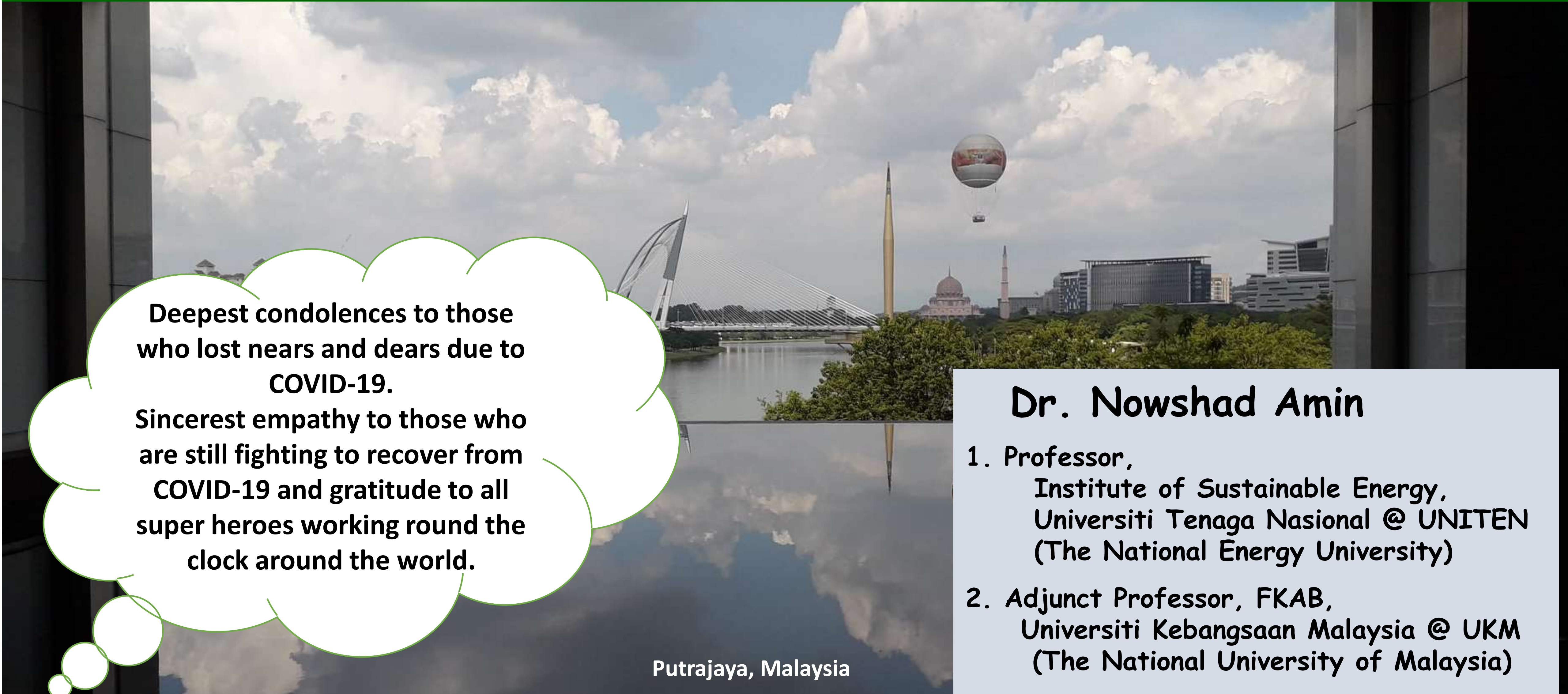
IEEE Electron Devices Society (EDS) Webinar, 15 April 2020
From Universiti Tenaga Nasional (UNITEN), Malaysia

Prospects and Limitations in Thin Film Photovoltaic Technology R&D



Deepest condolences to those who lost nears and dears due to COVID-19.
Sincerest empathy to those who are still fighting to recover from COVID-19 and gratitude to all super heroes working round the clock around the world.

Putrajaya, Malaysia

Dr. Nowshad Amin

1. Professor,
   Institute of Sustainable Energy,
   Universiti Tenaga Nasional @ UNITEN
   (The National Energy University)
2. Adjunct Professor, FKAB,
   Universiti Kebangsaan Malaysia @ UKM
   (The National University of Malaysia)

Acknowledgement

- Thin Film Solar PV R&D Group of Universiti Tenaga Nasional (@The Energy University) of Malaysia.
- Solar Energy Research Institute of Universiti Kebangsaan Malaysia (@The National University of Malaysia).
- Collaboration Partners around the world from both universities (TokyoTech, USF) and corporates.
- The Ministry of Education of Malaysia (MOE) as well as Ministry of Science and Technology of Malaysia (MOSTI-> MESTEC) for grants provided all these years.
- All the useful literatures that are being referenced from various sources/journals/proceedings.

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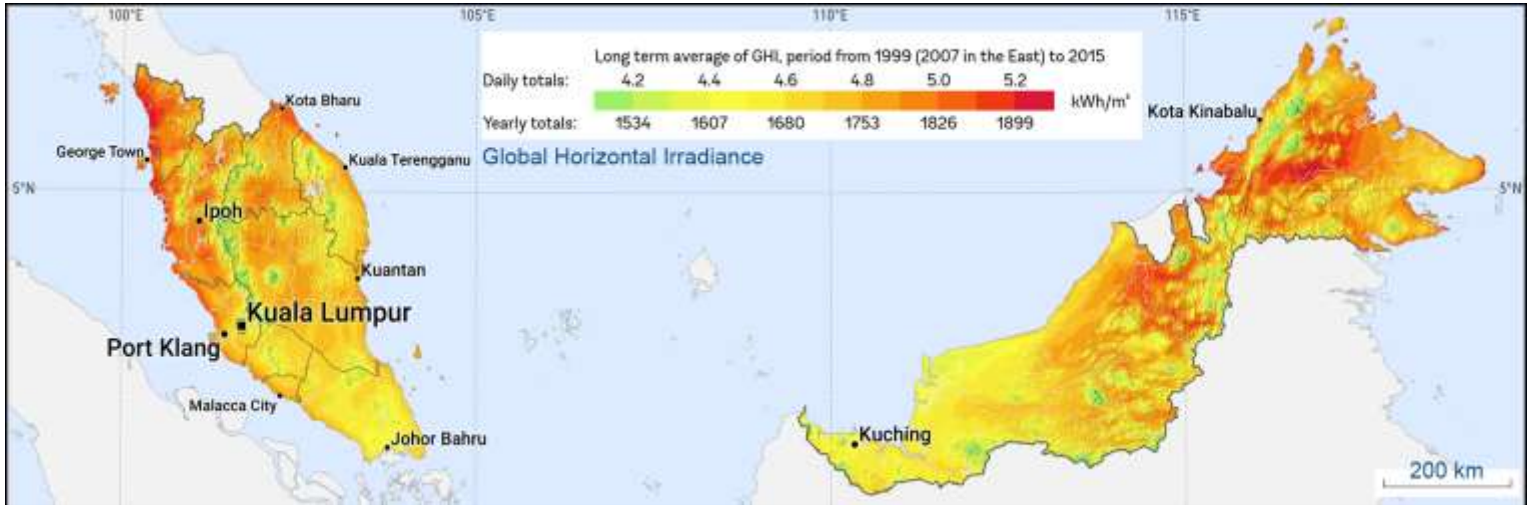
Our Collaborative Effort on Solar Photovoltaic Technology



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The National Energy University

Our Effort in High Impact Research on Energy

5 RESEARCH INSTITUTES

Key Outcomes

- Increased publications
- Increased research grants / consultancy revenues secured
- Increased principal researchers
- Increased postgraduate students / postdoctoral researchers

Institute of Power Engineering (IPE)

- Transmission and distribution technologies
- Power generation

University of Strathclyde Glasgow · Imperial College London

Institute of Sustainable Energy (ISE)

- Solar energy
- Wind technology
- Energy based on biofuel

The University Of Sheffield. · Imperial College London · DEAKIN UNIVERSITY AUSTRALIA

Institute of Energy Policy & Research (IEPRe)

- Energy economy
- Regulatory policy
- Social transformation

THE OXFORD INSTITUTE FOR ENERGY STUDIES · Massachusetts Institute of Technology · IEE JAPAN

Institute of Energy Infrastructure (IEI)

- Geospatial intelligence
- Energy water security
- Disaster risk reduction

DEAKIN UNIVERSITY AUSTRALIA · 東京大学 THE UNIVERSITY OF TOKYO · THE UNIVERSITY OF QUEENSLAND AUSTRALIA

Institute of Informatics & Computing in Energy (IICE)

- Data analytics
- Visual informatics
- Energy security

DCU DUBLIN CITY UNIVERSITY · Imperial College London · KING'S College LONDON

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The National Energy University

Institute of Sustainable Energy (ISE) @ UNITEN

BIOFUEL

HRES

SOLAR

WIND

SUSTAINABILITY

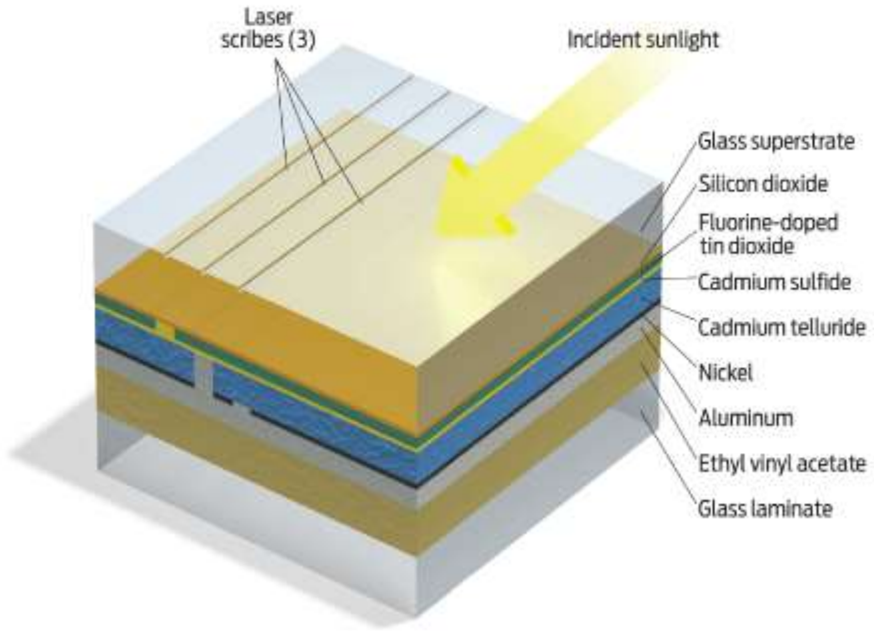
OUTLINE

- Introduction
- **Thin Film & Thin Film Deposition**
- Solar Cells
- Implication of Thin Films into Solar Cells
  - aSi
  - CdTe
  - CIS (CIGSSe, CZTS, CTS)
- Challenges and prospects
- Conclusion

Thin Films & Applications

- A **thin film** is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. The controlled synthesis of materials as thin films (a process referred to as deposition) is a fundamental step in many applications.
- Thin film technology is a "self organizing" structural evolution.

  Ex: In ancient times, people already knew how to beat gold into a thin film (<1 μm thickness) with hammers and knew how use this "gold leaf" for coating all kinds of stuff.
- Advances in thin film deposition techniques during the 20th century have enabled a wide range of technological breakthroughs in areas such as magnetic recording media, electronic semiconductor devices, LEDs, optical coatings (such as antireflective coatings), hard coatings on cutting tools, and for both energy generation (e.g. thin-film solar cells) and storage (thin-film batteries).



Applications:
Decorative coatings, Optical coatings, Protective coatings, Electrically operating coatings, Thin-film photovoltaic cells, Thin-film batteries

Thin Film Deposition

- The act of applying a thin film to a surface is *thin-film deposition* - any technique for depositing a thin film of material onto a substrate or onto previously deposited layers.

- "Thin" is a relative term, but most deposition techniques control layer thickness within a few tens of nanometres.

  Molecular beam epitaxy, Langmuir-Blodgett method, atomic layer deposition and molecular layer deposition allow a single layer of atoms or molecules to be deposited at a time.

- Thin film technology involves deposition of individual molecules or *atoms*.

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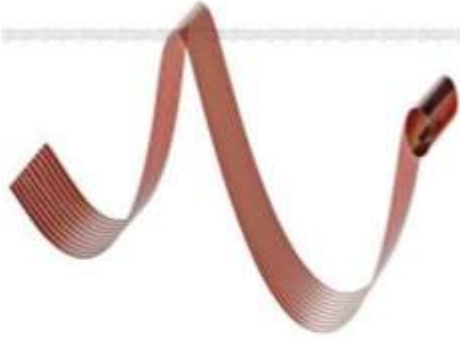
Solar Cells

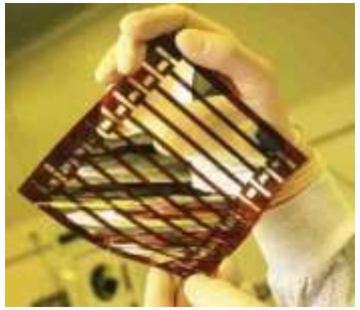
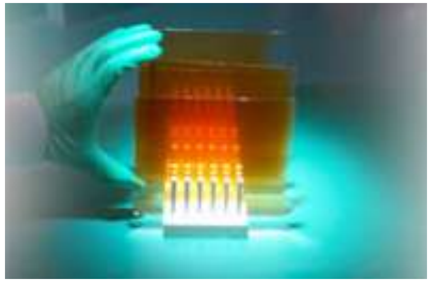
Solar cells operate by converting sunlight directly into electricity using the electronic properties of a class of material known as semiconductors and can be configured in many options like flexible, semi-transparent etc., besides rigid ones.







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Solar Cell Development

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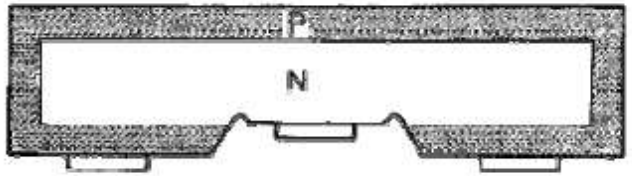
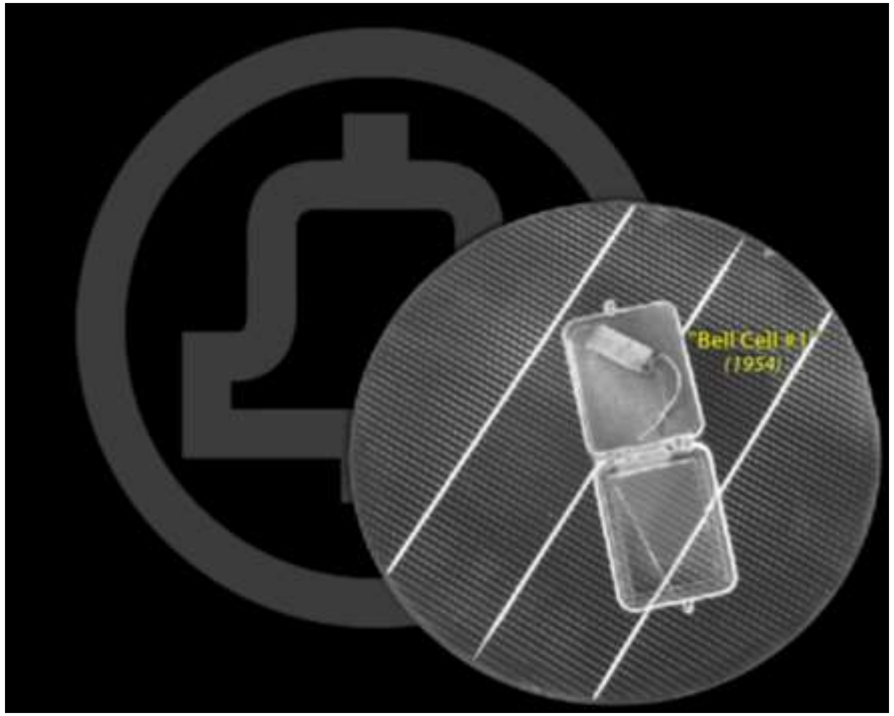
The National Energy University



D.M. Chapin (center), C.S. Fuller (right) and G.L. Pearson (left), "A New Silicon P-N Junction Photocell for Converting Solar Radiation into Electrical Power", J. Appl. Phys. **25** 676 (1954).



First photovoltaic structure that converted light to electricity with reasonable efficiency (6%)

Vast Power of the Sun Is Tapped By Battery Using Sand Ingredient

Special to The New York Times.

MURRAY HILL, N. J., April 25—A solar battery, the first of its kind, which converts useful amounts of the sun's radiation directly and efficiently into electricity, has been constructed here by the Bell Telephone Laboratories.

The new device is a simple-looking apparatus made of strips of silicon, a principal ingredient of common sand. It may mark the beginning of a new era, leading eventually to the realization of one of mankind's most cherished dreams—the harnessing of ...

... they had achieved an efficiency of 6 per cent in converting sunlight directly into electricity. This, they asserted, compares favorably with the efficiency of steam and gasoline engines, in contrast with other photoelectric devices, which have a rating of no more than 1 per cent.

With improved techniques the efficiency may be expected to be increased substantially, they added. They observed that nothing is consumed or destroyed in the energy conversion process and there are no moving parts, so ...

The New York Times: April 26, 1954
"Vast Power is Tapped by Battery Using Sand Ingredient"

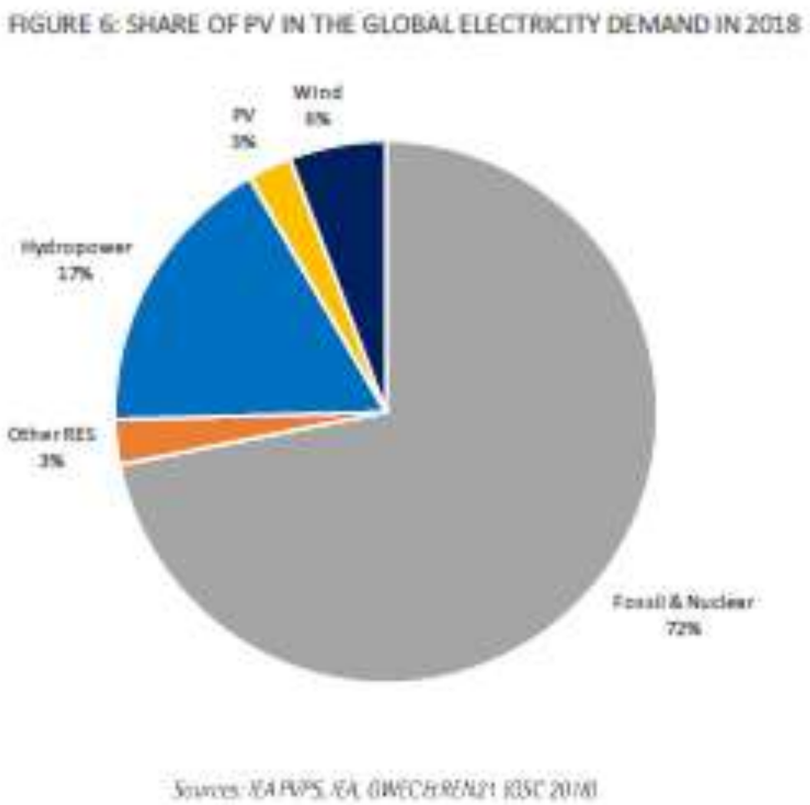
…may mark the beginning of a new era, leading eventually to the realization of one of mankind's more cherished dream —the harnessing of the almost limitless energy of the sun for the uses of civilisation".

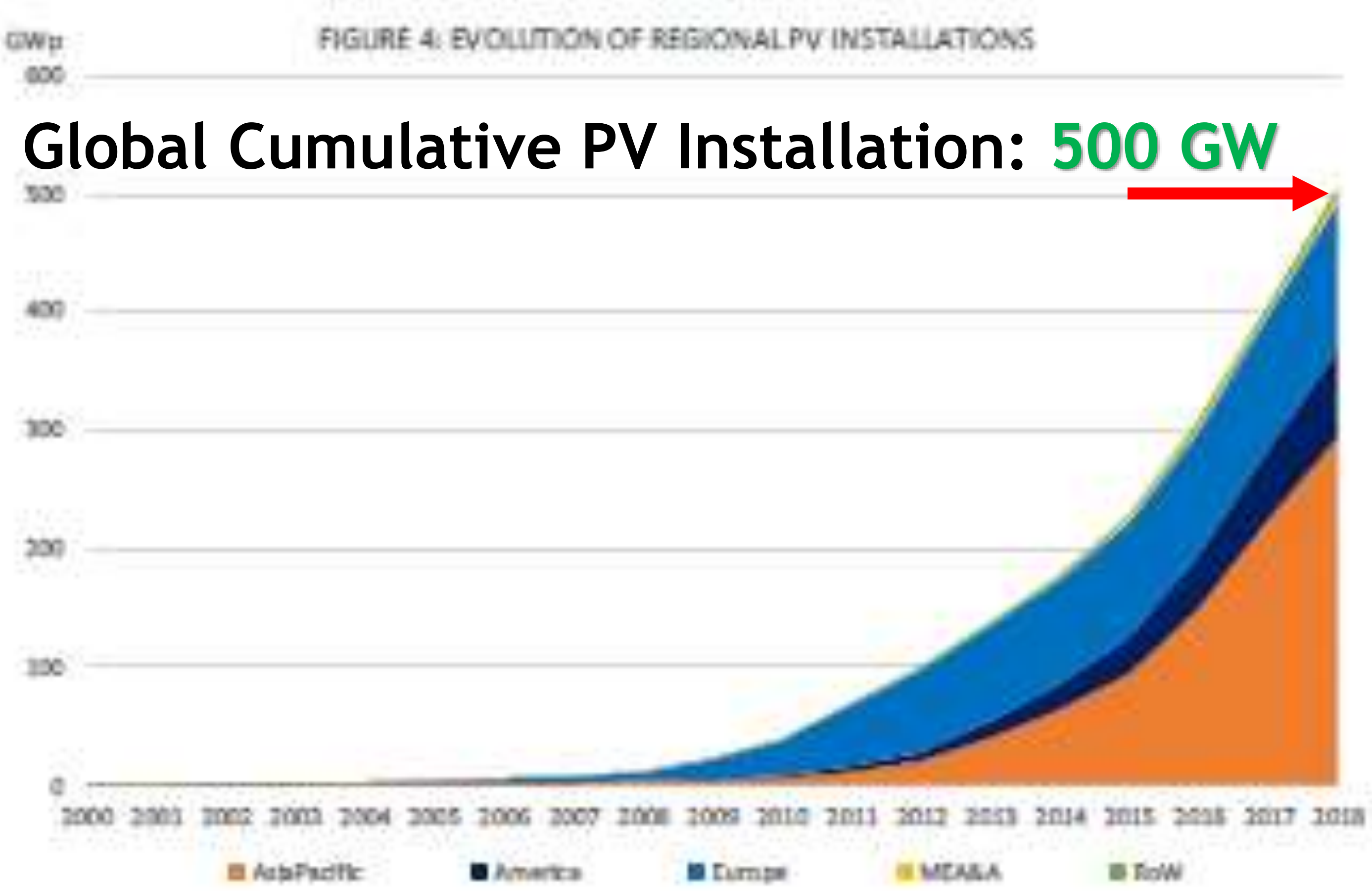
Evolution of Solar Panel Size

Purchased in 1992

460Wp possible nowadays

PV Scenario till 2018 (2019)

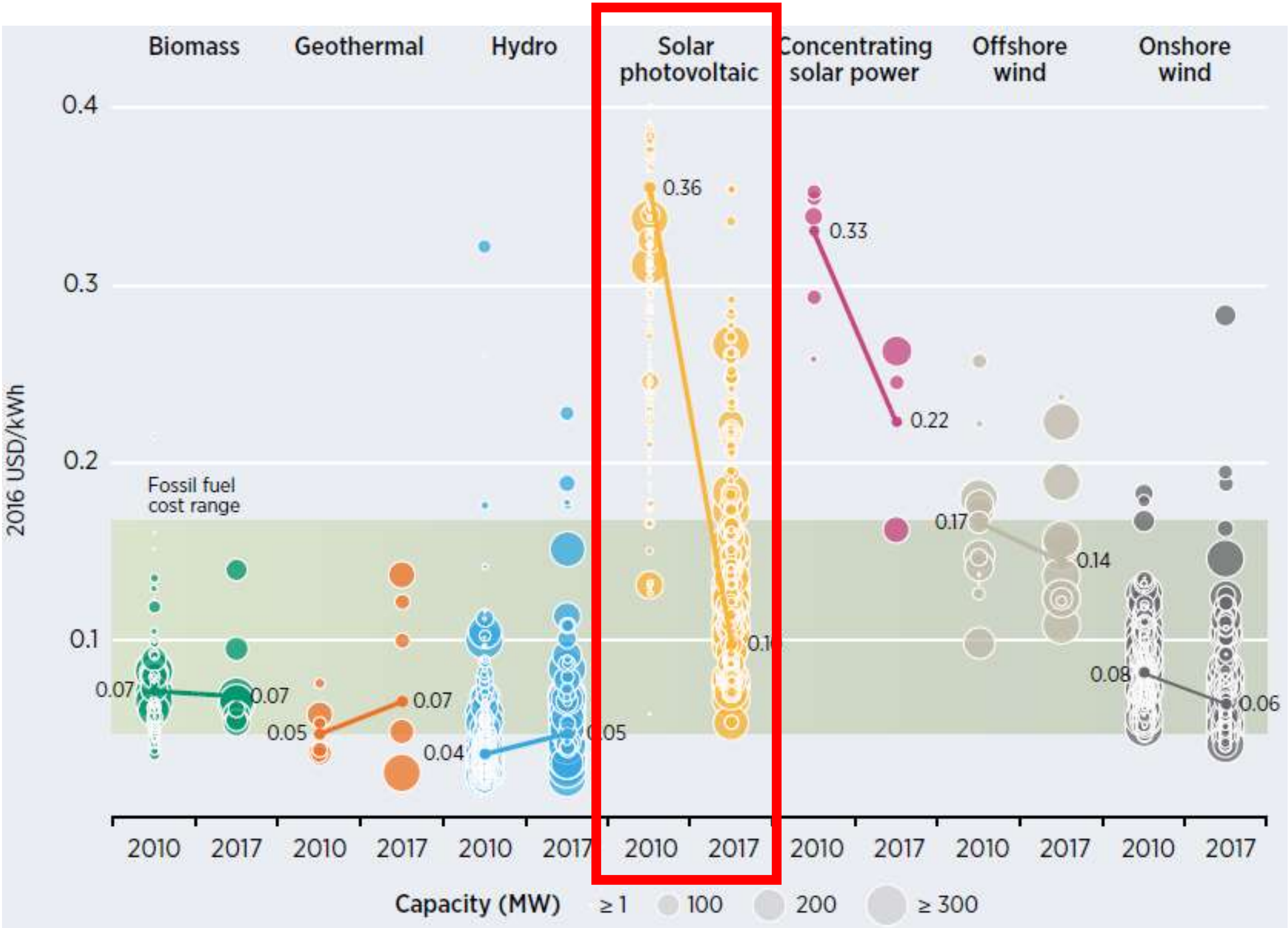




620 GWp
(by end of 2019)

Source: IEA-PVPS 2019 *Snapshot of Global PV markets*, April 2019

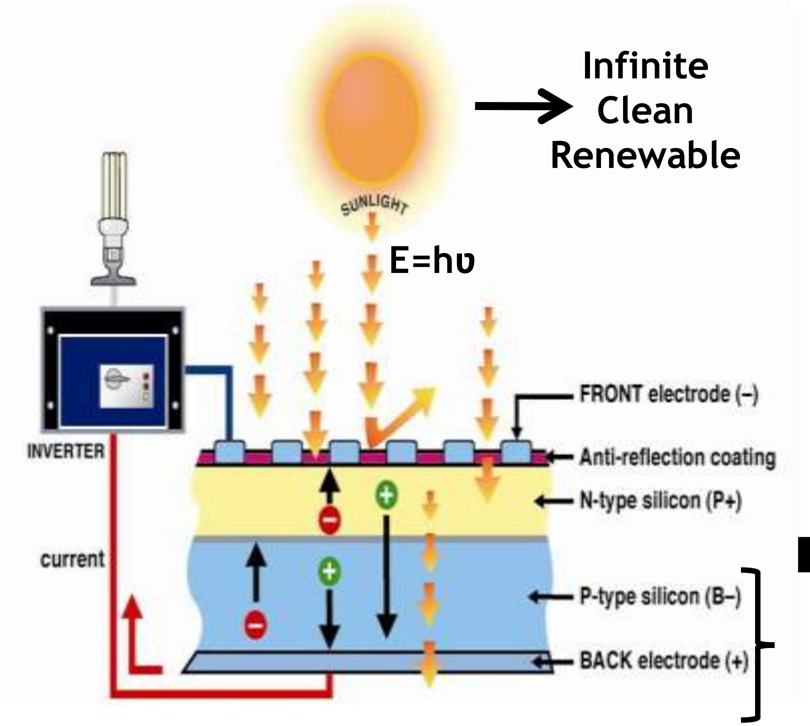
Global Levelised Cost Of Electricity (LCoE)
From Utility-scale Renewable Power Generation Technologies (2010 vs. 2017)



Source: International Renewable Energy Agency (IRENA), 2017

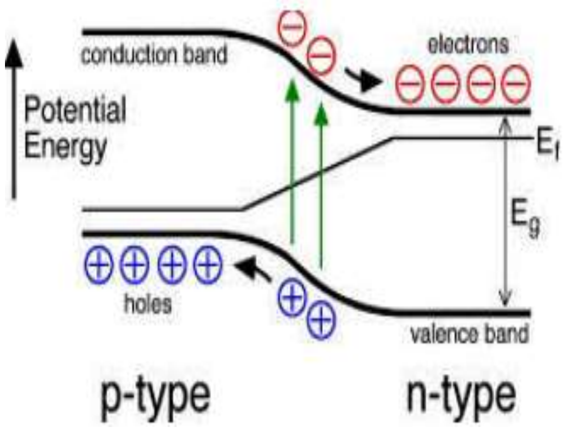
Photovoltaic (PV) Device/Cell

- Solar cell is a semiconductor device (large area p-n junction) that converts sunlight directly into electricity

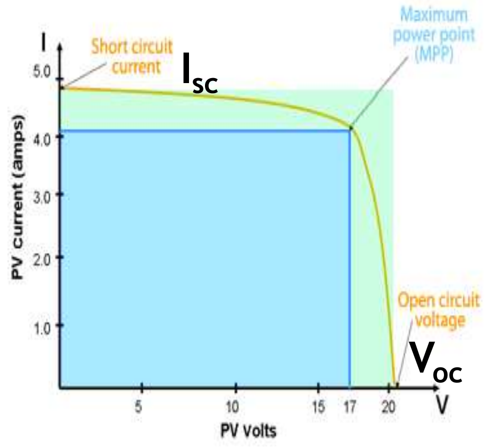


Basic Principle of Solar Cell Operation

Photovoltaic Conversion Efficiency (PCE %) = $\frac{P_{out}}{P_{in}} = \frac{I_{SC} \bullet V_{OC} \bullet FF}{P_{in}} \times 100\%$

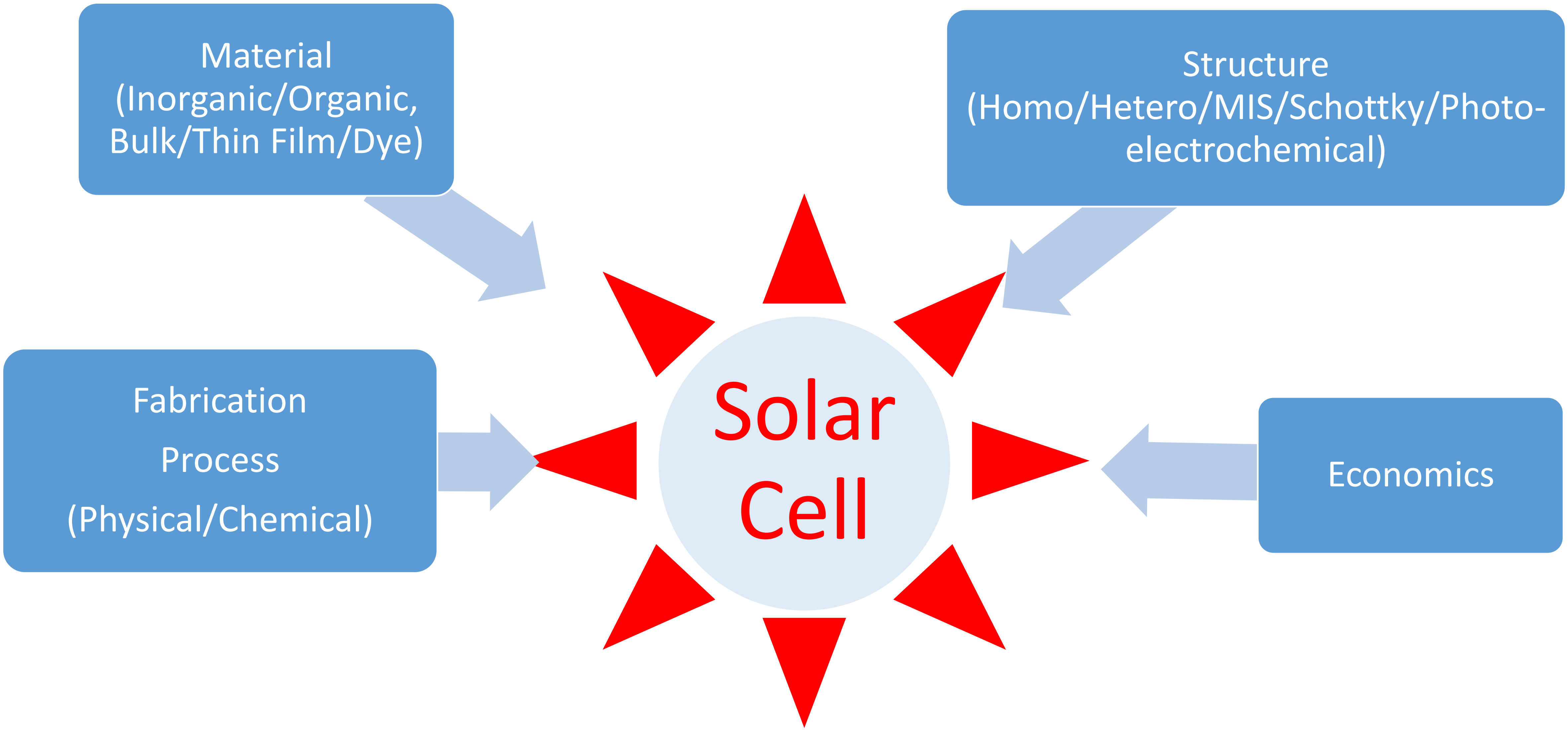


EHP Generation and Carrier Transport in p-n Junction



Solar Cell I-V Curve Under Illumination

Solar Cell Essentials



What is essential for an ideal Solar Cell ?

1. Cheap, Simple and Abundant Material
2. Integrated Large Scale Manufacturability
3. Cost, Long Durability as well as recyclability

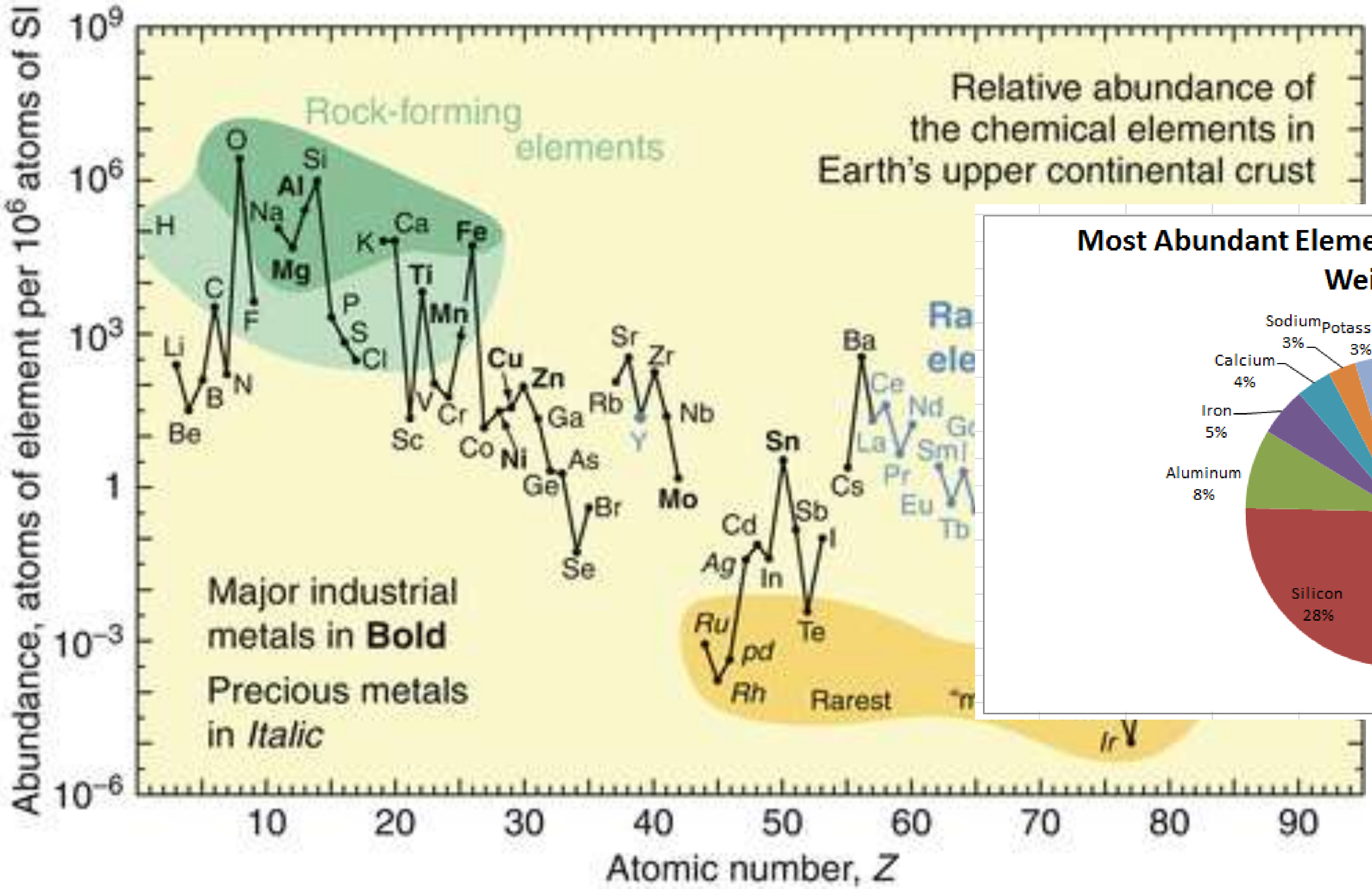
- HIGH ABSORPTION COEFFICIENT > 10^5 /cm with direct band gap ~1.5 eV
- JUNCTION FORMATION ABILITY
- HIGH QUANTUM EFFICIENCY
- LONG DIFFUSION LENGTH
- LOW RECOMBINATION VELOCITY
- ABUNDANT,CHEAP & ECO-FRIENDLY MATERIAL

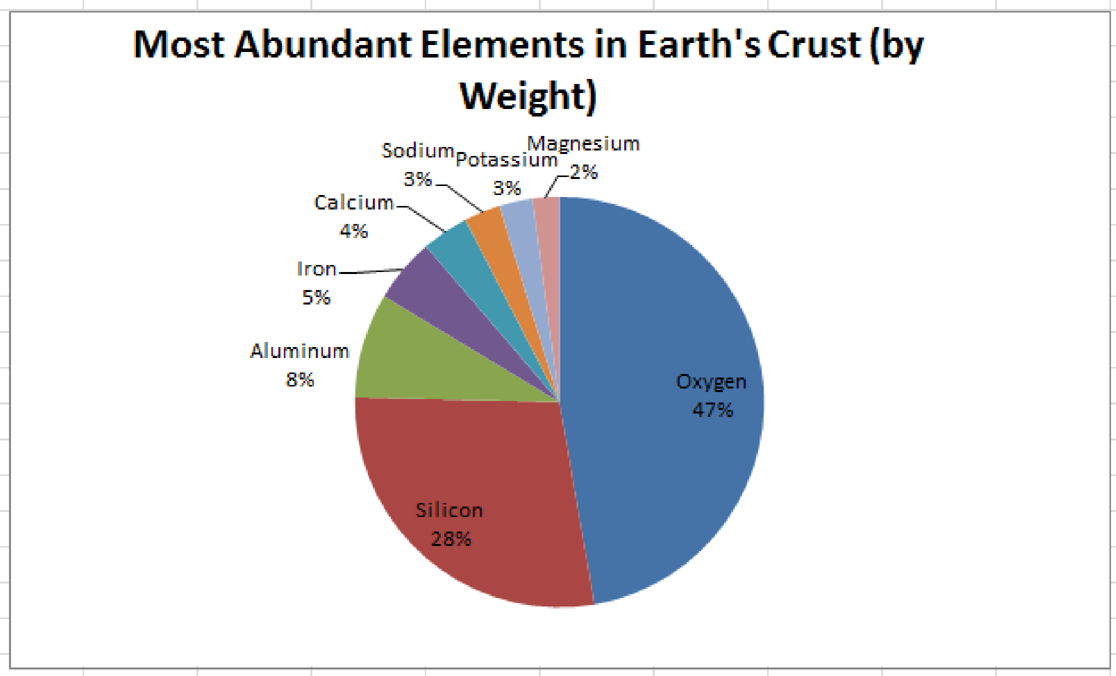
PV Materials & Devices

- CONVENIENCE OF SHAPES AND SIZES
- SIMPLE AND INEXPENSIVE INTEGRATED PROCESSING/MANUFACTURABILITY
- MINIMUM MATERIAL / WATT
- MINIMUM ENERGY INPUT/ WATT
- ENERGY PAY BACK PERIOD < 2 YEARS
- HIGH STABILTY and LONG LIFE (> 20 Years)
- COST (< 1$/Watt or lower)

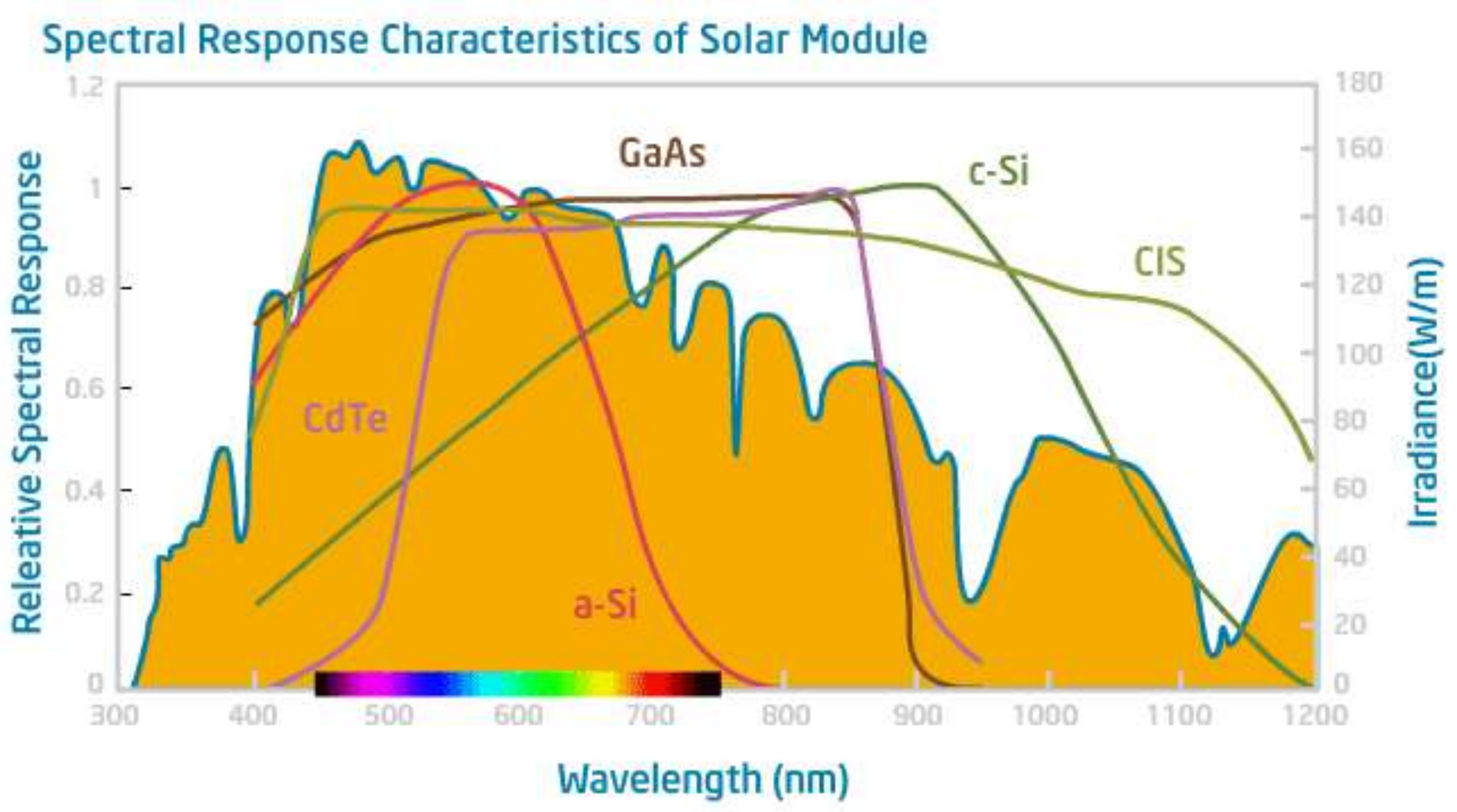
Manufacturability

Abundance Chart (Elements)





Prospects of PV Materials



[24] http://auo.com/print.php?sn=192&lang=en-US

Solar Cell Technologies

[Solar PV Applications Controllers, Systems]

[First Generation]:
Crystalline silicon solar cell (200-500 micron)

[Second Generation]:
Thin film solar cell (1-10 micron)

[Third Generation]:
DSSC, Organic, Perovskite, Multijunction, Futuristic

Crystalline Silicon cells

Mono-crystalline cells

Efficiency : 18%~25.6%

Multi-crystalline cells

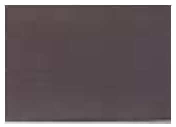
Efficiency : 17%~20.8%

Thin film PV

CdTe cells

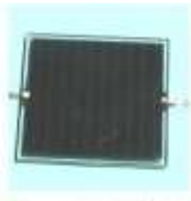
Efficiency : 18.3%~22.1%

Amorphous silicon cells



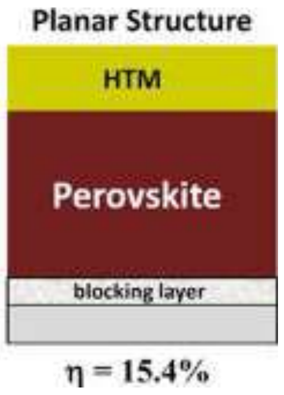
Efficiency : 13.4%

CIGS cells

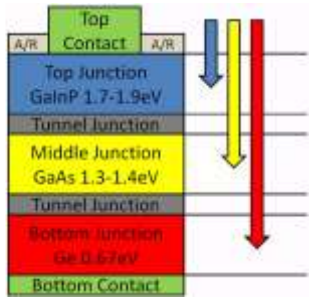


Efficiency : 20.4%~22.6%

Perovskite cells

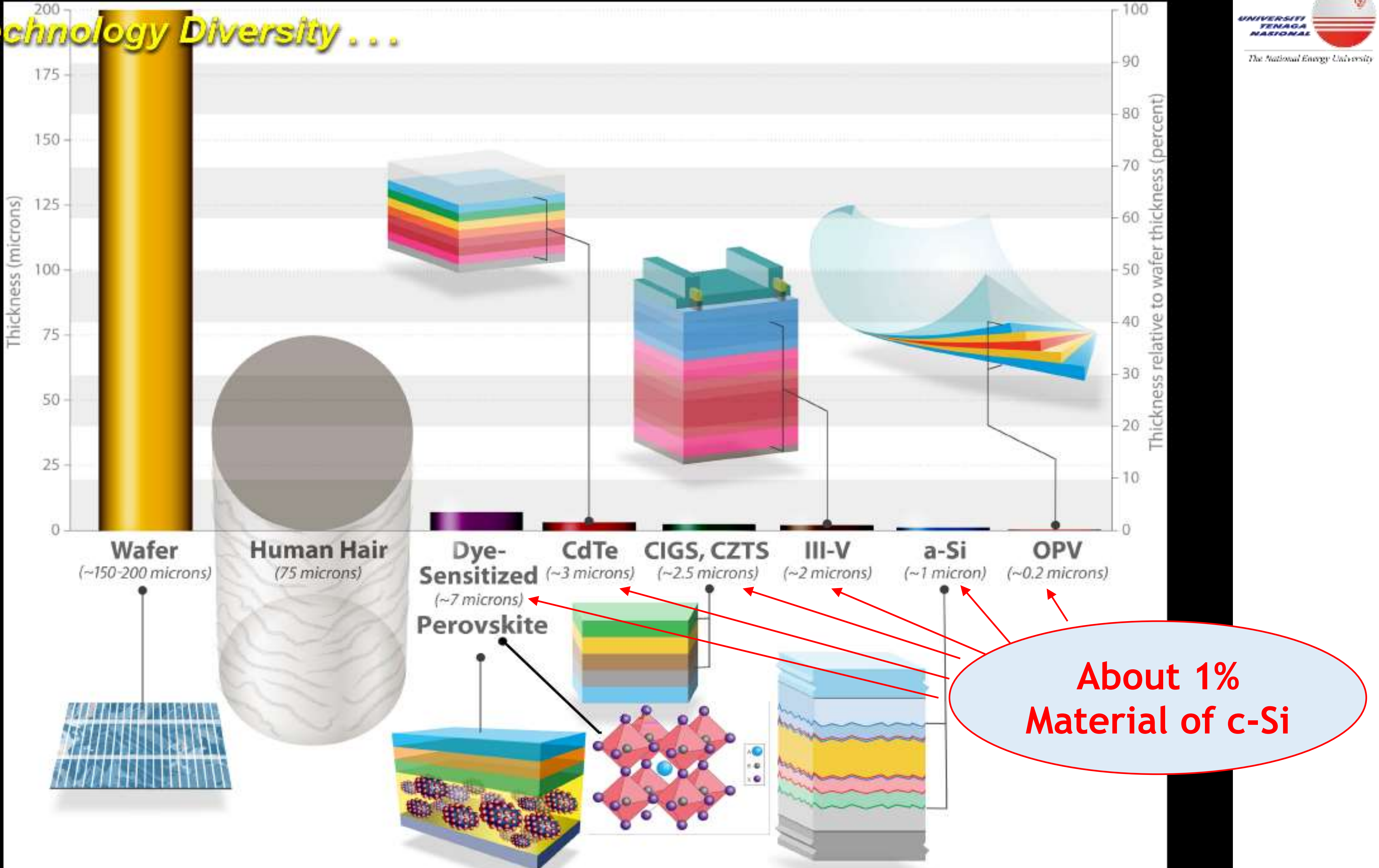


Novel Hybrid



Efficiency: 40%

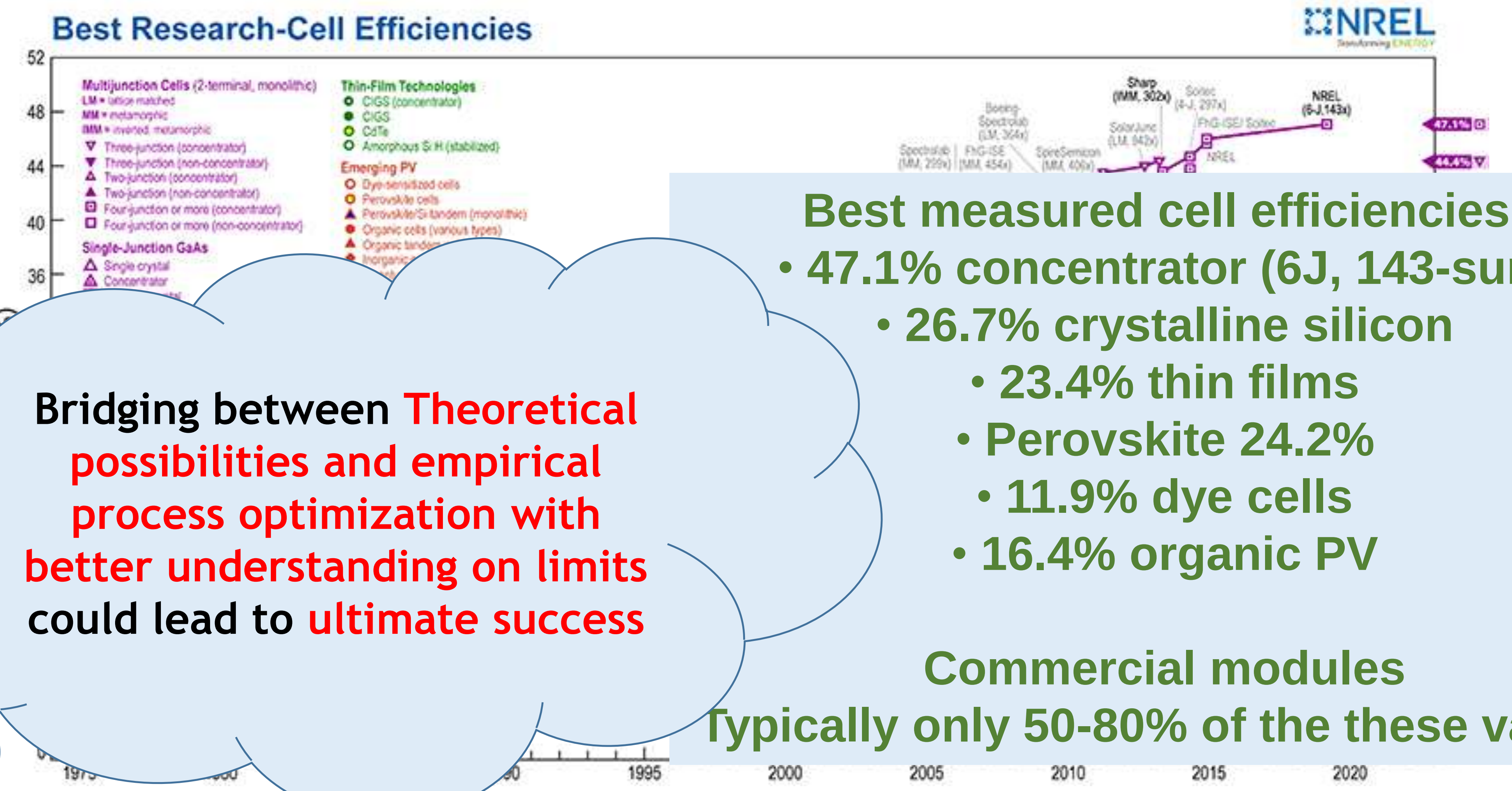
Technology Diversity . . .



Courtesy: Lawrence L. Kazmerski, *NREL*

Latest Chart Of Best Research-Cell Efficiencies (Up-to-date With The New World Record)

Source: NREL



Best measured cell efficiencies:

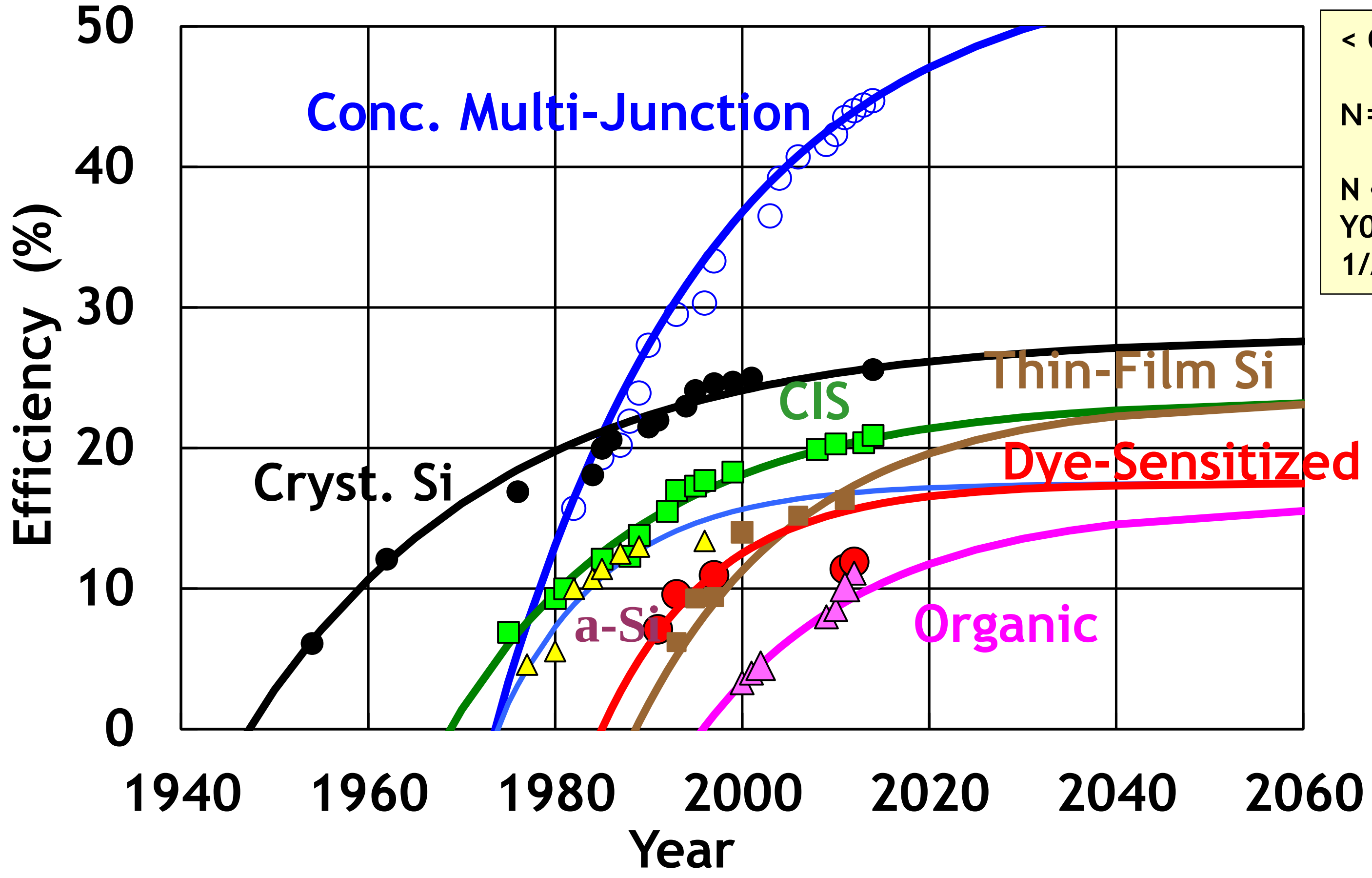
- 47.1% concentrator (6J, 143-sun)
- 26.7% crystalline silicon
- 23.4% thin films
- Perovskite 24.2%
- 11.9% dye cells
- 16.4% organic PV

Commercial modules Typically only 50-80% of the these values

Bridging between Theoretical possibilities and empirical process optimization with better understanding on limits could lead to ultimate success

Green MA, Dunlop ED, Levi DH, Hohl-Ebinger J, Yoshita M, Ho-Baillie AWY. Solar cell efficiency tables (version 54). Prog Photovolt Res Appl. 2019;27:565–575; https://doi.org/10.1002/pip.3171

Future Prediction of Various Solar Cells Efficiency



< Curve Fitting >

N=N∞＊[1-exp{(Y0−Y(x))/A}]

N ∞ ・・・ Ceiling on efficiency
Y0 ・・・・ Earliest year with experiment data report
1/A ・・・ Augmentation factor of efficiency

Original Paper : A. Goetzberger, J. Luther and G. Willeke, Solar Energy Materials and Solar Cells, 74, 1 (2002)
M. Yamaguchi, Proc. 19th European Photovoltaic Solar Energy Conference, (WIP, Munich, 2004) xl.

OUTLINE

- Introduction
- Thin Film & Thin Film Deposition
- Solar Cells
- **Implication of Thin Films into Solar Cells**
  - **aSi**
  - **CdTe**
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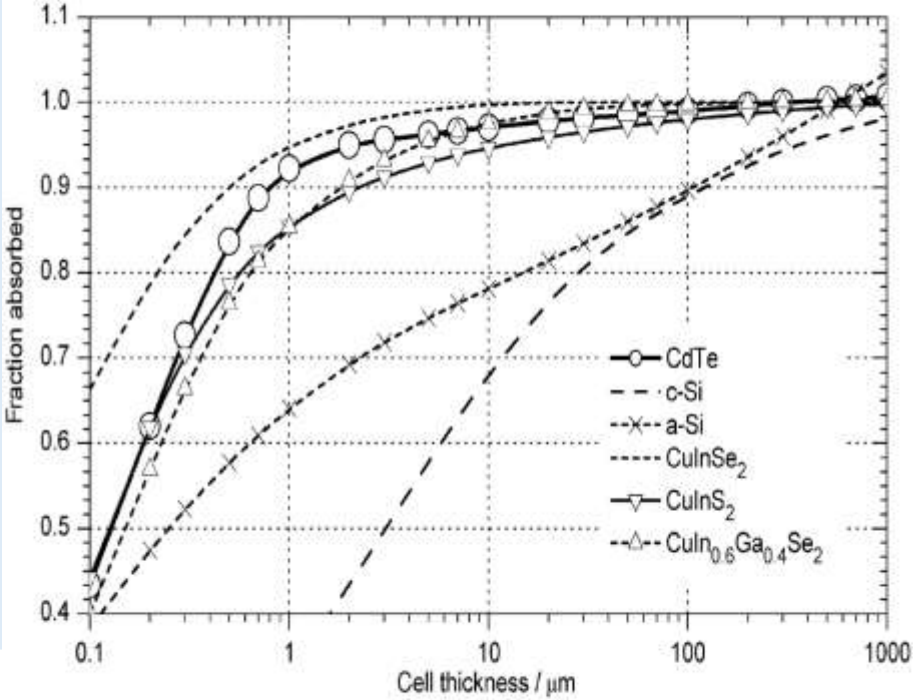
Thin Film PV

- THIN FILM SOLAR CELLS: 1-10 µm vs. Si 100-200 µm due to a higher optical absorption coefficient
- The thin film solar cells such as CdTe, a-Si and CIGS have greater advantages of significantly lower production cost over crystalline-silicon based cells
- Thinning will save material (About 1% Material of c-Si), lower production time and energy: all these factors will eventually decrease the cost and make it more popular
- Key Issues:
    - Long term stability (must be proven)
    - Manufacturability (no off-the-shelf equipment)
    - Performance (bridge gap between cells and modules)
        - Contacts
        - Buffers
        - Absorber



PV Technology: Thin Film

Thin Film

Thin film solar panels are made by placing thin layers of semiconductor material onto various surfaces, usually on glass. The term *thin film* refers to the amount of semiconductor material used. It is applied in a thin film to a surface structure, such as a sheet of glass. Contrary to popular belief, most thin film panels are not flexible. Overall, thin film solar panels offer the lowest manufacturing costs, and are becoming more prevalent in the industry.

There are three main types of thin film used:

– Cadmium Telluride (CdTe)

CdTe is a semiconductor compound formed from cadmium and tellurium. CdTe solar panels are manufactured on glass. They are the most common type of thin film solar panel on the market and the most cost-effective to manufacture. CdTe panels perform significantly better in high temperatures and in low-light conditions.

– Amorphous Silicon

Amorphous silicon is the non-crystalline form of silicon and was the first thin film material to yield a commercial product, first used in consumer items such as calculators. It can be deposited in thin layers onto a variety of surfaces and offers lower costs than traditional crystalline silicon, though it is less efficient at converting sunlight into electricity.

– Copper, Indium, Gallium, Selenide (CIGS)

CIGS is a compound semiconductor that can be deposited onto many different materials. CIGS has only recently become available for small commercial applications, and is considered a developing PV technology.

Solar Cell Technologies

Solar PV Applications Controllers, Systems

First Generation: Crystalline silicon solar cell (200-500 micron)

Second Generation: Thin film solar cell (1-10 micron)

Third Generation: DSSC, Organic, Perovskite, Multijunction, Futuristic

Crystalline Silicon cells

Mono-crystalline cells

Efficiency : 18%~25.6%

Multi-crystalline cells

Efficiency : 17%~20.8%

Thin film PV

CdTe cells

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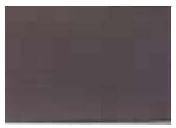
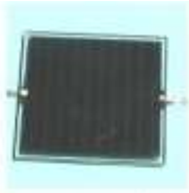
Amorphous silicon cells



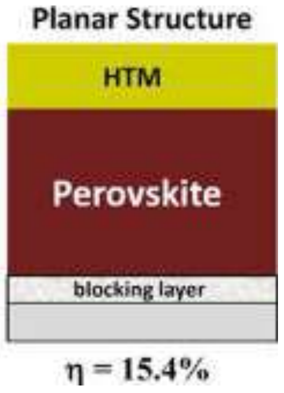
Efficiency : 13.4%

CIGS cells



Efficiency : 20.4%~22.6%

Perovskite cells



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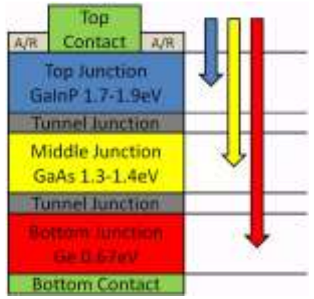
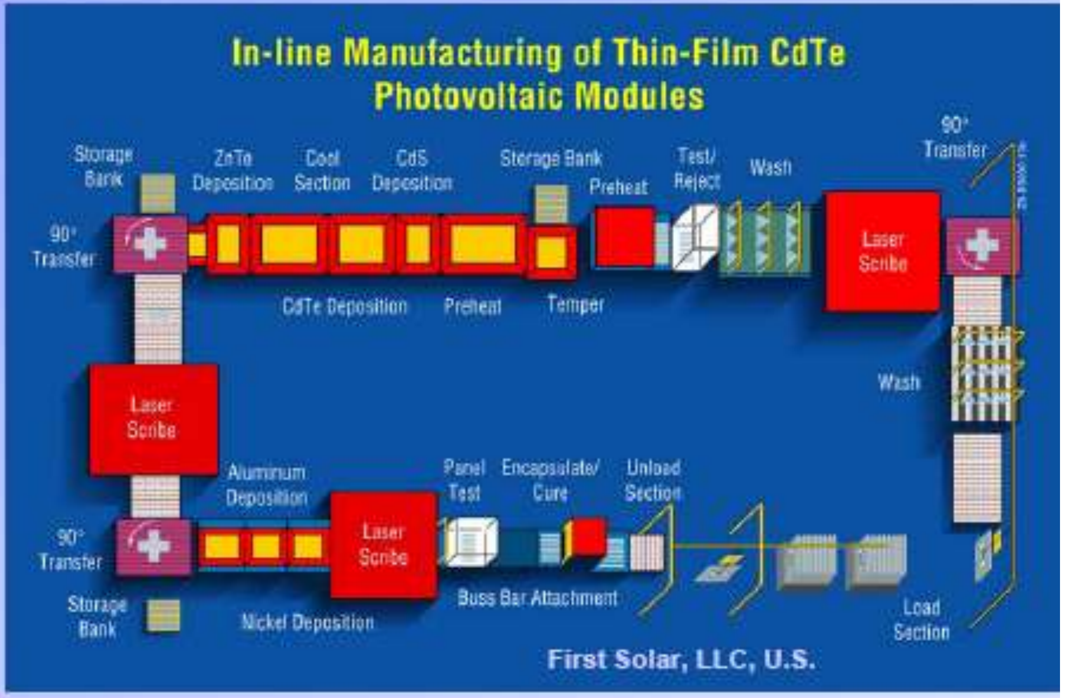


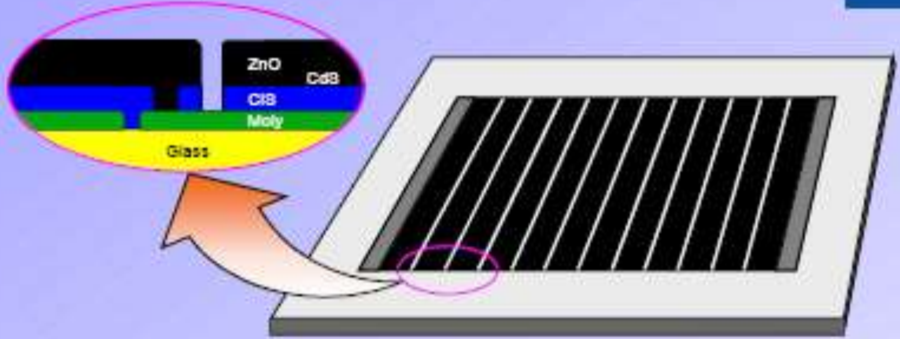
Efficiency: 40%

Thin Film PV Research Focuses

Thin-Film PV Technologies

- Low materials use (~1 μm vs. ~300 μm for Si) – direct bandgap absorbers
- Low-cost substrates (glass, stainless steel, plastics)
- High-throughput deposition processes (batch or continuous)
- Lower processing temperatures (less energy use); some non-vacuum
- Fewer processing steps for modules; integral interconnection of cells during film deposition





- Leading technologies:
  - Amorphous silicon (a-Si:H)
  - Cadmium telluride
  - Copper indium gallium diselenide (CIGS)
- Future technologies:
  - Thin (polycrystalline) silicon
  - Polycrystalline multijunctions

- Choice of materials dictated by efficiency, materials availability, ease of manufacturing, module reliability, market acceptance

Thin Film PV R&D

Thin Film Photovoltaic Laboratory

Thin Film PV Fabrication Facility

Annealing Chamber

Spin Coater

Ultrasonic Bath
Sonicator

Sputtering

Fumehood

Thermal Evaporator

Co-evaporation (MBE)

CBD Water Bath

Deionized (DI)
Water System

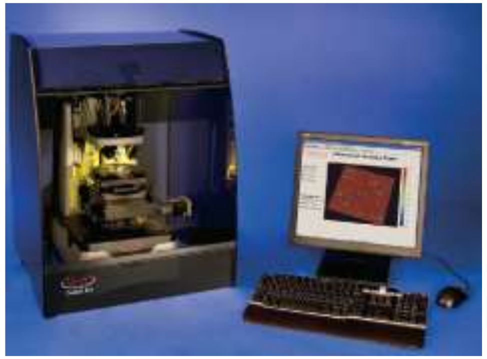
Thin Film PV Characterization

Optical Spectrometer

Hall Measurement System

Integrated LIV
with Class AAA
Solar Simulator

Surface Profilometer



Integrated Semiconductor-PV
Defect Measurement System

Quantum Efficiency
Measurement System

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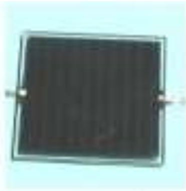

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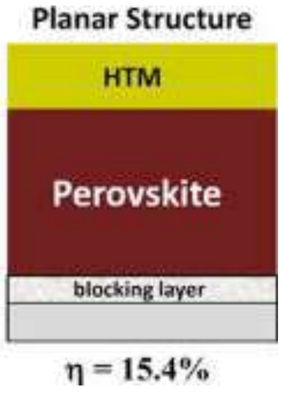
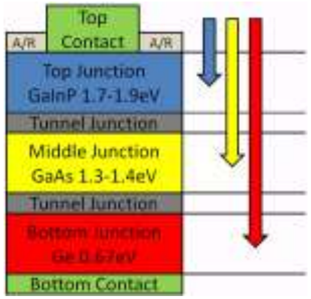
Perovskite cells



Novel Hybrid



Efficiency: 40%

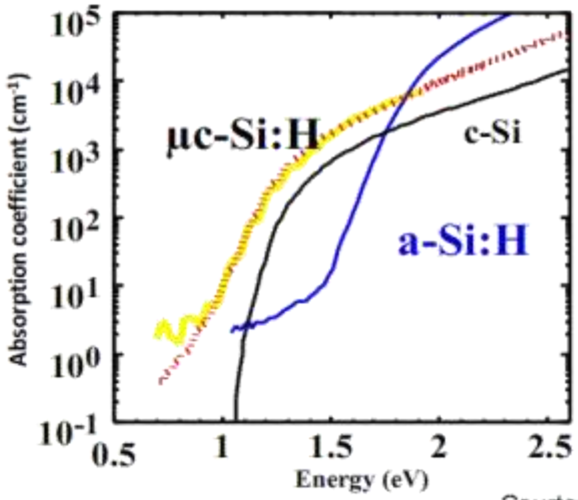
Thin Film PV Research Focus: a-Si

Why Amorphous Silicon as a PV Material?

- Amorphous Silicon has a very high absorption coefficient (> 10^5 cm^{-1}) over the major portion of the visible spectrum, making extremely thin film (100 – 500 nm) devices possible, leading to low material cost
- Low temperature deposition process can be used to uniformly coat extremely large areas (5.7 m^2)
- The deposition technique and by-products of the technique are environmentally benign making it a truly green manufacturing process
- The optical Bandgap of 1.7 eV lies close to the peak (1.5 eV) where high efficiencies are expected
- monolithic integration of individual cells is simple and done by selective laser ablation – allows for module voltage optimization
- Silicon and Hydrogen are abundant!
- The material can be doped p or n type (although not very efficiently) with boron or phosphorous respectively
- The material possesses the necessary electron and hole transport properties for p-i-n type solar cells

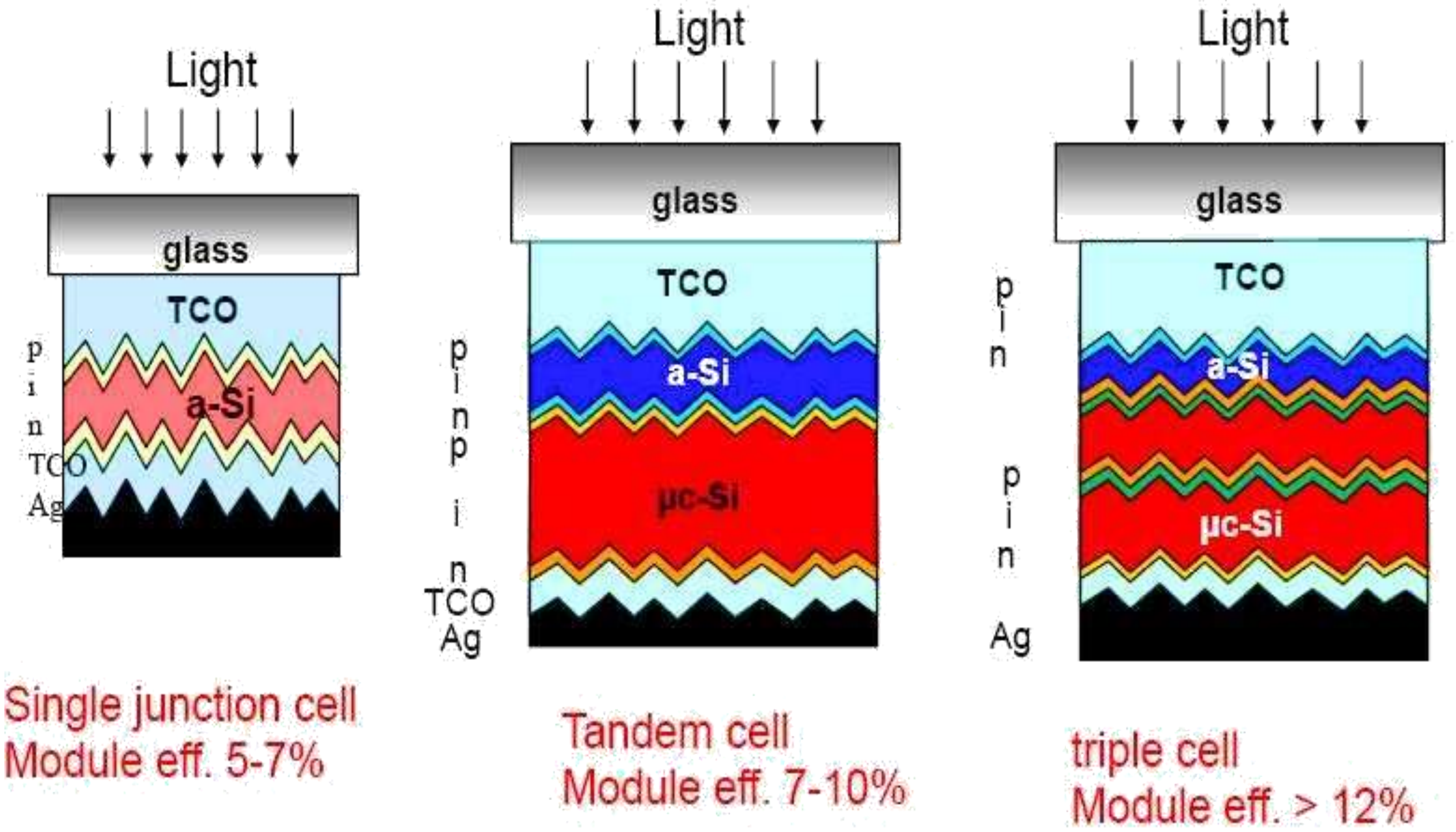
Absorption Coefficient of Si (change with crystalline state)

Different Eg → Different optical properties

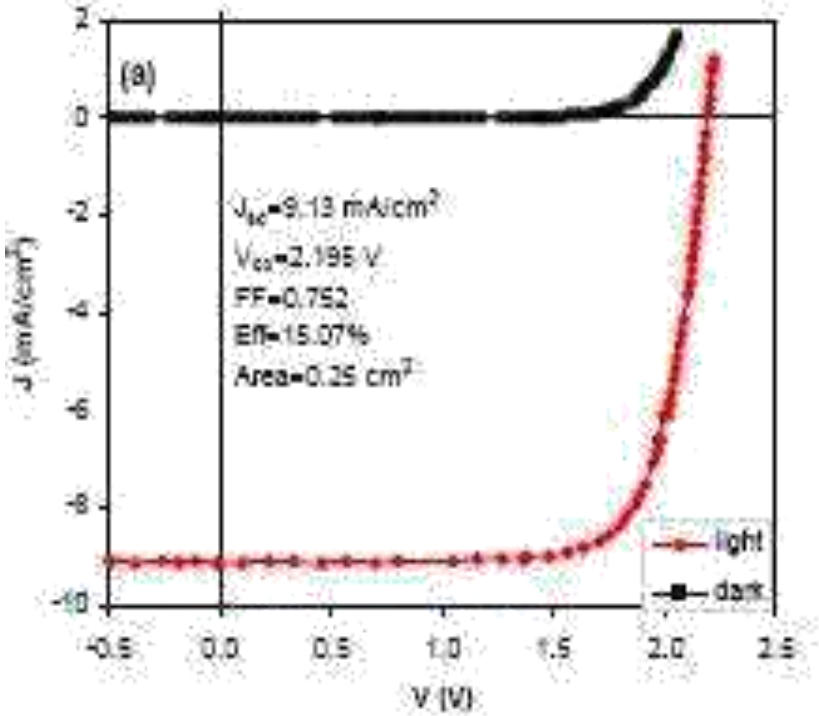


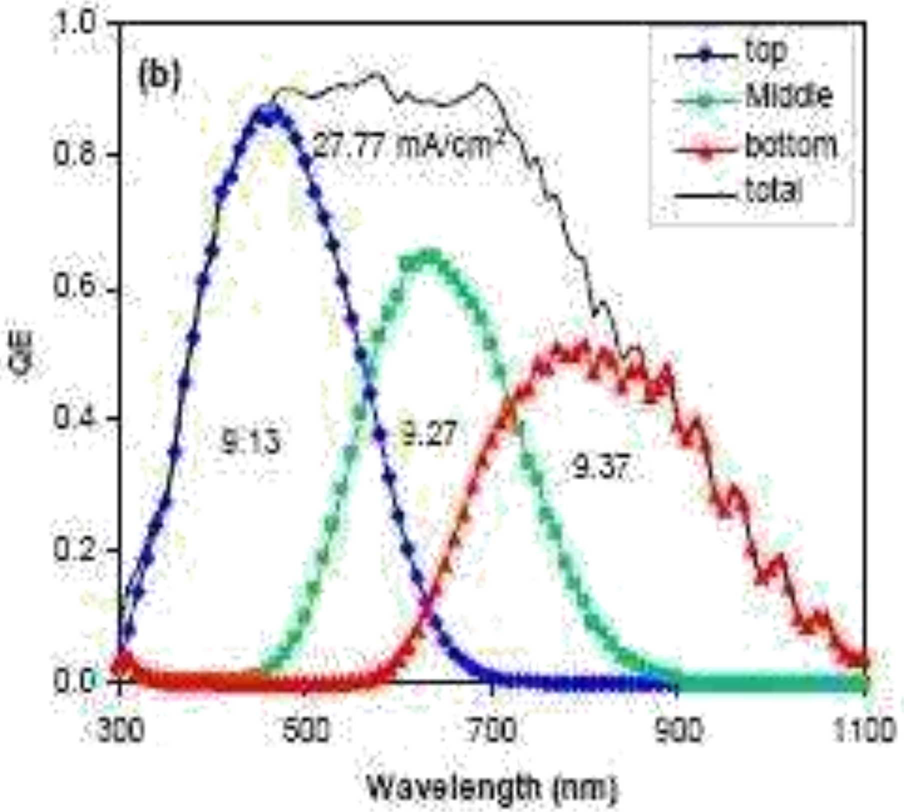
Courtesy : Vikram Dalal

Single, Tandem & Triple Junction Si Solar Cells



Triple Junction a-Si:H/SiGe:H/nc-Si:H Solar Cells





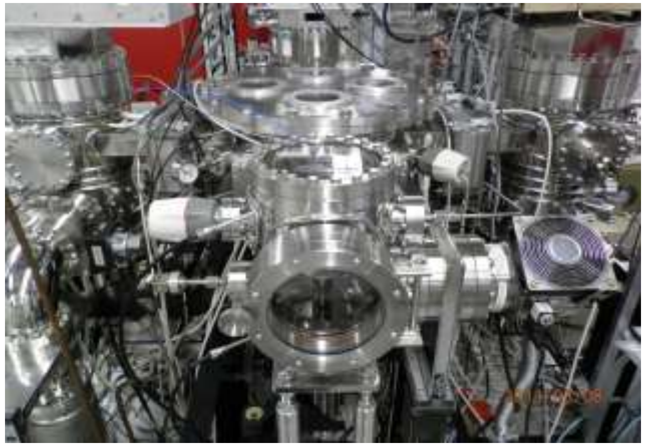
Initial efficiency: 15.1%; Stable efficiency: 13.3%

Green MA, Dunlop ED, Levi DH, Hohl-Ebinger J, Yoshita M, Ho-Baillie AWY. Solar cell efficiency tables (version 54). Prog Photovolt Res Appl. 2019;27:565–575; https://doi.org/10.1002/pip.3171

Fabrication of a-Si:H Solar Cell (1J)

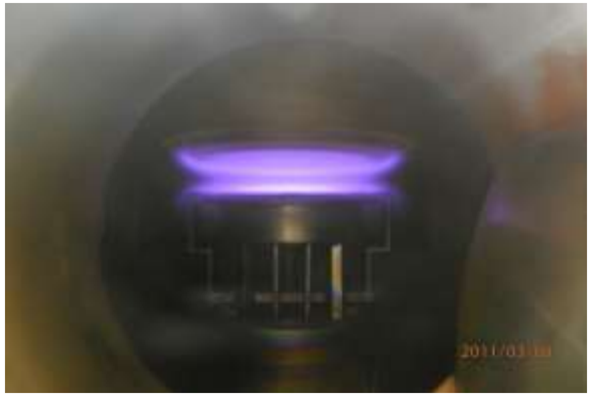
- PECVD is the best technique for a-Si:H Solar Cells

Glass	
SnO_2:F	Asahi Type-U, ~10 Ω/☐
p-a-SiC:H	RF-PECVD, 18 nm, ~2.0 eV
p-graded-buffer	RF-PECVD, 2 nm
i-a-Si:H	VHF-PECVD, 500 nm 1.75 eV
n-a-Si:H	RF-PECVD, 20 nm ~1.7 eV
ZnO:B	MOCVD, 70 nm
Ag	Evaporator, 60 nm
Al	Evaporator, 200 nm


Three chamber in-line PECVD system


Schematic diagram of PECVD with Load-lock and gas flow system


Substrates fixed in substrate holder


Plasma plume in PECVD chamber

IV Characteristics & Quantum Efficiency

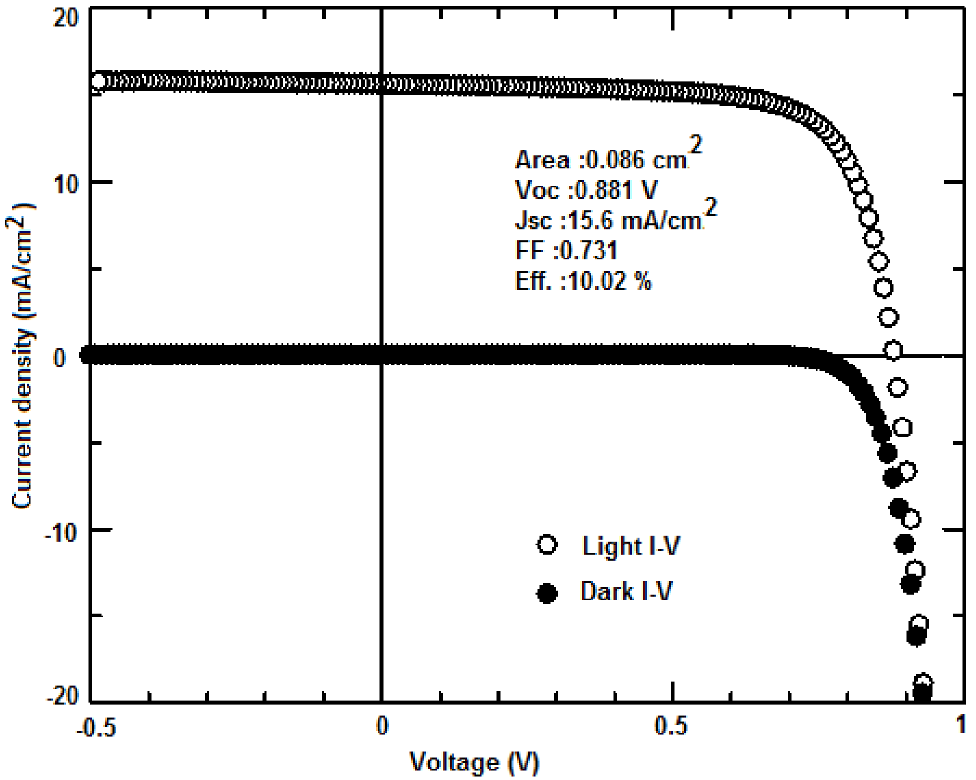
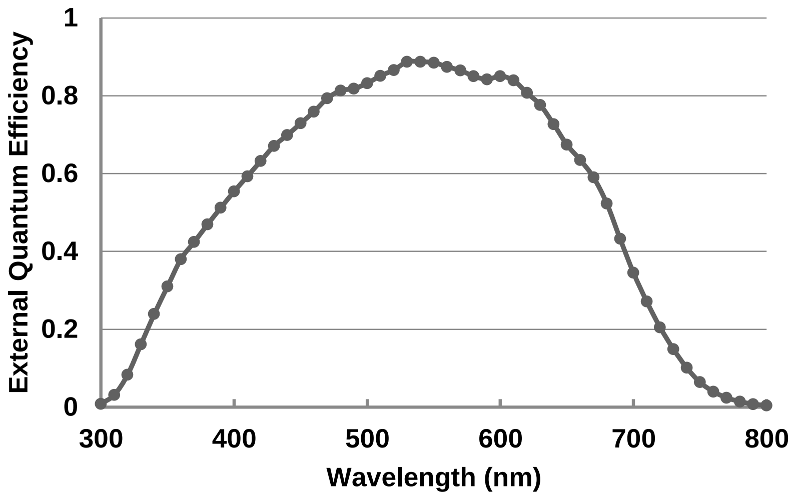
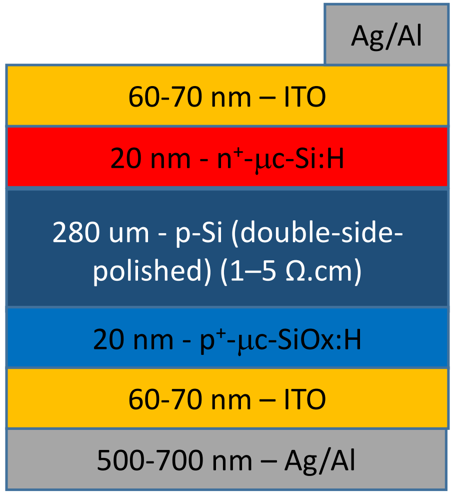


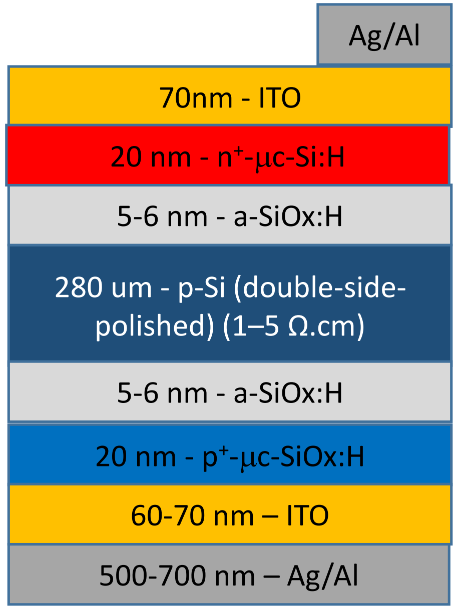
Photo and dark I–*V* characteristics of the *p-i-n* solar cell

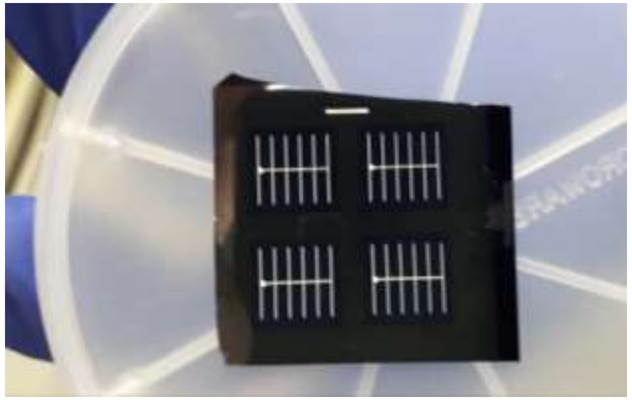


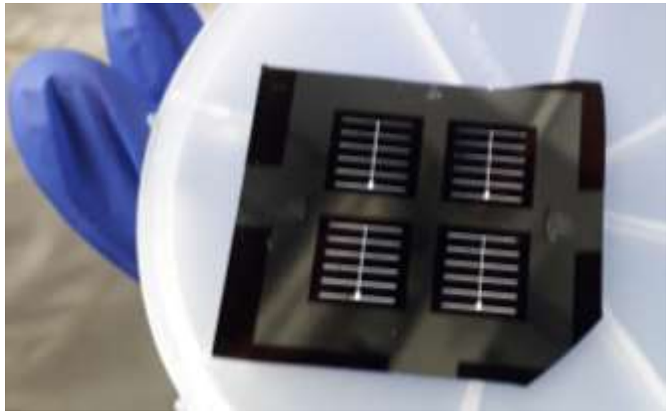
Quantum efficiency curve with wavelength in the range of 300-800 nm

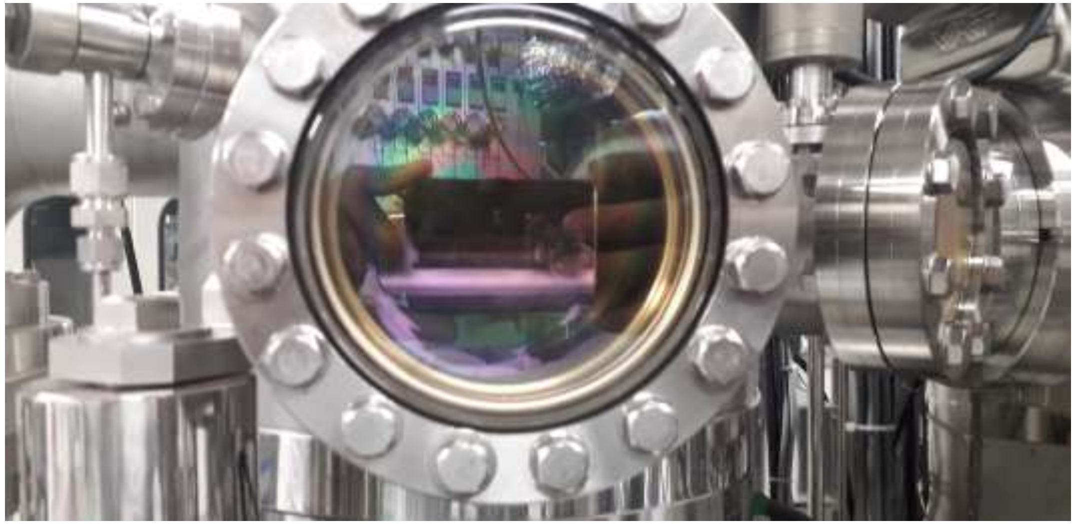
HIT Cells (Passivation Effect)



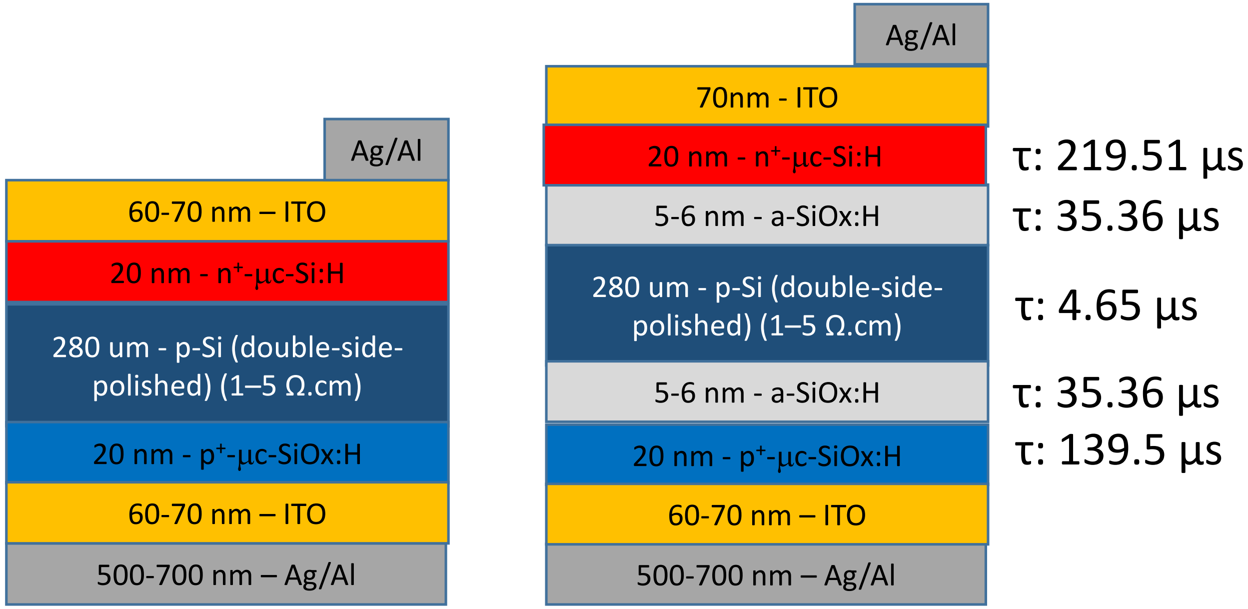




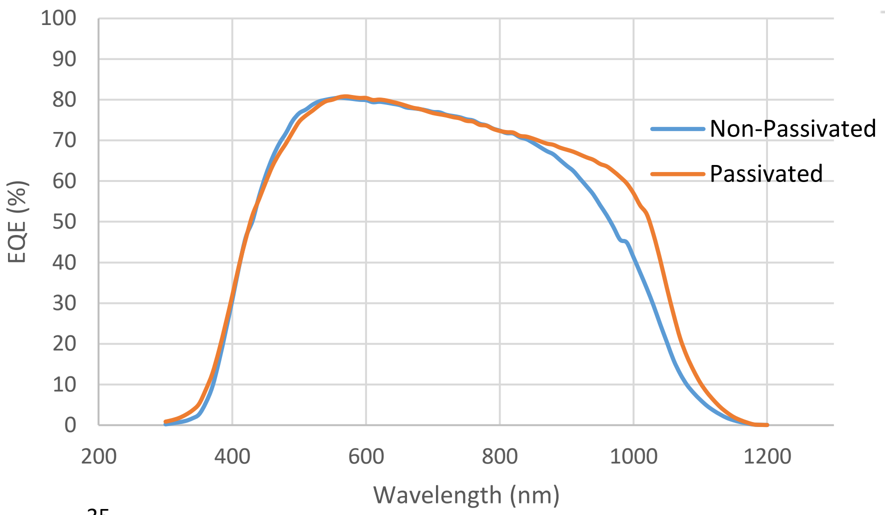


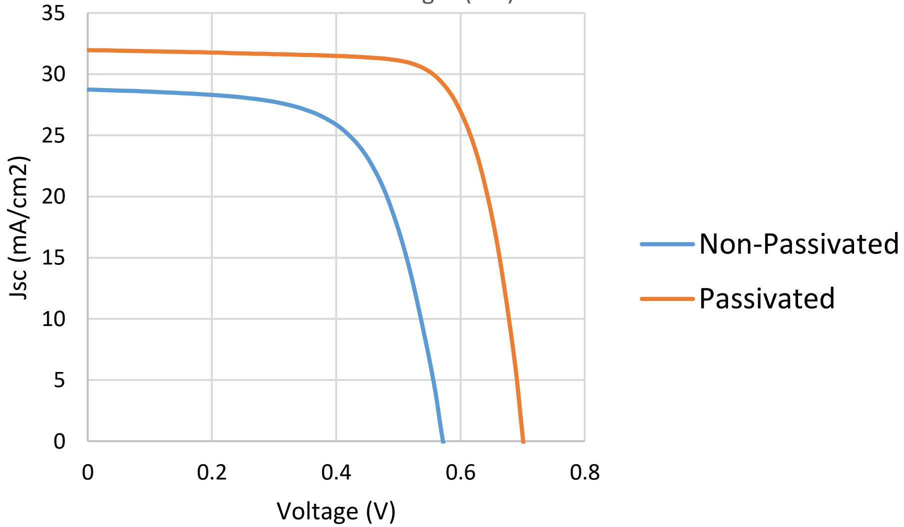


HIT Cells



Minority Carrier Lifetime (τ) was measured by quasi steady-state photo conductance (QSSPC).





Output Performance	Non-Passivated	Passivated
Jsc [mA/cm²]	28.742	31.9662
Voc [V]	0.572	0.701
Fill Factor	0.6418	0.746
Efficiency [%]	10.553	16.716
Series Resistance [ohm]	3.20E+00	1.95E+00
Shunt Resistance [ohm]	6.07E+02	1.26E+03

OUTLINE

- Introduction
- Thin Film & Thin Film Deposition
- Solar Cells
- **Implication of Thin Films into Solar Cells**
  - **aSi**
  - **CdTe**
  - **CIS (CIGSSe, CZTS, CTS)**
- Challenges and prospects
- Conclusion

Solar Cell Technologies

Solar PV Applications Controllers, Systems

First Generation: Crystalline silicon solar cell (200-500 micron)

Second Generation: Thin film solar cell (1-10 micron)

Third Generation: DSSC, Organic, Perovskite, Multijunction, Futuristic

Crystalline Silicon cells

Mono-crystalline cells

Efficiency : 18%~25.6%

Multi-crystalline cells

Efficiency : 17%~20.8%

Thin film PV

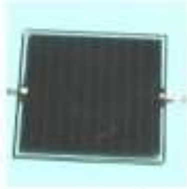
CdTe cells

Efficiency : 18.3%~22.1%

Amorphous silicon cells

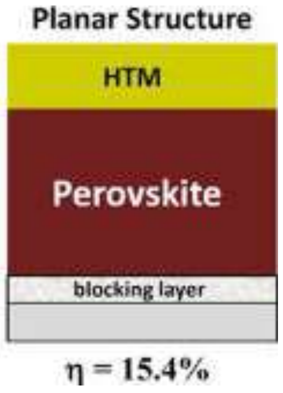
Efficiency : 13.4%

CIGS cells

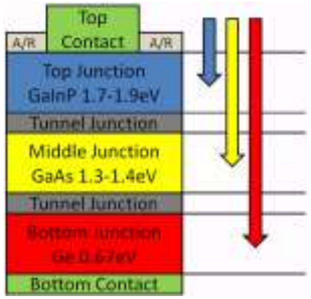


Efficiency : 20.4%~22.6%

Perovskite cells



Novel Hybrid

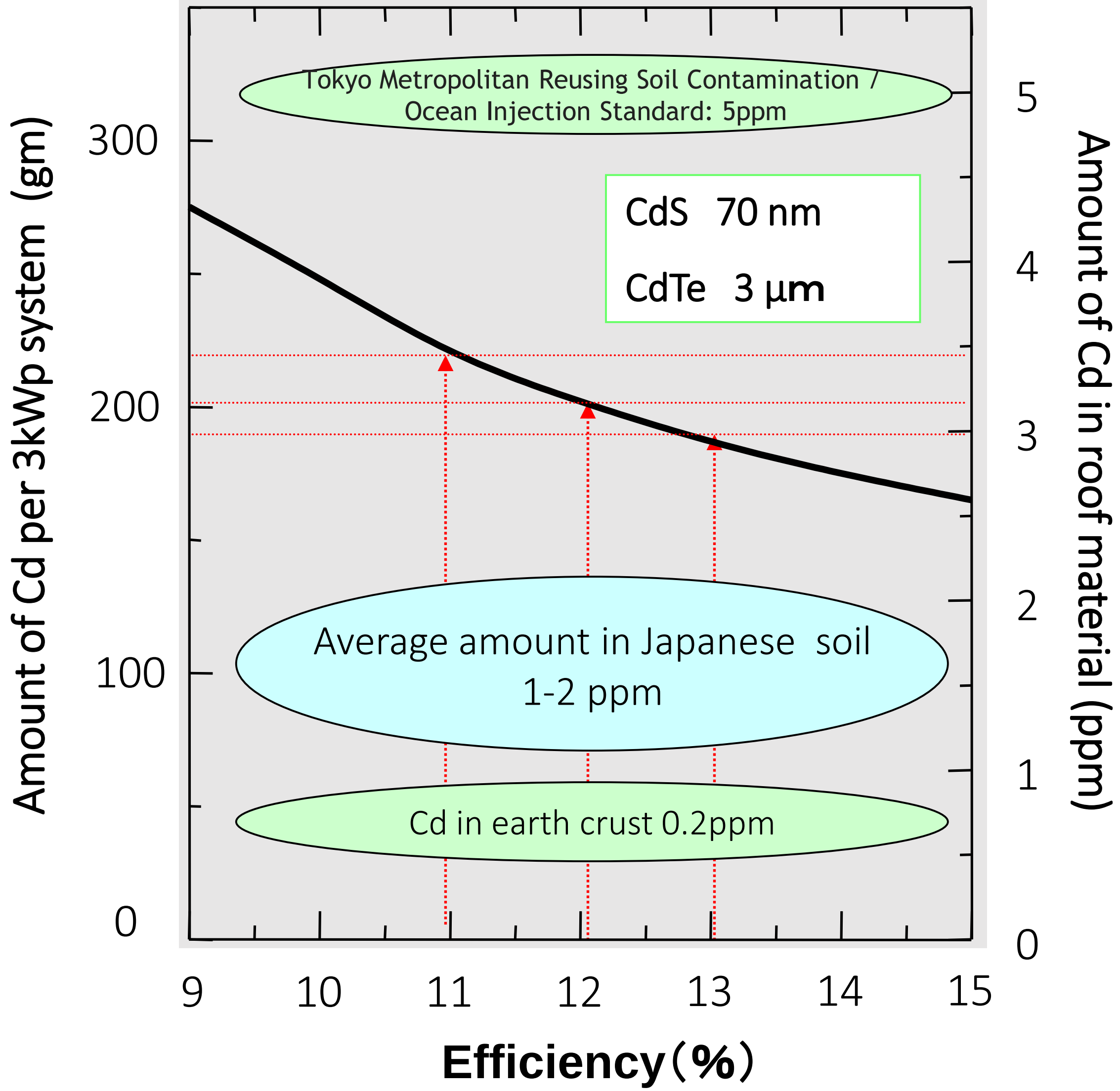


Efficiency: 40%

Thin Film PV Research Focus: CdTe

Advantages of CdTe Thin Film Solar Cells

- Bandgap 1.45 eV is almost optimum for PV
- The energy gap is 'direct'- strong light absorption
  - CdTe has a high absorption coefficient >5×10^5/cm
- Simple and variety of low cost deposition techniques
- Polycrystalline materials and glass, cheaper…
- PV modules seal the cadmium, encapsulate and can be recycled
  - Thus safe, Cd is only 3.27 g/m^2 of PV



The total house weight is 60 tons as a value assuming a lightweight steel frame structure, two stories, and a floor area of 85 sq.m.

Historical Chronology of CdTe Solar Cells

First CdTe-based Heterojunction Solar Cells was Reported on

"thin film" CdTe heterojuntions, n-CdTe/p-CuTe as early as 1963 by …

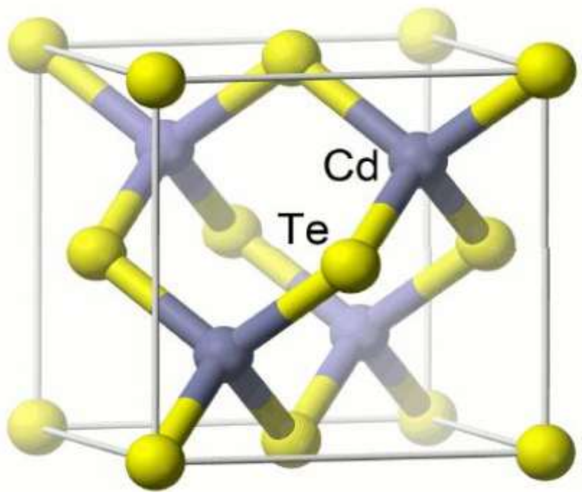
D. A Cusano, *"CdTe Solar Cells and Photovoltaic Heterojunctions in II-VI Compounds"*, Solid State Electronics, Vol, 6(3), (1963), 217-218.

CdTe Based Solar Cells

CdTe Single Junction Solar Cells	**1960, Vodakov et al, Single crystalline CdTe wafer, Eff. 4%**
$Cu_{2-x}Te$/CdTe Solar Cells	**1963, Cusano et al, n-CdS/CdTe/p-Cu_{2-x}Te, Eff. 6%**
CdS/single crystal CdTe Solar Cells	**1969, Adirovich et al, SnO_2/CdS/CdTe, Eff. 1%** **1977, Yamaguchi et al, p-CdTe/n-CdTe/n-CdS, Eff. 11.7%** **1982, Barbe et al, n-CdTe/p-CdTe, Eff. 10.7%**

Historical Background of CdTe (Deposition Process)

Thin Film CdS/CdTe Solar Cells



Screen Printing
1984, Matsumoto et al, CdS/CdTe/C:Cu/Ag, Eff. 12.8%

Electro-deposition
1991, Woodcock et al, CdS/CdTe, Eff. 14.2%

Close-Spaced Sublimation (CSS)*
1982, Tyan et al, ITO/CdS/CdTe, Eff. 10.5%
1992, Chu et al, SnO_2/CdS/CdTe/C:Cu, Eff. 15.8%
1997, Aramoto et al, ITO/CdS/CdTe/C:Cu/Ag, Eff. 16%

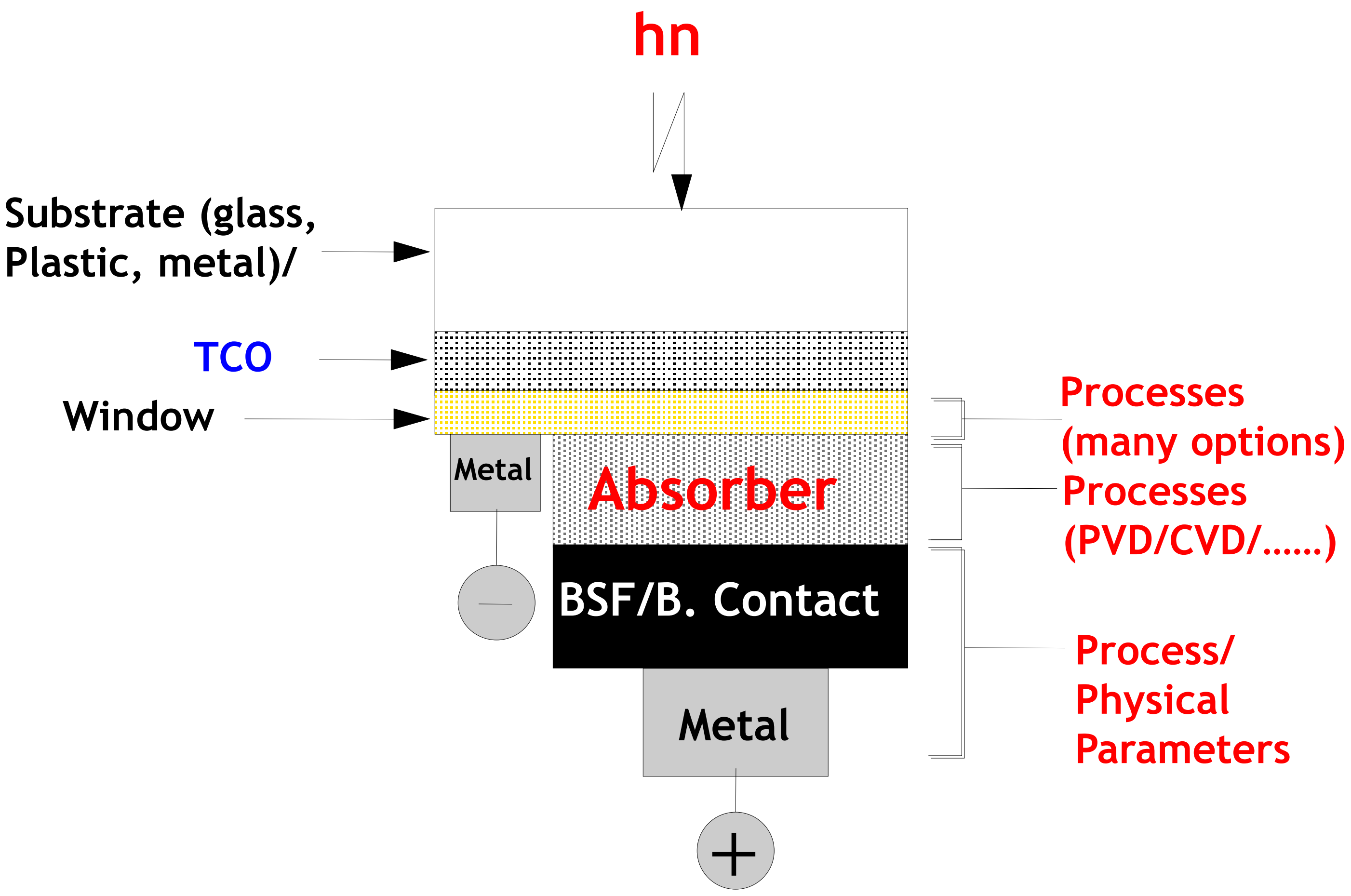
Magnetron Sputtering + CBD + CSS
2004, Wu et al, Cd2SnO4/Zn2SnO4/CdS/CdTe/Cu, Eff. 16.5%

CSS Process
2005, Gupta et al, CdS/CdTe, Eff. 11.8%

Undisclosed Process
2014, First Solar, USA, Eff. 21%

Undisclosed Process
2016, First Solar, USA, Eff. 22.1%

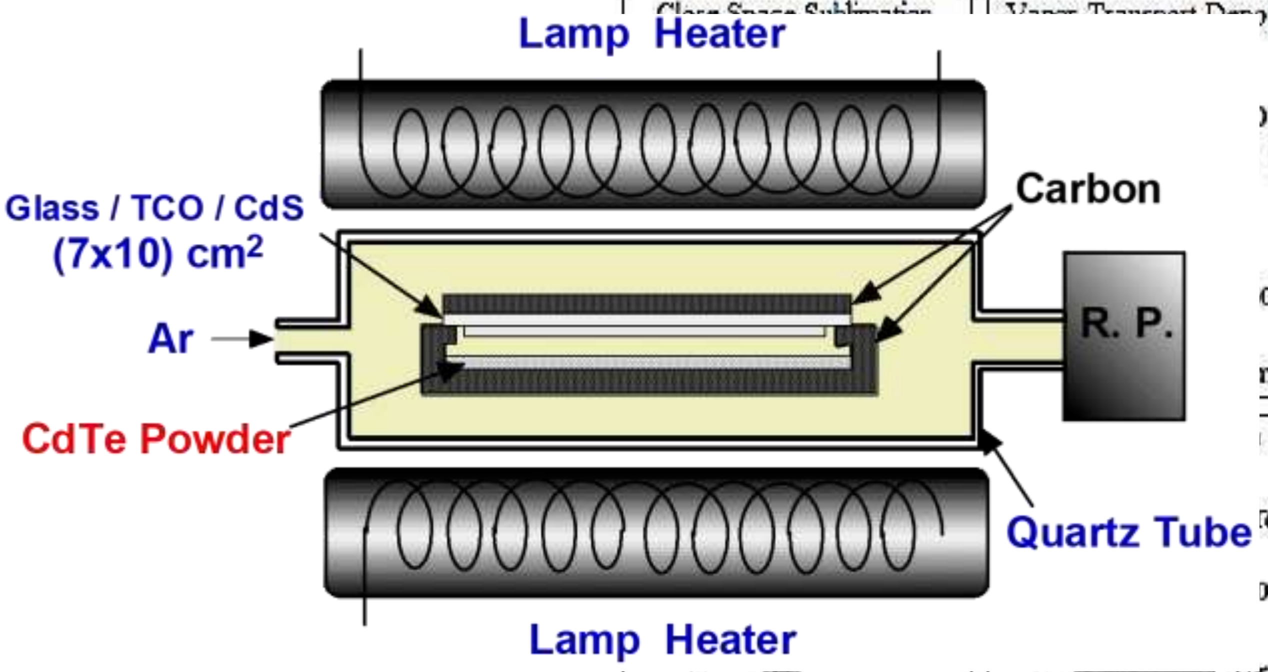
Developing Low Cost & High Eff. Solar Cells

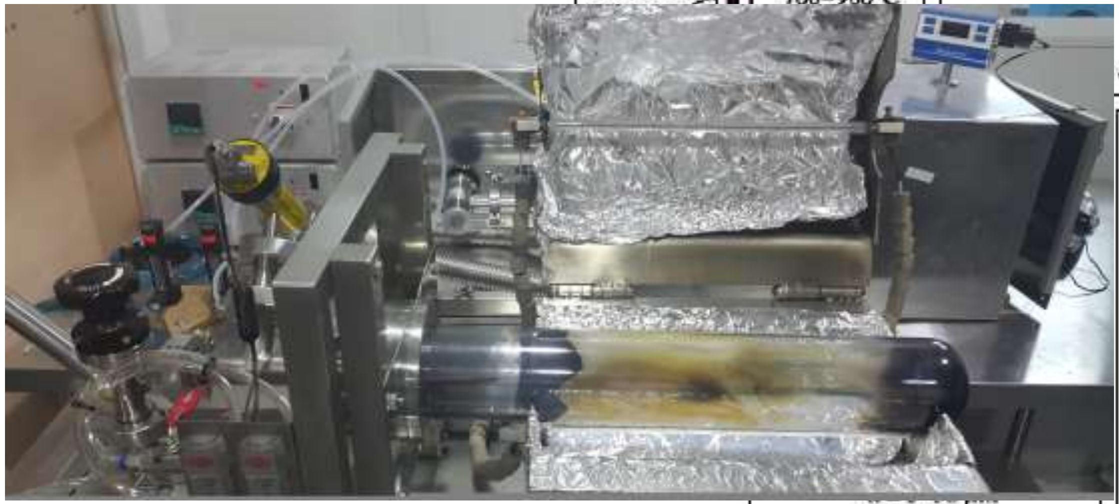


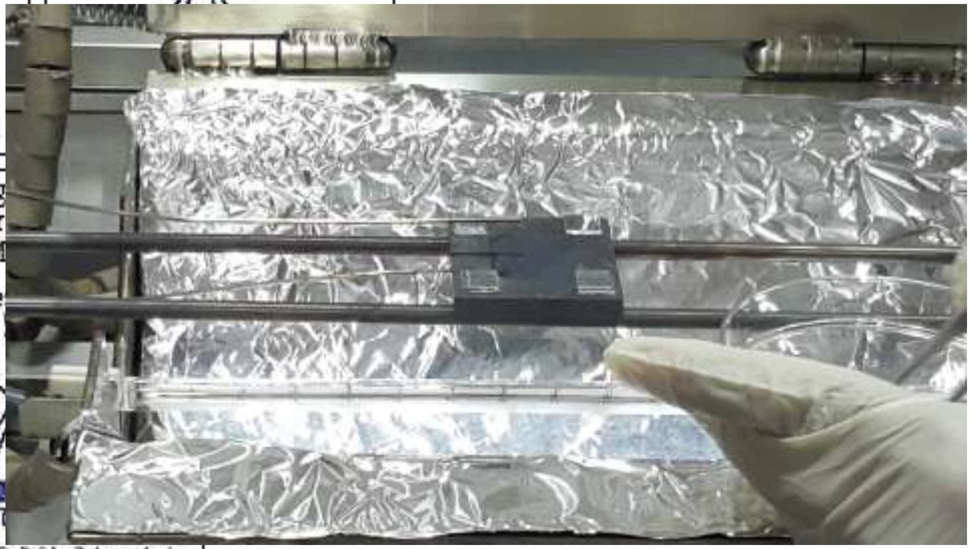
- *Glass:* Borosilicate, soda lime. Inexpensive, good optical properties, compatible with deposition process (T).
- *TCO/Buffers:* SnO_2, ITO, Cd_2SnO_4, ZnO, ZTO, In_2O_3 etc. Good electro-optical properties; compatible with subsequent processing steps; "buffers" important for thin CdS
- *CdS:* E_G=2.42 eV (510 nm); ~ 7 mA/cm^2 below 510 nm. Must be thin (600Å) and pinhole free. CdS:O used for record efficiencies
- *CdTe:* versatility in deposition technology; thickness 3-8 μm; thickness why not ~ 2 μm ? Can it be doped controllably?
- *Heat Treatment:* "activation" process; improves bulk and interface properties; carried out in the presence of $CdCl_2$.
- *Back Contact:* Various options most of which utilize Copper; doped graphite paste, ZnTe:Cu, etc. Stability? Cu-free Sb_2Te_3

Source: McCandless et al. 2004

Deposition Options and CSS

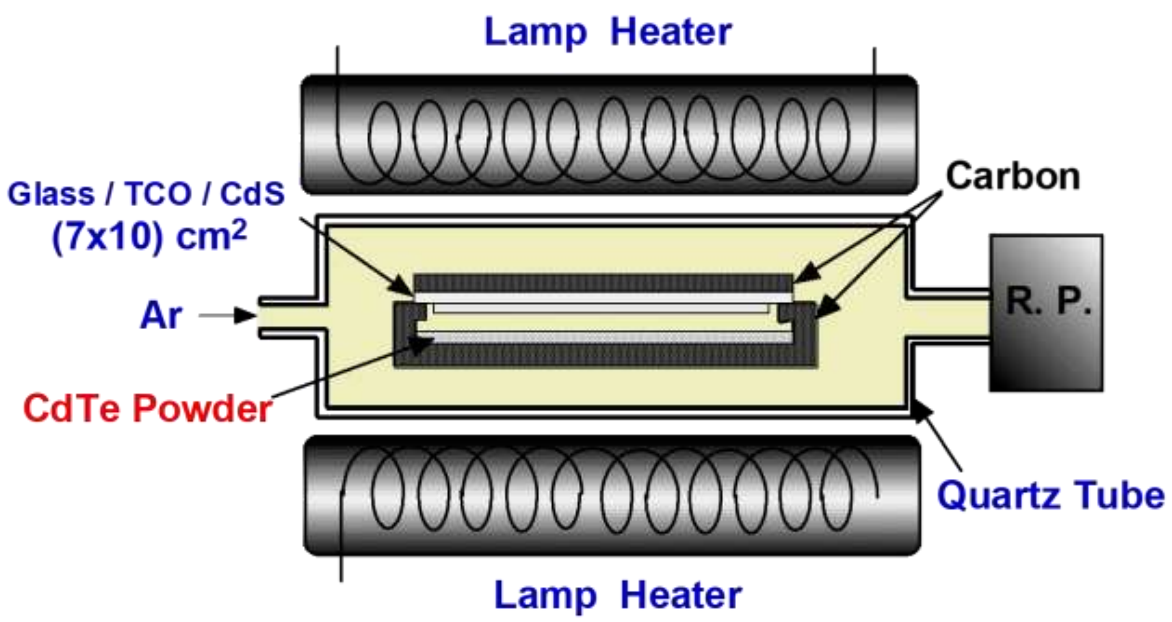


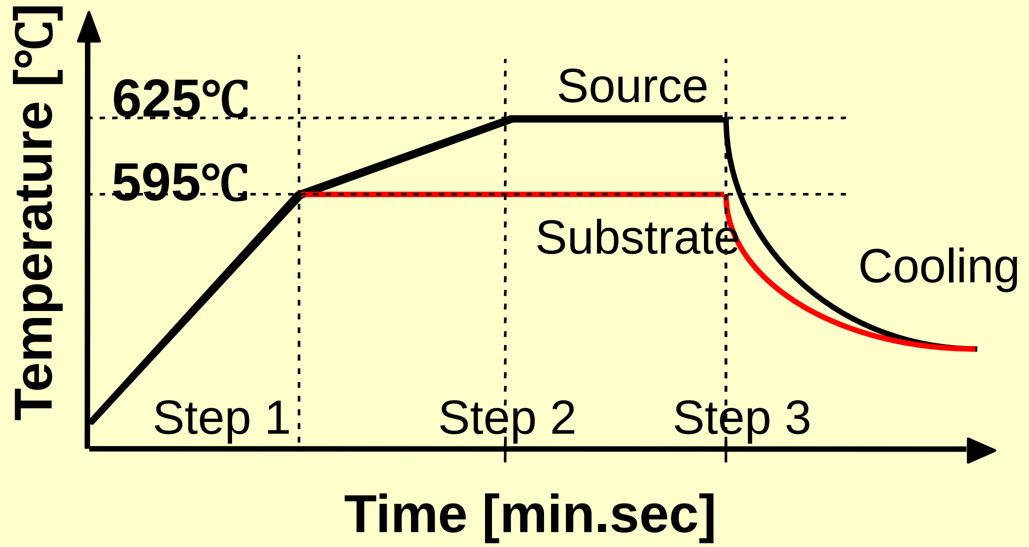




Source: McCandless et al. 2004

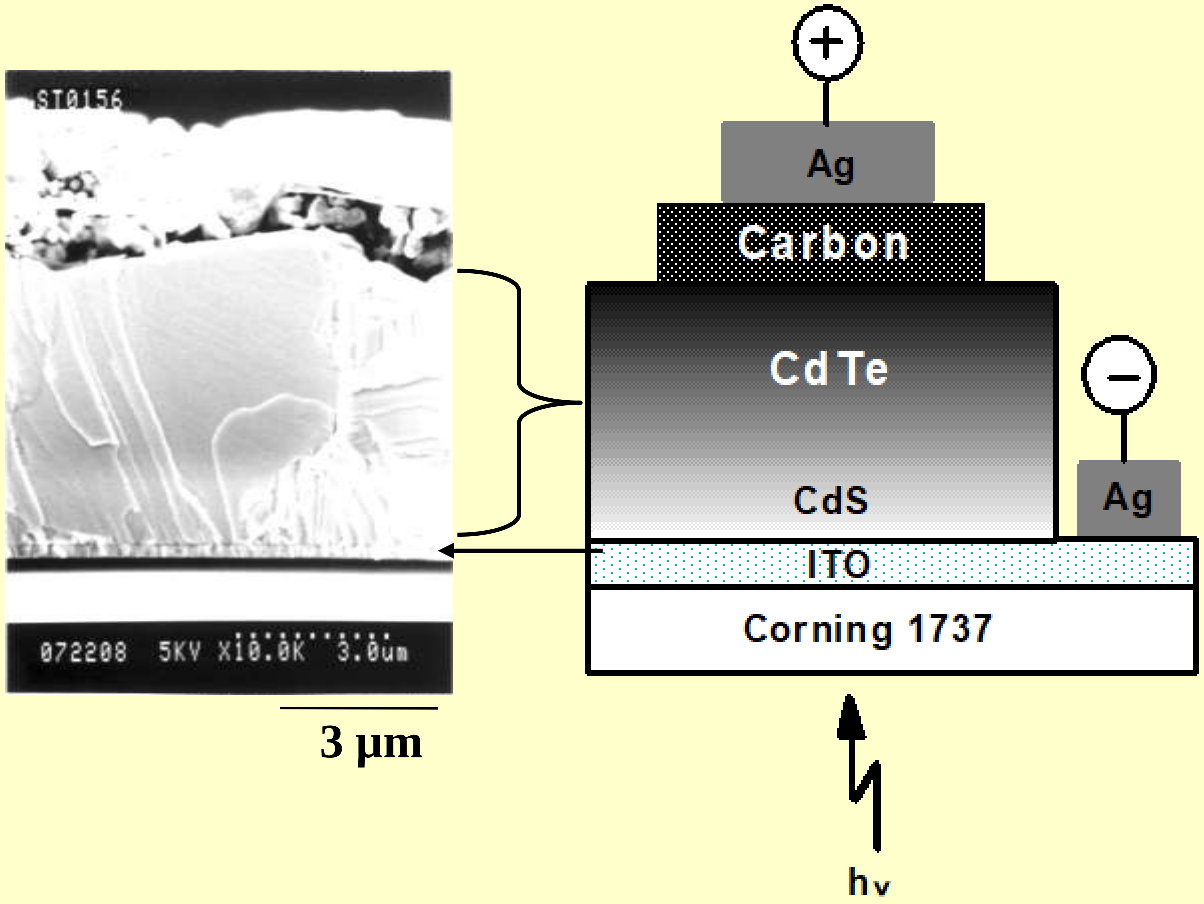
Temperature Profile of the CSS Growth Technique





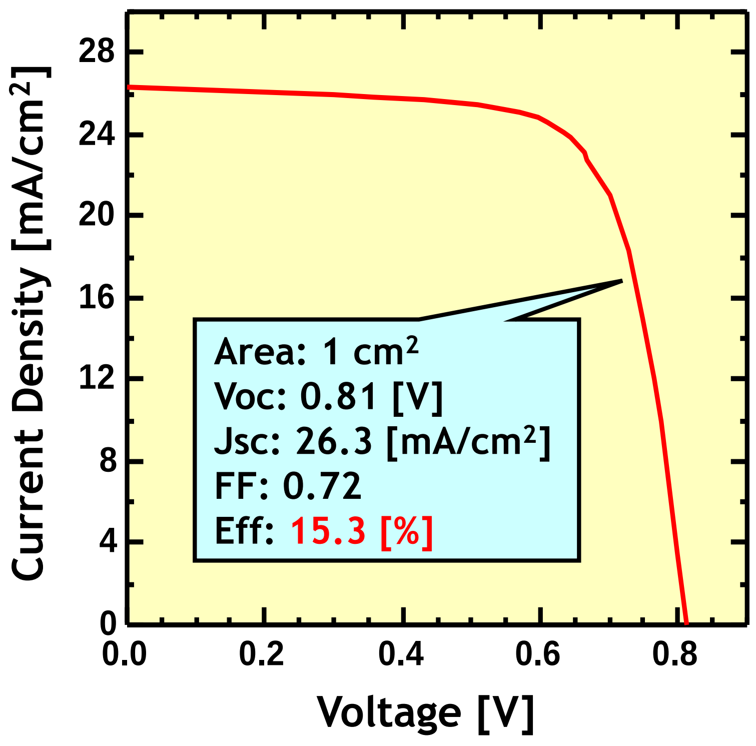
Example: 3min 26sec 1min 1min

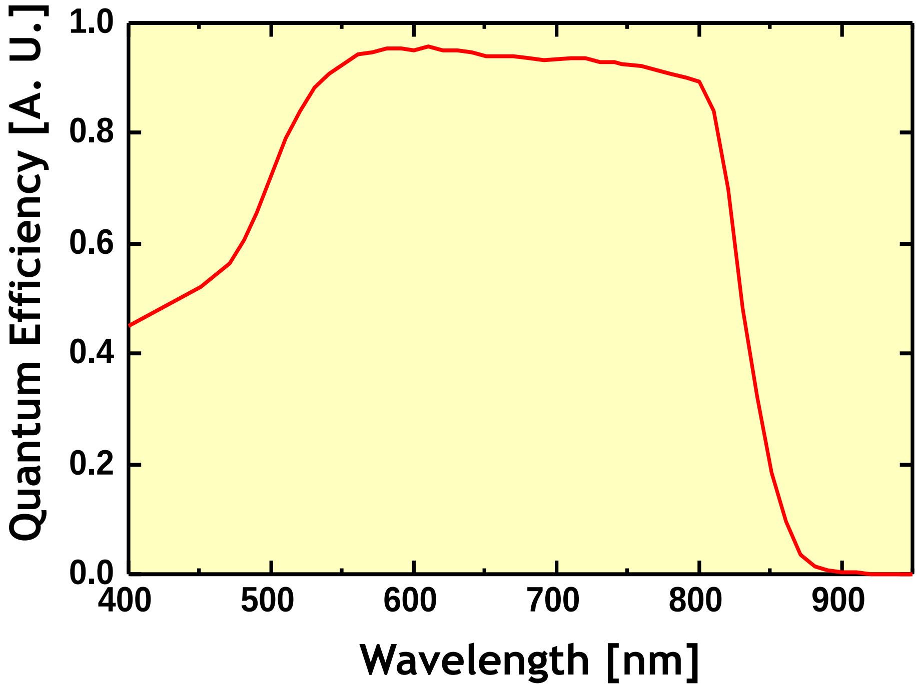
SEM Image of the CdS/CdTe Solar Cell Cross Section



I-V Characteristics & Spectral Response of CdTe Thin Film Solar Cells

CdTe Thickness: 7 μm

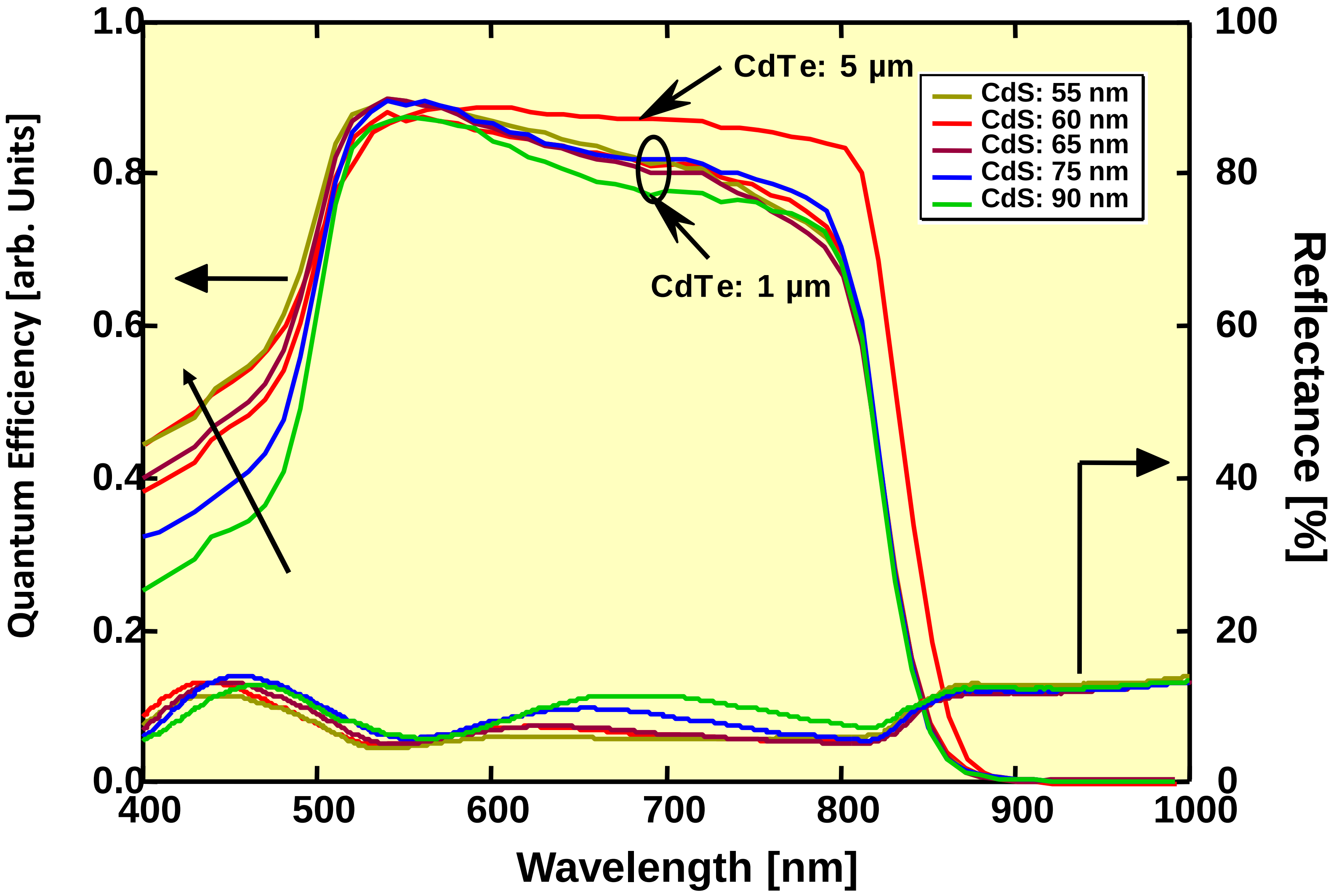




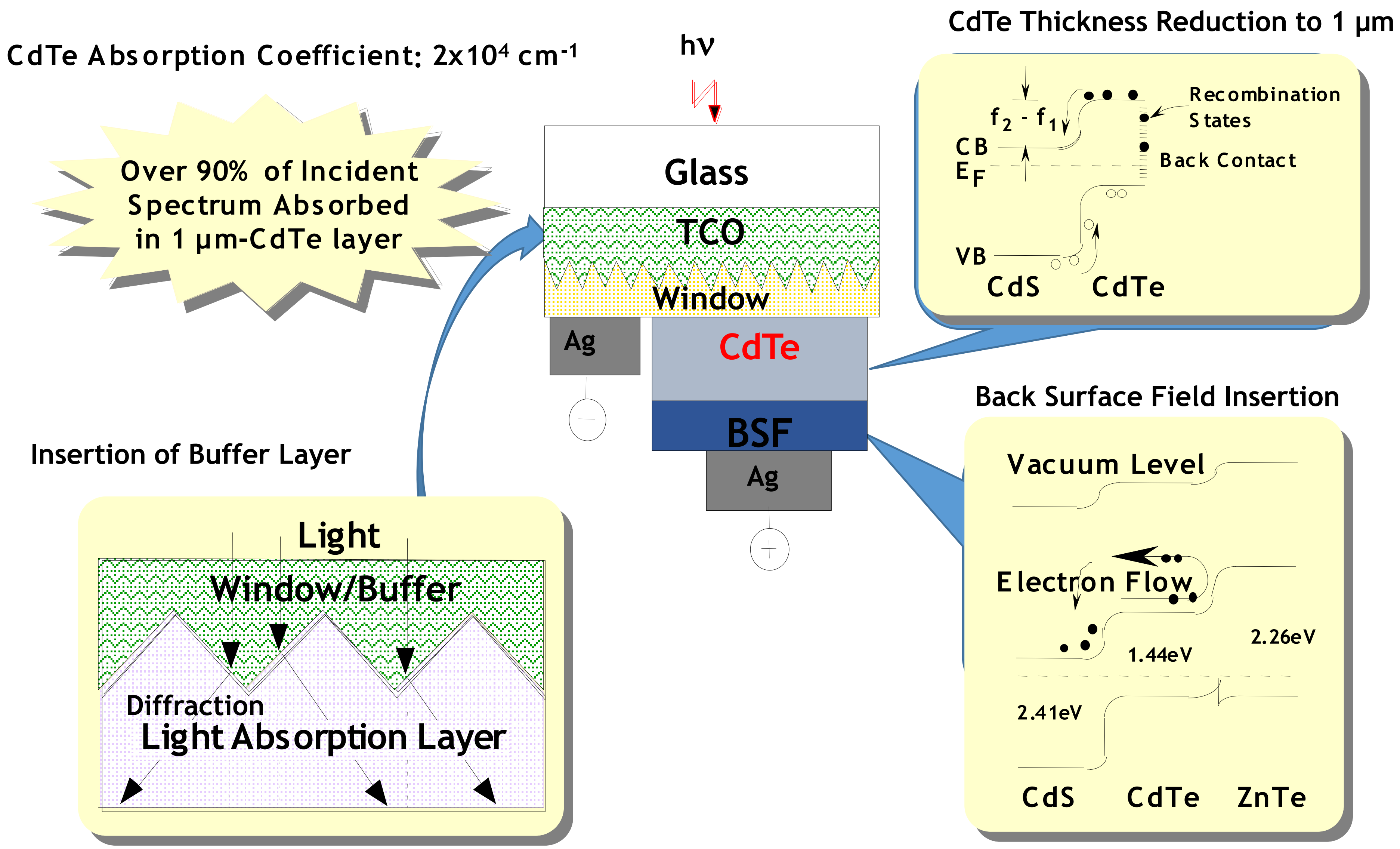
I-V Characteristics

Spectral Response

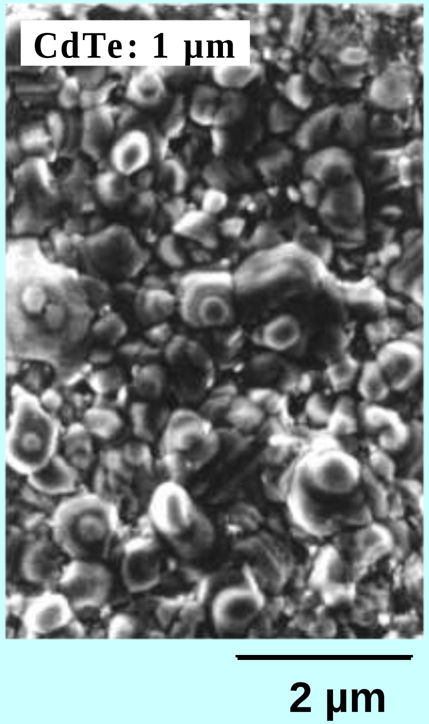
Spectral Response of the CdTe Solar Cell (The Effect of CdS Window Layer Thickness)

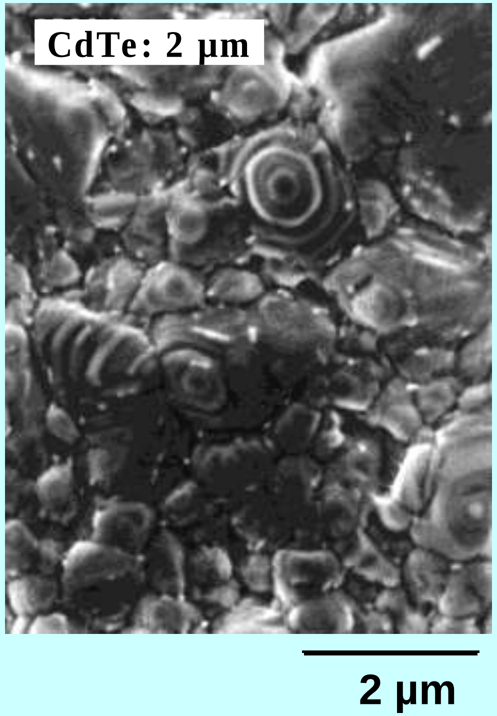


Research Prospects in CdTe Thin Film PV

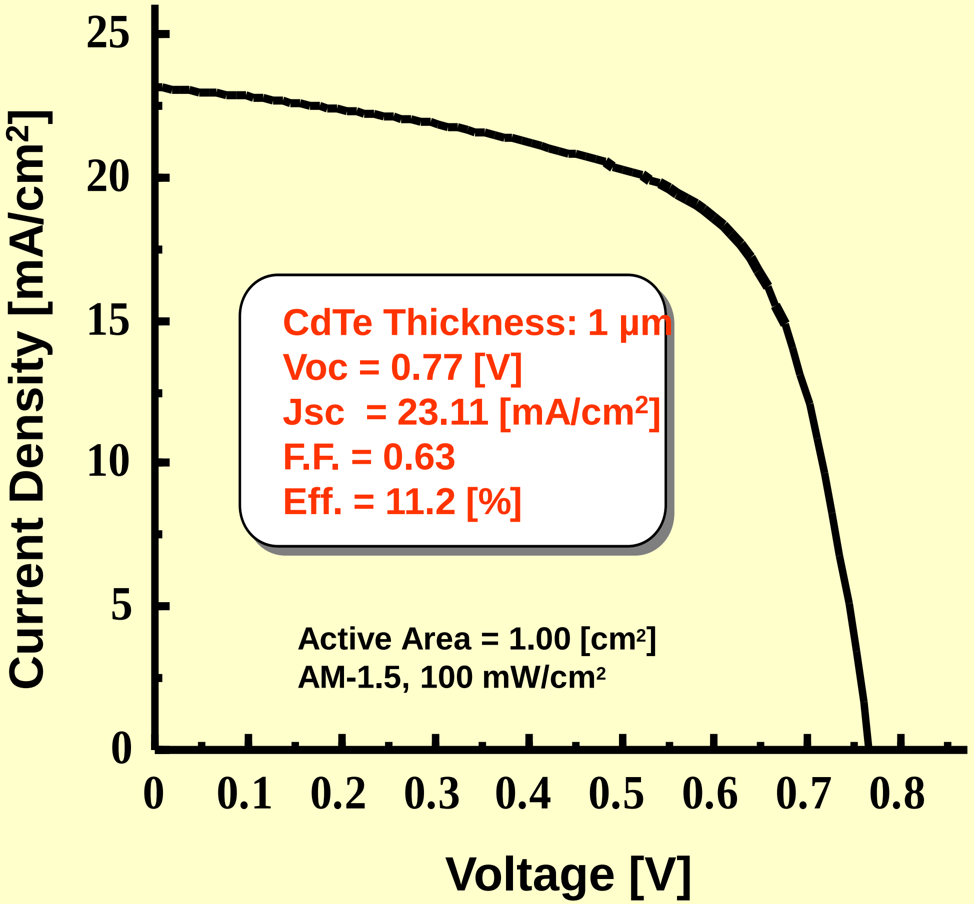


SEM Images of the CdTe Surface with Different Thickness (Grown by CSS)

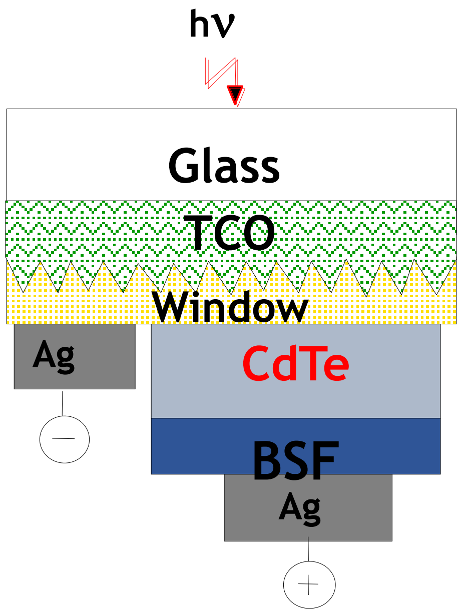


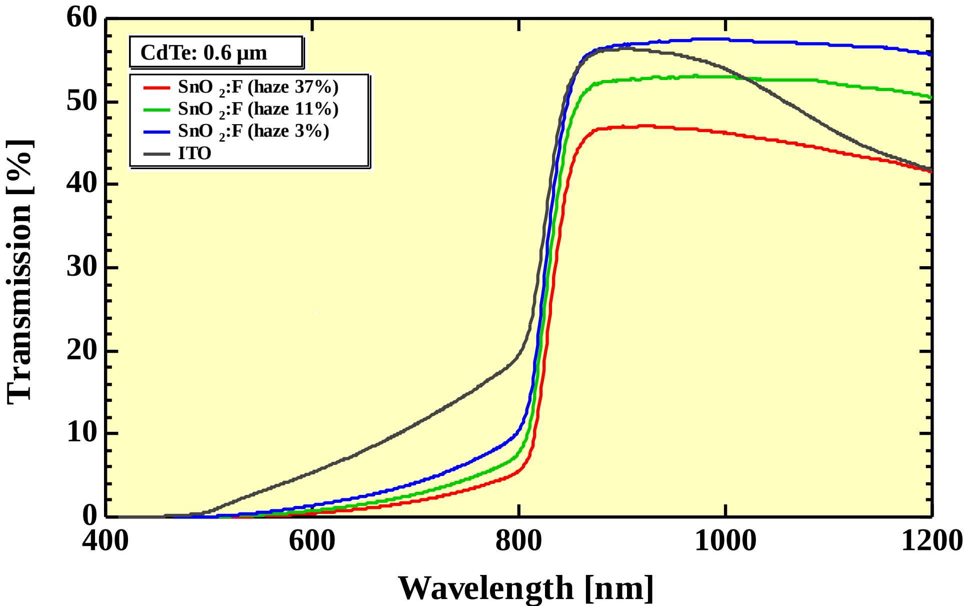


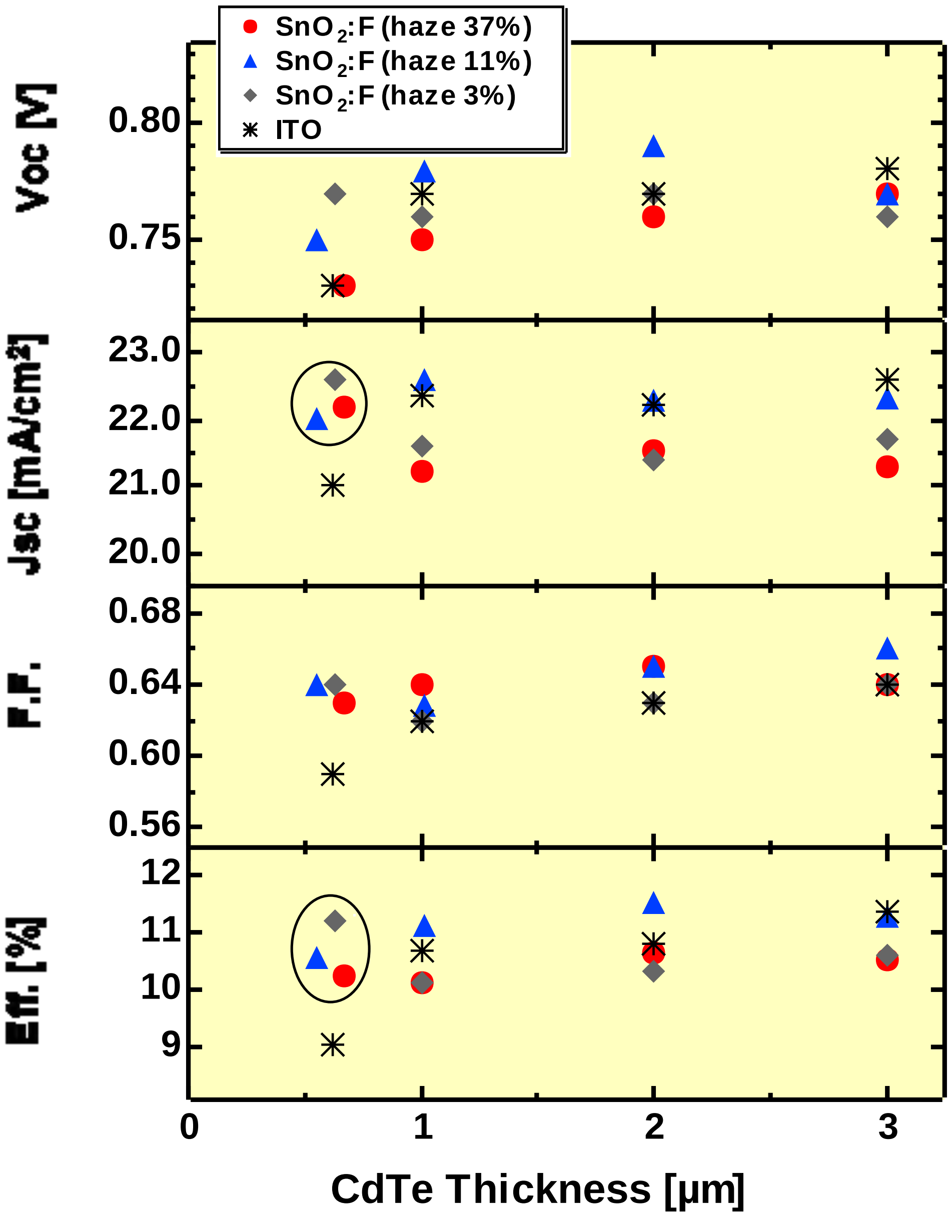
I-V Characteristics of 1 um-CdTe Thin Film Solar Cell



Textured Tin Oxide (SnO_2:F) for Ultra-Thin CdTe





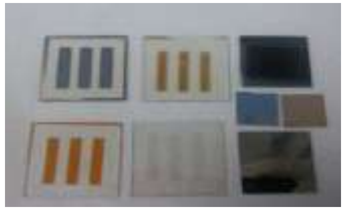


Universiti Kebangsaan Malaysia
The National University of Malaysia

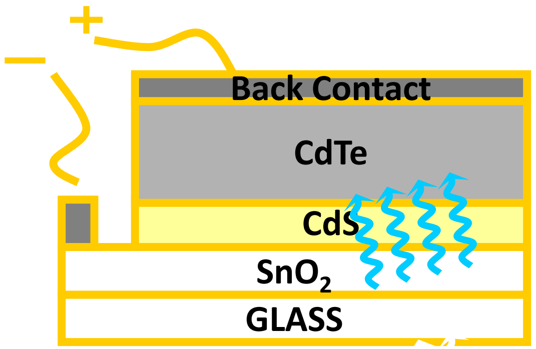
Continuous Fabrication Process

Universiti Tenaga Nasional
The National Energy University

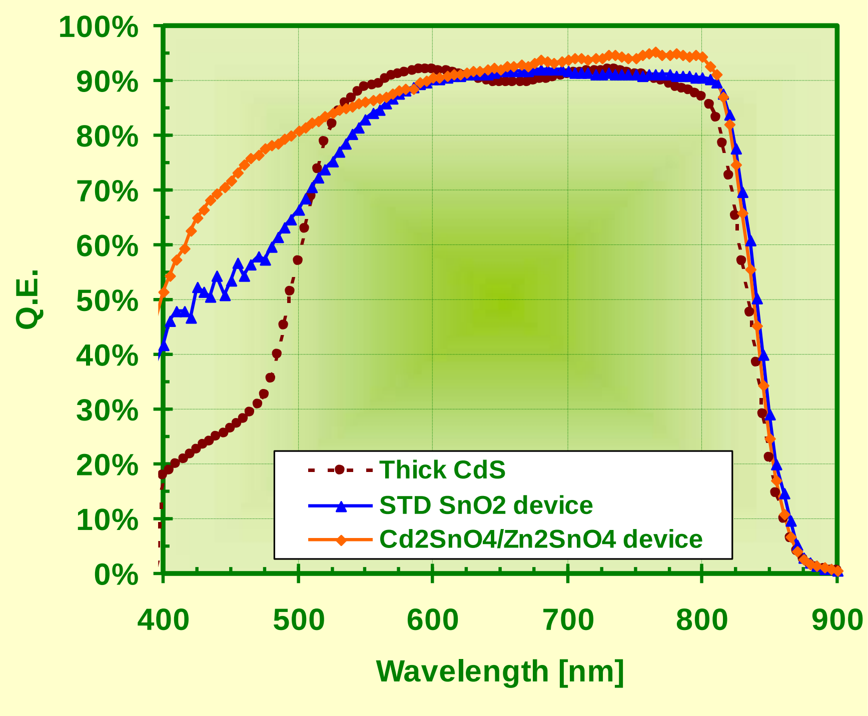
- ➢**Substrate Preparation**
- ➢**Magnetron Sputtering Chamber Preparation**
- ➢**Target Installation**
- ➢**Operation of Sputtering Growth**
- ➢**ZnO, CdS and CdTe deposition by RF Sputtering**
- ➢**Back contact Deposition by DC Sputtering**



Improving Performance: J_{SC}

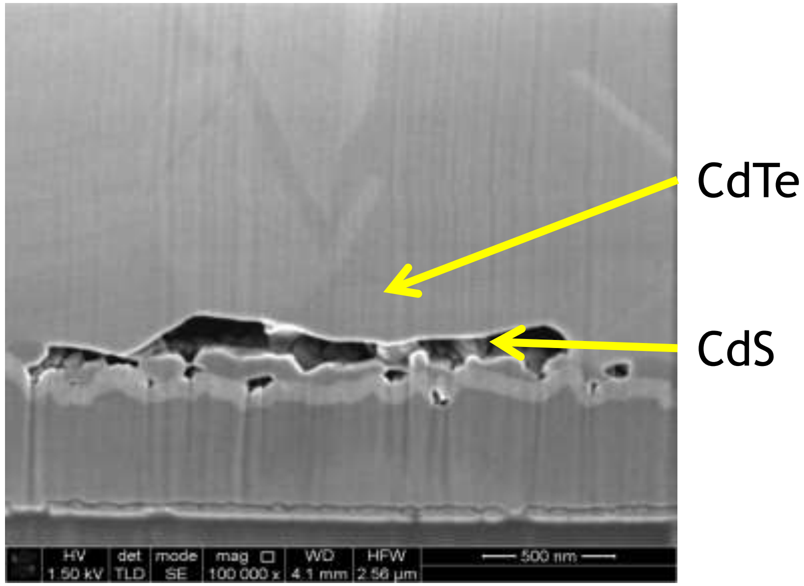


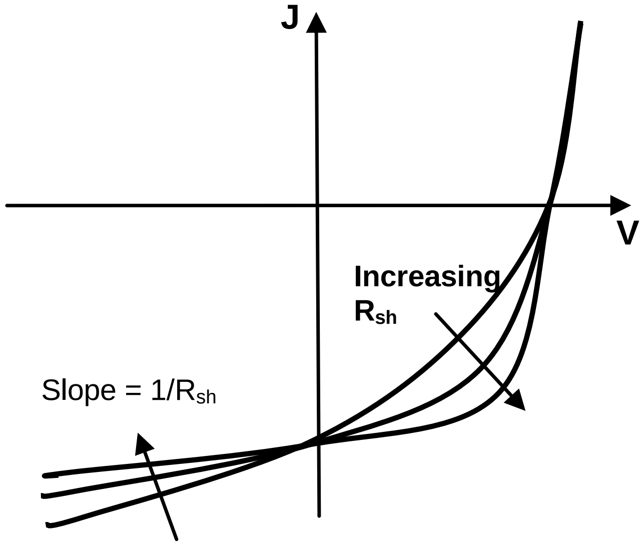
- Most promising avenue to higher J_{SC}'s is via "thinner" CdS
- Approximately 7 mA below 510 nm (max. 30 mA/cm^2)



- Choice of Window material for CdTe solar cell is limited by several considerations:
  1. The heterojunction should be designed so that most of the absorption occurs within the CdTe bulk.
  2. It must act as a highly transparent, and low-resistance window layer and not be responsible for carrier generation.
  3. It should have wide band gap
  4. It should have a small lattice mismatch with CdTe to avoid excessive interface recombination.
  5. It should have long-term stability,
  6. Finally, window material should be composed of elements that are slow to diffuse into CdTe.

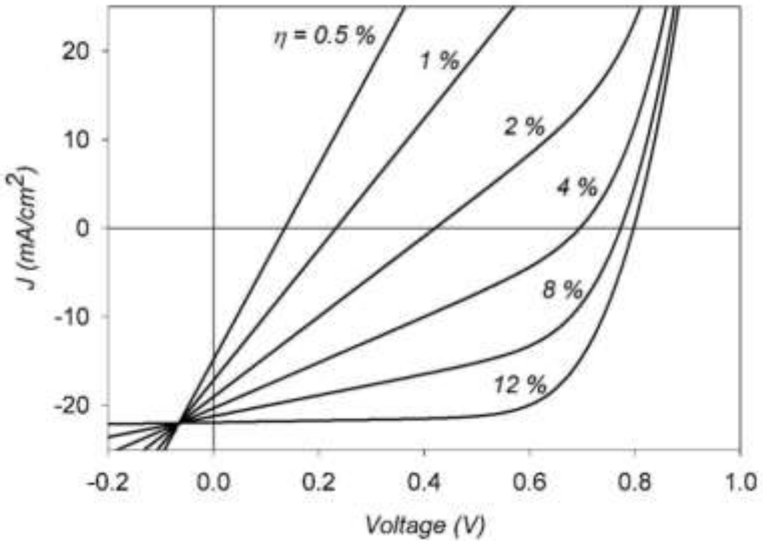
Defects in Interface Layers





Too thin CdS will lead to voids and shunt related losses - J_{sc} may increase but FF will decrease.

In severe cases where voids lead to TCO/CdTe interface regions, V_{OC} is also decreased



Effect of Substrate Temperature

Effect of source and substrate temperature

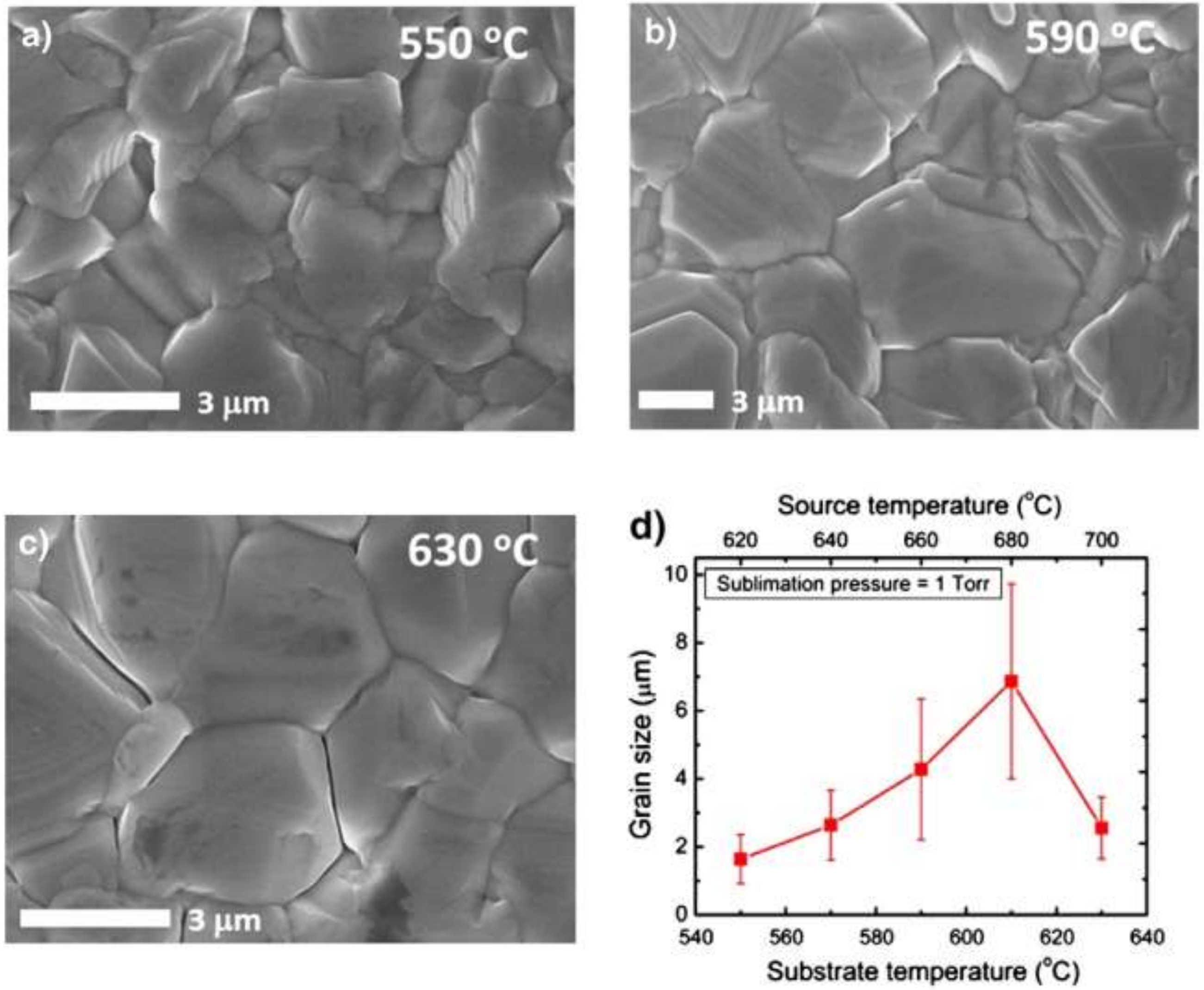
i) Vary the source and substrate temperatures with constant temperature difference.
ii) Vary the substrate temperature, keeping the source temperature constant.

Tsubstrate: 550 ~ 620° C,
Tsource : 560 ~ 700° C,
Ar Pressure: 1.8 ~ 2 Torr,

ΔT= 150, 100, 70, 75, 55, 25

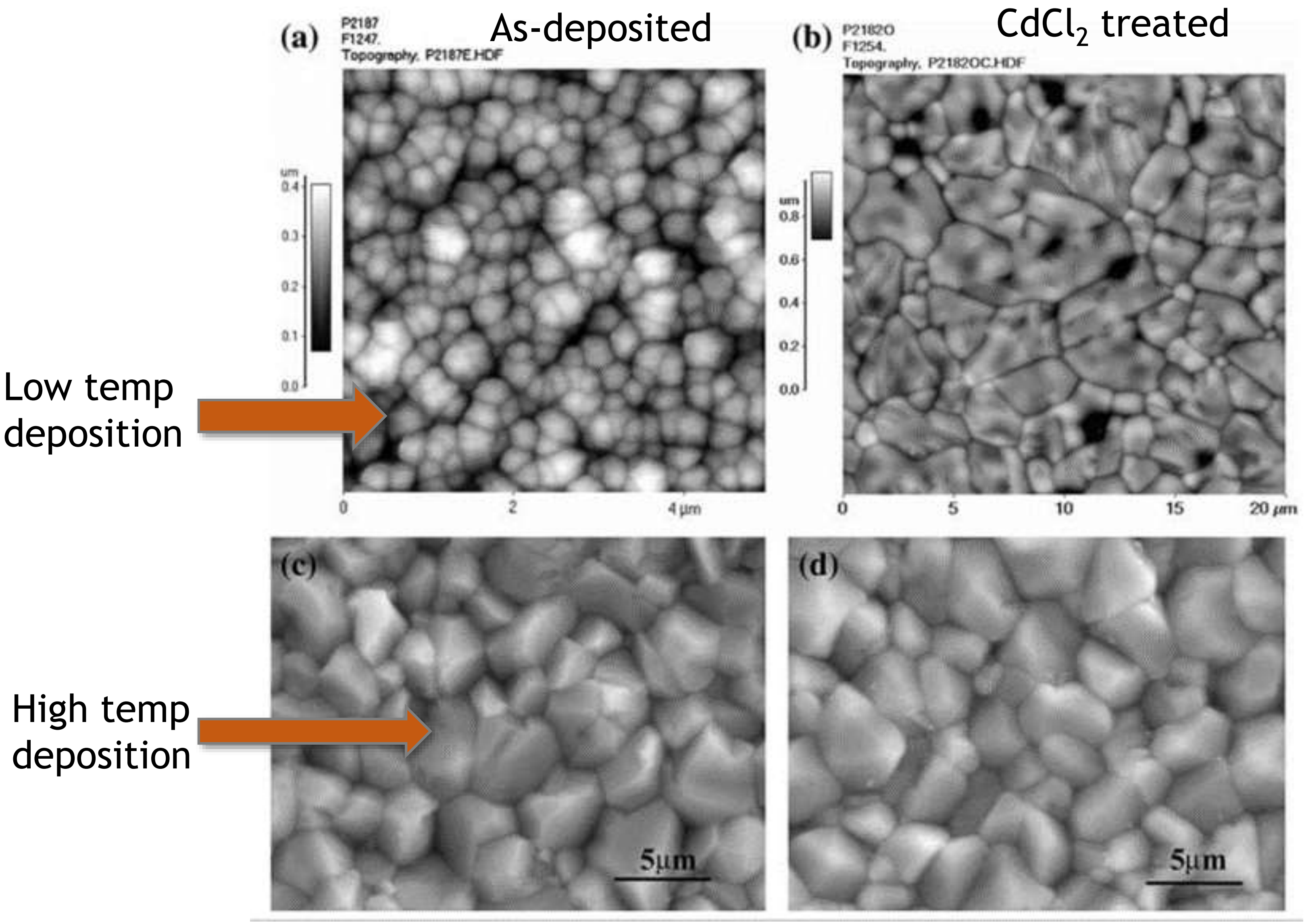
Spacing: 1~2 mm,

Deposition rate: 500nm/min

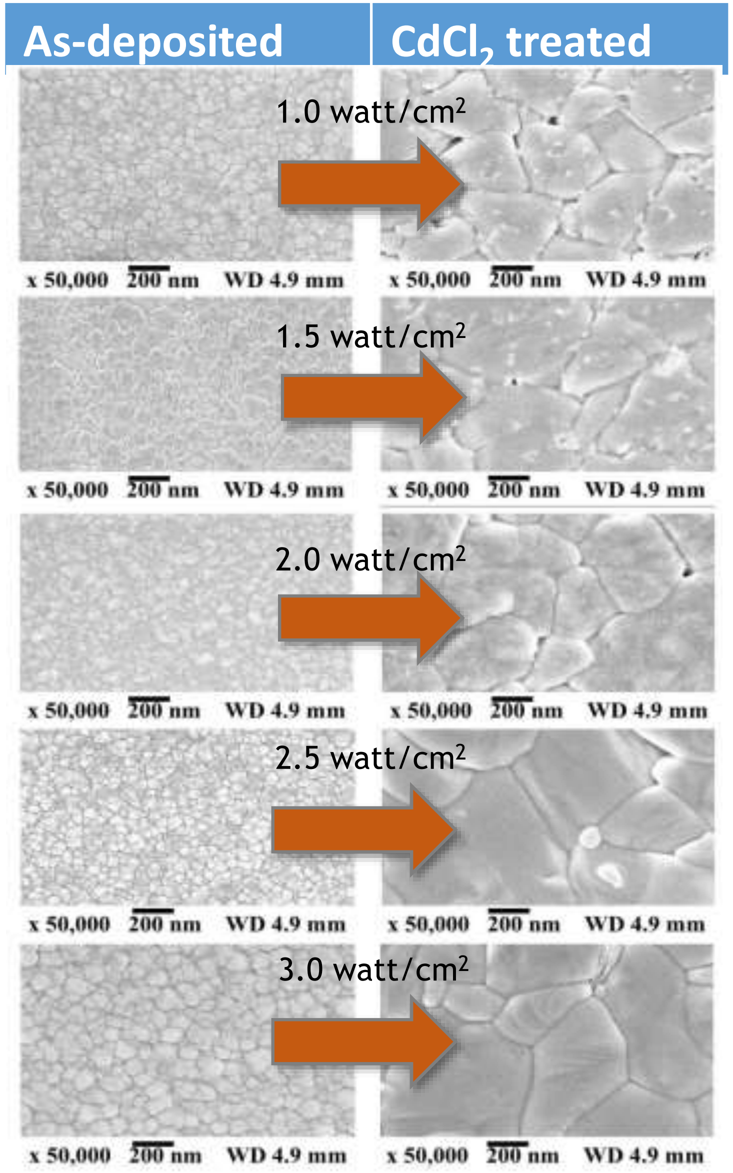


[14] Fabrication and characterization of high-efficiency CdTe-based thin-film solar cells on commercial SnO2:F-coated soda-lime glass substrates Naba R. Paudel ⁎, Yanfa Yan
[15] Growth and characterization of CdTe by close spaced sublimation on metal substratesA. Seth!, G.B. Lush!, J.C. McClure!,*, V.P. Singh", D. Flood#

Grain growth



CdTe Layer Deposition at Different RF power

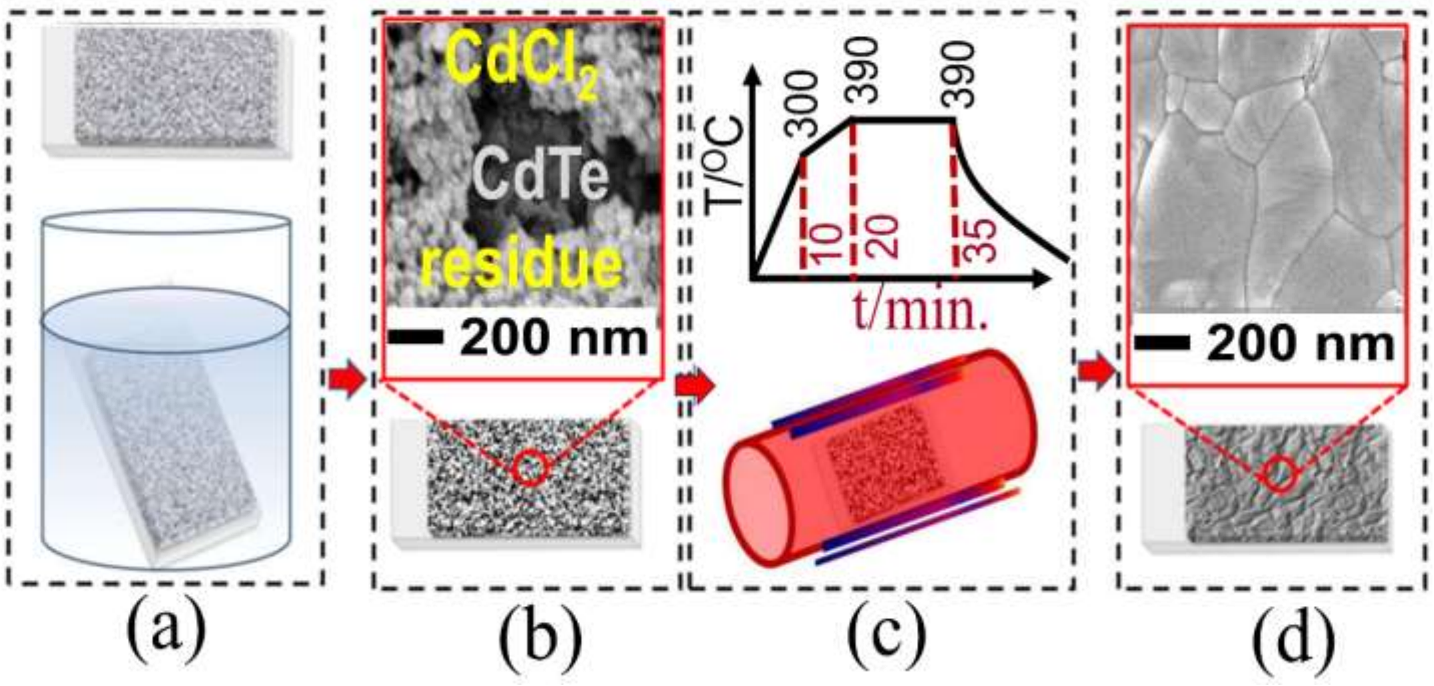


SEM images of CdTe thin films

Values of the electrical parameters of as-deposited & $CdCl_2$ treated CdTe thin films

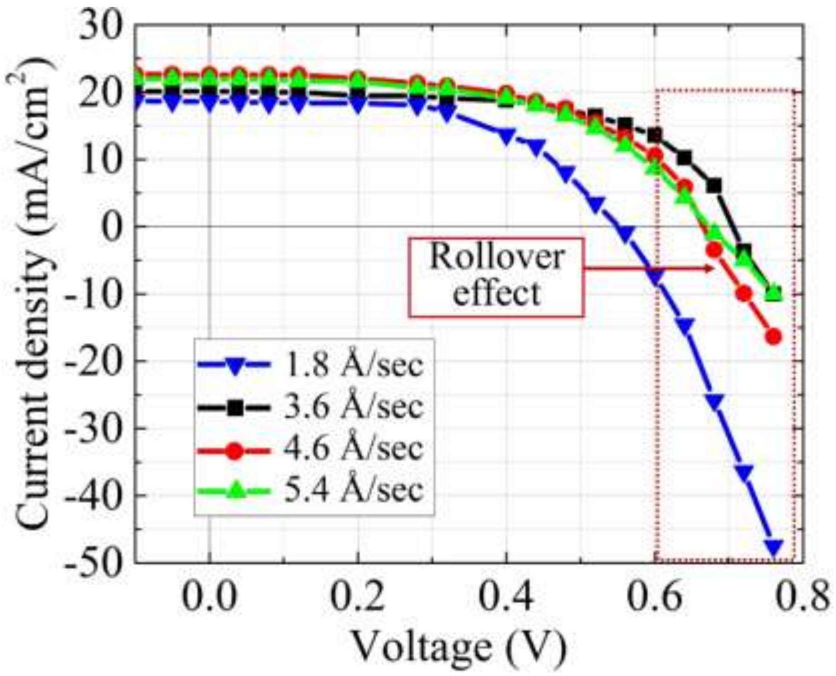
RF-power (watt/cm^2)	Resistivity x 10^4 (Ω-cm)	Carrier concentration x 10^{13} cm^{-3}
As-deposited		
1.0	3.41	1.45
1.5	1.51	4.52
2.0	9.19	0.12
2.5	1.06	0.78
3.0	**2.21**	**0.49**
CdCl2 treated		
1.0	2.68	2.24
1.5	4.43	10.43
2.0	1.24	13.45
2.5	1.59	7.30
3.0	**1.61**	**68.69**

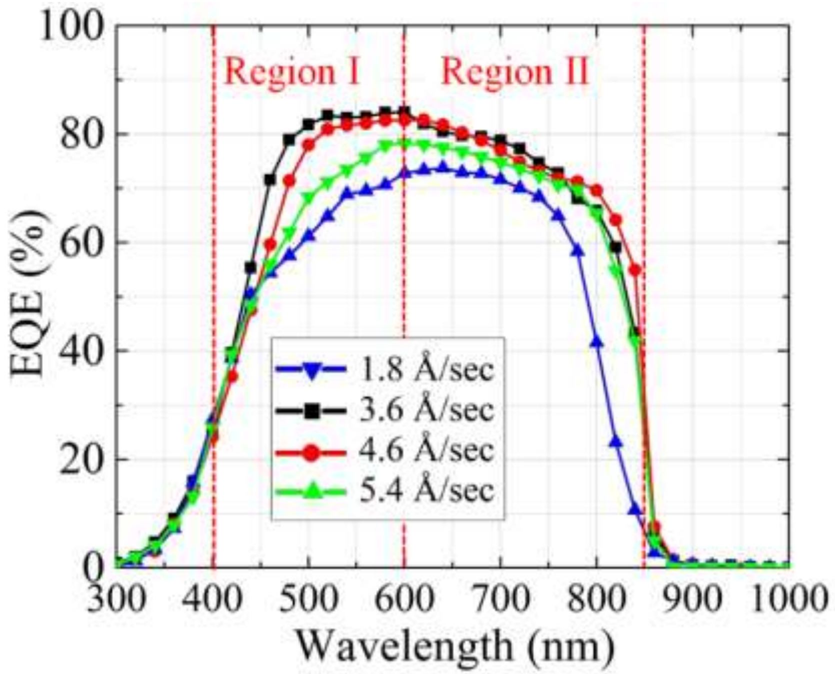
$CdCl_2$ Treatment on *CdS:O/CdTe* Stacks



Schematic illustration of the $CdCl_2$ heat treatment in steps. (a) Glass/CdTe stack immersion in 0.3 M $CdCl_2$ solution for 10 sec, (b) SEM morphology of naturally dried sample (c) thermal annealing process with the temperature profile (samples annealed for 15 min. at 390 ^oC in vacuum with 66.66 Pa of N_2/O_2 pressure) and, (d) SEM morphology of the cleaned (by warm water) sample

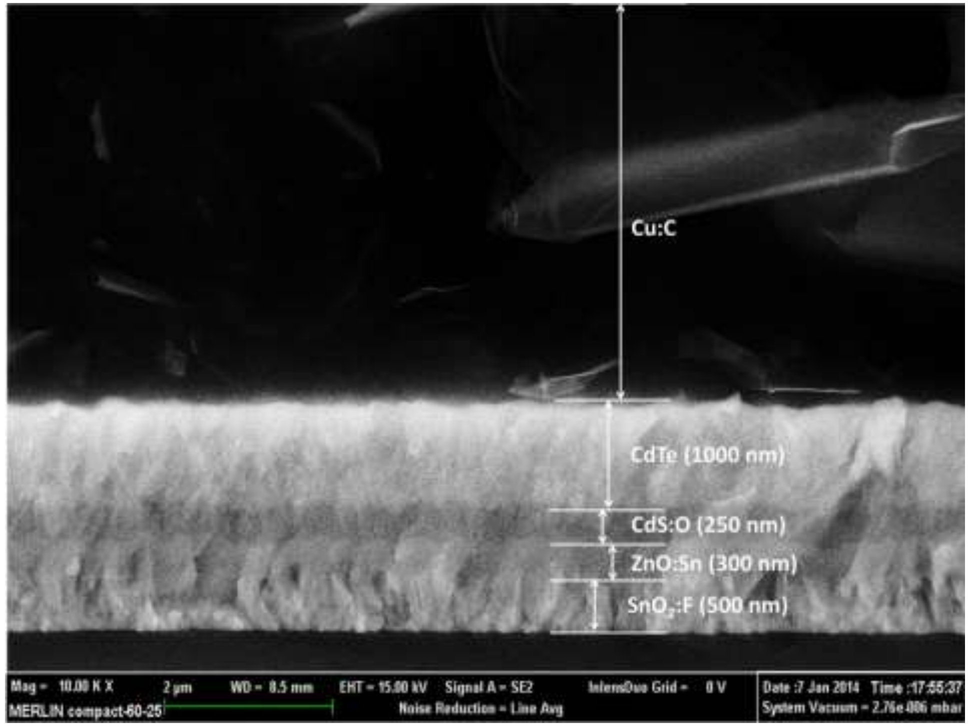
LIV and EQE

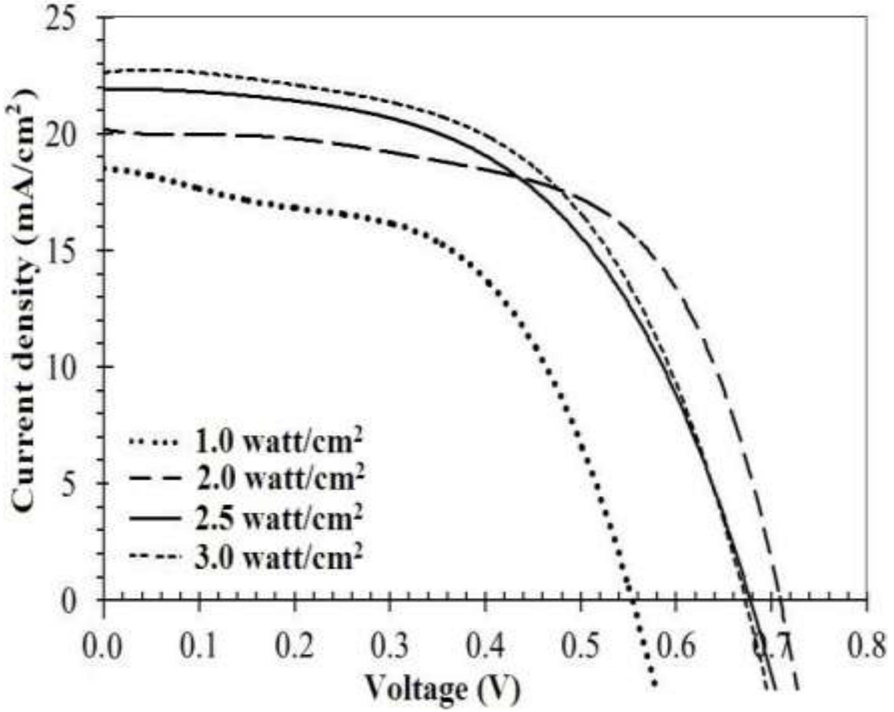




J-V curves (left) of the fabricated CdTe solar cell with respect to the growth rate in Sputtering; External quantum efficiency (EQE) (right) of the solar cells (decrease of QE from 600 nm to 800 nm indicates the increase of carrier recombination at the bulk of CdTe)

Achievement in Novel Approach
for CdTe Solar Cells





Cross sectional image & J-V curves of the ZnO:Sn/CdS:O/CdTe/Cu:C/Ag solar cells

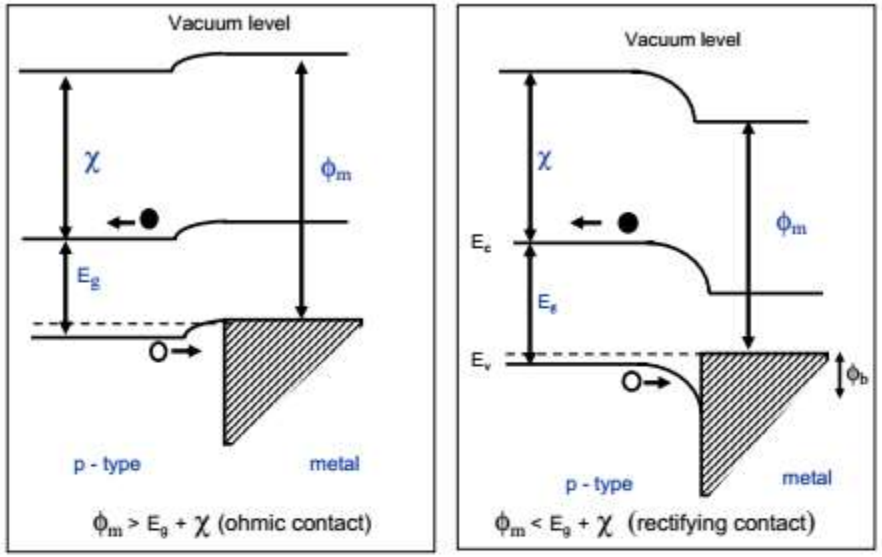
Table : Solar cell performance with FTO/ZnO:Sn/CdS:O/CdTe/Cu:C/Ag configuration

RF power (CdTe)	Voc (V)	Jsc (mA/cm^2)	FF (%)	Efficiency (%)	Cell area (cm^2)
1.0 $watt/cm^2$	0.56	18.58	59	6.14	0.25
2.0 $watt/cm^2$	0.72	20.11	65	9.41	
2.5 $watt/cm^2$	0.68	21.89	62	9.23	
3.0 $watt/cm^2$	0.67	22.55	68	10.27	

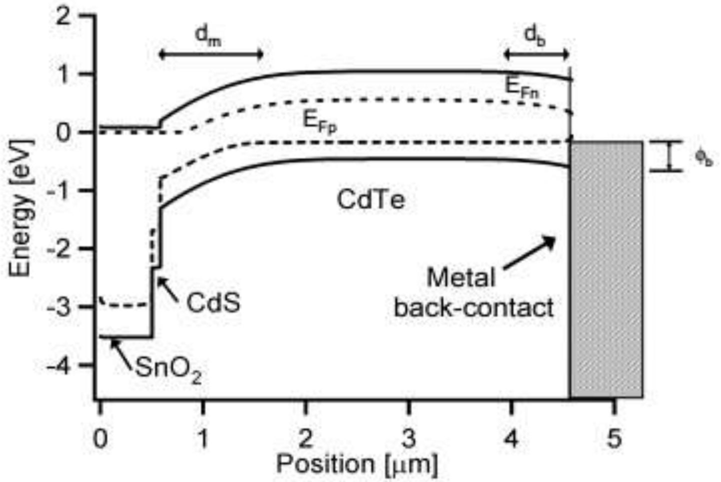
Back contact of CdTe

- Forming back contact to CdTe is problematic owing to the high electron affinity x_s = 4.5eV
- For Ohmic contact require a work function of > 6eV – No such metal exists!
- May contact with high work function metals (e.g. Au ~5.1eV) but a barrier still exists.

$$\phi_m \geq E_g + \chi \qquad \phi_m \leq E_g + \chi$$



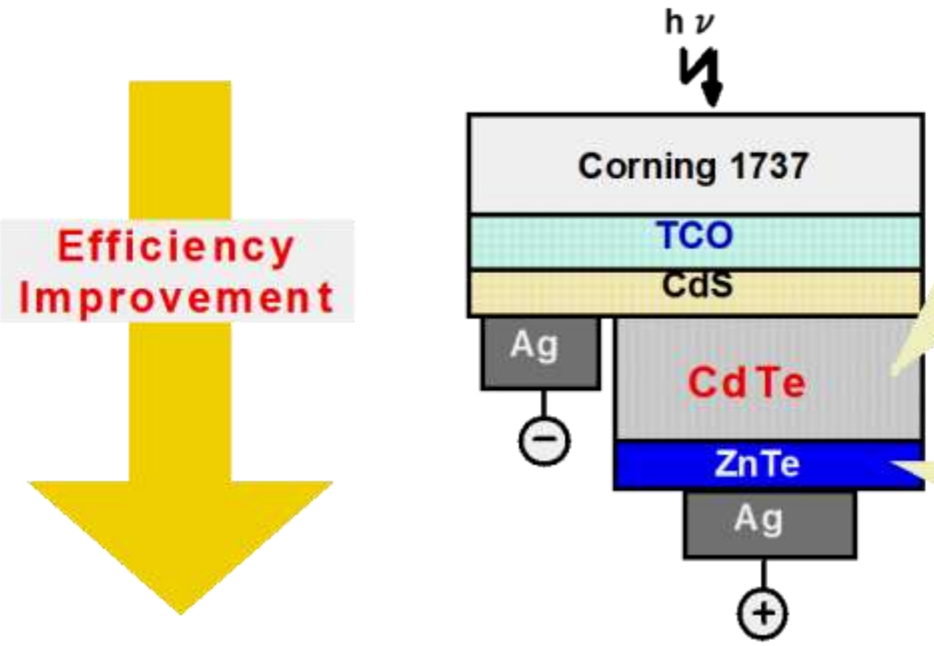
Ohmic and rectifying metal/p-semiconductor contacts.

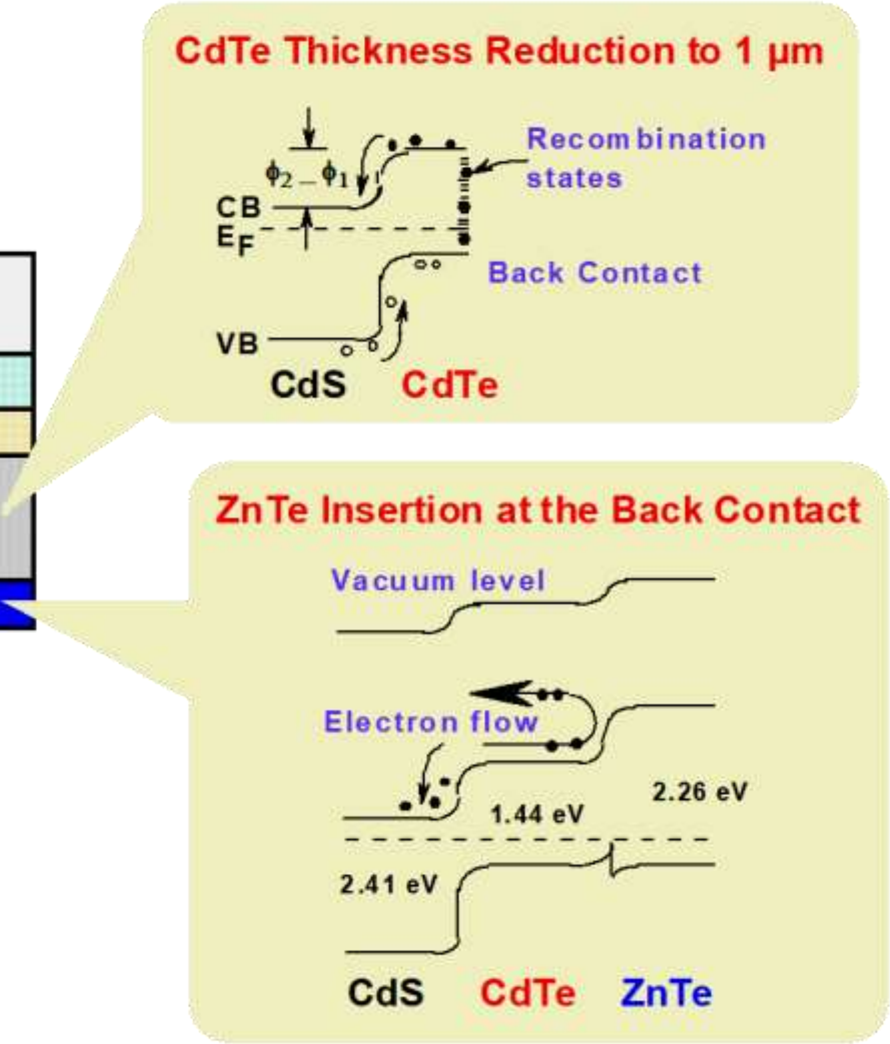


Metal	ϕ_m [eV]	ϕ_b [eV]
Ag	4.26	1.69
Al	4.28	1.67
Au	5.10	0.85
Cu	4.65	1.30
Cr	4.50	1.45
In	4.12	1.83
Mo	4.60	1.35
Ni	5.15	0.80
Pd	5.12	0.83
Pt	5.65	0.30
Sb	4.55	1.40
Te	4.95	1.00
Ti	4.33	1.62
V	4.30	1.65

Pseudo-Ohmic Contact – A Potential Key to Success

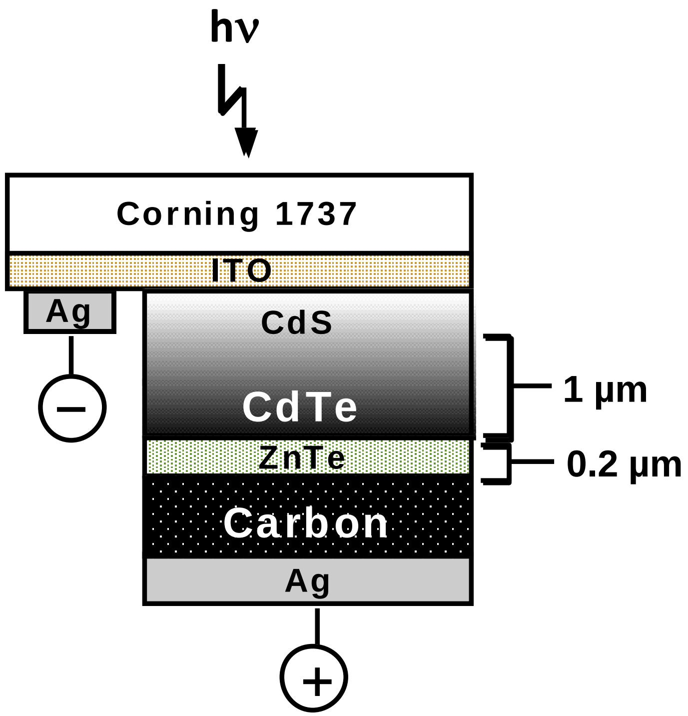
CdTe absorption coefficient: 2×10^4 cm^{-1};
1 µm-CdTe absorbs 90% of the incident spectrum.

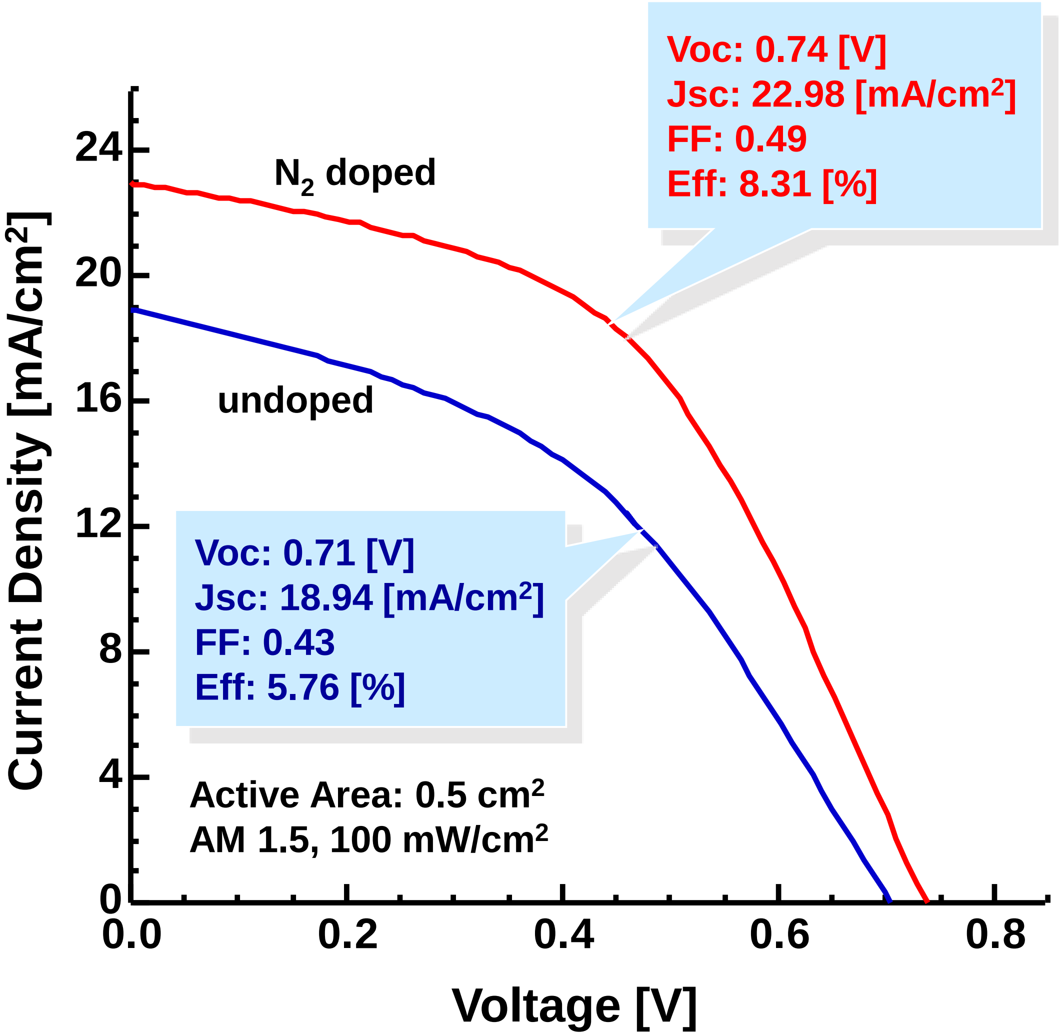




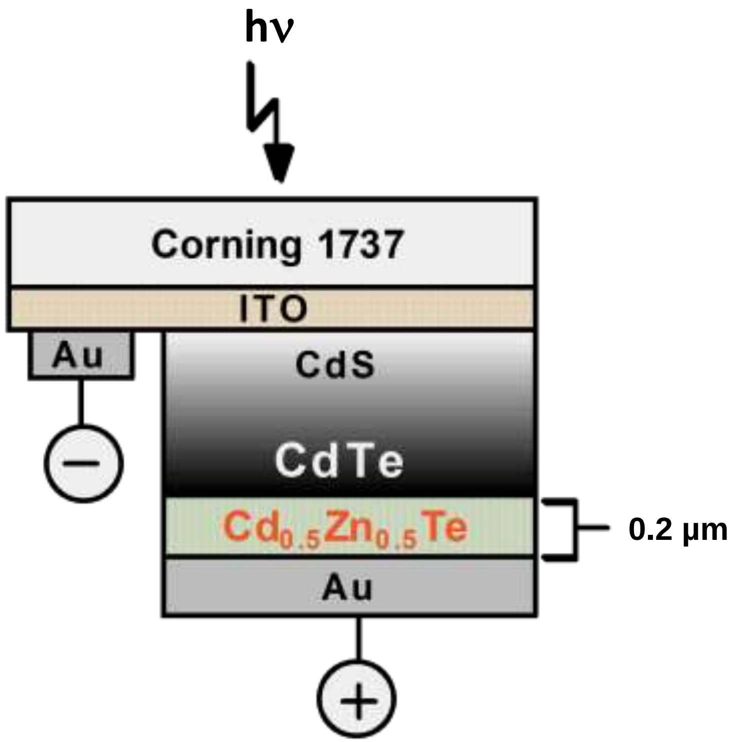
- **Reduction of Carrier Recombination Area.**
- **Enhancement of Optical Confinement.**
- **Reduction of Carrier Recombination at the Back Contact.**

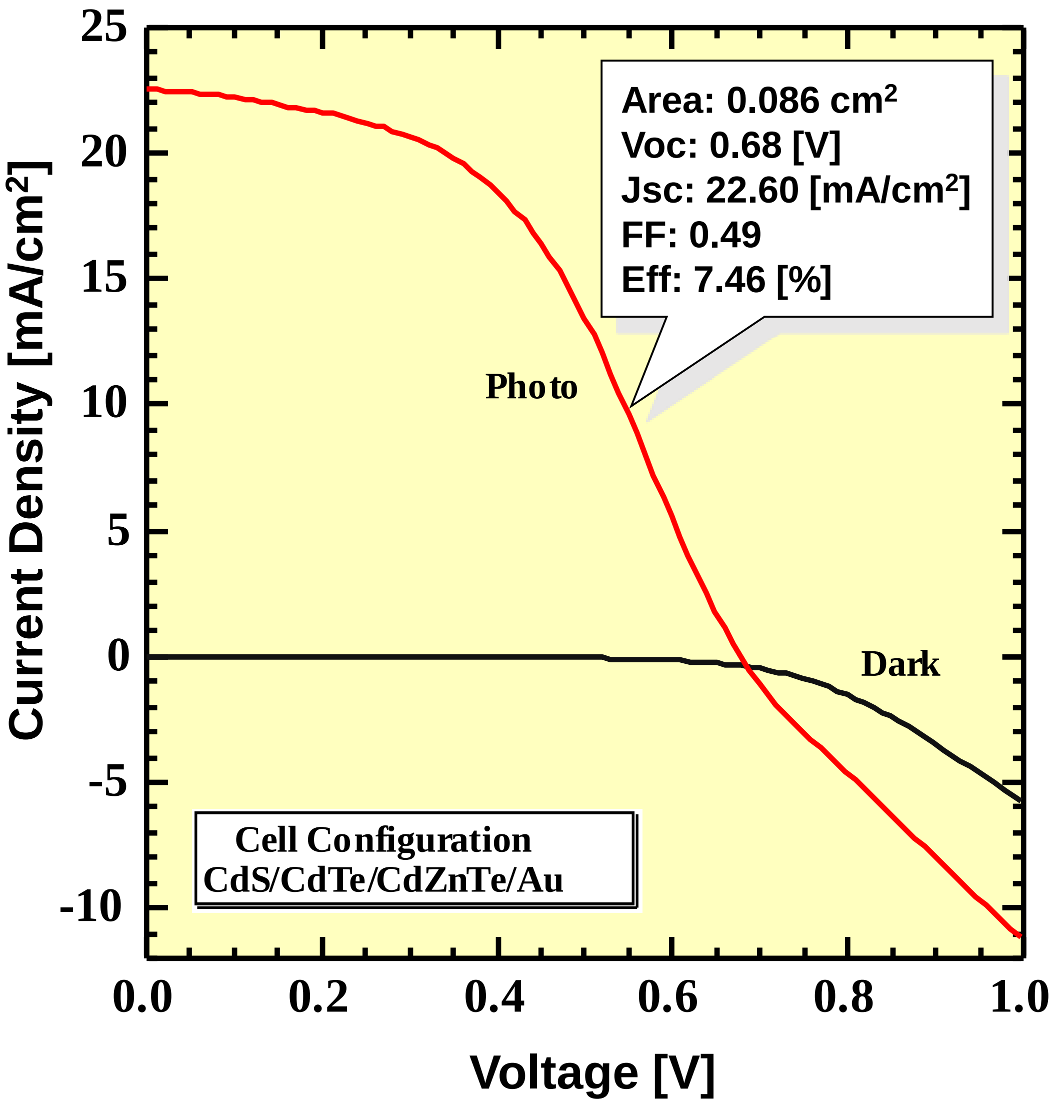
I-V Characteristics of CdS/CdTe/ ZnTe Solar Cell





I-V Characteristics of CdTe/ $Cd_{0.5}Zn_{0.5}Te$ Thin Film Solar Cell





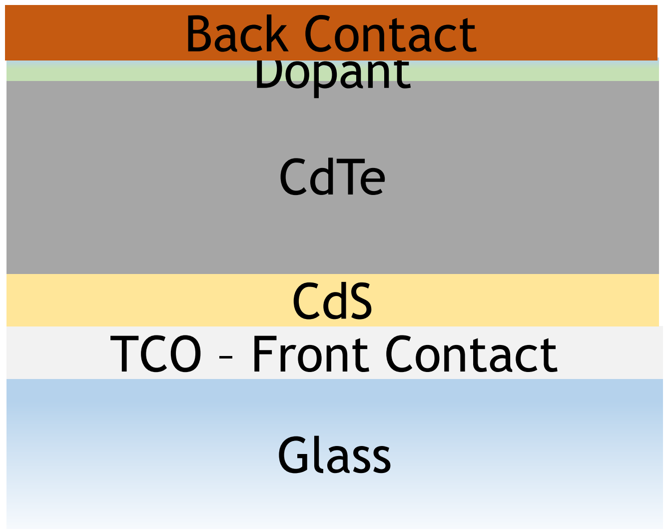
Ag & Na Doping Effect in CdTe Thin Film Solar Cells

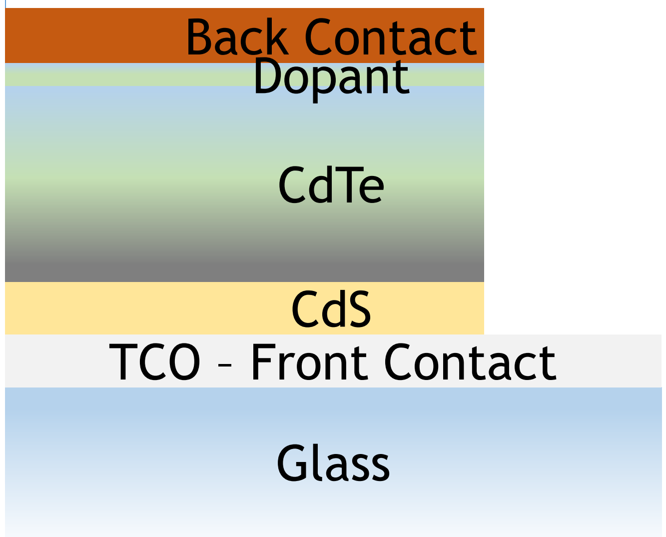
- V_{bi} is correlated to device performance ↔ V_{oc}
- Increase of acceptor concentration, N_A will shift Fermi to near E_v and shift up the E_c higher V_{bi} ↔ V_{oc}.

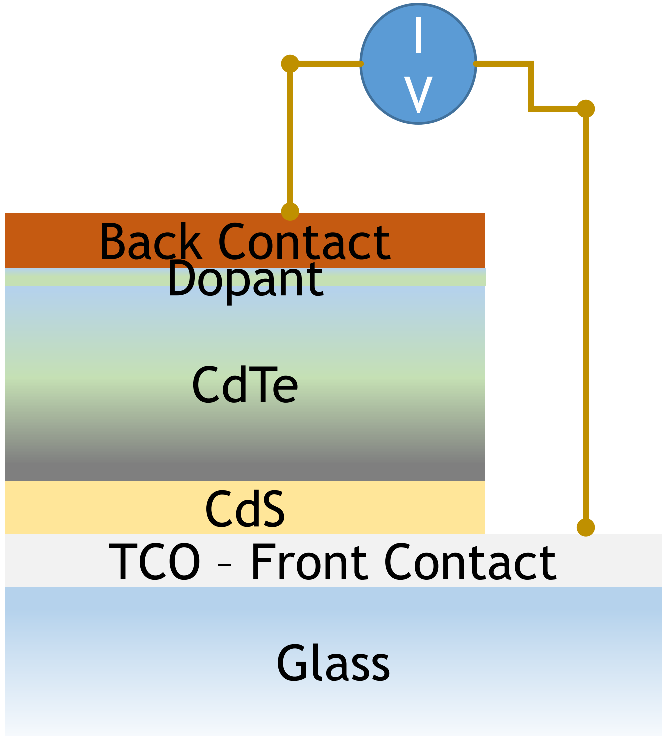
Doping (Ag, Na, Cu) + Back Contact → + Anneal → Mask + Etch + remove mask → Characterize

Nd:YAG laser at wavelength of 532 nm

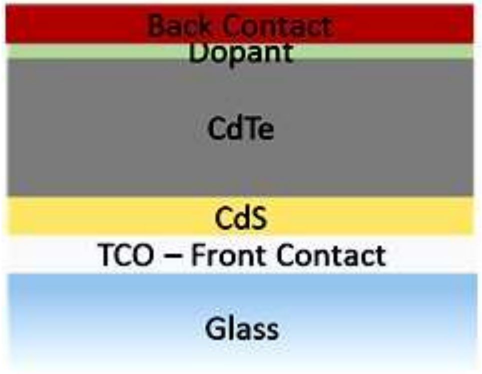
Copper (II) chloride ($CuCl_2$) and silver nitrate ($AgNO_3$) dip coating

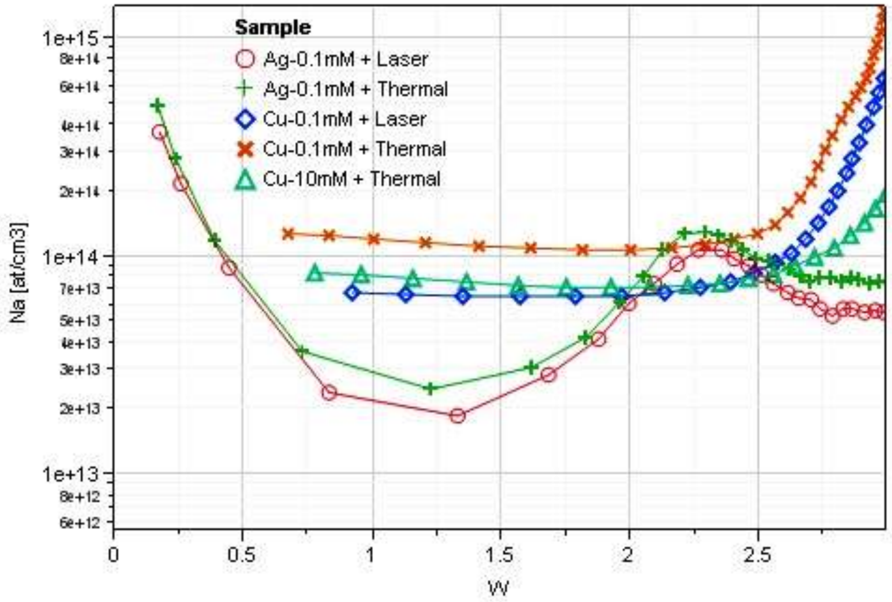


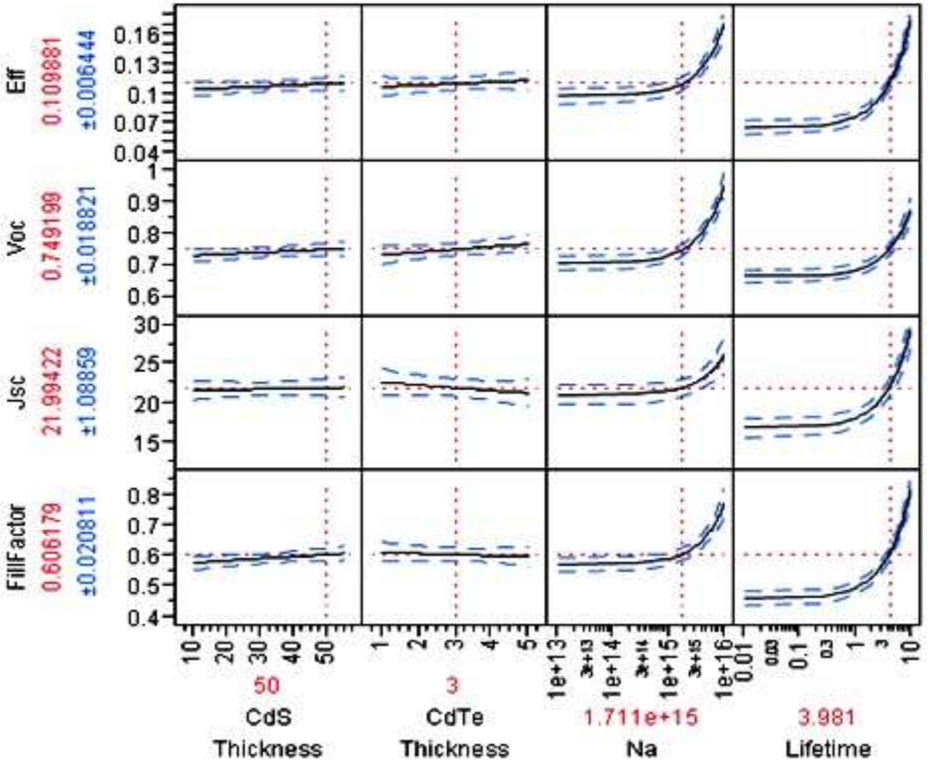


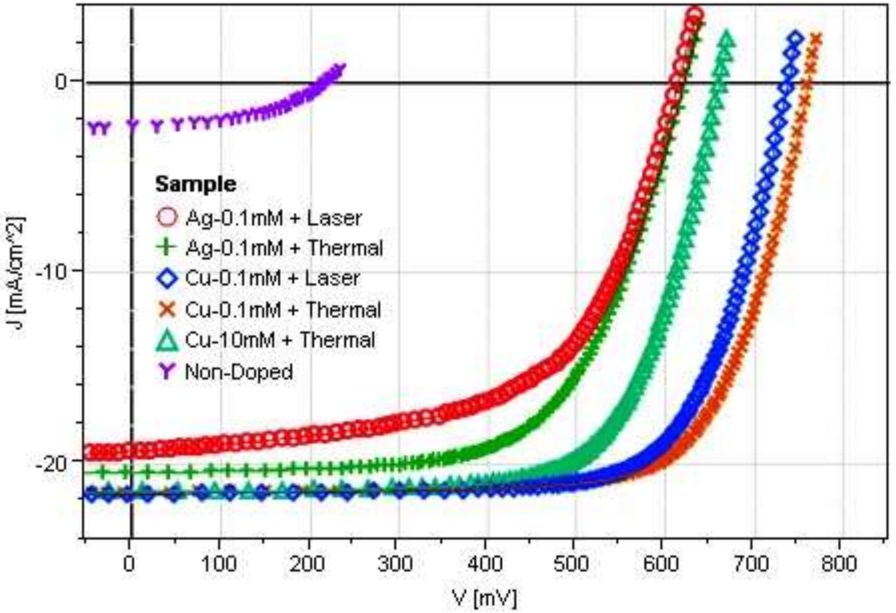


Ag & Na Doping Effect in CdTe Thin Film Solar Cells









CdTe Research Trend & Challenges

TABLE I
CDTE RECORD CELL *I–V* PARAMETERS

Year	Team	Eff	Voc	Jsc	FF
1993	USF*	15.8%	843	25.1	74.5%
1997	Matsushita[‡]	16.0%	840	26.1	73.1
2001	NREL*	16.4%	848	25.9	74.5
2001	NREL*	16.7%	845	26.1	75.5%
2011	FSLR*	17.3%	845	27.0	75.8%
2012	GE*	18.3%	857	27.0	79.0%
2012	FSLR*	18.7%	852	28.6	76.7%
2013	**FSLR[$]**	**19.0%**	**872**	**28.0**	**78.0%**
	Demtsu/Sites – Target	19.0%	900	27.0	78.5%

*NREL certified; ‡JQA certified; $Newport certified.

2016 highest Eff 22.1%* record cell from First Solar

- A lot of opportunity in Voc improvement.
- Primary research of in Voc improvement:
  - Interface optimization (back/front contact)
  - Improve carrier lifetime – better CdTe film quality (grain size, grain boundary, defects, fabrication process, etc..)
  - **Understand of doping capability of CdTe and improve carrier concentration.**

- ➢Thinner CdTe Absorber layer
- ➢Improvement of the back contact
- ➢Insertion of bi-layer
- ➢Optimizing process steps
- ➢Low temperature deposition techniques
- ➢Deposited layer quality improvement
- ➢Annealing ($CdCl_2$) treatment optimization

M. Gloeckler, I. Sankin, and Z. Zhao, "CdTe Solar Cells at the Threshold to 20% Efficiency", J. of Photovoltaics 3(4) 1389 - 1393 (2013)

First Solar

Kulim, Malaysia

6 Manufacturing Plants

Over 4,000 Skilled Associates

Over 3 Million Square Foot of Floor Space

2016 Total Annualized Capacity 2.5 GW

First Solar on CdTe Thin Film Solar PV

1. CdTe cell efficiency reaches > 22% and module performance > 18 %
2. Largest Module is over 460 Wp to date

From a visit on 5 Nov 2018

#9 Topaz Solar Farm, USA

2nd Generation
CdTe Based

Highlights:

Location: California, USA

Capacity: 550 MW

Area: 24.6-square-kilometer

Year: 2014

Cost: $2.5 billion

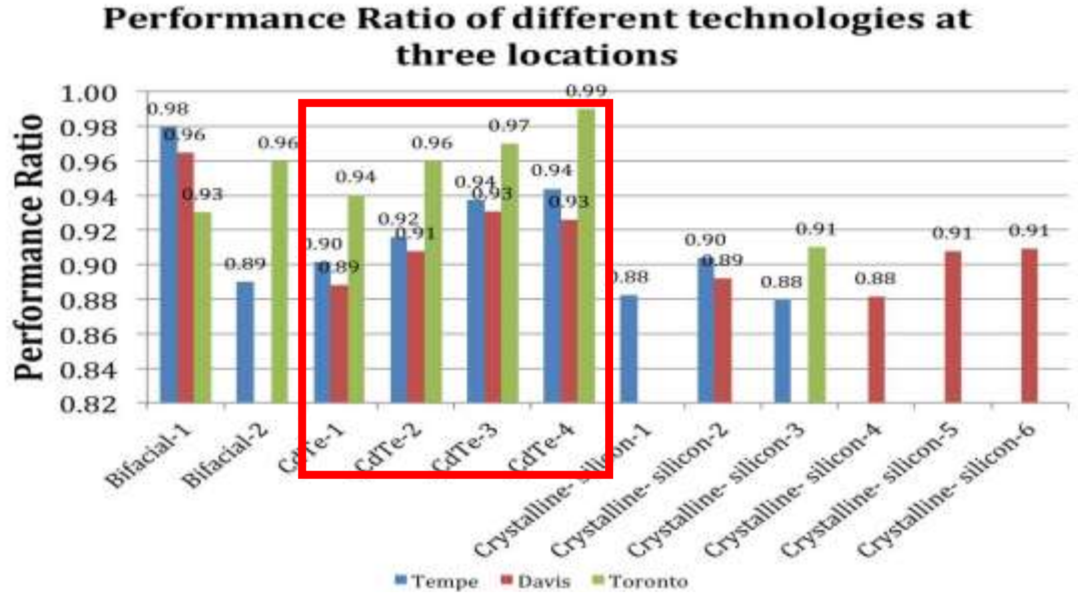
Modules: First Solar CdTe

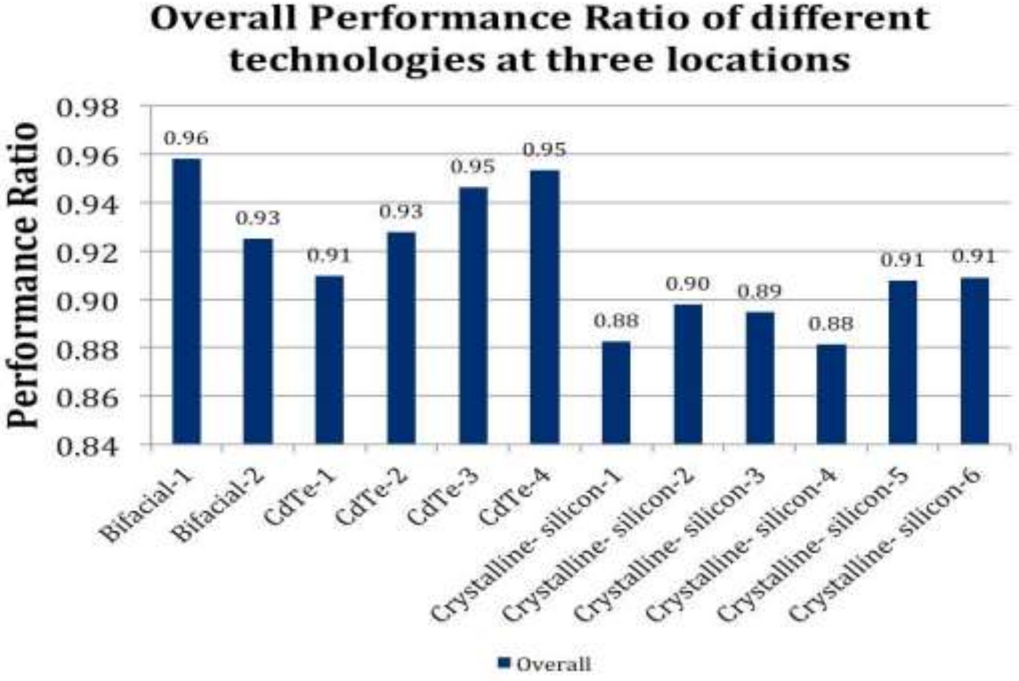
The plant could power 160,000 average California homes and displaces 377,000 tons of carbon dioxide annually which is equivalent to 73,000 cars being removed.

[20] http://earthobservatory.nasa.gov/IOTD/view.php?id=85403
[21] http://www.firstsolar.com/en/About-Us/Projects/Topaz-Solar-Farm
[22] http://www.dailymail.co.uk/sciencetech/article-2853208/Watch-world-s-largest-solar-power-plant-built-Huge-farm-generates-energy-160-000-homes-using-nine-MILLION-panels.html

CdTe Field Performance

- Independent test by TÜV Rheinland Photovoltaic Testing Lab shows CdTe has better than c-Si and comparable or better performance to c-Si bifacial cells technology.
  - Data collection – 1 year
- 3 different sites:
  - Tempe – hot climate, module temperature > 45 deg. C
  - Davis – Moderate climate, module temperature ~25 de. C.
  - Toronto – cold climate





https://www.greentechmedia.com/articles/read/who-wins-when-bifacial-thin-film-cdte-and-crystalline-silicon-face-off

OUTLINE

- Introduction
- Thin Film & Thin Film Deposition
- Solar Cells
- **Implication of Thin Films into Solar Cells**
  - aSi
  - CdTe
  - **CIS (CIGSSe, CZTS, CTS)**
- Challenges and prospects
- Conclusion

Solar Cell Technologies

[Solar PV Applications Controllers, Systems]

First Generation:
Crystalline silicon solar cell
(200-500 micron)

Second Generation:
Thin film solar cell
(1-10 micron)

Third Generation:
DSSC, Organic, Perovskite, Multijunction, Futuristic

Crystalline Silicon cells

Mono-crystalline cells

Efficiency : 18%~25.6%

Multi-crystalline cells

Efficiency : 17%~20.8%

Thin film PV

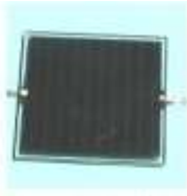
CdTe cells

Efficiency : 18.3%~22.1%

Amorphous silicon cells

Efficiency : 13.4%

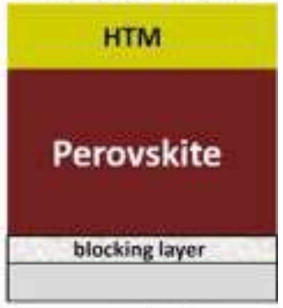
CIGS cells



Efficiency : 20.4%~22.6%

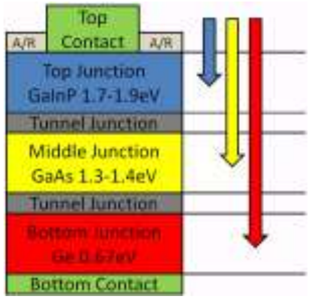
Perovskite cells

Planar Structure



$\eta = 15.4\%$

Novel Hybrid



Efficiency: 40%

Thin Film PV Research Focus: CIGS, CZTS, CTS

Brief History of CIGS Solar Cells

1839
Photovoltaic effect discovered by Becquerel

1950
6% efficient silicon solar cell was fabricated in Bell Labs

1954: Photovoltaic effect was discovered in CdS/CuS_2 devices

1960
14% efficient silicon solar cell was made

1974: First chalcopyrite solar cells with $CuInSe_2$ absorbers were made

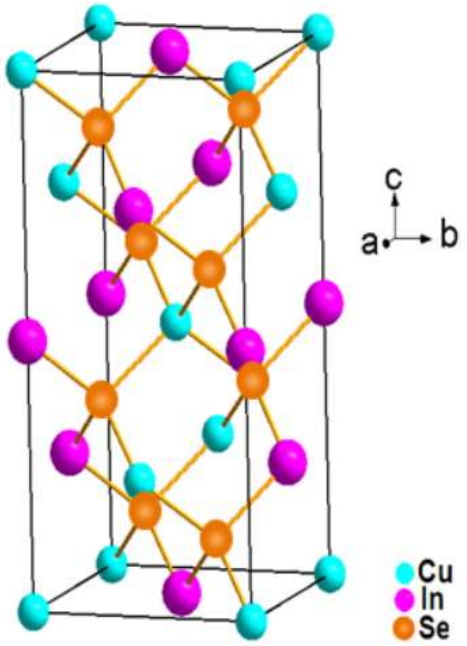
1975
12% efficient CdS/$CuInSe_2$ solar cell was made by scientists at Bell Labs

1980s
Corporations and research laboratories started developing CIGSe solar cells

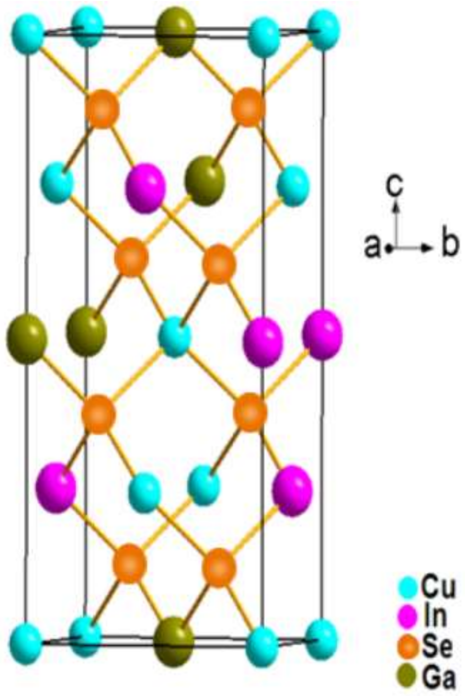
[1] RENEW SUST ENERG REV 43 (2015) 1073-1089
[2] Hamakawa, Y. (2004)

Absorber

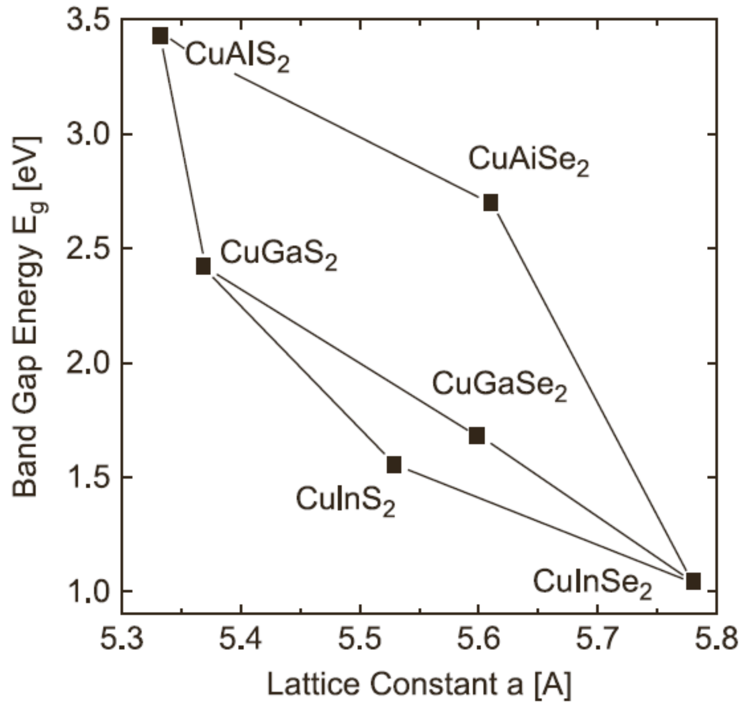
- $Cu(In,Ga)Se_2$ is an alloy of $CuInSe_2$ and $CuGaSe_2$.
  - Classified under I-III-VI_2 group of semiconducting materials (direct bandgap).
  - Crystallizes in the tetragonal chalcopyrite structure homogeneously.
  - Cu-based chalcopyrites span a wide range of bandgap energies that cover most of the visible wavelength spectrum.



Crystal structure of $CuInSe_2$



Crystal structure of $Cu(In,Ga)Se_2$

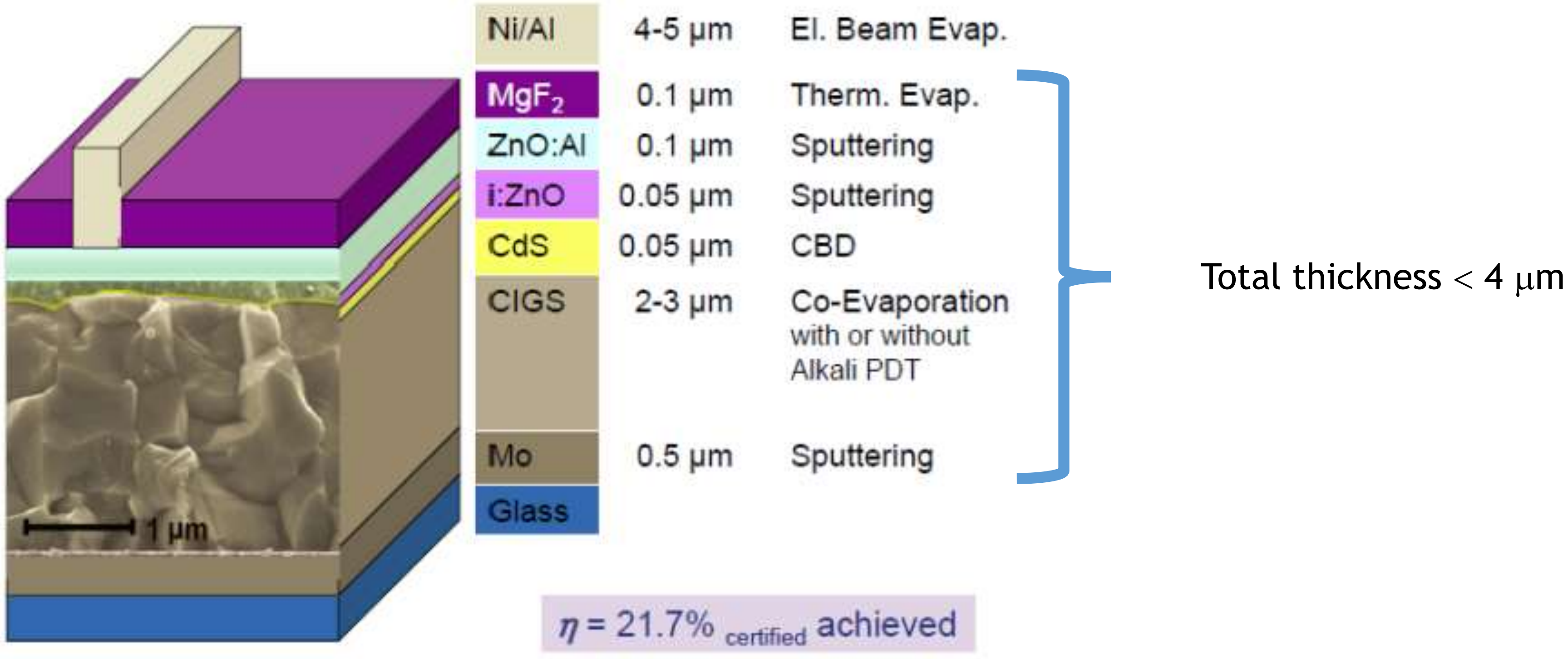


Bandgap energies (Eg) vs. lattice constant (a) of the $Cu(In,Ga,Al)(S,Se)_2$ alloy system

[11] BEILSTEIN J. NANOTECHNOL., 2014 (5), 1235–1244.
[14] McEvoy, A. et al. (2013)

Advantages of CIGS Solar Cells

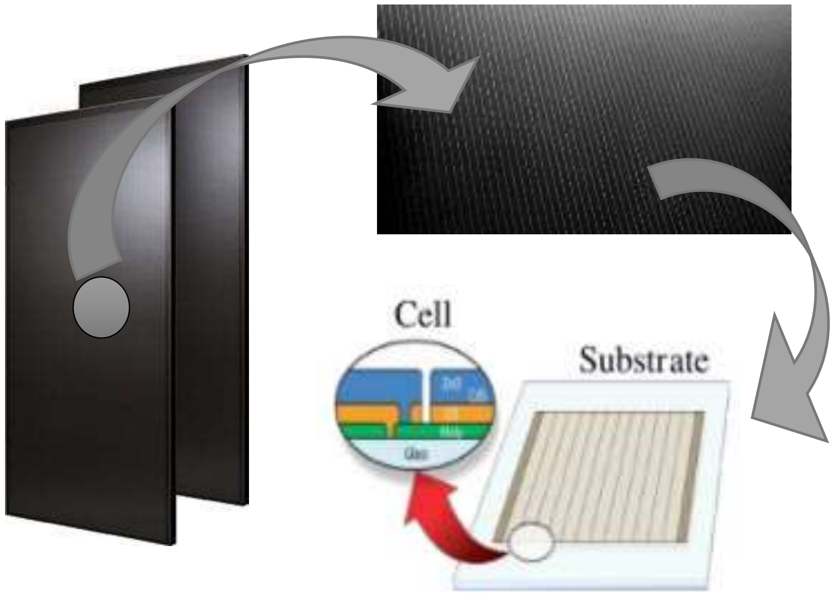
- Minimum use of materials



[17] Paetel, S. (2016)

Advantages of CIGS Solar Cells

- Monolithic connected modules offer better stability than soldered or bonded PV modules



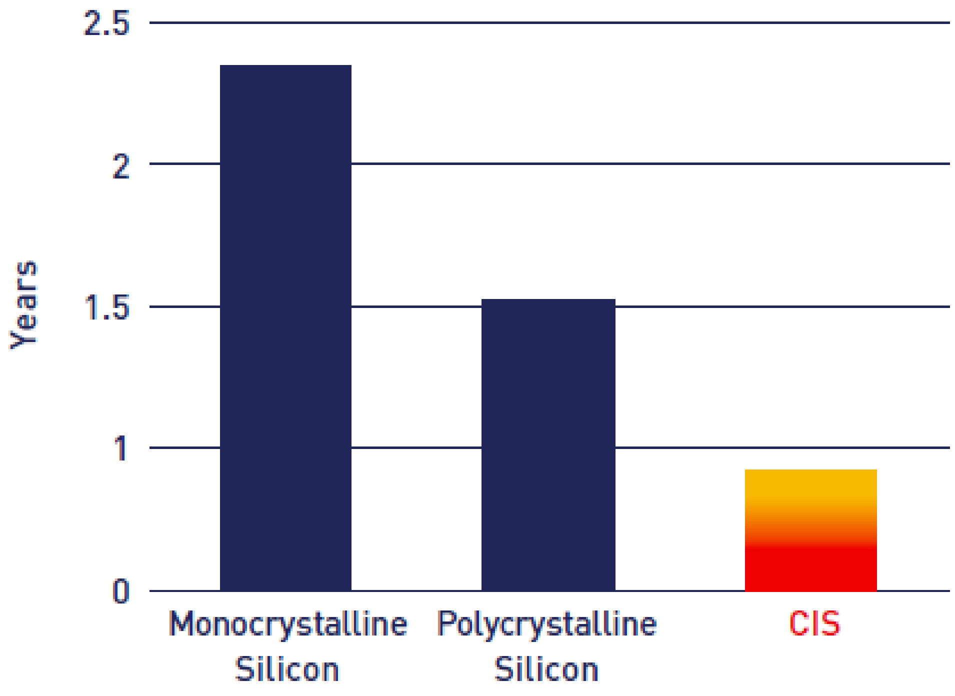
Monolithic integrated (MLI) CIGS PV module

- Modules are more aesthetically pleasing too

[4] http://cigs-pv.net/

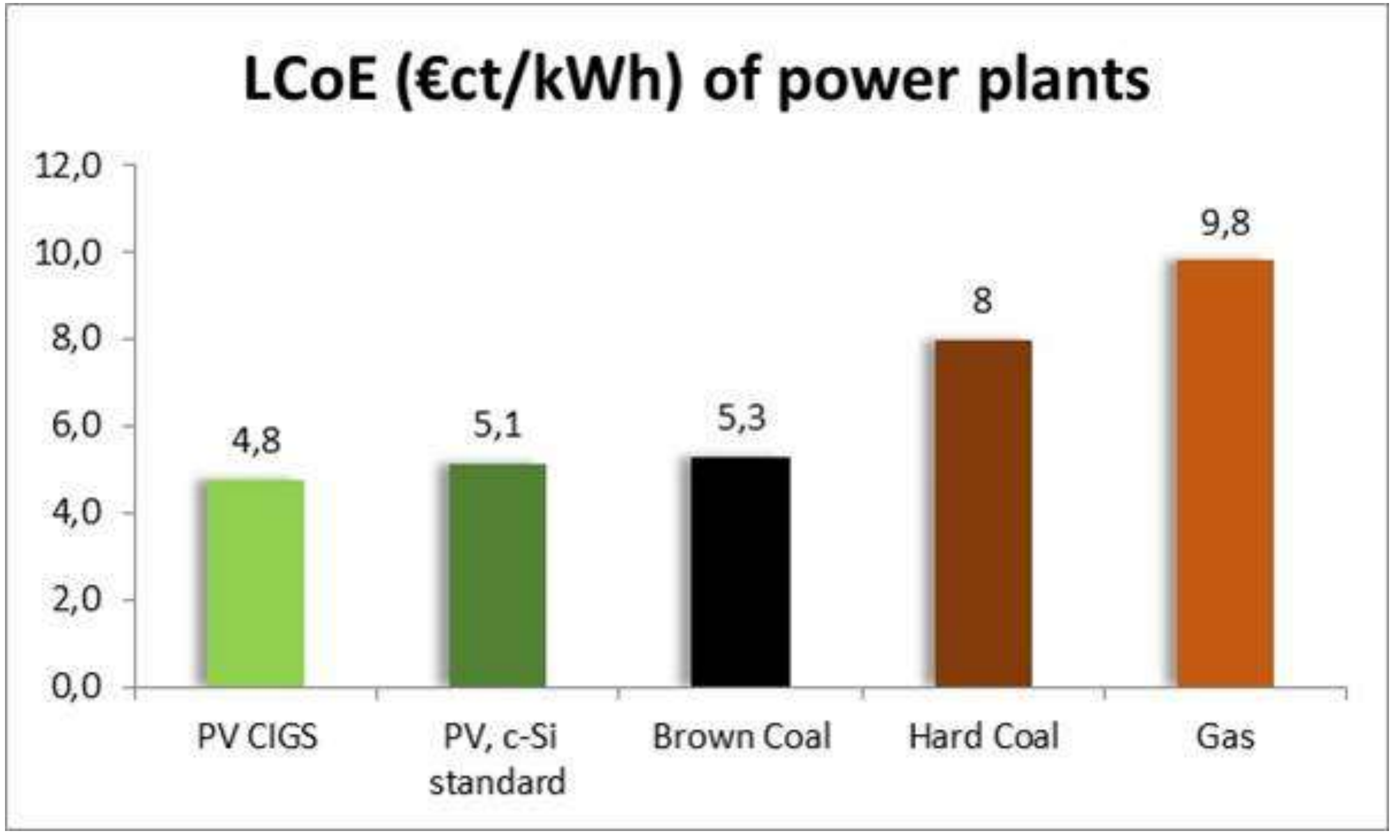
Advantages of CIGS Solar Cells

- Short energy payback time



CIGS modules require 60% less energy to produce than crystalline silicon panels.

- Low cost of electricity production & low carbon footprint



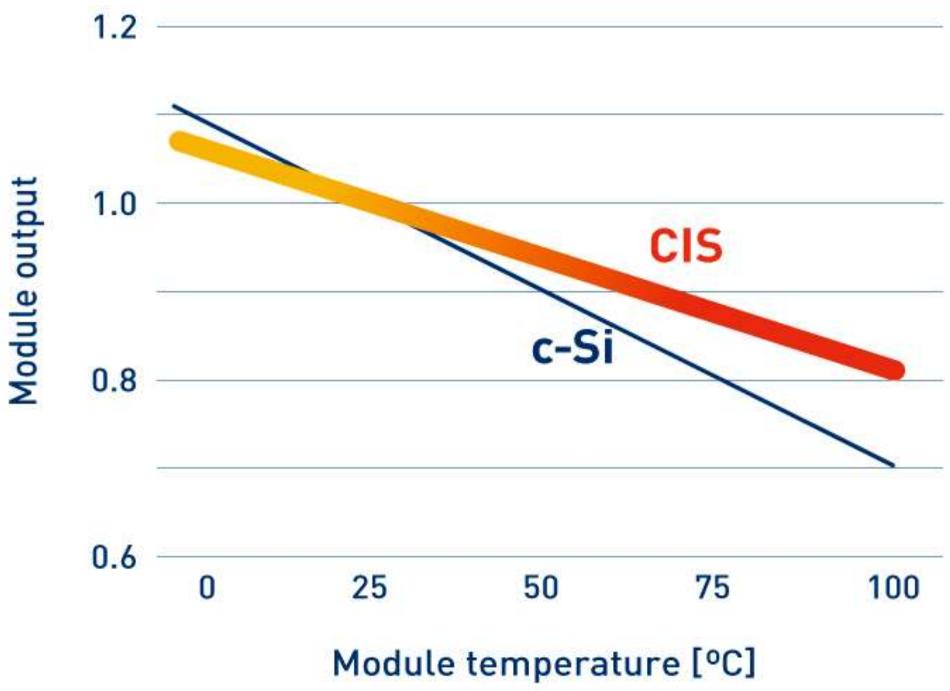
Source: Fraunhofer ISE/ IPA Dec. 2013

[6] http://www.solar-frontier.com/

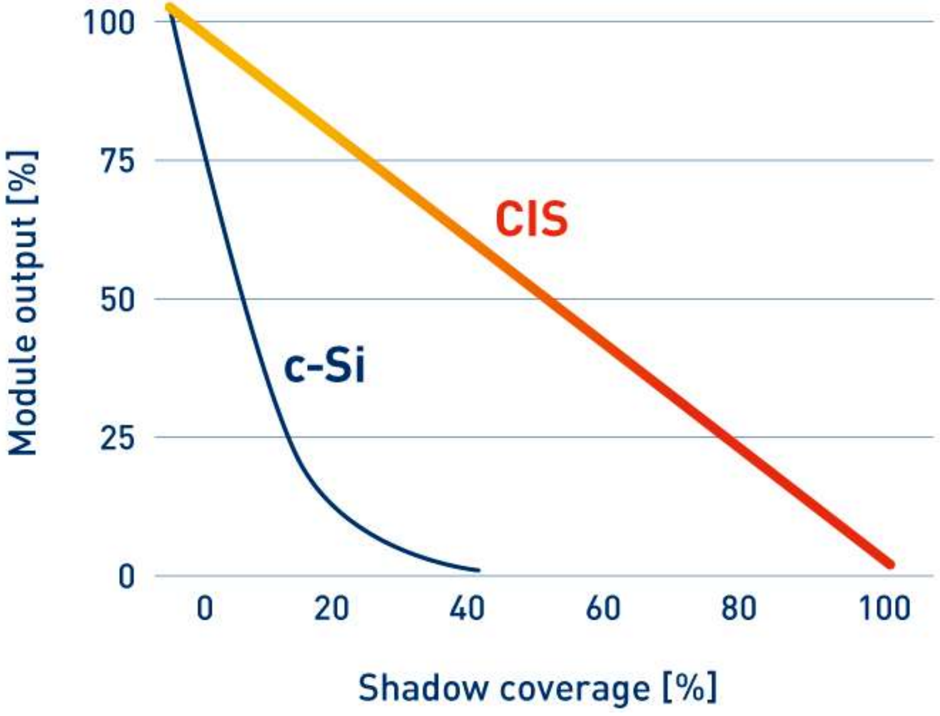
[4] http://cigs-pv.net/

Advantages of CIGS Solar Cells

- CIGS PV modules possess lower temperature coefficient than crystalline Si



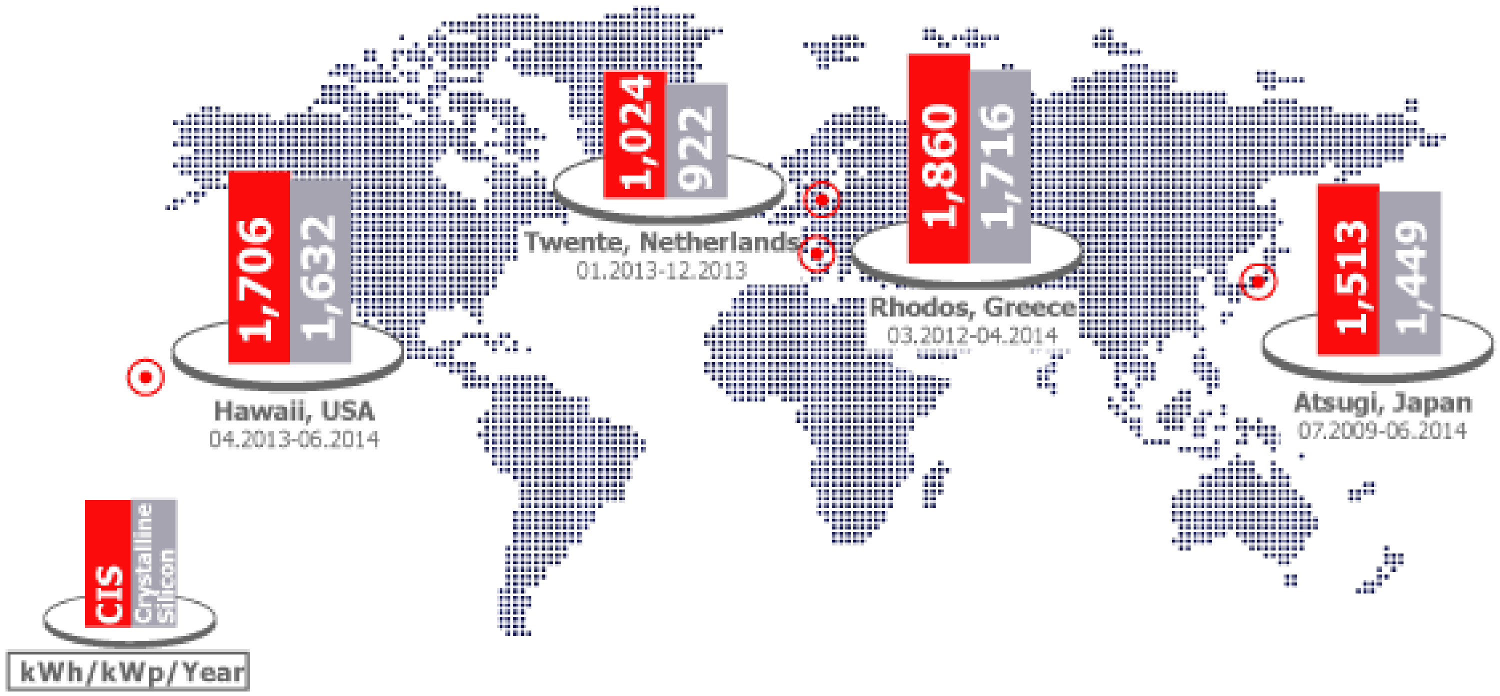
- CIGS PV modules has higher tolerance for shading



[6] http://www.solar-frontier.com/

Advantages of CIGS Solar Cells

- CIGS modules generate higher electricity (comparing with c-Si) in real world conditions (data from 4 different sites).



[6] http://www.solar-frontier.com/

Successful Commercialization

SOLAR FRONTIER

Founded	2006
Headquarters	Tokyo, Japan
Technology	Lead and Cadmium-free CIGS modules
Employees	~ 1,300
Product	• R&D and Production of CIGS modules • Sale of Solar Power Systems • Development of Power Plant Projects • Power Generation and Management
Investment	JPY 113 B
Capacity	1050 MW per annum

Highly automated production process

http://www.solar-frontier.com/

Solar Frontier (now IDEMITSU Kosan) on CIGS PV

Current Status of CIGS PV

Highest recorded efficiency for CIGS PV device to date:

- Cell: 22.6%
  - Reported by ZSW.
  - Size 0.5 cm².

ZSW's CIGS cell.

Solar Frontier's 22.3% CIGS cell (22.9% by SF, unverified)

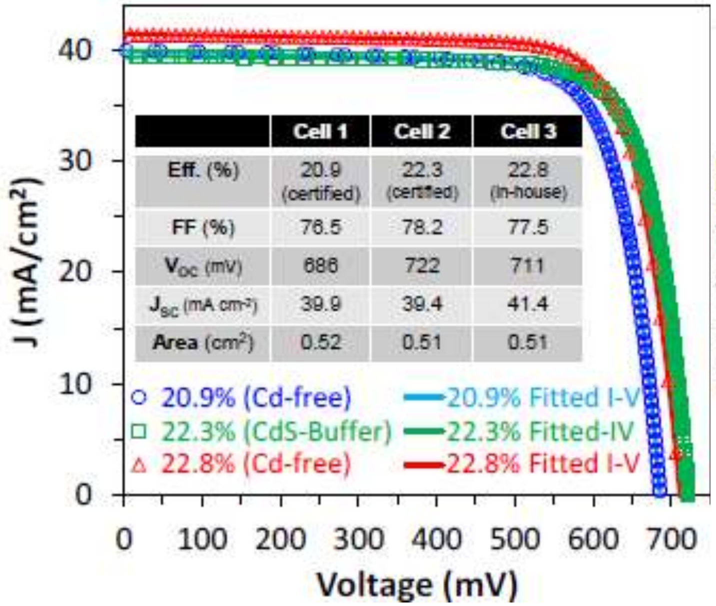
- Mini-module: 19.8%
  - Reported by Solar Frontier (now IDEMITSU KOSAN).
  - Size 7.5 cm × 5 cm.

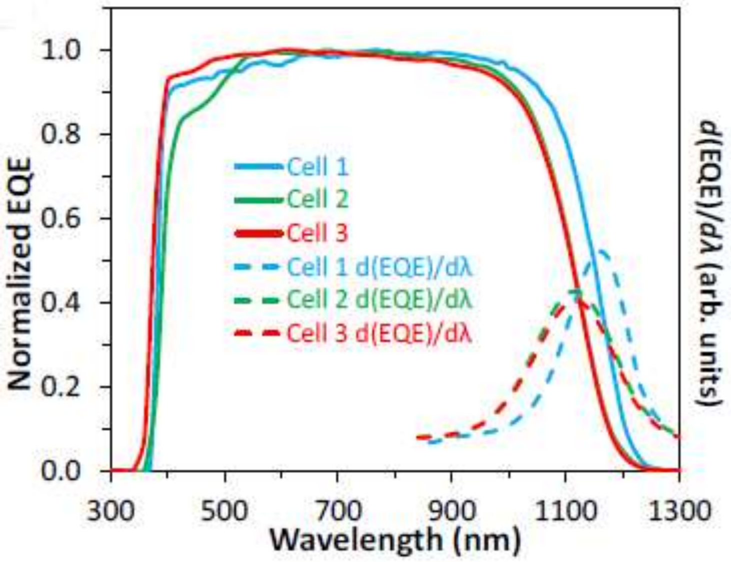
- Module: 19.2%
  - Produced by Solar Frontier (now IDEMITSU KOSAN).
  - Size: 30 cm × 30 cm.

[5] https://www.pv-magazine.com. 15 June 2016
[6] http://www.solar-frontier.com/eng/news/2017/0227_press.html

Recent Advances

Paper#1	Authors	Journal	Significant Findings
From 20.9 to 22.3% $Cu(In,Ga)(S,Se)_2$ solar cell: Reduced recombination rate at the heterojunction and the depletion region due to K-treatment	Kong Fai Tai, Rui Kamada, Takeshi Yagioka, Takuya Kato, and Hiroki Sugimoto	Japanese Journal of Applied Physics Year: 2017 (IF: 1.471, Q3)	• CIGS solar cells with intentional surface treatment with K-sources, coupled with the unintentional Na diffusion from the glass substrate, have consistently shown an improved open-circuit voltage (V_{OC}) and fill factor (FF) • Researchers compared the device characteristics of their previous world record holding solar cell of 20.9 % efficiency with their, at the time, record breaking cell of 22.3 % • Also tested was a solar cell with Cd-free buffer • Cell area: 0.5 cm^2 • K-treatment was found to enhance V_{OC} in all surface treated solar cells • **Recombination analysis suggests that the recombination rates at the interface and in the depletion region were largely reduced compared to untreated device** • **The reduced recombination rates are likely due to a decreased defect density on the absorber surface and depletion region**





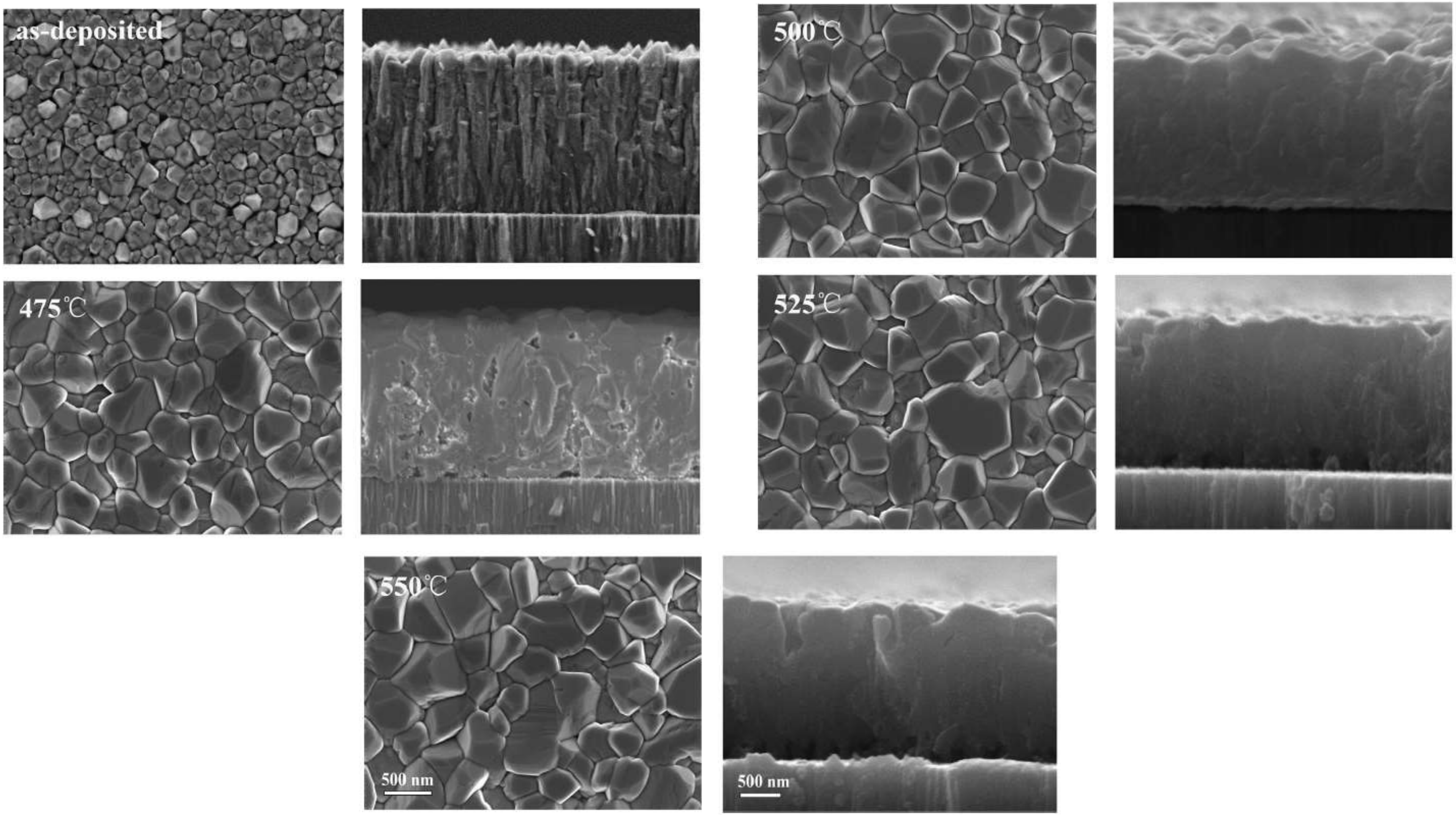
Recent Advances

Paper#2	Authors	Journal	Significant Findings
Record Efficiency for Thin-Film Polycrystalline Solar Cells Up to 22.9% Achieved by Cs-Treated $Cu(In,Ga)(Se,S)_2$	Takuya Kato, Jyh-Lih Wu, Yoshiaki Hirai, Hiroki Sugimoto, and Veronica Bermudez	IEEE Journal of Photovoltaics Year: 2019 (IF: 3.398, Q1)	• Researchers at Solar Frontier further improved their solar cell from 22.3% to 22.9% by replacing K-treatment with Cs-treatment during absorber layer preparation • Conventional sulfurization-after-selenization (SAS) process was also replaced with a Rapid Thermal Process (RTP) by increasing the temperature ramp rate from 8–10 to 200–300 °C/min • New SAS process led to better quality absorber layer manifested as reduced V_{OC} and the extended minority carrier lifetime • The combination of the modified absorber and Cs treatment enables an absorber having wider $E_{g,min}$ to increase V_{OC} more efficiently with increased carrier density, reduced defect density, and suppressed carrier recombination • Cell area: 1 cm^2 • Type of buffer layer: extremely thin CBD-CdS (10 nm) • The alkali treatment improves tolerance for reduced CdS thickness

Recent Advances

Paper#3	Authors	Journal	Significant Findings
Improving the lateral homogeneity of Cu(In, Ga)Se2 layers fabricated by RF magnetron sputtering from a quaternary ceramic target	Linquan Zhang, Longlong Zeng, Chunhong Zeng, Yunfeng Liang, Ruijiang Hong	Ceramics International Year: 2018 (IF: 3.450, Q1)	• Authors subjected the as-sputtered Cu(In,Ga)Se_2 films to annealing treatment at atmospheric pressure with added Se pellets • Annealing duration was 30 minutes • Annealing temperature investigated: 475, 500, 525 and 550 °C • The annealed films were compact and composed of well-faceted grains with sizes of approximately 500–1000 nm • The crystallinity of the annealed films was significantly enhanced without phase separation nor formation of secondary phases • Single-layered and compact films were formed by recrystallization of columnar grains during the annealing process (FESEM images are on the next slide) • Authors also reported that tensile stress that was introduced into the CIGS films during the sputtering process and was subsequently eliminated by annealing treatment • Tensile stress is usually the cause of delamination of the CIGS layer from the Mo back contact • The results indicate that annealing treatment, with the addition of Se pellets, is a feasible way to improve the lateral homogeneities in composition and morphology of sputtered Cu(In,Ga)Se_2 films

Recent Advances



Recent Advances

Paper#4	Authors	Journal	Significant Findings
Electrical characterization and comparison of CIGS solar cells made with different structures and fabrication techniques	Rebekah L. Garris, Steve Johnston, Jian V. Li, Harvey L. Guthrey, Kannan Ramanathan, Lorelle M. Mansfield	Solar Energy Materials and Solar Cells Year: 2018 (IF: 6.019, Q1)	• The researchers studied the similarities and differences between high quality CIGS solar cells made with various structures and fabrication techniques • The underlying electrical behavior governing the performance of these CIGS-based solar cells were investigated • CIGS solar cell samples were obtained from different research laboratories and industrial companies (see Table 1 on the following slide) • Performance parameters of the CIGS samples, shown in Table 2, indicate that despite significant differences in cell structures, fabrication techniques, carrier-density depth profiles, and activation energies, the device performance was similar • Cross-sectional EBIC signals overlaid on FESEM images showed that the different growth processes and composition variations affected the electric field distribution in the CIGS devices (see Figure 1 on slide 8) • This is a strong indicator that current collection profile in a device is influenced by the type substrate and the absorber deposition process

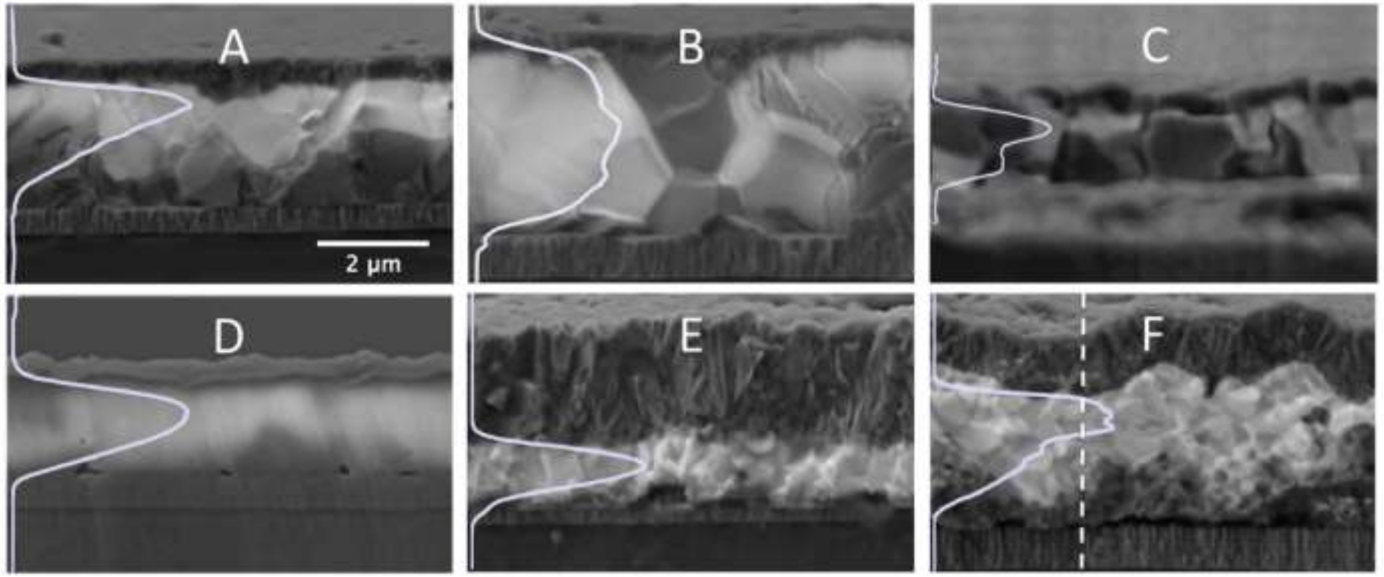
Recent Advances

Table 1
Summary of cell structures and fabrication processes for six different fabricators, reprinted from [1].

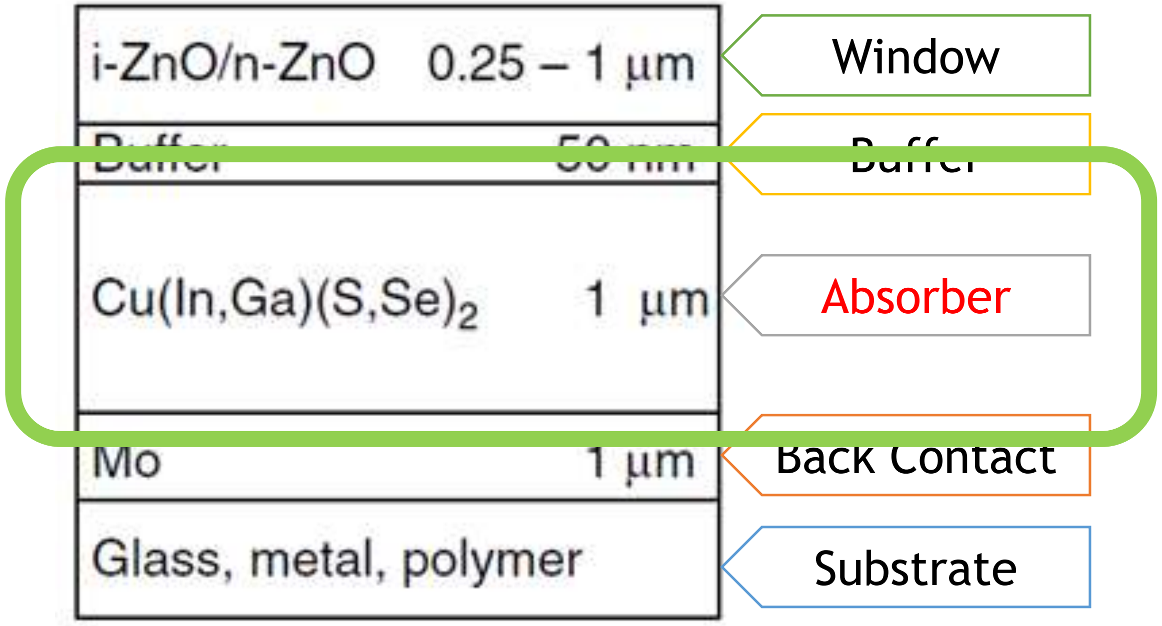
Fabricator	Substrate	Absorber process	Absorber	Buffer	Cell structure
A	Glass	Three-stage Co-evaporation	$Cu(In,Ga)Se_2$	CdS	ZnO:Al/i-ZnO/CdS/CIGS/Mo
B	Glass	Three-stage Co-evaporation	$(Ag,Cu)(In,Ga)Se_2$	CdS	ITO[a]/i-ZnO/CdS/ACIGS/Mo
C	Stainless steel (R2R[b])	Co-sputtering	$Cu(In,Ga)Se_2$	CdS	ZnO:Al/i-ZnO/CdS/CIGS/Mo
D	Stainless steel (R2R)	Three-stage Co-evaporation	$Cu(In,Ga)Se_2$	CdS	ITO/i-ZnO/CdS/CIGS/Mo
E	Glass	Metal-precursor reaction with H_2Se/H_2S	$Cu(In,Ga)(S,Se,S,See)_2$	Thin CdS	ZnO:B/ZnO/CdS/CIGSSe/Mo
F	Glass	Metal-precursor reaction with H_2Se/H_2S	$Cu(In,Ga)(S,Se,S,See)_2$	Thin Zn(O,O,S)	ZnO:B/ZnO/Zn(O,O,S)/CIGSSe/Mo

Table 2
Parameter table from J-V curves of representative devices, reprinted from [1].

Sample	V_{OC} (mV)	J_{SC} (mA/cm^2)	*FF* (%)	η (%)	E_g (eV)
A	701	34.3	80.7	19.4	1.17
B	742	33.0	77.8	19.1	1.22
C	698	32.3	77.4	17.5	1.22
D	656	34.3	69.3	15.6	1.18
E	571	34.6	72.3	14.3	1.09
F	669	38.3	73.2	18.8	1.05



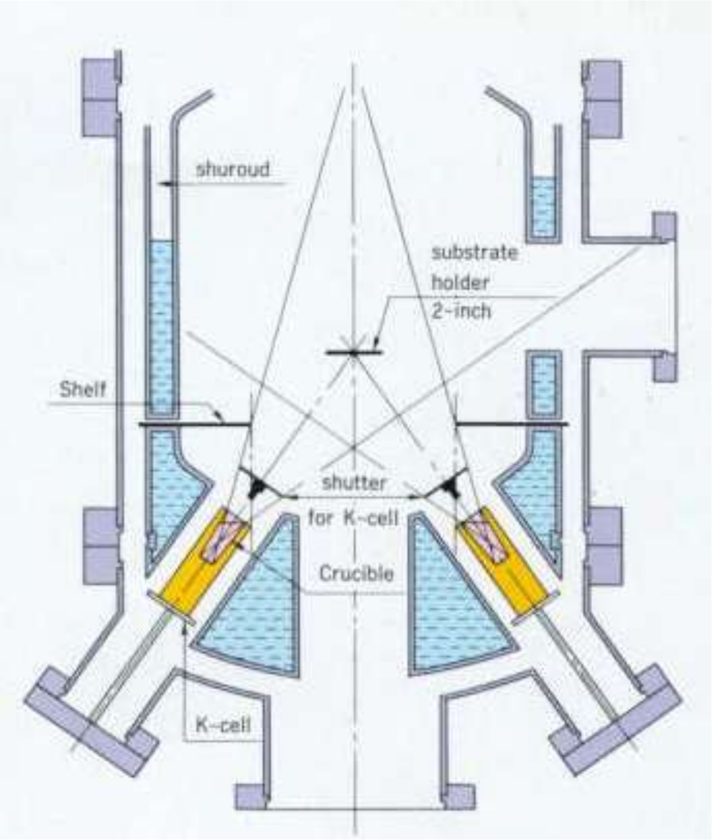
Device Fabrication (CRUCIAL)



Co-evaporation

Co-evaporation

Co-Evaporation System (MBE) for CIGS Thin Film Growth - 1



Substrate holder(2 inch,800℃,rotation)

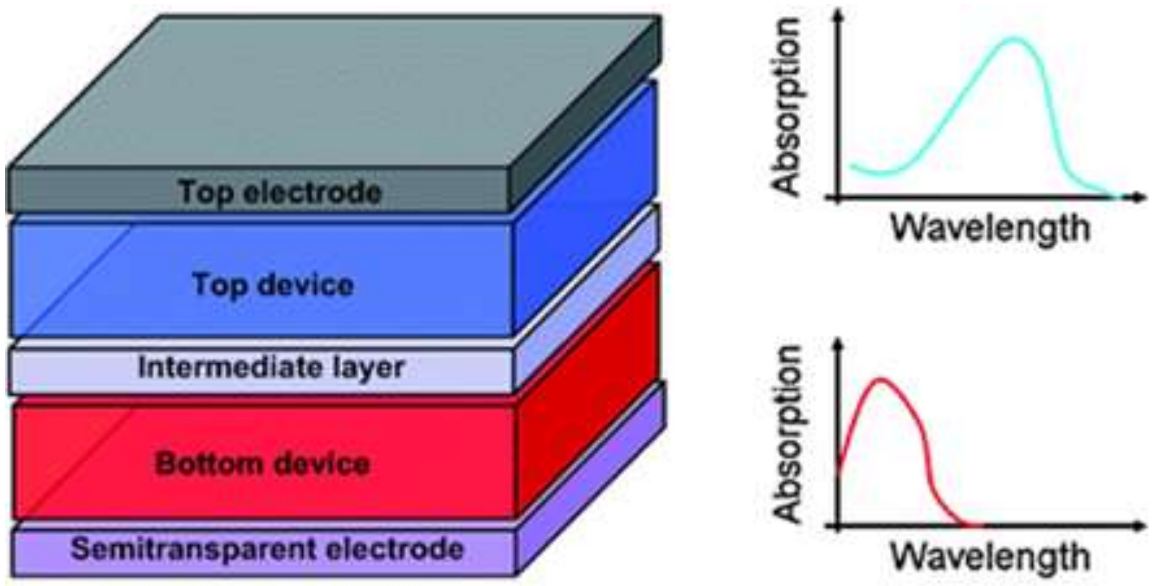
Growth chamber(φ406×600,Liq N2 shuroud)

K-cell(Max1200℃,5～25cc,PBN crucible,shutter)

Valved cracking cell(max500℃,shutter)

Prospects of CIGS PV Device

- The ability to tailor the bandgap of CIGS devices to create larger bandgap absorber layers opens up the possibility of using CIGS in tandem PV devices.



CZTS (Se) Cell

- Band Gap :1.4-1.6 eV – Direct
- Deposition Techniques : PVD;Sputtering;Spray Pyrolysis; Electrodeposition; Screen Printing
- Theoretical Efficiency : ~30%
- Efficiency Obtained : up to about 9.6 % ⟶ 11%
- Abundant, cheap and green materials

Problems :

- Multiphasic ;Mixed Phases (monoclinic,orthorhombic,cubic,tetragonal,stannite)
- Multistructural;Structural and Electronic Inhomogeneities
- Difficult to control complicated synthesis process
- Time and temperature stability questionable

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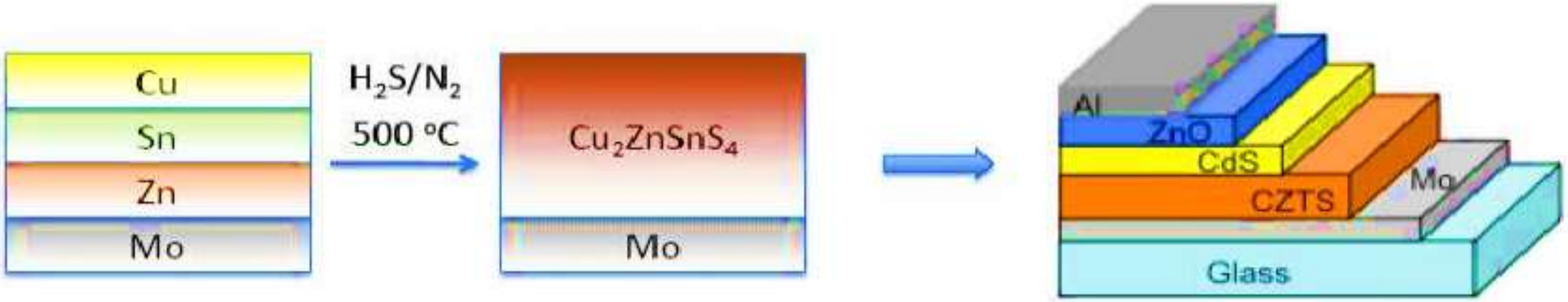
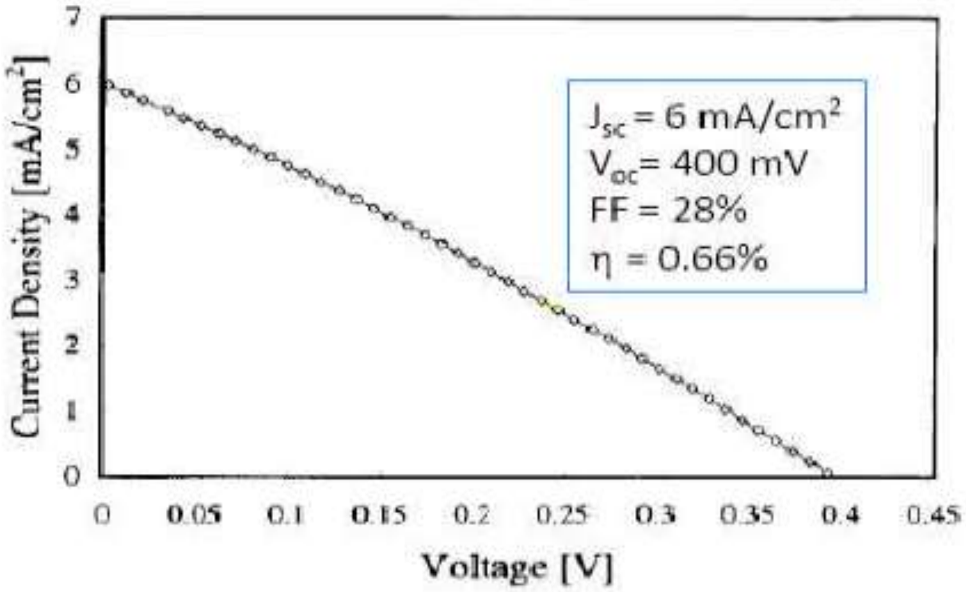
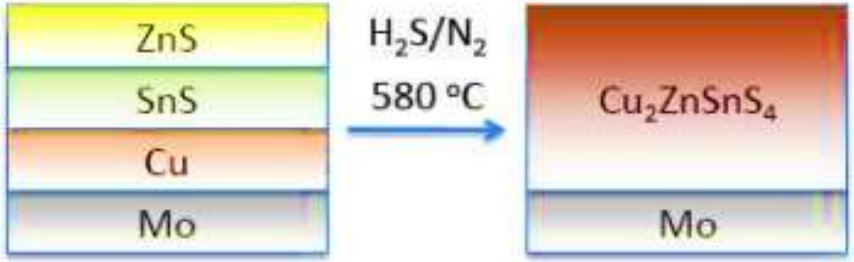
CZTS Solar Cells by Sulfurization of a stack of evaporated Zn/Sn/Cu films

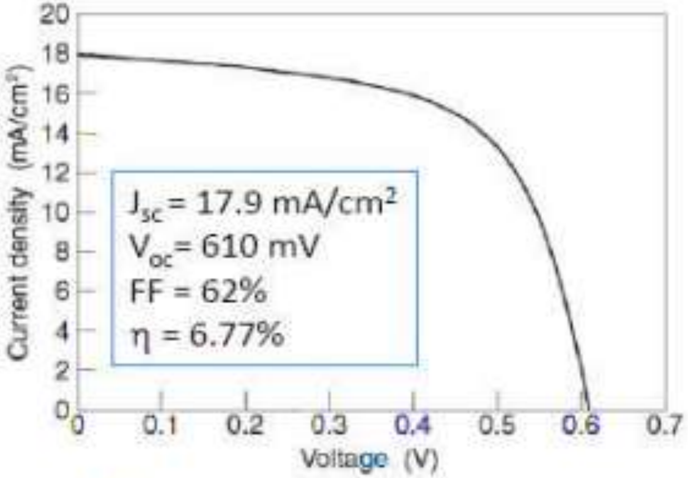


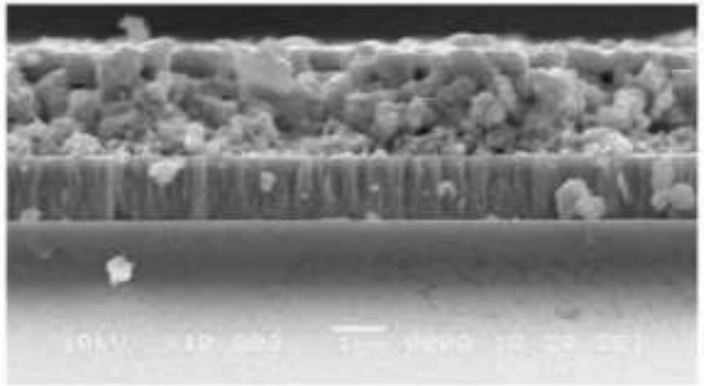


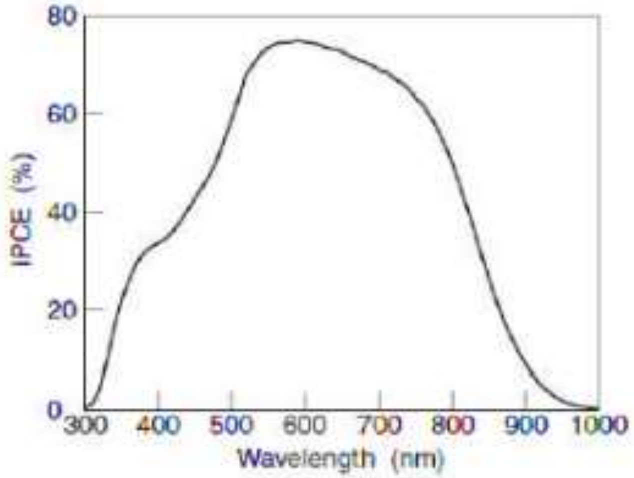
Katagiri et al. Sol Energ. Mater. Sol. C. , **49**, 407 (1997).

CZTS Solar Cells by Sulfurization of co-sputtered Cu, SnS and ZnS film



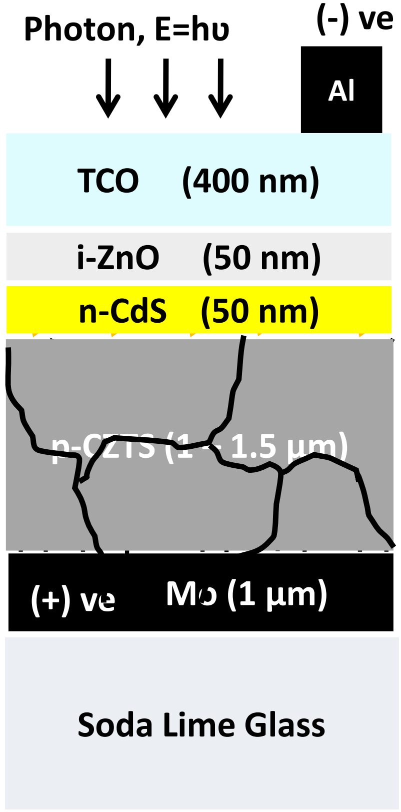






Katagiri et al. Applied Physics Express, **1**, 041201 (2008).

CZTS Device Fabrication



Thermally Evaporated

RF-Sputtered

Chemical Bath Deposited

3. KCN Etching

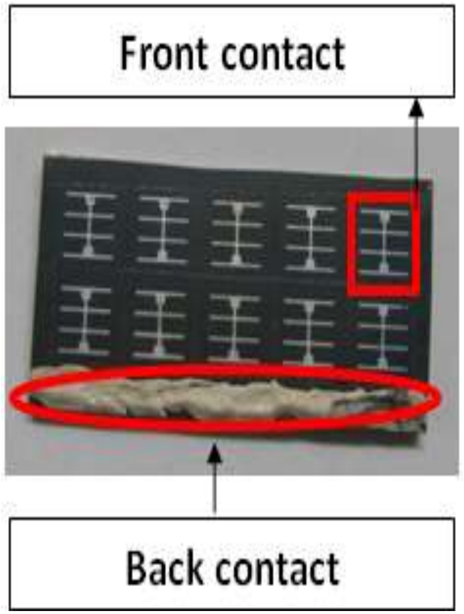
2. Sulphurization Process

1. Single Step RF-Sputtered CZTS Precursor

DC-Sputtered

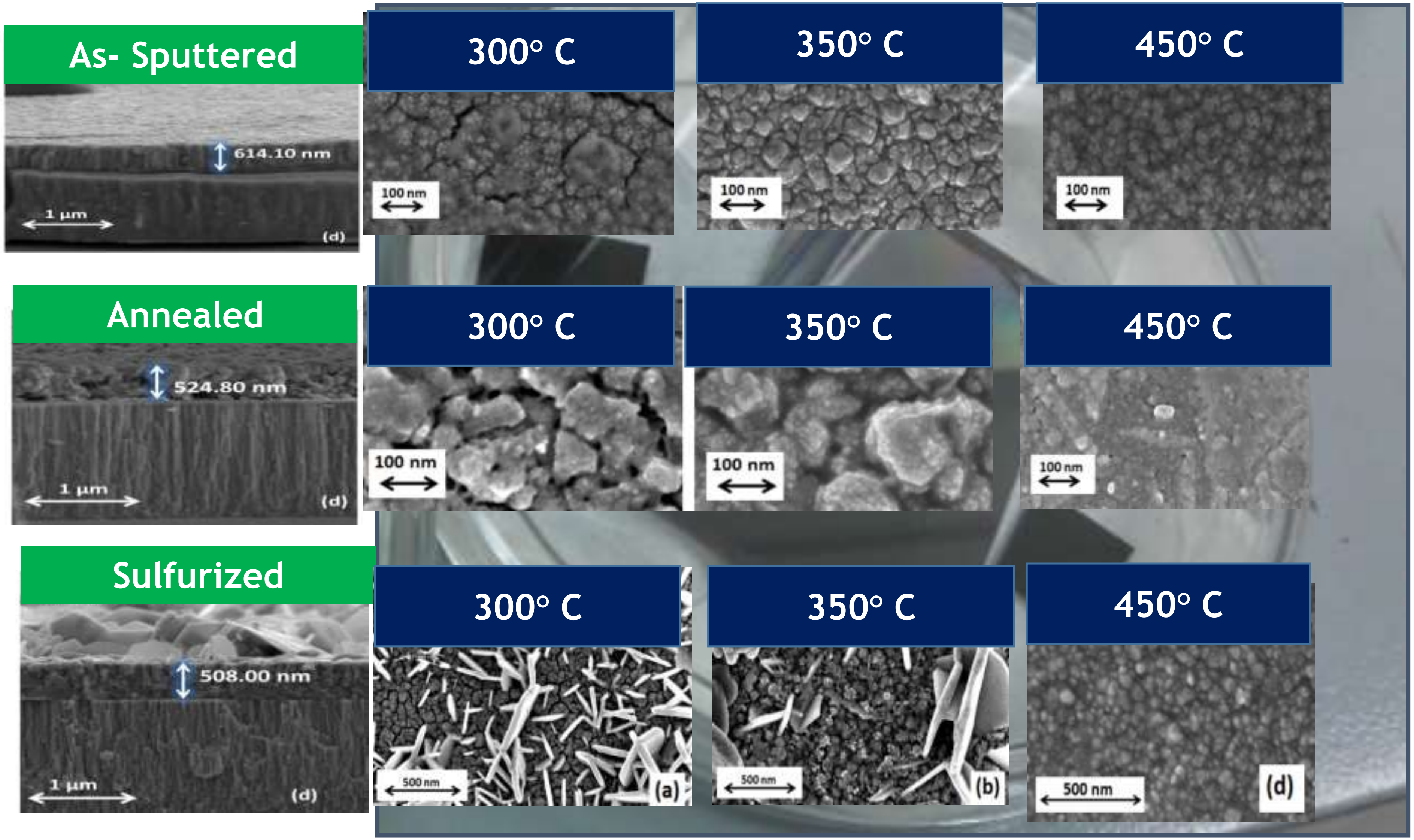
Ultrasonification & N_2 drying

Step by Step CZTS Device Fabrication Process



Practical CZTS Device

THIN FILM DEPOSITION & CHARACTERIZATION OF CZTS



Scanning Electron Microscopy (SEM)

CZTS at Present

Sulphurization Process Parameters

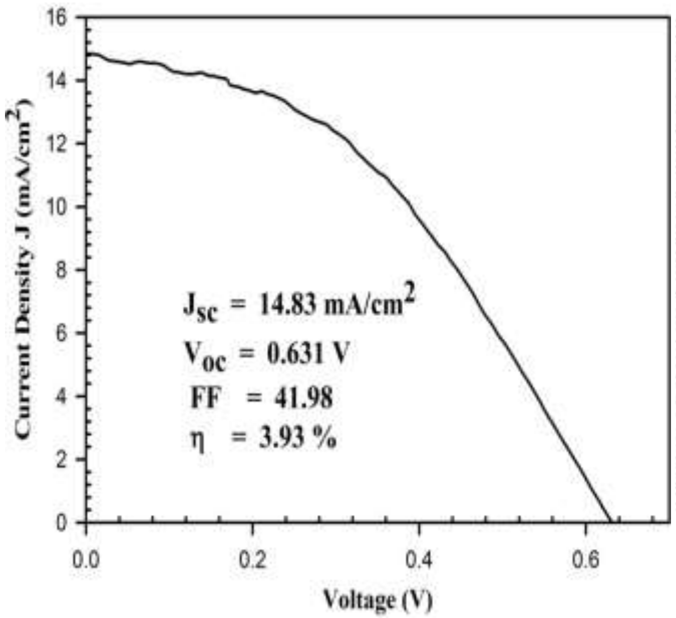
Parameters	Condition
Stack Configuration	SLG/Mo/CZTS
Heating Ramp-Rate	5 ˚C/Minute
Cooling Rate	Natural cooling
Base Pressure	0.0001 ATM (90 mTorr)
Working Pressure	0.5 ATM (380 Torr)
Background Gas	Purified N_2 (99.99 %)
Sulphur Content	62.50 mg
Holding Time	45 Minutes
Sulphurization Temperature	560 ˚C

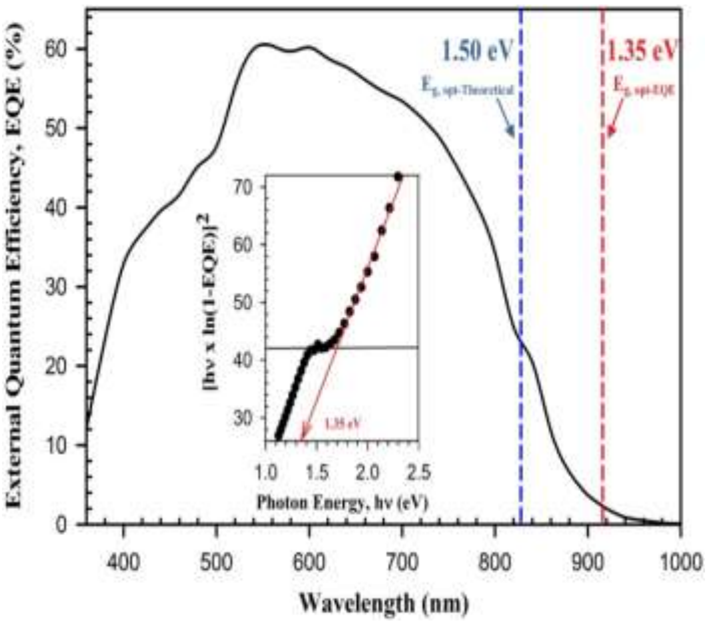
KCN Etching 10 wt%, 2 Minutes

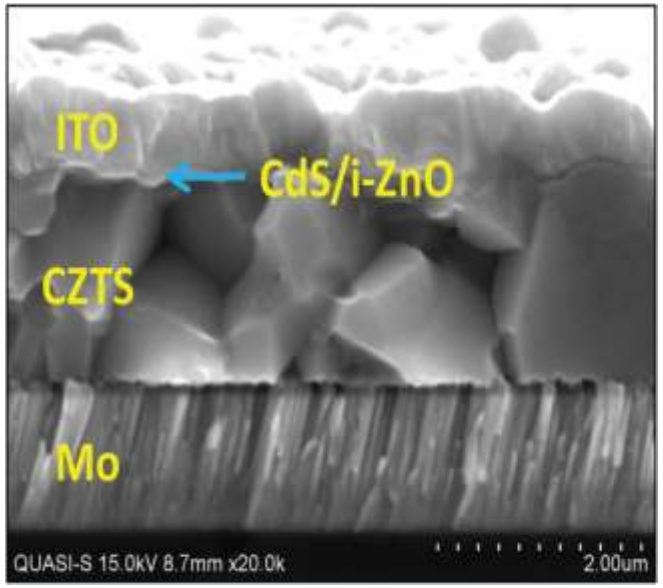
CdS by CBD, 68 ˚C to 70 ˚C

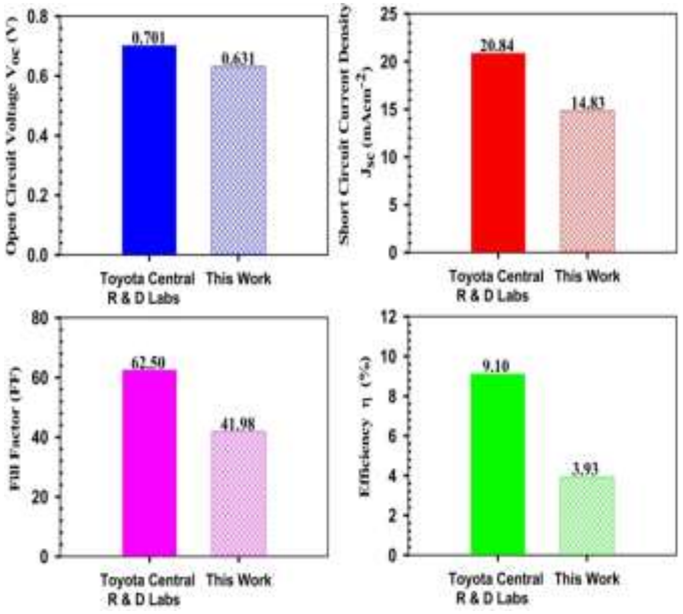
i-ZnO, ITO & Al Layers

Mechanical Scribing









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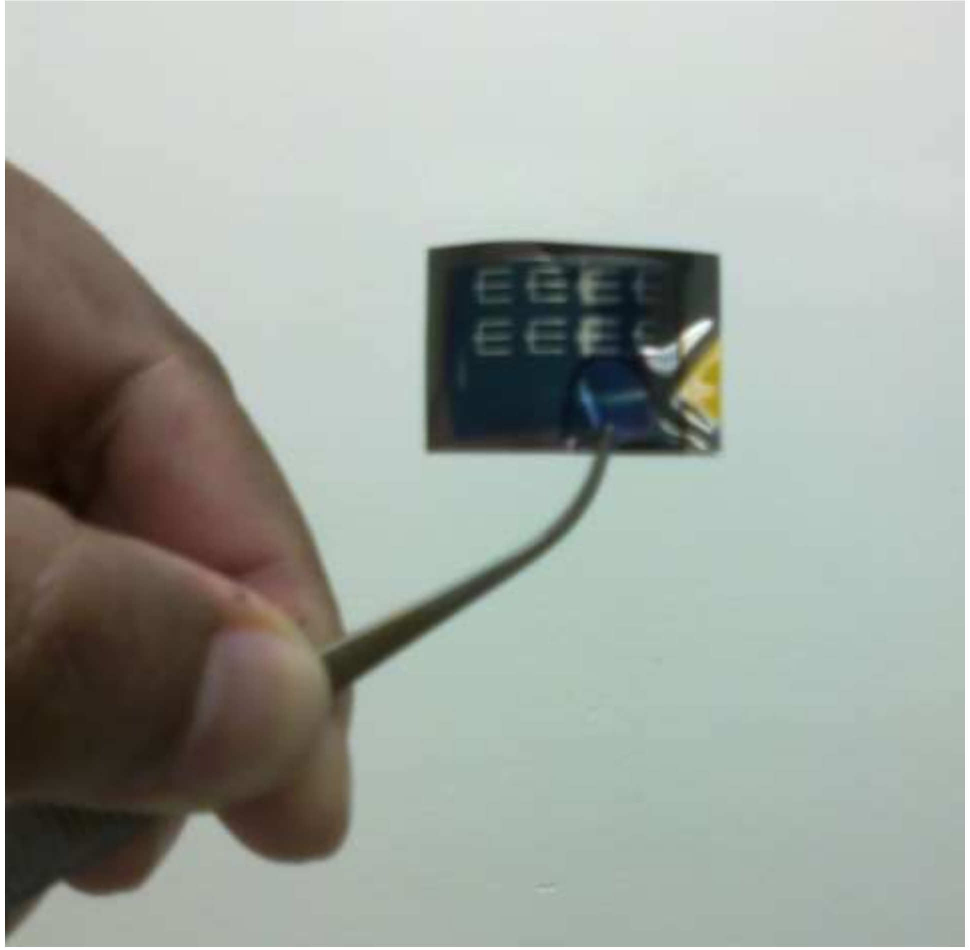
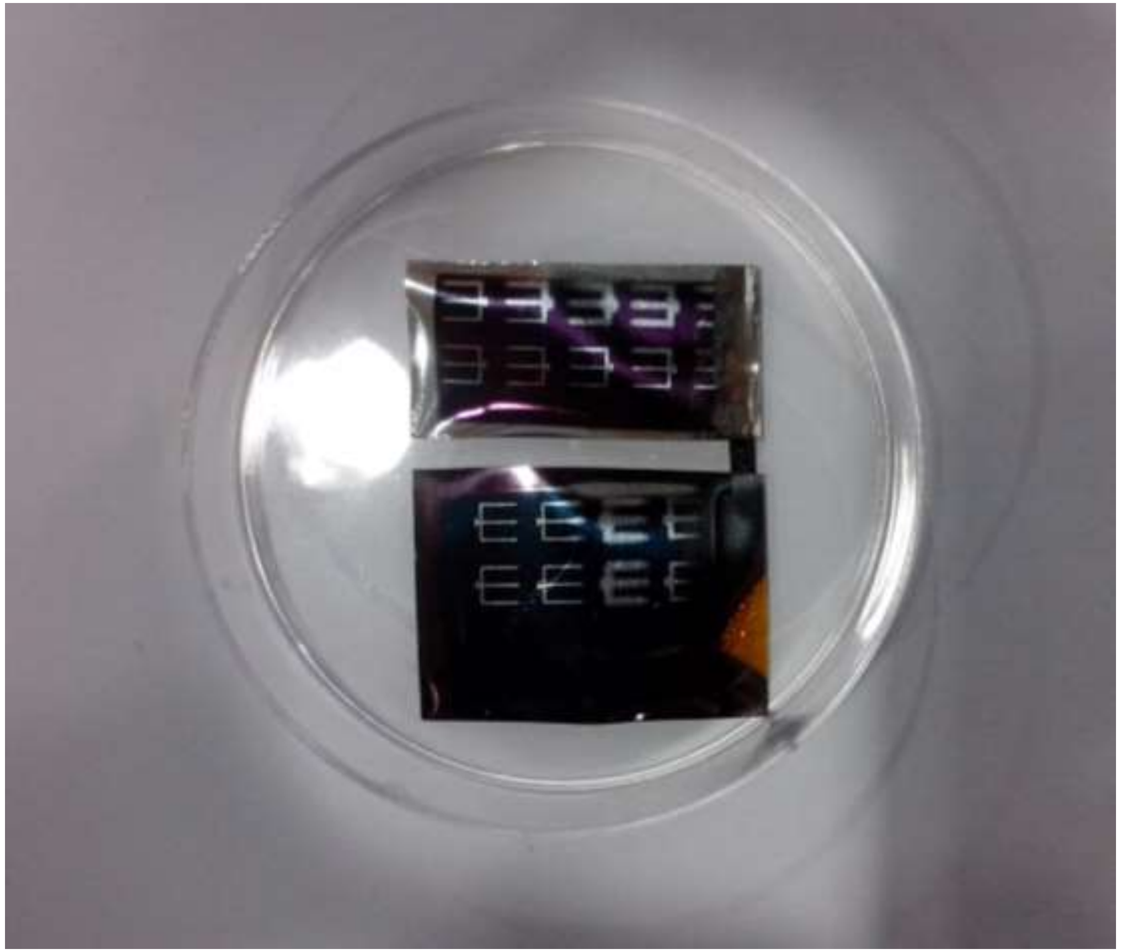
CZTS Flexible Solar Cells





Cu2ZnSnS4 solar cells with over 10% power conversion efficiency

Recent Advances

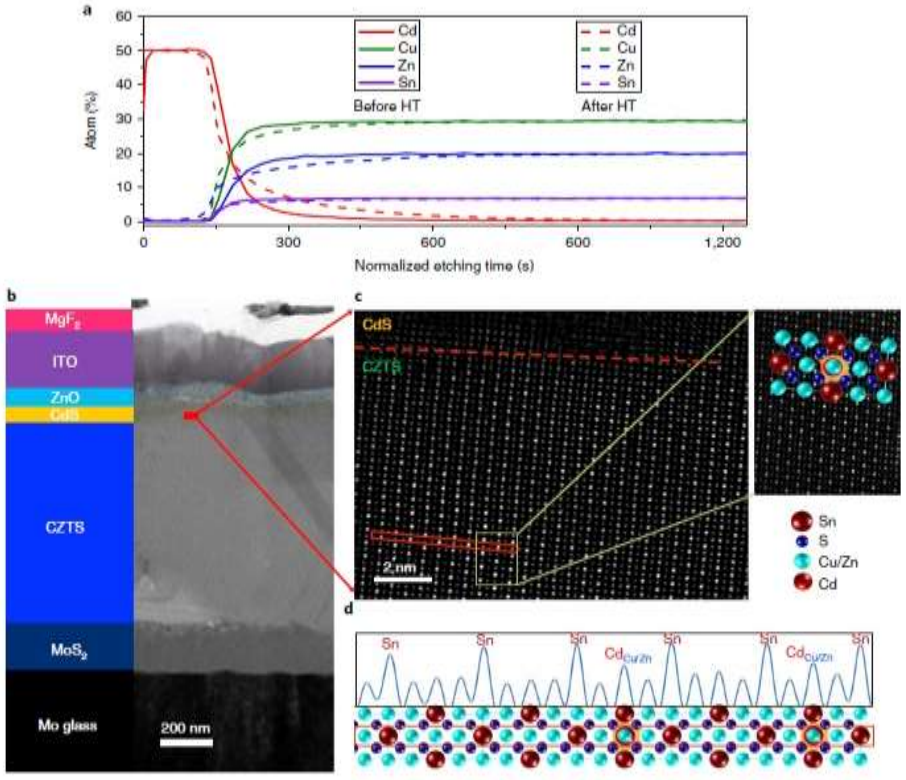


Fig. 3 | Elemental inter-diffusion and high-resolution imaging. a, XPS elemental profiles of heterojunction with and without the heat treatment (HT) process. b, Bright-field TEM cross-sectional image of CZTS device with the HT process, with the corresponding device structure schema shown left. c, Filtered atomic resolution HAADF image taken at the region near the CdS/CZTS interface. d, The intensity profile in a row of cations is marked by the red rectangle showing the cation exchange (Cd occupying Cu/Zn site).

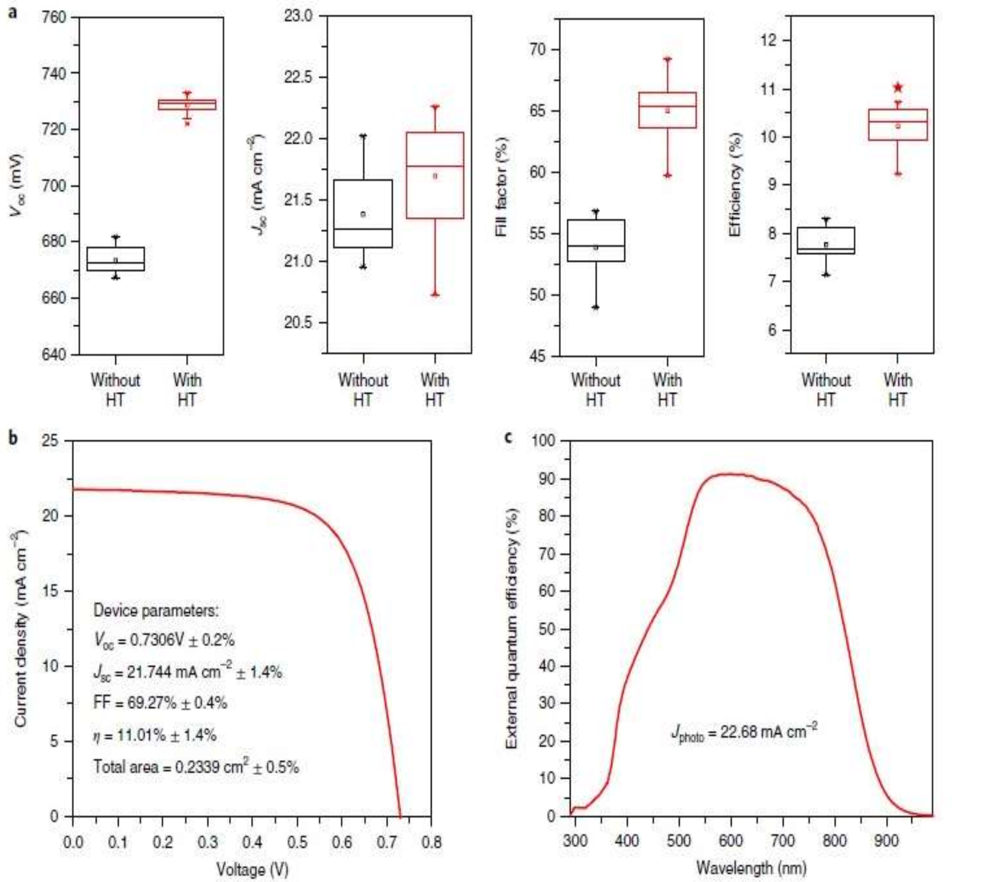


Fig. 1 | Photovoltaic device properties for the 11.0% efficient solar cell. a, Statistical box plot of device performance parameters with and without optimized HT. The box plot denotes median (centre line), mean value (dots), 25th (bottom edge of the box), 75th (top edge of the box), 95th (upper whisker) and 5th (lower whisker) percentiles. The sample size in each column is 10 devices. The red star denotes the efficiency of champion cell. b, Certified J–V curve and c, EQE curve for the highest efficiency Cu_2ZnSnS_4 device using the HT process.

Table 1 | Detailed device performance parameters estimated for a one-diode model.

CZTS device	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF(%)	Eff (%)	$R_{S,L}$ (Ω cm^2)	$G_{S,L}$ (mS cm^{-2})	A	J_0 (A cm^{-2})
Without HT	672.5	20.65	56.29	7.82	4.40	0.56	2.61	9.0×10^{-7}
With HT	730.6	21.74	69.27	11.01	2.58	0.98	1.44	6.8×10^{-11}

Ref: Yan et.al., Nature Energy 2018

High Efficiency CTS and CTGS Thin-Film Solar Cells

Recent Advances

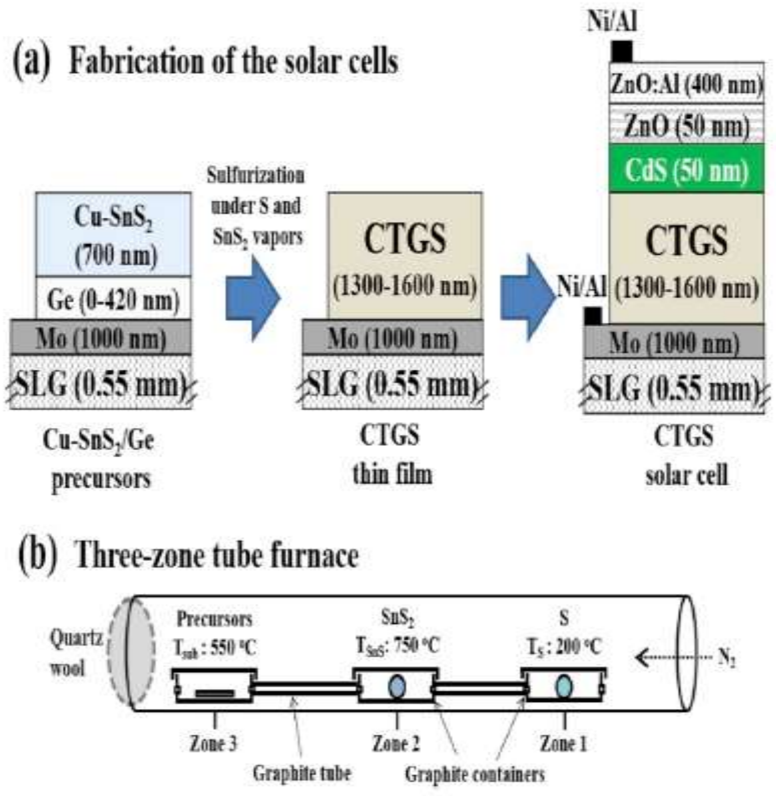


Fig. 1. (a) Structures of stacked precursors, CTGS thin film, and CTGS solar cell, as well as (b) schematic of three-zone tube furnace for sulfurization of the stacked precursors to form the CTGS thin films under S and SnS_2 vapors.

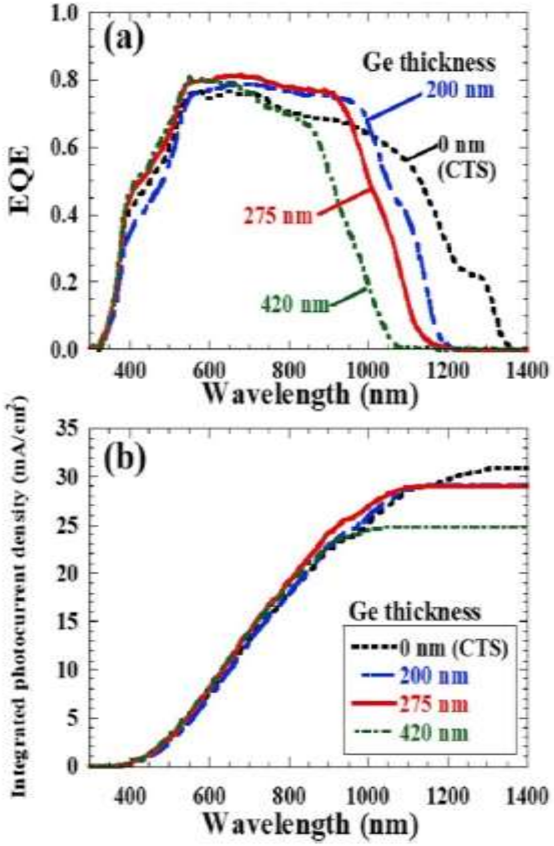


Fig. 6. (a) EQE spectra and their integrated photocurrent densities of the CTGS solar cells at each Ge thickness of 0, 200, 275, and 420 nm in Fig. 5.

Table 2

Photovoltaic performance parameters, E_g, $V_{OC,def}$, E_A, CBO, and E_U of the CTGS solar cells at each Ge thickness of 0, 200, 275, and 420 nm in Fig. 5. The E_g of the CTGS absorbers was estimated from the first EQE derivative.

Ge thickness (nm)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	η (%)	E_g (eV)	$V_{OC,def}$ (V)	E_A (eV)	CBO (eV)	E_U (meV)
0 (CTS)	31.1	0.251	45.4	3.6	0.95	0.700	0.70	−0.20	21
200	29.3	0.370	51.2	5.6	1.08	0.710	0.81	−0.33	22
275	29.4	0.344	49.7	4.9	1.14	0.796	0.80	−0.39	30
420	23.9	0.311	37.2	2.8	1.22	0.909	0.75	−0.47	32

Ref: Hayashi et.al., SOLMAT 2020

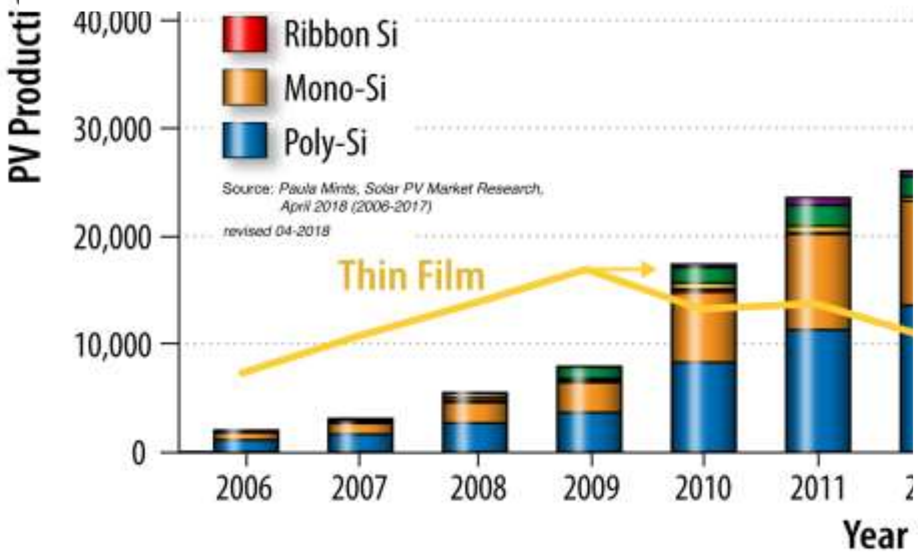
OUTLINE

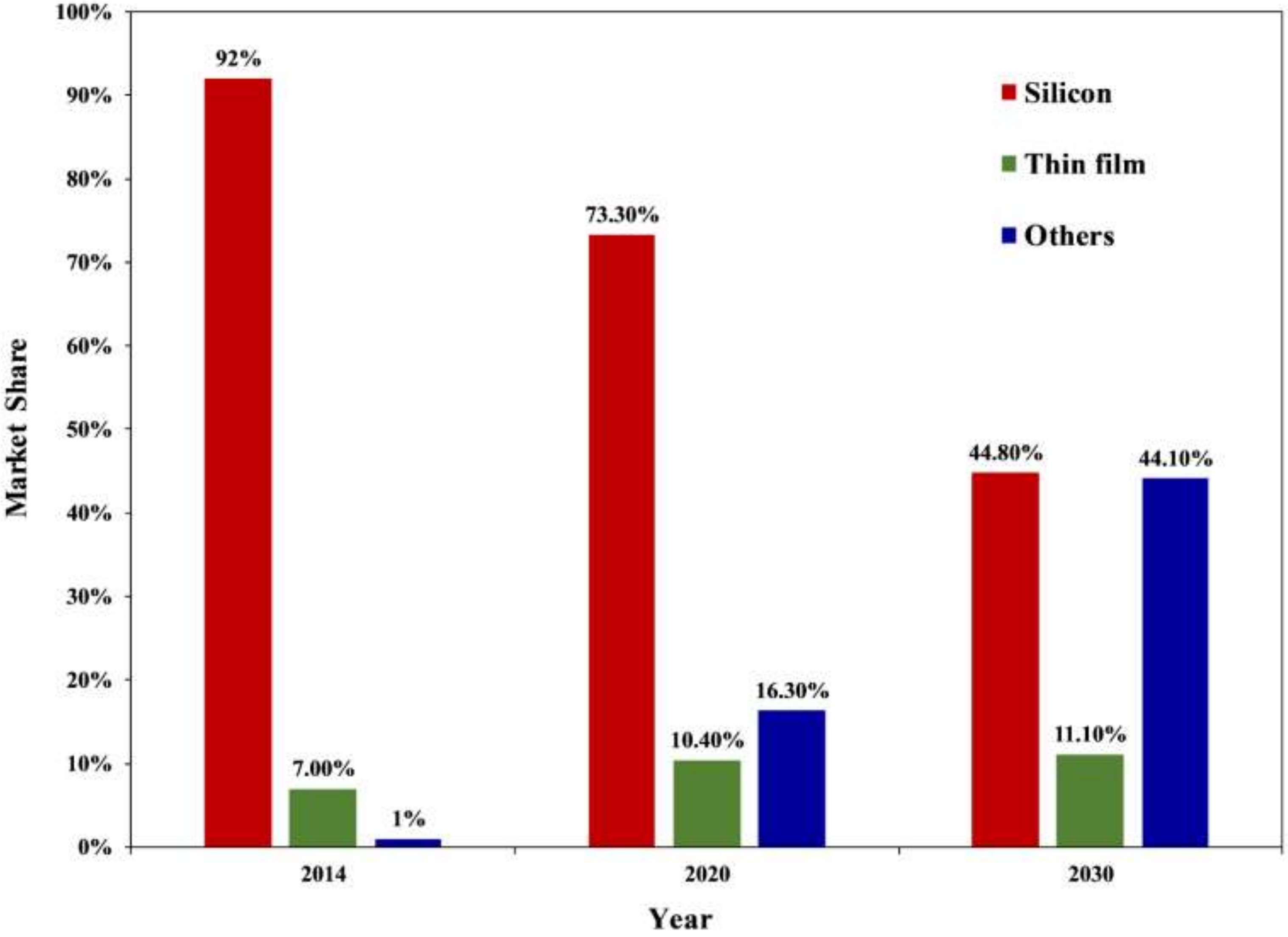
- Introduction
- Thin Film & Thin Film Deposition
- Solar Cells
- Implication of Thin Films into Solar Cells
  - aSi
  - CdTe
  - CIS (CIGSSe, CZTS, CTS)
- **Challenges and prospects**
- Conclusion

Market Share Projection of PV Panels by Technology Type (2014-2030)

- Market share of c-Si PV panels is projected to decrease from 92% to 44.8% between 2014 and 2030.

- The third-generation PV panels are predicted to reach 44.1%, from a base of 1% in 2014, over the same period.

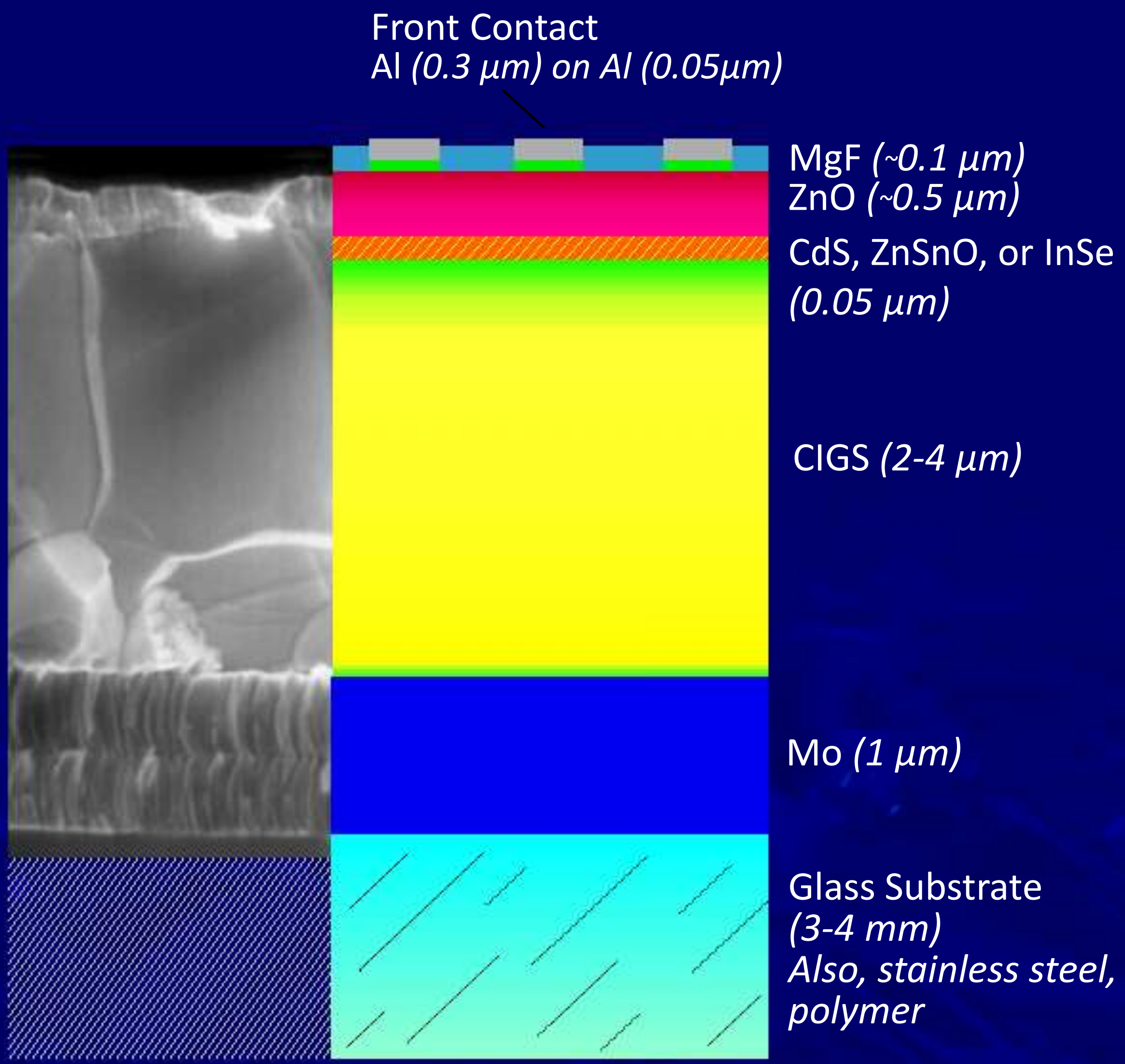




Thin Films: The commercial leaders

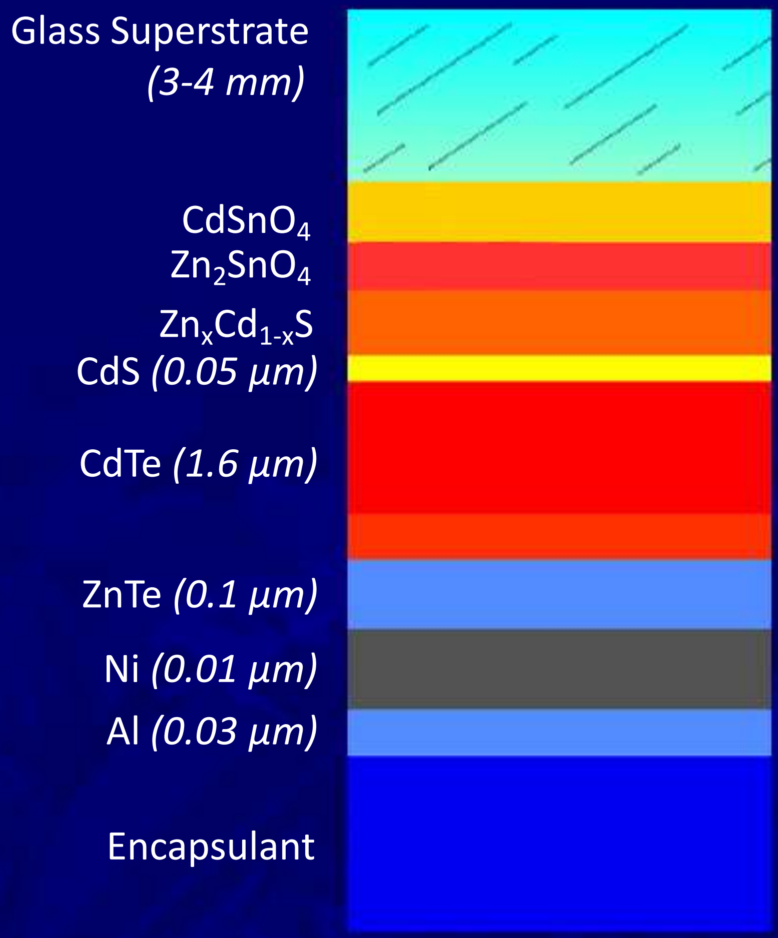
$Cu(InGa)(S,Se)_2$ Thin Film Cell

Best Research: 22.9% - Solar Frontier

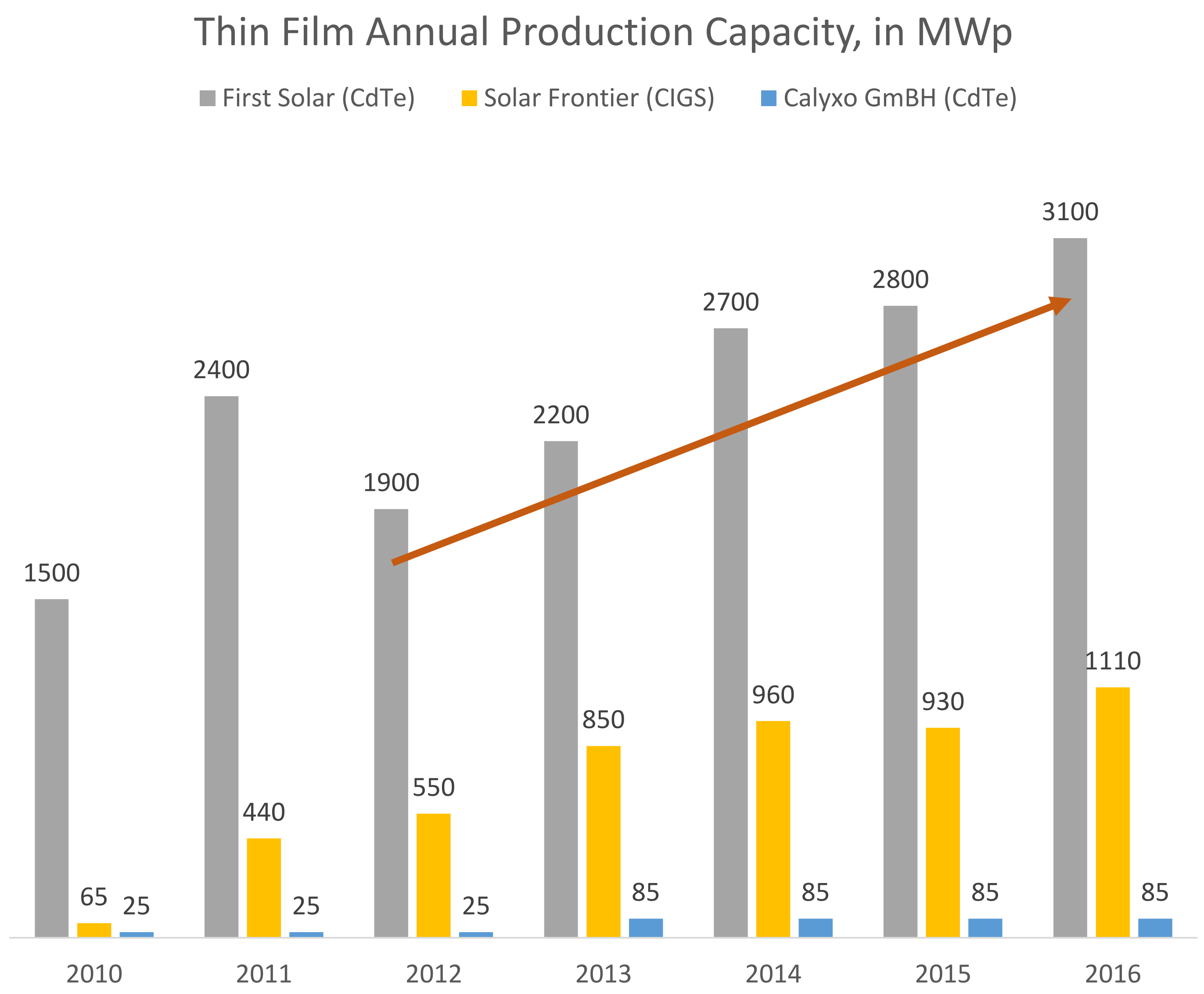


CdTe Thin Film Cell

Best Research: 21.1% - First Solar



Thin Film (CdTe & CIGS) Production Capacity



- First Solar (CdTe) dominates the thin film module manufacturer segment with 3.1GWp annual capacity in 2016.
    - From 2012, First Solar capacity increase with module efficiency improvement without new plant investment [1].

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PV Technology Comparison: Thin Film vs Multicrystalline Silicon

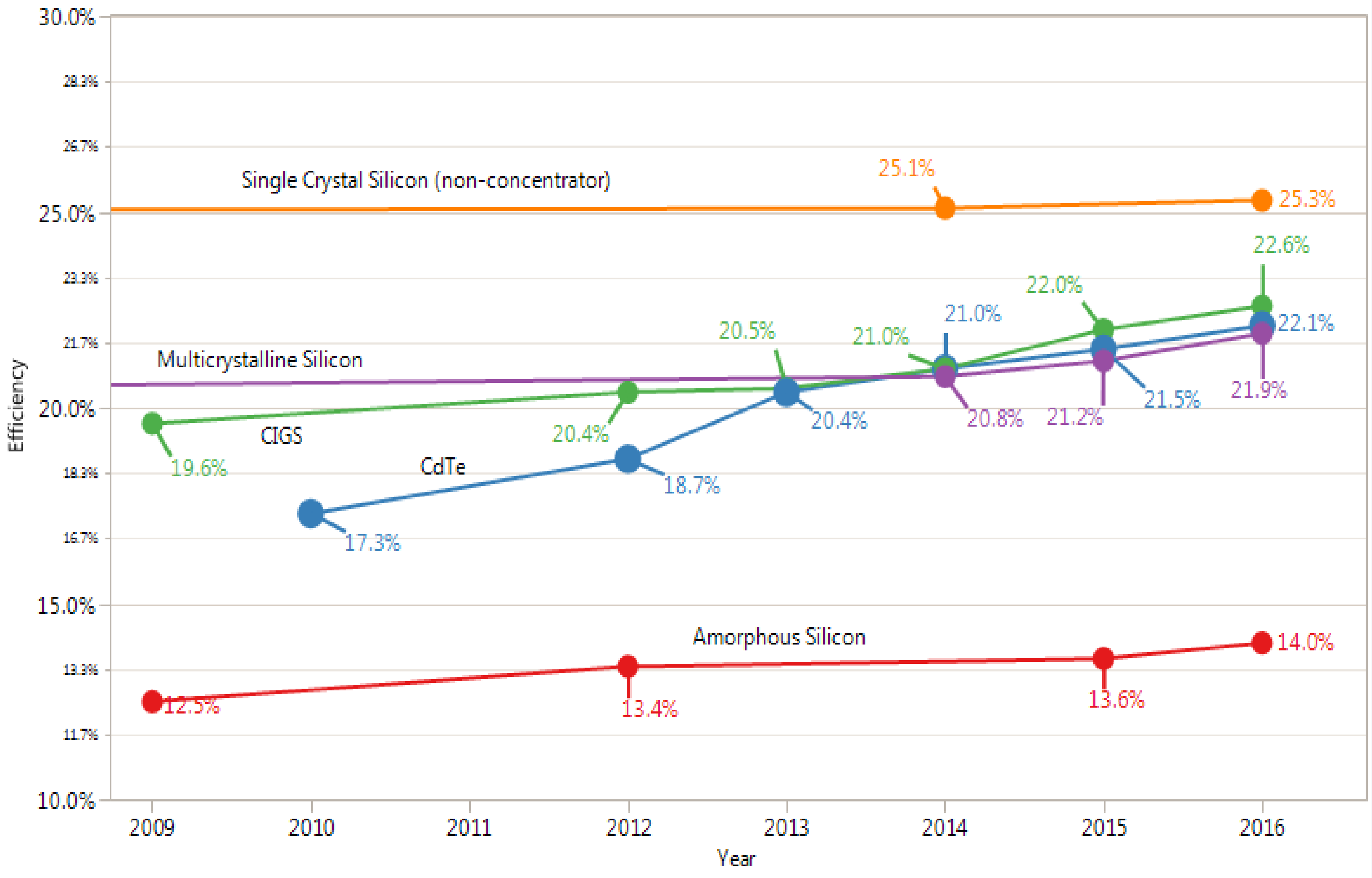
Universiti Tenaga Nasional The National Energy University

	a-Si	CdTe	CIGS	Multi c-Si
Best research-cell efficiency	**14.0% [1]**	**22.1% [1]**	**22.6% [1]**	**21.9% [1]**
Best solar module efficiency	12.3% [1]	18.6% [1]	17.5% [1]	19.9% [1]
Commercial module efficiency	10.0% (Sharp) [3]	17.0% (First Solar) [5]	14.2% (Solar Frontier) [2]	17.3% (Trina) [6]
Module Temperature Coefficient (Pmpp)	**-0.24%/°C [3]**	**-0.28%/°C) [5]**	**–0.31 %/K [2]**	**-0.41%/°C (Trina) [6]**
Advantages	Mature technology Excellent for small devices (e.g. pocket calculators)	Low cost manufacturing Lower temperature coefficient	High efficiency Glass or flexible substrates Lower temperature coefficient	Mature technology High volume production, competitive cost.
Disadvantages	Low efficiency High cost equipment, less popular now as lower Si price	Medium efficiency Rigid glass substrates Cd toxicity is a concern	High cost & traditional process Quarternary compound, complicated process control. No Cd	Medium efficiency Poorer temperature coefficient
Major manufacturers (2016 production capacity)	Sharp**, Uni Solar**	First Solar (3100MW) [5], Calyxo (85MW)	Solar Frontier (1110MW) [2]	Trina Solar (4825MW*) [6], Hanhwa Q-Cells (4583MW*) [9], Canadian Solar (5232MW*) [7], JA Solar (4920MW*) [8]

- CdTe and multicrystalline Si are competing best research cell and module efficiency and translate to commercialize module's efficiency.
- CIGS slow adoption to commercial.
- Temperature coefficient of thin films are better.

*Crystalline Si supplier capacity includes total mono and multicystalline.
**No data available, estimate a-Si production capacity is very low with Si price reduce tremendously in the past several years.

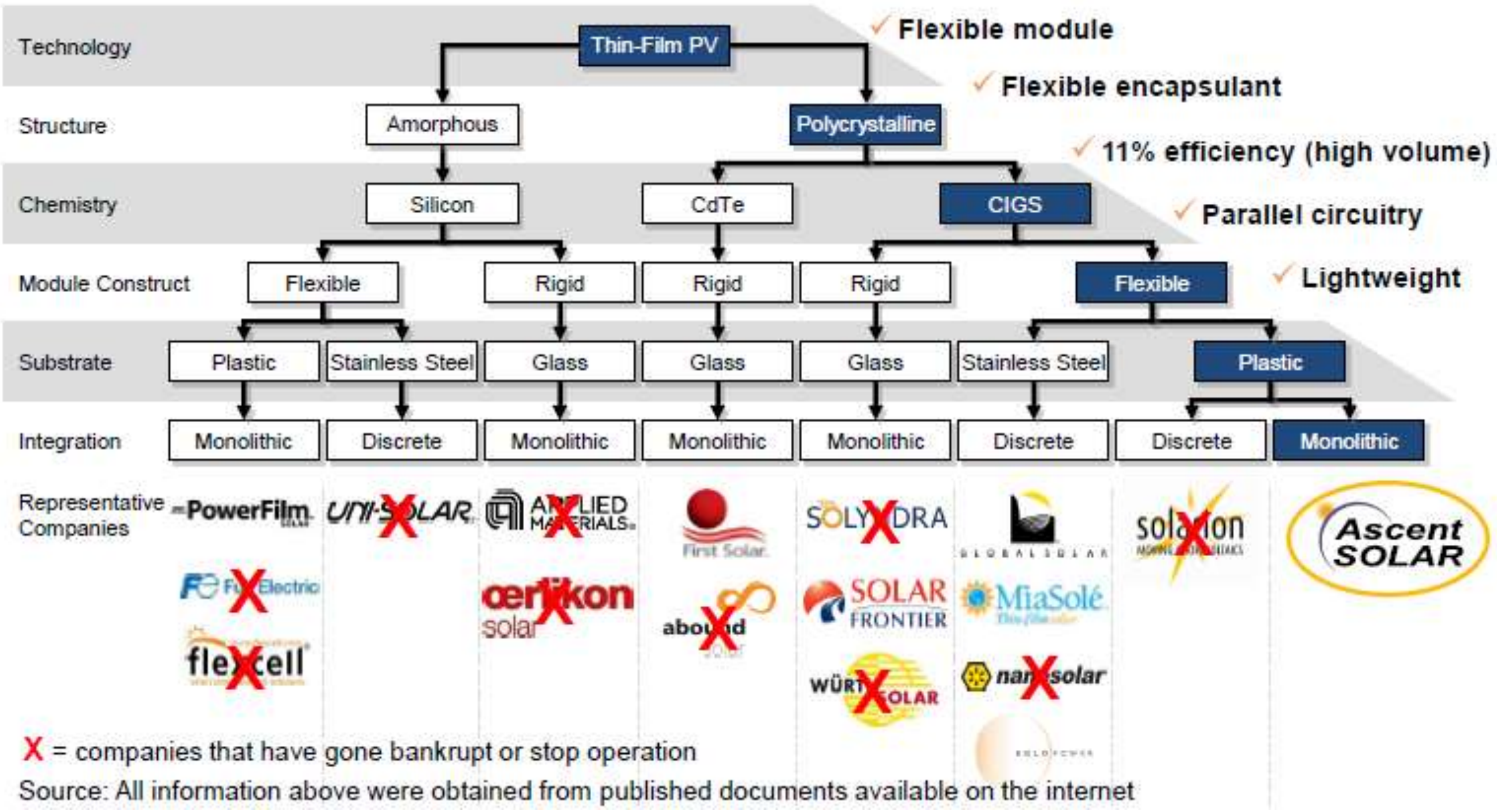
Best Efficiency Record: Snapshot of CdTe, a-Si, CIGS & c-Si



Source: https://www.nrel.gov/pv/assets/images/efficiency-chart.png

- Rapid development of CdTe and CIGS in the past 6 years.
- CdTe has the highest development with +4.8% efficiency improvement in 6 years. CIGS has +3% increment over the past 7 years.
  - Corporate spending for R&D and commercialize fund: First Solar utilized 4% - 5% of annual revenue. Spent $130M or 4.2% of total revenue in 2016 [1].
- Multicrystalline Si has some momentum recently with n-type high performance cells [2] from Fraunhofer Institute for Solar Energy Systems ISE. Still slow efficiency improvement compare to thin film.
- Monocrystalline Si and amorphous Si performance has very less efficiency improvement in the last 5 years.

The Casualties



Bankability

The capacity or capability to manufacture or produce a product competitively (e.g., with an acceptable profit, reliability, etc.)

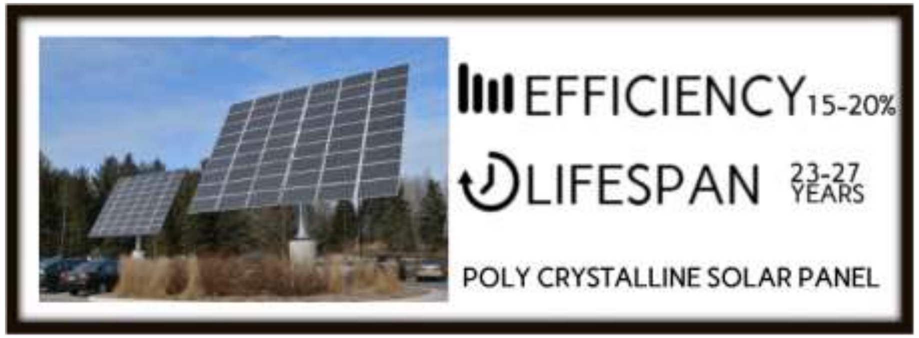
[22] Ascent Solar Investor Presentation (March 2016).

Challenges to Thin Film Technology Commercialization

1. Technical:
   - Continue adopt and translate record cells/module efficiency to high volume production → involve high capital investment.
   - Possible risk and challenge in high volume manufacturing, product performance and customer acceptance. Needs to deliver cost structure as forecast to remain competitive.
   - New innovation – potential commercialization of new disruptive technology (Perovskite/c-Si Tandem junction) that could produce higher efficiency at lower cost.
   - Innovation of lower cost c-Si raw material (fluidize bed poly, cheaper lower energy/higher purity ingot).
2. Economical:
   - Cost per watt pressure: Chinese manufacturers expansion and domestic demand will be the key. Cost per watt crash in 2H-2016 might be repeated if China's domestic demand shrink as 13th 5-year plan exceeded the target 3 years ahead.
     - Cost per watt < $0.30 – thin film manufacturers have to increase production capacity and produce at cheaper cost to maintain return margin and sustain competitive.
   - International trade barrier – introduction of impose tax to PV module in high PV demand countries will slow down the PV sector grow.
3. Political:
   - Governments abrupt energy policy change and benefit energy sources other than PV, e.g: US pulling out of Paris Agreement, promote traditional energy sources.
   - Unstable political regions delay the PV adoption: Middle east.

End of Life Recycling R&D Prospects

Industry standard warranty from Tier 1 manufacturers



Green PV Lifestyle Requirement

Preferred options for PV waste management

- As research and development (R&D) and technological advances continue with a maturing industry, the composition of panels is expected to require less raw material.

- Rapid global PV growth is expected to generate a robust secondary market for panel components and materials.

- As current PV installations reach the final decommissioning stage, recycling and material recovery will be preferable to panel disposal.

Source: IEA,End-of-Life PV 2016

Innovation in Approach:
Materials by Design + Artificial Intelligence

“Edisonian Approach” - *Conventional trial-by-error science*

“Materials-by-Design” - *Inverse process: Define desired materials functionalities and work backward to computationally define (determine) best-of-class materials*

Courtesy: Lawrence L. Kazmerski

Conclusion

1. Thin Film PVs are finally demonstrating their potential to provide affordable solar generated electricity
2. Leading thin film PV material – CdTe & CIS – have come a long way since its inception
   - The devices are becoming significantly more complex
   - Although much is known about the leading thin film PV, unresolved issues and open questions remain
3. Further advances in performance require improved understanding of the materials that comprise the solar cell, the key interfaces, and the device operation models (AI may be implemented)
   - Control of absorber properties
     - improve carrier lifetimes (therefore collection)
     - control doping concentration
   - Better contacts (front and back)
     - to improve yield
     - to improve performance
4. Scopes for Industry
   - Off-the-shelf manufacturing equipment
   - In-line diagnostics for improved quality control/yield
   - Validation of long term reliability
   - Bridge the performance gap between small cells and commercial modules
   - Sustainable Recycling process of end-of-life PV panels

Current R&D Priorities

- **Materials and Devices**
- **Manufacturing**
- **Reliability**

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