

## PV Technology:

### Lecture 8: Inorganic Thin-film Solar Cells

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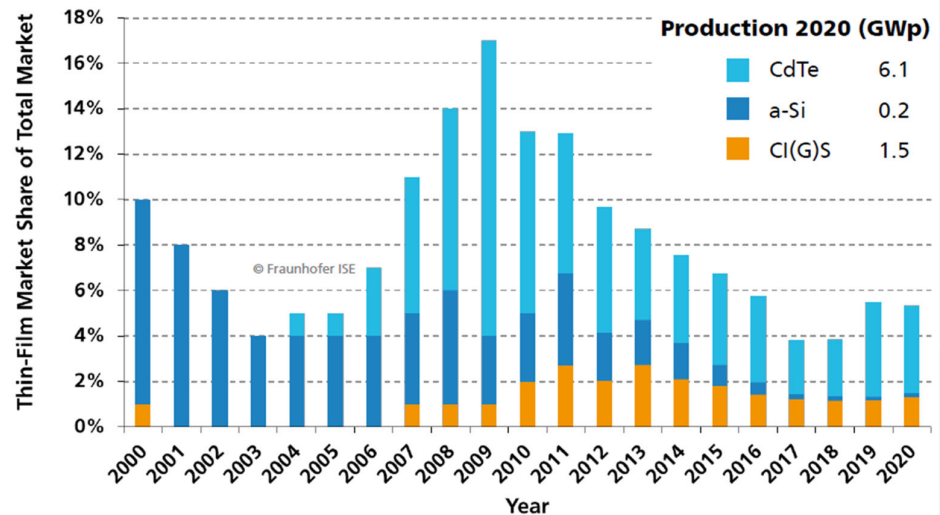
## Thin Film PV

General motivation for thin-film PV:

- Technical:
  - Significant losses during wafering process
  - Solar cells end up inside a sheet of glass anyway, so why not use the glass as a substrate to deposit onto?
  - With good light trapping  $\Rightarrow$  don't need 200  $\mu\text{m}$  of Si, 2  $\mu\text{m}$  of semiconductor enough (even with Si)
  - Potentially higher throughput
- Marketing: More uniform product appearance
- Economic:
  - Very energy-intensive process growing MG-Si, and then either Cz c-Si or mc-Si ingots
  - Thus, can possibly have a cost advantage

# PV Market Today

- Thin-film PV represents ~5% of global annual production
- Had largest market share in 2009  $\pm$  2 years  $\Rightarrow$  years when there was a Si shortage
- Cadmium telluride (CdTe) clearly has largest share
- Copper indium gallium diselenide (CIGS) second
- Amorphous silicon (a-Si) PV market share shrinking



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Source: <https://www.ise.fraunhofer.de/en/downloads-englisch/pdf-files-englisch/photovoltaics-report-slides.pdf>

## Comparing Thin Film PV Modules



Photo: Manz



Photo: First Solar



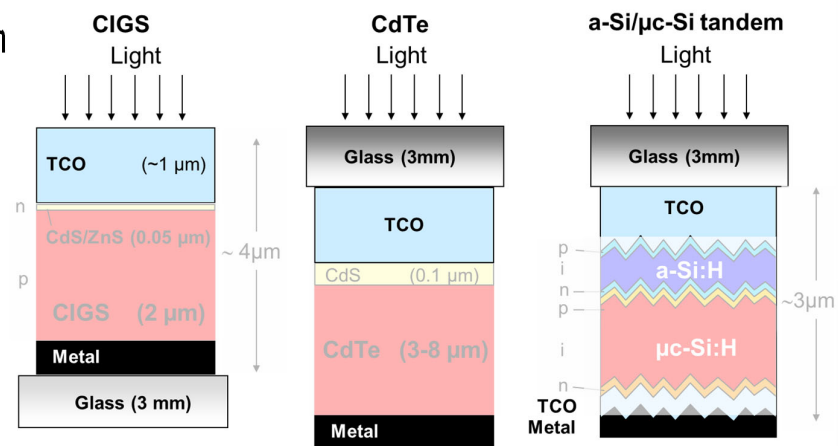
Photo: Schott Solar

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# Comparing Thin Film Solar Cells

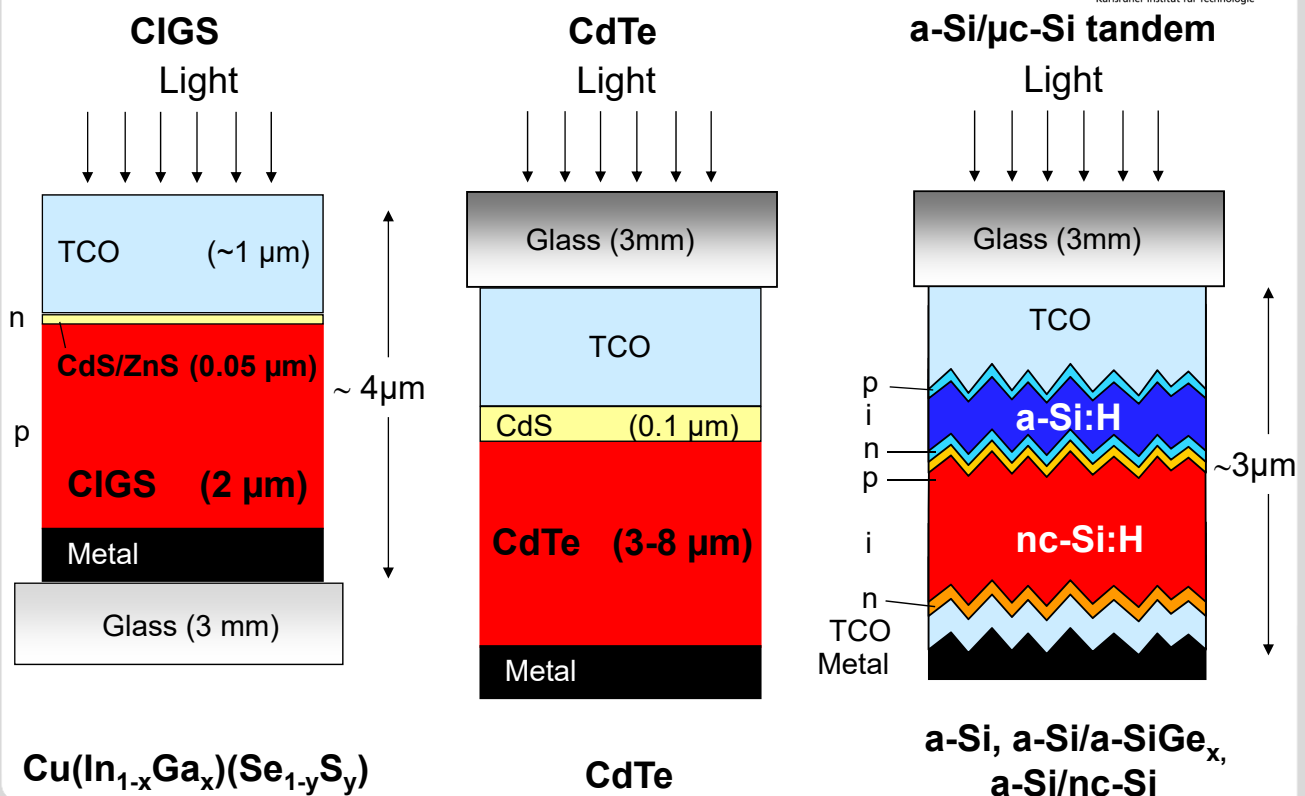
What do all thin-film PV devices have in common?

- Glass substrate (e.g. CIGS) or superstrate (e.g. CdTe, a-Si)  
– other materials also used, e.g. stainless steel, polymer foil
- Transparent conducting oxide (TCO) to extract current from the top-side of the device
- Thin absorber layers: 100nm – 5μm
- *pn* or *pin* junction
- Rear metal contact



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# Comparing Thin Film Solar Cells



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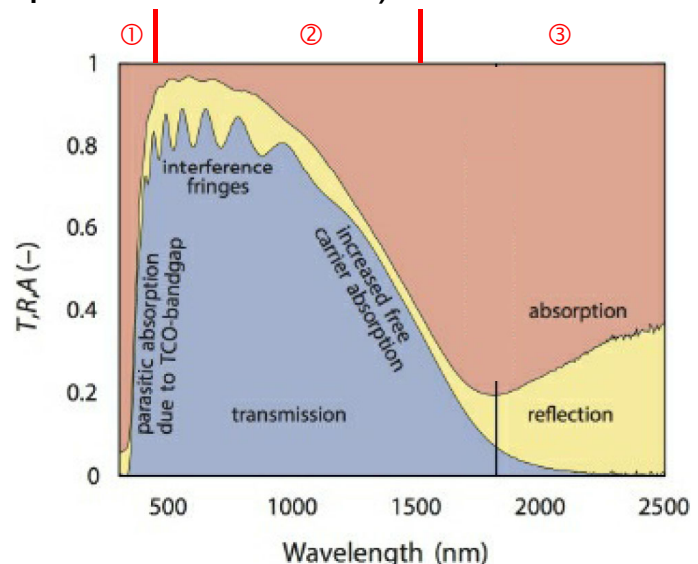
# Transparent Conducting Oxides

- TCO layer has two roles:
  - i) acts as electric front contact of solar cell
  - ii) guides incident light to the active layers
- Thus, TCO needs to be both i) highly conductive and ii) highly transparent in the active wavelength range
- Typical TCO layers are made from:
  - fluorine-doped tin oxide (FTO, or  $\text{SnO}_2:\text{F}$ ),
  - aluminium-doped zinc oxide (AZO, or  $\text{ZnO}:\text{Al}$ ),
  - indium tin oxide (ITO) – mixture ~90% indium oxide ( $\text{In}_2\text{O}_3$ ) and ~10% tin oxide ( $\text{SnO}_2$ )
  - hydrogen-doped (hydrogenated) indium oxide ( $\text{In}_2\text{O}_3:\text{H}$ )
- Films are deposited using such as sputtering (AZO, ITO), or chemical vapour deposition based techniques (others)

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# Transparent Conducting Oxides

- Typical transmission ( $T$ ), reflection ( $R$ ) and absorption ( $A$ ) spectra of  $\text{ZnO}:\text{Al}$  layer – divided into three regions:
- ① at short  $\lambda$ ,  $T$  is very low due to high absorption of light (energy greater than bandgap of TCO material)
- ② in this region,  $T$  is high  $\Rightarrow$  interference fringes can be used to estimate film thickness
- ③ in the NIR region  $A$  increases again  $\Rightarrow$  “free carrier absorption” (FCA)

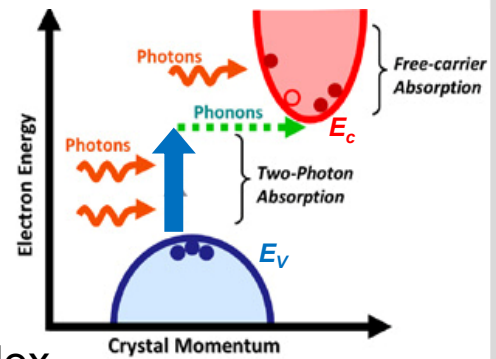


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Source: textbook

# Transparent Conducting Oxides

- FCA: a material absorbs a photon and a carrier ( $e^-$  or  $h^+$ ) is excited from an already-excited state to another unoccupied state in same band
- This intraband absorption is parasitic – not useful like interband absorption
- Material properties link to refractive index  $n$  and extinction coefficient  $k$  of TCO material
- With more metallic-like properties  $\Rightarrow k$  will increase  
 $\Rightarrow$  material exhibits both higher reflection and absorption
- TCO should be highly transparent in active region of absorber, but electrical properties of TCO improve when free carrier density is greatest  
 $\Rightarrow$  Trade-off between optical and electrical properties



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Source: [https://www.osa-opn.org/home/articles/volume\\_20/issue\\_6/features/green\\_silicon\\_photonics/](https://www.osa-opn.org/home/articles/volume_20/issue_6/features/green_silicon_photonics/)

# Transparent Conducting Oxides

- Of all commercial-scale TCOs, best performer is ITO
- However, indium is a rare element with a very low abundance of 0.05 ppm in Earth's crust (similar to silver)
- Thus, less preferable for TW-scale PV
- Motivation to use other TCO materials, e.g. abundance of elements much better in AZO and FTO: aluminium 7.96%, zinc 65 ppm, fluorine 525 ppm, tin 2.3 ppm



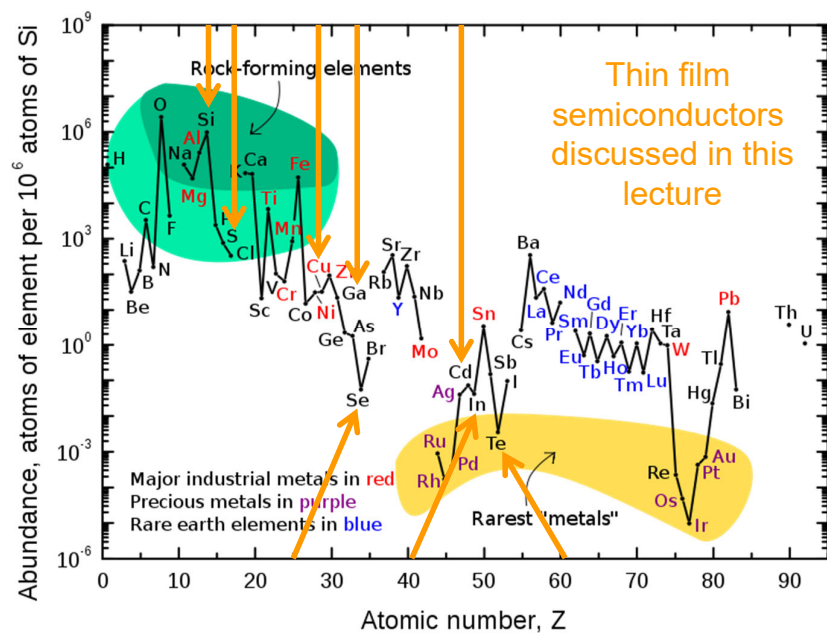
# Materials Abundance

Many different semiconductors are used for thin-film solar cells

Some semiconductors require very rare elements, e.g. indium (In), selenium (Se), or tellurium (Te)

To realise TW-scale PV, solar cells should ideally be based on abundant elements

Also, ideally elements that are potentially toxic (e.g. Cd) should also be avoided



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Source: [http://en.wikipedia.org/wiki/Abundance\\_of\\_the\\_chemical\\_elements](http://en.wikipedia.org/wiki/Abundance_of_the_chemical_elements)

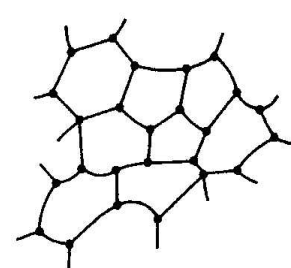
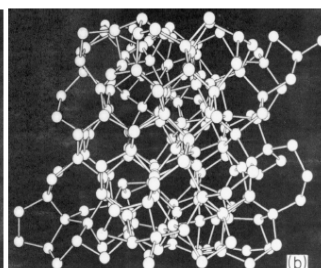
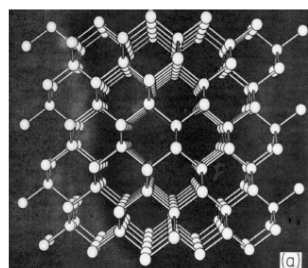
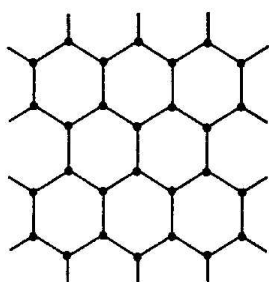
## Amorphous vs Crystalline Silicon

“Amorphous” commonly refers to non-crystalline materials:

- chemical bonding of atoms nearly unchanged from crystals, e.g. Si still bonded to Si
- But small, disorderly variations in the angles between the bonds  $\Rightarrow$  eliminates regular lattice structure

c-Si

a-Si



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## a-Si:H Solar Cells

- First thin films of amorphous silicon (a-Si) layers deposited in 1965 using a silane ( $\text{SiH}_4$ ) gas as precursor
- But took another 10 years to discover that a-Si actually had semiconducting properties
- Not recognized immediately that hydrogen plays very important role and that this is this actually an alloy of silicon and ~10% hydrogen
- Thus, electronic grade material is called **hydrogenated amorphous silicon (a-Si:H)**
- First successful a-Si:H solar cell with  $\eta = 2.4\%$  was reported in 1976

## a-Si:H Solar Cells

Back then, seemed promising technology due to:

- i) a-Si:H has a direct bandgap
  - ⇒ high absorption coefficient ( $\alpha$ ) in visible spectrum
  - ⇒ 1  $\mu\text{m}$ -thick a-Si:H layer can absorb 90% of above-bandgap solar energy
- ii) PECVD technique allowed for production of a-Si:H films over  $>1\text{m}^2$  area and at low-T (100–250°C)
  - ⇒ low T enables use of low cost substrates, e.g. glass, metal or polymer foils
  - ⇒ also opened up possibility of flexible PV modules
- iii) Possibility of “bandgap engineering”

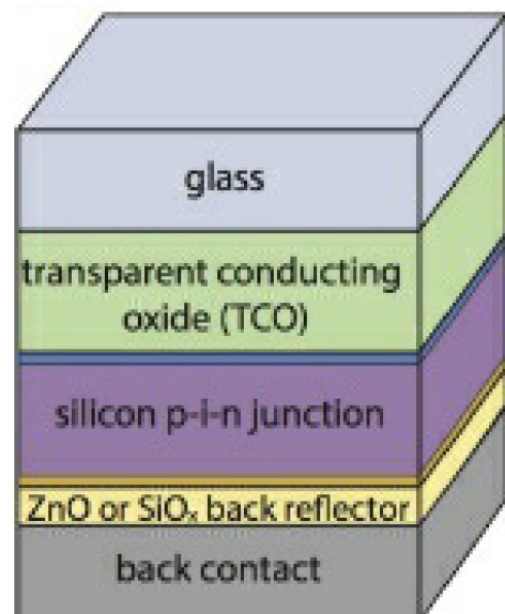
## a-Si:H Solar Cells

- Compared to c-Si, a-Si:H films have a high amount of defects ( $\sim 10^{16}/\text{cm}^3$ , c.f. below detection limit for c-Si)
- Due to the disordered structure, not all electrons able to bond with the neighbouring Si atoms  $\Rightarrow$  dangling bonds act as defects that limit the lifetime of the excited charge carriers
- SRH recombination  $\Rightarrow$  reduces diffusion length,  $L$
- Due to high defect density,  $L$  in a-Si:H is only  $\sim 100\text{nm}$  (and even 2-3 orders of magnitude lower when  $n$ - or  $p$ -doped)
- Thus, cannot rely on diffusion for transport of charge carriers in thick a-Si:H absorber
- Therefore, a-Si:H devices are not based on a  $p$ - $n$  junction like wafer-based c-Si solar cells

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## a-Si:H Solar Cells

- Instead, a-Si:H cells based on a  $p$ - $i$ - $n$  junction  $\Rightarrow$  thicker intrinsic  $i$  layer (undoped) sandwiched between very thin  $p$ - and  $n$ -doped layers
- Thicknesses:  
 $i$ -layer  $\sim 300\text{nm}$  thick, while  $p$ - and  $n$ -doped layers are only  $\sim 10\text{ nm}$  thick
- Between highly-doped  $p$ - and  $n$ -doped layers  $\Rightarrow$  built-in electric field across  $i$ -layer (absorber) created



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Source: textbook



# a-Si:H Solar Cells

- Remember: diffusion length,  $L_D$ :

$$L_D = \sqrt{D\tau} = \sqrt{\frac{\mu\tau k_B T}{q}}$$

(noting that both lifetime  $\tau$  and mobilities  $\mu$  are 50-1000x lower in a-Si:H compared to c-Si)

- Instead: drift length,  $L_E \equiv$  average distance a carrier can travel with its drift velocity in an electric field  $E$  before it recombines

$$L_E = v_E \tau = \mu \tau |\vec{E}|$$

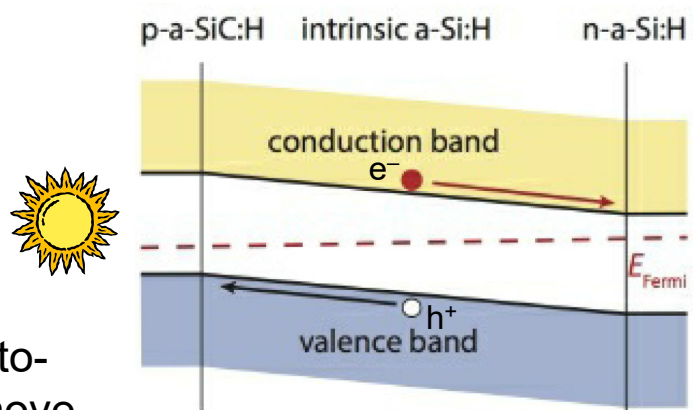
= 1  $\mu$ m assuming that we have a voltage drop of 1V over a 1  $\mu$ m absorber thickness (roughly what we have in a-Si:H solar cell), indicating that  $|\vec{E}| = 10^4$  V/cm

- In such a device, where electronic drift due to electric field is the dominant transport mechanism  $\Rightarrow$  called a drift device

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# a-Si:H Solar Cells

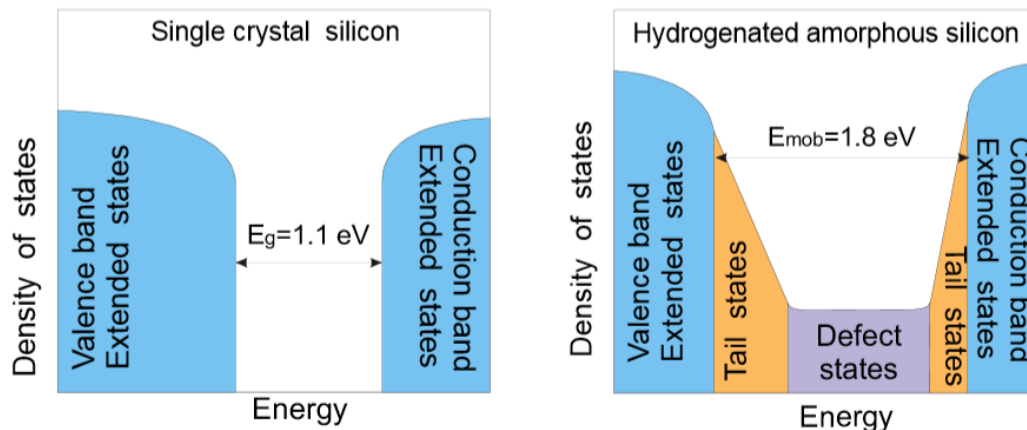
- Electronic band diagram : the slope in the intrinsic film reflects the built-in electric field
- Due to the electric field, photo-generated charge carriers move through the intrinsic layer
- $h^+$  move up slope in the valence band towards  $p$ -type layer,  $e^-$  move down slope in conduction band towards the  $n$ -layer
- In  $p$ -layer, the  $h^+$  are majority charge carriers  $\Rightarrow$  dominant transport mechanism is diffusion (similarly for  $e^-$  in  $n$ -layer)  $\Rightarrow$  but due to short diffusion lengths, both  $p$ - and  $n$ -layers must be very thin



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# a-Si:H Solar Cells

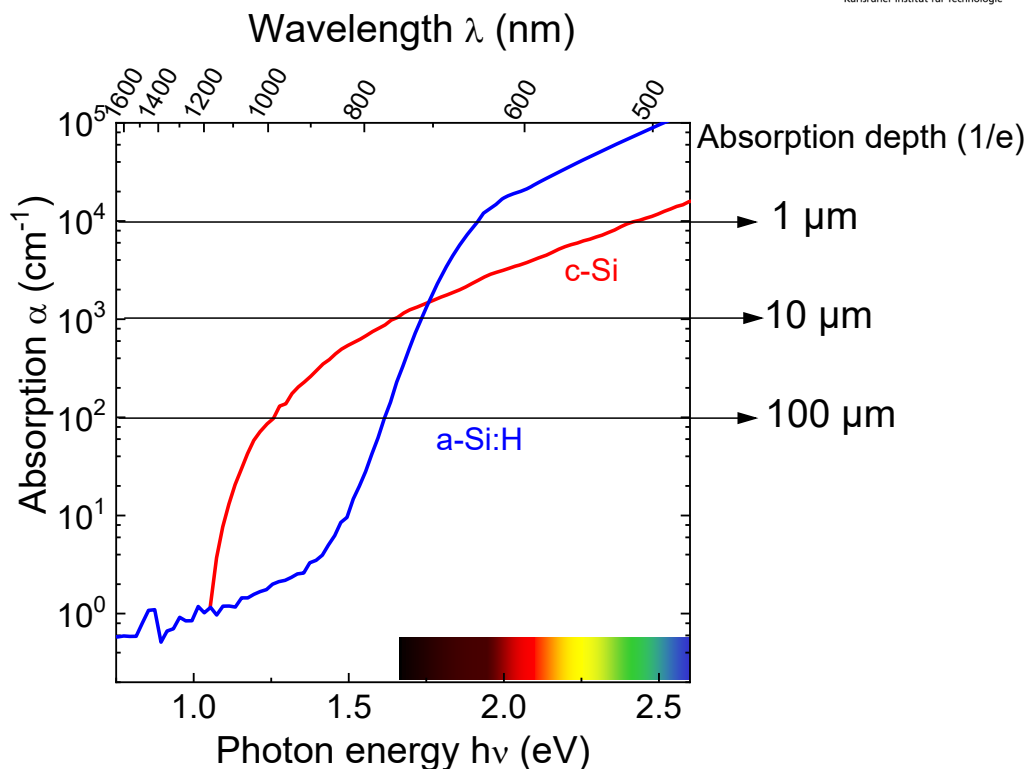
- a-Si:H has direct bandgap  
⇒ thus high absorption  $\sim 10^5 \text{ cm}^{-1}$
- But bands are "smeared" due to band tails and defect states  
⇒ no clear bandgap ⇒ thus often refer to "optical bandgap"  
vs. "electrical bandgap" (i.e. there might be absorption at longer  $\lambda$  but is it useful?)



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Source: [http://ocw.tudelft.nl/fileadmin/ocw/courses/SolarCells/res00030/CH7\\_Thin\\_film\\_Si\\_solar\\_cells.pdf](http://ocw.tudelft.nl/fileadmin/ocw/courses/SolarCells/res00030/CH7_Thin_film_Si_solar_cells.pdf)

# a-Si:H Solar Cells

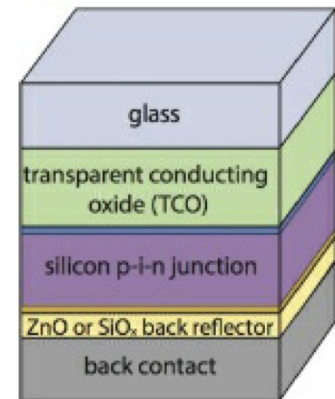


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Source: Courtesy of FZJ – IEF 5

# a-Si:H Solar Cells

- Cell deposited in superstrate configuration
- Means that light encounters the layers in order that they were deposited in production process
- When we talk about a “p-i-n device”, this also indicates the order of depositions
- Glass is typically used as superstrate because it:
  - i) is highly transparent;
  - ii) can handle the conditions during cell deposition;
  - iii) can be supplied pre-coated with a TCO;
  - iv) is cheap; and
  - v) serves as excellent mechanical and environmental protection of the solar cell.

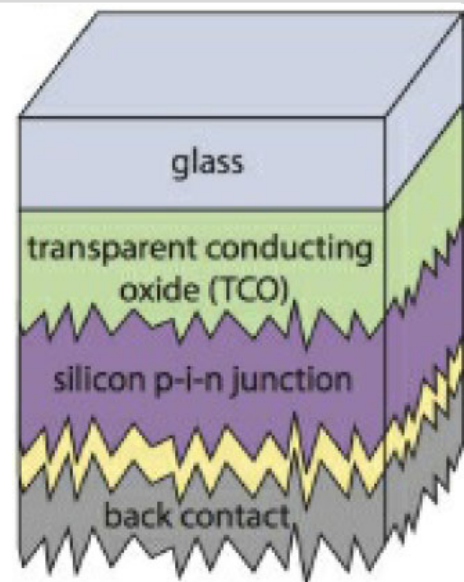


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Source: textbook

# a-Si:H Solar Cells

- Typically, a-Si:H solar cells are not planar devices  $\Rightarrow$  instead are deposited on nanotextured TCO
- Textured TCO scatters incident light  $\Rightarrow$  helps increase average pathlength of photons  $\Rightarrow$  increase amount of light absorbed without increasing the thickness of absorber layer  $\Rightarrow$  higher  $J_{sc} \Rightarrow$  higher  $\eta$  (N.B. similar motivation for pyramid texture in c-Si)
- $E_g$  of a-Si:H is  $\sim 1.75$  eV  $\Rightarrow V_{oc}$ 's  $\sim 1.0$  V  $\Rightarrow$  limited by high levels of SRH recombination
- Only absorbs  $\lambda < 700$  nm  $\Rightarrow$  highest  $J_{sc}$ 's achieved in single-junction a-Si:H device  $\sim 17\text{--}18$  mA/cm<sup>2</sup> at average EQE  $\sim 75\%$

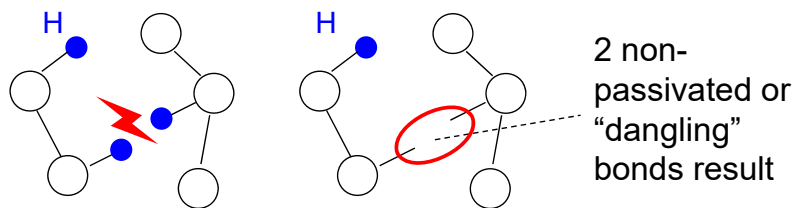


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Source: textbook

# a-Si:H Solar Cells

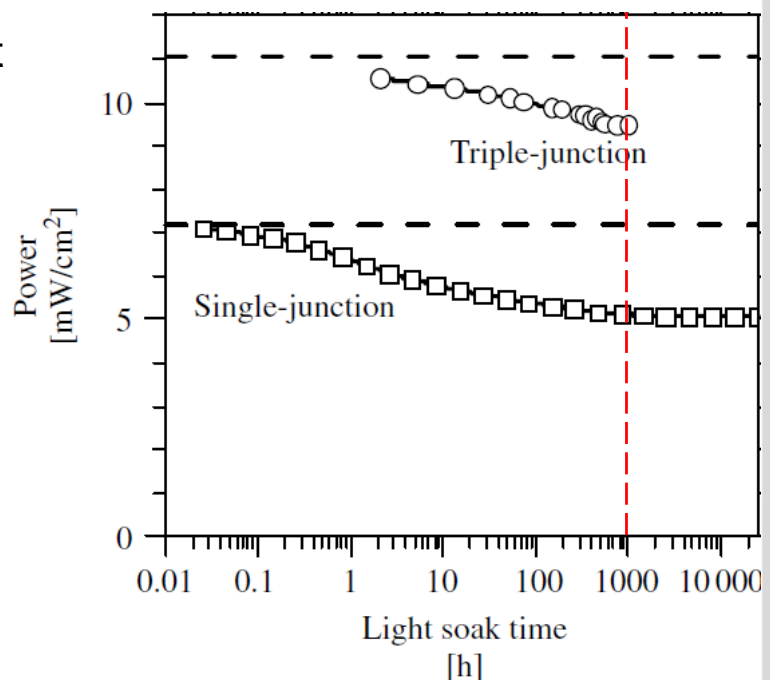
- Light-induced degradation (Staebler–Wronski effect, SWE)  
⇒ biggest challenges for a-Si:H thin-film solar cells
- Mechanism: recombination of light-excited charge carriers uses energy to break weaker bonds and creates metastable defects in absorber layer ⇒ forms dangling bonds, that lie within the bandgap ⇒ increased defect density leads to increased recombination ⇒ lower  $\eta$



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# a-Si:H Solar Cells

- SWE: after ~1000 hours of illumination,  $\eta$  stabilizes at 80–85% of initial  $\eta$  value and then remains stable
- Effects can be somewhat minimized but never avoided completely
- Highest stabilized single-junction lab-scale solar cell  $\eta = 10.1\%$  (Oerlikon Solar, Switzerland)
- a-Si:H modules  $\eta$  more typically 3 – 4%



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# a-Si:H Solar Cells

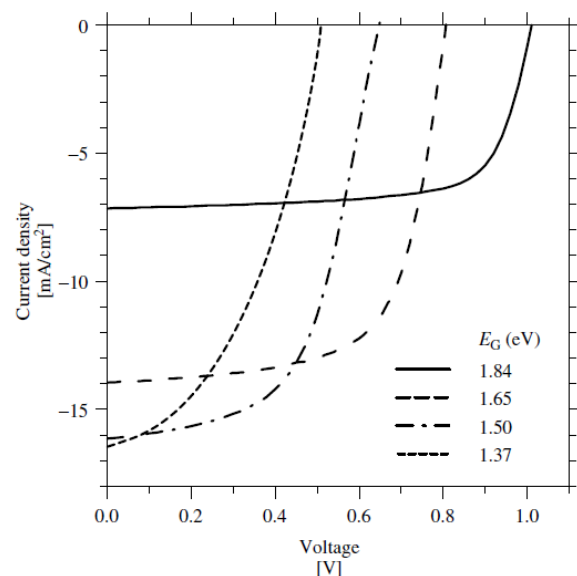
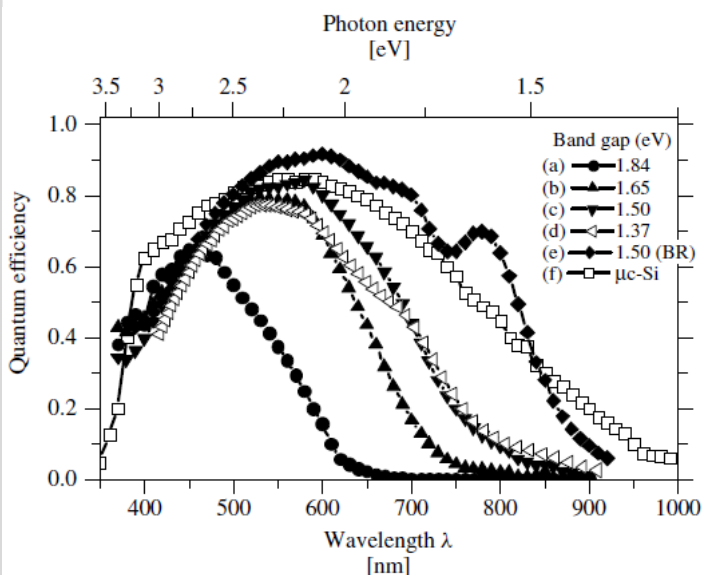
## Bandgap Engineering:

- Alloying of Si with elements, such as Ge and C, can be realised during thin film deposition
- Inclusion of C in a-Si:H increases  $E_g$  (~2.0 eV for a-SiC:H)
- Inclusion of Ge in a-Si:H decreases  $E_g$  (~1.0 eV for a-Ge:H)
- Resulting alloys have wide range of bandgaps

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# a-Si:H Solar Cells

- E.g. a-Si:H (1.84 eV) vs devices made from a-SiGe:H mixtures
- Increased Ge content  $\Rightarrow$  lower  $E_g \Rightarrow$  longer EQE response  $\Rightarrow$  higher currents  $\Rightarrow$  lower voltages

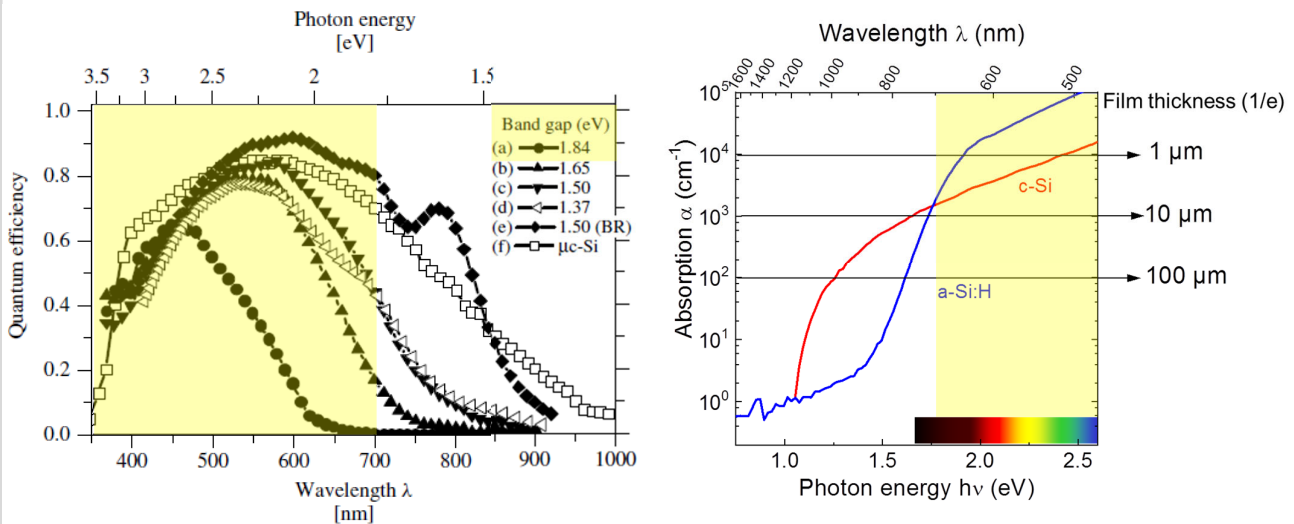


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Source: "Amorphous Silicon-based Solar Cells" by Deng and Schiff (2002), in *Handbook of Photovoltaic Science and Engineering*, edited by A. Luque and S. Hegedus

# a-Si:H Solar Cells

- Reminder: not all absorption is useful
- e.g. optical absorption data of a-Si:H looks like it should respond to 1100nm light, but electrically the solar cell does not respond to light with  $\lambda > 700\text{nm}$



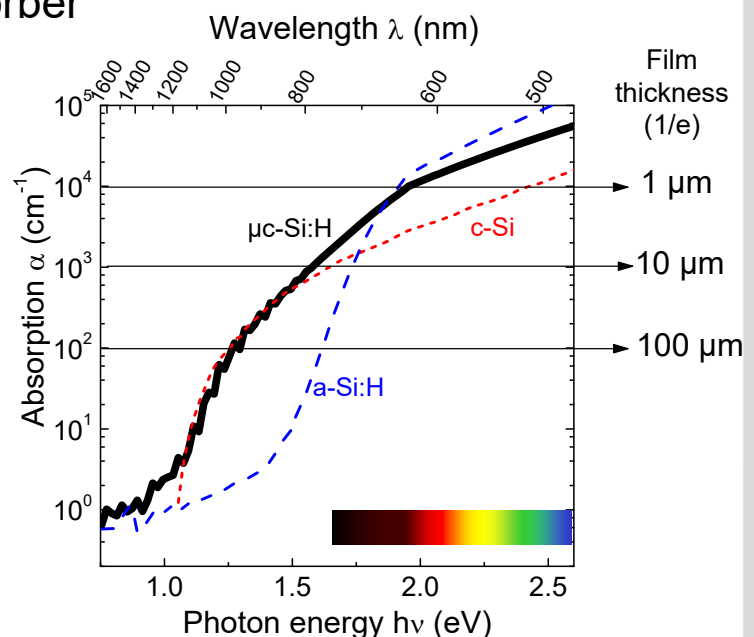
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Source: "Amorphous Silicon-based Solar Cells" by Deng and Schiff (2002), in *Handbook of Photovoltaic Science and Engineering*, edited by A. Luque and S. Hegedus

# a-Si:H Solar Cells

## Bandgap Engineering:

- Also, hydrogenated micro- ( $\mu\text{c-Si:H}$ ) and nanocrystalline silicon (nc-Si:H) as possible absorber
- Also suffers less from SWE
- Bandgap similar to c-Si and also indirect
- But to harvest  $>700\text{nm}$  range (where a-Si:H responds poorly), thicker films (1 – 3  $\mu\text{m}$ ) and light-trapping required



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Source: Courtesy of FZJ – IEF 5



# a-Si:H Solar Cells

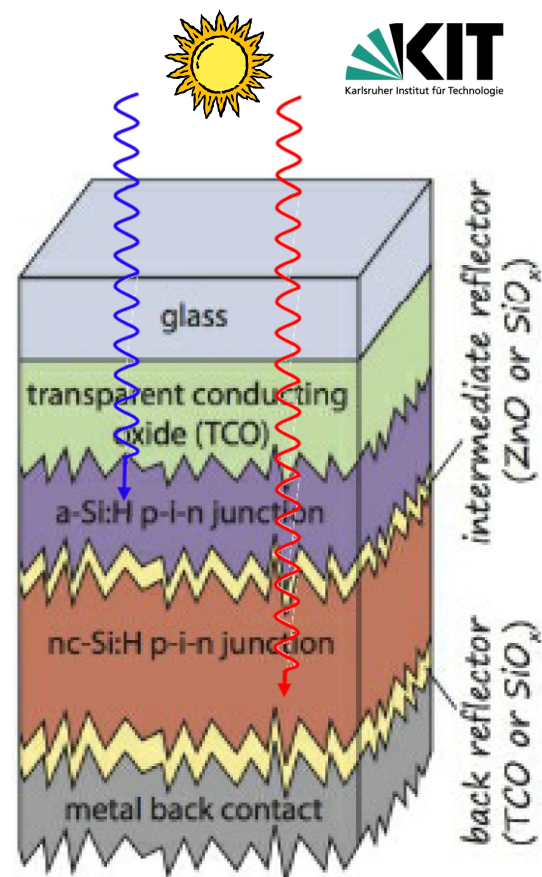
## Multijunction (also called tandem) solar cells:

- Multijunction solar cell approach allows for absorbing a wider range of photons  $\Rightarrow$  stack higher bandgap a-Si:H solar cell on top of lower bandgap a-SiGe:H or nc-Si:H
- Solar cell with the highest bandgap is used as a top cell that converts the most energetic photons into electricity, while the lower bandgap material is used for the bottom cell and converts the lower energetic photons
- Add voltages of the two solar cells together
- The current is determined by the minimum current flowing in each device  $\Rightarrow$  thus tandem solar cells require “current matching” (*discussed in more detail in tandems lecture*)

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# a-Si:H Solar Cells

- With a-Si:H can have double- and triple-junction devices
- Common device was “micromorph” solar cell  $\Rightarrow$  with a-Si:H top cell and nc-Si:H bottom cell
- Blue and green short- $\lambda$  light is absorbed in top cell, generating  $e^-h^+$  pairs, while longer- $\lambda$  (red and NIR) light is absorbed in bottom cell, also generating  $e^-h^+$  pairs

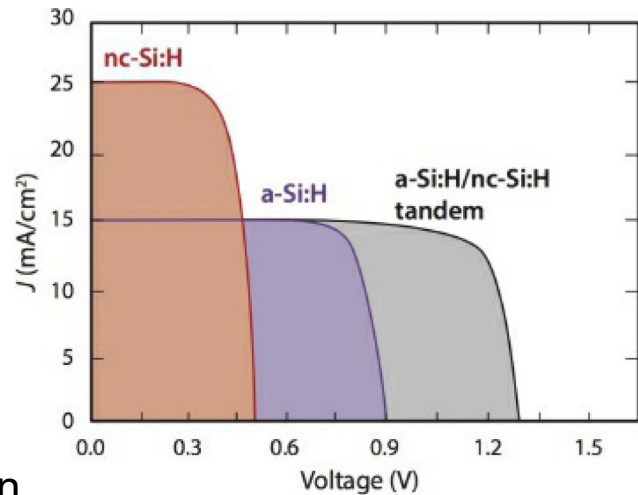


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Source: adapted from textbook

## a-Si:H Solar Cells

- Total current density = that of junction with the lowest current density  $\Rightarrow$  optimized multijunction cell  $\Rightarrow$  current densities in each subcell have to be matched
- a-Si:H:  $V_{oc} = 0.9 \text{ V}$   
 $J_{sc} = 15 \text{ mA/cm}^2$
- nc-Si:H:  $V_{oc} = 0.5 \text{ V}$   
 $J_{sc} = 25 \text{ mA/cm}^2$
- a-Si:H/nc-Si:H tandem:  
 $J_{sc} \sim 15 \text{ mA/cm}^2$   
 $V_{oc}$  of bottom cell will be slightly lower than for each single junction cell as  $V_{oc} \propto \ln(J_{ph}/J_0)$

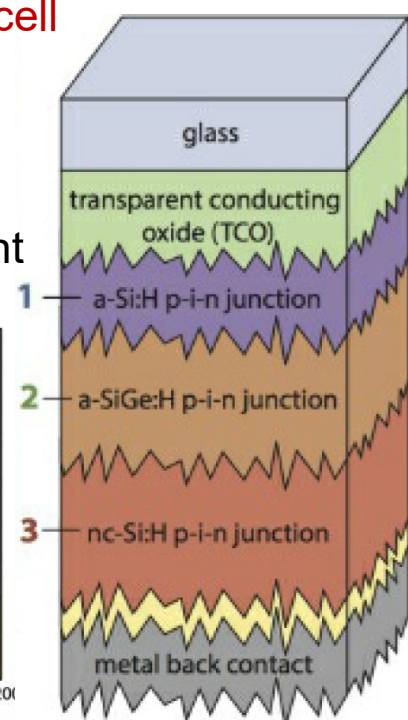
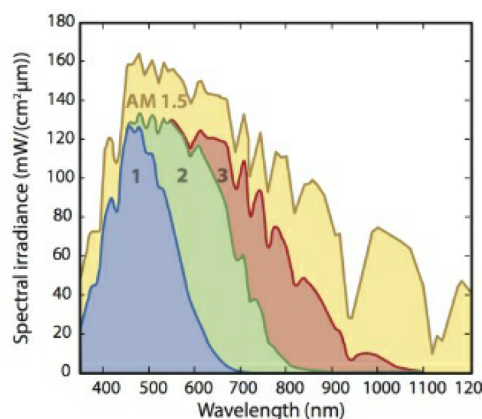


Current record double-junction has  $\eta = 12.3\%$  (Kaneka)

## a-Si:H Solar Cells

- United Solar Ovonic triple-junction devices: **1) a-Si:H top cell;** **2) a-SiGe:H middle cell;** **3) nc-Si:H bottom cell**
- Significant overlaps between EQE spectra  $\Rightarrow$  optimising thin-film multijunction solar cells  $\Rightarrow$  complex interplay between various absorber thicknesses and light management concepts
- Optimise under AM1.5G standard spectrum...?

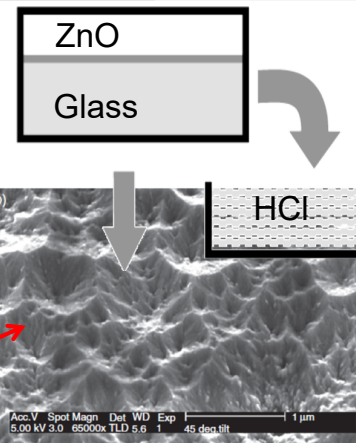
Highest initial cell  $\eta = 16.3\%$   
( $\eta \sim 12\%$  stabilized,  
 $\eta \sim 7\%$  module)



# a-Si:H Solar Cells

Fabrication steps for single-junction *pin* a-Si:H superstrate technology:

1. Glass cleaning (abrasive + washing)
2. Front contact:
  - sputtering of 50nm SiO<sub>2</sub> (as Na diffusion barrier)
  - deposition ~600nm TCO (can be ITO, FTO, **AZO** - last two can be textured)
3. Structuring of front contact (laser patterning and wet chemical cleaning)
4.  $\left. \begin{array}{l} 10\text{-}20 \text{ nm } p\text{-type a-Si:H} \\ 300\text{-}500 \text{ nm } i\text{-type a-Si:H} \\ 10\text{-}20 \text{ nm } n\text{-type a-Si:H} \end{array} \right\} \text{pin junction deposited using PECVD with SiH}_4 + \text{H}_2 \text{ gases, along with diborane (B}_2\text{H}_6\text{) for } p\text{-doping and phosphine (PH}_3\text{) for } n\text{-doping}$
5. Sputtering of back Al contact (or evaporation)
6. Laser welding of contact strips
7. Testing



*N.B. This describes fabrication of a solar cell, but thin-film PV usually deposited as a module directly  $\Rightarrow$  covered in PV module lecture*

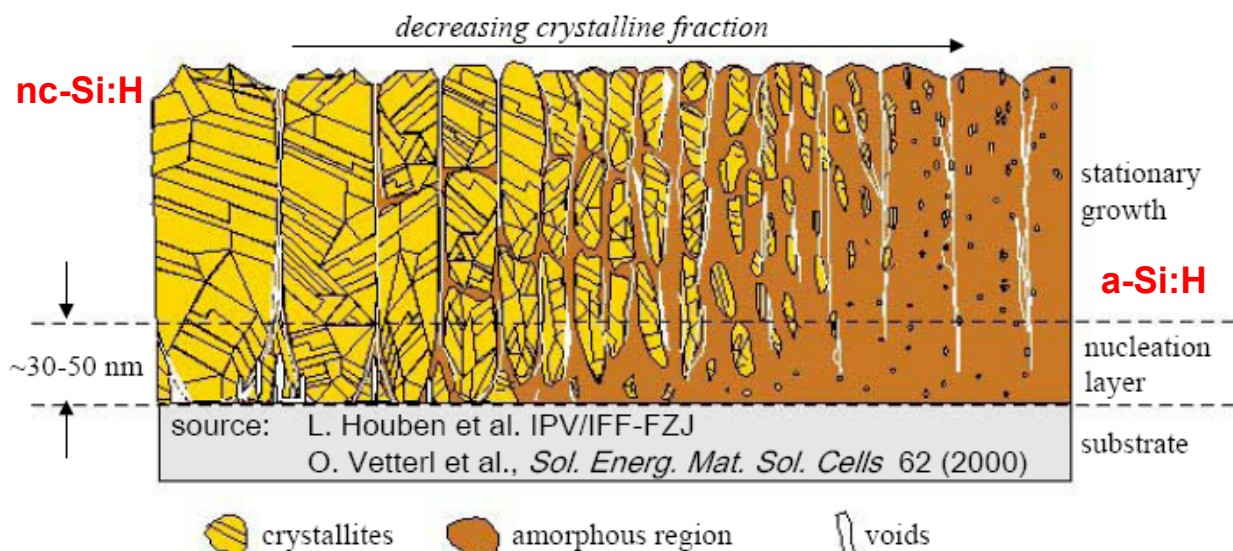
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# a-Si:H Solar Cells



- PECVD used for deposition of both a-Si:H and nc-Si:H – just vary deposition parameters (temperature and H<sub>2</sub> ratio)

influence of deposition parameters: silane concentration, power, frequency, temperature, ...



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# Thin-Film Crystalline Si Solar Cells

Why not use crystalline silicon for thin-film PV?

- Non-toxic and earth abundant material (unlike In, Cd, Te, etc)
- Doesn't degrade like hydrogenated amorphous silicon (a-Si:H)
- Thin films made of very small-grained material, called microcrystalline silicon ( $\mu\text{c-Si}$ ) – but no hydrogen
- Still indirect bandgap material  $\Rightarrow$  light absorption challenging
- Complex device processing, high-T processes needed
- Never achieved  $\eta > 10\%$  for full-size ( $\sim 1\text{m}^2$ ) modules

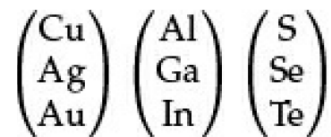


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Source: <http://www.pressebox.de/pressemitteilung/csg-solar-ag/Dr-Ottmar-Koeder-wird-neues-Vorstandsmitglied-fuer-den-Bereich-Produktion-der-CSG-Solar-AG/boxid/186646>

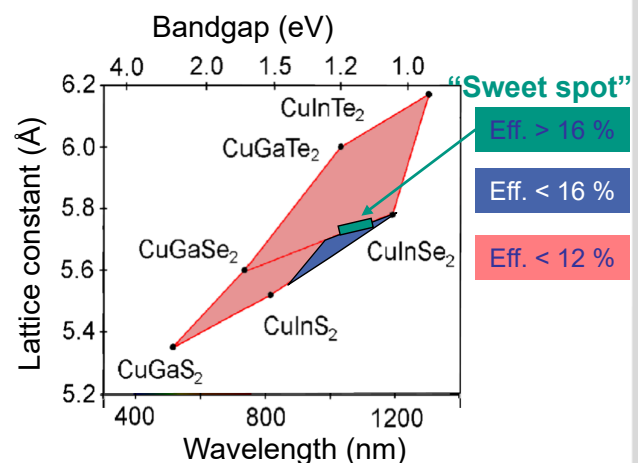
## CIGS solar cells

- Chalcogenides include semiconductors containing elements S, Se or Te
  - Copper indium gallium selenide (CIGS)
  - Cadmium telluride (CdTe)



- Change In:Ga ratio  $x$  and Se:S ratio  $y \Rightarrow$  tune bandgap of  $\text{Cu}(\text{In}_x\text{Ga}_{1-x})(\text{Se}_y\text{S}_{1-y})_2$

e.g.  $\text{CuInSe}_2$  has  $E_g = 1.0$  eV, while  $\text{CuInS}_2$  has  $E_g = 1.5$  eV, and  $\text{CuGaSe}_2$  has  $E_g = 1.7$  eV



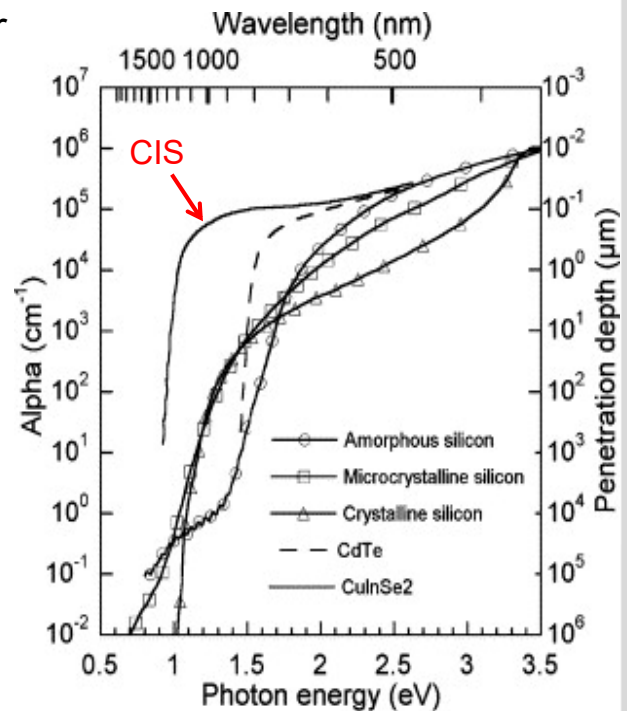
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Source: textbook  
Powalla (ZSW)



# CIGS solar cells

- CIGS is a direct bandgap semiconductor material
- High absorption coefficient over broad wavelength range
- Absorber thickness of 1–2  $\mu\text{m}$  sufficient to absorb a large fraction of above-bandgap light
- Typical diffusion length is about few  $\mu\text{m}$
- CIGS is  $p$ -type  $\Rightarrow$  resulting from intrinsic defects in material (Cu deficiencies)

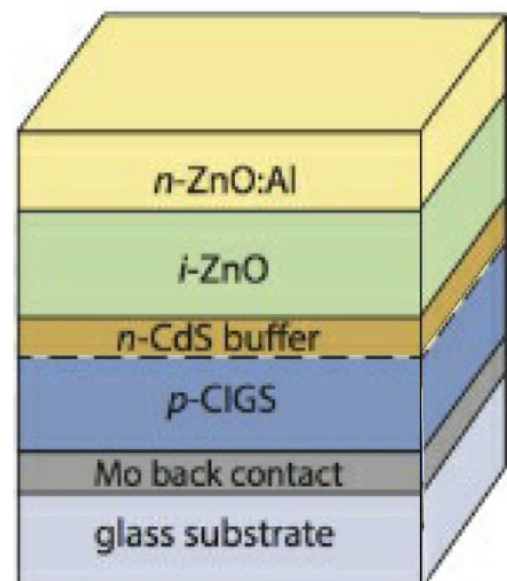


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Source: Powalla (ZSW)

# CIGS solar cells

- Typical CIGS solar cell deposited on glass substrate
- Molybdenum (Mo) layer ~500 nm thick deposited as rear contact
- $p$ -type CIGS absorber layer deposited (up to 2  $\mu\text{m}$  thick)
- $p$ - $n$  junction formed by depositing thin (~50 nm thick) cadmium sulphide (CdS) buffer
- Then intrinsic zinc oxide ( $i$ -ZnO) layer deposited (role not fully understood), followed by TCO based on Al-doped ZnO

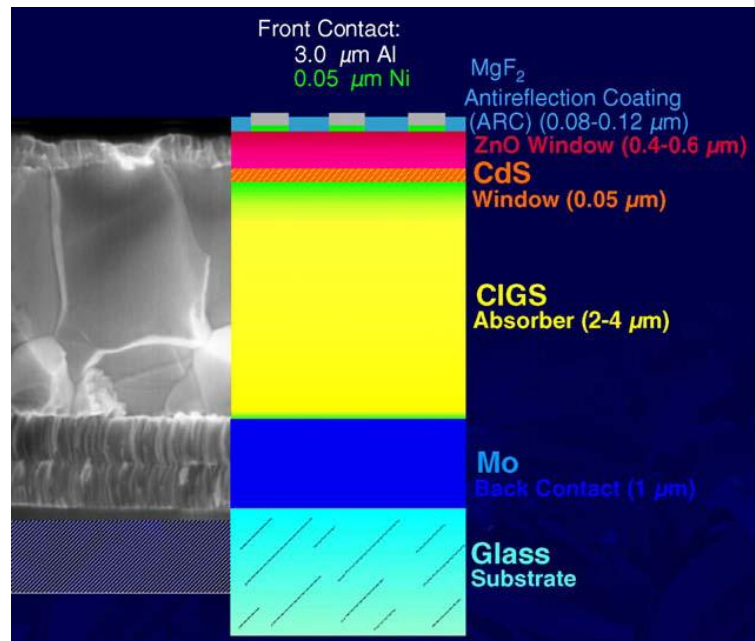
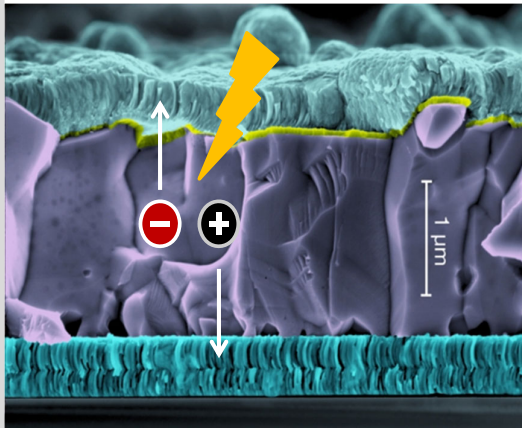


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Source: adapted from textbook

# CIGS solar cells

- Grain boundaries largely run vertically through the absorber  
⇒ less damaging than horizontal grain boundaries;
- CIGS solar cells are (roughly) planar devices  
⇒ no texturing needed for high light absorption

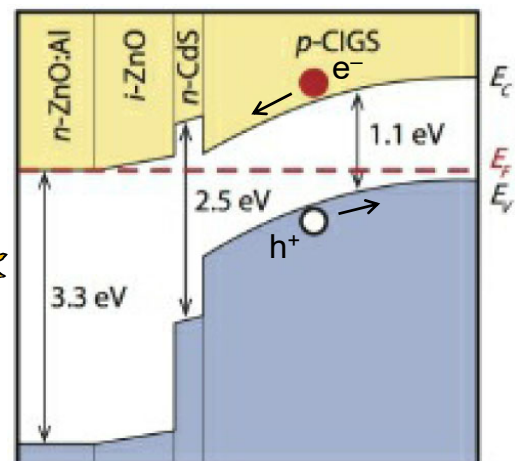


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Source: [https://en.wikipedia.org/wiki/Copper\\_indium\\_gallium\\_selenide\\_solar\\_cells](https://en.wikipedia.org/wiki/Copper_indium_gallium_selenide_solar_cells)  
ZSW Annual Report 2008

# CIGS solar cells

- Light enters cell from left, via the ZnO ⇒ high bandgap of  $E_g = 3.3$  eV minimizes parasitic absorption losses
- *n*-type CdS buffer layer has  $E_g = 2.5$  eV
- Commercial *p*-type CIGS absorber layer  $E_g = 1.1$  eV, achieved using  $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$  with  $x \approx 0.3$
- Bandgaps of *n*- and *p*-type materials are different ⇒ CIGS considered as heterojunctions (c.f. Si homojunction)
- Role of sodium (Na)  
⇒ reduces recombination at grain boundaries in CIGS (like H<sup>+</sup> in Si) ⇒ Na-source in soda-lime glass (window glass)



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Source: textbook

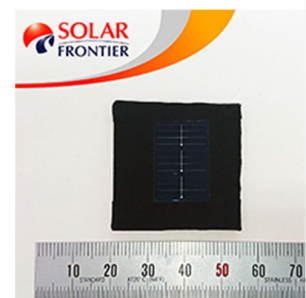


# CIGS solar cells

- Fabrication of CIGS solar cells – many different approaches:
  - i) co-evaporation under vacuum conditions via crucibles of copper, gallium, indium and selenium onto heated substrate
  - ii) sputtering onto a non-heated substrate, then thermally annealed in presence of selenium vapour
- Variety and complexity of reactions taking place during the ‘selenization’ process  $\Rightarrow$  CIGS properties difficult to control
  - iii) Non-vacuum techniques based on depositing nanoparticles of the precursor materials onto substrate then sintering the film  $\Rightarrow$  plus then followed by selenization step

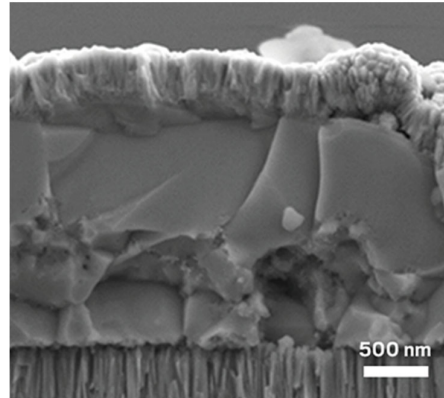
# CIGS solar cells

- CIGS solar cells have achieved one of the highest conversion efficiencies for thin-film PV
- Previous solar cell efficiency record held Centre for Solar Energy and Hydrogen Research (ZSW, Stuttgart) with  $\eta = 22.6\%$  for CIGS  $\Rightarrow$  working with Manz AG for commercialisation
- Overtaken by Solar Frontier (Japan) with  $\eta = 23.3\%$  (1cm<sup>2</sup> device with  $V_{oc} = 734$  mV,  $J_{sc} = 39.58$  mA/cm<sup>2</sup>, FF = 80.4%)  $\Rightarrow$  notably for a Cd-free CIS device
- Despite the very high  $\eta$ , CIGS technology faces challenges:
  - i) complex deposition process; ii) achieving uniform large-area depositions with iii) a high production yield



# Kesterite solar cells

- Indium is a very rare element, but crucial to CIGS solar cells  
⇒ scarcity may prevent upscaling of CIGS PV to TW scale
- Also, current thin-film display industry depends on In as well, with ITO is integrated in many display screens.
- Cadmium is toxic but efforts underway to replace Cd with Zn
- Kesterite  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$  is based on abundantly available and non-toxic elements
- Record efficiency was  $\eta = 12.6\%$  (IBM, 2013)
- Challenge controlling defects and presence of unwanted phases



Three layers (top to bottom):  
Indium tin oxide, nondoped zinc oxide, cadmium sulfide

Copper zinc tin selenide ( $\text{Cu}_2\text{ZnSnSe}_4$ ) doped with germanium

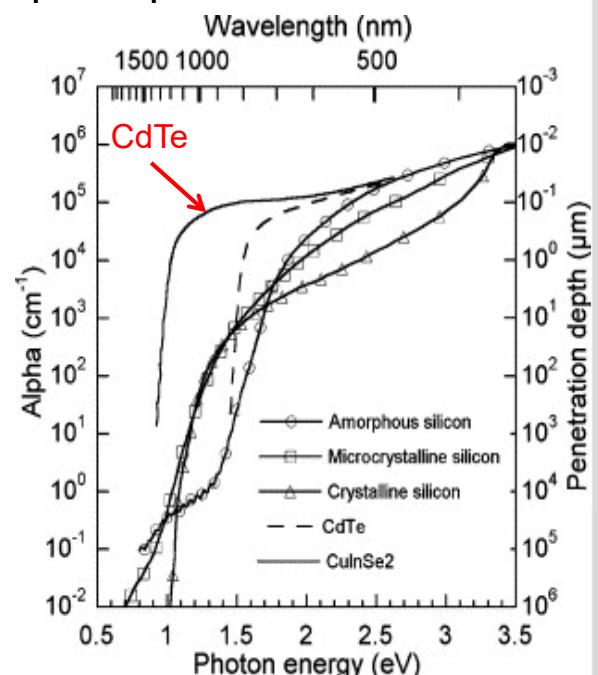
Molybdenum substrate

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Source: <https://cen.acs.org/articles/96/i7/Kesterite-solar-cells-ready-shine.html>

# CdTe solar cells

- Cadmium telluride (CdTe) PV – the thin-film technology with currently lowest demonstrated cost per Wp
- CdTe: *p*-doped semiconductor with  $E_g = 1.44$  eV ⇒ close to ideal for single-junction device
- CdTe is a direct bandgap material ⇒ only few  $\mu\text{m}$  of CdTe required to absorb all above-bandgap photons
- History: first suggested for PV in 1956, followed by first solar cells being made in the 1960s, with  $\eta = 5\%$  devices made in 1972

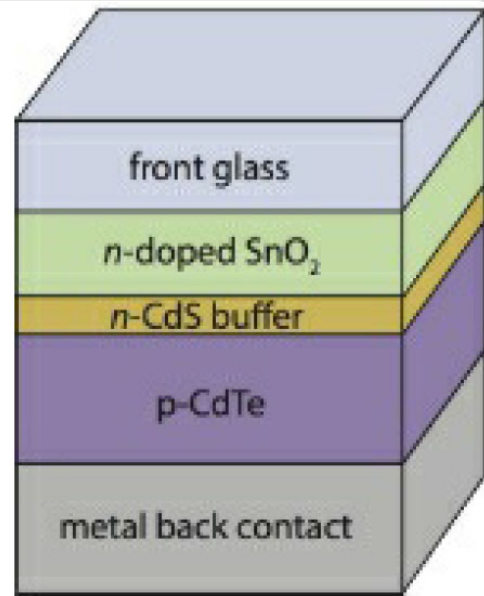


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Source: Powalla (ZSW)

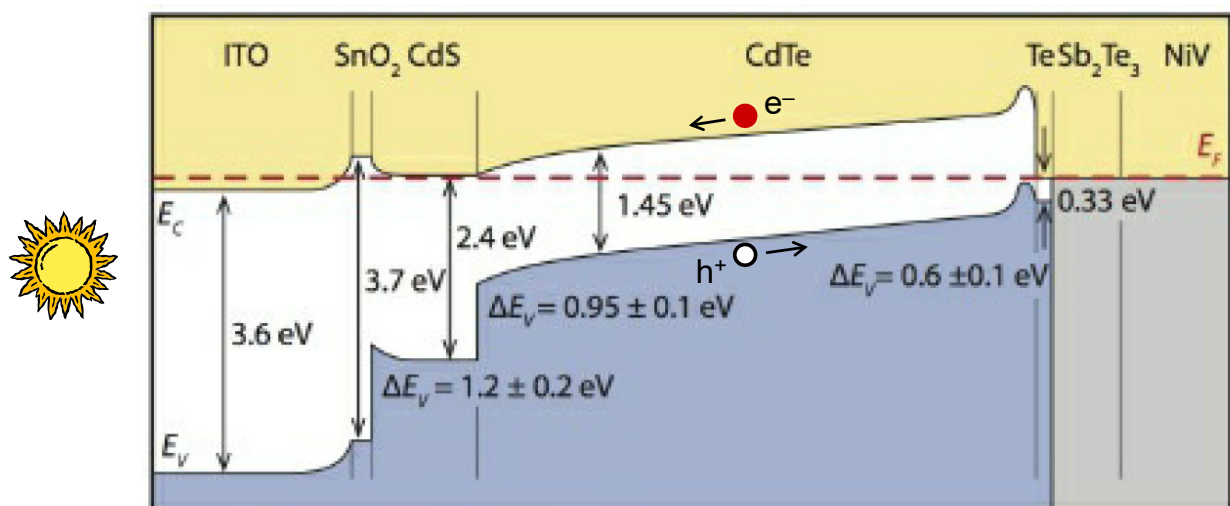
## CdTe solar cells

- First, TCO front deposited onto glass superstrate (ITO with tin oxide layer)
- $n$ -type layer is CdS (same as for CIGS but thicker)
- Then,  $p$ -type CdTe absorber layer (few  $\mu\text{m}$  thick ) is deposited
- Making a good back contact on CdTe is challenging due to limited choice of acceptable metals
- Thus, often another semiconductor material is added to improve the contact, e.g. antimony telluride layers in combination with molybdenum rear metal contact (*not discussed in detail here*)



## CdTe solar cells

- CdS/CdTe is a heterojunction (like for CIGS)
- Light-excited minority electrons in the  $p$ -layer are separated at the heterojunction and collected at the TCO-based front contact. The holes are collected at the back contact.

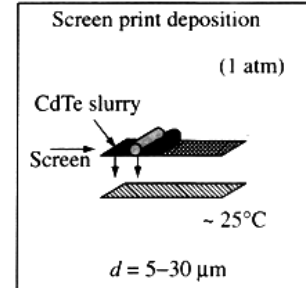
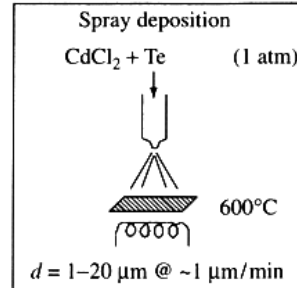
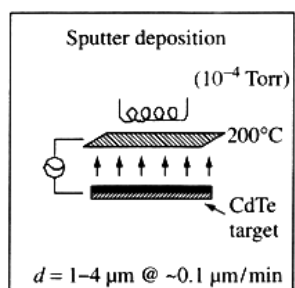
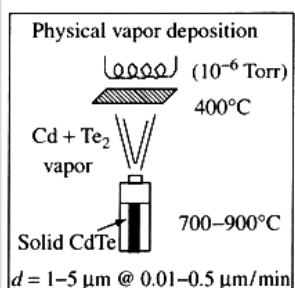
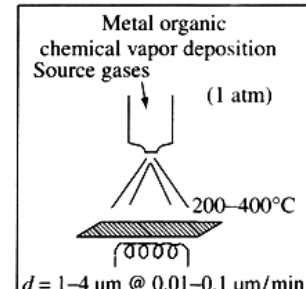
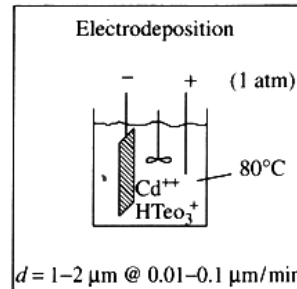
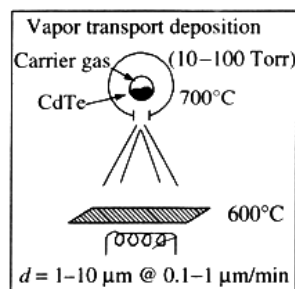
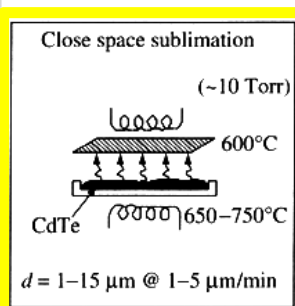


# CdTe solar cells

- CdS/CdTe layers are processed using the closed-space sublimation (CSS) method
- *Sublimation*  $\equiv$  transition of substance directly from solid to gas phase, without passing through intermediate liquid phase
- Source consists of granules/powders of CdTe
- Source material and substrate are placed close together (mm – cm) under vacuum conditions
- Both source and substrate are heated  $\Rightarrow$  source is at higher temperature than substrate  $\Rightarrow$  temperature difference is the driving force for thin film deposition on substrate
- Glass limits temperatures that can be used

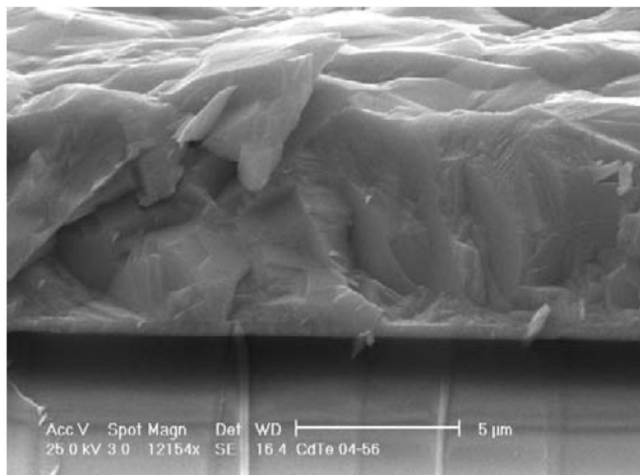
# CdTe solar cells

- At least eight different ways of depositing CdTe layers:



# CdTe Solar Cells

- Cross-sectional image via scanning electron microscopy (SEM) of device from Antec Solar (Germany)
- Note, very rough surfaces



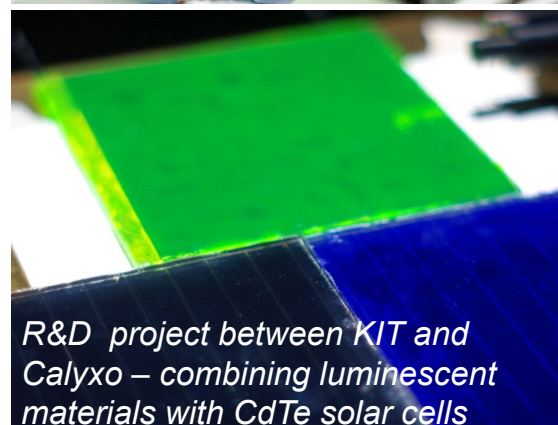
metallischer Rückkontakt - 250 nm
Te - 20 nm
CdTe - 8 μm
CdS - 150 nm
SnO <sub>2</sub> - 30 nm
ITO - 240 nm
Glassubstrat

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Source: Diss. Fritsche, TU Darmstadt 2003

# CdTe Solar Cells

- First Solar (USA) – leading CdTe PV module producer and current world record solar cell efficiency
- $\eta = 22.1\%$  for  $0.5 \text{ cm}^2$  device with  $V_{oc} = 887 \text{ mV}$ ,  $J_{sc} = 31.69 \text{ mA/cm}^2$ ,  $FF = 78.5\%$
- Three German CdTe PV producers (“second solars”):
  - Antec Solar
  - Calyxo
  - CTF-Solar (German R&D, manufactured in China)



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Sources: <https://www.greentechmedia.com/articles/read/first-solar-hits-record-22-1-conversion-efficiency-for-cdte-solar-cell>  
Ross et al., Solar Energy Materials and Solar Cells 103 (2012): 11-16.



# CdTe Solar Cells

- Although Cd is toxic, insoluble compounds like CdTe and CdS are much less toxic than elementary Cd
- Still very important to prevent Cd from entering into ecosystem
- First Solar producing ~5.6 GWp/year  
⇒ ~5% of total Cd consumption
- Recycling schemes established have been set up for installed CdTe solar modules ⇒ fund where \$0.05/Wp of purchase price set aside to cover cost of recycling at end-of-module lifetime
- Another challenge is supply of Te ⇒ one of rarest elements (abundance similar to Pt)
- Also Te not used for many other applications, hence dedicated Te mining not explored (currently by-product of Cu mining – 1000 tonnes Cu ⇒ 1kg of Te)

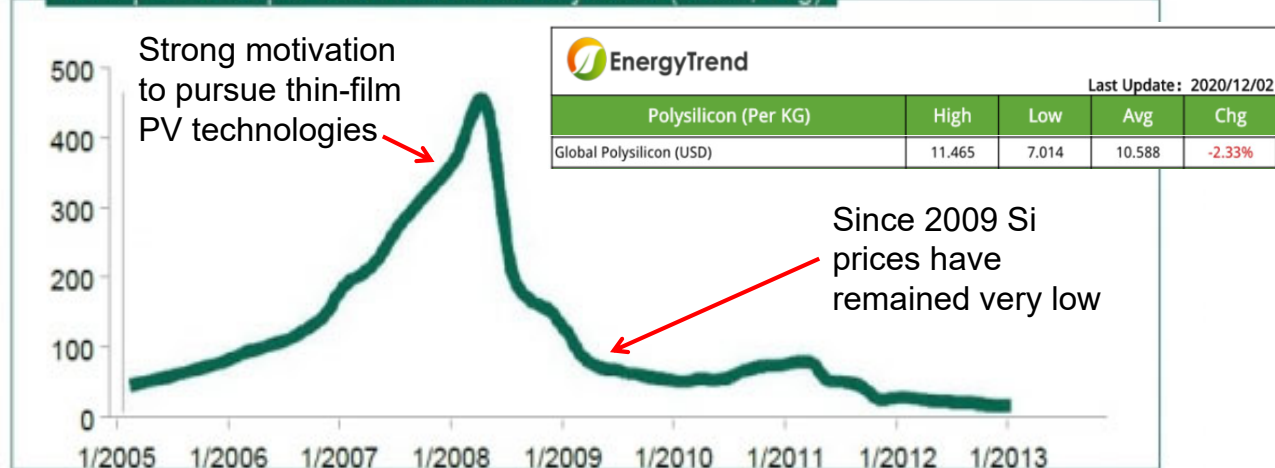
51

Sources: <https://www.greentechmedia.com/articles/read/first-solar-hits-record-22-1-conversion-efficiency-for-cdte-solar-cell>  
Ross *et al.*, Solar Energy Materials and Solar Cells 103 (2012): 11-16.

# Silicon vs Thin-film PV

AVERAGE PRICE OF SOLAR-GRADE SILICON FELL BY HALF IN PAST YEAR

Development of Spot-Market Prices for Polysilicon (in US\$ / kg)



**WACKER** Annual Press Conference 2012  
March 14, 2013, slide 14

Source: Timminco Solar, Photon

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Source: [http://www.pv-tech.org/news/polysilicon\\_prices\\_at\\_wacker\\_fell\\_50\\_in\\_2012](http://www.pv-tech.org/news/polysilicon_prices_at_wacker_fell_50_in_2012)

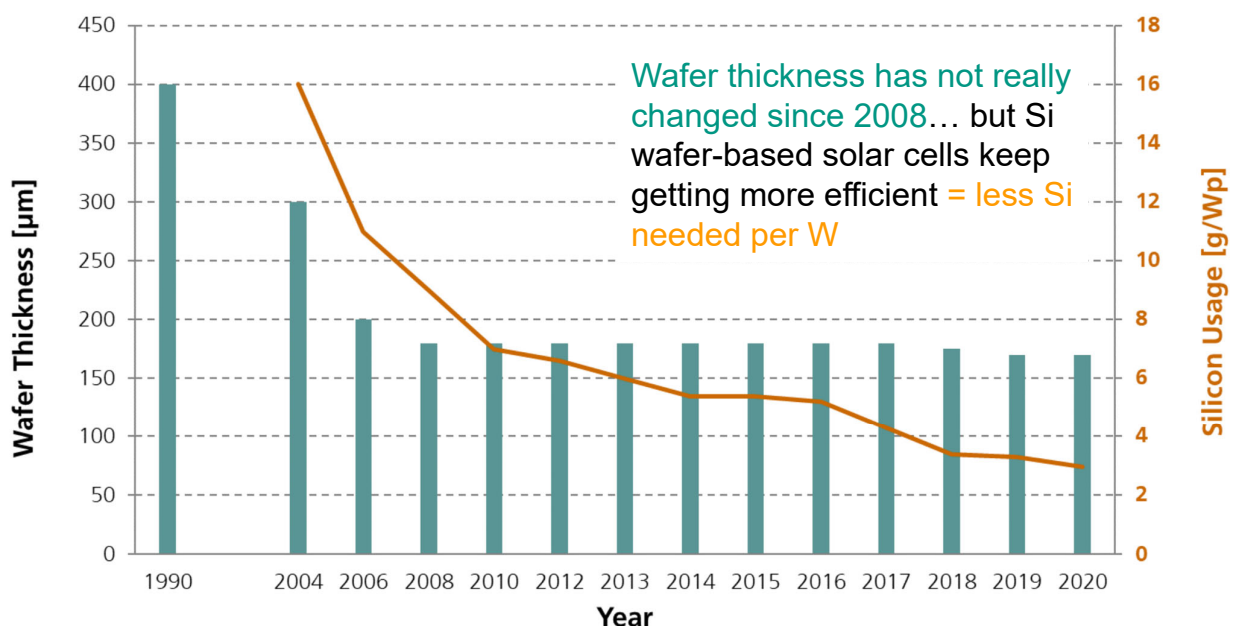


# Silicon vs Thin-film PV

- Huge demand for PV in mid-2000's  $\Rightarrow$  over-demand & under-supply of Si  $\Rightarrow$  Si prices sky-rocketed  $\Rightarrow$  two responses:
  - 1) huge investment in thin-film PV technologies to move away from wafer-based Si;
  - 2) but at same time, massive plants for poly-Si manufacturing were being built
- Global recession started in 2008  $\Rightarrow$  investors have no money  $\Rightarrow$  massively reduced demand  $\Rightarrow$  made worse by massive over supply of poly-Si  $\Rightarrow$  bottom dropped out of wafer-based silicon solar market  $\Rightarrow$  Si PV manufacturers forced to cut costs to stay in business and take loans from government (e.g. China)  $\Rightarrow$  many EU Si PV companies go bankrupt  $\Rightarrow$  thin-film PV technologies largely still developing and cannot compete  $\Rightarrow$  many go bankrupt between 2010 – 2012

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# Silicon vs Thin-film PV

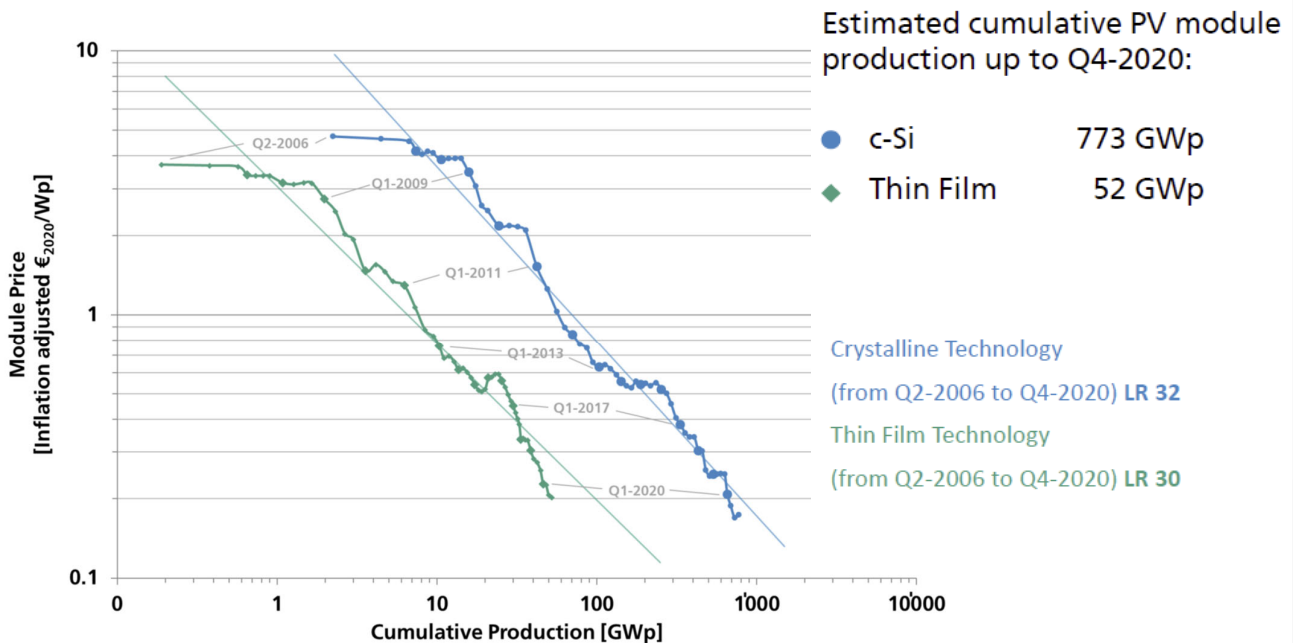


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Source: <https://www.ise.fraunhofer.de/en/downloads-englisch/pdf-files-englisch/photovoltaics-report-slides.pdf>

# Silicon vs Thin-film PV

- Learning rate (LR) for thin-film PV slower than for c-Si PV

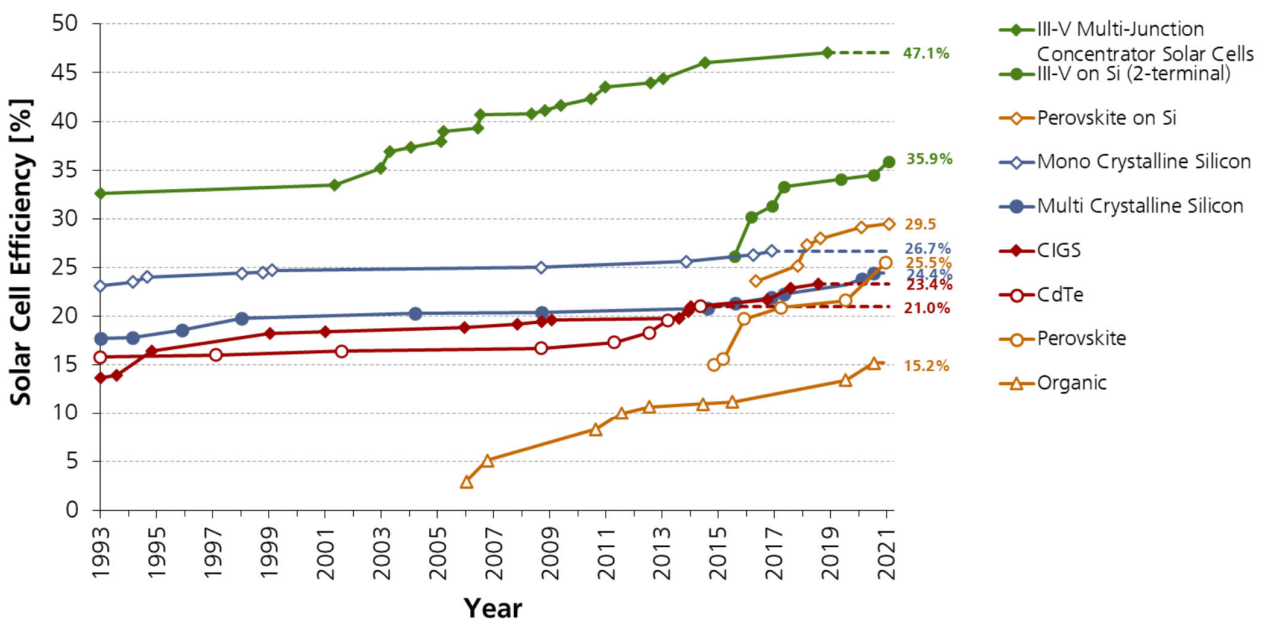


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Source: <https://www.ise.fraunhofer.de/en/downloads-englisch/pdf-files-englisch/photovoltaics-report-slides.pdf>

# Silicon vs Thin-film PV

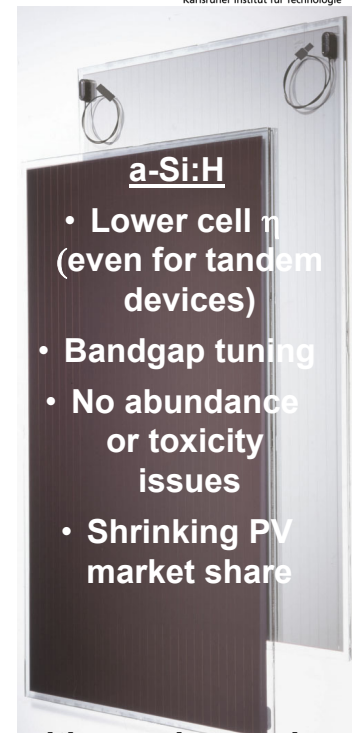
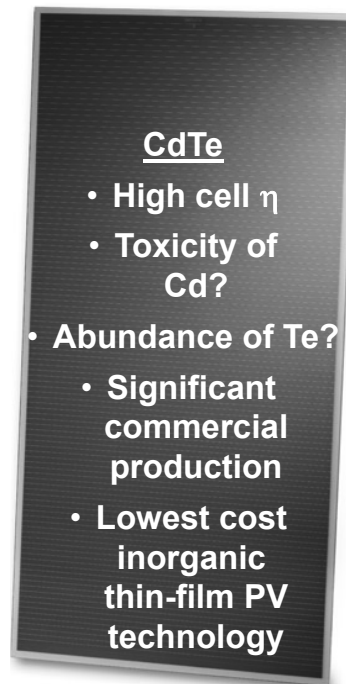
- c-Si and mc-Si solar cell efficiencies hardly increasing (approaching  $\eta \sim 30\%$  theoretical efficiency limit) – CdTe and CIGS also no recent progress
- Most rapidly increasing efficiency is for perovskite solar cells (and tandems of perovskite on Si)



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Source: <https://www.ise.fraunhofer.de/en/downloads-englisch/pdf-files-englisch/photovoltaics-report-slides.pdf>

# Comparing Thin Film PV Modules



***All thin-film PV technologies finding it tough to compete with ever-increasing efficiencies and ever-reducing costs of c-Si wafer-based solar cells***

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Photo: Manz

Photo: First Solar

Photo: Schott Solar

## Thin-Film PV Summary

- Range of materials can be used for thin-film solar cells:
  - i) a-Si:H (incl. a-Si:H/nc-Si:H tandems) and thin-film c-Si
  - ii) CIGS
  - iii) CdTe
- Main goal was to move away from energy intensive process of making c-Si, but ultimately thin-film struggles on cost
- a-Si and thin-film Si never achieved  $\eta > 10\text{-}11\%$  large-area  $\Rightarrow$  cannot ignore “balance-of-systems” (BoS) costs
- CIGS and CdTe exhibit higher efficiencies but issues with abundance and toxicity remain  $\Rightarrow$  compatible with TW-scale?
- c-Si fabrication processes are simple and robust  $\Rightarrow$  plus c-Si also very stable  $\Rightarrow$  hard for a new technology to beat
- Thin-film PV market not growing  $\Rightarrow$  main hope lies in the perovskites (and their tandems with c-Si)?

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## Homework: a-Si:H solar cells

- What role does H play in a-Si:H?
- Why is it necessary to make a *pin*-junction out of a-Si:H material? (or why won't a *pn*-junction made from a-Si:H work very well?)
- How does the Stäbler-Wronski Effect (SWE) affect the performance of a-Si:H-based devices?
- Describe one way of introducing light-trapping into a a-Si:H solar cell.
- With two elements can Si be alloyed to tune the bandgap of a-Si:H solar cells up and down?
- What is the critical issue to consider when fabricating a tandem/multijunction solar cell? State why.

## Homework: a-Si:H solar cells

- Reading Chapter 13 textbook