

Why don't we have inexpensive PV systems made from Earth-Abundant elements?

Roy G. Gordon
Harvard University



ACS National Meeting, August 12, 2014
San Francisco, CA

Photocatalytic Conversion of H₂O to H₂ and O₂

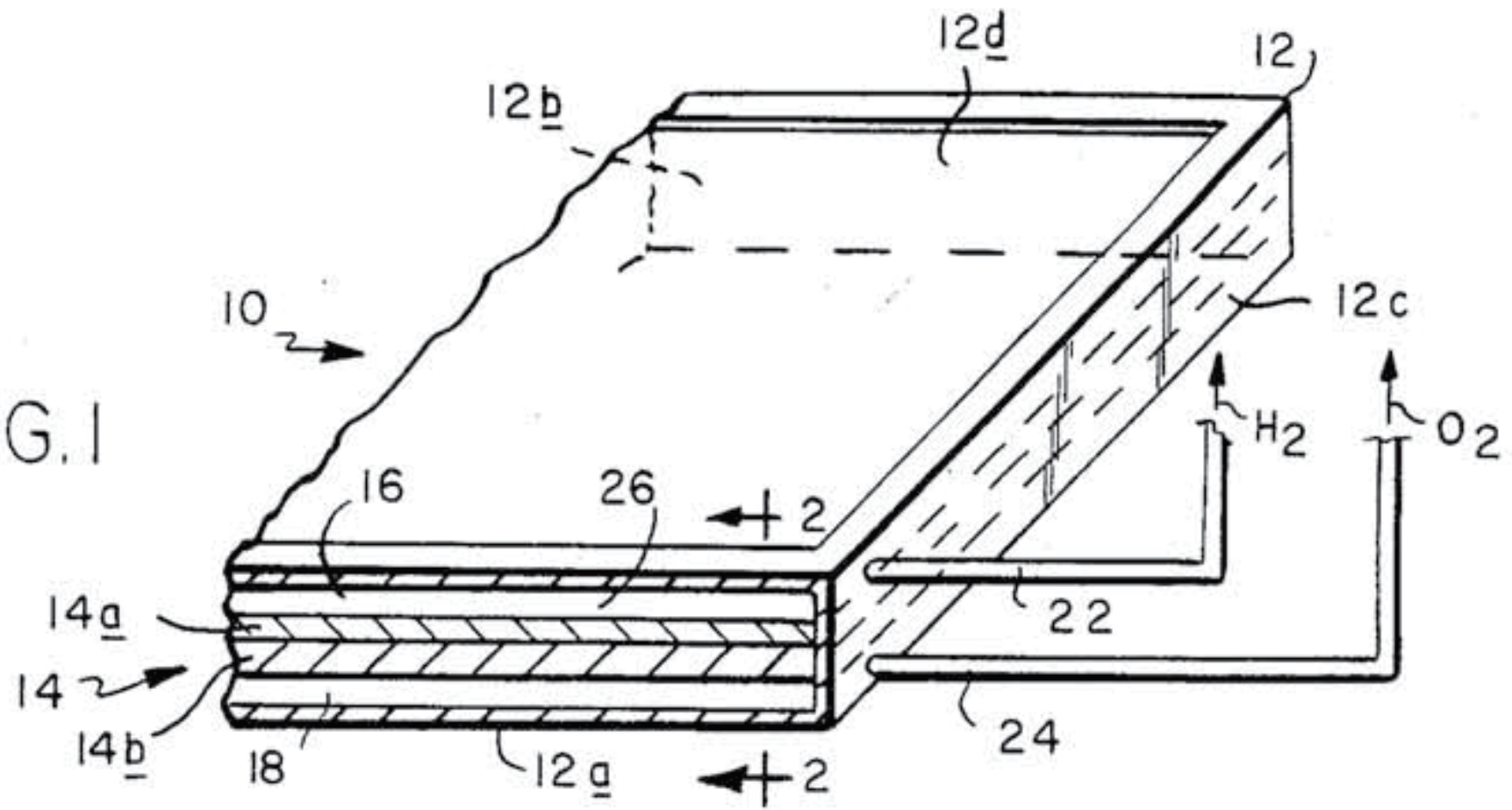
United States Patent [19]

[11] Patent Number: 4,650,554

Gordon

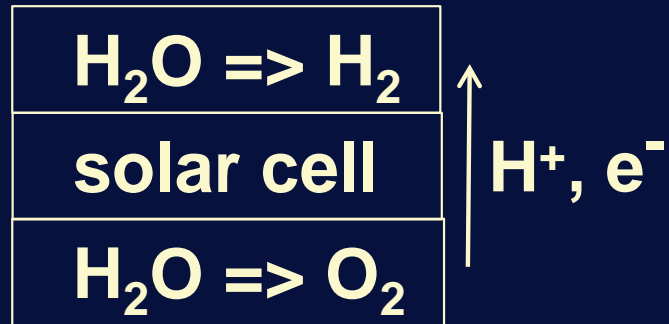
[45] Date of Patent: Mar. 17, 1987

FIG. 1



2 Strategies for Solar to Stored Energy

This symposium:

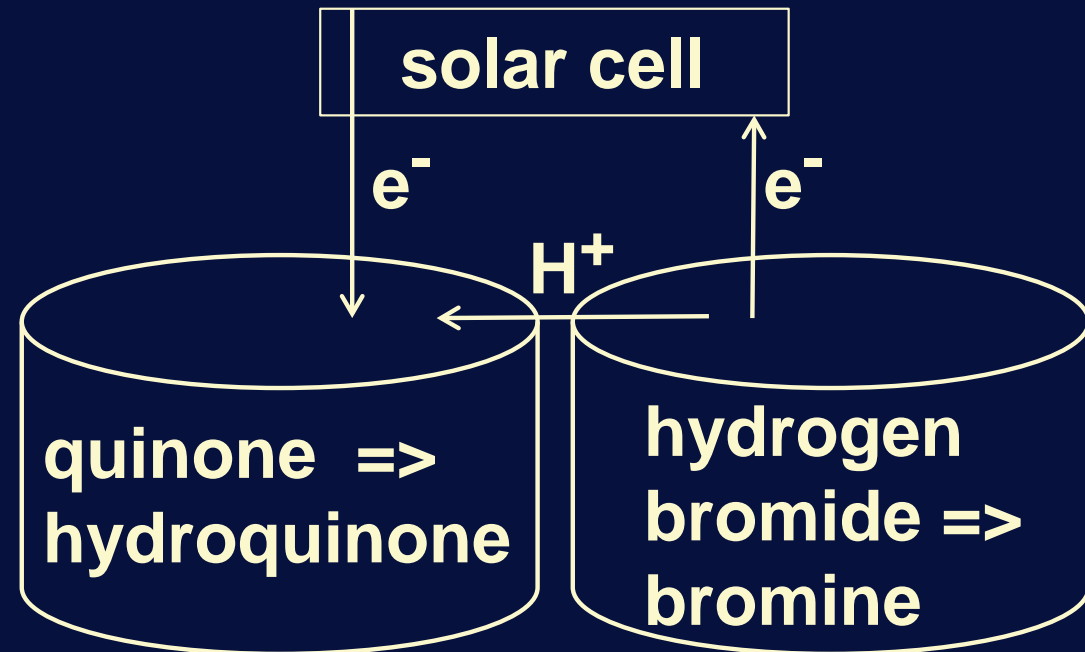


explosive H_2 gas

electrocatalysts needed

corrosion of solar cell

Our strategy:



non-flammable water solutions

no electrocatalysts needed

solar cell protected from water

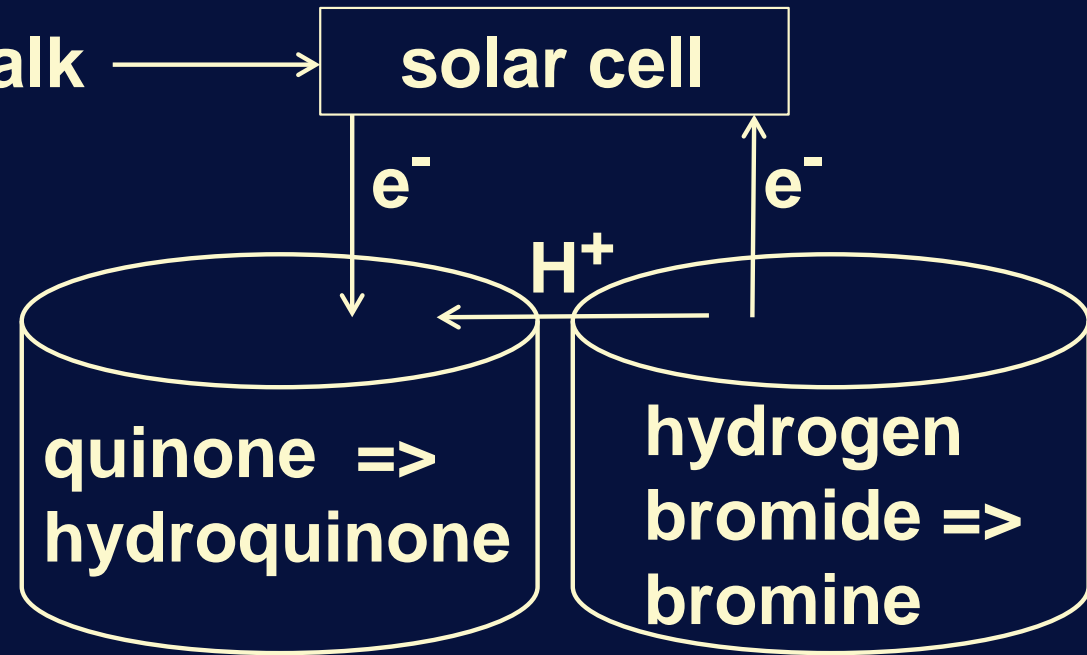


Harvard Strategy for Solar to Stored Energy

The subject of my talk



My collaboration on a flow battery for grid-scale storage of electricity: the subject of Mike Aziz's talk at 4pm today.



Outline

amount of solar energy

photovoltaic (PV) solar cells

abundant materials for large-scale thin-film PV

high-volume production of inexpensive thin-film PV

tin oxide – transparent electrode for PV



Solar Land Area Requirements - Global

Generating 15 TW (total primary power used by humans)

with 15 % efficiency requires collector area

$$= (15 \times 10^{12} \text{ W}) (200 \text{ W m}^{-2})^{-1} (0.15 \text{ efficiency})^{-1} = 5 \times 10^{11} \text{ m}^2$$

Total land area of the earth is $1.5 \times 10^{14} \text{ m}^2$

$$\text{Collector fraction} = 5 \times 10^{11} \text{ m}^2 / 1.5 \times 10^{14} \text{ m}^2 = 0.0033$$

0.33 % of land area could generate all the power now used



Solar Land Area Requirements - Global



20 TW from 6 Boxes at 3.3 TW Each



Solar Land Area Requirements - US

U.S. Land Area: $9.1 \times 10^{12} \text{ m}^2$

Average solar insolation: $>200 \text{ W/m}^2$

U.S. Primary Power Consumption: 3.3 TW

U.S. Electricity Consumption = 0.4 TW

To supply **all** US **primary** power from PV:

$$3.3 \times 10^{12} \text{ W} / (2 \times 10^2 \text{ W/m}^2 \times 15\% \text{ Efficiency}) = 1.1 \times 10^{11} \text{ m}^2$$

$$\text{Requires } 1.1 \times 10^{11} \text{ m}^2 / 9.1 \times 10^{12} \text{ m}^2 = \mathbf{1.2\% \text{ of Land Area}}$$

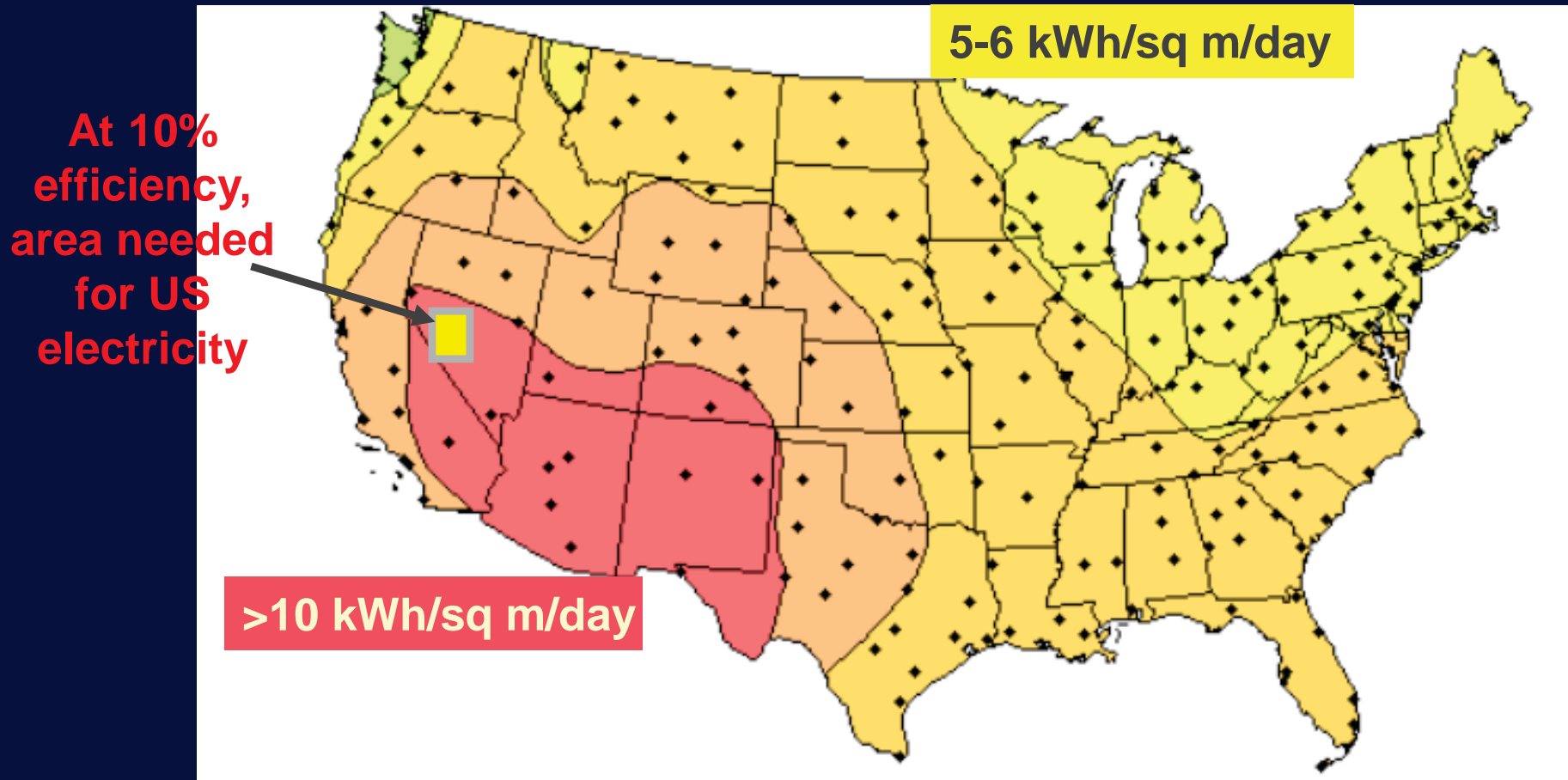
To supply **all** US **electrical** power from PV:

$$0.4 \times 10^{12} \text{ W} / (2 \times 10^2 \text{ W/m}^2 \times 15\% \text{ Efficiency}) = 1.3 \times 10^{10} \text{ m}^2$$

$$\text{Requires } 1.3 \times 10^{10} \text{ m}^2 / 9.1 \times 10^{12} \text{ m}^2 = \mathbf{0.15\% \text{ of Land Area}}$$



Convenient truth: a small area can supply our electricity



PV on all US rooftops could meet US electricity demand



PV on my home in Cambridge, MA

20 panels of polycrystalline Si x 1.5 m²/panel = 30 m²

x 3 kWh / m² / day x 0.13 efficiency => 12 kWh/day

Average power 12 kWh/day x 1 day/24 h = 0.5kW

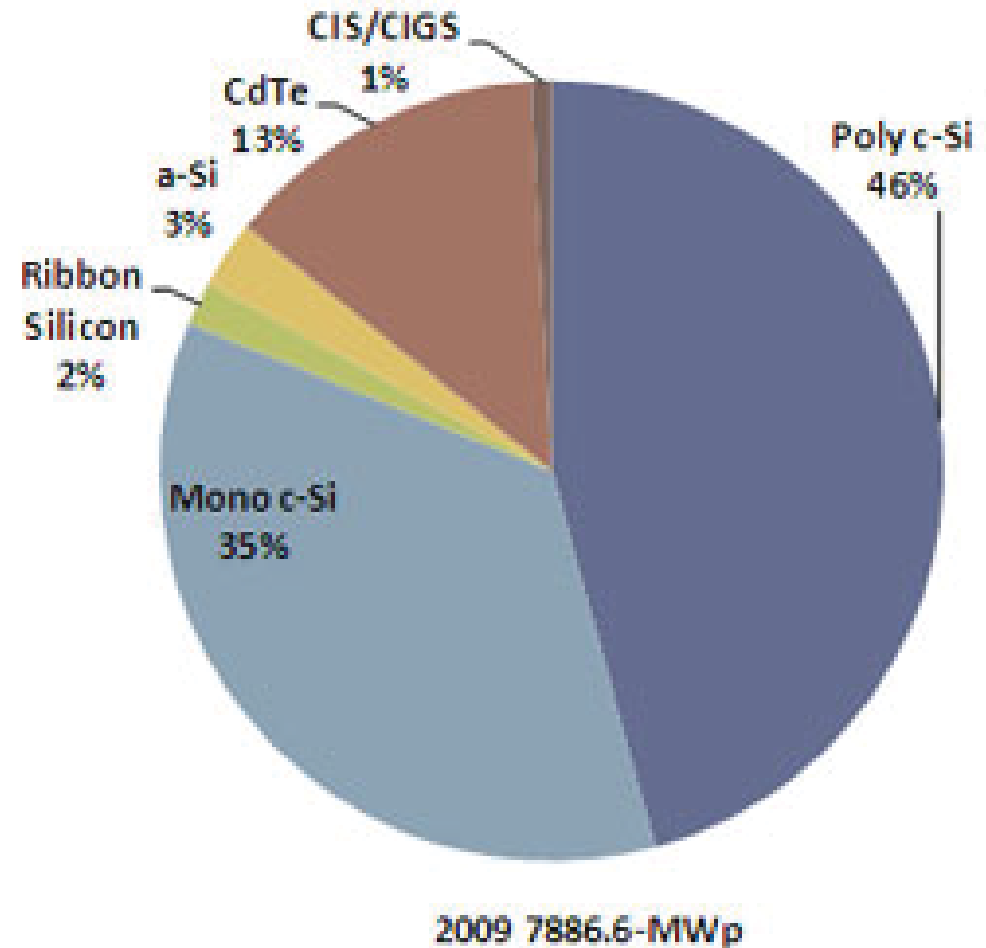
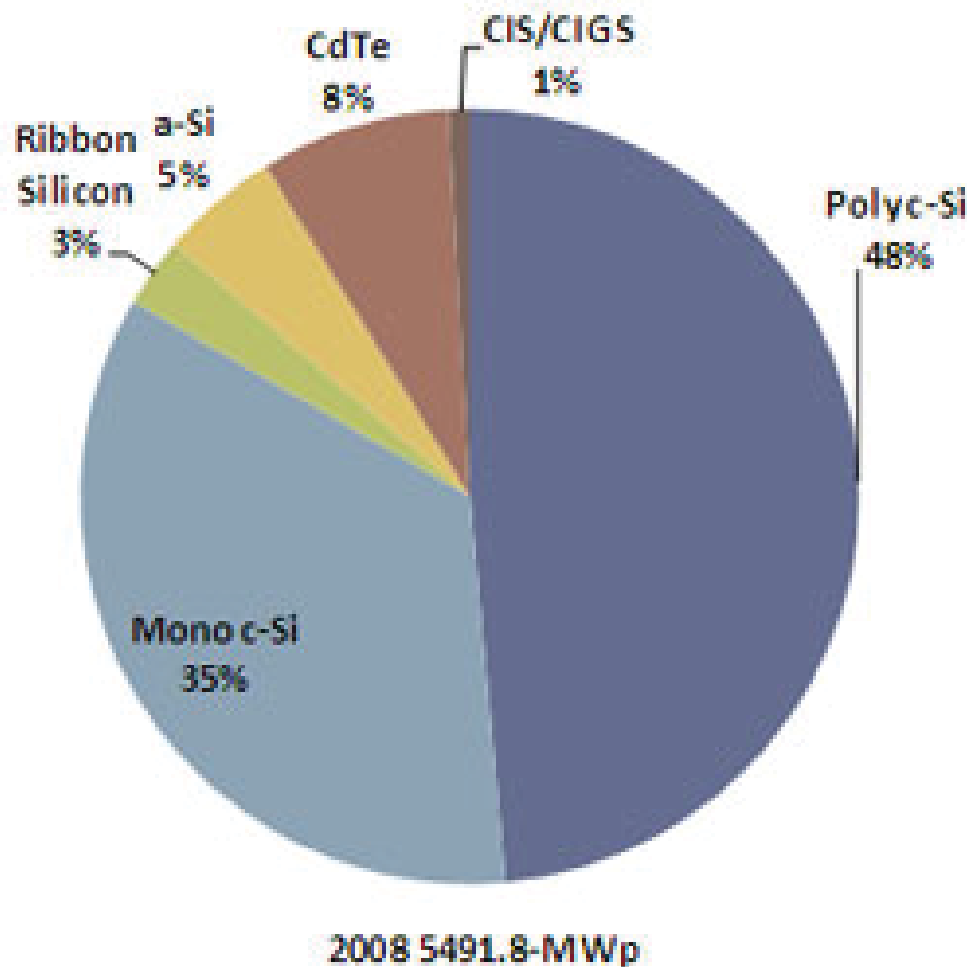
Typical household in US uses 1.3kW electric.

By replacing lights with LEDs and old appliances, we should be able to reduce our usage to 0.5 kW, the average input from our solar panels



Market Shares of PV Technologies

Technology Shares 2008/2009



Mostly silicon, < 20 % thin films

Current Commercial PV Materials

Crystalline Si:

expensive purification, not integrated, (rare silver)

CdTe:

rare tellurium, toxic cadmium and tellurium

Amorphous Si-Ge:

low efficiency, slow deposition

Cu(In,Ga)Se₂ (CIGS):

rare indium, gallium, toxic selenium

Dye-sensitized:

rare ruthenium and platinum

None of these cell designs meet the criteria:

abundant, inexpensive and non-toxic elements



Why is PV Expensive?

Production is too slow

=> make solar cells very quickly

Too many separate pieces connected by wires

=> integrate directly without wires

Rare, expensive elements now used: Ag, In, Ga, Te, Se

**=> use abundant and inexpensive elements:
copper, zinc, tin, oxygen, sulfur, aluminum**



How to make lots of inexpensive solar cells

small amounts of materials

high absorption coefficients => thin films

rapid, continuous production on large areas

< few seconds for depositing thin films

integrated series interconnections of cells

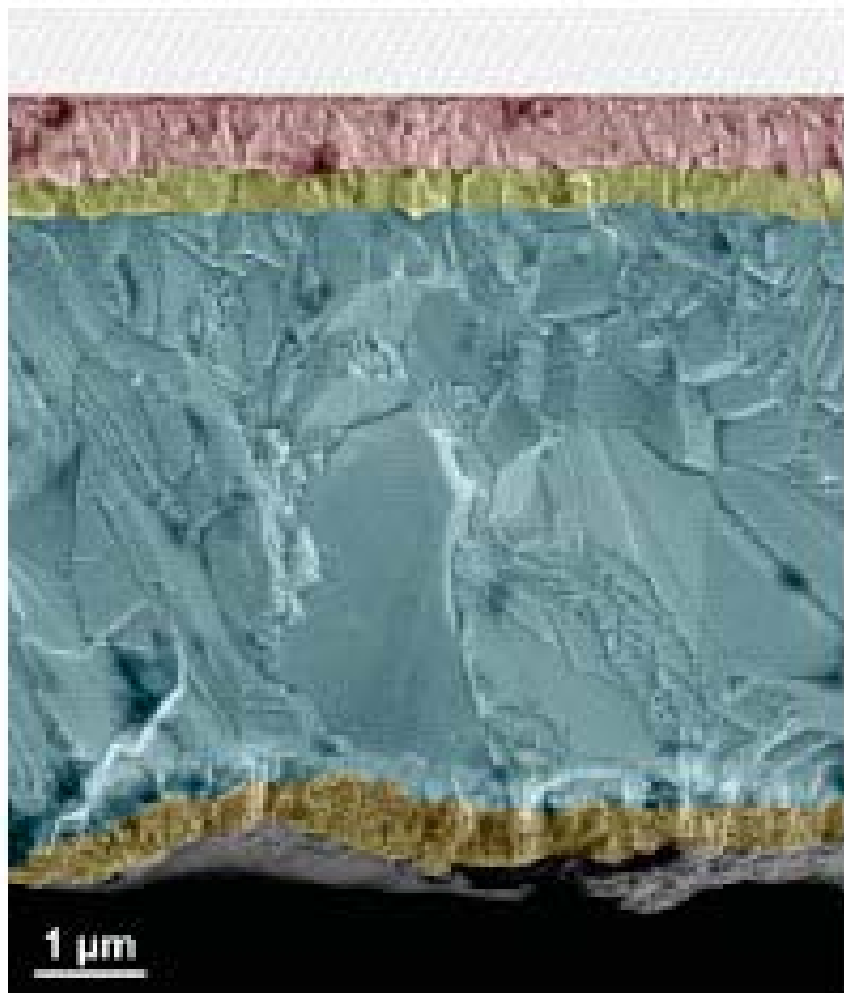
inexpensive, abundant elements

nontoxic elements

product durable for long lifetimes (> 20 years)



Structure of CdTe Thin-Film Solar Cells



Glass

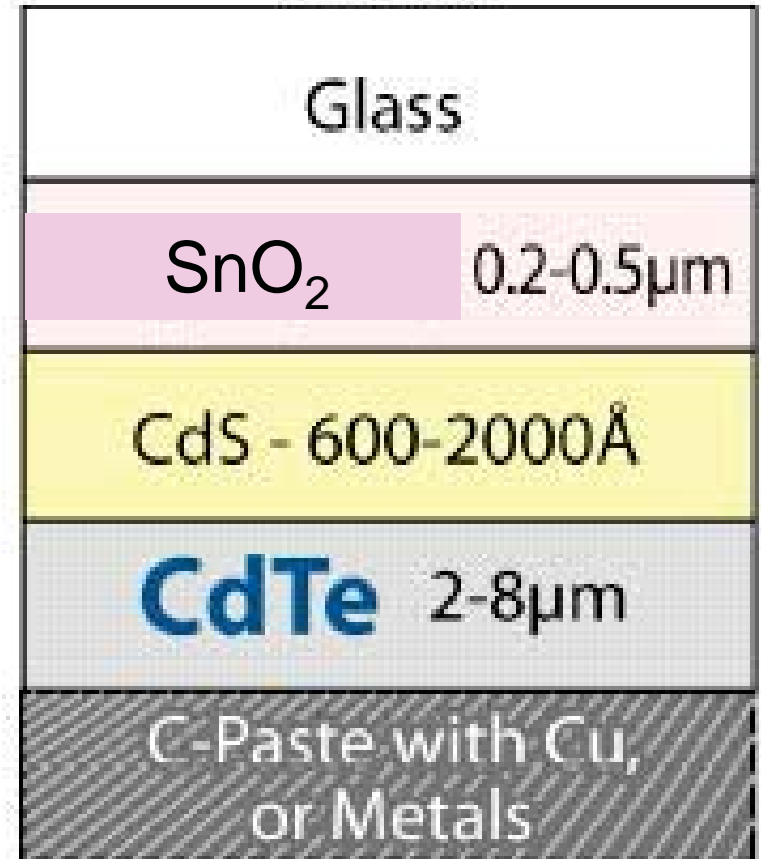
SnO₂

CdS

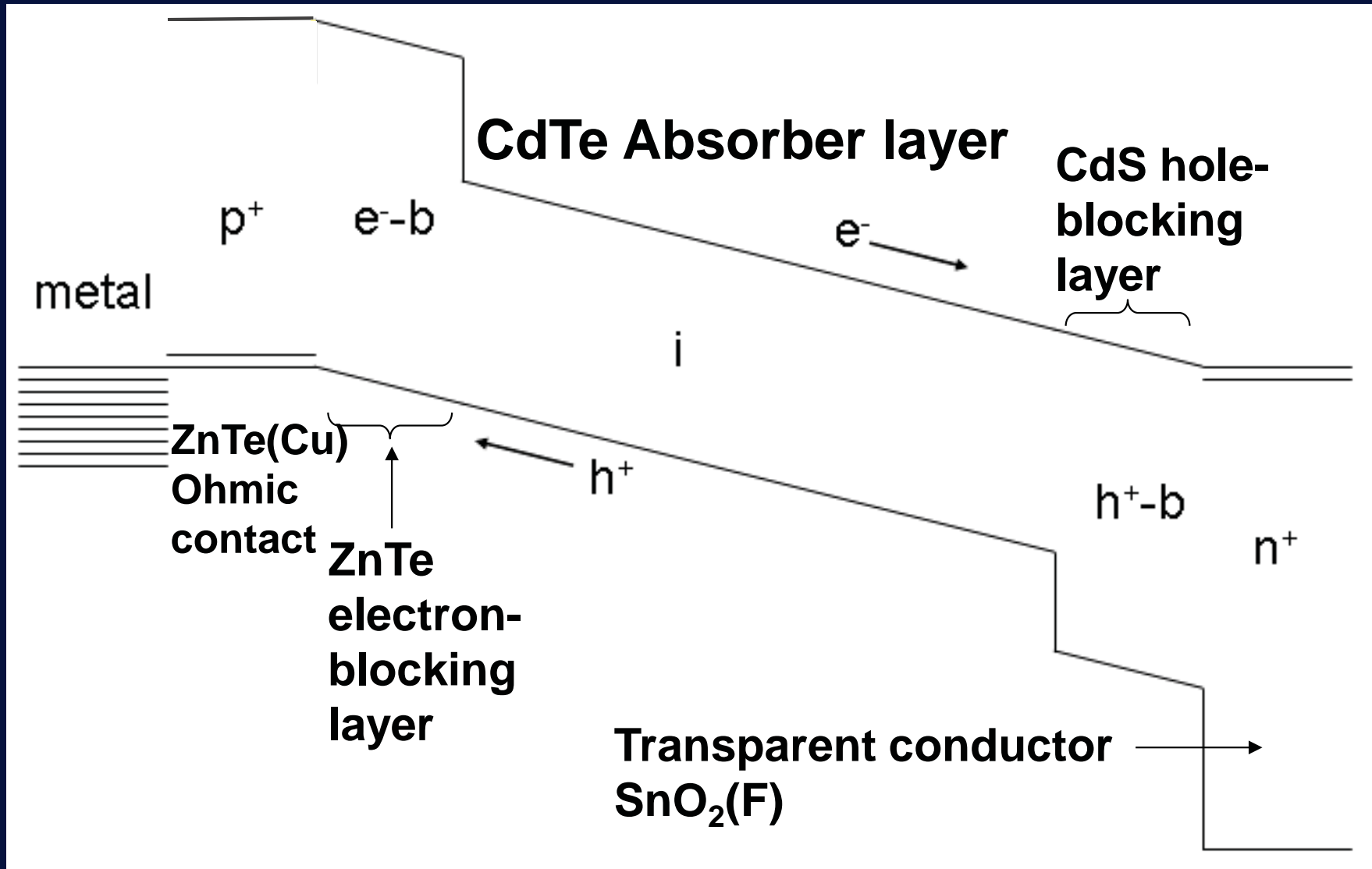
CdTe

ZnTe:Cu

Ti



Band Diagram for a Thin-Film CdTe Solar Cell



How Much Material is Needed for Solar Cells?

A typical thin-film cell is $2 \mu\text{m} = 2 \times 10^{-6} \text{ m}$ thick

The area required to supply current energy use is $5 \times 10^{11} \text{ m}^2$

The volume of thin-film material is
 $= (2 \times 10^{-6} \text{ m}) \times (5 \times 10^{11} \text{ m}^2) = 1 \times 10^6 \text{ m}^3$

10^6 m^3 of $\text{Cu}(\text{In,Ga})\text{Se}_2 \Leftrightarrow 1.4 \times 10^9 \text{ kg}$ of indium

Total recoverable reserves of In in Earth's crust $\sim 6 \times 10^6 \text{ kg}$.
enough to make 0.5% of the required solar cells

10^6 m^3 of $\text{CdTe} \Leftrightarrow 3.3 \times 10^9 \text{ kg}$ of tellurium

Total recoverable reserves of Te in Earth's crust $\sim 3.7 \times 10^7 \text{ kg}$.
enough to make $\sim 1 \%$ of the required solar cells



Which Elements are Sufficiently Abundant?

Enough Si, Al, Zn, Cu & Sn to make all the solar cells needed

Enough non-metals C, N, P, O, S, F, Cl, Br, I are available

Transition metals Fe, Mn, etc. don't make efficient solar cells

Organics are unlikely to be stable for 20 years in sunlight

Avoid toxic elements like As, Cd, Se, Te, Be, Pb



Thin-Film PV Absorbers Made of Abundant Elements

Main Absorber Material	Band gap (eV)	Actual Efficiency	Theoretical Maximum
SnS	1.1	5%	32%
Cu ₂ O	2.0	5%	23%
Zn ₃ P ₂	1.3	6%	33%
Cu ₂ ZnSn(S,Se) ₂	1.3	13%	33%
(CH ₃ NH ₃)Pb(I,Cl) ₃	1.5	16%	33%
(CH ₃ NH ₃)Sn(I,Br) ₃	1.5	6%	33%

$\text{Zn}_3\text{P}_2 + \text{H}_2\text{O} \Rightarrow \text{PH}_3$ (highly toxic phosphine gas)

Selenium (Se) and lead (Pb) are toxic

(CH₃NH₃)Sn(I,Br)₃ is air-sensitive and water-soluble

More research is needed to improve their efficiency.



Possible Scalable Materials for Solar Cells

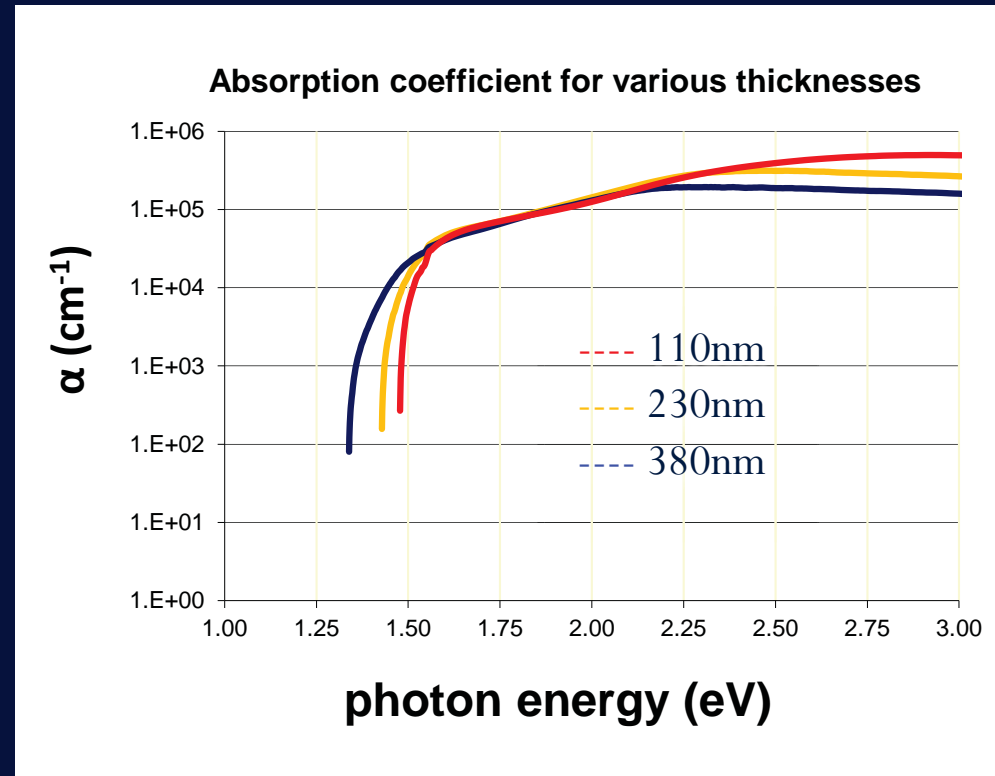
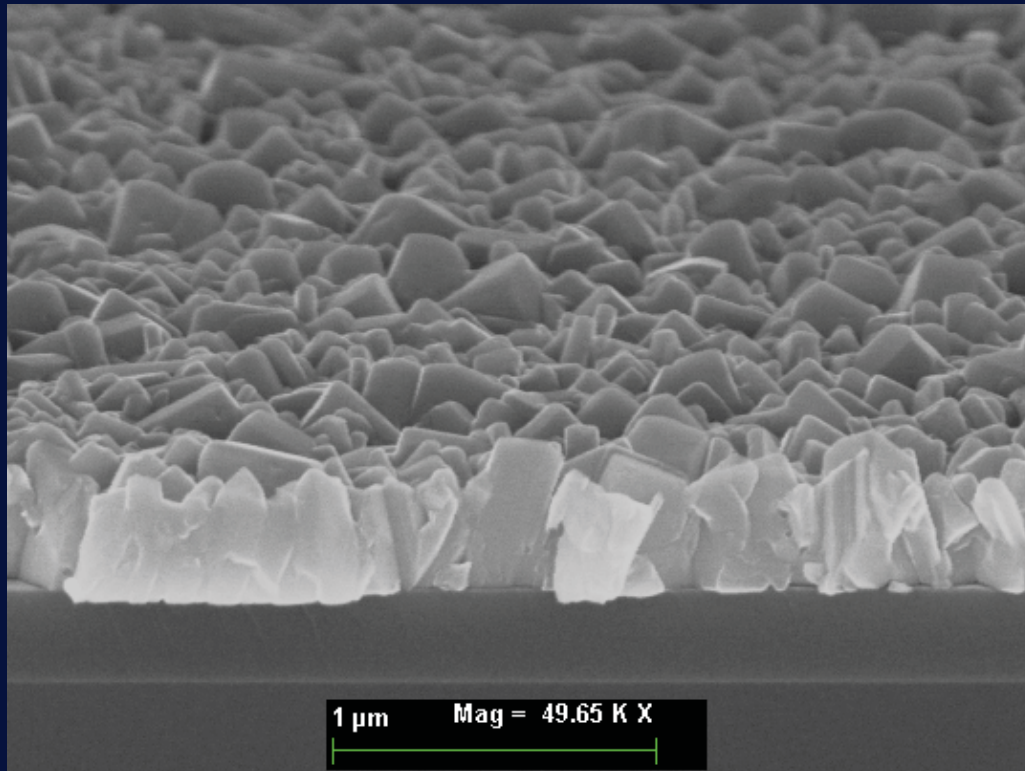
function of layer	possible materials
transparent support, protection	soda-lime glass
n+ transparent conductor, front electrode	SnO ₂ (F) or ZnO(F)
electron transparent, hole-blocking	Zn(O,S) or (Zn,Mg)O
light absorber, charge separator	SnS or Cu ₂ O
hole-transparent, electron-blocking	(Mo,W)O _{3-x}
reflective conductor, back electrode	Cu or Al

All elements sufficiently abundant, inexpensive & non-toxic



An Absorber with Abundant, Non-toxic Elements

Tin monosulfide, SnS



$\alpha > 10^5 \text{ cm}^{-1}$ strong absorption of visible light

→ need $< 0.5 \mu\text{m}$ thickness to absorb 98% of light

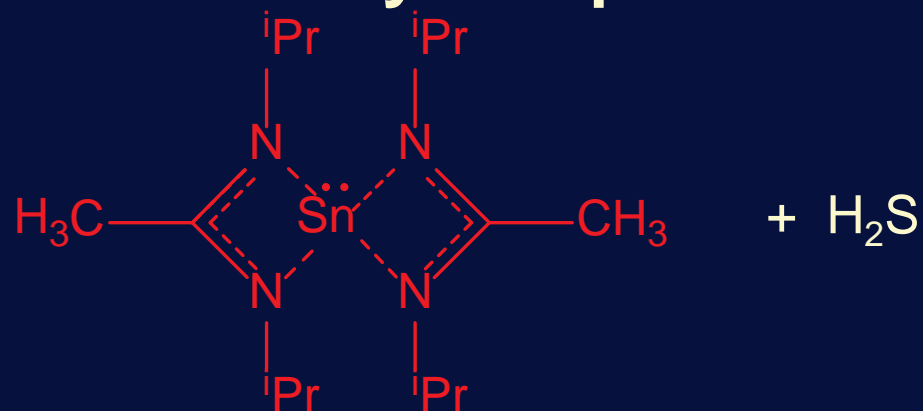


Deposition of SnS Absorber Layer

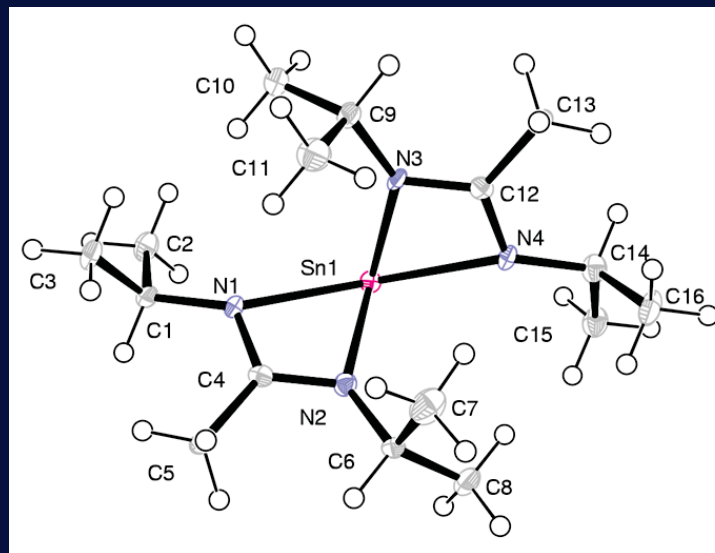
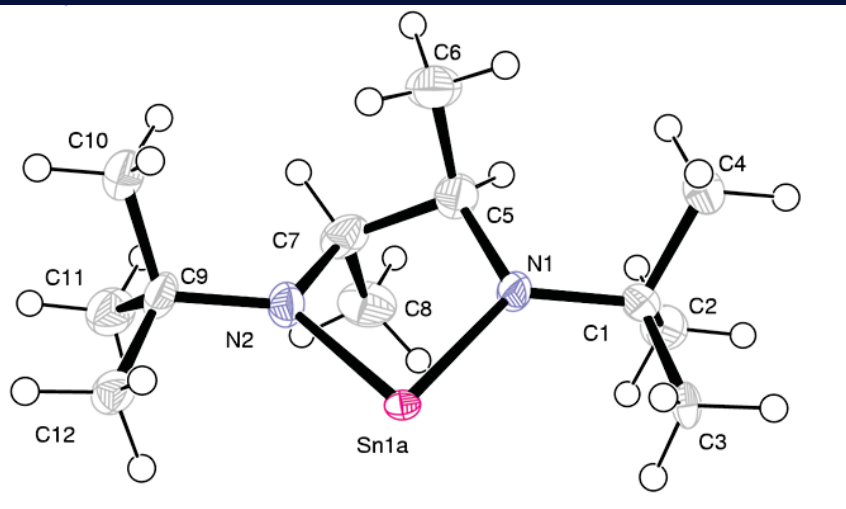
Chemical vapor deposition or atomic layer deposition:



or



+ H₂S

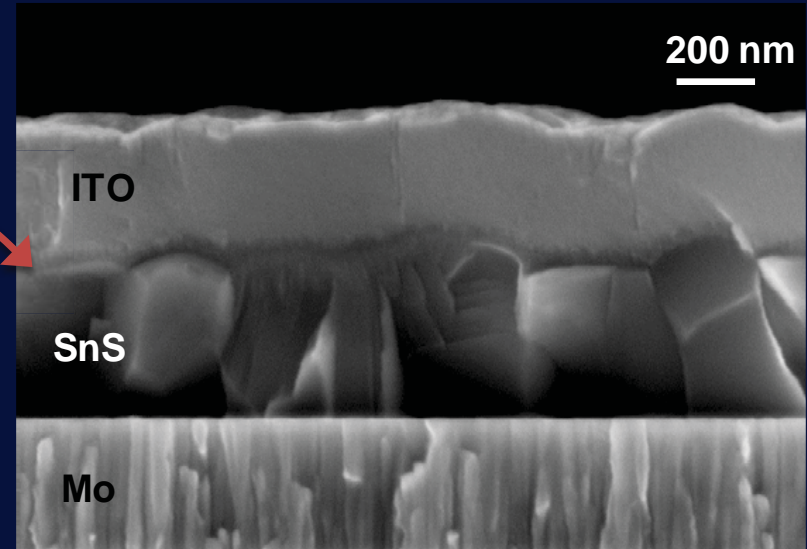
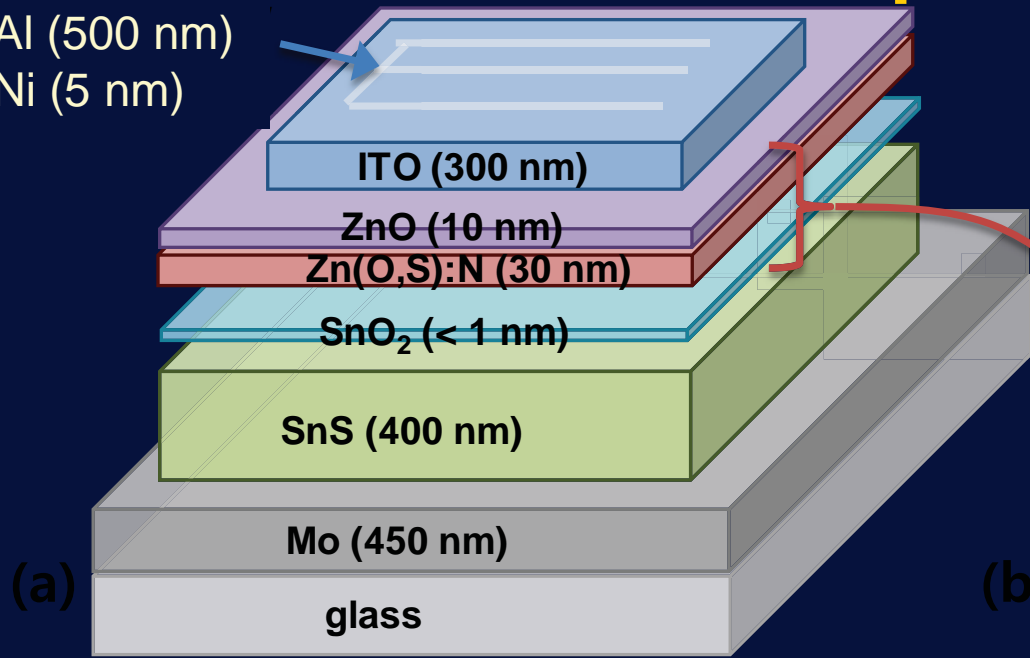


Sang Bok Kim, Prasert Sinsersuksakul, Adam S. Hock, Robert D. Pike, Roy G. Gordon
Chemistry of Materials **26**,3065 (2014)



Current Champion SnS PV Cells

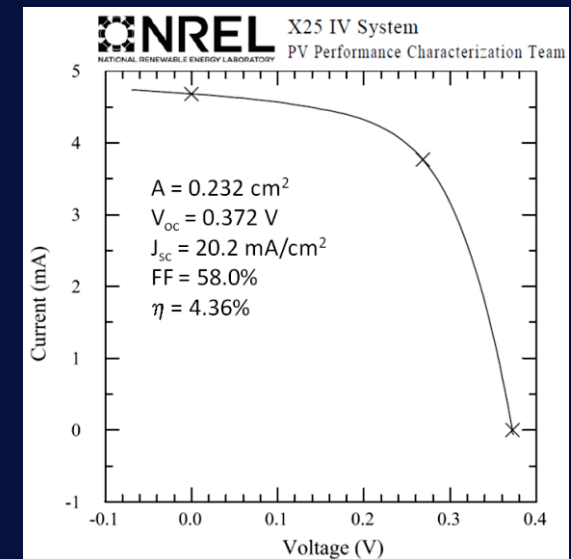
Al (500 nm)
Ni (5 nm)



NREL-certified efficiency 4.36%

Best recent cell: 4.68%

Theoretical maximum: 32%



Prasert Sinsersuksakul, Leizhi Sun, Sang Woon Lee, Helen Hejin Park, Sang Bok Kim, Chuanxi Yang, and Roy G. Gordon, *Advanced Energy Materials* (in press) (2014)

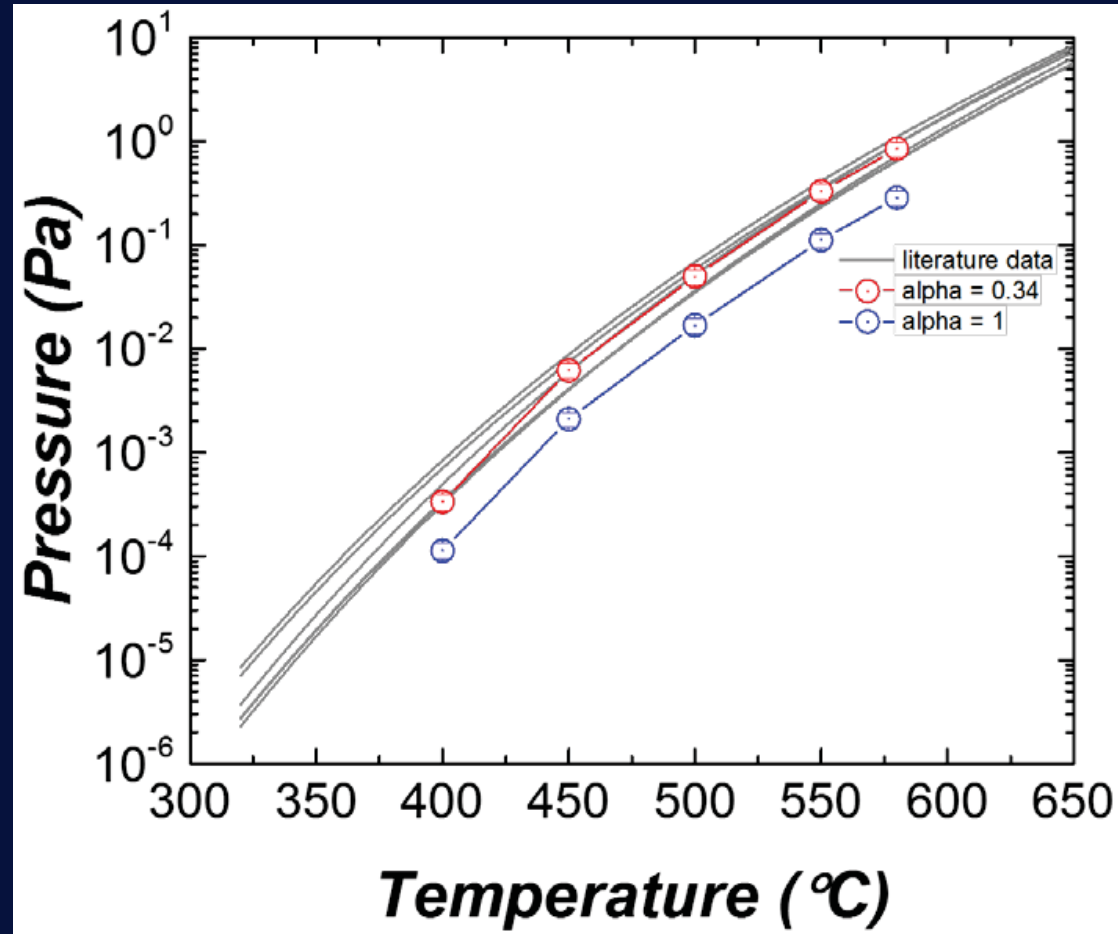


Sublimation of SnS Absorber Layer

SnS evaporates congruently like CdTe

=> 4% efficient solar cells

Could be produced rapidly by close-spaced sublimation as in First Solar's CdTe process

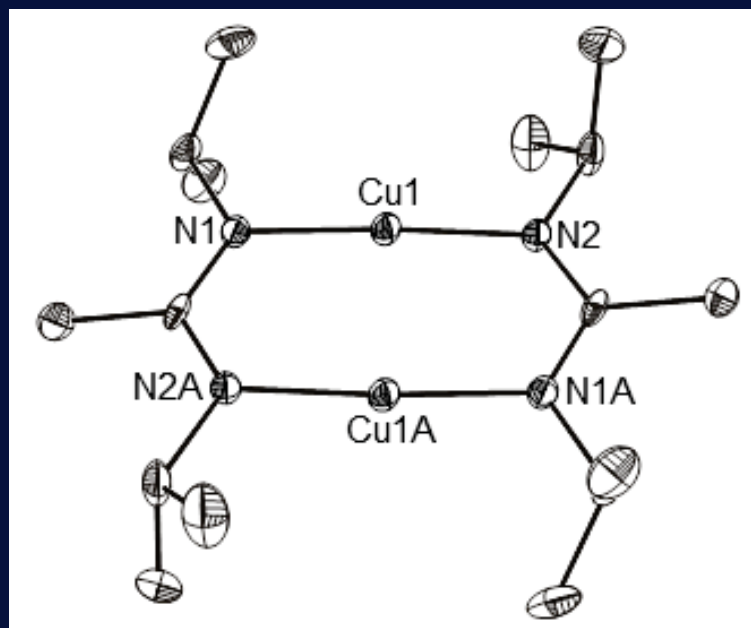
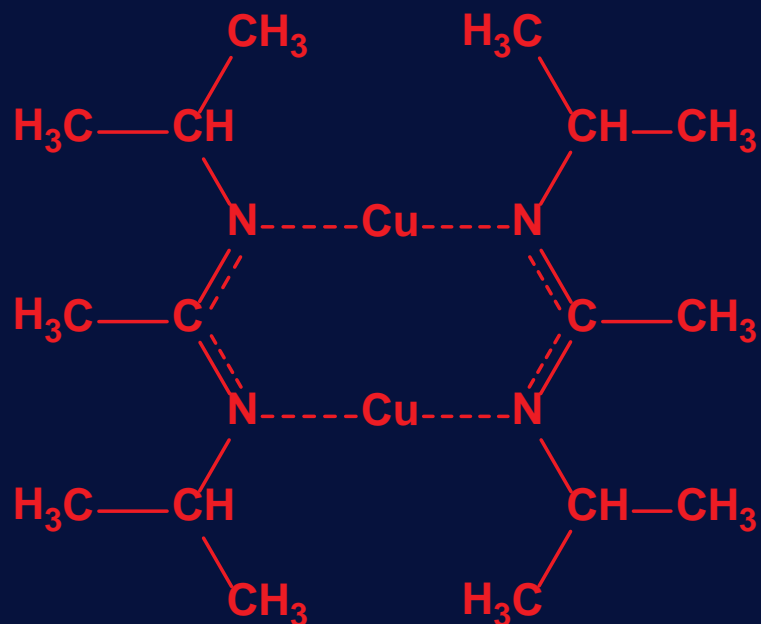


Vera Steinmann, R. Jaramillo, Katy Hartman, Rupak Chakraborty, Riley E. Brandt, Jeremy R. Poindexter, Yun Seog Lee, Leizhi Sun, Alexander Polizzotti, Helen Hejin Park, Roy G. Gordon, and Tonio Buonassisi, *Advanced Materials* (in press, 2014) DOI: 10.1002/adma.201402219



Depositing Cu₂O

By Chemical Vapor Deposition or Atomic Layer Deposition:



+ H₂O vapor

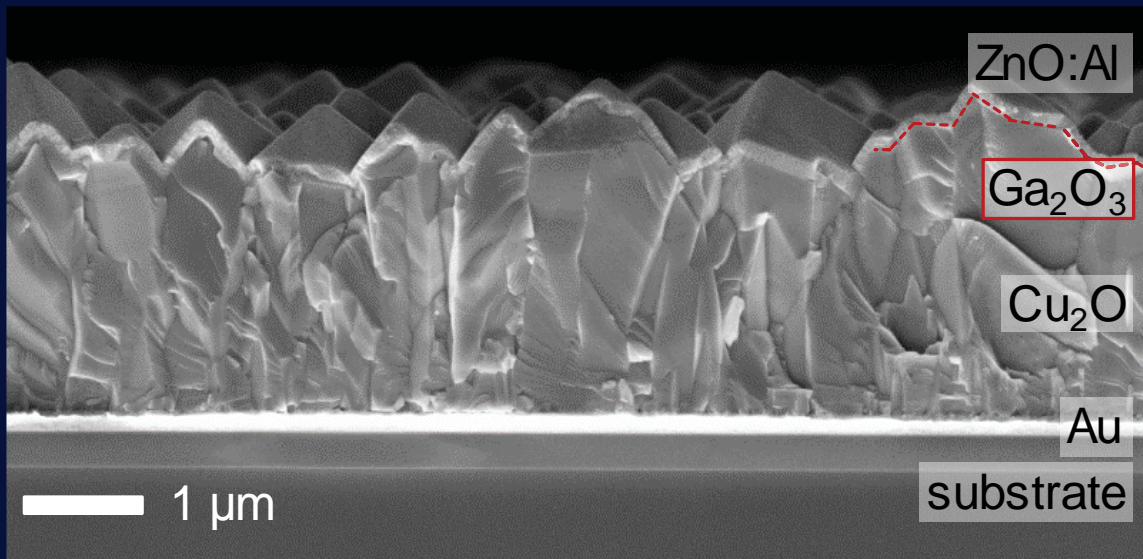
Hoon Kim, Harish B. Bhandari, Sheng Xu, Roy G. Gordon,
J. Electrochemical Society, **155**, H496 (2008)

By Electrodeposition from water-based electrolyte:

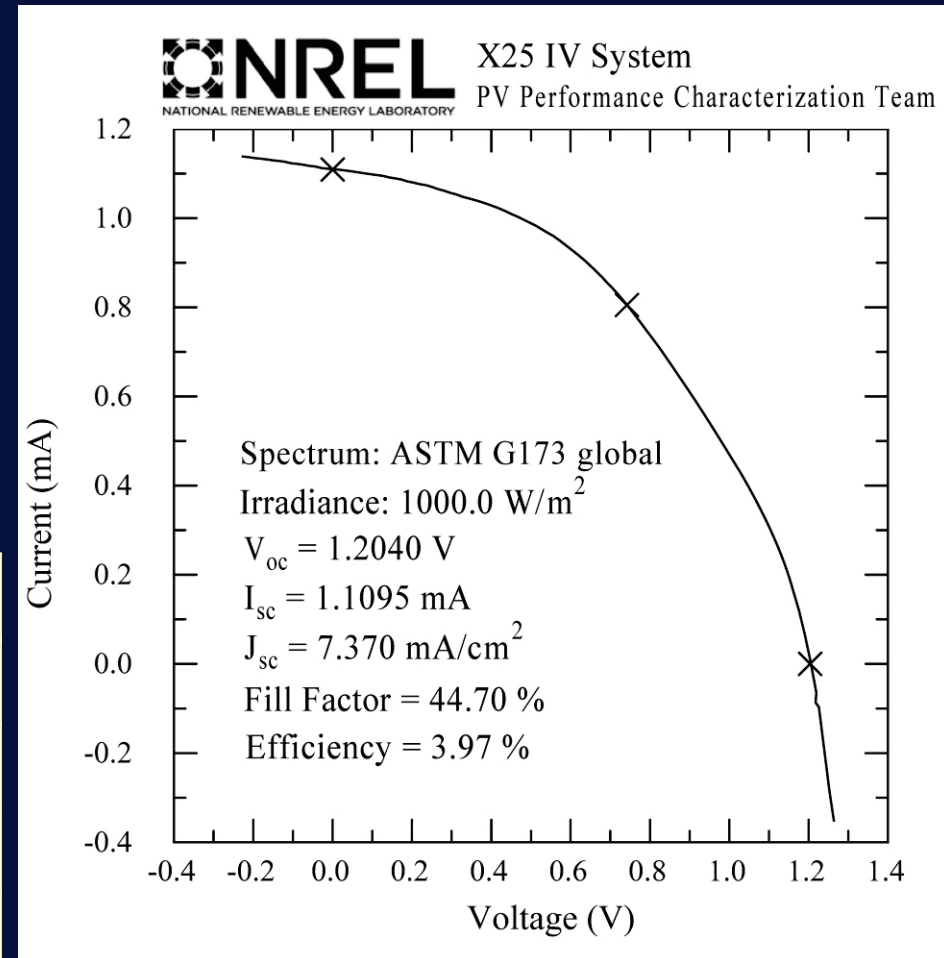
Yun Seog Lee, Danny Chua, Riley E. Brandt, Sin Cheng Siah, Jian V. Li,
Jonathan P. Mailoa, Sang Woon Lee, Roy G. Gordon, and Tonio Buonassisi,
Advanced Materials (2014); 10.1002/adma.201401054



Cu₂O Solar Cells



layer	function	thick
MgF ₂	antireflection	95 nm
n+ ZnO(Al)	transparent contact	80 nm
n Ga ₂ O ₃	electron transmission	10 nm
p Cu ₂ O	absorber	2 μm
Au	reflective back contact	200 nm



Yun Seog Lee, Danny Chua, Riley E. Brandt, Sin Cheng Siah, Jian V. Li, Jonathan P. Mailoa, Sang Woon Lee, Roy G. Gordon, and Tonio Buonassisi, *Advanced Materials* (2014); 10.1002/adma.201401054



Methods for Improving SnS & Cu₂O PV Cells

More efficient collection by optimizing depositing and annealing:
atmosphere with well-controlled activities of elements
optimized time-temperature profile
adding dopants to passivate grain boundaries

Improve back contact:

higher reflectivity to near infrared light
lower recombination velocity by reflecting electrons

Buffer layer

wider band gap, so more transparent to blue end of spectrum
reduced recombination rate near the junction
higher conductivity buffer near the transparent conductor

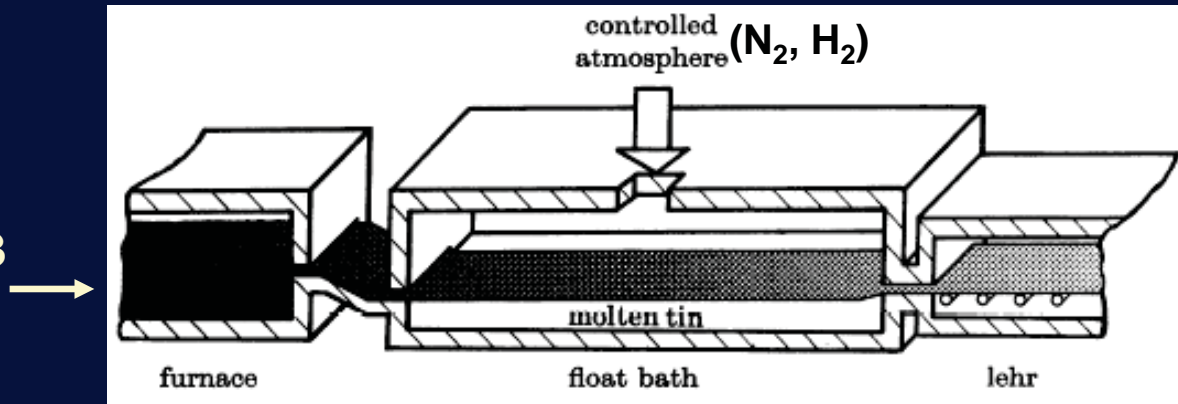
Front contact:

transparent conductor with lower work function
more transparent front conductor
antireflection coating

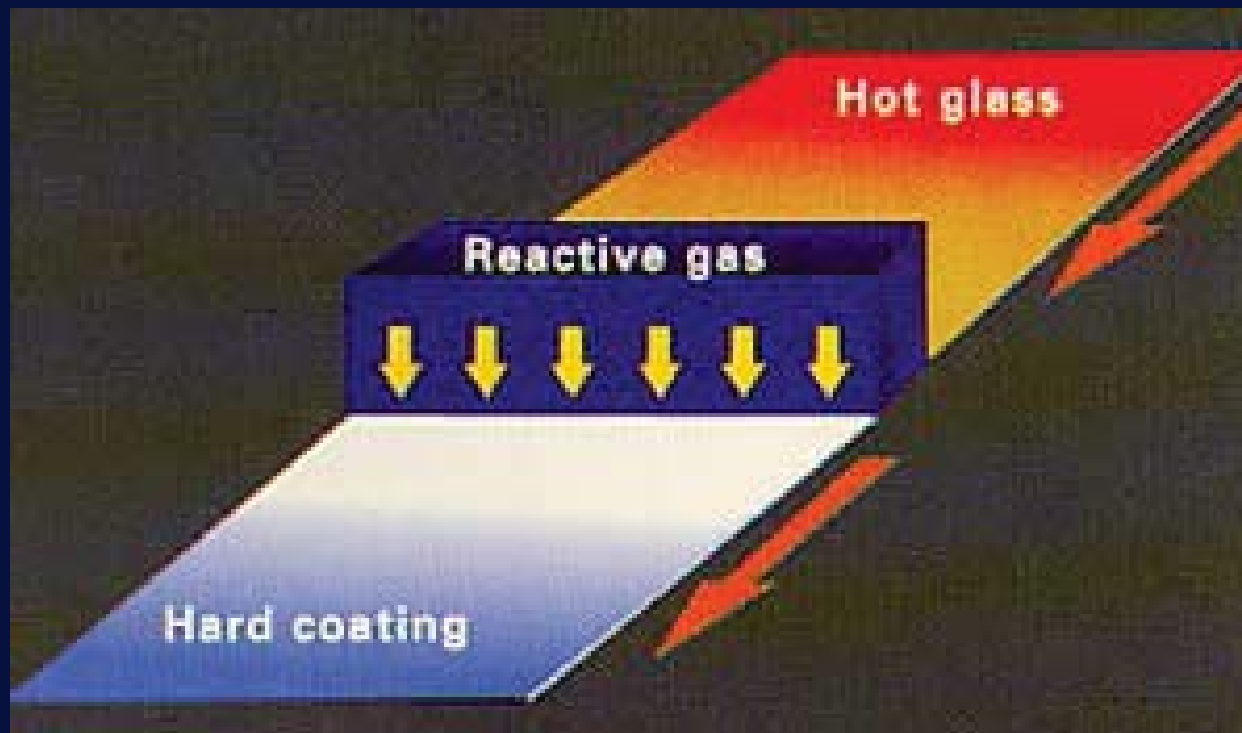


How windows are coated as the glass is made

SiO_2 ,
 Na_2CO_3
etc. in



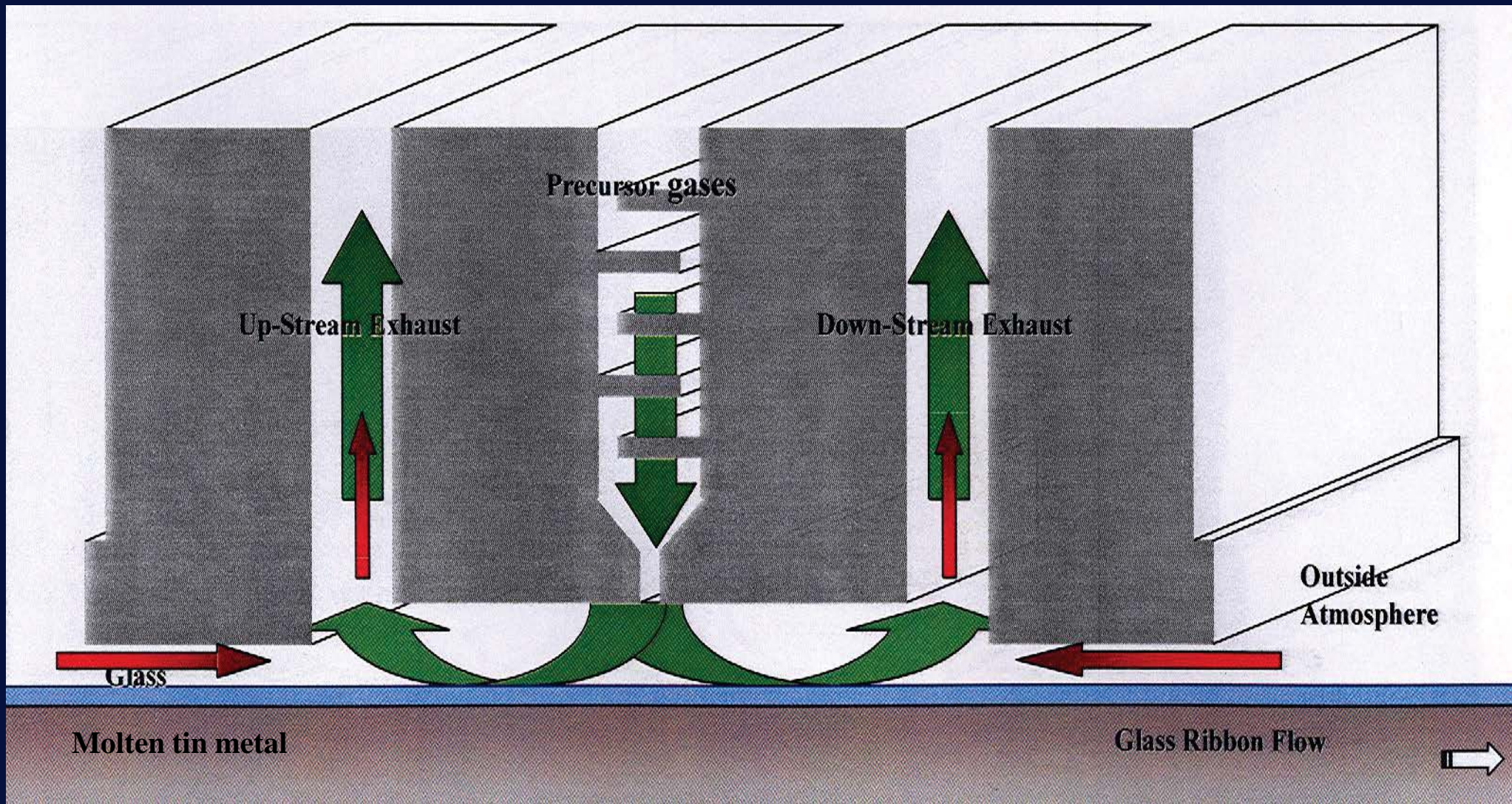
The float process for making flat glass



Chemical Vapor Deposition (CVD) on glass just after it is made



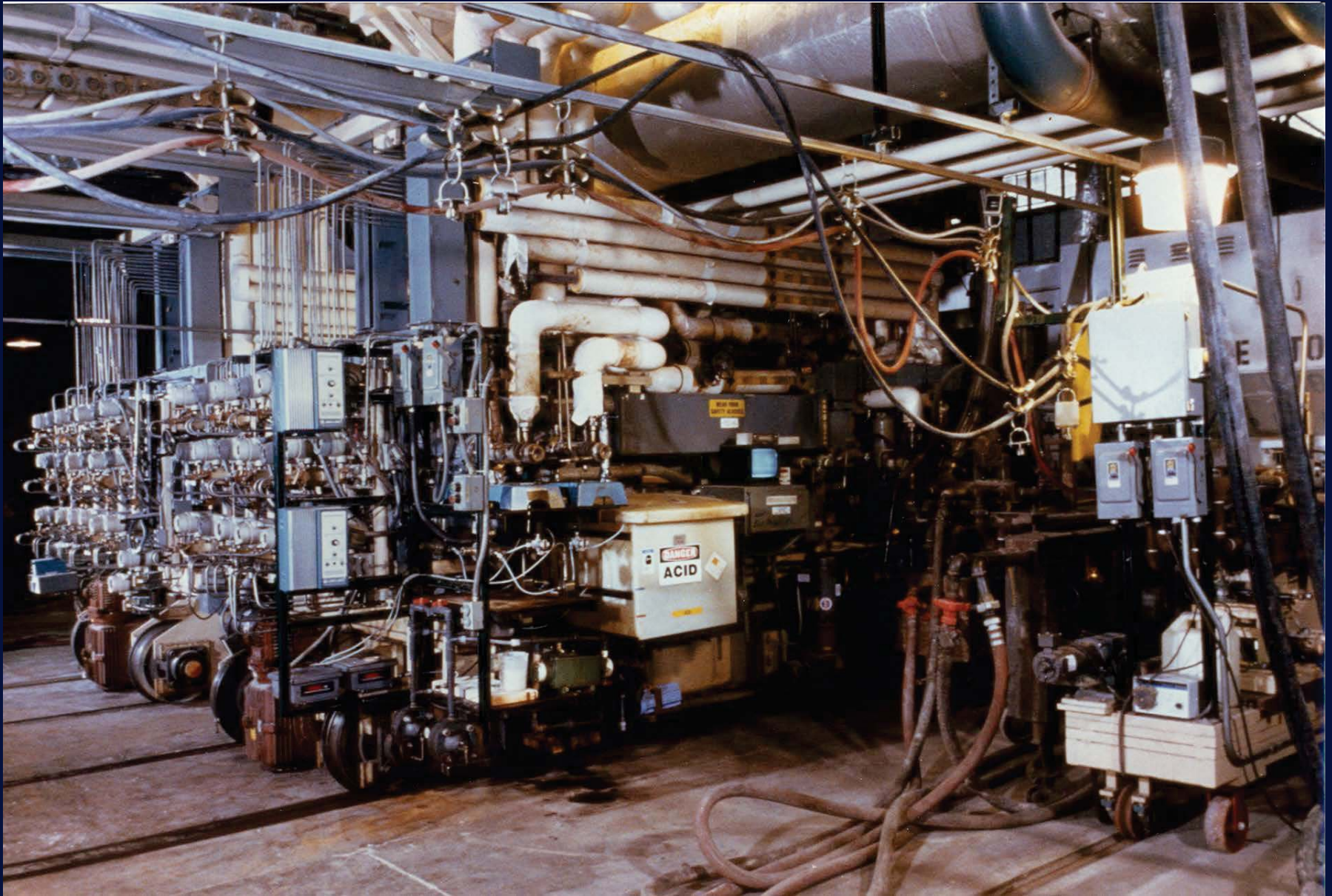
CVD SnO₂ on hot glass ribbon



A given area of glass spends a few seconds under the coater.



CVD coaters in a glass factory



Makes very inexpensive tin oxide coatings ($< \$1 / \text{m}^2$)

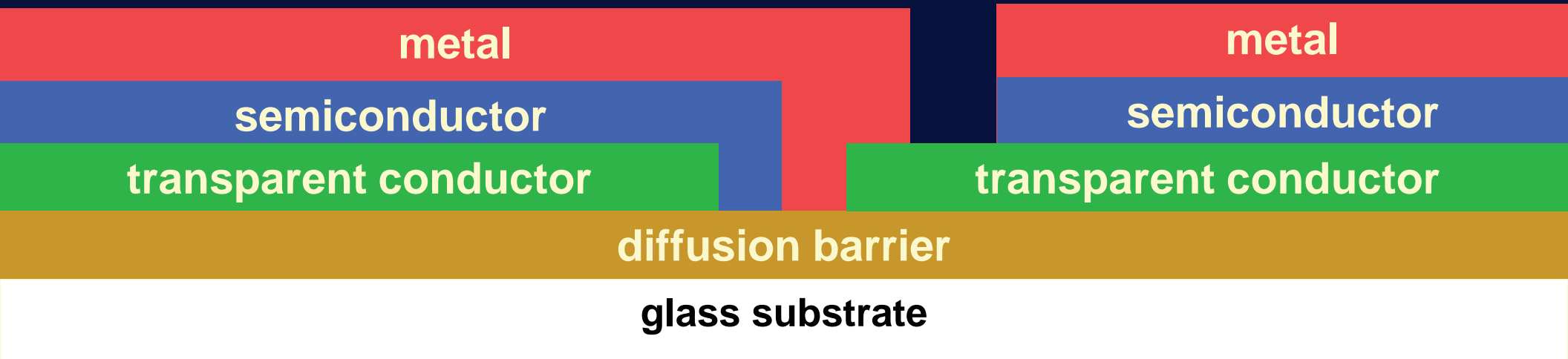


Integrated Connections between solar cells

The solar cells also need to be connected in series to increase the output voltage

To do this on-line, lasers should etch one layer selectively without disturbing the layers below.

Avoids the high cost of wired connections between cells



Why will On-line Solar Cells be Inexpensive?

Coater technology already developed for window coatings

Production costs: mainly precursor materials

Little energy input beyond what is used in glass production

Low handling costs because integrated into glass production

Low assembly costs because of integrated cell structure



Scientific and Technical Challenges

Find sufficiently rapid CVD reactions to make materials with

only abundant elements

inexpensive precursors

high purity

few defects

high speed deposition

compatible ranges of deposition temperature

stable and strongly adherent interfaces



Economics of PV

CdTe thin film cells are currently the lowest cost PV

First Solar Co. makes CdTe PV panels at $< \$0.60/\text{peak watt}$

The average energy production rate would be about 5 times lower, taking into account night and cloud cover.

Balance of system and installation would \sim triple the cost.

Thus, $\$0.60 \times 5 \times 3 \sim \$9/\text{average watt produced}$.

If the lifetime of the modules is 20 years, the cost of power is $\$9/[(8766 \text{ hrs/yr}) \times (20 \text{ yrs}) \times (1 \text{ kW} / 1000 \text{ W})] \sim \$0.05 / \text{kW-hr}$, less than electricity from fossil fuel plus environmental costs.





"Look up, you fools!"



Summary

Solar energy can supply all human needs for energy

**Inexpensive solar electricity can come from PV
using solar cells made from earth-abundant elements**

**Production of the PV cells should be
very fast
integrated interconnections
produced continuously during glass production**

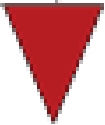
**Storing electricity must be less expensive
metal-free flow batteries (Aziz talk: 4pm today)**



Acknowledgements

- Prasert Sinsermsaksakul, Leizhi Sun, Helen Heijin Park, Sang Bok Kim, Danny Chua, Chuanxi Yang, Sang Woon Lee, Adam S. Hock, Ashwin Jayaraman, Rachel Heasley
- MIT PVLab: Tonio Buonassisi, R. Jaramillo, Yun Seog Lee, Katy Hartman, Riley E. Brandt, Vera Steinmann, Rupak Chakraborty, Alexander Polizzotti, Sin Cheng Siah, Juan V. Li, Jonathan P. Mailoa, N. Mangan
- Paul Cizek (NREL) for certification of solar cells
- Precursors: Dow Chemical, Sigma-Aldrich and Strem Chemical
- U.S. National Science Foundation; U.S Department of Energy
- Facilities at Harvard's Center for Nanoscale Systems (CNS), a member of the National Nanotechnology Infrastructure Network, supported by the U. S. National Science Foundation

Harvard University
Center for
Nanoscale
Systems



How Much Solar Energy?

1.2×10^5 terawatts of solar energy reaches earth's surface

**1 terawatt = 10^{12} watt = 10^{12} joules / second = 1 trillion watts
= 10^3 gigawatts = 10^6 megawatts = 10 billion 100 watt lights**

One year contains about 8766 hours.

1.2×10^5 terawatt / 8766 ~14 terawatt ~ total human energy use

Energy in 1 hr of sunlight = total human energy use in a year

