UNIVERSITÀ DEGLI STUDI DI MILANO BICOCCA

Silicon, the key element for photovoltaic energy: past, present and future perspectives

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AVOGADRO COLLOQUIA 2019

Società Chimica Italiana

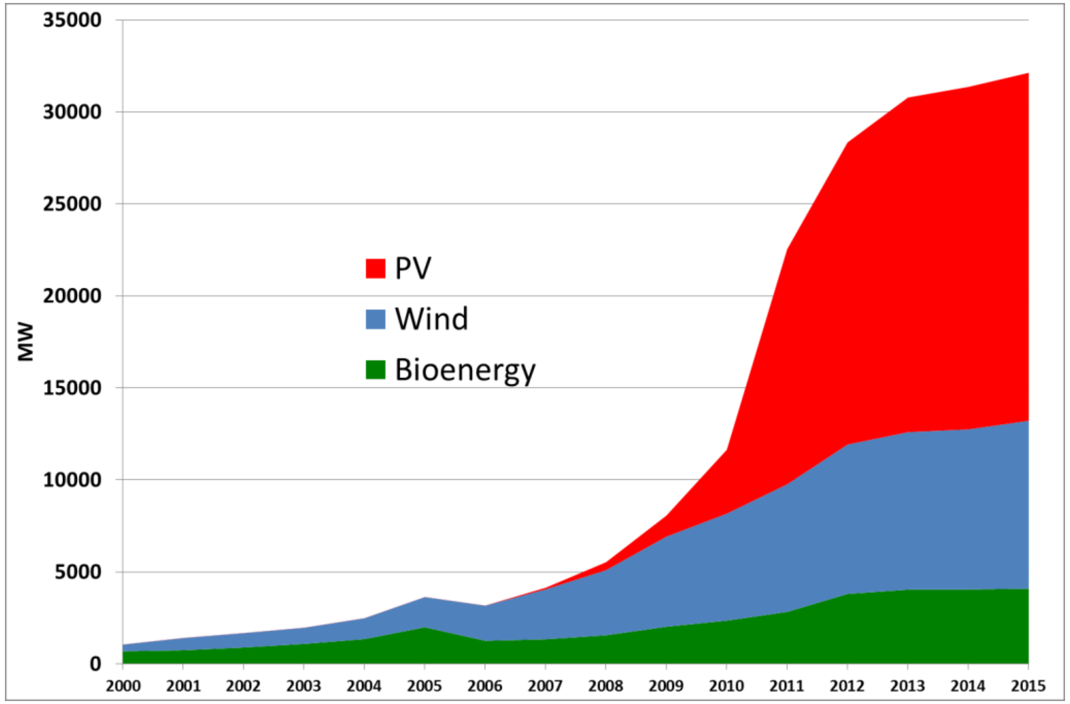
United Nations
Educational, Scientific and
Cultural Organization

2019 IYPT
International Year
of the Periodic Table
of Chemical Elements

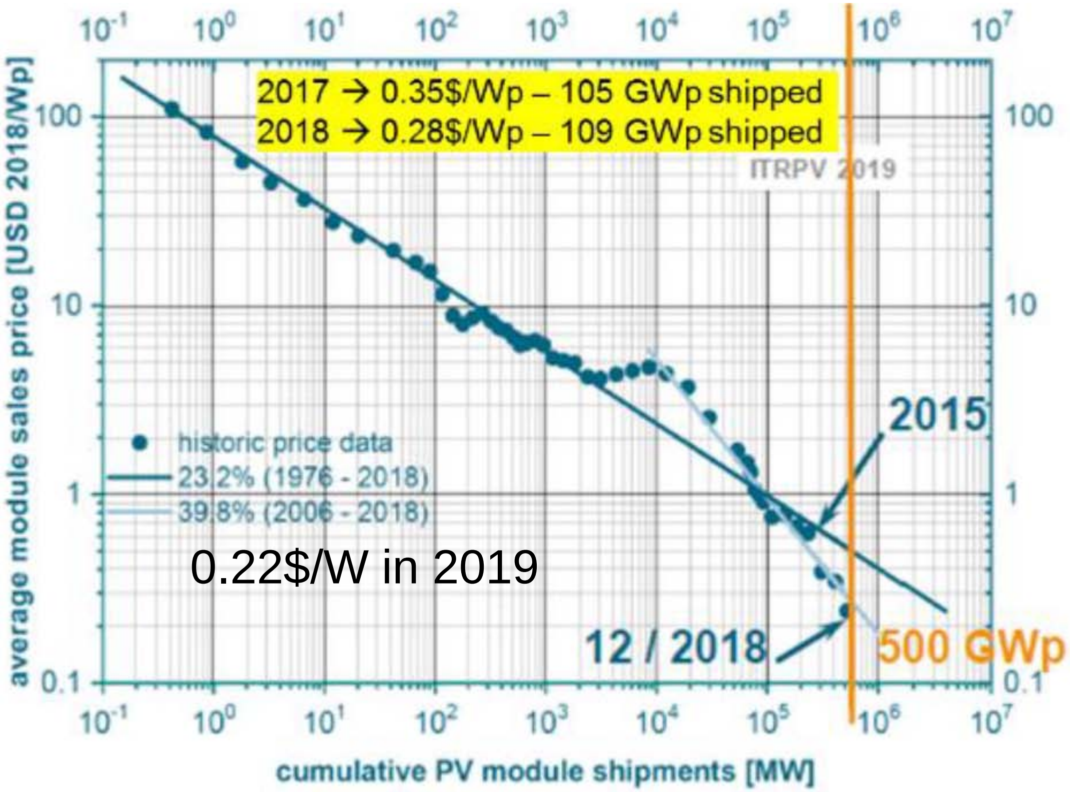
Consiglio Nazionale
delle Ricerche

PV Facts

- Photovoltaic (PV) energy is one of the most promising emerging renewable technologies
- Cumulative PV capacity grew at 49%/yr on average since 2003
- Total global capacity overtook 510 gigawatts (GW) in 2019



Source: International Energy Agency (IEA) , Bloomberg New Energy Finance

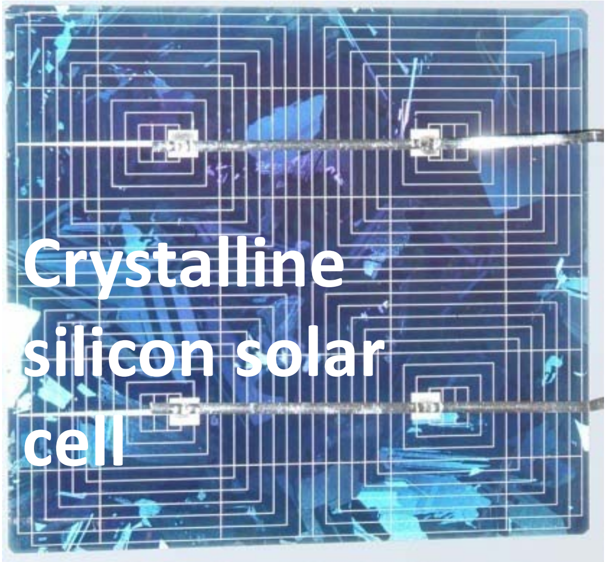


Key role for PV energy in the future
4 600 GW of installed PV capacity by 2050 would avoid the emission of up to 4 gigatonnes (Gt) of CO_2 annually

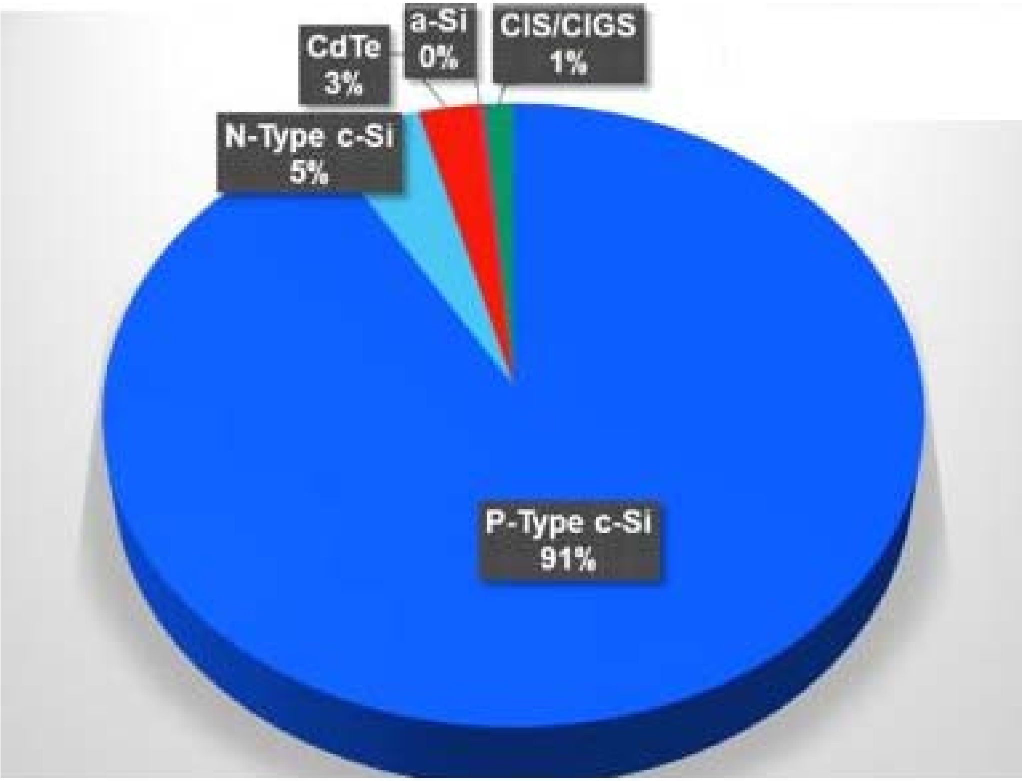
Madrid COP25
United Nations
Climate Change

Which technology is responsible for that ?

14
Si
28.085



Crystalline silicon solar cell



From an historical point of view

Alexandre-Edmond Becquerel

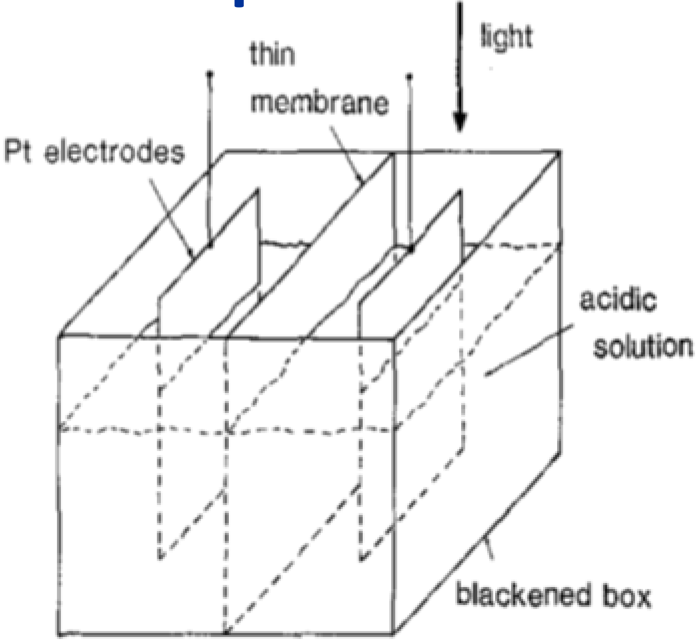
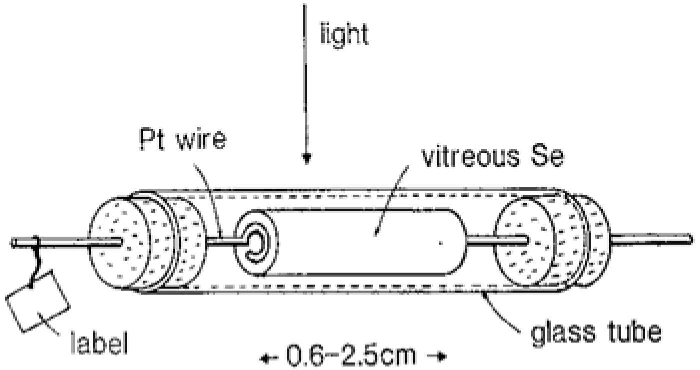
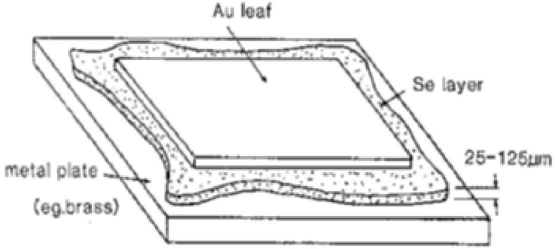


Diagram of apparatus described by Becquerel (1839)

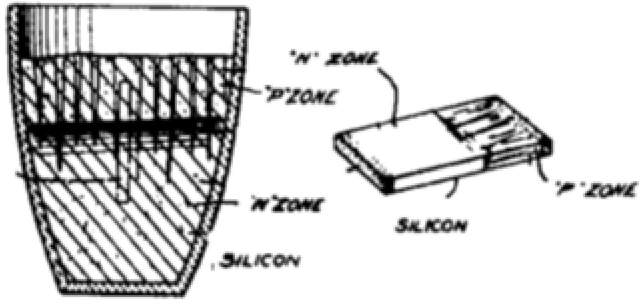


: Sample geometry used by Adams and Day (1876)



Thin film selenium cell demonstrated by Fritts in 1883.

η=1%

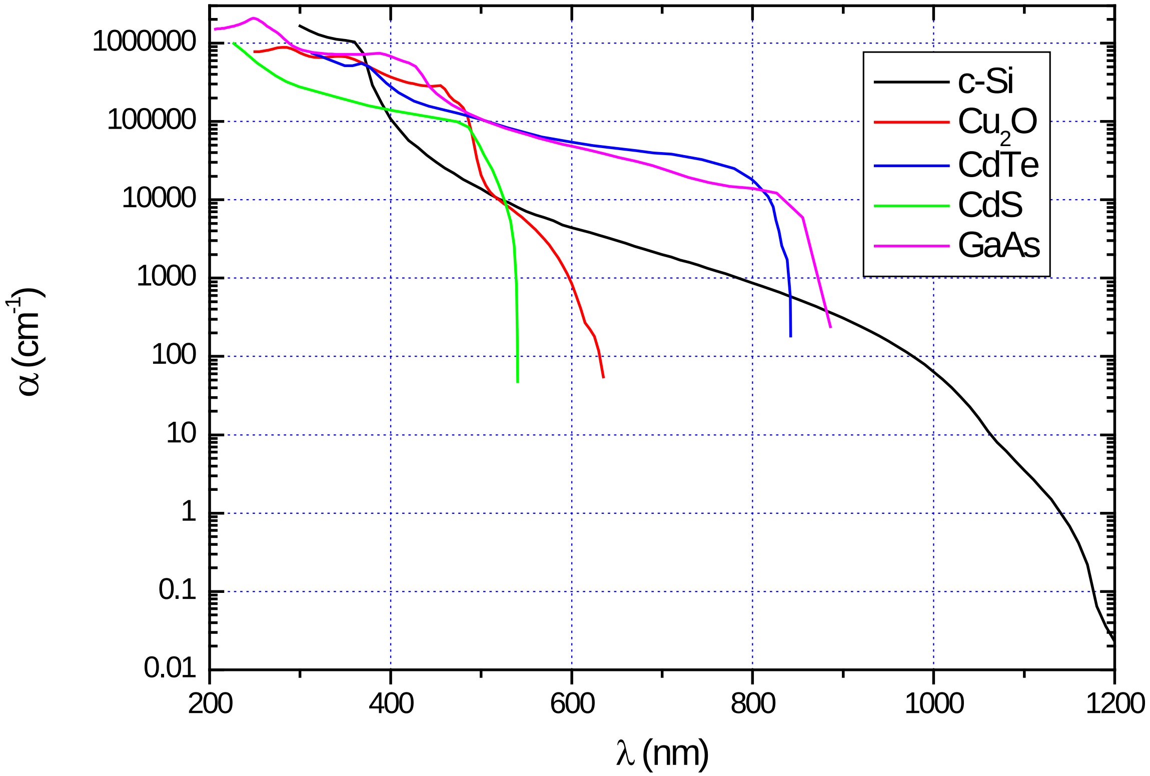


First silicon solar cell Ohl in 1941 η= 1%

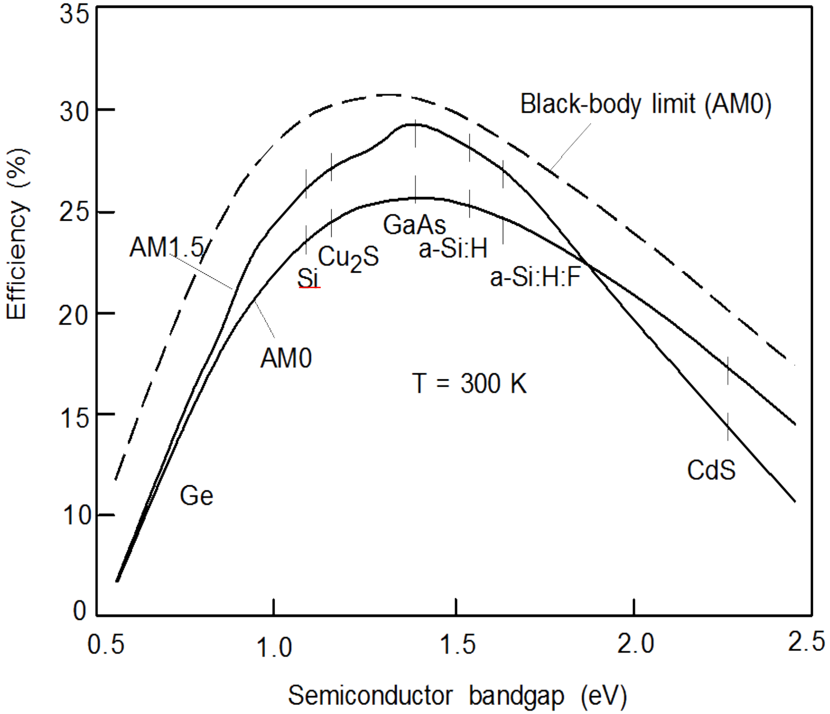
p-n junction based Si cell @ Bell laboratories in 1954 η= 6%

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

- ✓Availability (Si is the 2° most abundant element)
- ✓No toxicity
- ✓Low cost (0.22 $/W)
- ✓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)

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

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Si
28.085

*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

Silicon production

Si metallurgic production
From quartz and carbon

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

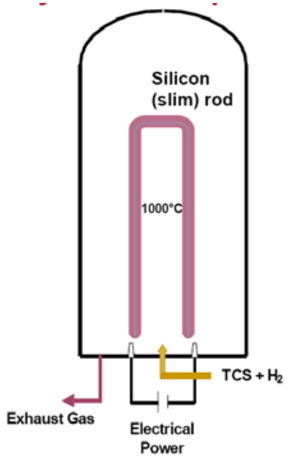
1- 3% of impurities

Si reaction with HCl

$SiHCl_3$ purification via distillation

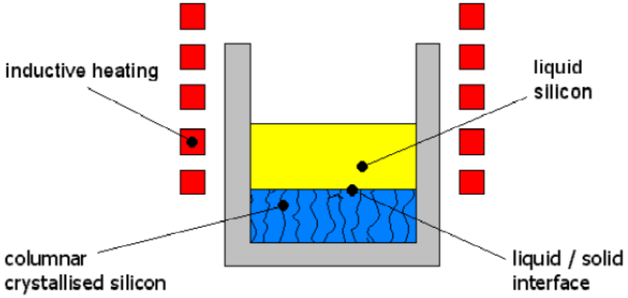
Electronic grade silicon

Polysilicon deposition

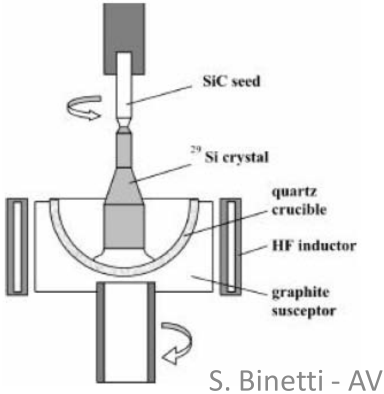


99,9999999% (9N) or even 11N purity

80% of 100.000 Si tons produced are for PV market

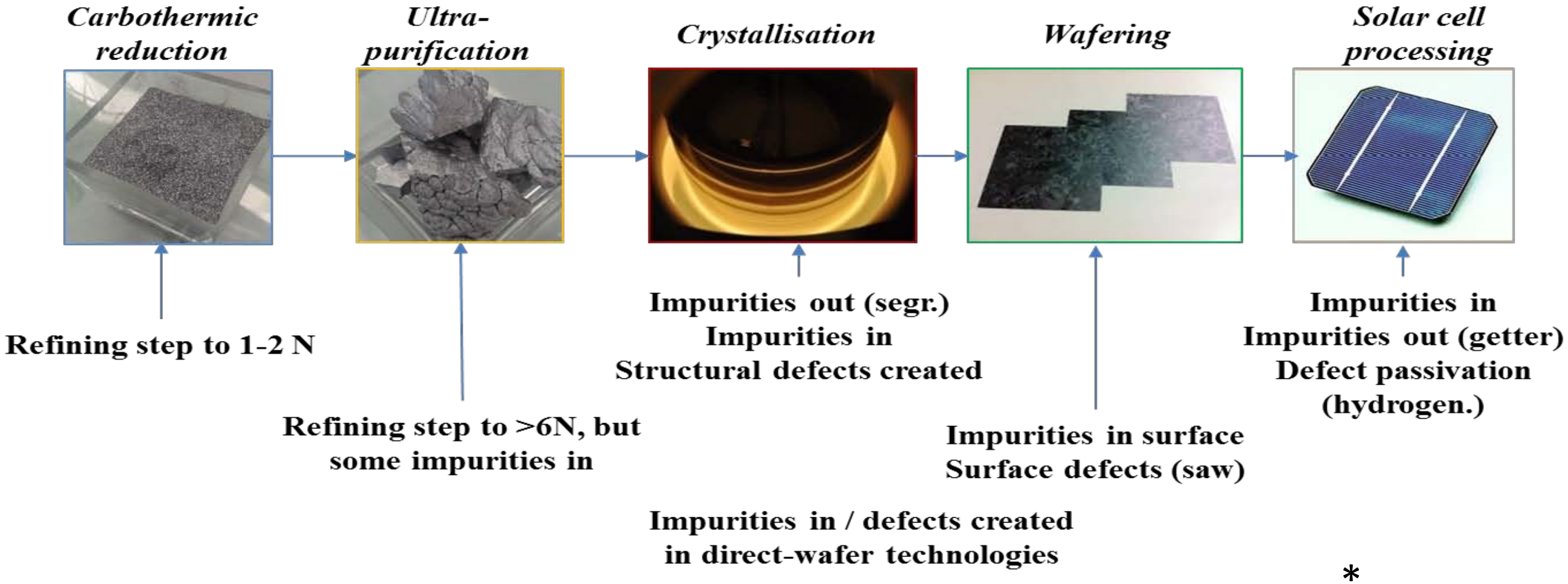


Si multicrystalline



Si monocrystalline

Silicon solar cells



*

Producing the best quality feedstock is not the end of the story :

The process involves a number of steps, with the potential incorporation of contaminants, but with the opportunity to rearrange the impurities

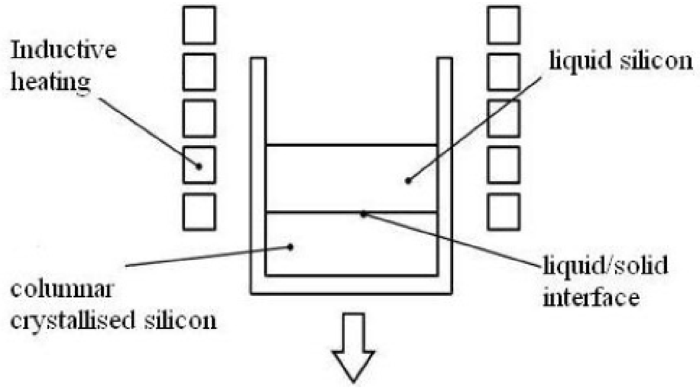
The optimization of every step of the process was the **key** of the Si solar cell’s success

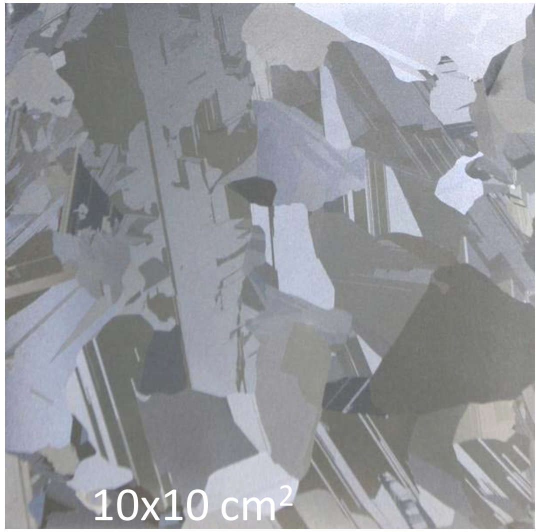
Important Role of Chemistry !

*C.Del Canizo, S. Binetti, T. Buonassissi in “*Purity Requirements for silicon in PV application* “ Solar Silicon Processes: Technologies, Challenges, and Opportunities CRC press ***(2016)***

Multicrystalline silicon growth process

DS growth process avoids the costly pulling sytem





$\eta = 22\ \%$

High density of dislocations and grain boundaries
$[B] = 10^{16} - 10^{17}$ at/ cm^3
$[O] = 1 - 20$ ppma ; $[C] = 1-10$ ppma ; $[Fe] < 10^{15}$ at/cm^3


Poly Silicon Casting

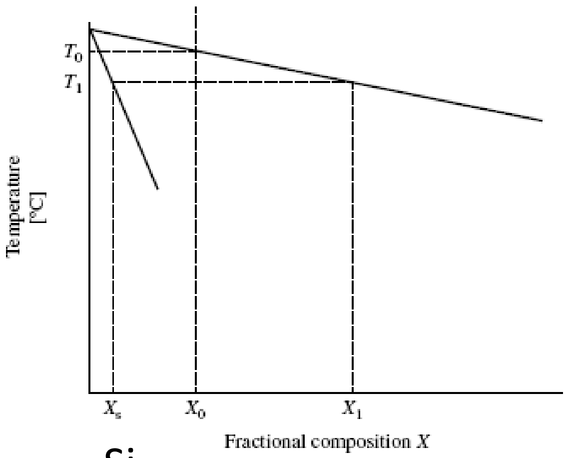

Multi-Crystalline Silicon Ingot


Blocking Silicon


Silicon Brick

The silicon blocks are sawn into wafers by multiwire sawing

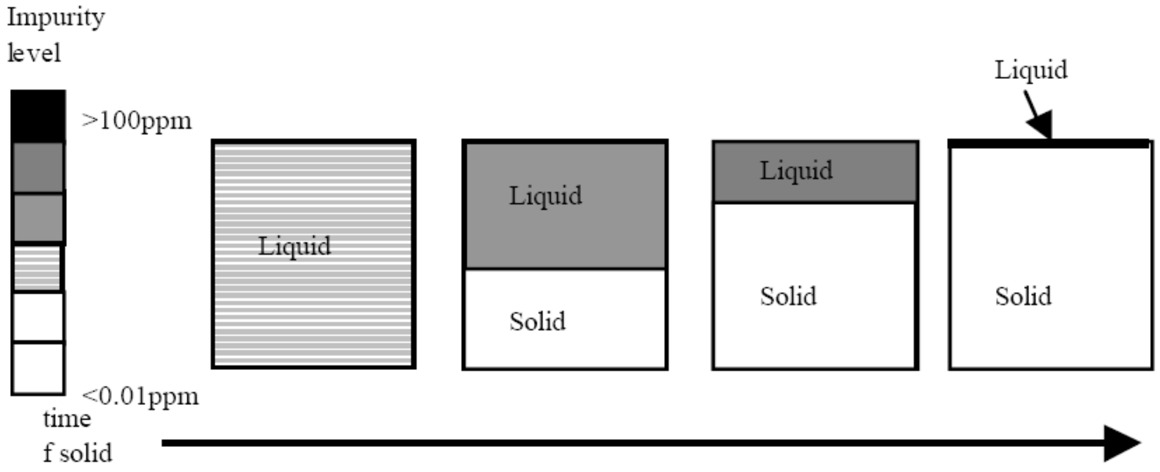
Purification by crystallization



Si

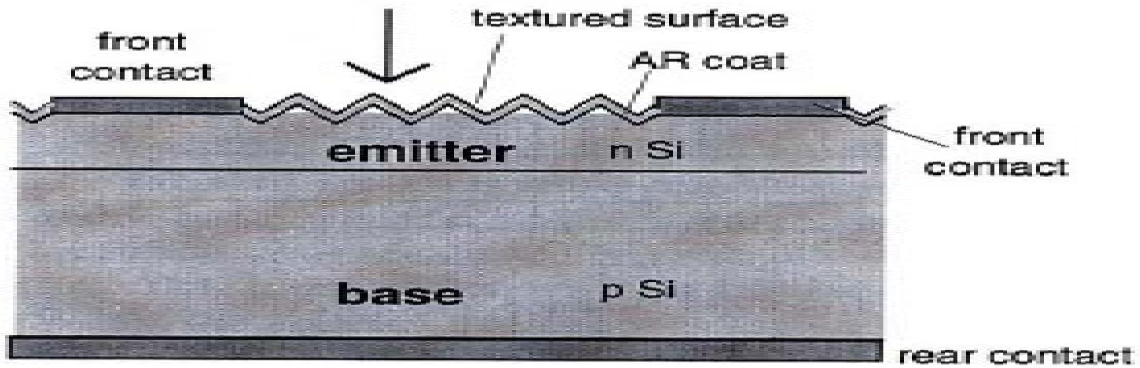
Segregation coefficient of metals

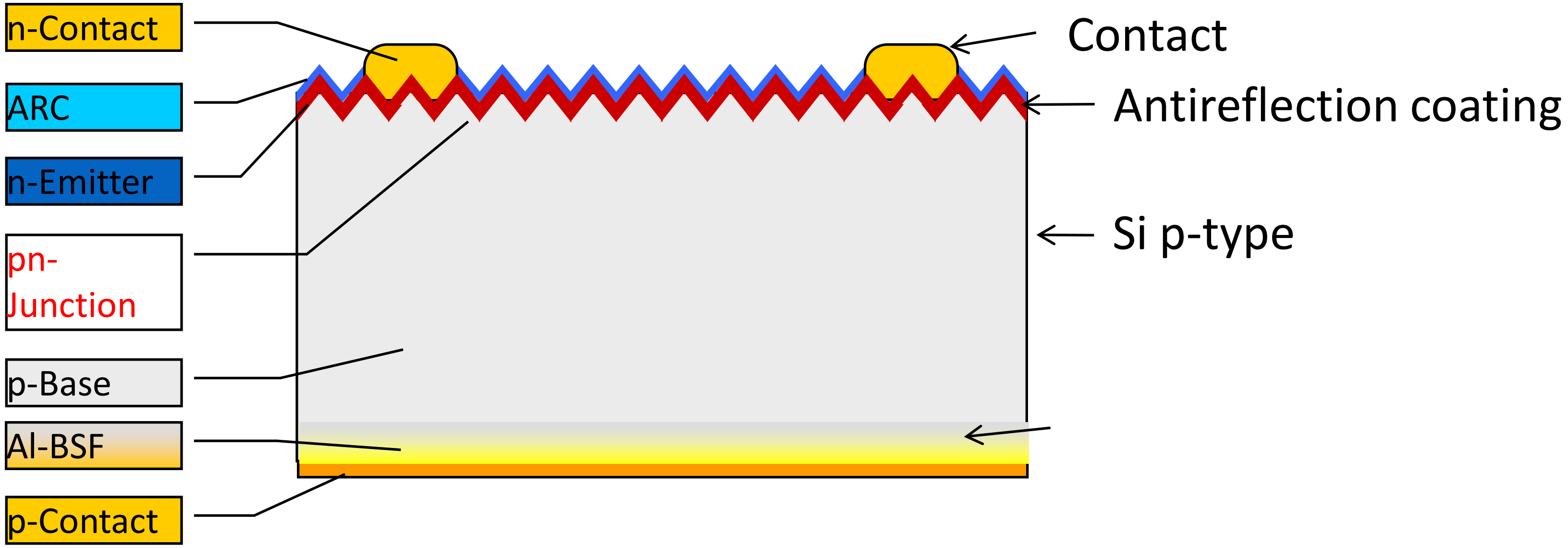
$$K = \frac{C_s}{C_l} < 1$$



Reduction of metal impurities up to less than few ppma

Silicon solar cell's process: state of the art




n-Contact

ARC

n-Emitter

pn-Junction

p-Base

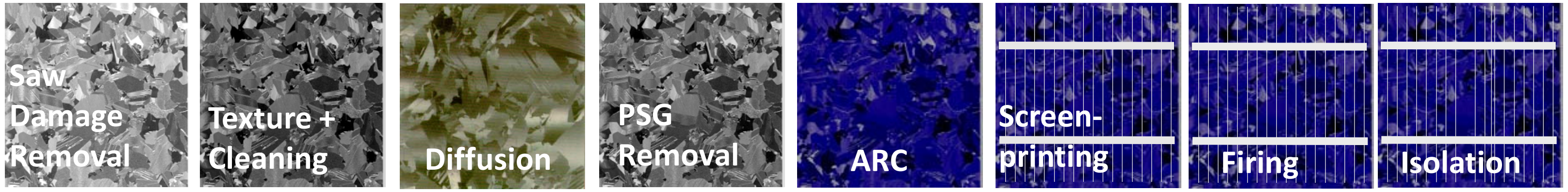
Al-BSF

p-Contact

Contact

Antireflection coating

Si p-type


Saw Damage Removal

Texture + Cleaning

Diffusion

PSG Removal

ARC

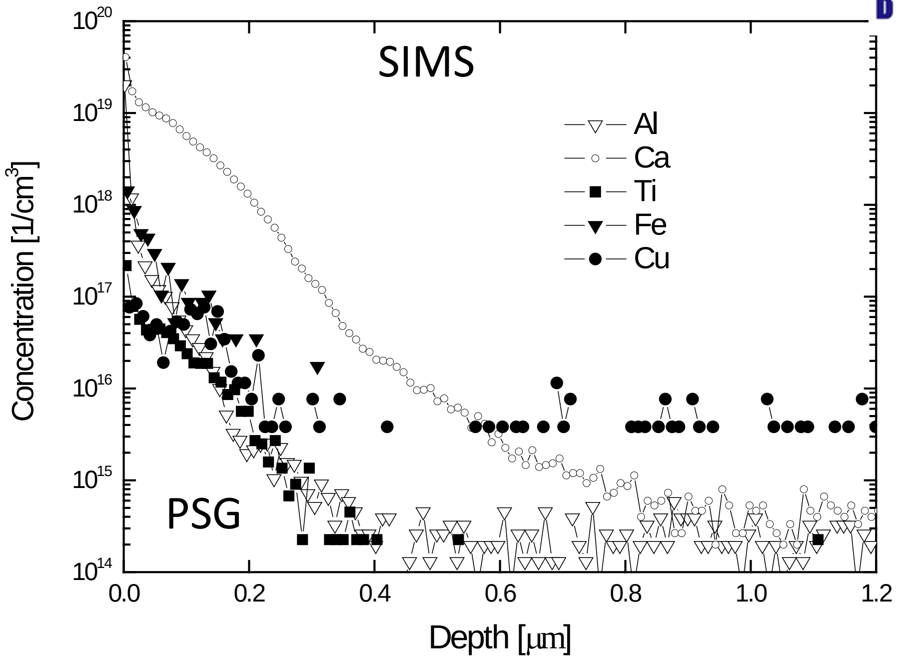
Screen-printing

Firing

Isolation

Junction formation: positive impact

Annealing in nitrogen saturated with phosporous oxycloride ($POCl_3$)



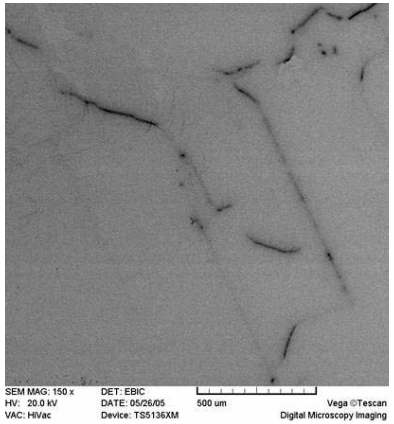
Lifetime increases by P gettering process

$$Me_S + Si_I \Leftrightarrow Me_I$$

Injection of point defects and diffusion versus the PSG layer of metals

In mc-Si: impact of impurities segregation on elecrical activities of defects

E.B.I.C.



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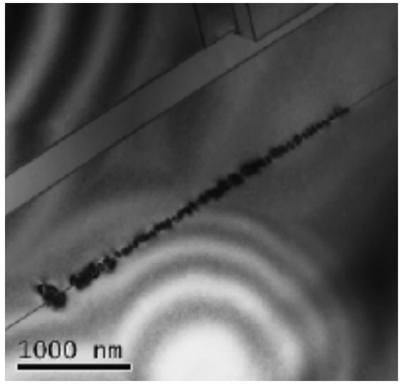


S. Pizzini et al . *J. Electrochem. Soc.*, vol. 135, no. 1, pp. 155–165, 1988.

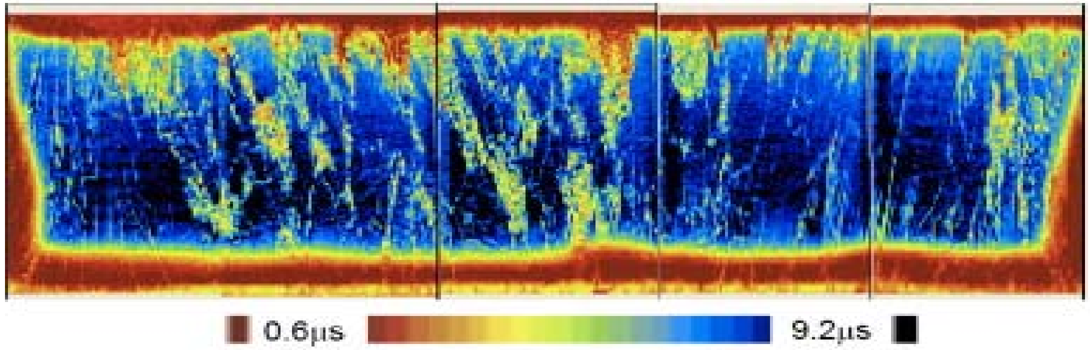
M. Acciarri, & S. Binetti et al. Prog in PV (2007)
J. Libal & S. Binetti et al JAP **104**, 104507 2008
S. Binetti et al. Materials Science & Engineering B **159,** (2009) 274

Antireflection coating: positive impact

Incorporation of atomic hydrogen from the SiNx:H anti-reflection coating and its diffusion into the bulk : Passivation of dislocations and Grain boundaries

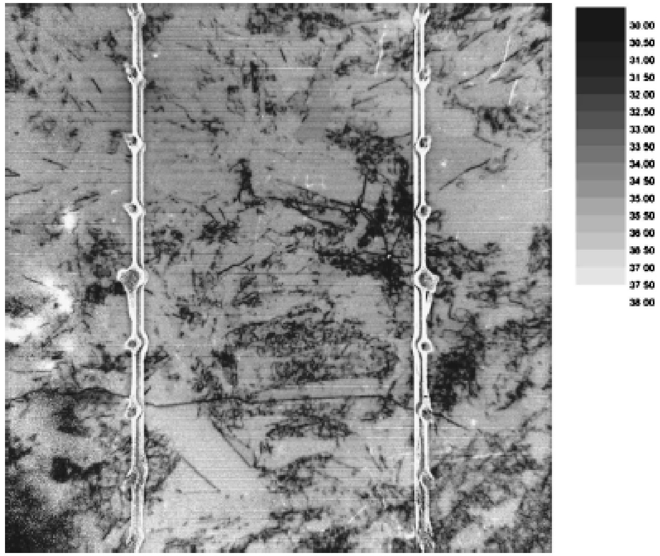
All the process has been optimizated also by developing of **analytically in line tools** like PL mapping , PV scans or μPCD

Lifetime mapping of a mc-Si ingot



S. Binetti et al. , Materials Sci. Eng. B 36, 68 (1996)

PL map



T. Trupke et al. Appl. Phys. Lett., 044107, (2006)
S. Binetti et al. Solmat 130 (2014)696

Silicon production

Si metallurgic production
From quartz and carbon

SiO_2+ C -> SiC+ SiO_2-> Si+ SiO+ CO

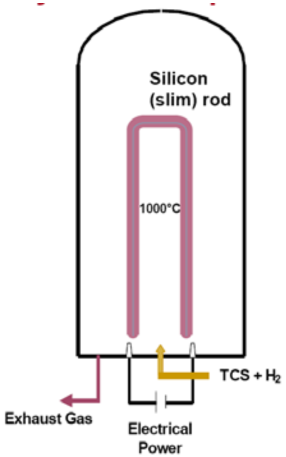
1- 3% of impurities

Si reaction with HCl

$SiHCl_3$ purification via distillation

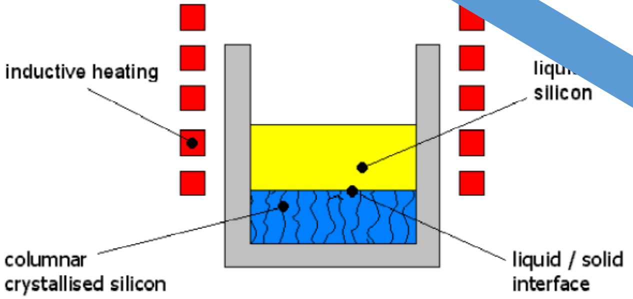
Electronic grade silicon

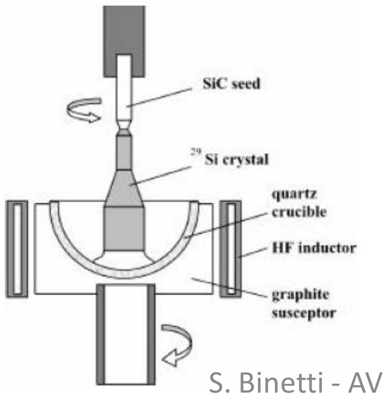
Polysilicon deposition



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

Si multicrystallin





mc-Si :

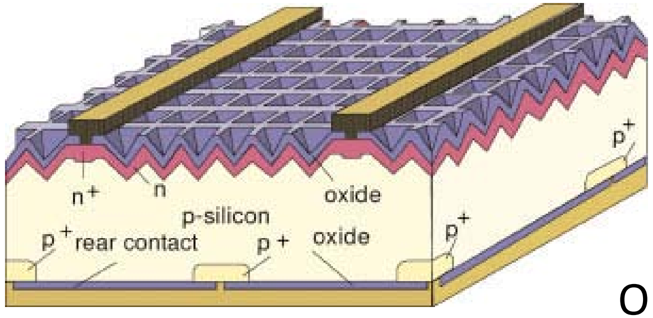
- possibility of using Up graded MG silicon (η= 19%)
- new advanced casting technologies under development

The technology has led us towards higher efficiency solar cells

- PERL cells (by UNSW)

  record of efficiency: 26.7 %

  Commercial efficiency: η=22 % *(Suntech)*

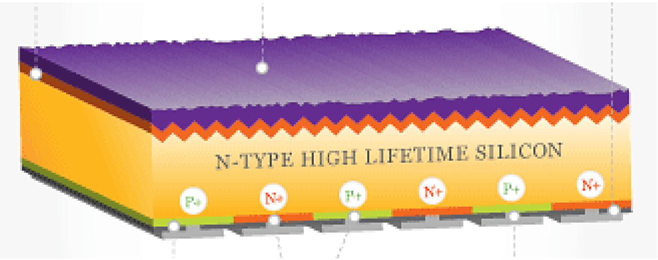


Optimizing :

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

- Based on n type Silicon :

  commercial η=25.5% (*Sunpower*)

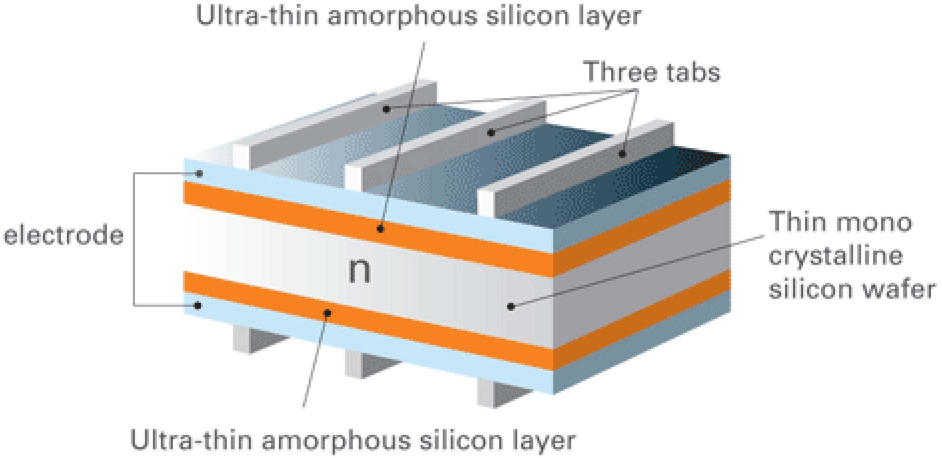


- HIT structure : c-Si with a double a-Si/c-Si heterojunction on n-type *(Sharp -Sanyo)*

  η= 25.6 % (R&D)

  η=21 % (in production)

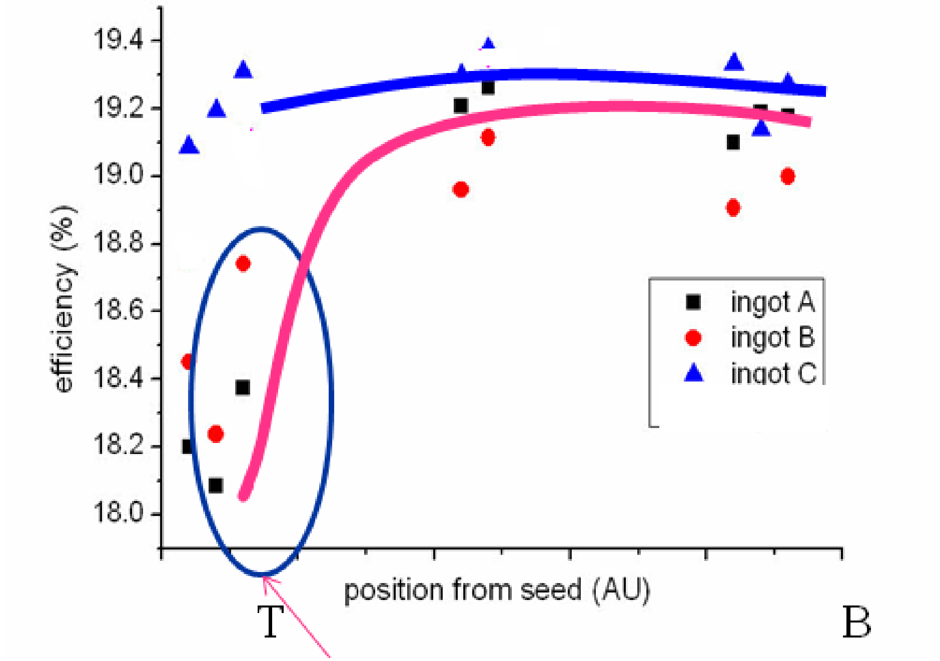
HIT® Solar Cell Structure



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

Current research activity: closing the gap and studying the remaining defects

Ingot	Ingot Classification	Doping	Resistivity [Ωcm]	Oi [ppma]
A	**Reference**	**n-type**	**1 – 5**	**<18 , 7.8 -8.6 at /cm^3**
B	**Low Grade Polysilicon**	**n-type**	**1 – 5**	**<18 8.1- 9.3 at /cm^3**
C	**Low Oxygen level**	**n-type**	**1 - 5**	**<16 7.2 -7.6 at /cm^3**



G. Colletti et al. Solmat 130, 647 (2014) ; A.Le Donne, S. Binetti *, et al . Applied Physics Letter 109, (2016), 033907

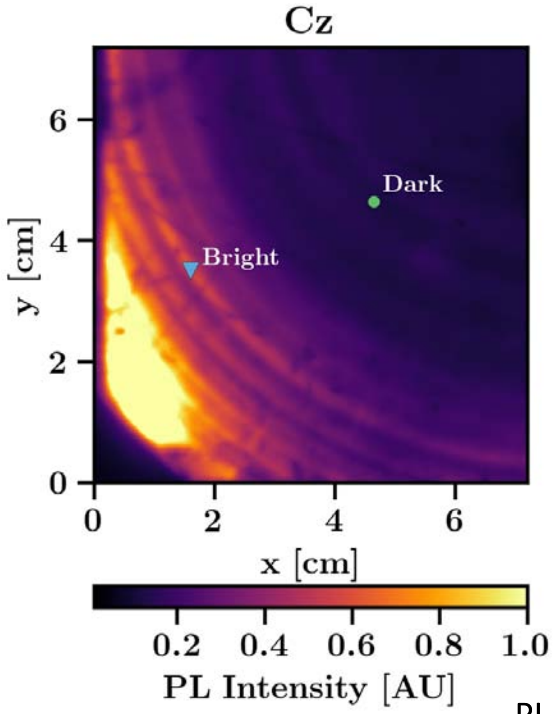
Standard n-type cell processing on wafers coming from different CZ ingots and ingot positions

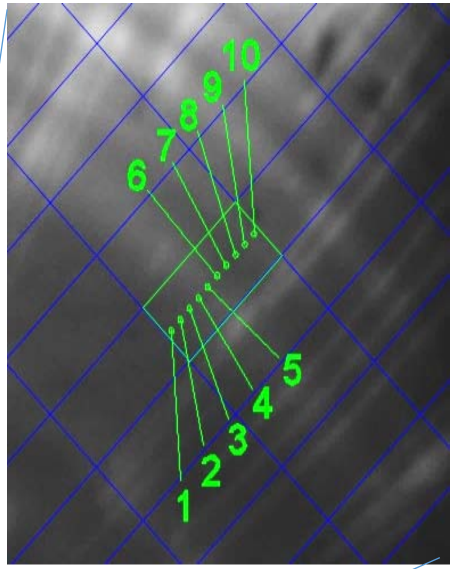
Cells of ingot A,B show evidence of decrease of η % in the seed side

(High oxygen concentration)

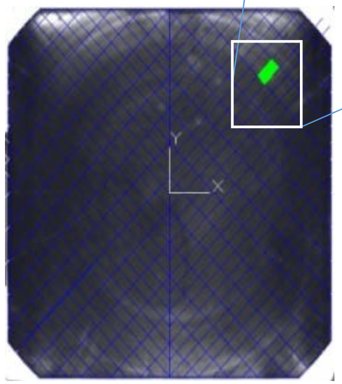
The reason behind the decrease in efficiency

- Room Temperature PL images of the band-to-band (BB) emission shows the bright/dark rings (striations)
- Dark striations correspond to lower effective minority carrier lifetime than the bright striations.
- No direct correlation exists between the feedstock quality and the occurrence of striations (Absence of striations in the middle and bottom wafers of the REF/LGP ingots and in the whole LOO)





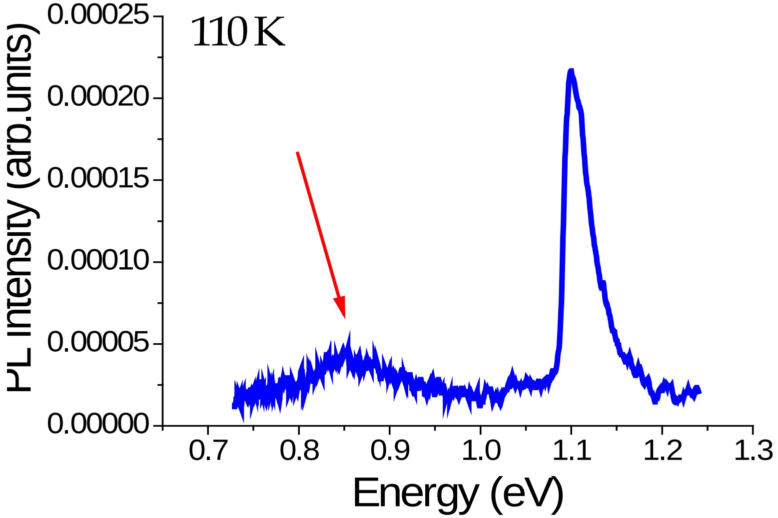
PL imaging

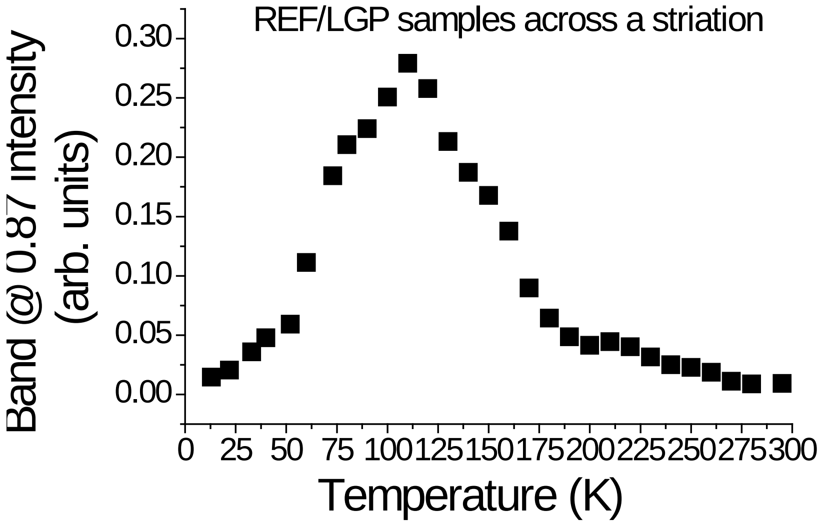


A. Le Donne, S. Binetti * & G. Coletti Applied Physics Letter 109, (2016), 033907

Photoluminescence results

On striations





Position of the band (0.87eV) and temperature dependence associated to oxide precipitates

SiO_x nanoprecipitates (density about 10^{11} cm^{-3}) formed during the pulling growth are responsible of the efficiency's decreases

Possible solution: dissolution treatment

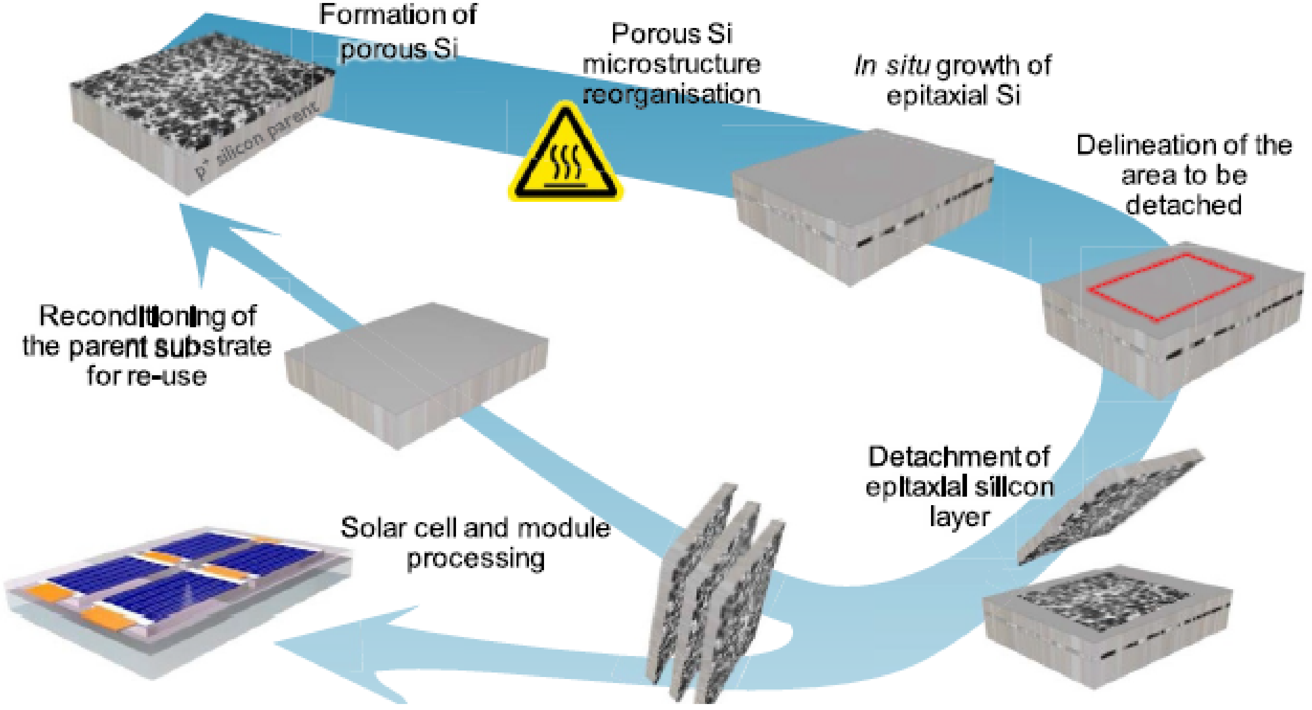
S. Binetti, et al. J.Appl. Phys. 92, 2437 (2002) ; E. Leoni , S. Binetti, et al. J Electrochemical Society 151, G866 (2004)

What’s next ?

Silicon for Product or Building Integration Photovoltaic and Vehicle Integration PV (VIPV)

Flexible Si modules with efficiency > 20 %

Huge cost saving potential for Si PV by using less Si per module and by reducing energy consumption



η= 20.6 % 43 μm thick ; 156x156 mm^2 by ISE- Fraunhofer

H. S. Radhakrishnan et al. Solar Energy Materials and Solar Cells 203 (2019) 110108

What's next?

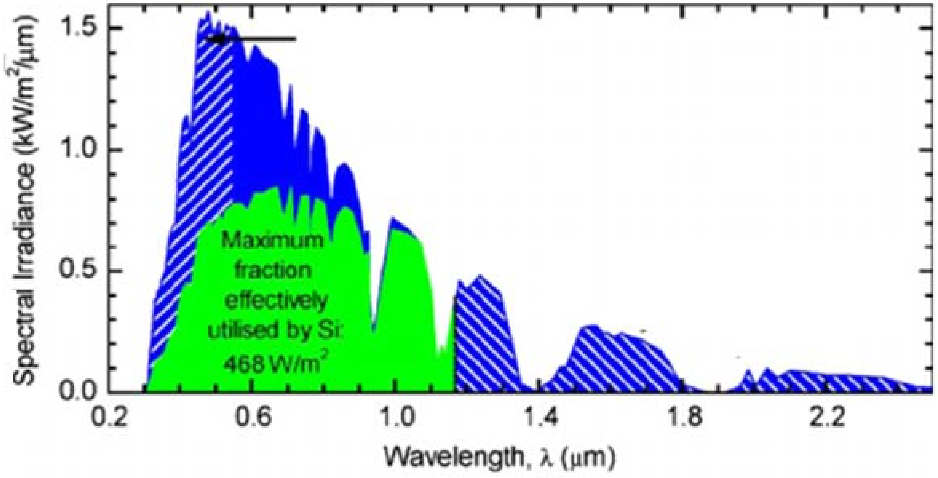
Overcoming the single junction limit (28%)

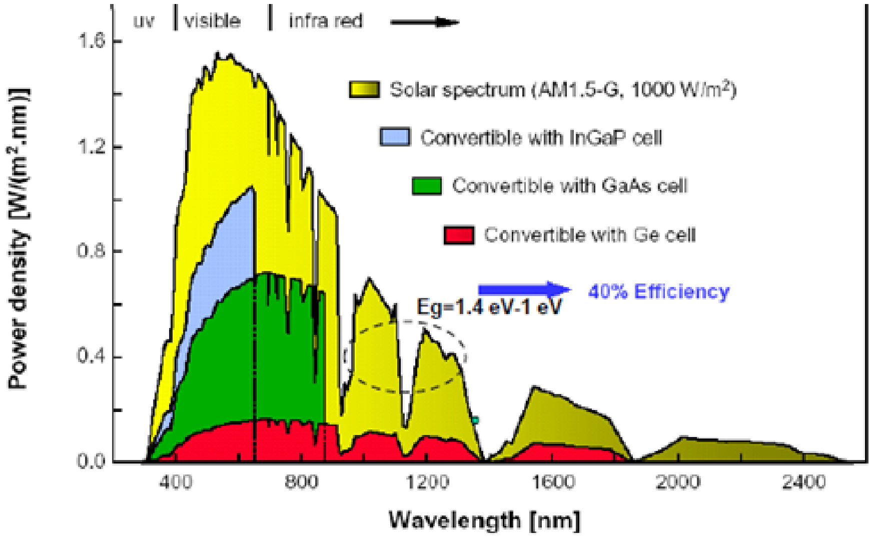
Aiming to approach the thermodynamic limit

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

↓

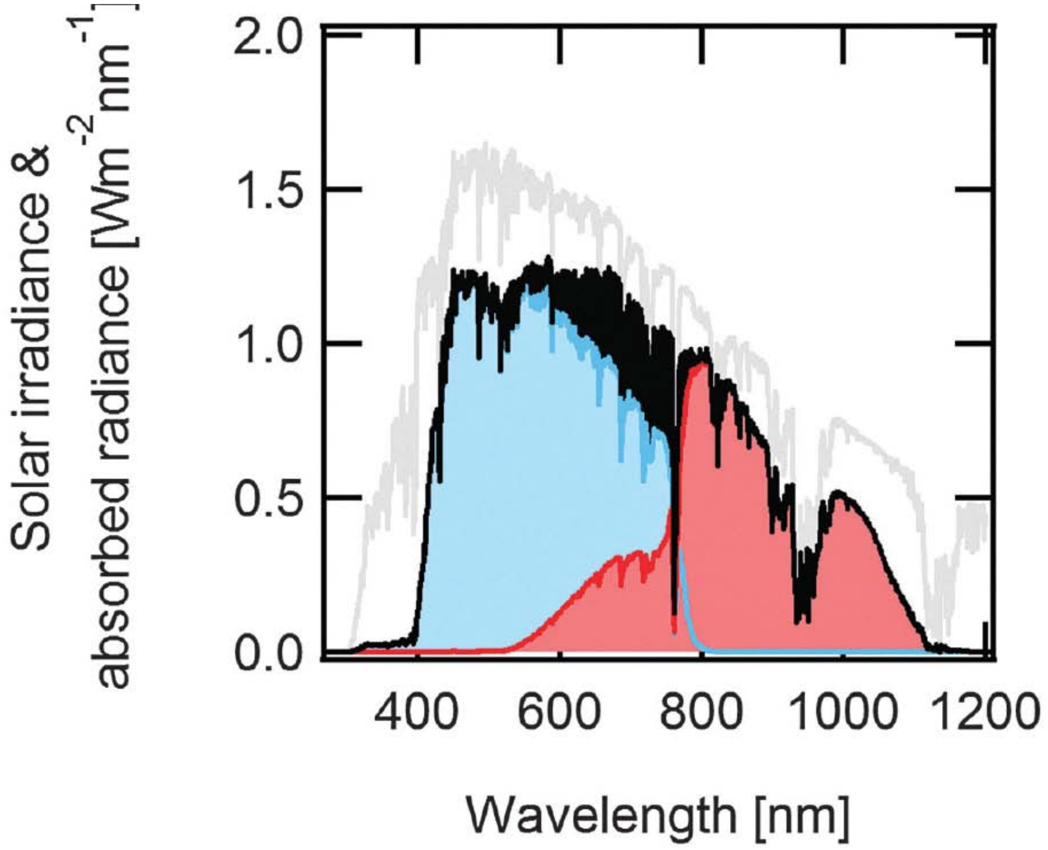
Multijunction solar cells concept



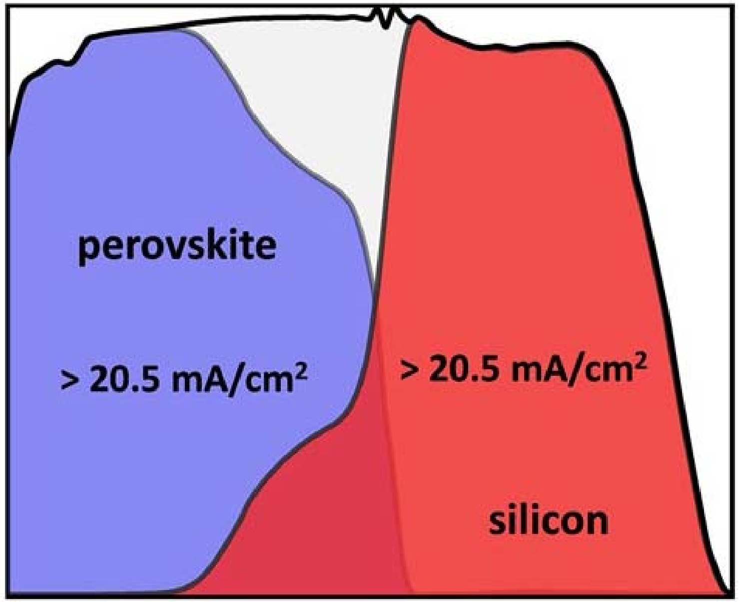


Tandem solar cell

Theoretical efficiencies up to 44 % @1 SUN



Perovskite on silicon

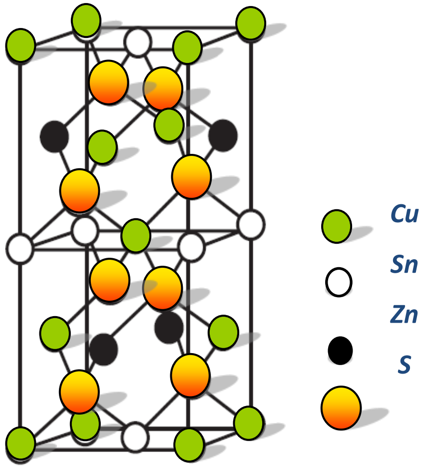


Oxford PV’s 1 cm^2 perovskite-silicon tandem solar cell has achieved a 28% conversion efficiency

Nano-Micro Lett. (2019) 11:58

Main open questions: lifetime and stability

Cu_2ZnSnS_4 for Si tandem solar cell



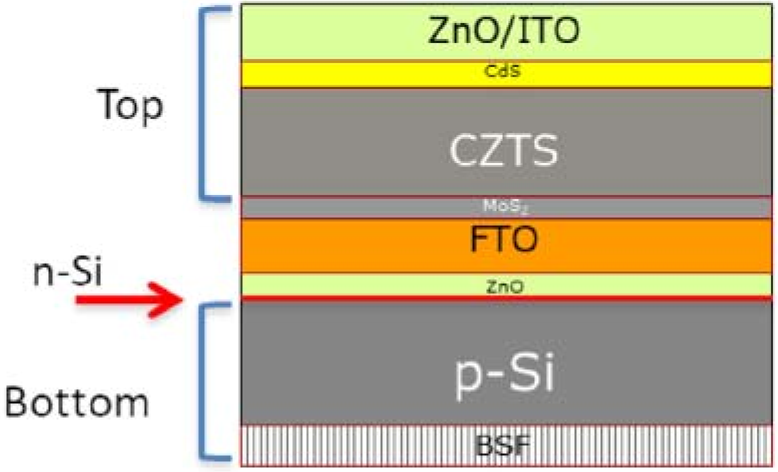
- Cu_2ZnSnS_4 (CZTS) Enviromentally friendly, low cost, many deposition methods
- High stability
- E_g can be tuned between 1.45 and 1.65 eV (DIRECT)
- High absorption coefficient (> 10^4 cm^{-1})
- *Efficiency record* η_{record}= 11% * (CZTS) - 12.6% (CZTSSe)

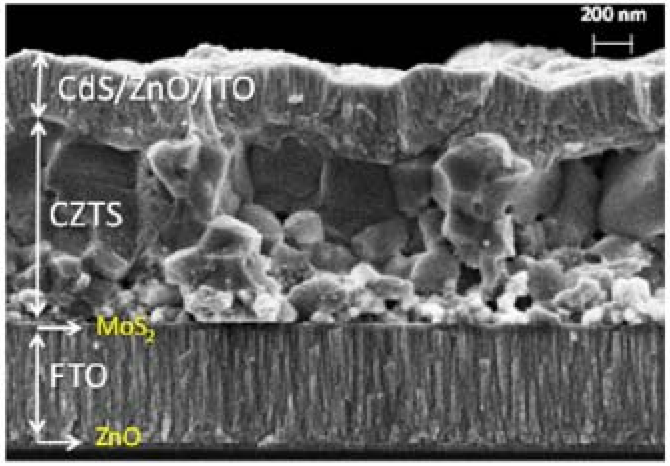
*C.Yan et al. Nature Energy 2019, 3- 764

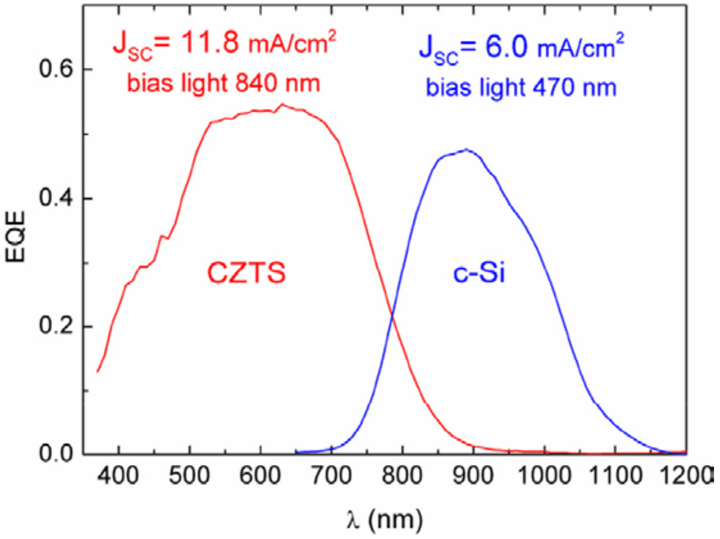
The first working monolithic tandem cell, with Voc = 950 mV and η= 3.5%,

V. Trifiletti et al., Chemistry Select 2019, 4, (17), 4905-4912.

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







Silicon based solar cells' evolution

- 1950s: development of both crystal growth and junction diffusion techniques
- 1970s: development of shallow junctions, photolithographically metallisation, antireflection coatings and surface texturing.
- 1980-2000: improvements in mc-Si , surface and contact passivation, bulk lifetimes
- 2000-2022: further optimization reaching the theoretical limit also in modules
- 2020–2030: flexible Si modules & tandem Si-solar cells
- 2030 - ?: building cells with Si from end of life modules: 1.7 millions of tons in 2030

There is still room for chemistry-related research activity

Acknowledgements

Si-related European projects

- 1990-1993 EU project “Concepts for high efficiency multicrystalline silicon solar cells (Multi-Chess I)
- 1993-1996 EU project “Concepts for high efficiency multicrystalline silicon solar cells (Multi-Chess II)
- 1996-1999 EU “Cost Effective Solar Silicon Tecnology (COSST)
- 2000-2003 FP5 Fast in Line characterization tools for crystalline silicon material and cell process quality control in the PV industry (FAST-IQ)
- 2002-2005 FP5 N-type Solar Grade Silicon for Efficient Solar Cells (NESSI)
- 2005-2008 FP6 "Nanocrystalline silicon film for Photovoltaic andOptoelectronic application (NanoPhoto)
- 2014-2017 FP7 “Cost-reduction through material optimisation and Higher EnErgy outpuT of solAr PV modules (CHEETACH)

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Si

28.085

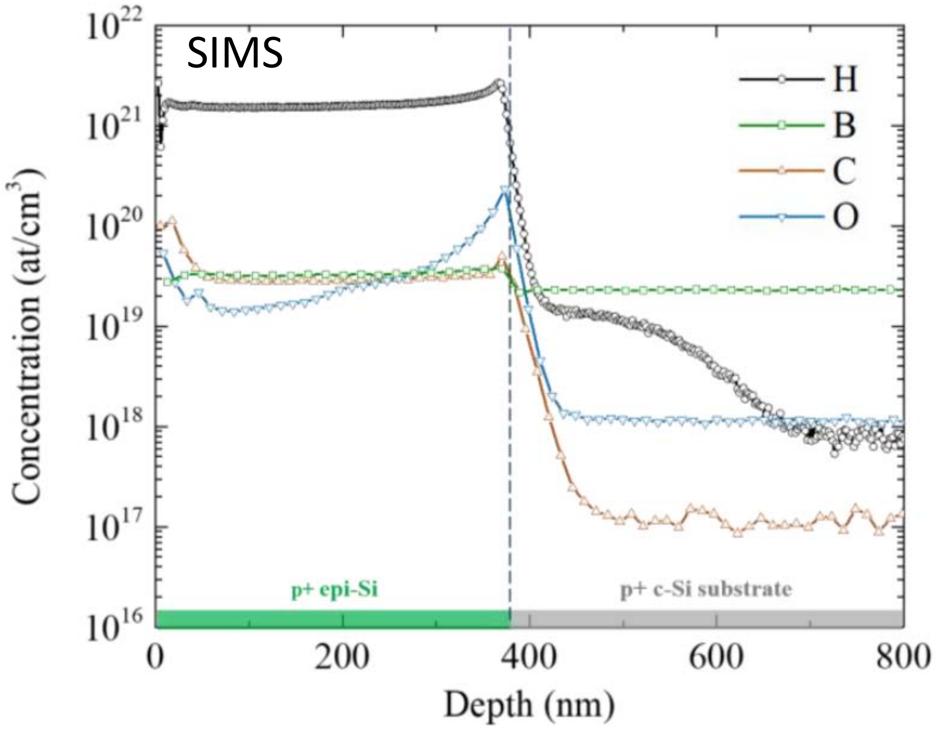
Thank you for your kind attention

Backup

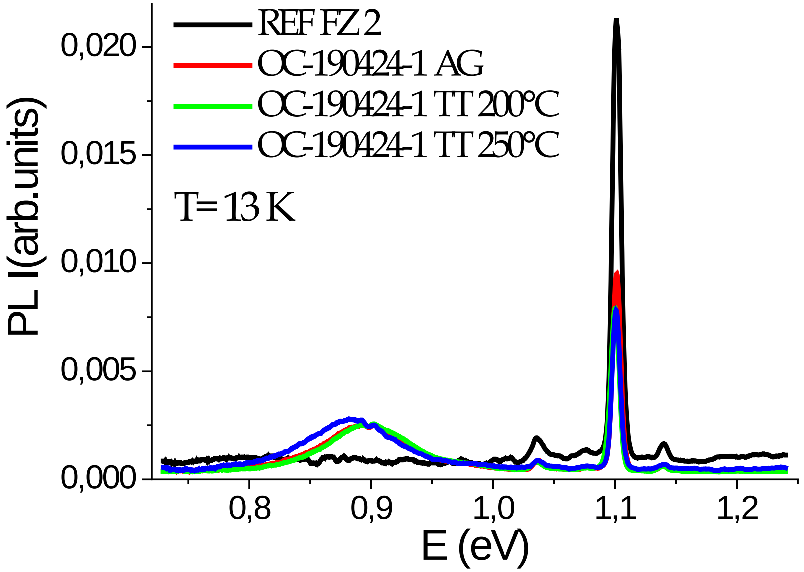
Boron emitter p^{+} epi –Si by low temperature PECVD

Advantages: lower thermal budget, control of doping profile

Several epi layers annealed from 175 -220 °C (B-H)



HTREM measurement in progress



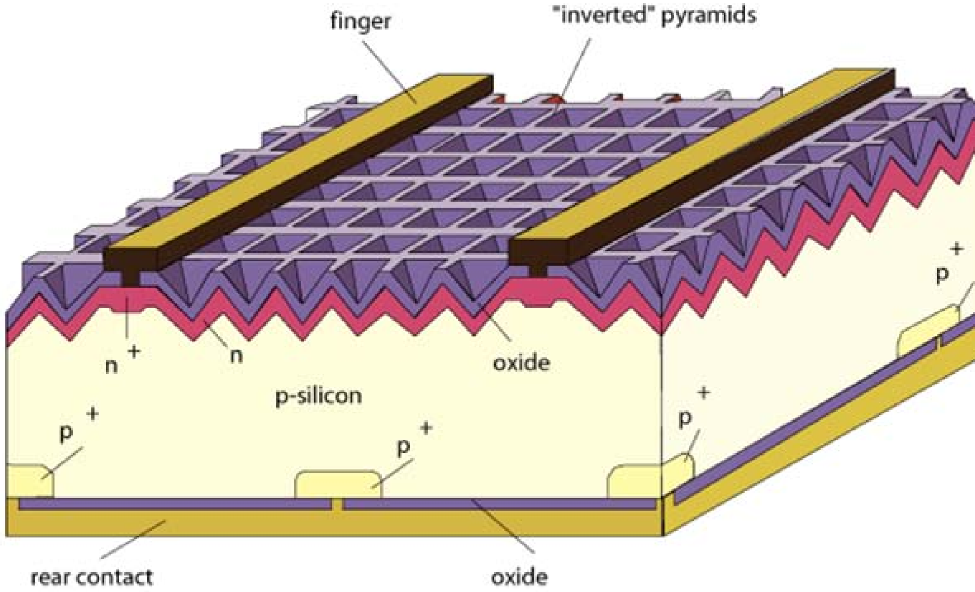
Platelets like exdended defects due to H*

M. Chrostowski , J.Alvarez , A. Le Donne, S. Binetti, Pere Roca Cabarrocas , Materials 2019, 12(22), 3795

High efficiency solar cells :

- **PERL (P**assivated **E**mitter **R**ear **L**ocally diffused cell
  developed by UNSW in 1990

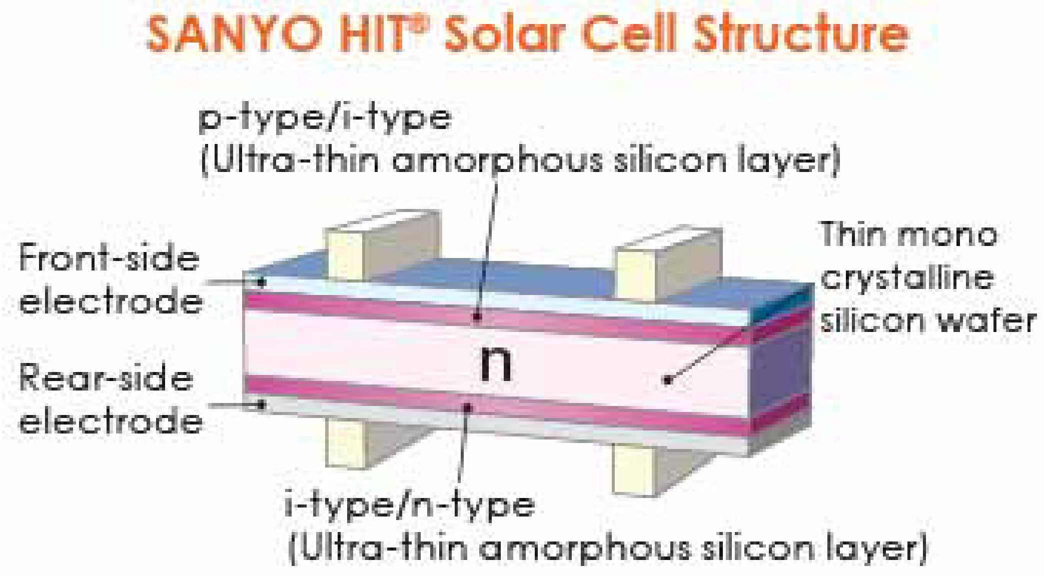
1. top surfaces is textured with inverted piryamid structures
2. double layer ARC (MgF2 and ZnS)
3. reduction of the contact area at the front side to reduce the shadin losses
4. In the emitter: high doping under the front metal grid to reduce the related contact resistance and low doping for the rest of the emitte. Then the uncovered emitter is also easy to passivate.
5. Back contact optimized by point contacts and passivation layers



η=25.5 %

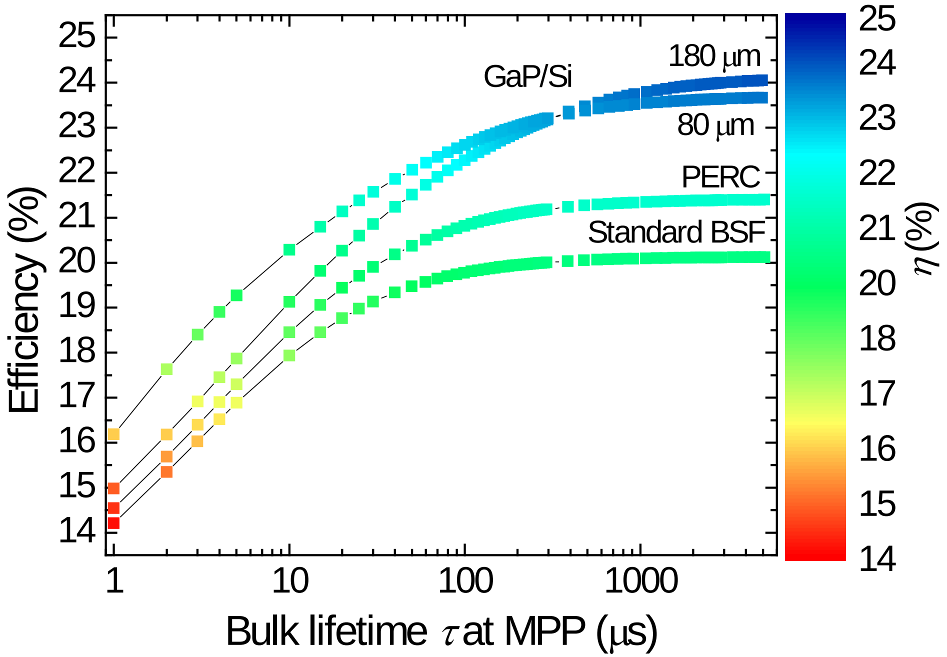
HIT cell

- Several advantages:
  1. a high open circuit voltage due to the potentiality of HJ and due to the good silicon surface passivation promoted by the a-Si:H lyer,
  2. No high treatment
  3. Amorphous layer works as a passivating layers
  4. a better response as a function of the operating temperature with respect to conventional silicon base

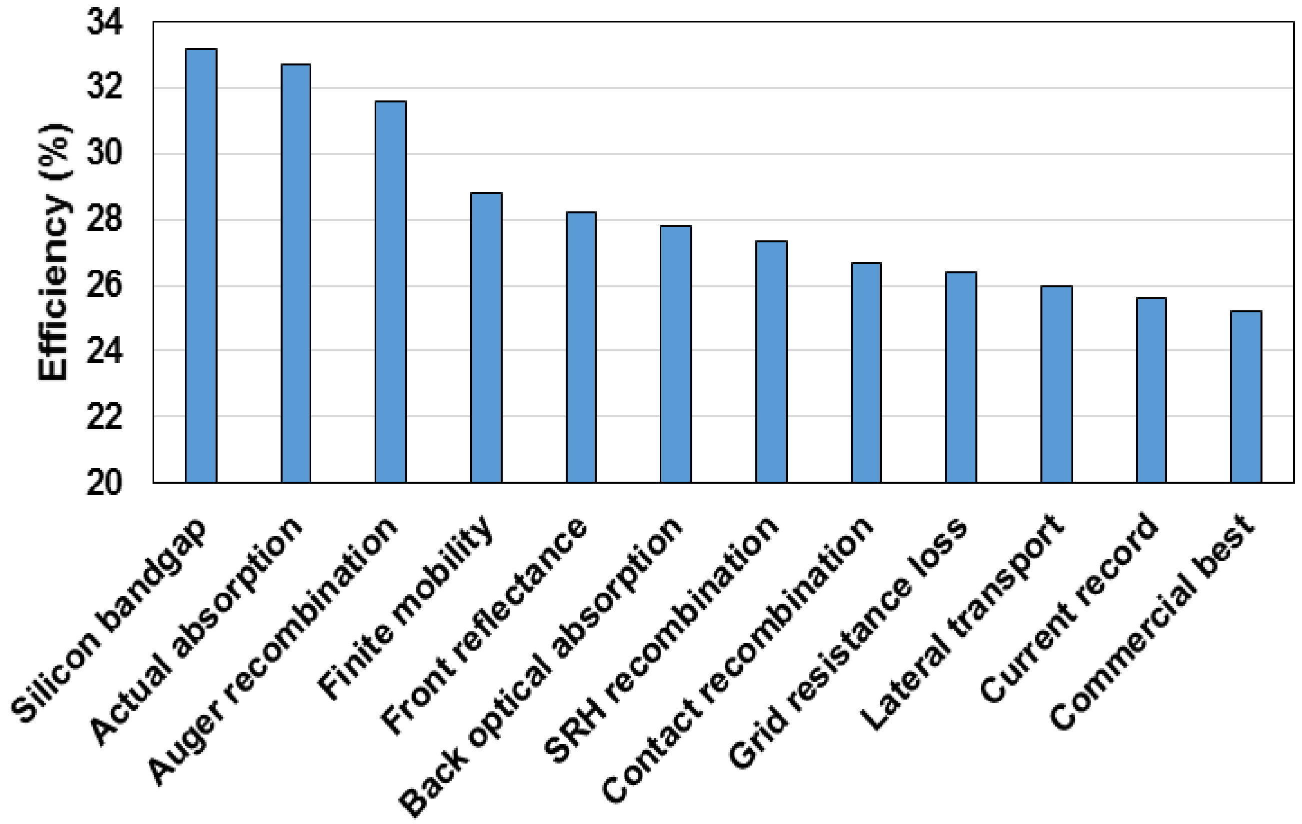


X 100 µm

η= 25,6 % Voc= 0.74 eV



- Given a substrate with a certain concentration of impurities and defects at the end of the cell process, which translates in a certain lifetime, Figure indicates the efficiency that can be achieved, depending on the cell architecture


Efficiency (%)
34
32
30
28
26
24
22
20
Silicon bandgap
Actual absorption
Auger recombination
Finite mobility
Front reflectance
Back optical absorption
SRH recombination
Contact recombination
Grid resistance loss
Lateral transport
Current record
Commercial best

High quality CZTS thin films by wet process

Aim: Develop a simple , cheap , no toxic process **based on the sol-gel technique**

Molecular inks :

CZTSsol was prepared by dissolving in DMSO:

- $Cu(CH_3COO)_2·H_2O$;
- $SnCl_2·2H_2O$;
- $Zn(CH_3COO)_2·2H_2O$.

After complete dissolution, thiourea was added.

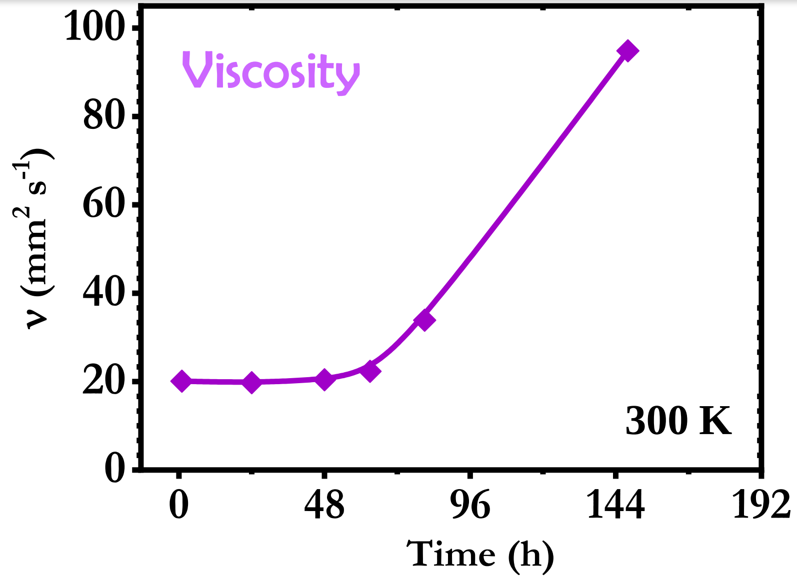
We investigated the composition and stability of the molecular ink

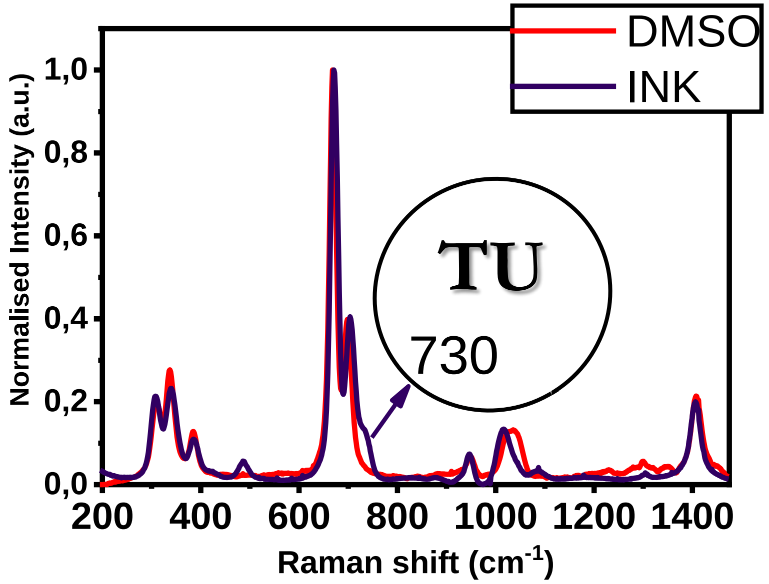
V. Trifiletti et al., Chemistry Select 2019, 4, (17), 4905-4912.

Sol-gel evolution

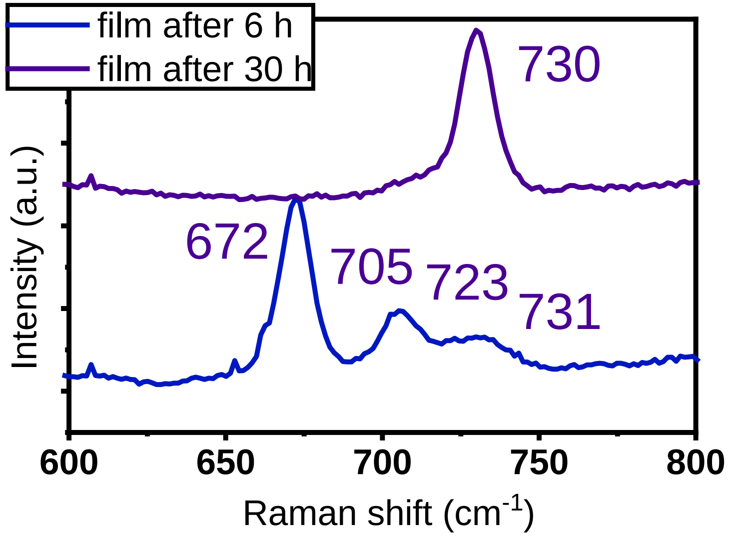
Ink composition :
$Cu(CH_3COO) \cdot H_2O$
$Zn(CH_3COO) \cdot 2H_2O$
$SnCl_2 \cdot 2H_2O$
in (**DMSO** and **TU**)

V. Trifiletti et al., Chemistry Select 2019, 4, (17), 4905





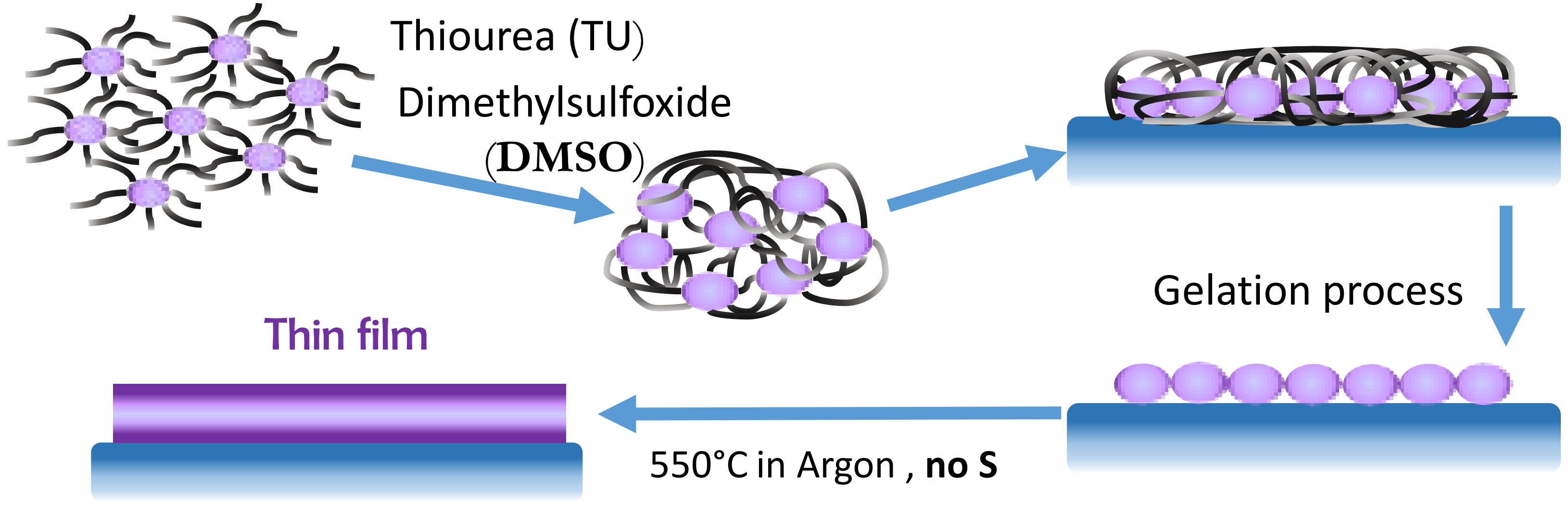
The Sol-gel viscosity increases due to polycondensation process, until the ink evolves to gel



After drying in air the DMSO signal disappears, and after 30 hours the thiourea signal splits in bands that are assigned to the metals coordinate by TU.

Kesterite thin films by non toxic solution process

Several deposition methods



1 **Precursor Ink**

Metal salts

Thiourea (TU)

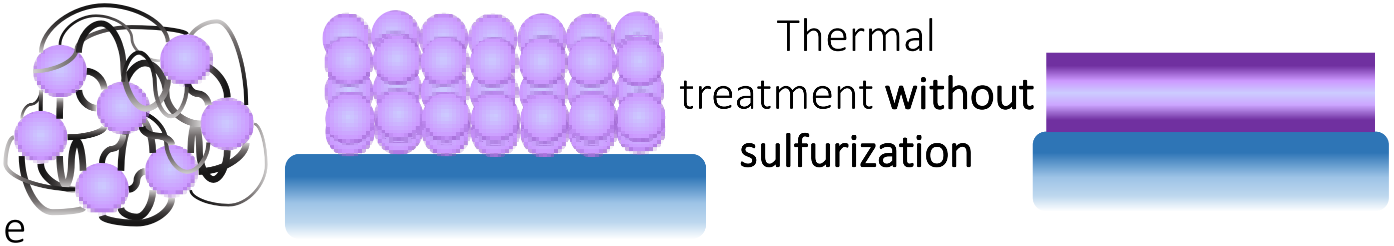
Dimethylsulfoxide (**DMSO**)

Spreading on FTO Glass or Mo coated glass

Gelation process

550°C in Argon , **no S**

Thin film



2 **Precursor-ink**

Spin Coating on substrates on FTO or Mo Glass)

Cu_2ZnSnS_4 Thin-film

Metal salts

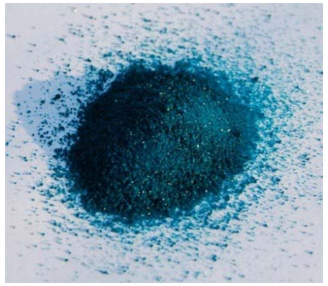
Thiourea

Dimethylsulfoxide

Thermal treatment **without sulfurization**

3 **Precursor-ink** + a ink jet printer (in progress)

V. Trifiletti et al., Chemistry Select, 2019



$Cu(CH_3COO)_2 \cdot H_2O$

0.8 mmol

$Zn(CH_3COO)_2 \cdot 2H_2O$

0.5 mmol

$SnCl_2 \cdot 2H_2O$

0.5 mmol

Thiourea

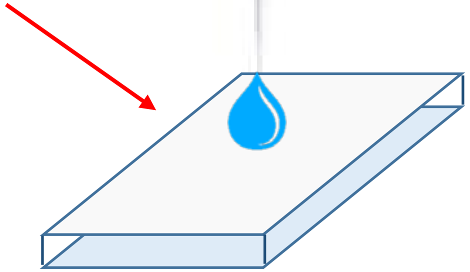
9.0 mmol

<u>Solvent:</u>
DMSO 3.0 mL

Thin films were fabricated by
1) a direct drop-casting of the solution
2) Gelation in 30’ at RT after droplet deposition

loading
<u>1st Layer: 4 µL/cm^2</u>
<u>2nd Layer: 6 µL /cm^2</u>

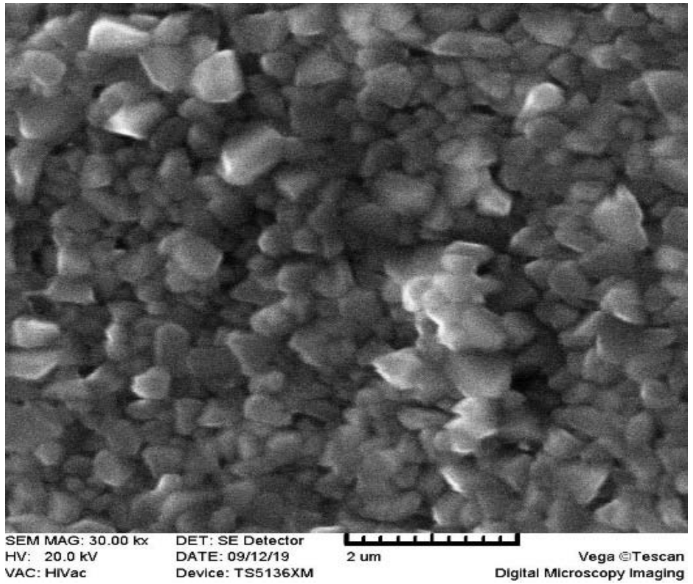
3) 1st and 2nd Layer:
Oven annealing in Argon
@ 550 °C

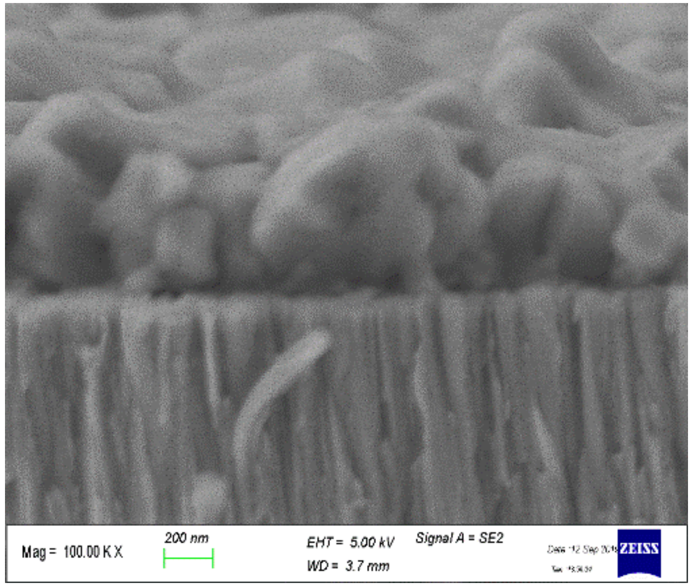


final thickness:
1.2 -1.5 µm

Optimization of the solution/film

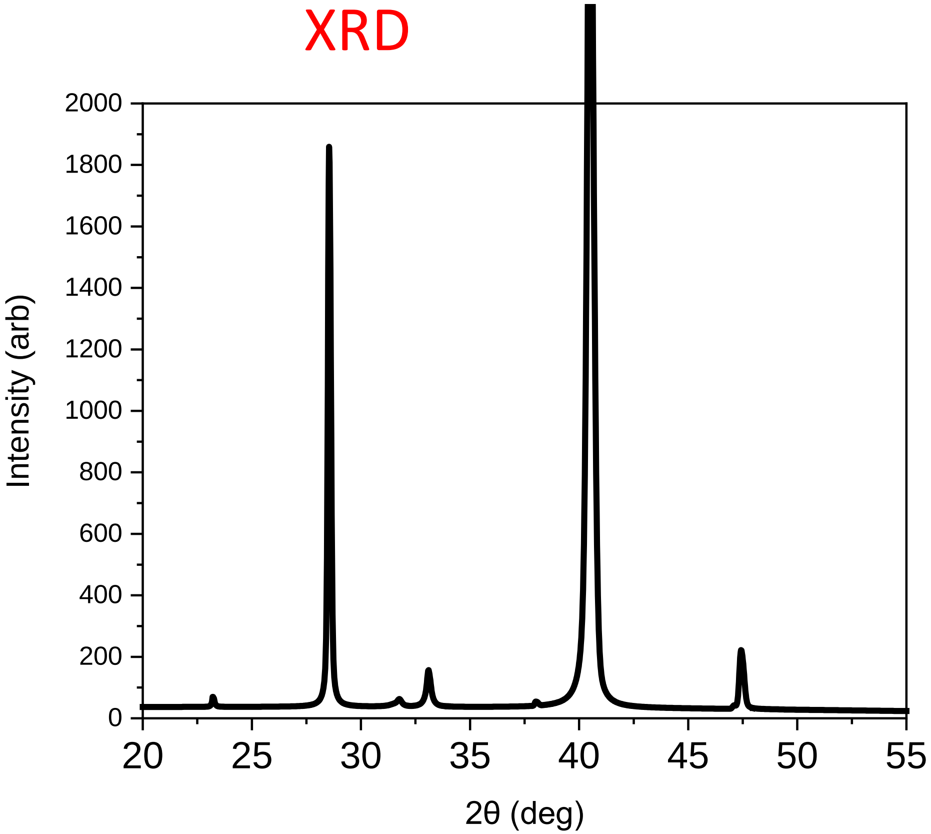
Entry#	Cu/(Sn+Zn)	Zn/Sn	Thiourea [conc.]
1	1.00	1	3.7 M
2	0.91	1	3.7 M
3	0.86	1	3.0 M
4	0.83	1	3.0 M
5	0.80	1	3.0 M
6	0.80	1.1	3.0 M
7	0.80	1.2	3.0 M
8	0.80	1.2	2.3 M



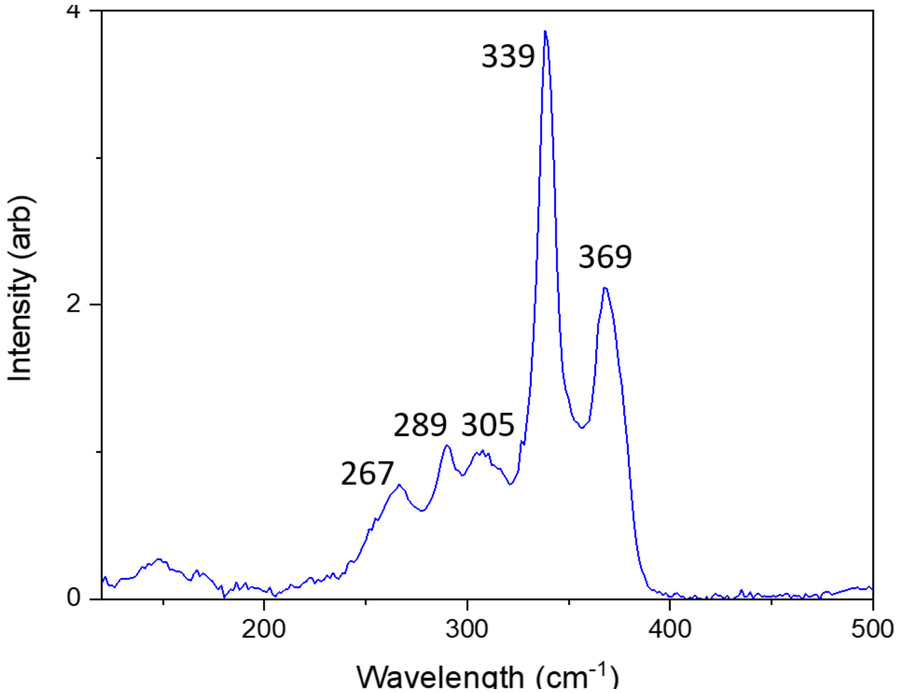


CZTS drop casting samples: material properties

XRD



Raman Spectra

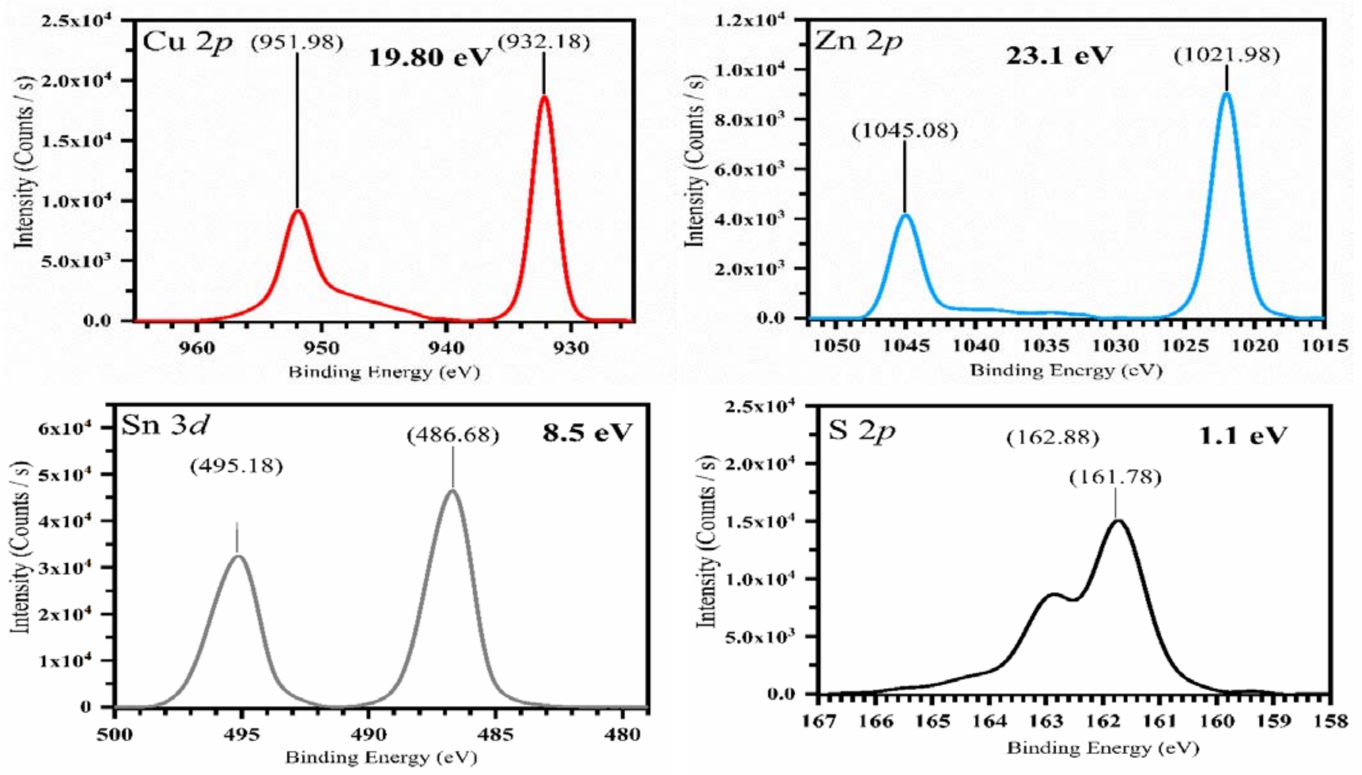


2θ = 16.5, 18.4, 23.3, 28.7, 33.2, 47.5

Unpublished results

XPS analysis on CZTS film

From Ms. Sally Luong, Dr Vanira Trifiletti and Dr Oliver Fenwick
School of Engineering and Materials Science ,Queen Mary University of London



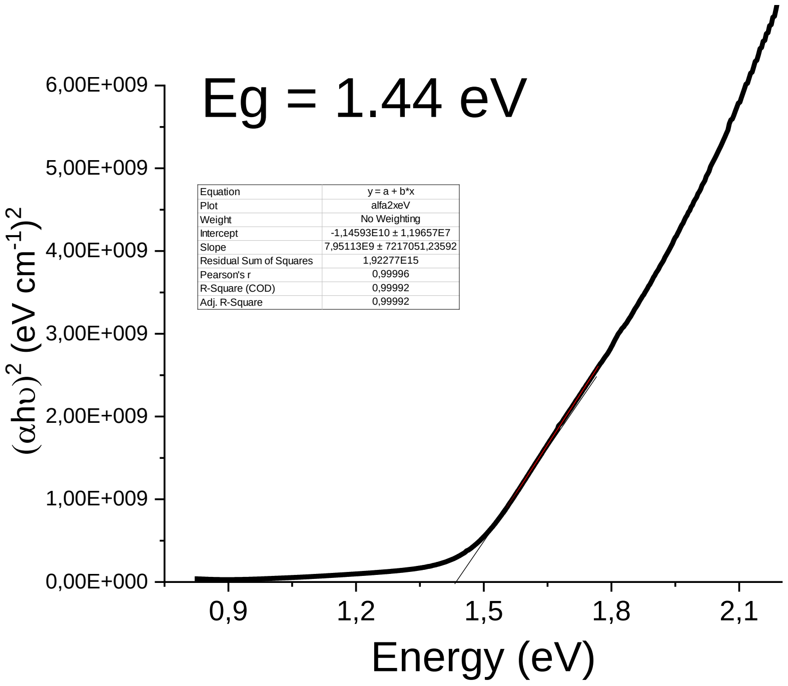
Ion Beam Etch:
30 sec x 3 times
(30 nm each time)
Energy 8000 eV
Raster size 1 mm
Cluster size 1000

Cu, Zn, Sn, and S oxidation states: Cu (I), Zn (II), Sn (IV) and S (II)

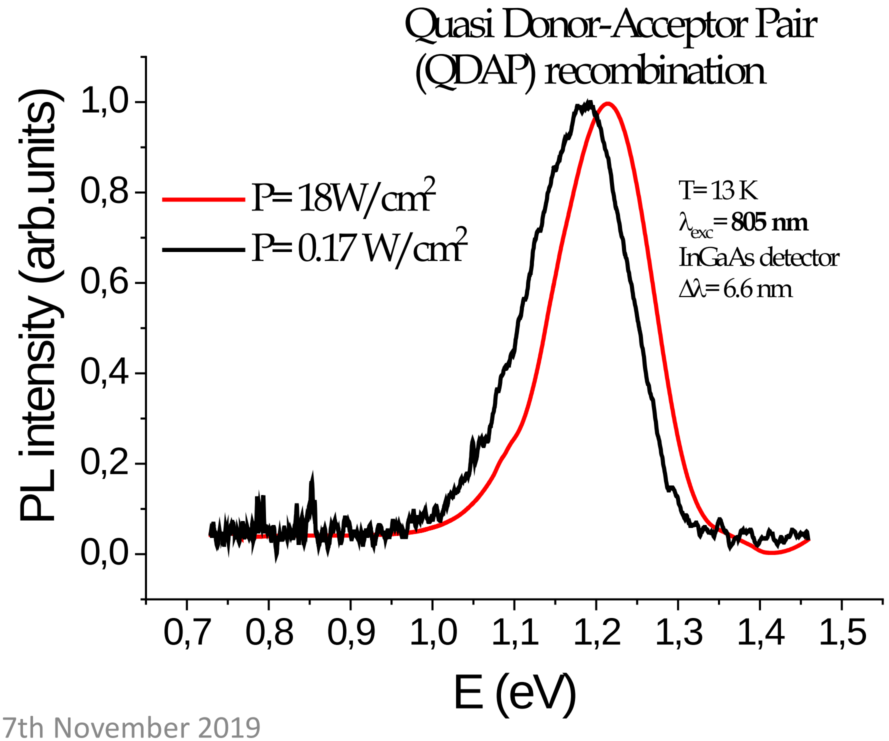
Sample #2

Unpublished results

Band gap and PL


Eg = 1.44 eV

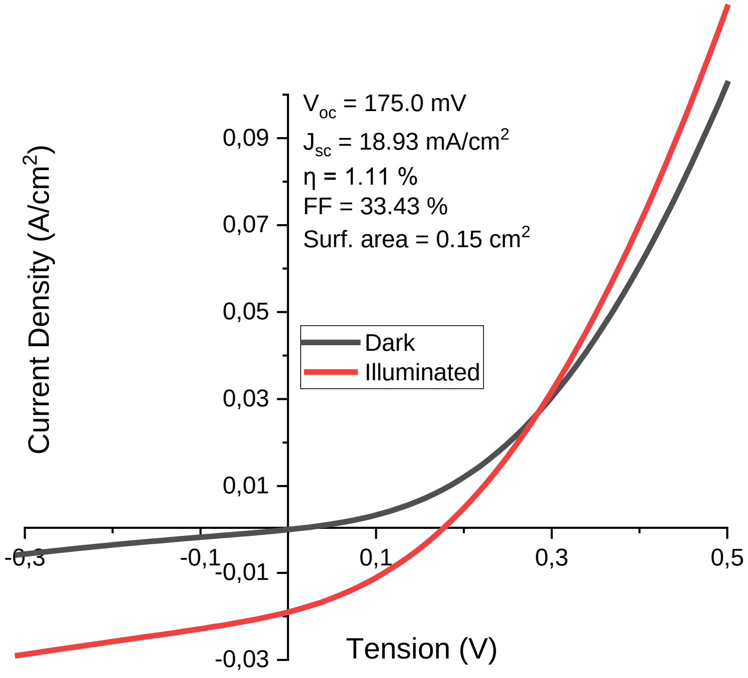
Equation	y = a + b*x
Plot	alfa2xeV
Weight	No Weighting
Intercept	-1,14593E10 ± 1,19657E7
Slope	7,95113E9 ± 7217051,23592
Residual Sum of Squares	1,92277E15
Pearson's r	0,99996
R-Square (COD)	0,99992
Adj. R-Square	0,99992

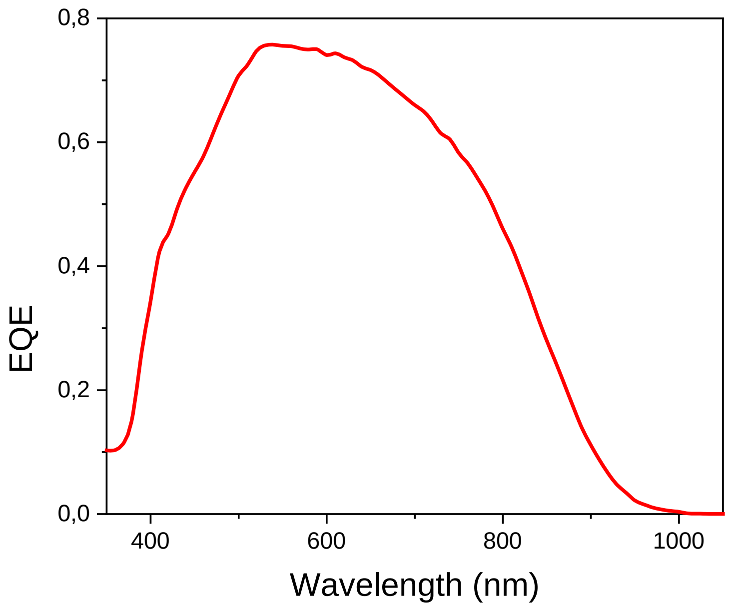

Quasi Donor-Acceptor Pair (QDAP) recombination

T= 13 K
λ_{exc} = **805 nm**
InGaAs detector
$\Delta\lambda$ = 6.6 nm

Unpublished results

Device Performance





V_{oc} = 175.0 mV → **Modest V_{oc}**

J_{sc} = 18.93 mA/cm^2 → **Respectable J_{sc}**

η = 1.11 %

FF = 33.43 %

SCAPS software simulation indicates problems at the interface with the back contact

Unpublished results

Tuning the gap

$Cu_2Zn_{1-x}Fe_xSnS_4$

Molecular inks :

CZFTS sol was prepared by dissolving in DMSO:

- $Cu(CH_3COO)_2 \cdot H_2O$;
- $SnCl_2 \cdot 2H_2O$;
- $Zn(CH_3COO)_2 \cdot 2H_2O$.
- $Fe(CH_3COO)_2$

After complete dissolution, thiourea was added.

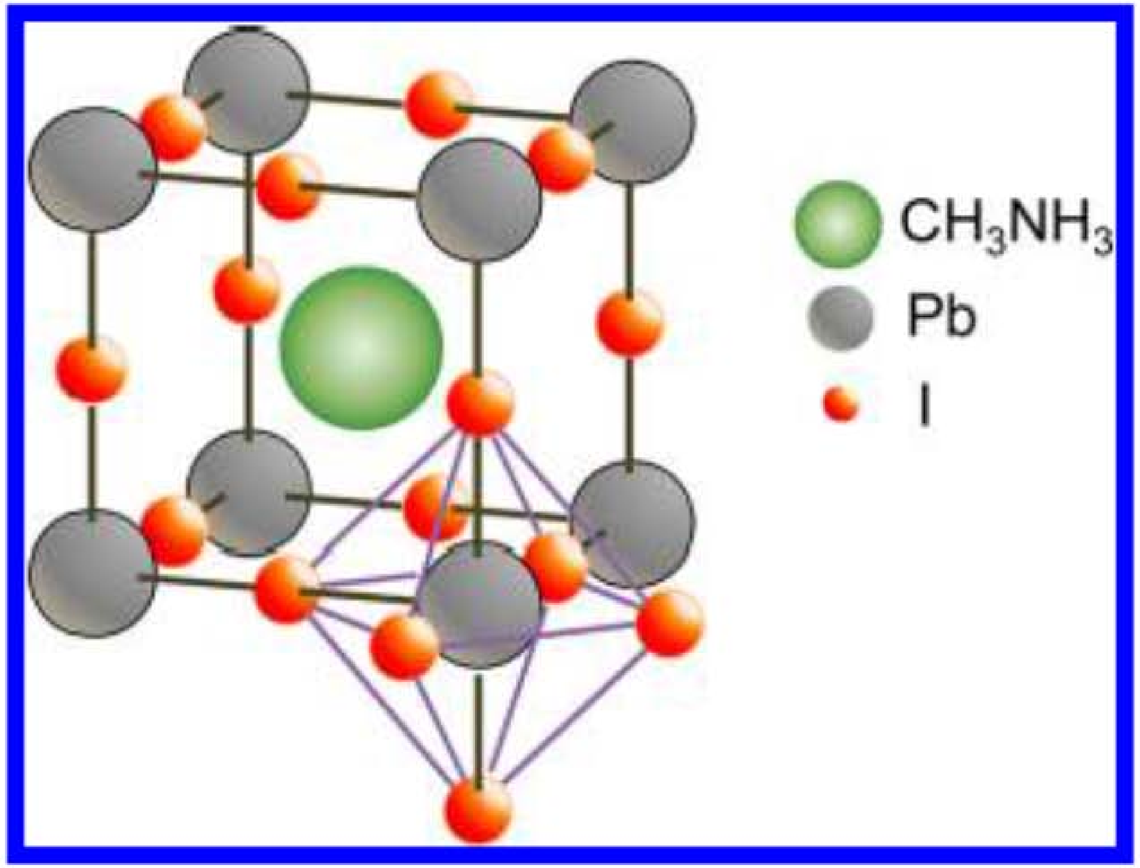
$Cu_2Zn_{1-x}Fe_xSnS_4$

Ink is spread on Mo SLG and HT @550 °C in S
Preliminary thin film results very promising

Perovskite-based solar cells

A new age for low cost high-efficiency PV

ABX_3 (RNH_3PbI_3)



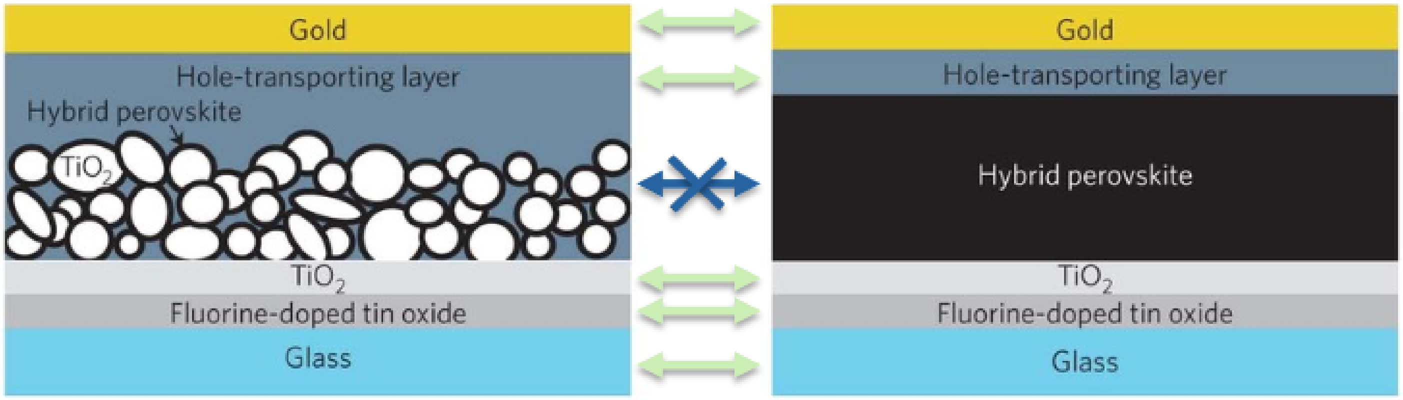
Park, N.-G. *J. Phys. Chem. Lett.* **2013**, *4*, 2423 (perspective)

Perovskite-based solar cells

A new age for low cost high-efficiency PV

ABX_3

$PbI_2 + CH_3NH_3I \rightarrow CH_3NH_3PbI_3$

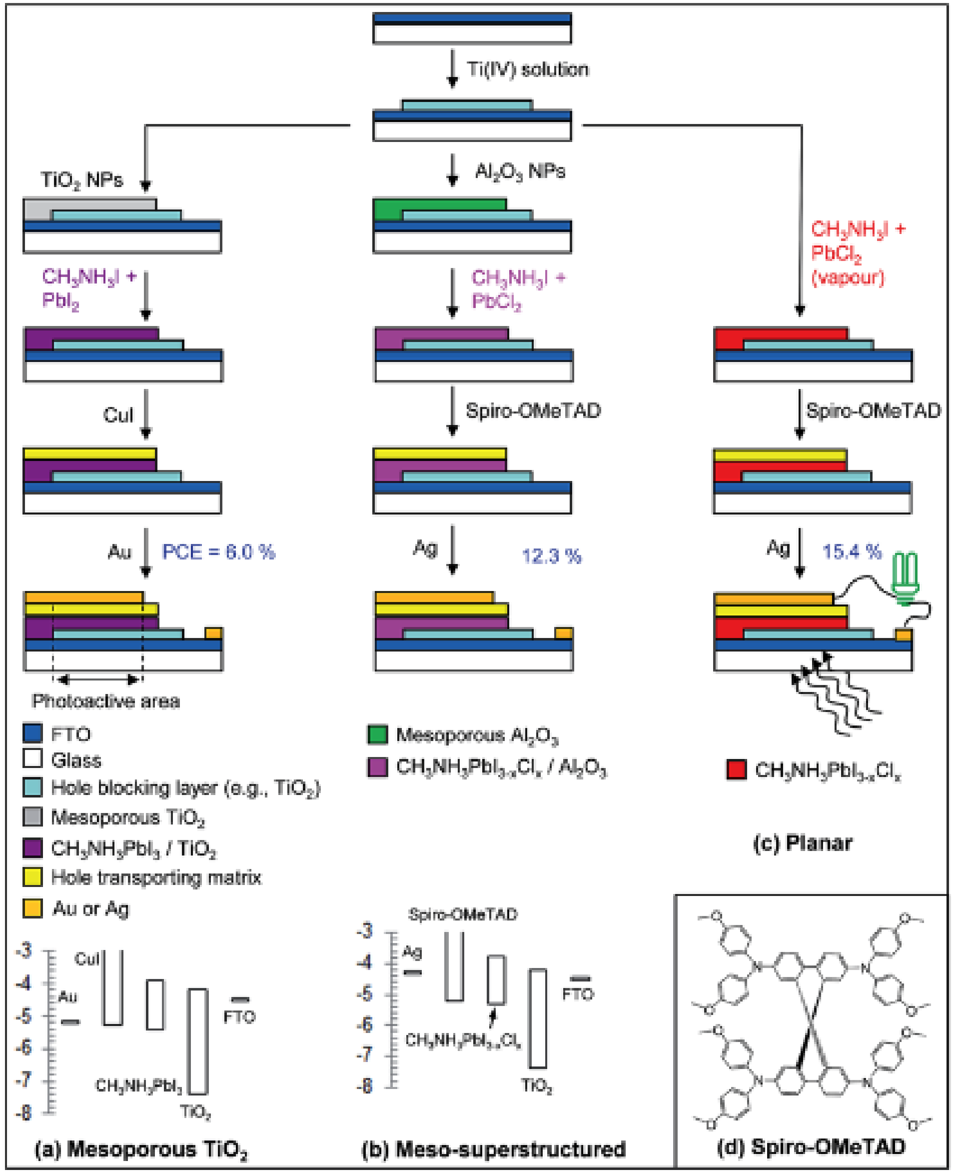


mesoporous PSC

planar PSC

Perovskite-based solar cells: preparation

1. FTO cleaning
2. Hole blocking layer (TiO_2 compact layer) (by spin coating or spray pyrolysis): 50-100 nm
3. Mesoporous TiO_2 layer (by screen printing and sintering): 300-600 nm
4. Perovskite layer (one- or two-step sequence)
5. HTM layer (spiroOMeTAD or other HTM) (by spin coating)
6. Evaporation of photocathode metal contact (Au or Ag)
7. Encapsulation and measurement



Yan, J. F.; Saunders, B. R. *Rsc Adv* **2014**, *4*, 43286

Perovskite-based solar cells

PROS

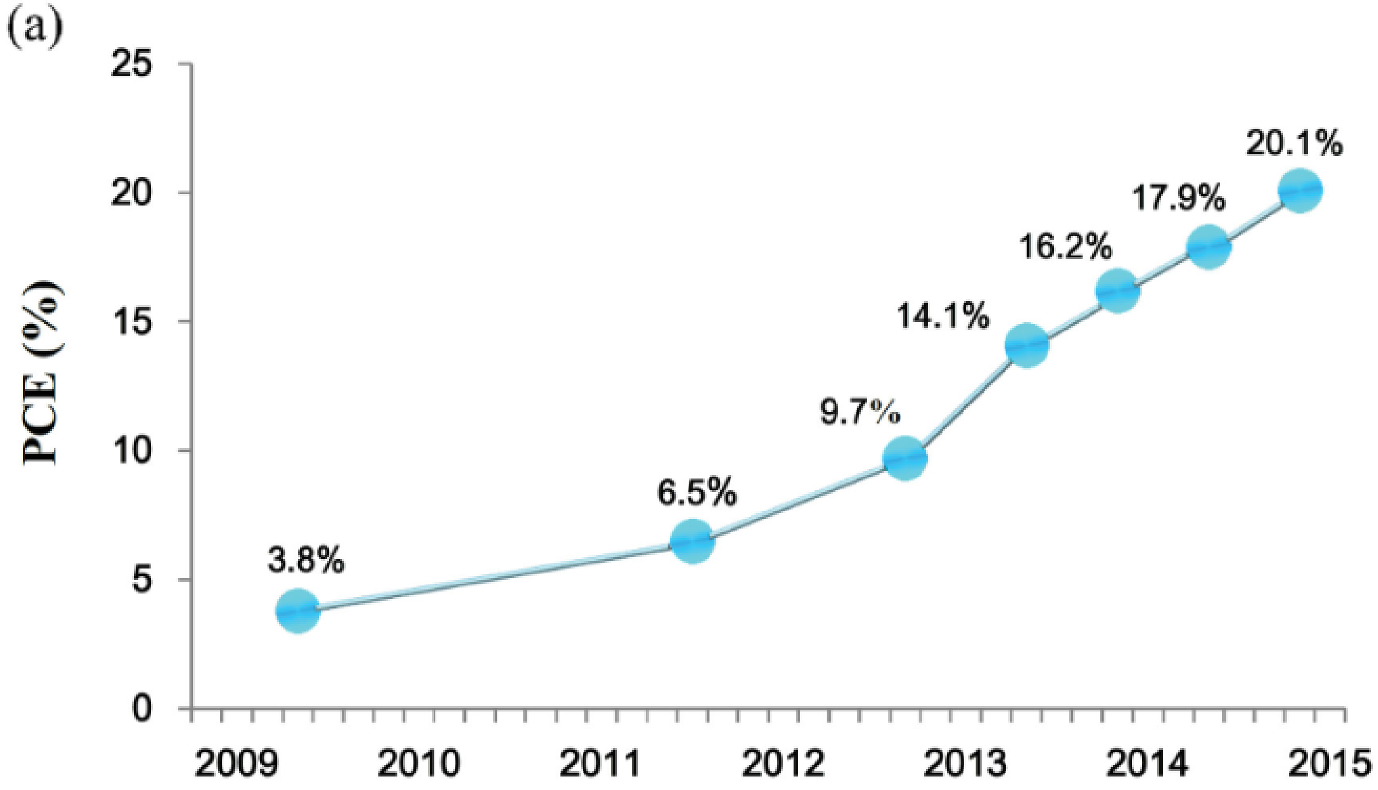
- strongly absorbing over a broad range (< 1 μm thin films)
- ideal for solid-state cells
- act as HTM and ETM as well
- lower loss-in potential and higher voltages (0.4 V)
- 20% efficiency reached
- extremely low cost

CONS

- dissolve or decompose in the electrolyte (no liquid electrolytes)
- toxicity of Pb components
- full device stability in moisture and air to be proven
- degradation with UV light

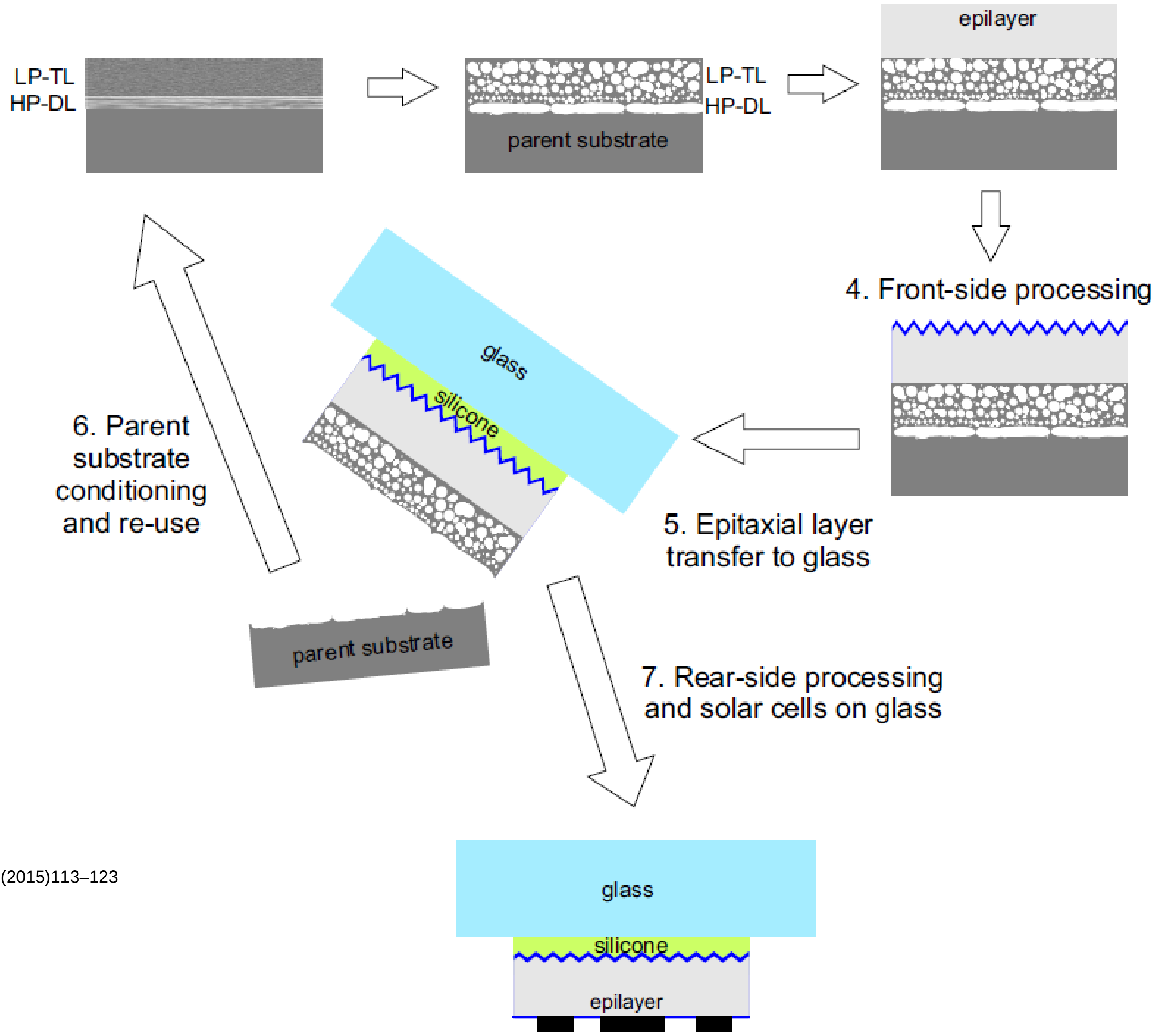
Perovskite-based solar cells

World record efficiencies



- ✧ Last certified value: 20.1%
- ✧ World record (EPFL): 25.2% *(2019)*

Addressing the challenge of automated handling of foils to high mechanical yield ad throughput during cell fabrication



4. Front-side processing

5. Epitaxial layer transfer to glass

6. Parent substrate conditioning and re-use

7. Rear-side processing and solar cells on glass

Solar EnergyMaterials&SolarCells135(2015)113–123

- Energy payback time for Si solar cells
- Northen Europe : 2, 5 years
- South 1, 5 years
- Pv system located in Sicily with mc-Si modules has an Energy pay back time of around 1 year !
- www.ise-frauhofer.de

Assuming 30 year system life **Silicon** PV systems will provide a net gain of 28-29 years of pollution free and greenhouse gas free electrical generation

47

Ag

Silver

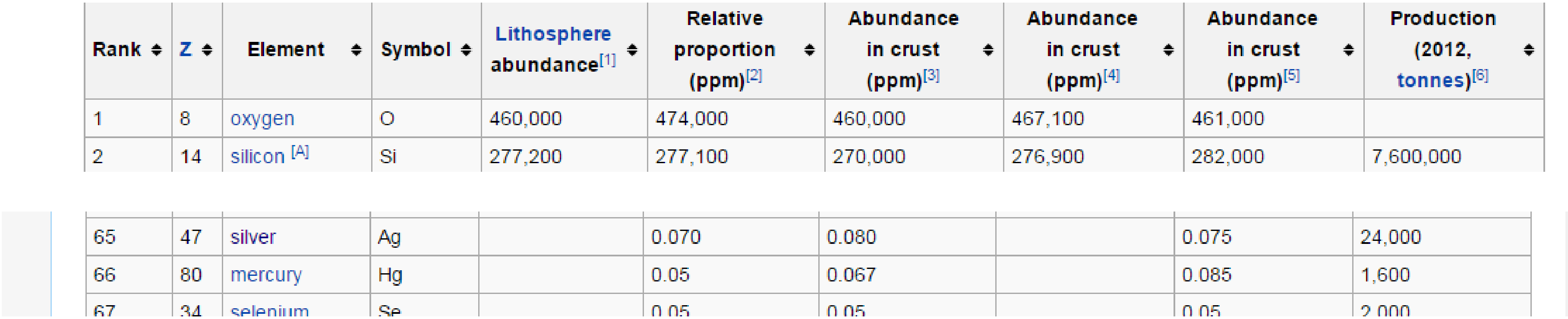
107.868

it's a necessary component in photovoltaic solar cells in the form of paste used as a conductor.

In 2014 this sector accounted for 56% of overall demand for the silver.

The solar industry alone used at least 70 million ounces of silver in 2015.

- the average solar panel contains between 15 and 20 g of silver: (10 g /m^2)
- solar could equal or exceed the silver volumes previously used in the photographic film industry



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
67	34	selenium	Se		0.05	0.05		0.05	2,000

L.Grandel, A. Thorenz Renewable Energy 69 (2014) 157 -166

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*

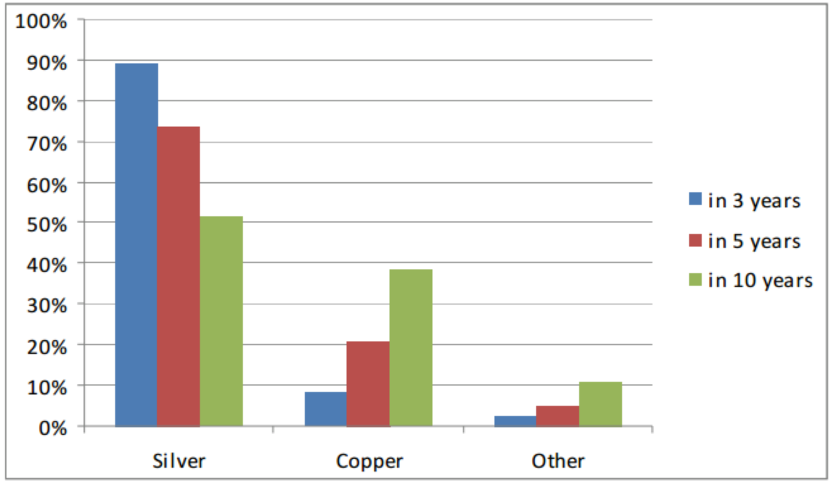
	Silver content [kg/m^2]	kg/MW
Fresnel reflector	0.001	13.75
Parabolic trough	0.001	3.75
Solar power tower	0.001	7.57

Photo courtesy of AREVA Solar

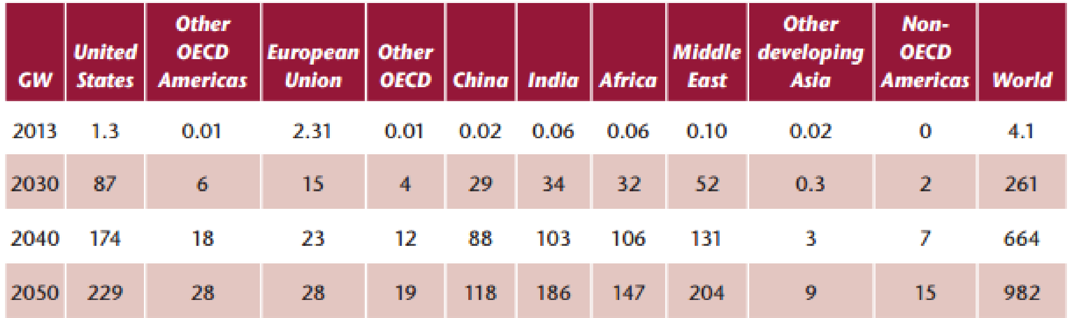
* Renewable Energy 69 (2014) 157

Silver' s matter

The cumulative PV capacity aimed for 2050 exceeds known silver reserves



Considering also for CSP capacities by region in 2030 and 2050 forecast



GW	United States	Other OECD Americas	European Union	Other OECD	China	India	Africa	Middle East	Other developing Asia	Non-OECD Americas	World
2013	1.3	0.01	2.31	0.01	0.02	0.06	0.06	0.10	0.02	0	4.1
2030	87	6	15	4	29	34	32	52	0.3	2	261
2040	174	18	23	12	88	103	106	131	3	7	664
2050	229	28	28	19	118	186	147	204	9	15	982

*The International Energy Agency (IEA) Roadmap 2014

Solution

1. reduce the use of Ag (the target is up to 0.82 g/m^2)
2. Silver replacement
3. Develop other PV technologies that do not contain any silver

Silver Replacement

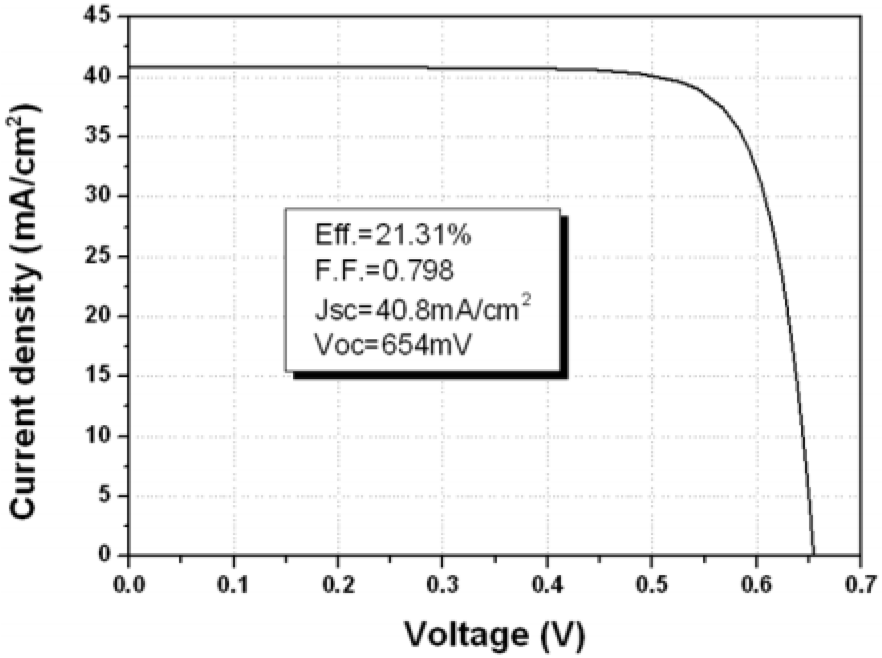
•Two metals were chosen as alternative contacting material: nickel and zinc.
Ni is cheap and can make a good contact to Si by means of Ni silicides

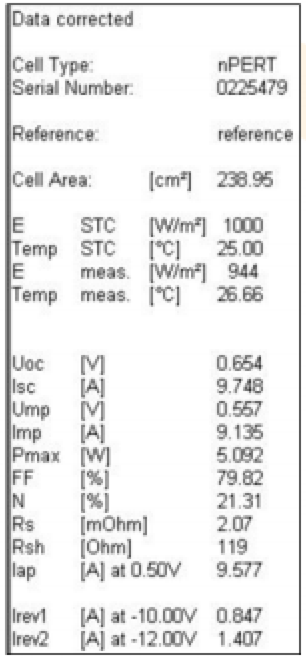
-higher specific electrical resistivity than silver: Ni = 8.7 Ω cm and Zn = 6.1 Ω cm as compared to Ag = 1.6 Ω cm , which makes it necessary to increase the line conductivity of the fingers in a second printing step for example by Cu paste.

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

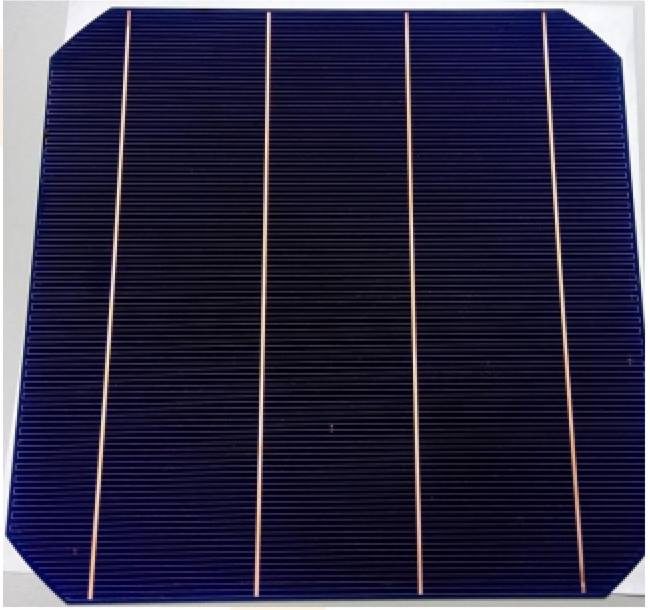
S. Kluska et al. Electrical and Mechanical Properties of Plated Ni/Cu Contacts for Si Solar Cells, 5th Metallisation Workshop, 2015. UNSW http://www.motechsolar.com/

>21% Cell Efficiency





```
Data corrected

Cell Type:                    nPERT
Serial Number:                0225479

Reference:                    reference

Cell Area:          [cm²]     238.95

E      STC      [W/m²]   1000
Temp   STC      [°C]     25.00
E      meas.    [W/m²]    944
Temp   meas.    [°C]     26.66


Uoc    [V]                0.654
Isc    [A]                9.748
Ump    [V]                0.557
Imp    [A]                9.135
Pmax   [W]                5.092
FF     [%]                79.82
N      [%]                21.31
Rs     [mOhm]             2.07
Rsh    [Ohm]              119
Iap    [A] at 0.50V       9.577

Irev1  [A] at -10.00V     0.847
Irev2  [A] at -12.00V     1.407
```



I-V curve of Motech plated n-PERT solar cell

n-PERT (Passivated Emitter, Rear Totally Diffused)

Best cell efficiency with different metallization

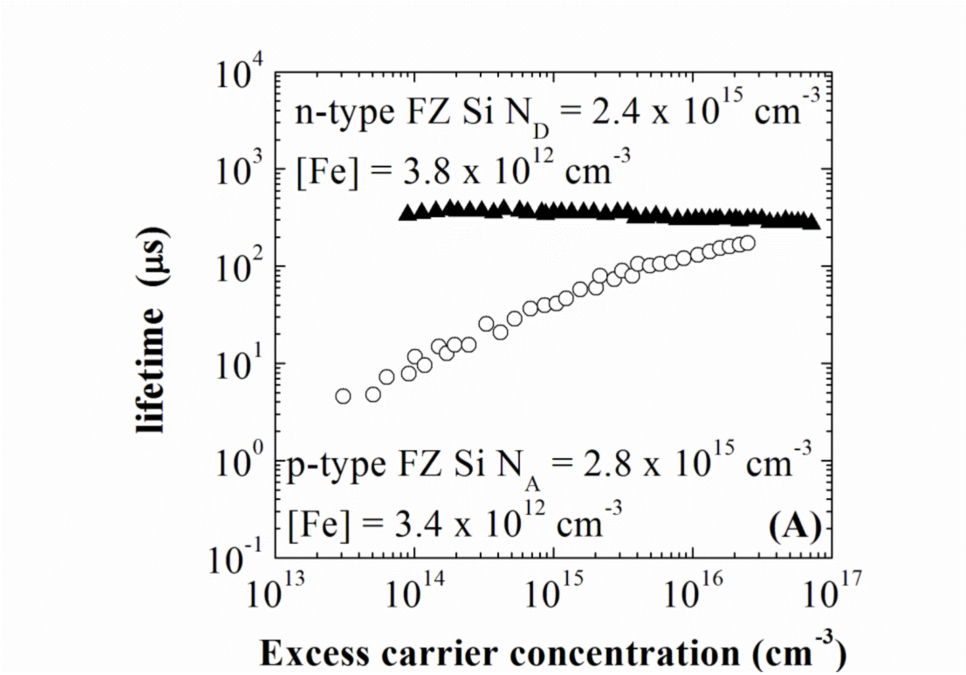
Conditions	Eff. (%)	FF	Voc (mV)	Jsc (mA/cm²)
Ag/Al paste	20.90	0.801	655	39.84
Ni/Cu/Sn	21.31	0.798	654	40.80

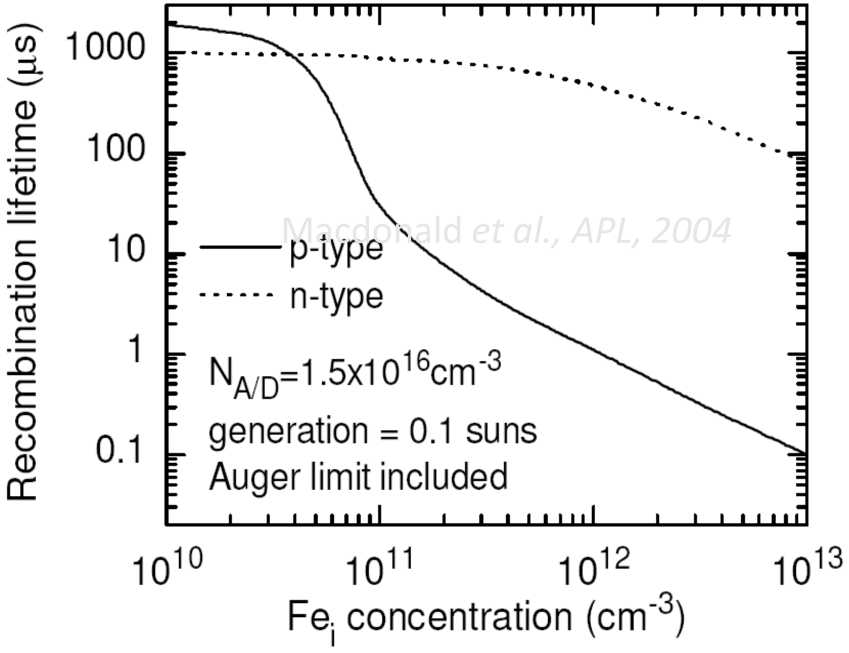
n-*type* silicon

- No Boron

-Most impurities in silicon as Fe capture electrons easier than holes.

- Minority carriers specie in p-type silicon: electrons ☹
- in **n-type** silicon: holes ☺

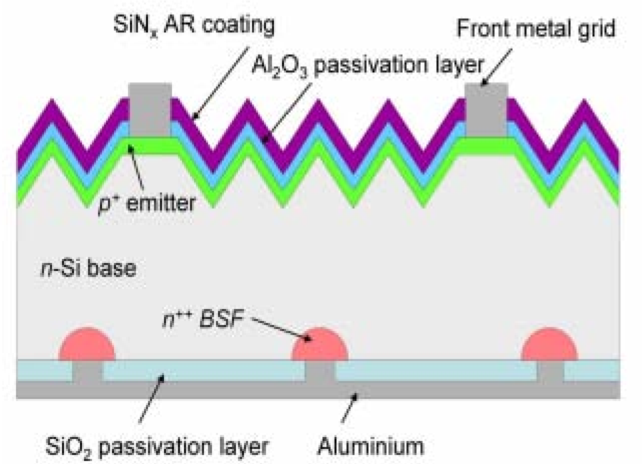




Source: Francesca Ferrazza ENI

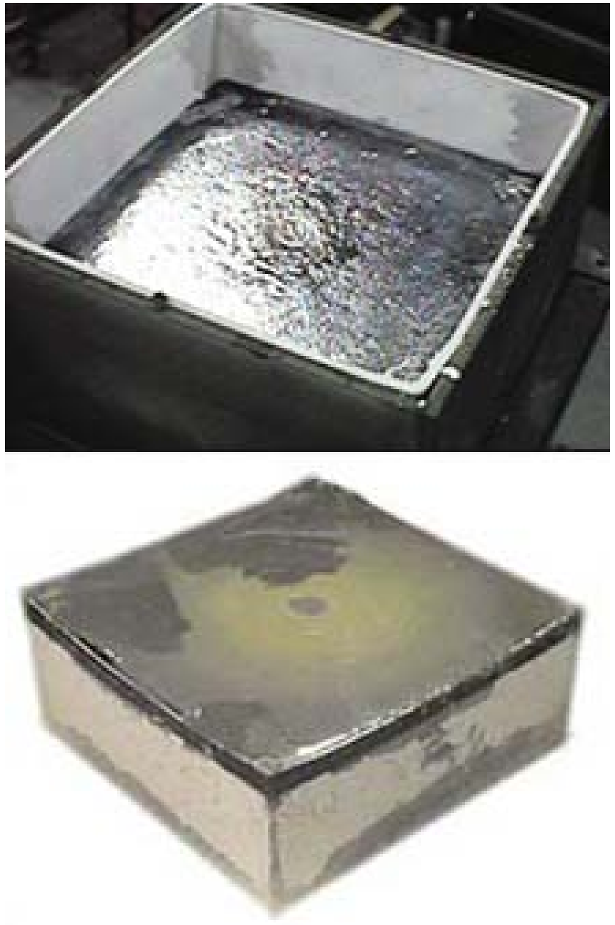
In n-type Fe is less active as recombination center

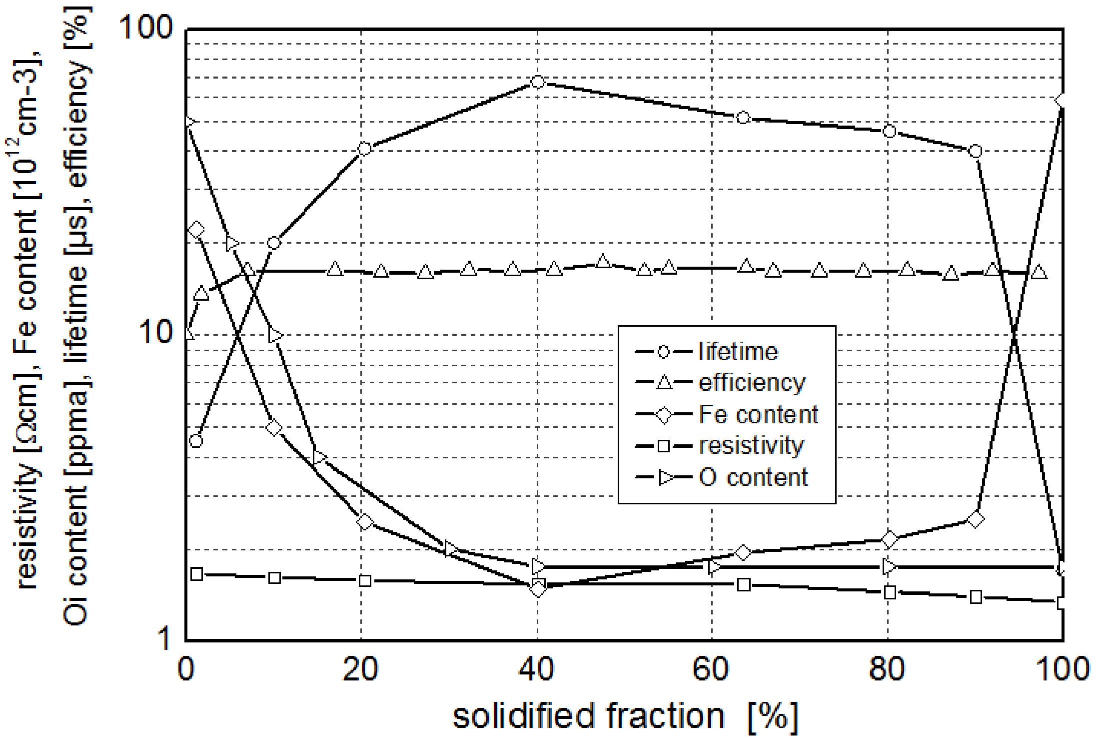
n-type cell back



In summary, an exceptionally high conversion efficiency of 23.2% for an n-type PERL solar cell with a front side B-doped emitter has been reported. The highest reported efficiencies on n-type material were 22.7% 681 mV on a backside-contact solar cell , 22.7% 702 mV on a rear emitter PERT solar cell.23 T

Effect of impurities on lifetime



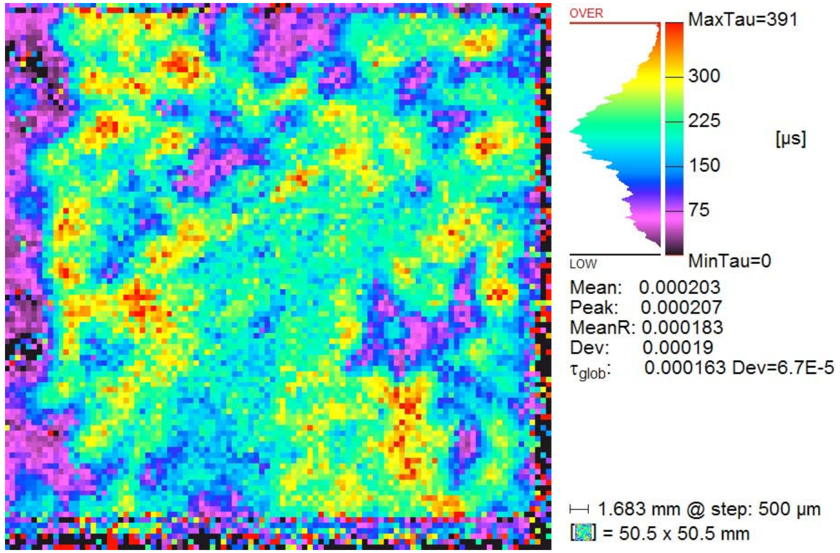


Iron

Effetto impurezze e difetti su proprietà elettriche : lifetime (τ)

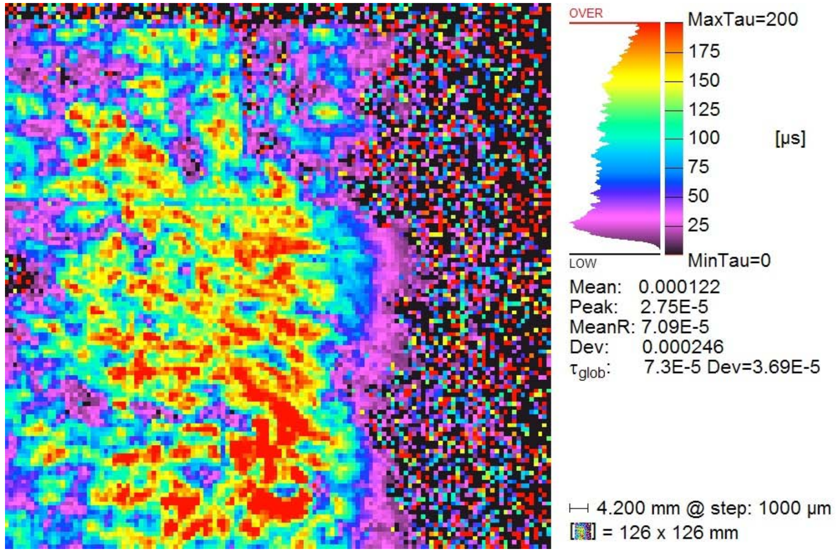
mappe di tempo di vita (τ)

120x120 mm



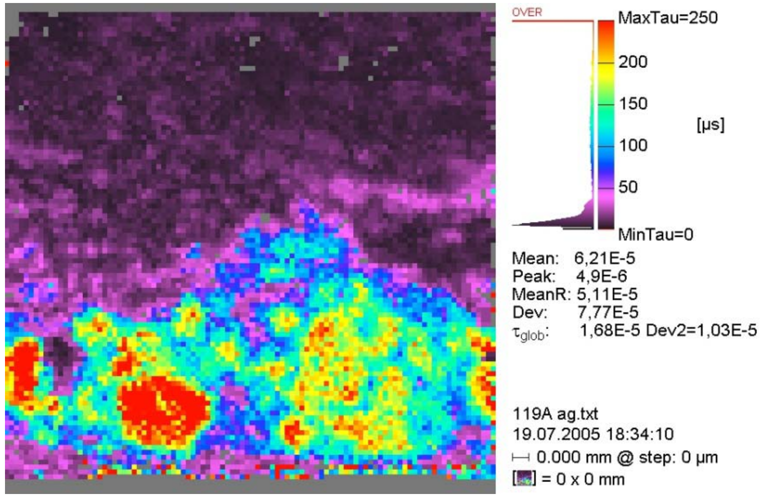
Mean: 0.000203
Peak: 0.000207
MeanR: 0.000183
Dev: 0.00019
τ_{glob}: 0.000163 Dev=6.7E-5

1.683 mm @ step: 500 µm
= 50.5 x 50.5 mm



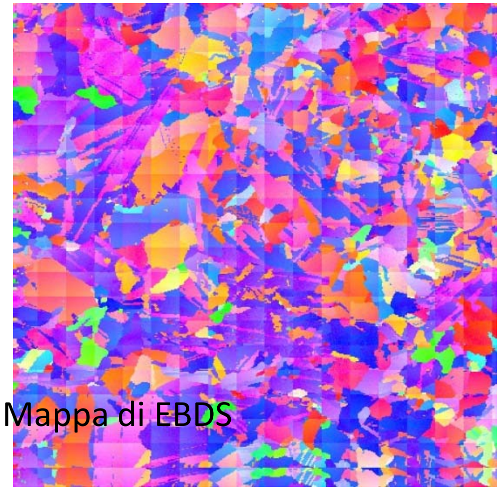
Mean: 0.000122
Peak: 2.75E-5
MeanR: 7.09E-5
Dev: 0.000246
τ_{glob}: 7.3E-5 Dev=3.69E-5

4.200 mm @ step: 1000 µm
= 126 x 126 mm



Mean: 6,21E-5
Peak: 4,9E-6
MeanR: 5,11E-5
Dev: 7,77E-5
τ_{glob}: 1,68E-5 Dev2=1,03E-5

119A ag.txt
19.07.2005 18:34:10
0.000 mm @ step: 0 µm
= 0 x 0 mm



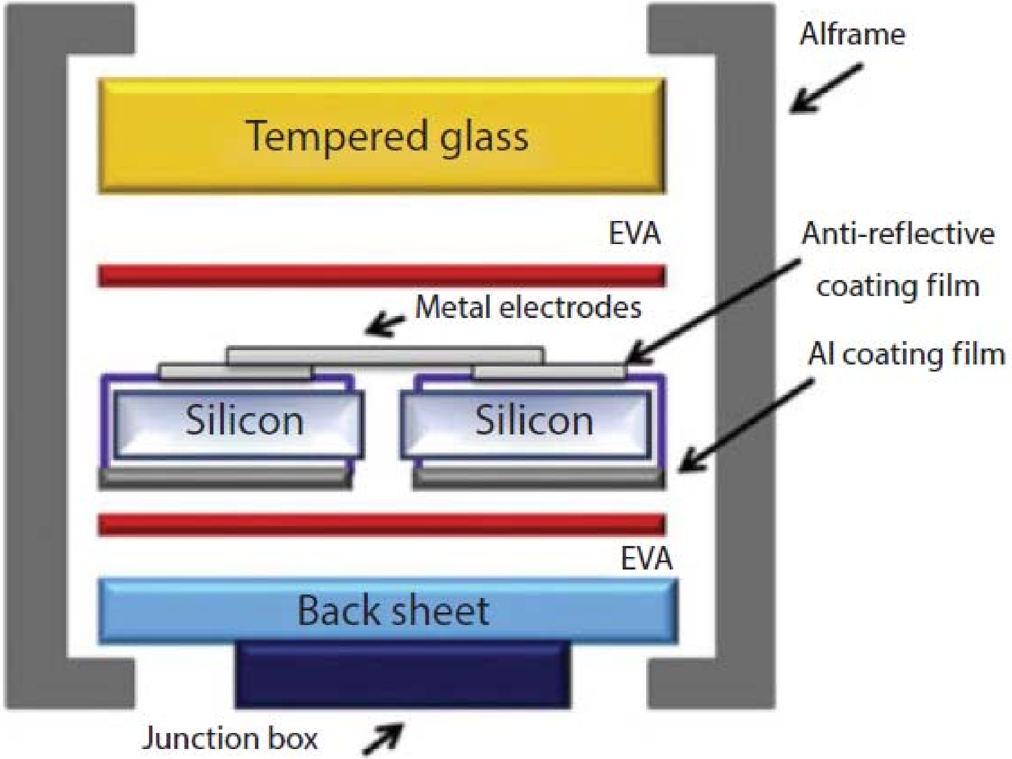
Mappa di EBDS

Recycling process

The amount of waste PV panel is estimated to reach 9.57 million tonnes in 2050 *

Material	Cryst. Si
glass	60 – 85%
aluminium	10 – 20 %, 0%
polymers	7 – 10%
interconnectors	Cu, solder coated ca. 1%
Solar Cells	ca. 3 %


PV CYCLE - Recycling of silicon base...



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

*Bio Intelligence Service (BioIS), Study on photovoltaic panels supplementing the impact assessment for a recast of the WEEE directive – Final report, 2011

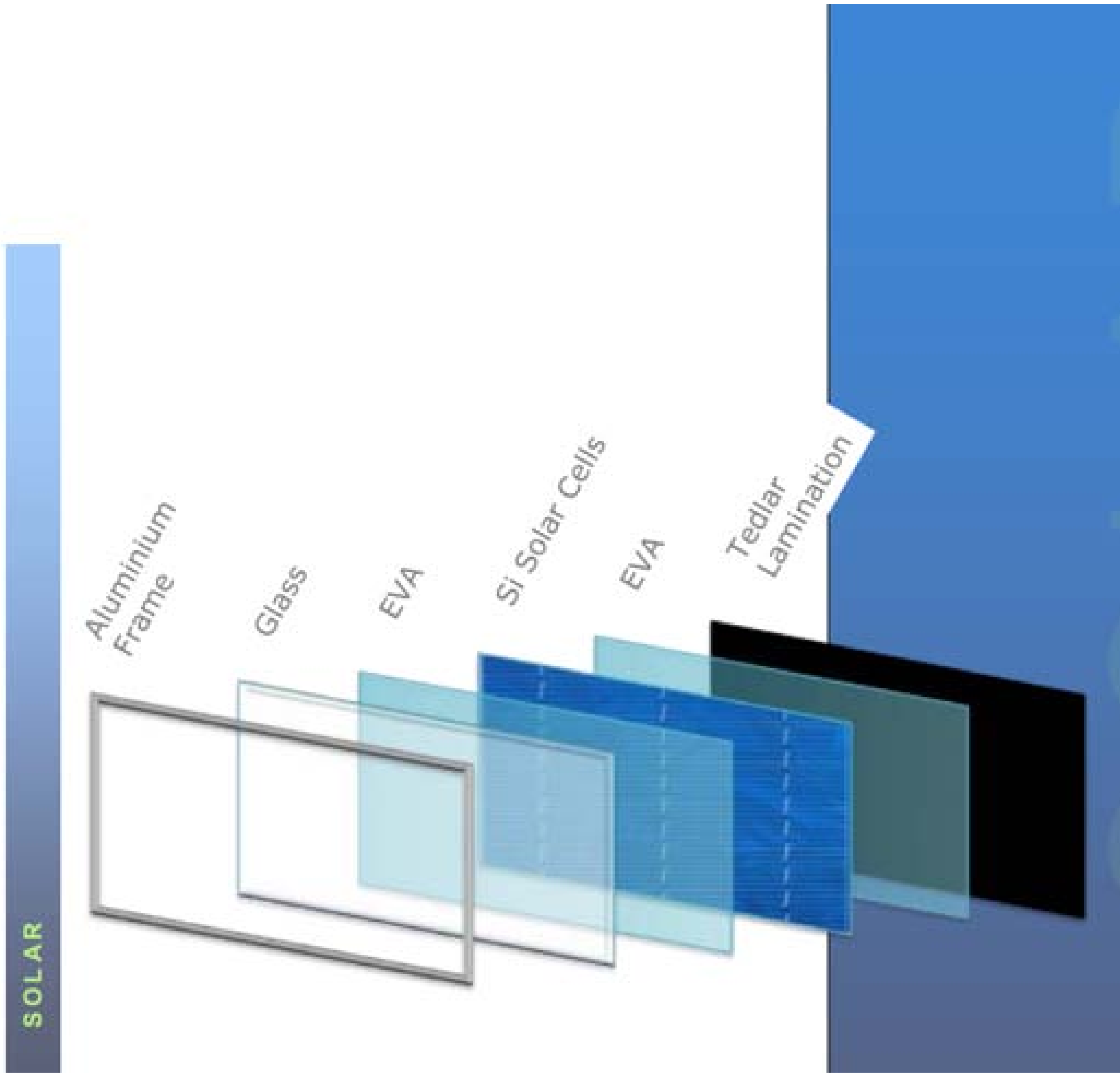
EU PROJECT SASIL, Project “Full Recovery End of Life Photovoltaic – FRELP”

Busbar Copper coated with a tin-lead alloys

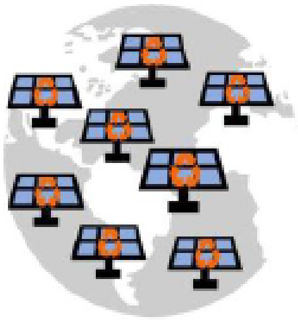
Metal	**Weight (%)**
Copper	83
Lead	7
Tin	10

Average material distribution of a c-Si cell.

Material	**Weight %**	**Deviation (±2σ)**
Silicon	96.74	±0.38
Silver	1.26	±0.02
Aluminum	1.12	±0.21
Copper	0.94	±0.03
Chromium	0.14	±0.01
Lead	0.10	±0.01

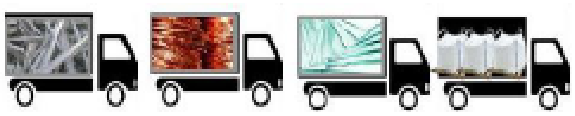


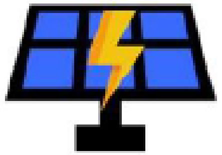
Challenge and opportunity of PV waste



A growing wave of PV wastes is expected globally, starting in Europe where PV was first installed. PV waste recycling is legally regulated only in the EU.

Economic solutions for a high-value recycling of all valuable materials are urgently needed.



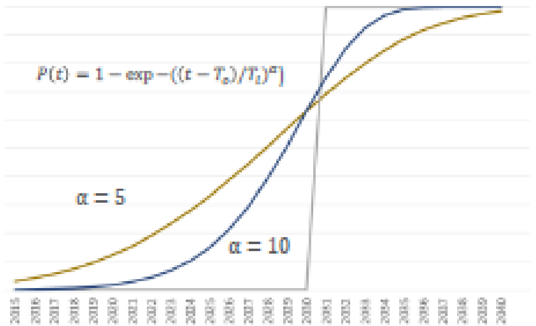


Up to now, PV manufacturers are not systematically using recycled materials.

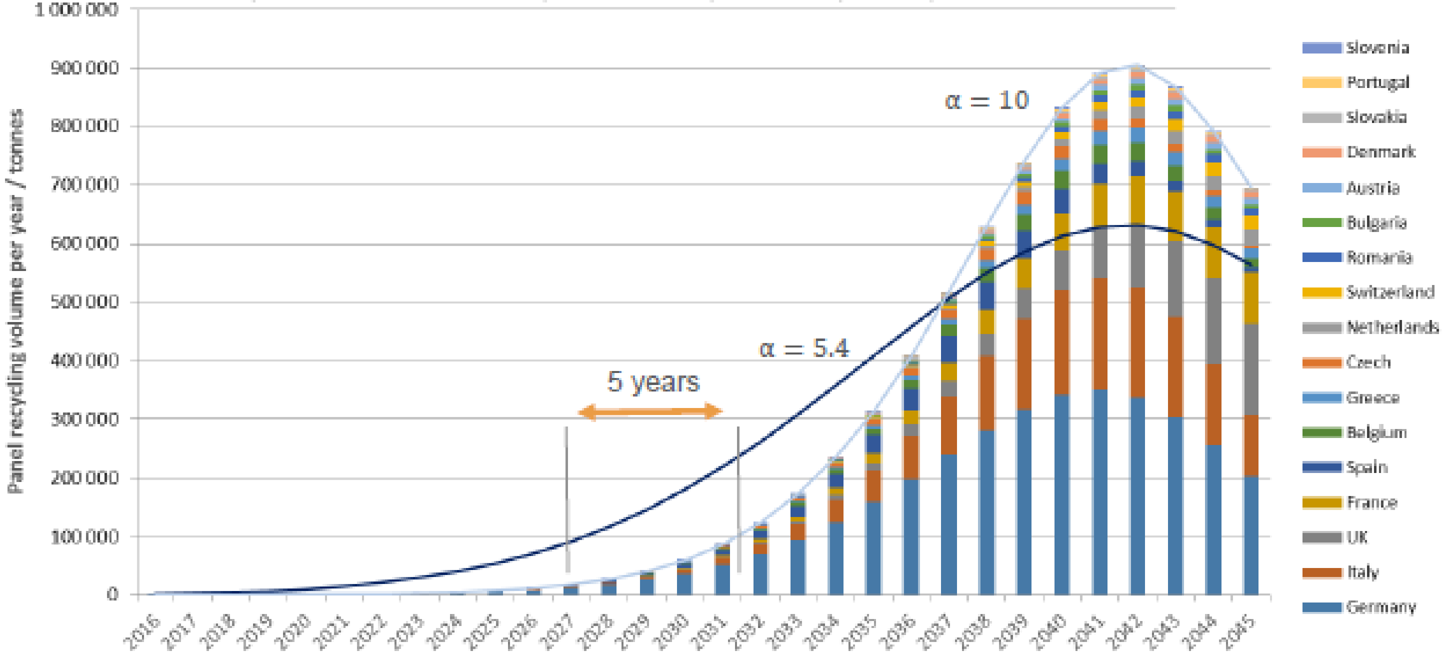
End-of-life panel waste volumes

- The modeling shows that the peak of European end of life waste will occur in 2042 (~ independent of the slope factor)
- The slope factor changes substantially the onset of panel waste
- For example, the date estimated for 100 000 tonnes of annual waste changes by 5 years according to common slope factors

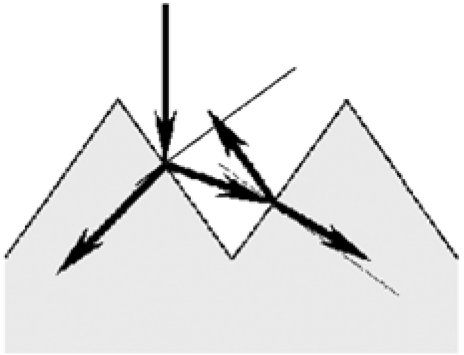
Weibull failure distribution for panels installed in 2000 with 30 year lifetime



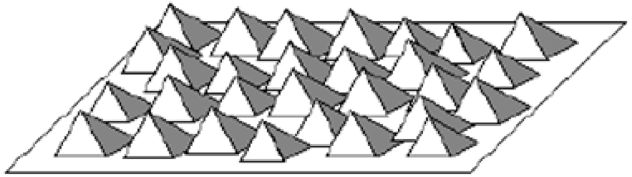
Yearly waste volumes in Europe for two slope factors (tonnes) – CABRISS model

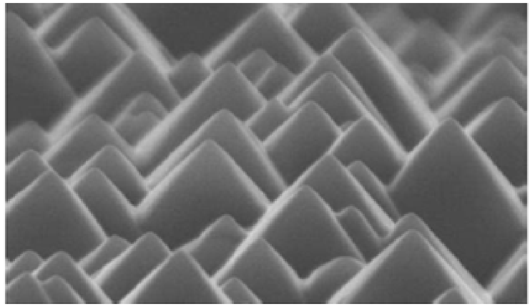


Texturization process



- Reduces the reflection
- increase the optical path : a solar cell with no light trapping features may have an optical path length of one device thickness, while a solar cell with good light trapping may have an optical path length of 50, indicating that light bounces back and forth within the cell many times.

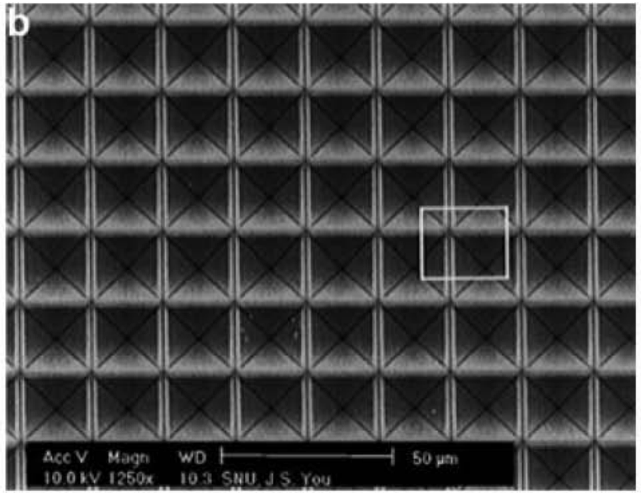




Random distributed pyramids :

Mono Si : KOH or NaOH-based : 5% 80°C , 15’

Poly : HNO_3 + HF



Uniform inverted pyramids:

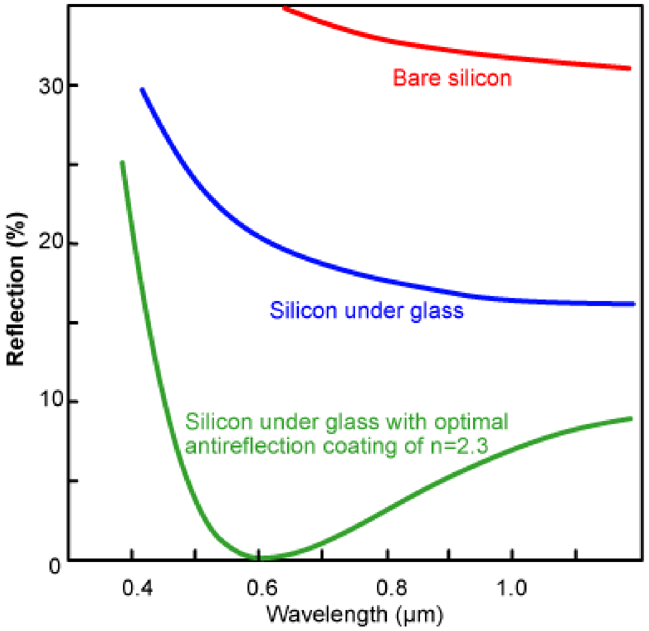
Etching mask on (100) Si (+ I_{sc}=1 mA /cm^2)

Anti-reflection and passivation layer

- The loss by reflection must be reduced
- The surface recombination of photogenerated carriers must be minimized

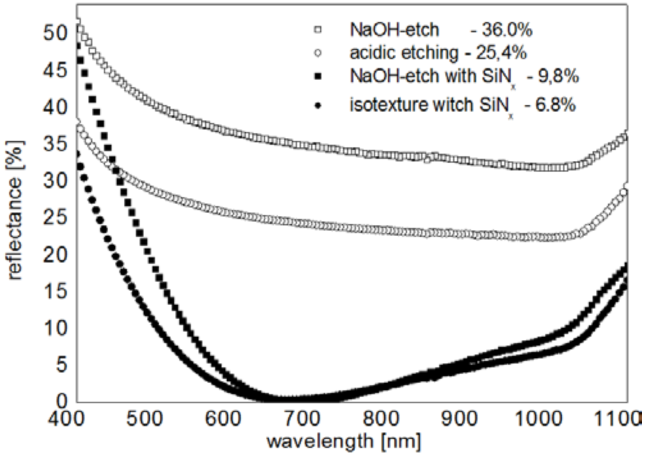
PECVD deposition of SiNx :

In order to reach the deep blue colour and thereby minimise the reflectance, a layer thickness of ca. 70 nm is deposited. The dielectric layer has additional benefits for the solar cell. As the layer is hydrogen (H) rich, the surface and the bulk is passivated by H, as it attaches to Si dangling bonds.

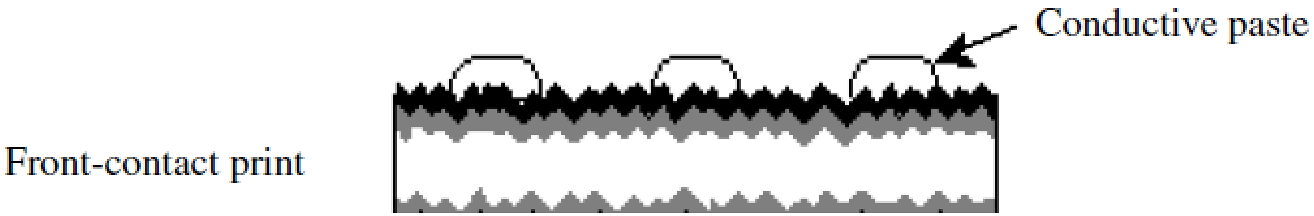


x = 70 nm

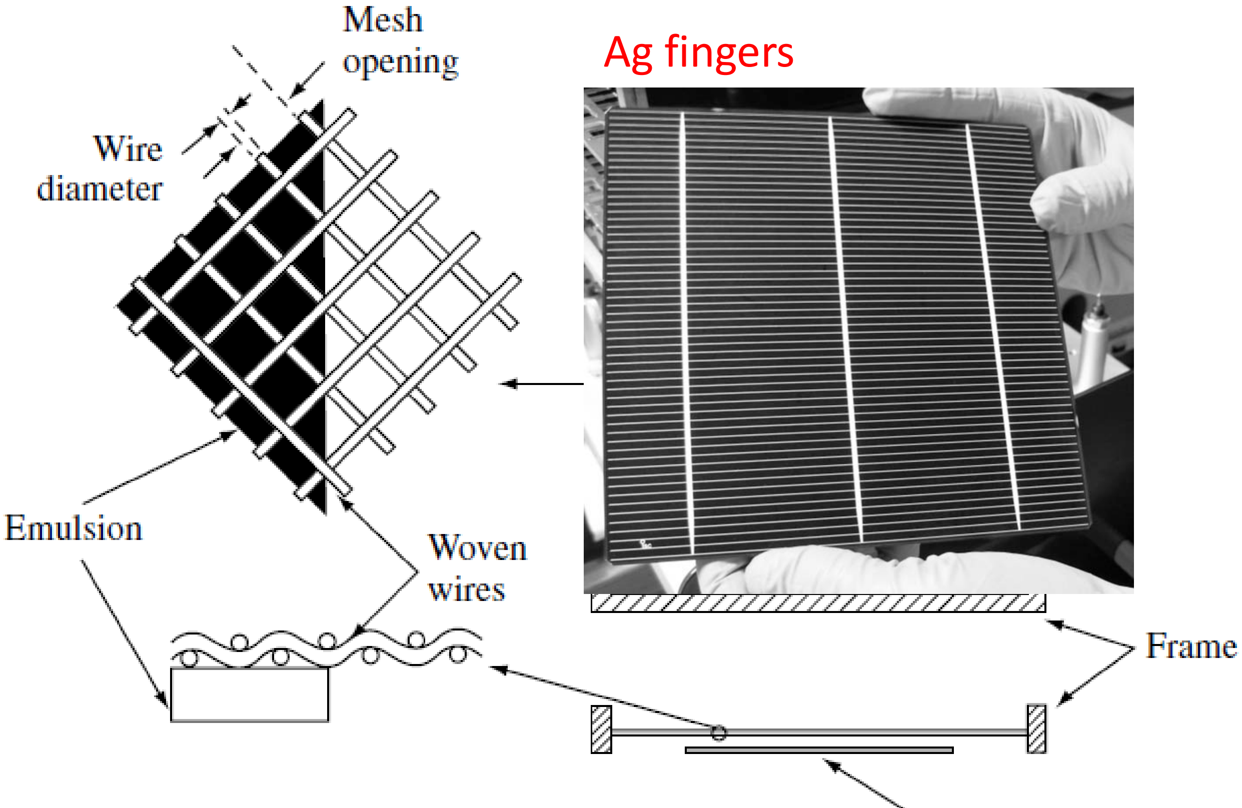
Color blue



Contacts



Front contact : screen printing method + annealig @ 100-200 °C (most widely used)



Ag fingers

Rear contact fully covered by a Al paste

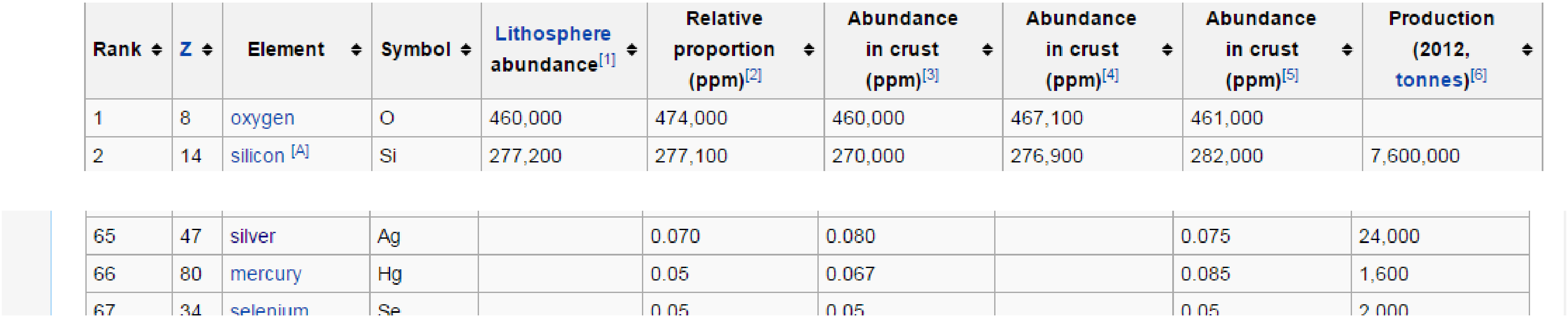
47
Ag
Silver
107.868

it’s a necessary component in photovoltaic solar cells in the form of paste used as a conductor.

In 2014 this sector accounted for 56% of overall demand for the silver.

The solar industry alone used at least 70 million ounces of silver in 2015.

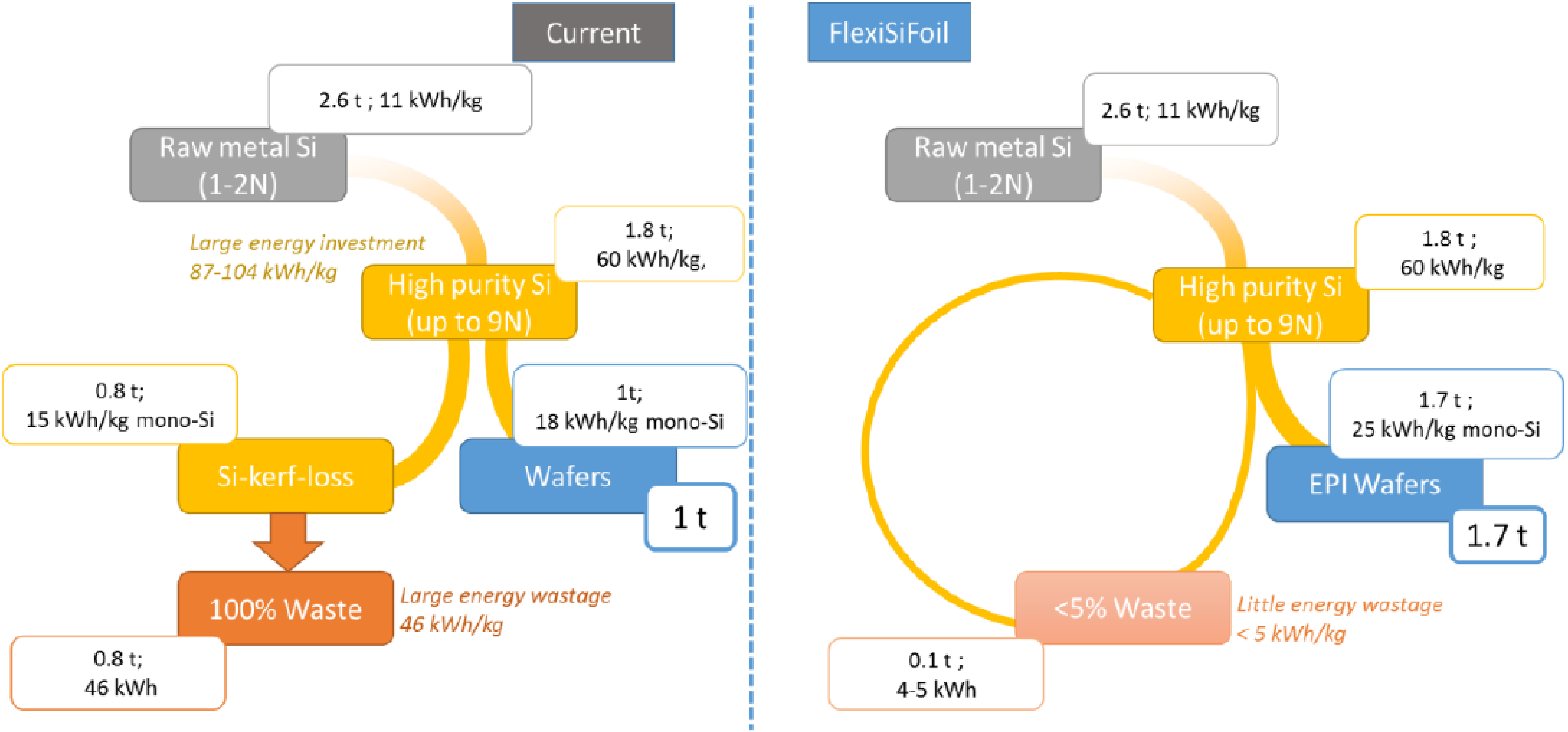
- the average solar panel contains between 15 and 20 g of silver: (10 g /m^2)
- solar could equal or exceed the silver volumes previously used in the photographic film industry

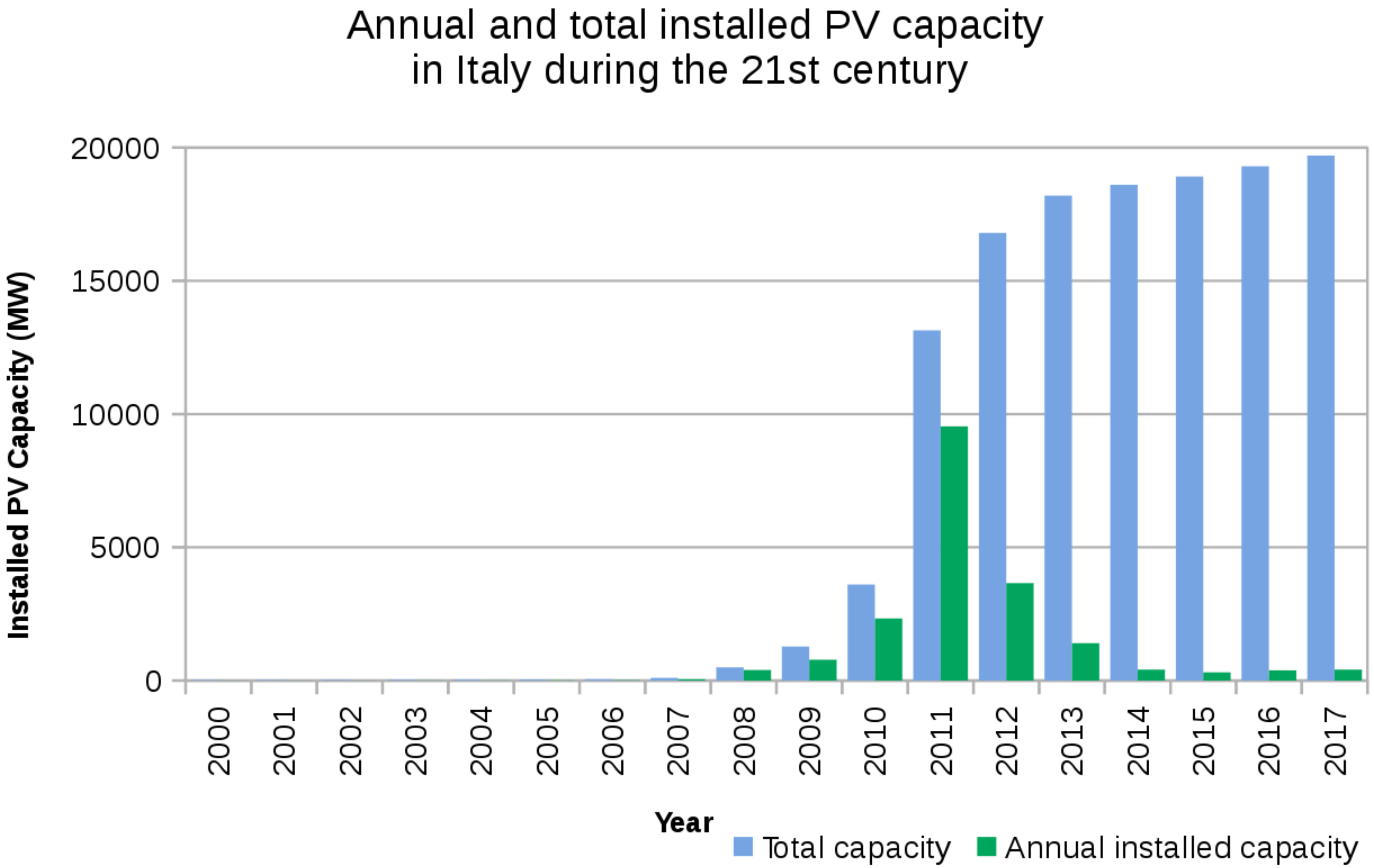


Rank	Z	Element	Symbol	Lithosphere abundance[1]	Relative proportion (ppm)[2]	Abundance in crust (ppm)[3]	Abundance in crust (ppm)[4]	Abundance in crust (ppm)[5]	Production (2012, tonnes)[6]
1	8	oxygen	O	460,000	474,000	460,000	467,100	461,000	
2	14	silicon [A]	Si	277,200	277,100	270,000	276,900	282,000	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
67	34	selenium	Se		0.05	0.05		0.05	2,000

L.Grandel, A. Thorenz Renewable Energy 69 (2014) 157 -166

Estimated energy and material consumption for the Epi-Foil process, compared with current state of the art mono-Si wafer manufacturing process. For the current state-of-art 2.6 t raw metal Si/1.8 t poly-Si is required to produce 1 t of mono-Si wafers.





Annual and total installed PV capacity in Italy during the 21st century

Key role of PV forecasts in all major future energy scenarios

Based on current market trends it has been estimated that :

- ➢ PV has the potential to meet 15 % EU electricity demand in 2030
- ➢ PV can give considerable contribution to the reduction of CO_2 emissions, since the carbon footprint of PV systems is up to 65 times lower than that of fossil fuel-based electricity, with no CO_2 emissions during operations

4 600 GW of installed PV capacity by 2050 would avoid the emission of up to 4 gigatonnes (Gt) of CO_2 annually

United Nations
Climate Change

The COP21's overarching goal from Paris to reduce greenhouse gas emissions and to limit the global temperature increase clearly showed that expectations for PV are high, confirmed by COP25

Availaibility

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

Production of silicon : In 2006 the silicon demand for solar surpassed for the first time that for electronics, and now more than 80% of the 100,000 tons produced by the industry were dedicated to the PV market .