Raw materials in solar cells: state of art and perspective

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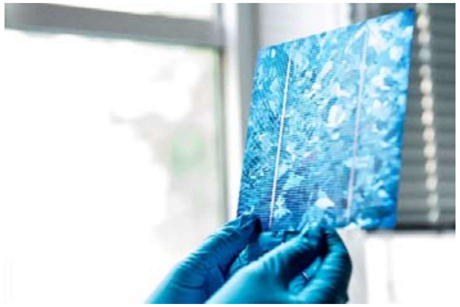
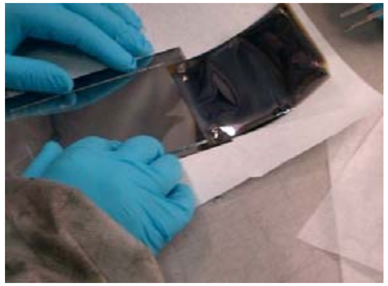
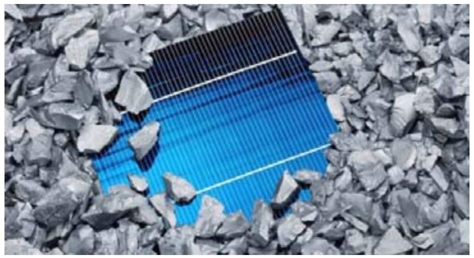


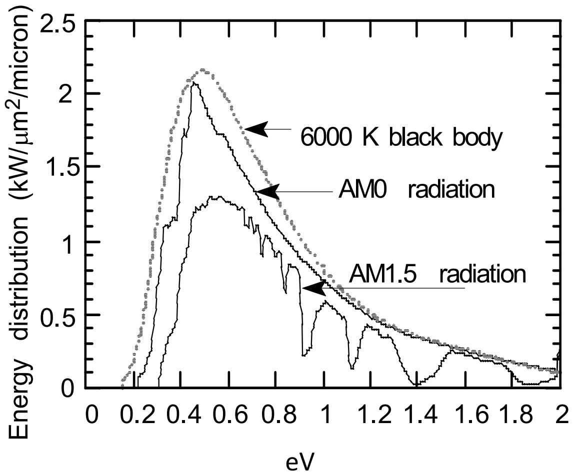


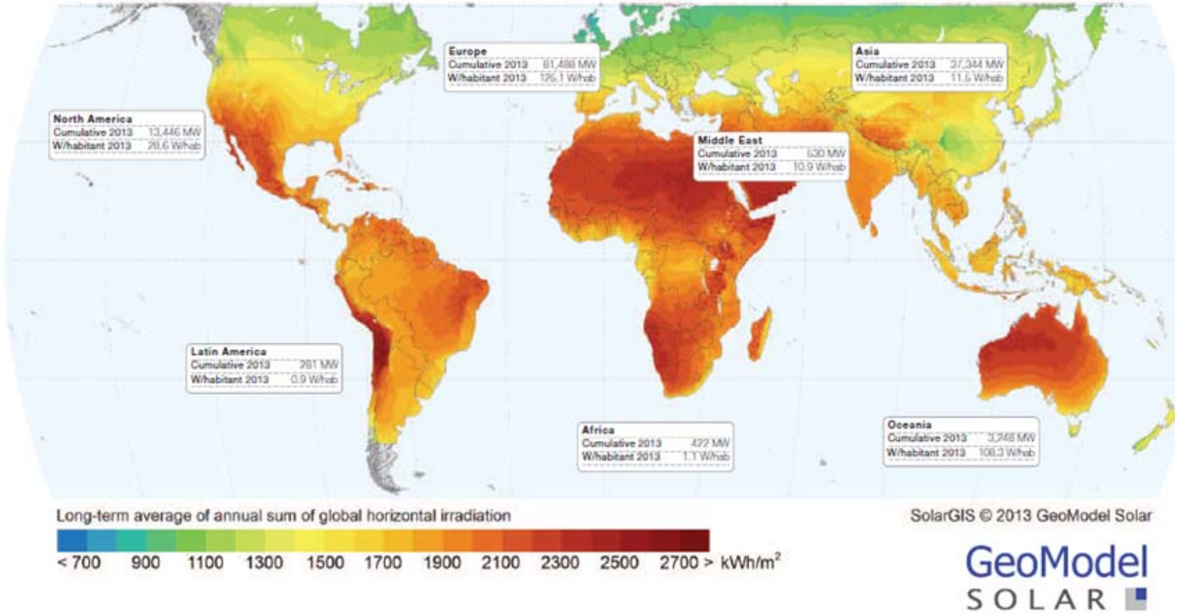



Solar energy

Solar Energy is the most important resource for humanity

Sunlight is
- abundant (the amount of power that the Sun deposits per unit area on earth is $= 1368\ W/m^2$
- inexhaustible (the sun will last for more than 4 billion years)
- well distributed over the planet.





https://ec.europa.eu/jrc/en/pvgis

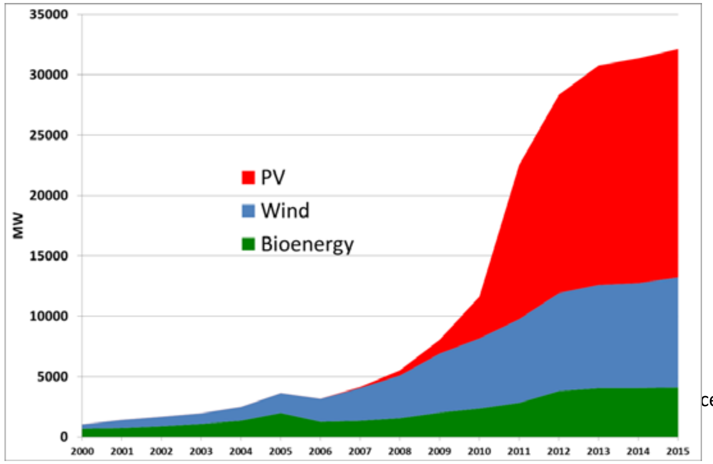
The solar energy reaching the earth's surface in one day exceeds humankind's total energy requirements for 30 years

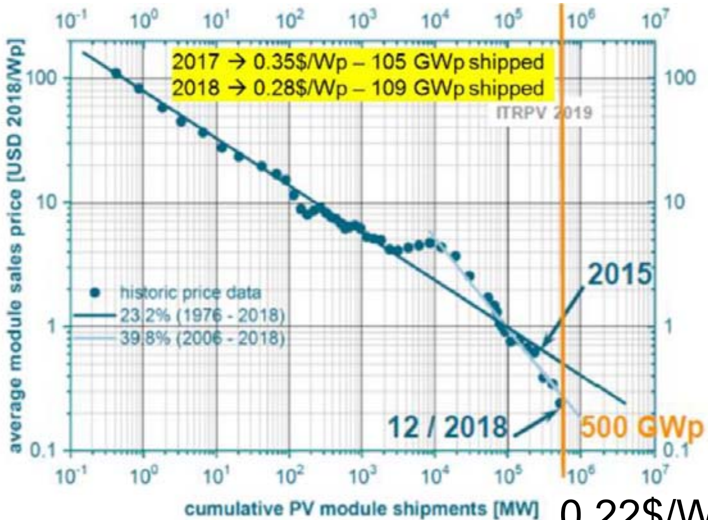
The sunlight can be converted into electricity by a Photovoltaic device

S.Binetti 2020/2021 (University of Milano-Bicocca)

Photovoltaic energy : Facts

- Photovoltaic (PV) energy is one of the most promising emerging renewable technologies
- Cumulative PV capacity grew at 37%/yr on average since 2003
- Total global capacity overtakes 750 gigawatts (GW) in 2020





0.22$/W in 2019

Grid parity has been achieved!

Key role of PV forecasts in all energy scenarios

Based on current market trends it has been estimated that:

- PV has the potential to meet 15% of the EU electricity demand in 2030.
- PV can give considerable contribution to the reduction of CO_2 emissions

In 2020 the global electricity capacity is currently over 7 TW

- 750 GWp of solar panels produces about 1.5% of the current global electricity capacity

By 2050 the global power demand will be 30 TW

- 70 - 100 TWp of solar panels will be necessary in order to meet 50% of the global energy demand by PV
- 100 TW of installed PV would avoid the emission of up to 100 gigatonnes of CO_2 annually

The expectations for PV are high: The Terawatt ERA of PV plant must be reached

Have we a reliable and low-cost supply of raw materials for the TW ERA of PV technology ?

Today

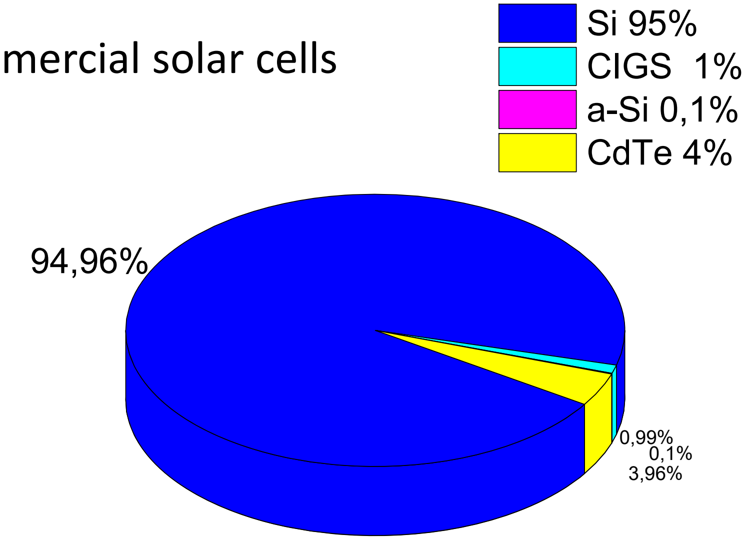
Which material is responsible for this impressive PV development?

14

Si

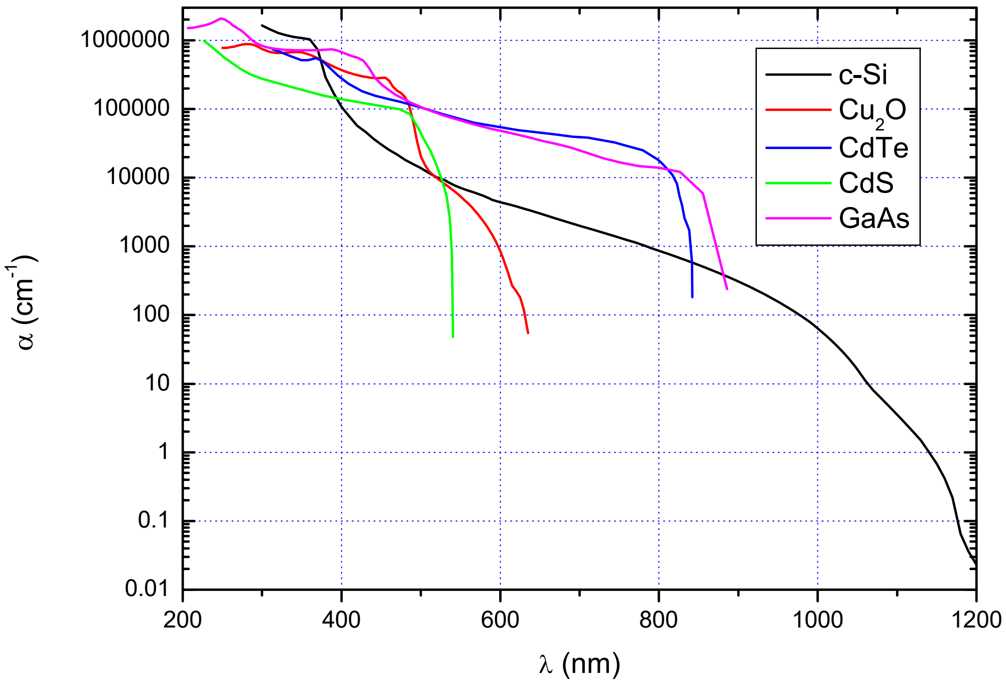
28.085

Commercial solar cells

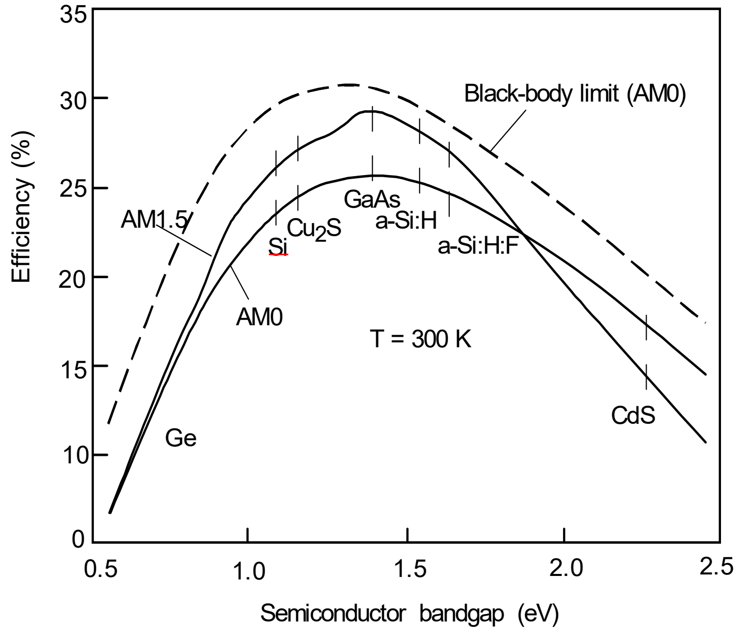


From a physical properties point of view

Absorption



Energy gap



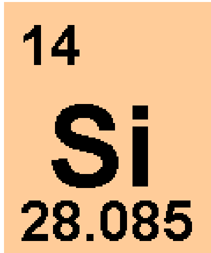
W.Schockley, H. Queisser JAP 32 (1961) 510

Silicon is not the best material!

Silicon solar cell's advantages

- ✓ Low cost (0.22 $/W)
- ✓ Availability
- ✓ No toxicity
- ✓ Efficiency
- ✓ Long lifetime
- ✓ Sustainability
- ✓ Recycling process

→ **Up to now Silicon has no competitors!**



Availaibility: silicon

14
Si
28.085

Silicon constitutes about 26% of the Earth’s crust and it is the second most abundant element in weight

Most of the earths’ crust is made up of silica and miscellaneous silicates associated with aluminium, magnesium and other elements

No Toxicity issues

Silicon production

Si metallurgic production
From quartz and carbon

$SiO_2 + C \rightarrow SiC + SiO_2 \rightarrow Si + SiO + CO$

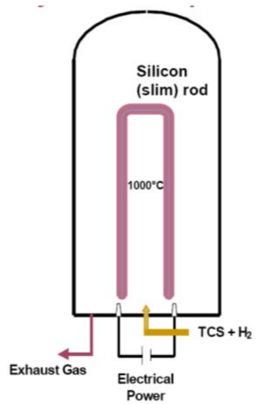
1- 3% of impurities

Si reaction with HCl

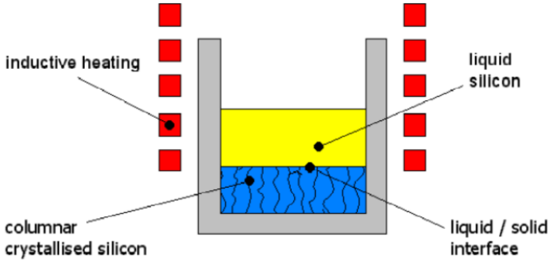
$SiHCl_3$ purification via distillation

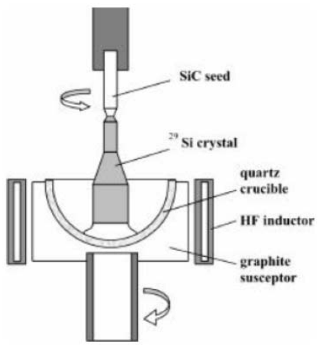
Electronic grade silicon

Polysilicon deposition



99,9999999% (9N) or even 11N purity



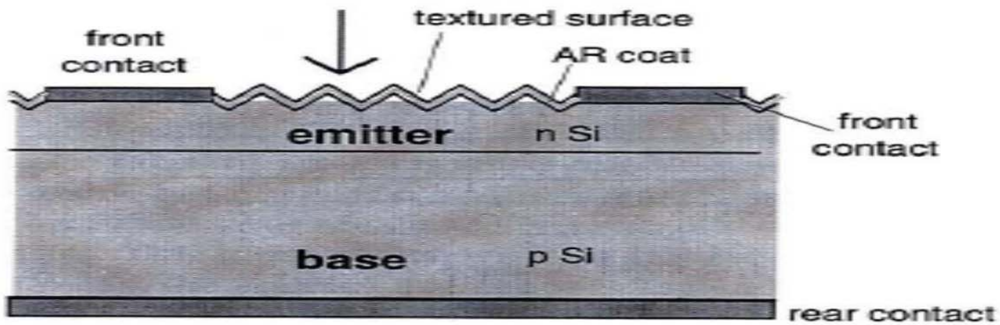


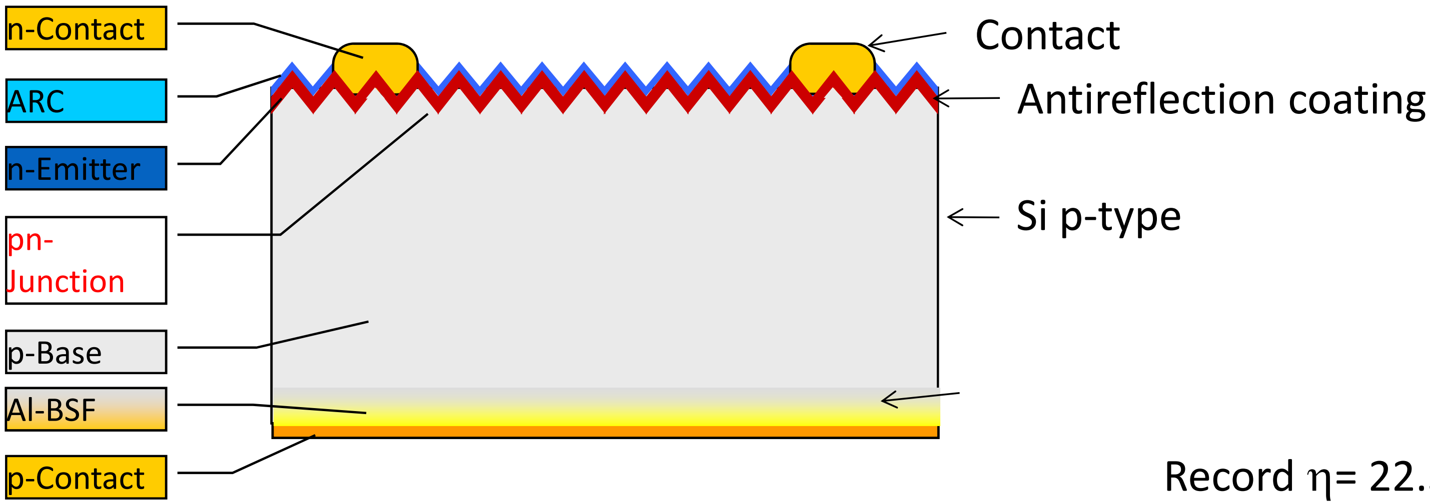
Si multicrystalline

Si monocrystalline

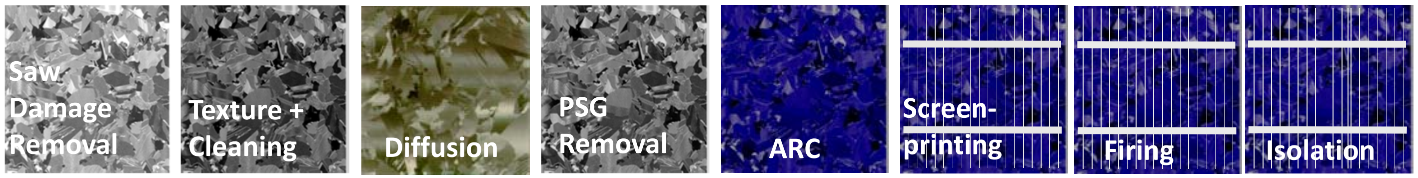
than 80% of the 100,000 tons produced are dedicated to the PV market

Silicon solar cell's process: state of the art



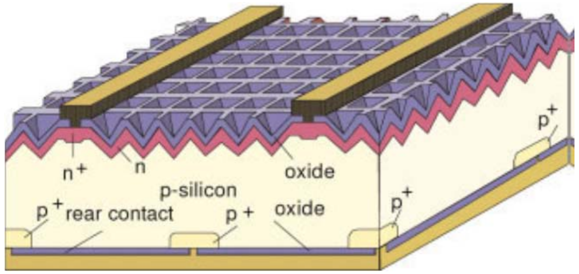


Record η= 22.3 %

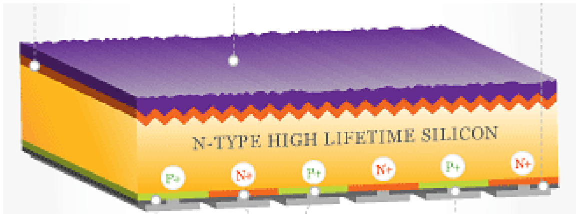


The technology has led us towards higher efficiency solar cells

- PERL cells (by UNSW)
  record of efficiency: 26.7 %
  Commercial efficiency: η=22 % *(Suntech)*

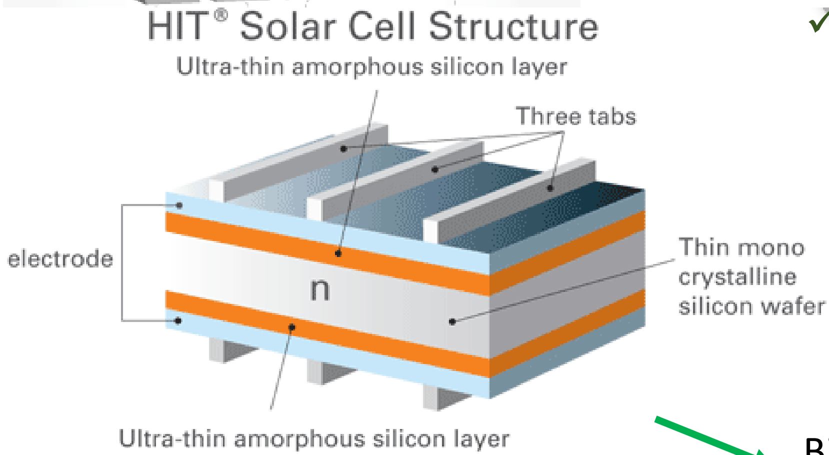


- Based on n type Silicon :
  commercial η=25.5% (*Sunpower*)



Optimizing :
- ✓ Texturization
- ✓ Surface passivation
- ✓ Contacts
- ✓ Material lifetime
- ✓ Junction

- HIT structure : c-Si with a double a-Si/c-Si heterojunction on n-type *(Sharp -Sanyo)*
  η= 25.6 % (R&D)
  η=21 % (in production)



Bifacial panel 3SUN
Enel green power

Efficiency is very close to the maximum value (28%)

Silicon solar cell's advantages

- ✓Low cost (0.22 $/W)
- ✓Availability
- ✓No toxicity
- ✓Efficiency (26.7%) - module efficiency (18 % mc–Si- 22 % mono Si)
- ✓Long lifetime (35 yr)
- ✓**Sustainability ***

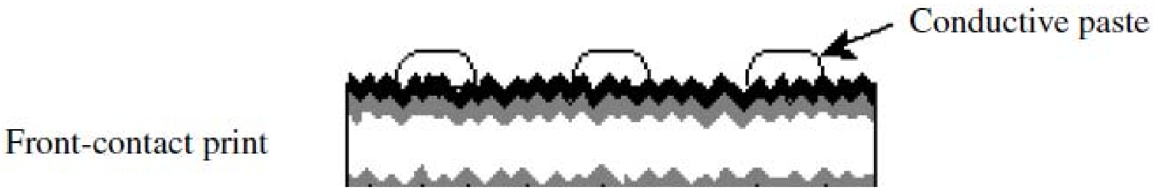
Recycling process

Assuming 30 year system life Silicon PV systems will provide a net gain of 29 years of pollution free and greenhouse gas free electrical generation

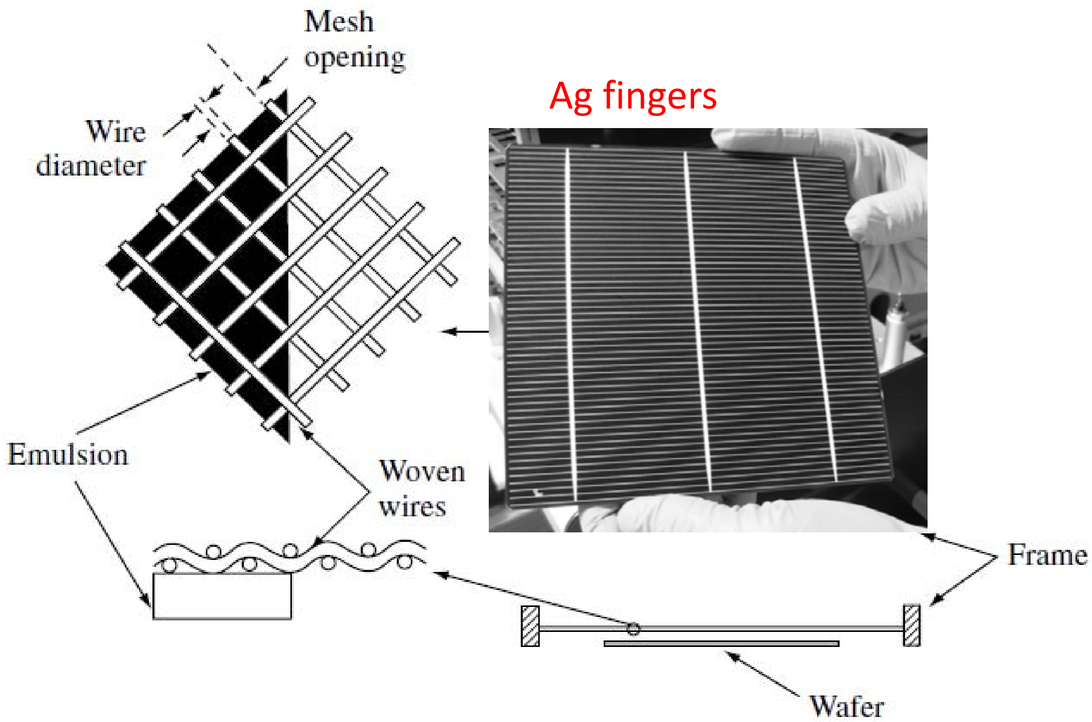
The **energy pay back time** of silicon solar cell is 1 – 1, 5 years

14
Si
28.085

Metallic Contacts



47
Ag
Silver
107.868



The average solar panel contains between 15 and 20 g of silver: (10 g /m^2- 130 mg per cell)

Silver' s matter

Rank	Z	Element	Symbol	Lithosphere abundance[1]	Relative proportion (ppm)[2]	Abundance in crust (ppm)[3]	Abundance in crust (ppm)[4]	Abundance in crust (ppm)[5]	Production (2012, tonnes)[6]
1	8	oxygen	O	460,000	474,000	460,000	467,100	461,000	
2	14	silicon [A]	Si	277,200	277,100	270,000	276,900	282,000	7,600,000
65	47	silver	Ag		0.070	0.080		0.075	24,000
66	80	mercury	Hg		0.05	0.067		0.085	1,600

Today the production of solar panels is estimated to use 20% of the globe's yearly industrial silver consumption

Silver and other PV technologies

- Concentrated solar power CSP : systems of mirrors or lenses that concentrate solar light into a small device
- Silver is essential for this technology, since due to its superior light reflectivity characteristics it is the first choice of material for such mirrors.

Silver requirement for the various concentrated solar power technologies*

	Silver content [kg/m^2]	kg/MW
Fresnel reflector	0.001	13.75
Parabolic trough	0.001	3.75
Solar power tower	0.001	7.57

* Renewable Energy 69 (2014) 157

Photo courtesy of AREVA Solar

Silver’ s matter

100 TW of installed PV plant aimed for 2050 will exceed silver reserves

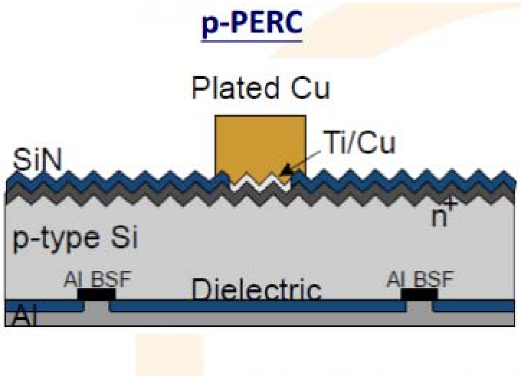
Solution

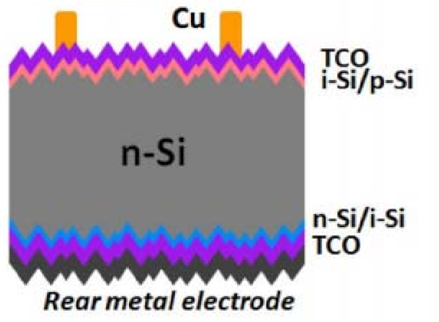
1. reduce the use of Ag (the target is up to 65 mg per cell in 2028)
2. Silver replacement
3. Recycling
4. Develop other PV technologies that do not contain any silver

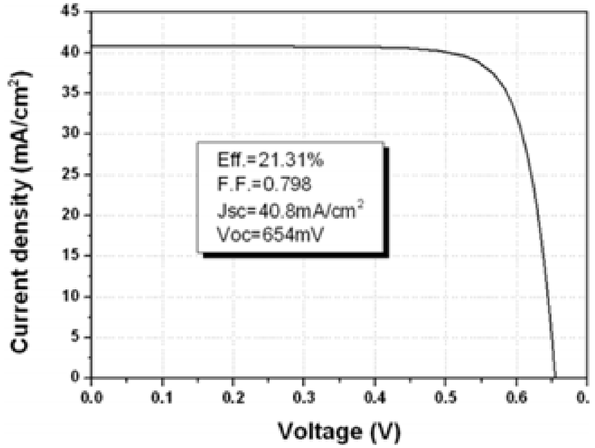
Silver Replacement

Cu plating applicable to all types of Si solar cells

Ni/Cu plating : advantages ;
Stable , low cost , high conductivity







High efficiency

S. Kluska et al. Electrical and Mechanical Properties of Plated Ni/Cu Contacts for Si Solar Cells, 5th Metallisation Workshop, 2015. UNSW

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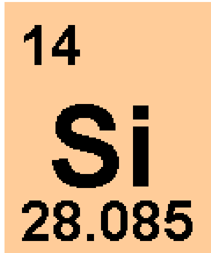
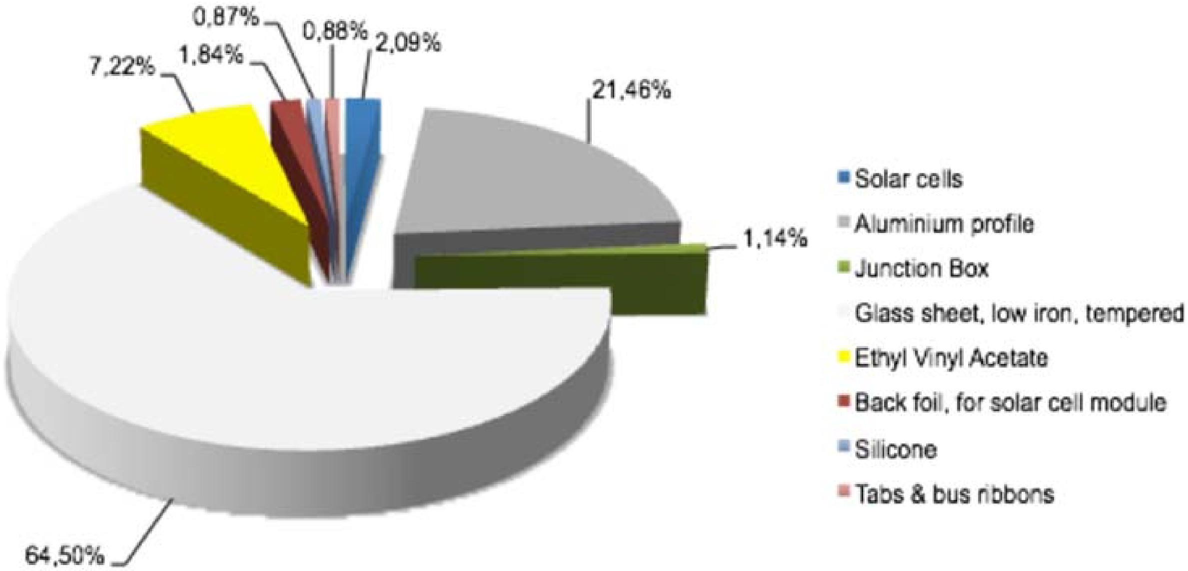
- ✓Long lifetime (35 yr)
- ✓Sustainability
- ✓**<u>Recycling process</u>**



Silicon Recycling process

- The amount of waste PV panel is estimated to reach 9.57 million tonnes in 2050
- Recycling 1 tonne of Si PV modules saves about 1.2 tonnes of CO_2 emission

https://www.youtube.com/channel/UCly9FyqW-9gbIkhxPeKnl7w



Source: M.J. de Wild-Scholten, Energy research Center of the Netherlands, Petten, The Netherlands

PV CYCLE achieves 96% recycling rate for silicon based PV modules

See RM@school TOOLKIT Recycling of silicon based PV modules in https://rmschools.isof.cnr.it

Silicon solar cell’s advantages

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- ✓No toxicity
- ✓Efficiency (26.7%) - module efficiency (18 % mc–Si- 22 % mono Si)
- ✓Long lifetime (35 yr)
- ✓Sustainability
- ✓Recycling process (PV CYCLE achieves 96% recycling rate for silicon based PV modules)

✓No toxicity

→ **Up to now Silicon has no competitors !**

14
Si
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*Assuming 30 year system life Silicon PV systems will provide a net gain of 29 years of pollution free and greenhouse gas free electrical generation
The energy pay back time of silicon solar cell is 1 – 1, 5 years

Material and devices
beyond silicon: in production and emerging

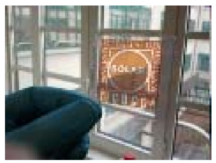
- **c-Silicon solar cells**

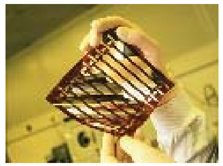
  Today, approximately 95 % of cumulative installed PV modules are based on crystalline silicon (c-Si) technology.

- **Inorganic thin-film technologies**
  - **a-Si-H, µc-Si-H, nc-Si**
  - **CdTe, CIGS Cu(In,Ga)Se_2**
  - **New material : CZTS**

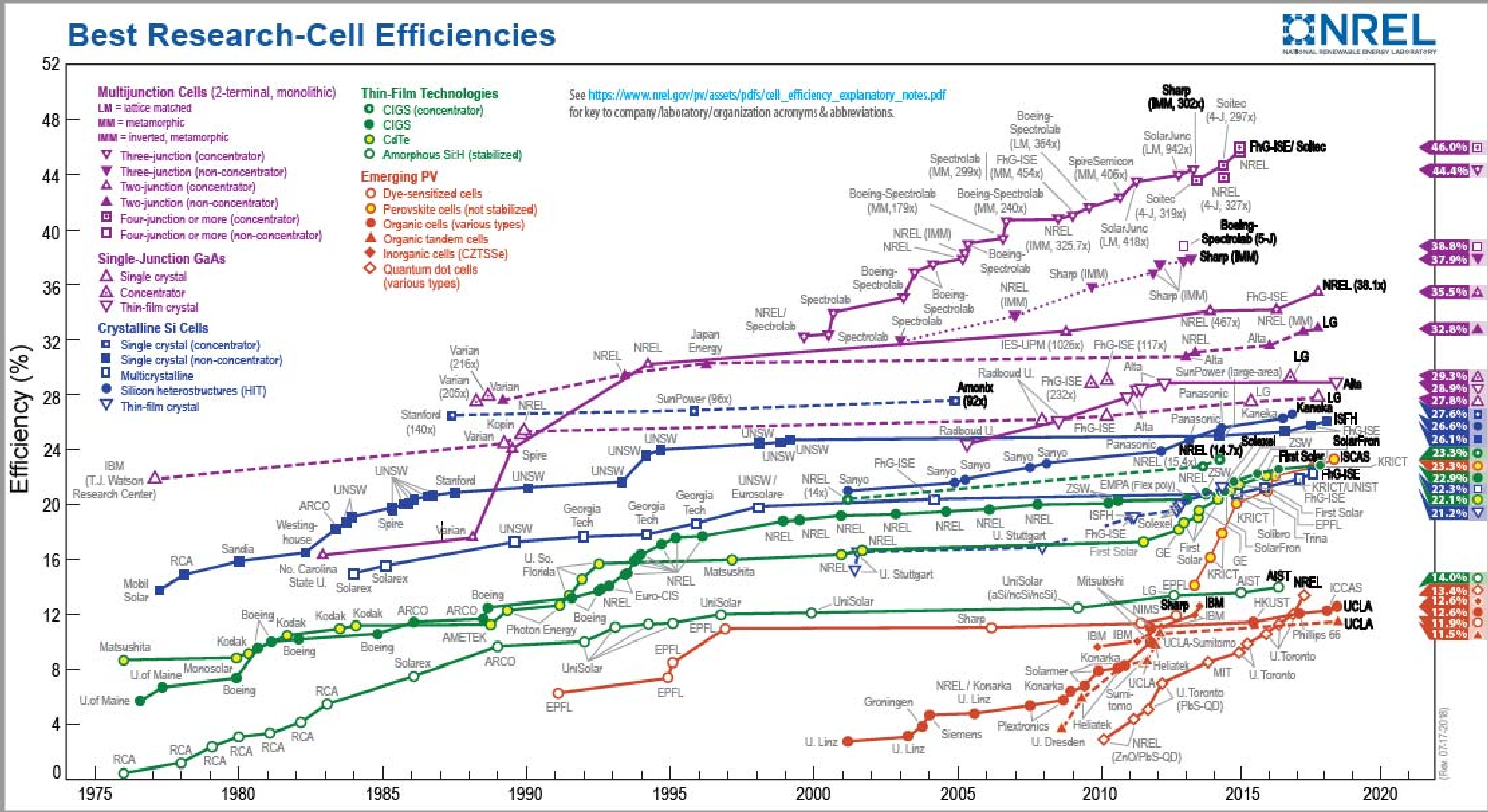
- **III-V (multijunction solar cells** (**GaAs- AlGaAs/GaAs/Ge**)
  - High efficiency (32 %)
  - high cost for space or concentration application

- **Organic and hybrid organic inorganic based thin film technologies**
  - Printing on large areas has been demostrated
  - Low cost of the active material and of the substrates
  - Open questions: scaled-up module prototypes, low lifetime and durability and a lack of standardized stability data





PV technologies and lab scale cell efficiency



S.Binetti 2020/2021 (University of Milano-Bicocca)

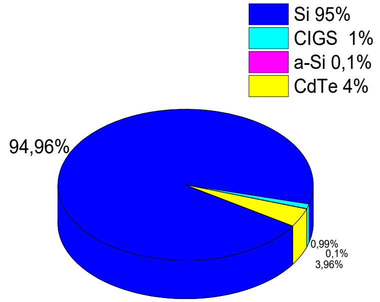
http://www.nrel.gov/

Inorganic Thin film technologies

The market is much smaller than the silicon's one (<6%)
Thin Film manufacturers are suffering from sharp decrease of prices of crystalline silicon PV.

Advantages:

- reduced quantity of active materials (few μm)
- monolithical integration: all production steps in one line
- high automation of production lines (glass-in/module-out);
- low energy consuming process (Short energetic payback< 1 year)
- low cost substrates (glass, polymers, metal)
- a broader spectrum absorption range, better weak light performance
- flexible substrates customized integrated solution on flexible substrate

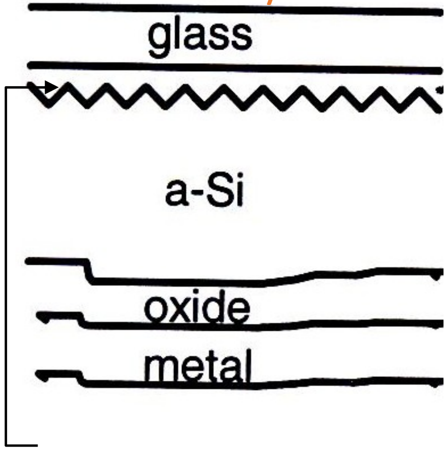


BIPV

Competitiveness of thin film PV depends on :
conversion efficiency in module (should be $\eta > 22$ %)

Inorganic thin film solar cells

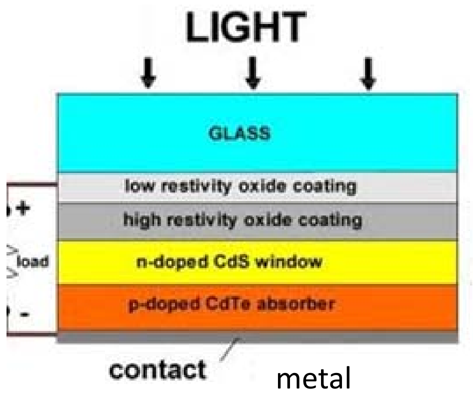
a-Si or nc-Si/a-Si



Amorphous silicon

- a-si Mature technology
- Turn-key factories available
- Simplicity
- Use of abundant material
- Light induced degradation effect
- Low efficiency

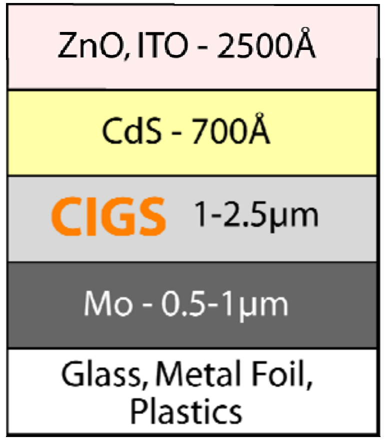
CdTe



CdTe :

- Medium efficiency (η = 11% - 15%)
- Easy to process
- Low cost manufacturing
- Potential row material scarcity (Te= 0.005 ppm)
- Currently rigid modules only
- Toxicity and recycling

CIGS – Cu(In,Ga)Se_2



- Record of Efficiency (21.7 %)
- Intrinsic p-type doping
- Direct bandgap
- Flexible substrates
- material scarcity

Cu(In,Ga)Se_2 (CIGS) thin film solar cells

✓record efficiencies 22.9 % for small cells and 16.5 % for production size modules
(Total world-wide CIGS production capacity is ~2 GWp/a)
✓ Better weak light performances

✓Diversification of production and design of CIGS modules
- Flexible and light weight CIGS modules for PIPV and BIPV

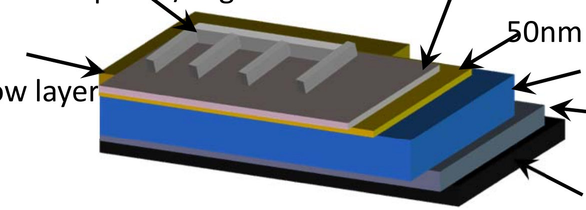


image: Manz AG

✓CIGS can be used in tandem devices (η> 30 %)
✓Lower temperature coefficients,
✓ good low light performance,
✓ short energy payback time

http://cigs-pv.net/white-paper-for-cigs-thin-film-solar-cell-technology/

Critical Metals in Inorganic thin film PV Technologies

Abundance in Earth's Crust of the elements

Cu 0.0068 %
Zn 0.0078 %
Sn 0.00022 %
Ga= 0.0019%
Se= 5x 10^{-6}%
In = 0.00016%

Ga = 19 ppm
In= 0.25 ppm
Se = 0.05 ppm

A.Le Donne, V. Trifiletti & S. Binetti "New Earth-Abundant Thin Film Solar Cells Based on Chalcogenides" Frontier in Chemistry 2019

✓The current indium extraction rate permit to estimate a global CIGS solar module production less than 10 GWp

✓Due to the adverse effects on the environment and human health, the supply and use of cadmium is restricted in Europe under the REACH regulation

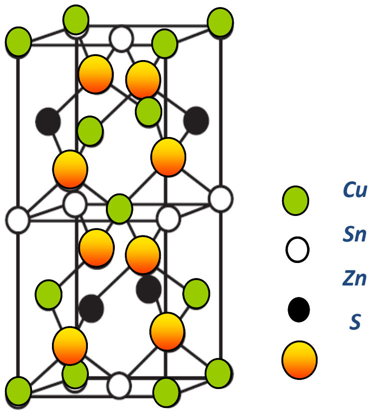
✓High price

To raise the competitiveness of thin films modules, rare and toxic elements should be avoided in all layers

NEW absorbers based on more abundant elements are required for the TERAWATT challenge

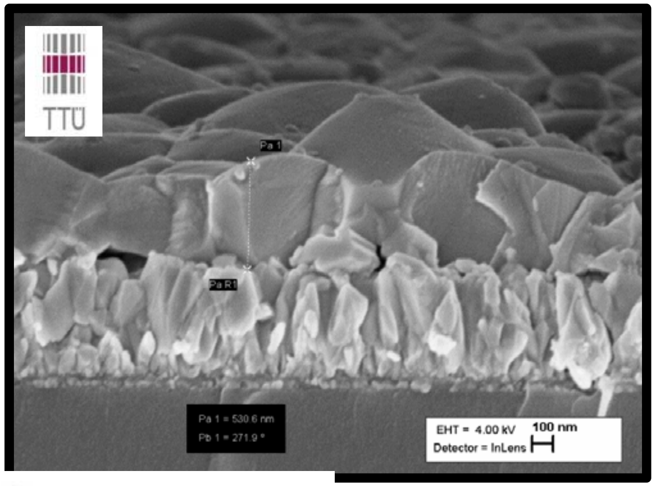
Strong constraints impose to investigate new materials

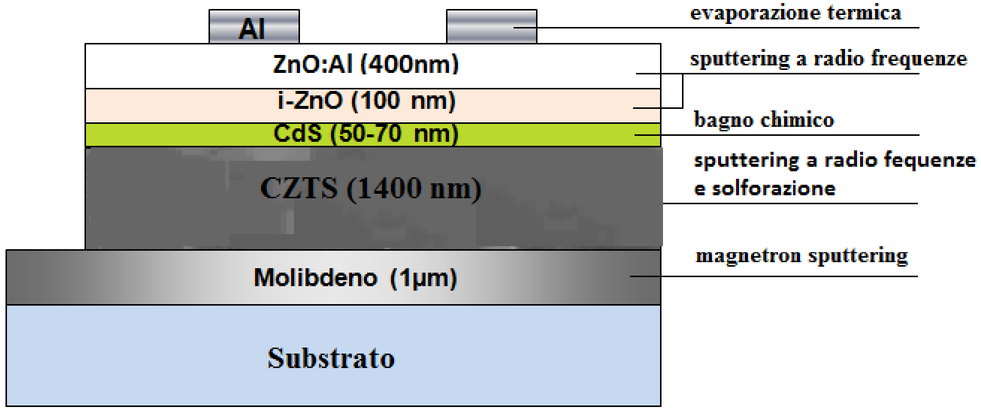
Kesterite - Cu_2ZnSnS_4



- Cu_2ZnSnS_4 (CZTS) Enviromentally friendly, low cost, many deposition methods
- High stability
- E_g can be tuned between 1.45 and 1.65 eV (DIRECT)
- High absorption coefficient (> 10^4 cm^{-1})
- *Efficiency record* η_{record}= 11% * (CZTS) - 12.6% (CZTSSe)

*C.Yan et al. Nature Energy 2019, 3- 764





Organic Photovoltaics

Pros:

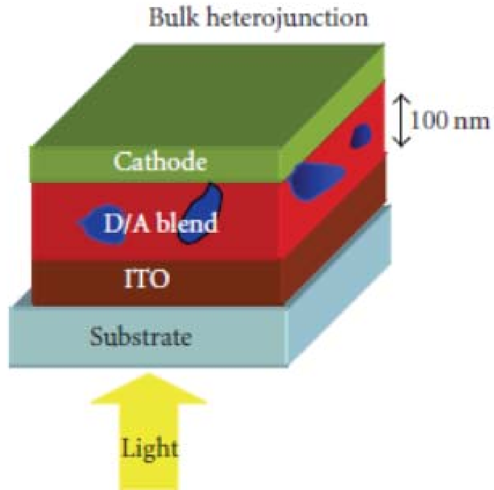
low production cost

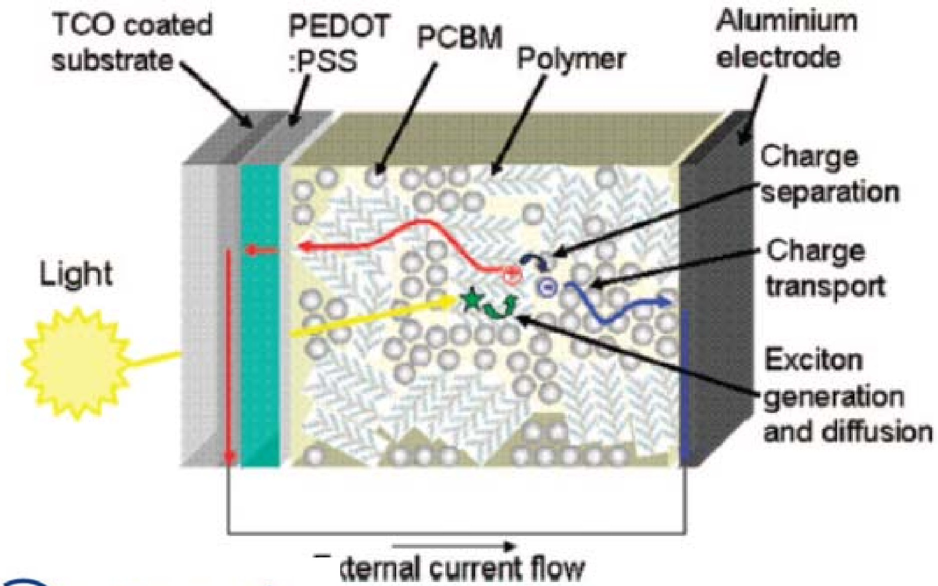
can be integrated into flexible substrates

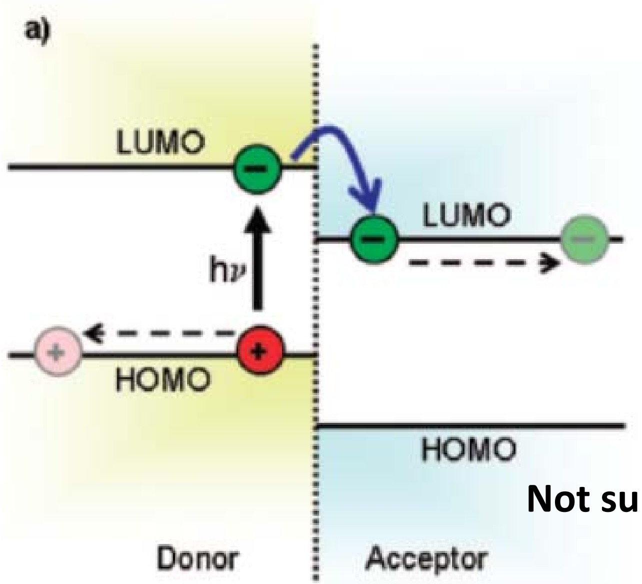
Cons

Low performance (3-5 % in module)

Low stability (2 years)



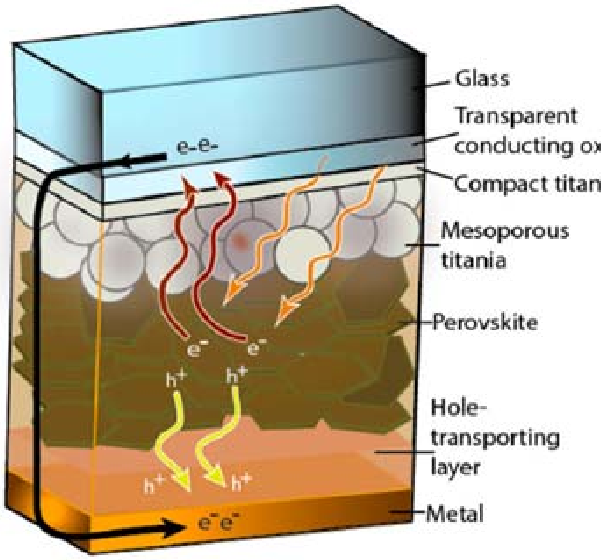


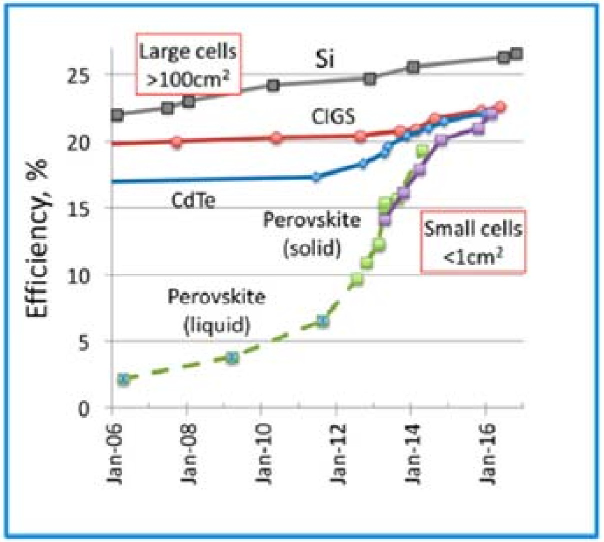


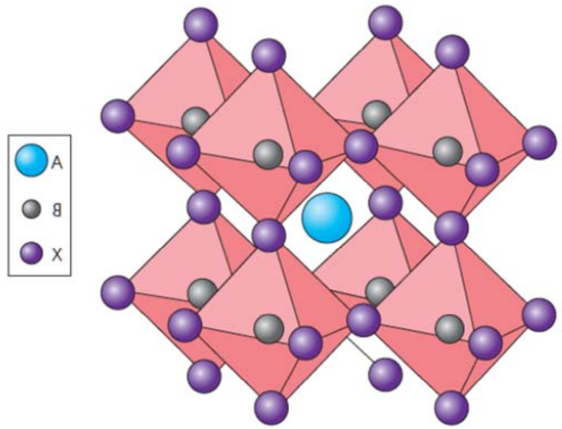
Not suitable for TERAWATT generation

Perovskite-based solar cells : a new comer

A new age for low cost high-efficiency PV ?







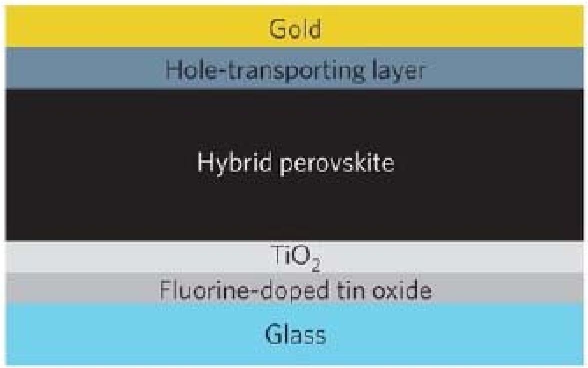
Methylammonium lead triiodide : A= CH_3NH_3 , B = Pb , X = I

Green, M. A.; Ho-Baillie, A. *Acs Energy Lett* **2017**

Perovskite-based solar cells

PROS
- strongly absorbing (< 1 μm thin films)
- ideal for solid-state cells
- act as HTM and ETM as well
- higher voltages (0.4 V)
- 24% efficiency reached
- extremely possible low cost

CONS
- dissolve or decompose in the electrolyte (no liquid electrolytes)
- Toxicity of Pb
- no stability in moisture and air
- degradation with UV light
- use of Au (Ag) as back contact



planar PSC

What's next?

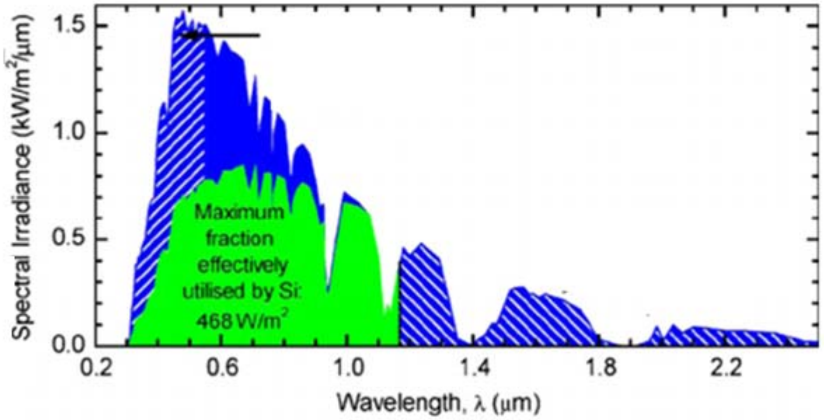
Increase the efficiency

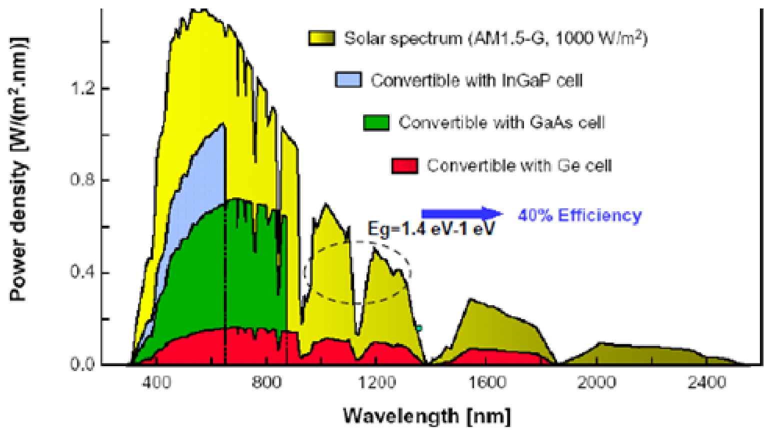
Overcoming the single junction limit (28%)

Aiming to approach the thermodynamic limit

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{5778}{300} = 93\%$$

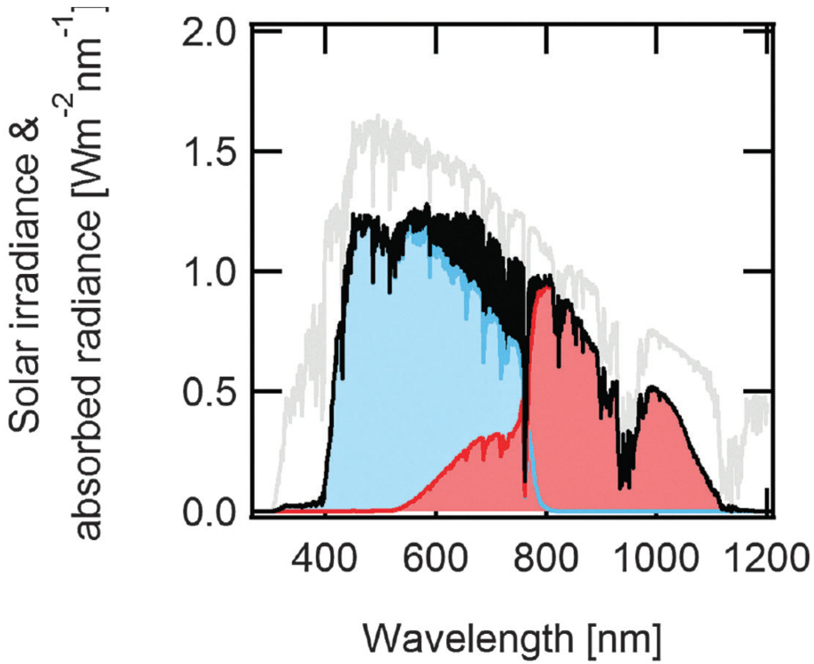
Multijunction solar cells concept and low cost

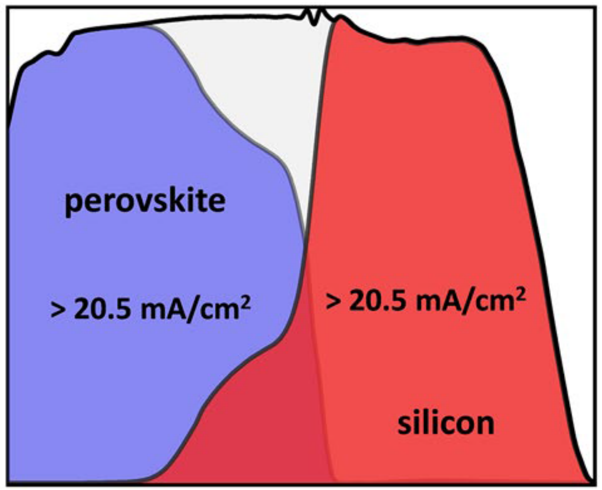




Tandem solar cell

Perovskite on silicon





Oxford PV's 1 cm^2 perovskite-silicon tandem solar cell has achieved a 28% conversion efficiency

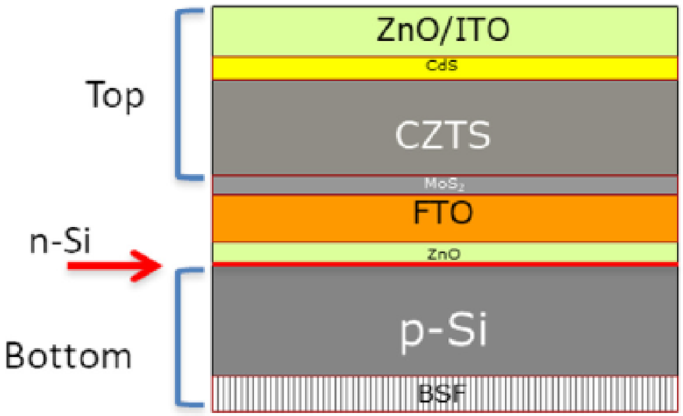
Main open questions: lifetime and stability and Pb

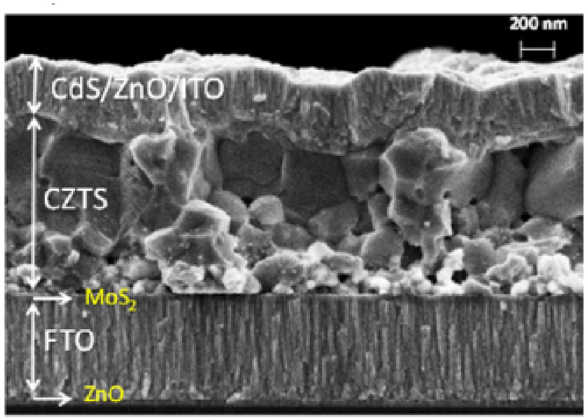
Does not make sense

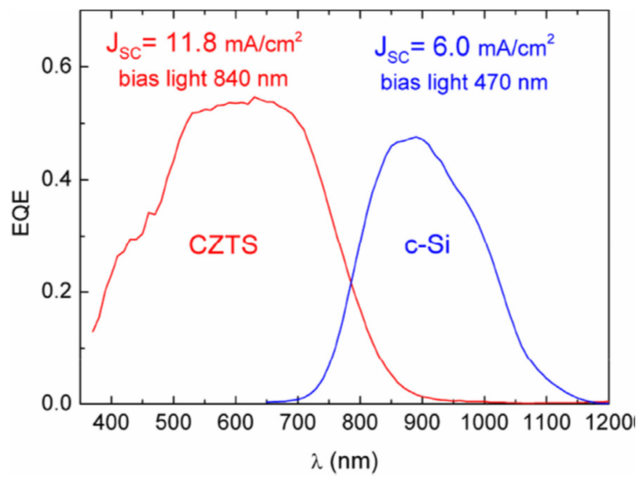
Nano-Micro Lett. (2019) 11:58

Cu_2ZnSnS_4 for Si tandem solar cell

The first working monolithic tandem cell, with Voc = 950 mV and η= 3.5%,







M. Valentini et al. Solar Energy 190 (2019) 414–419

Advantage : the same lifetime and stability and abundance on the earth crust of silicon

Conclusions

The “ideal” material for solar cells

- Energy Band gap between 1.1 - 1.7 eV
- High absorption coefficient
- Availability
- No toxicity
- Growth processes with high throughput and low carbon foot print
- Low energy pay back
- High stability

The “ideal ” solar cells

- Low cost
- High efficiency
- High lifetime
- High Stability
- Suitable for Product or Building integration
- With a cost effective recycling solutions

Take home messages

- As a renewable energy source, the only limitation of solar power is **our ability** to turn it into electricity in an efficient and cost-effective way
- The installed panels need to reach 100TWp by 2050 to reduce CO_2 emission by 25% from the 2020 level
- **Silicon could reach 100 TWp if we can substitute silver**
- There are some concepts developed in laboratories that can have potentiality (tandem solar cells with earth abundant top cell)
- From a research point of view it is important to support the development of a broad portfolio of options and technologies in PV field but

IT IS NECESSARY to develop new PV devices based on abundant material, with high efficiency and with a cost effective recycling solutions for the end of life module

Thanks for your kind attention!

MIB-SOLAR

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The MIB-SOLAR Center was established in 2010 at the Department of Materials Science (University of Milano-Bicocca) to promote and encourage study and research of new materials and devices related to solar energy in its various forms including:

- solar energy as a source of renewable energy in photovoltaic processes;
- solar energy as a source of renewable energy in photovoltaic and photocatalytic effects of different processes

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