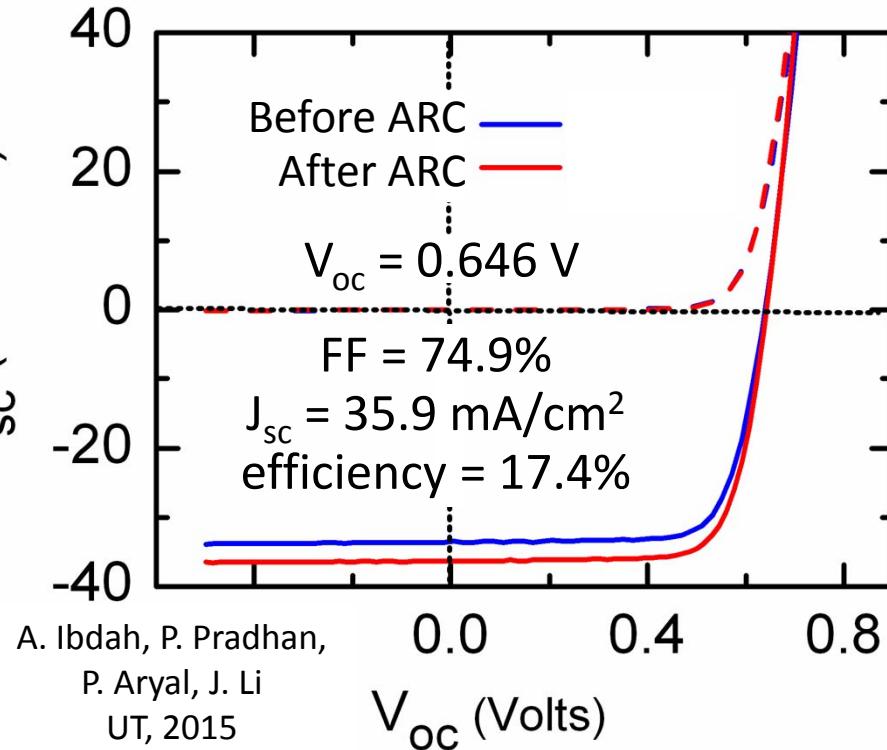
**WRIGHT CENTER** for  
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AND COMMERCIALIZATION



THE UNIVERSITY OF  
**TOLEDO**  
1872

## Feed-forward Optimization of Final Antireflection Coating (ARC) on CIGS Solar Cell

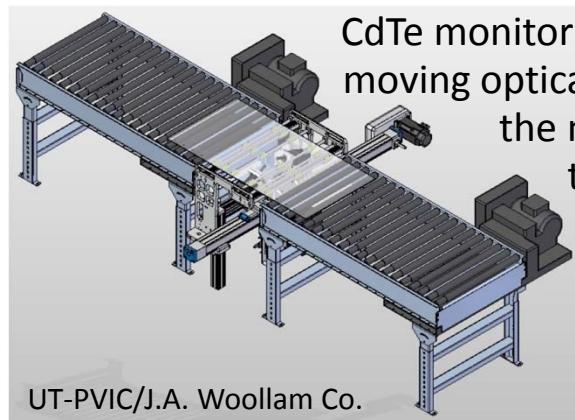
- Starting from the multilayer model add two layer ARC and simulate the  $J_{sc}$  gain
- Deposit optimum ARC, measure EQE and compare with optimized simulation





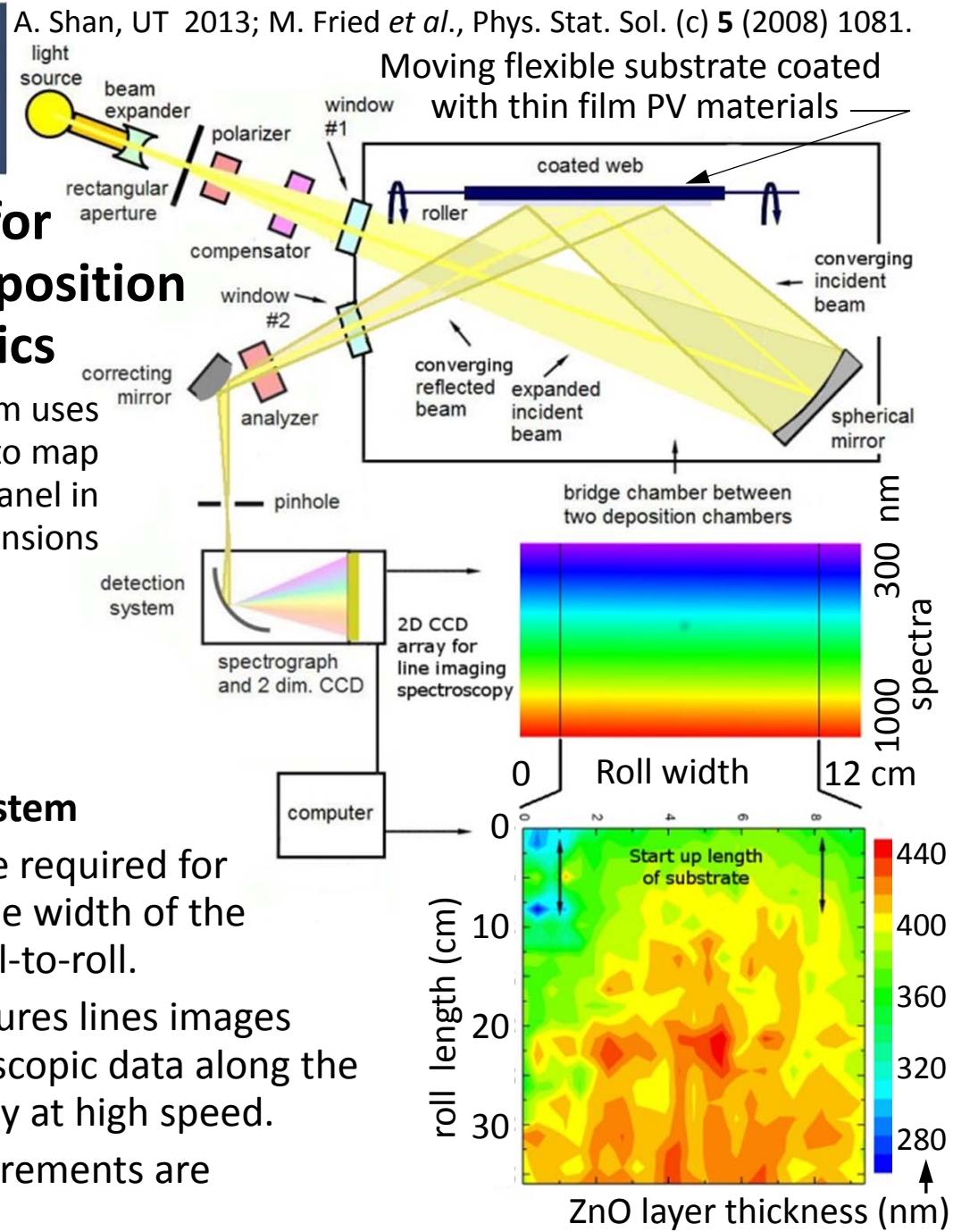
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## In-line Monitoring System for Feedback in Roll-to-Roll Deposition of CIGS Flexible Photovoltaics



UT-PVIC/J.A. Woollam Co.

CdTe monitoring system uses moving optical heads to map the moving panel in two dimensions



### Characteristics of new monitoring system

- No moving optical components are required for mapping; optical system images the width of the flexible PV material as it moves roll-to-roll.
- A two-dimensional CCD array captures lines images along one dimension and spectroscopic data along the second dimension – simultaneously at high speed.
- Multiple angle of incidence measurements are performed over the surface.



## Summary

- Second generation or thin film photovoltaics technology continues to provide advantages of lower cost and broader applications compared to first generation or crystalline Si technology.
- The current winning thin film technology, CdTe, is the product of Toledo area expertise emerging from the glass industry; low cost coated glass is the foundation of this success.
- Thin film PV poses scientific and technological challenges in translating recent high-efficiencies achieved for laboratory cells to modules fabricated on automated production lines.
- Advanced metrologies in which polarized electromagnetic waves are reflected from PV modules will serve as critical components of the production lines of the future.



## Acknowledgments

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Prakash Koirala  
Puja Pradhan  
Xinxuan Tan

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Sylvain Marsillac, Old Dominion Univ.  
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Ambalanath Shan

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Ken Kormanyos, Calyxo USA  
Amy Loyer, Calyxo USA  
Chris Michalski, Calyxo USA  
Akihiko Sakamoto, NEG  
Dave Strickler,  
NSG-Pilkington

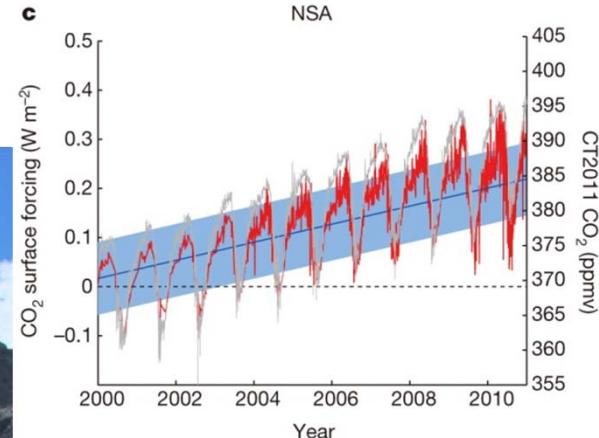




**Thank you for your attention! Questions?**



**Grinnell Glacier ... melting, Glacier National Park, 2013**



Radiative forcing is defined as a change in the difference between the solar irradiance incident on the Earth and the irradiance returning to space (in  $\text{W/m}^2$ ).

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[www.flickr.com/photos/wldrns/](http://www.flickr.com/photos/wldrns/)