Laboratory for Photovoltaics and semiconductor physics

uni.lu UNIVERSITÉ DU LUXEMBOURG

10 YEARS 2007-2017

Thin film solar cells: from fundamental scientific challenges to industrial potential

Daniel LINCOT

Institut de Recherche et Développement sur l'Energie Photovoltaïque (IRDEP),

UMR EDF-CNRS-Chimie ParisTech, Chatou

Institut Photovoltaïque Ile de France (IPVF)

IPVF INSTITUT PHOTOVOLTAÏQUE D'ILE-DE-FRANCE

www.ipvf.fr

IRDEP INSTITUTE OF R&D ON PHOTOVOLTAIC ENERGY

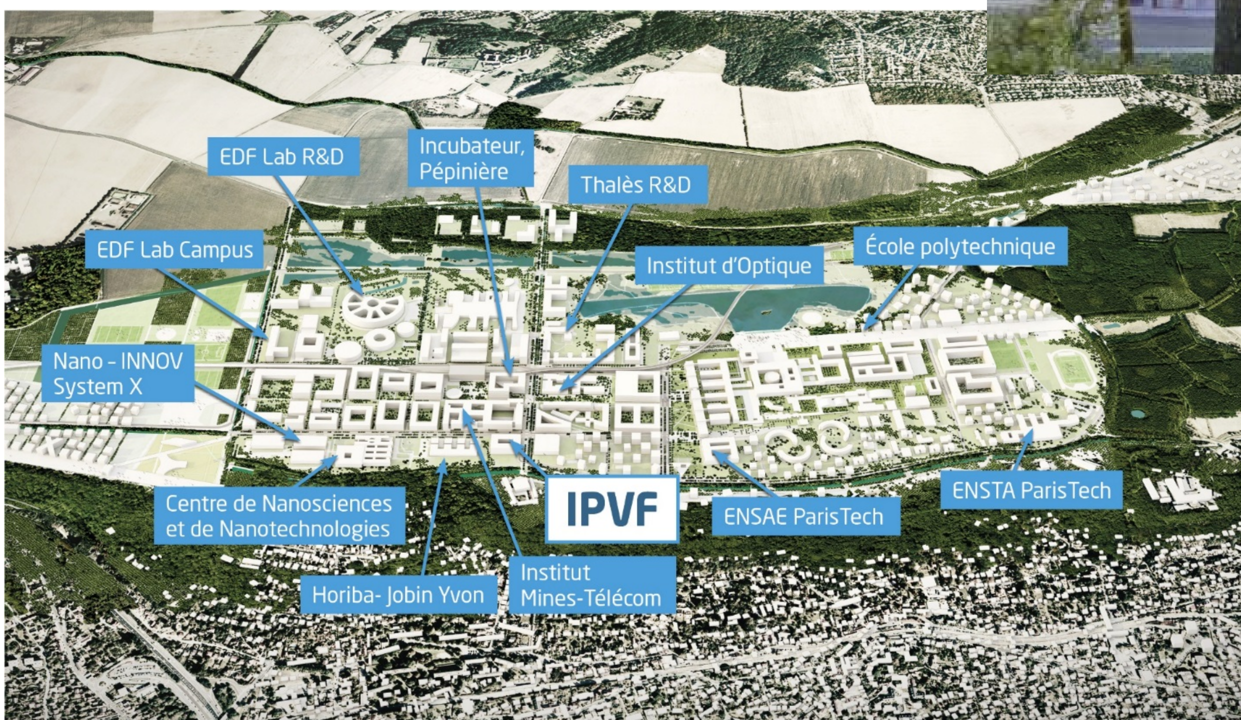
cnrs | dépasser les frontières

EDF LEADING THE ENERGY CHANGE

Chimie ParisTech

IPVF Building at the earth of the New Paris Saclay Campus

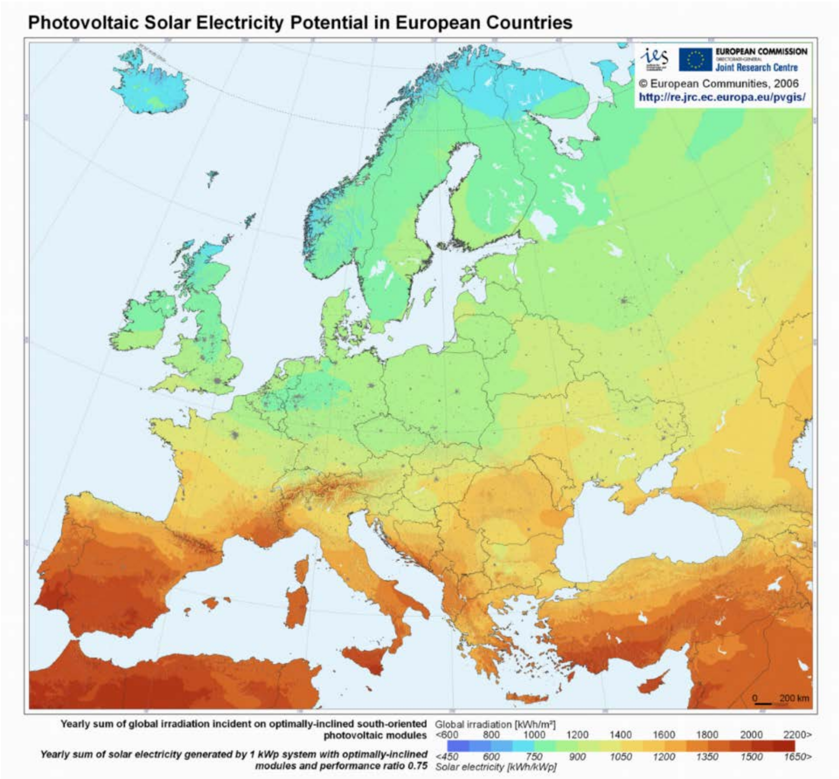
End 2017



Why Photovoltaics ?

The enormous ressource of renewable energy from the sun

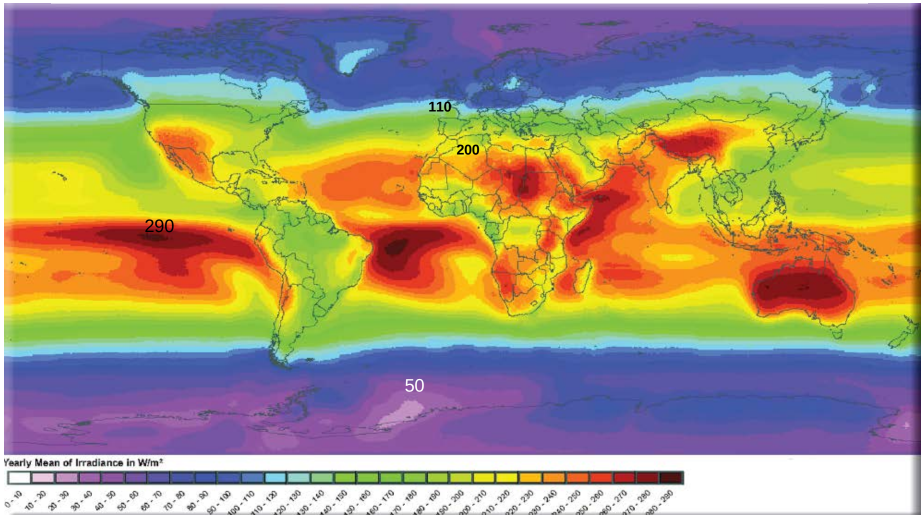
Sunny day : about 1 GW / km^2



Un m^2 reçoit de 0,8 à 3 MWh/an

Tableau - Bilan énergétique à la surface de la Terre (1 TW = 10^{12} watts) (d'après [1]).

Puissance solaire incidente (hors atmosphère) 173 000 TW	
Réflexion directe	52 000 TW (30 %)
Conversion directe en chaleur	78 000 TW (45 %)
Évaporation de l'eau	39 000 TW (22 %)
Vent et vagues	3 600 TW (2 %)
Photosynthèse	40 TW (0,02 %)
Marées : 3 TW	
Géothermie : 32,3 TW	

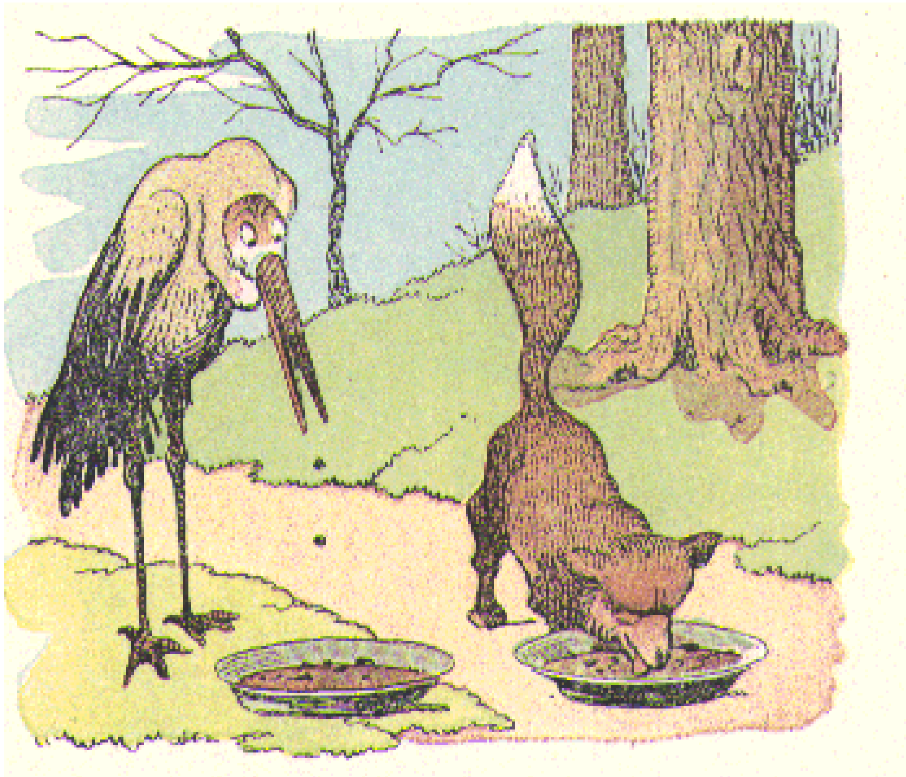


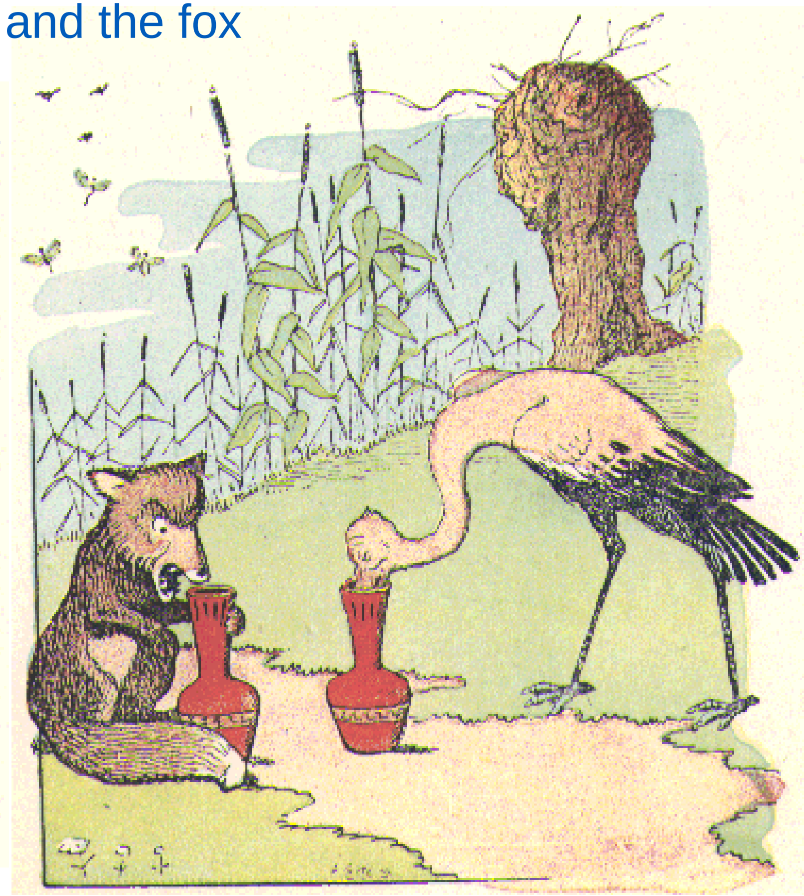
Solar ressource at the ground level : 120 000 TW (120 millions de GW)

Mean power of energy consumption by humanity: 17 TW (about 7000 times less)

Having an energy source is not sufficient :
We need to discover the right technologies for using it

Jean de la Fontaine: The stork and the fox

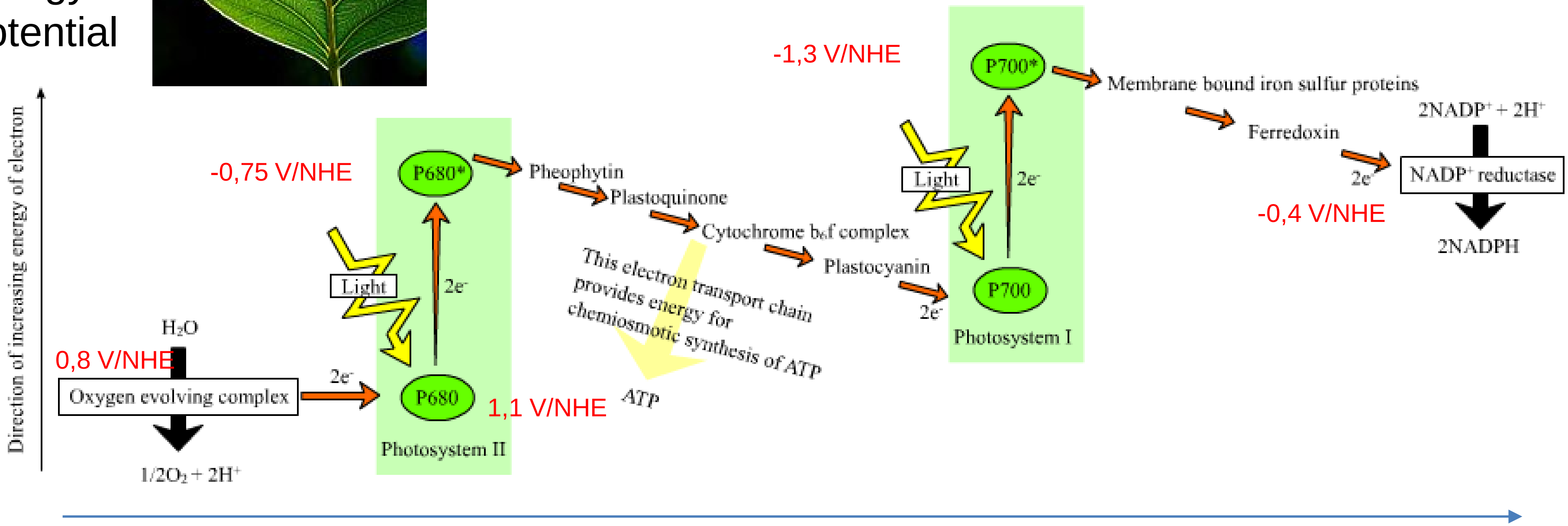




Source : fergant.clg61.ac-caen.fr

Photovoltaics at the heart of Natural Photosynthesis

Energy Potential

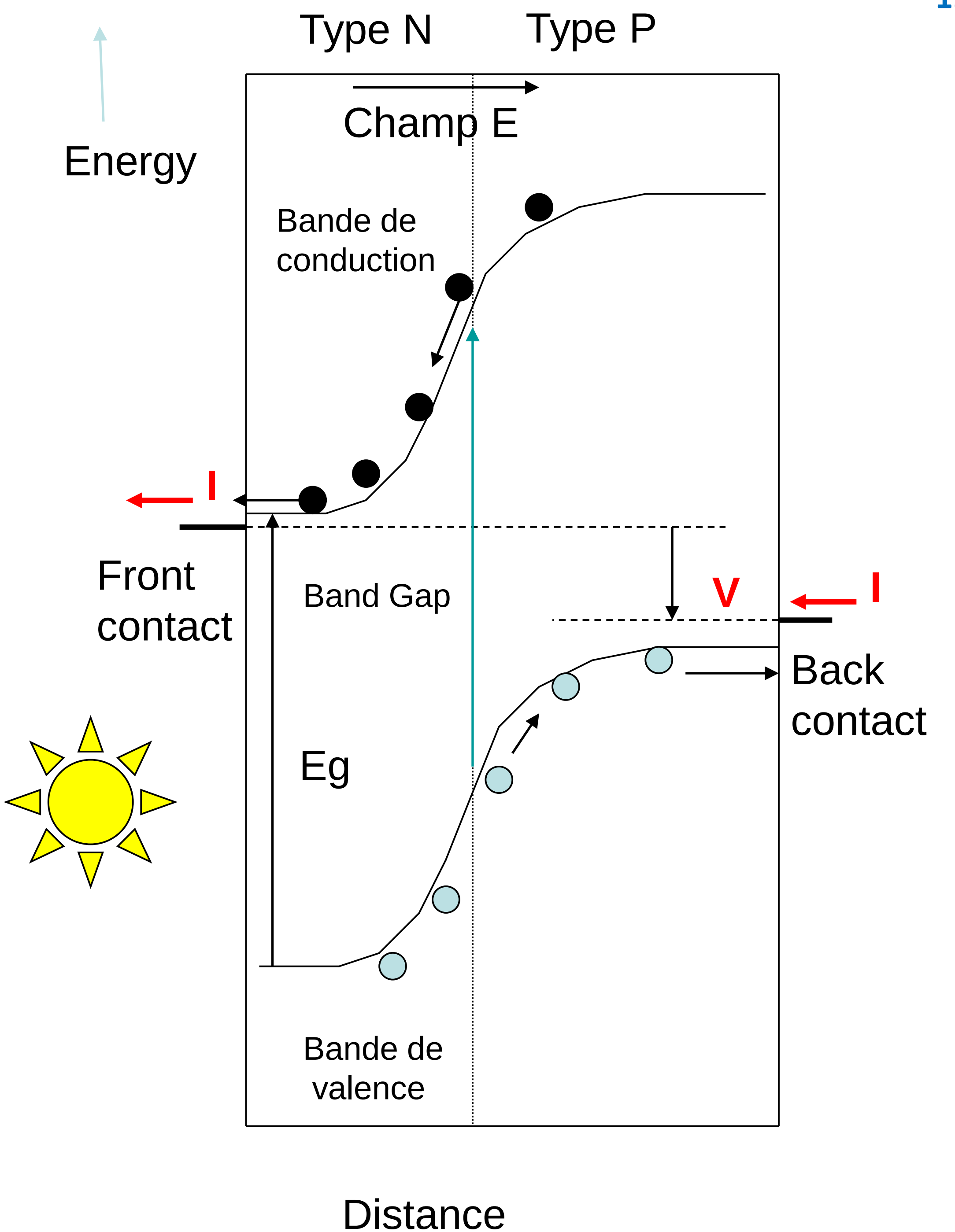


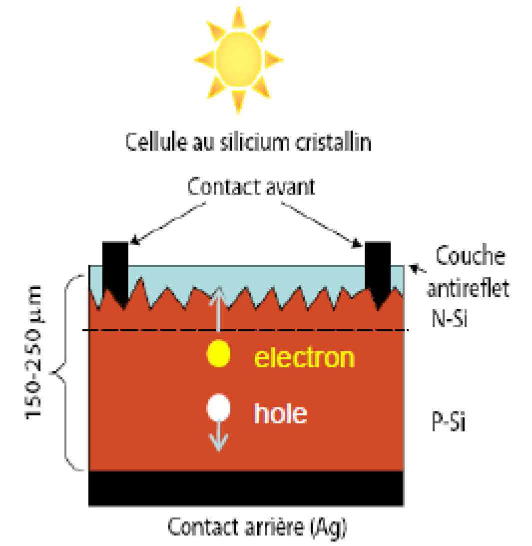
Distance

$$6CO_2 + 6H_2O \xrightarrow{\text{Light}} C_6H_{12}O_6 + 6O_2$$

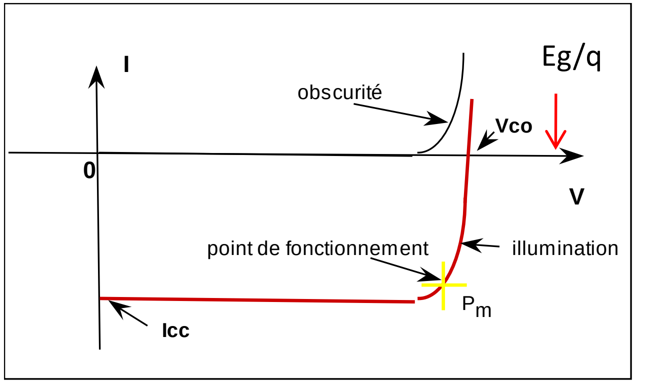
Carbon dioxide + Water → Sugar + Oxygen

1954 : Silicon solar cells The big jump !





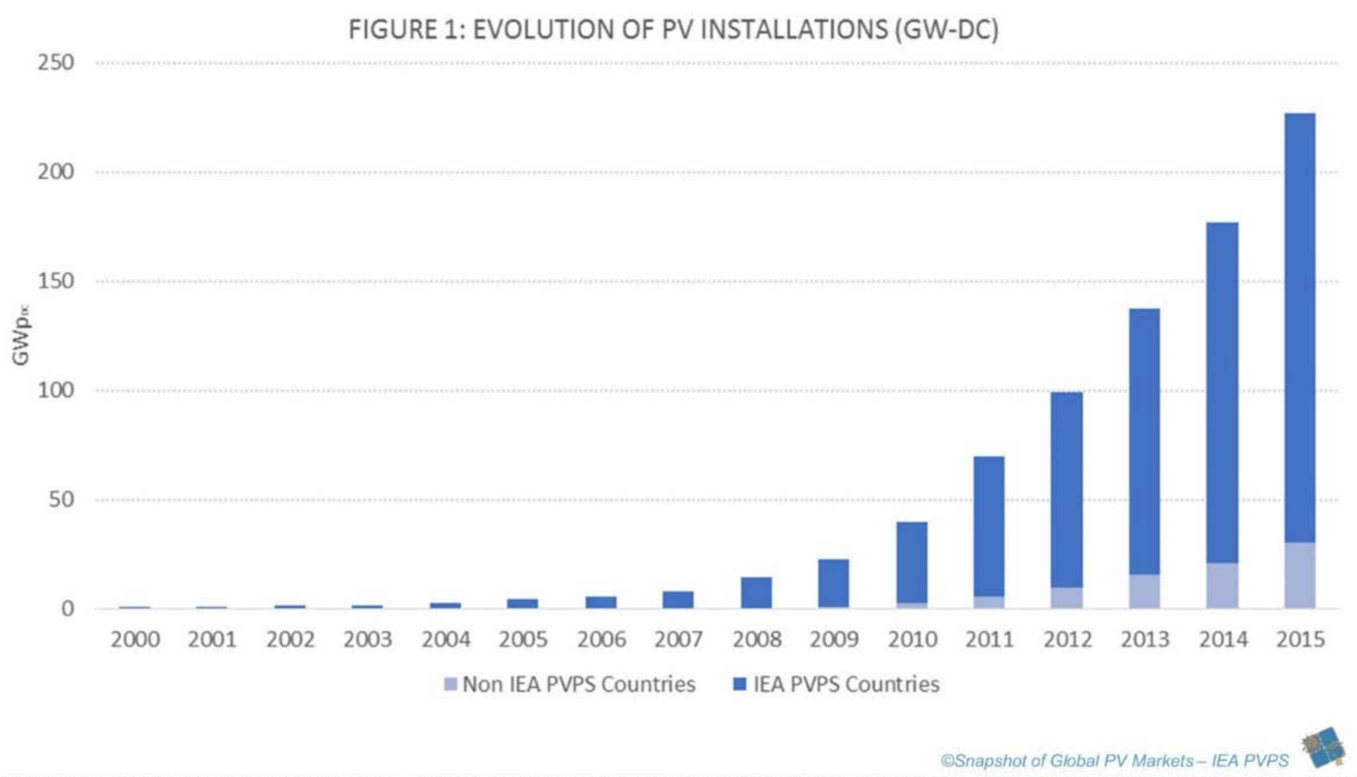
Current voltage-curves



$$I = I_0 [\exp(qV/nkT) - 1] - I_L$$

Light power , P_{lum} :1000 W/m^2
Electrical power : $P_{el} = VI$
Efficiency : $R = P_{el}/P_{lum}$

2000 : Photovoltaics becomes a major energy source



2015 : 220 GW (1,3% of world electricity production)

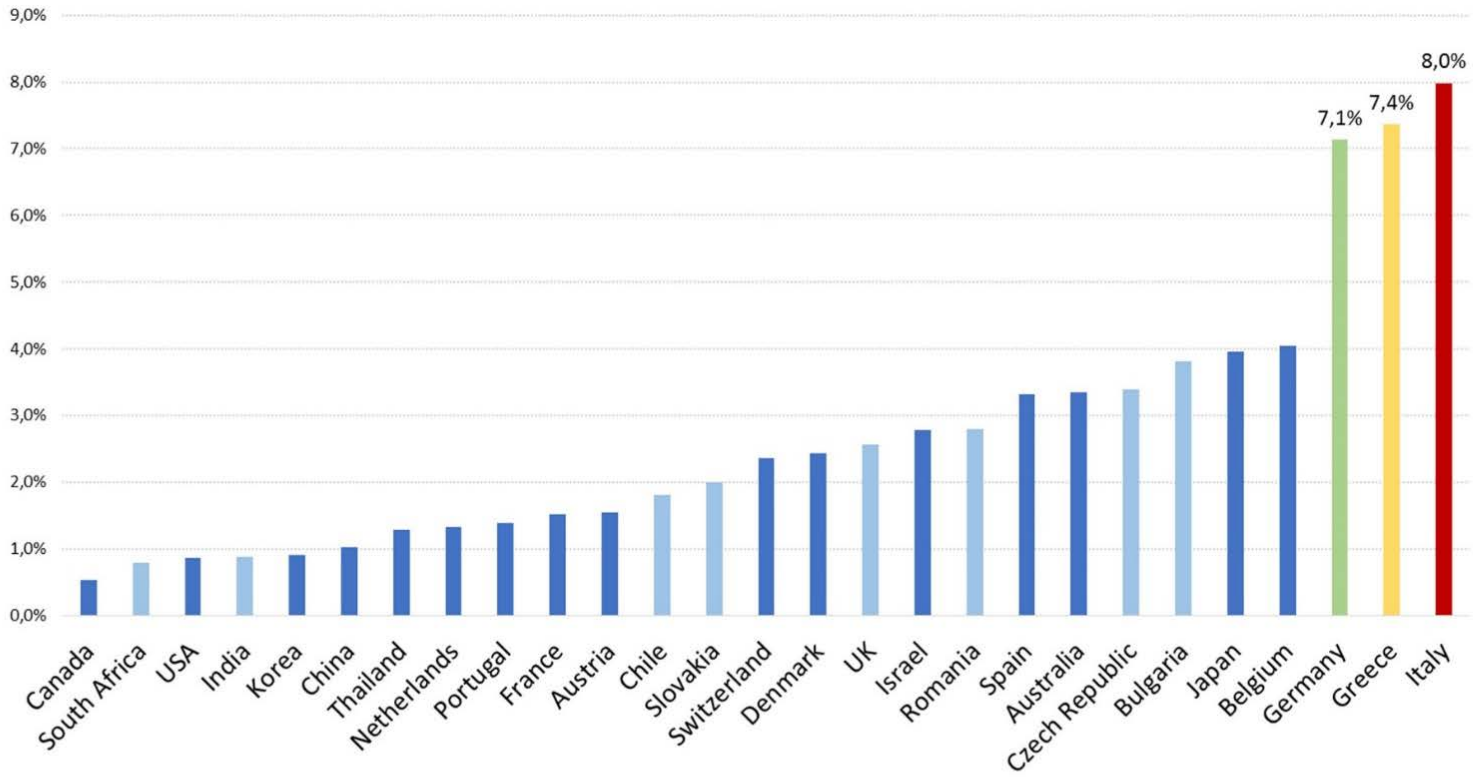
2016 : 300 GW (75 GW in 2016 with 35 GW in China)

Projection 2020 : 500 GW

Projection 2050 : 4,5 TW , 16% of World Electricity (AIE)

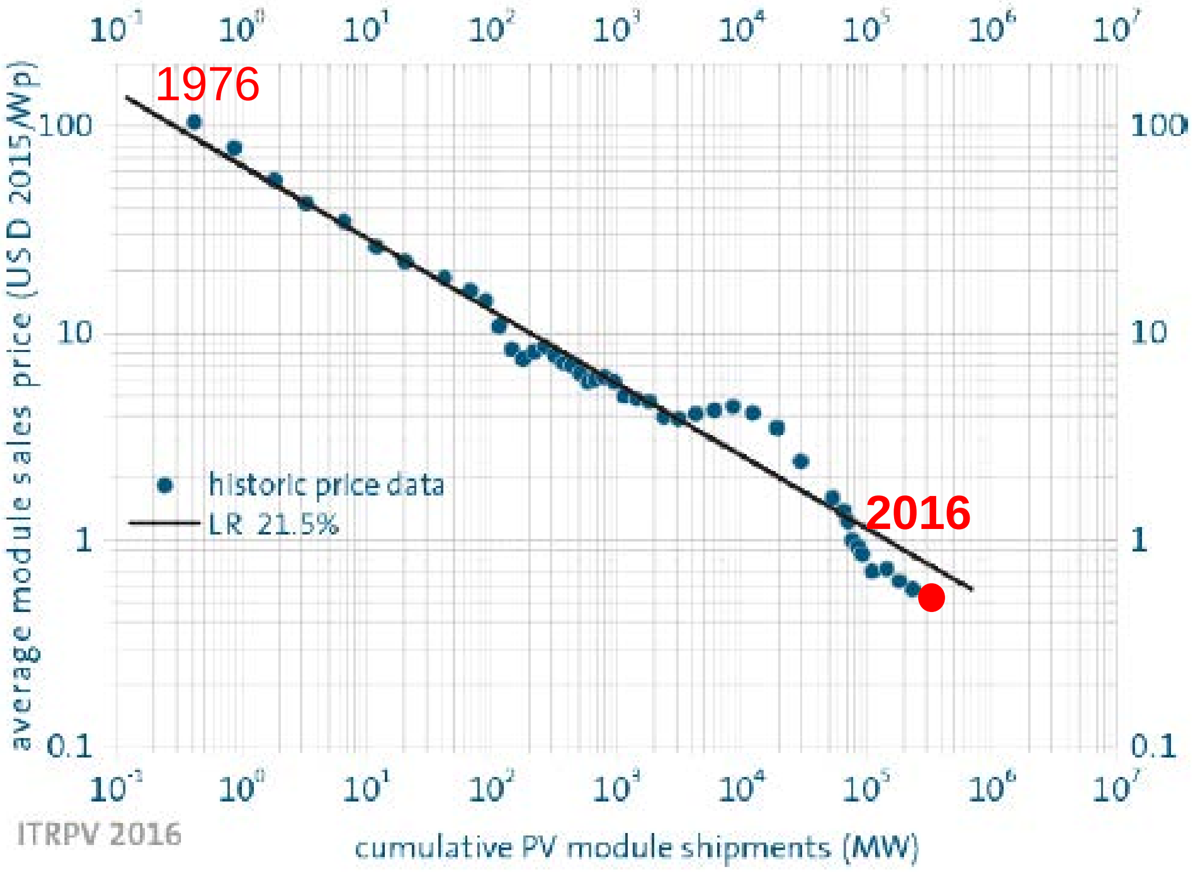
The fast introduction of PV in the electricity sector

FIGURE 4: NATIONAL PV PENETRATION IN % OF THE ELECTRICITY DEMAND BASED ON 2015 CAPACITIES



©Snapshot of Global PV Markets – IEA PVPS

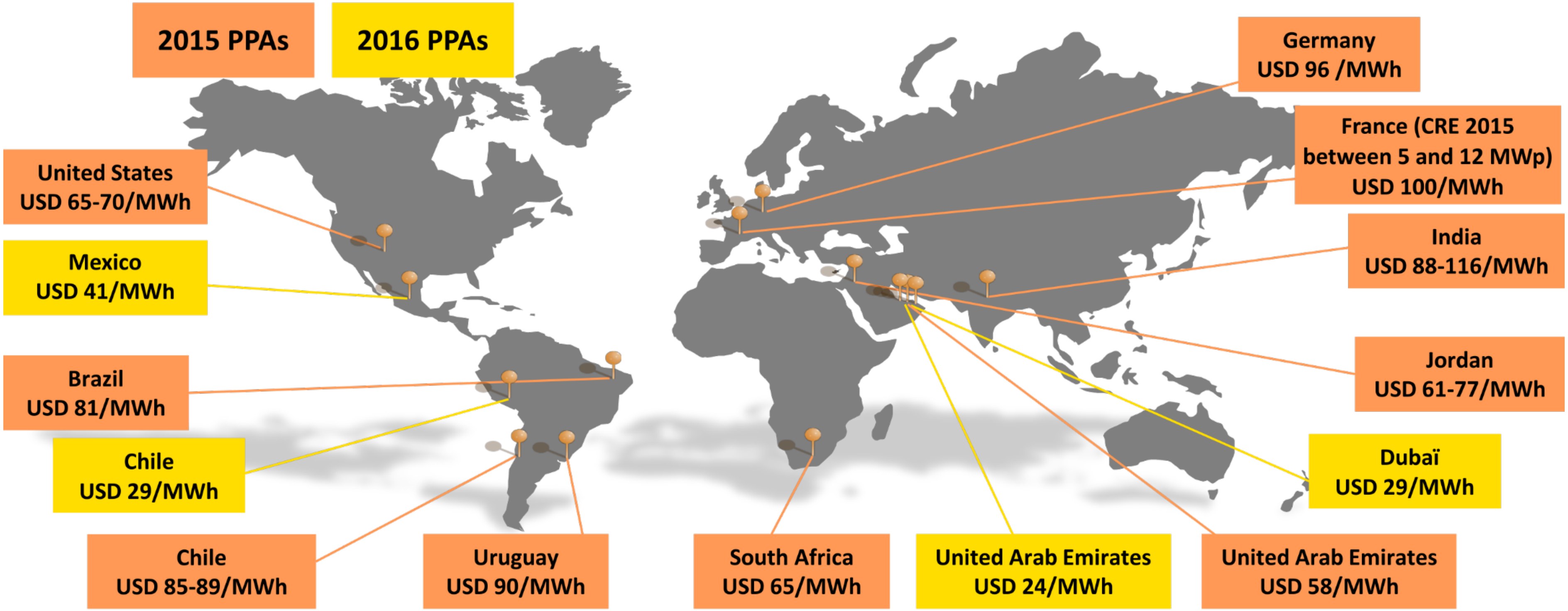
The reason : Economic competitiveness of photovoltaics
The price/cost experience curve



0.3 $/W

Competitiveness of solar electricity prices

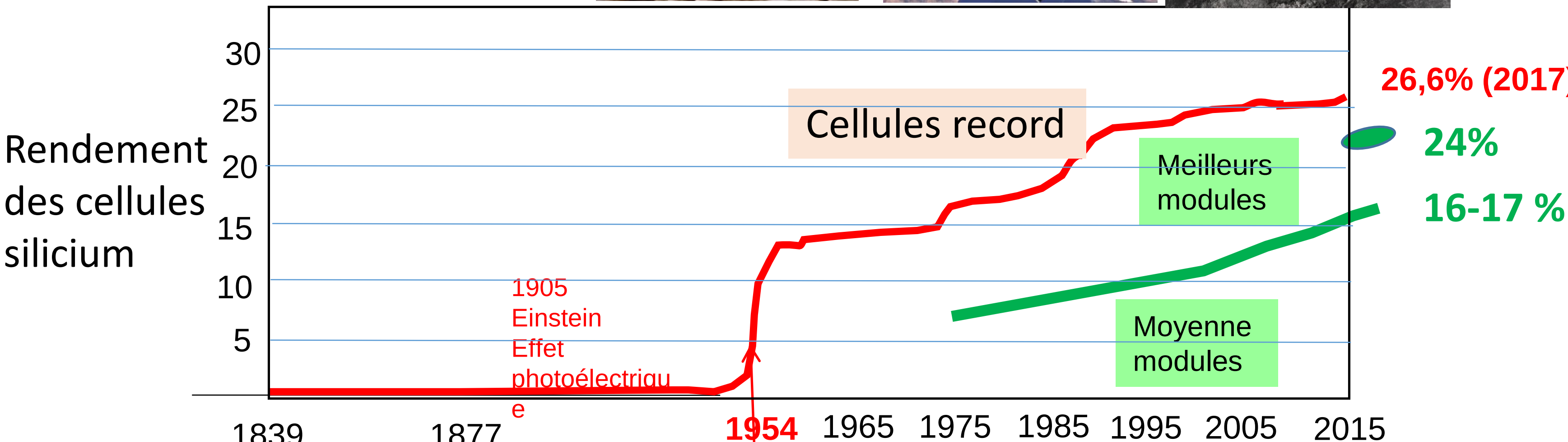
Recent announced long-term contract prices for new solar electricity

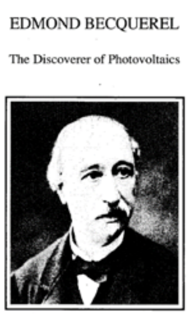


This map is without prejudice to the status or sovereignty over any territory, to the delimitation of international frontiers and boundaries and to the name of any territory, city or area

Adapted from IEA Renewable Energy Medium Term Market Report 2015

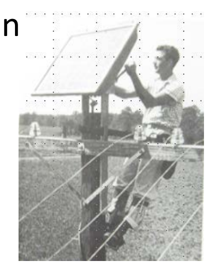
The « épopée » of Photovoltaics : Silicon solar cells





W.G. Adams
& R.E. Day
Cellules
Se 1%

Chapin &Fuller
&Person
Si(6%)



nature energy

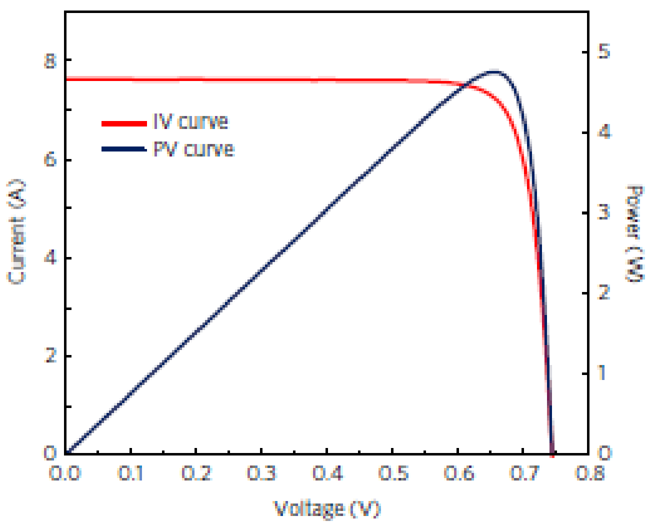
ARTICLES

PUBLISHED: 20 MARCH 2017 | VOLUME: 2 | ARTICLE NUMBER: 17032

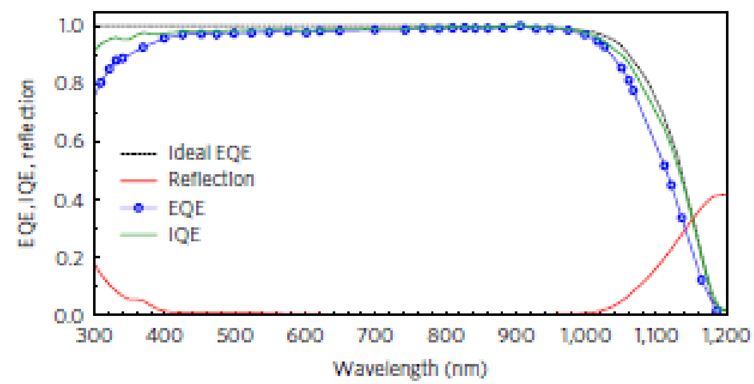
Silicon heterojunction solar cell with interdigitated back contacts for a photoconversion efficiency over 26%

Kunta Yoshikawa*, Hayato Kawasaki, Wataru Yoshida, Toru Irie, Katsunori Konishi, Kunihiro Nakano, Toshihiko Uto, Daisuke Adachi, Masanori Kanematsu, Hisashi Uzu and Kenji Yamamoto

2017 :record 26,6% (Kaneka)



Current voltage curve

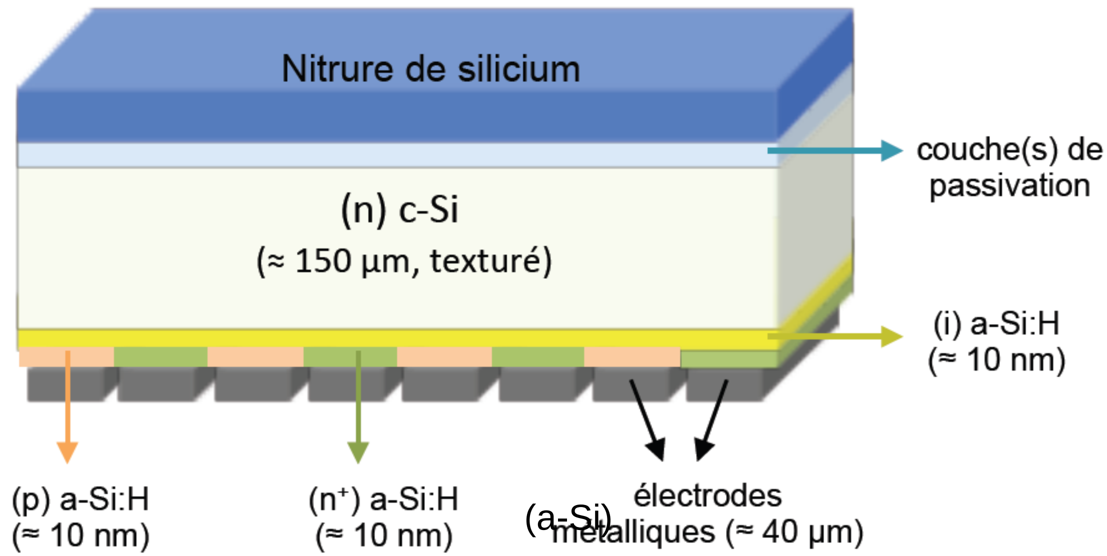


Spectral Response

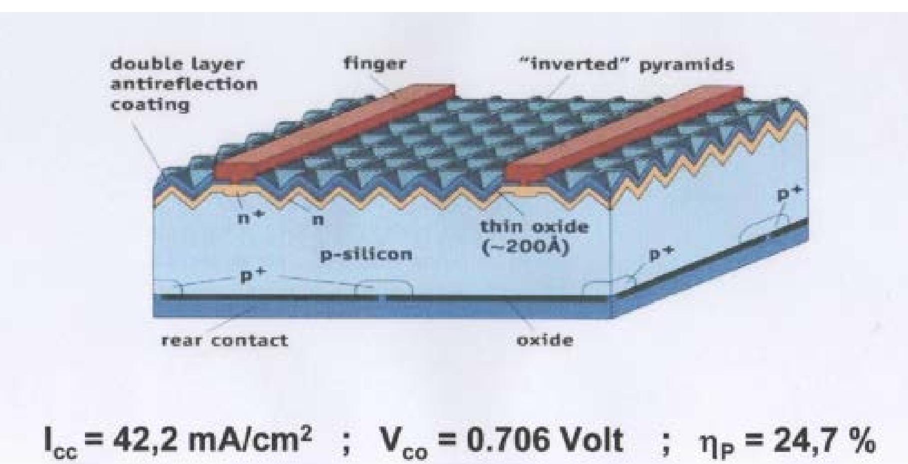
Next objective: 27,1 % (theroetical efficiency 29.1%)

Key of success : Alliance of microelectronics and photovoltaics

2014
Hétérojonctions
(HIT) à contact arrière

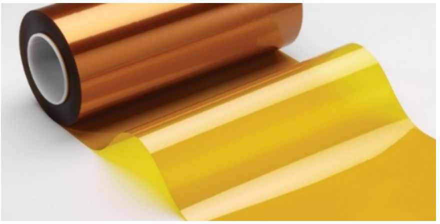


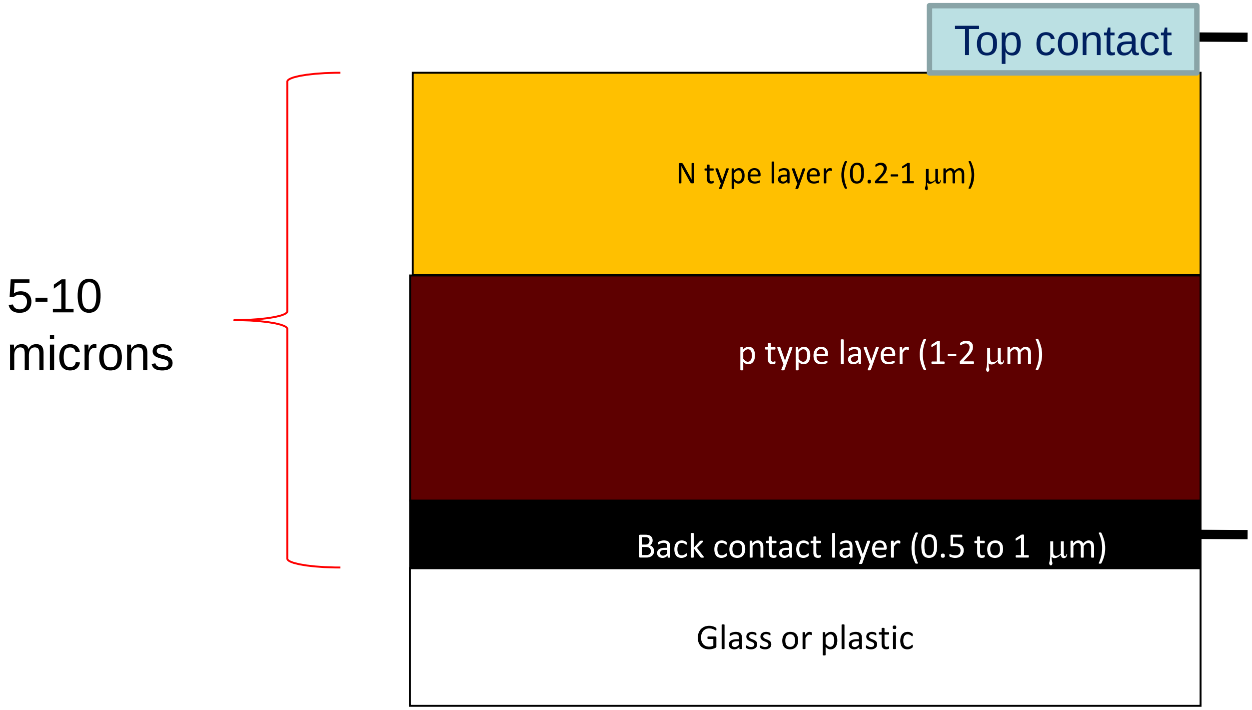
1999
homojonctions



Why Thin film solar cells ?

Thinner, Simpler, lighter, Cheaper





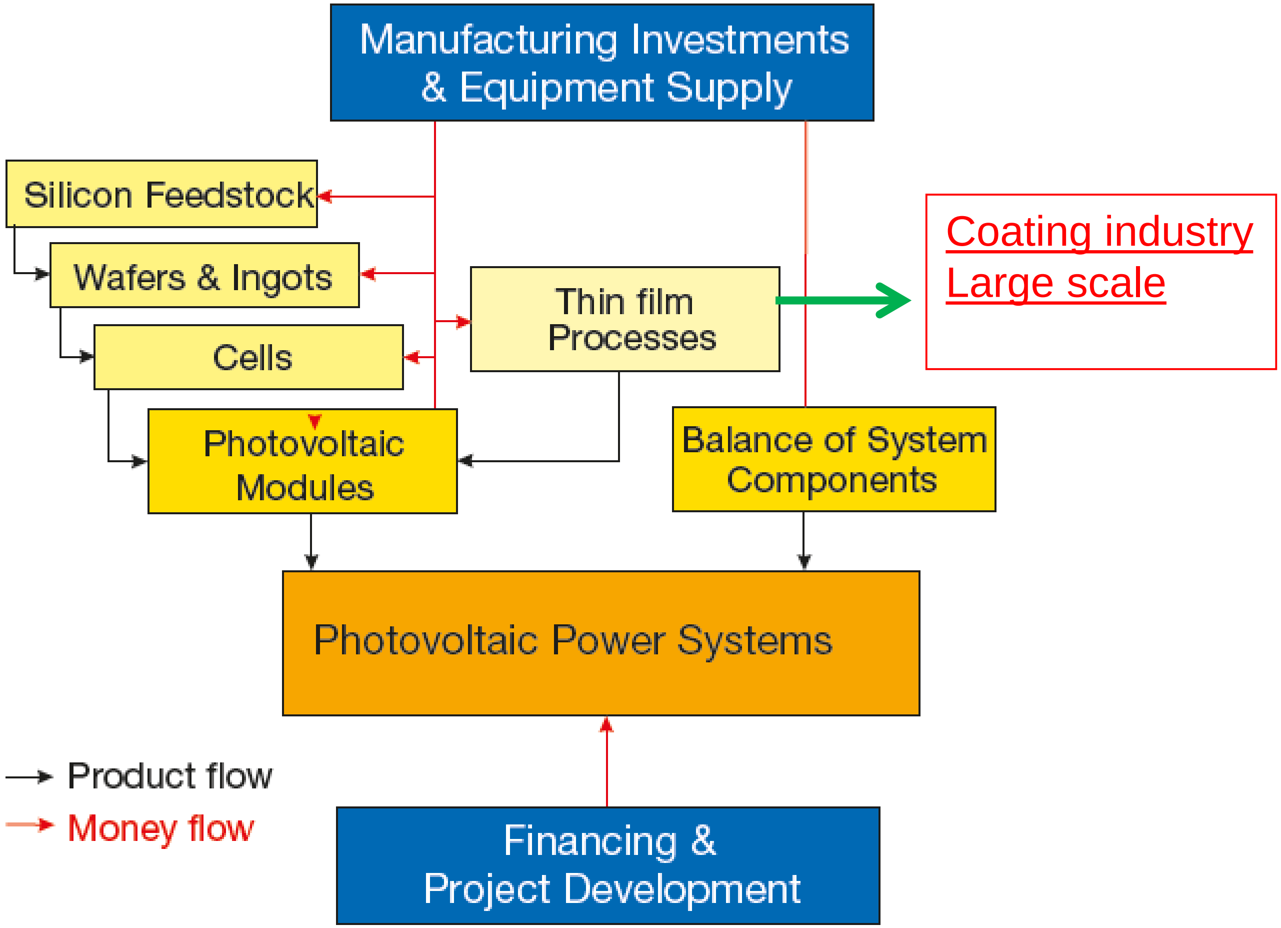


Figure 11 – Photovoltaic (PV) industry supply chain

Rapport IEA-PVPS 2011

1960-1973

The ancestor : Copper Sulfide solar cells

The thin film dream : Space application

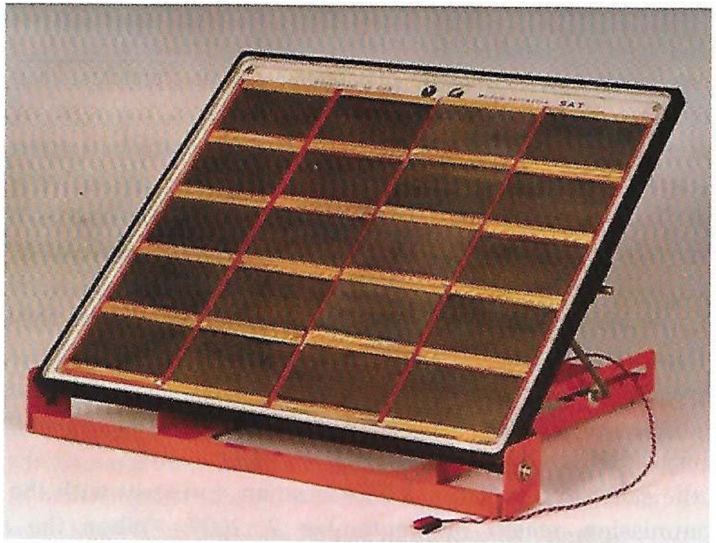


Figure 3. A French PV generator of CdS from 1973.

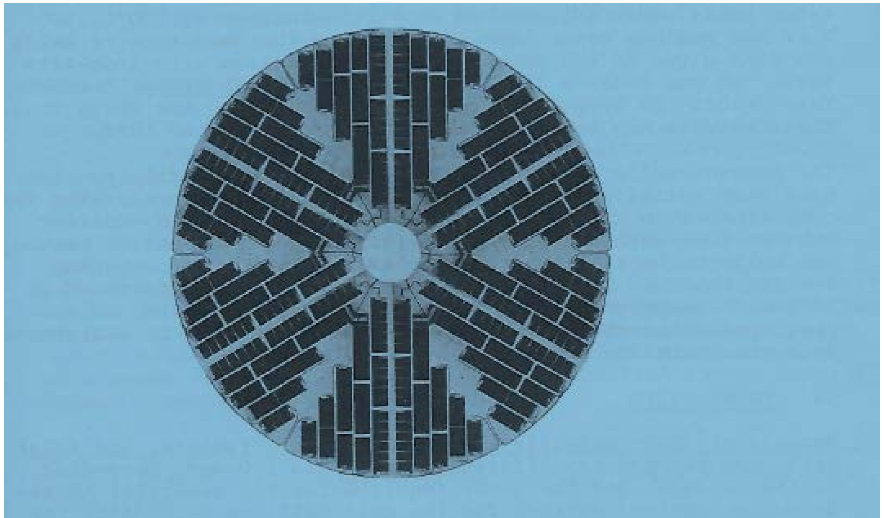


Figure 8 - Essor balloon solar generator, diameter: 2 m, maximum power: 70 watts under 100 mW cm^{-2} AM1, 35°C

Kapton-Silver-CdS-Cu_2S

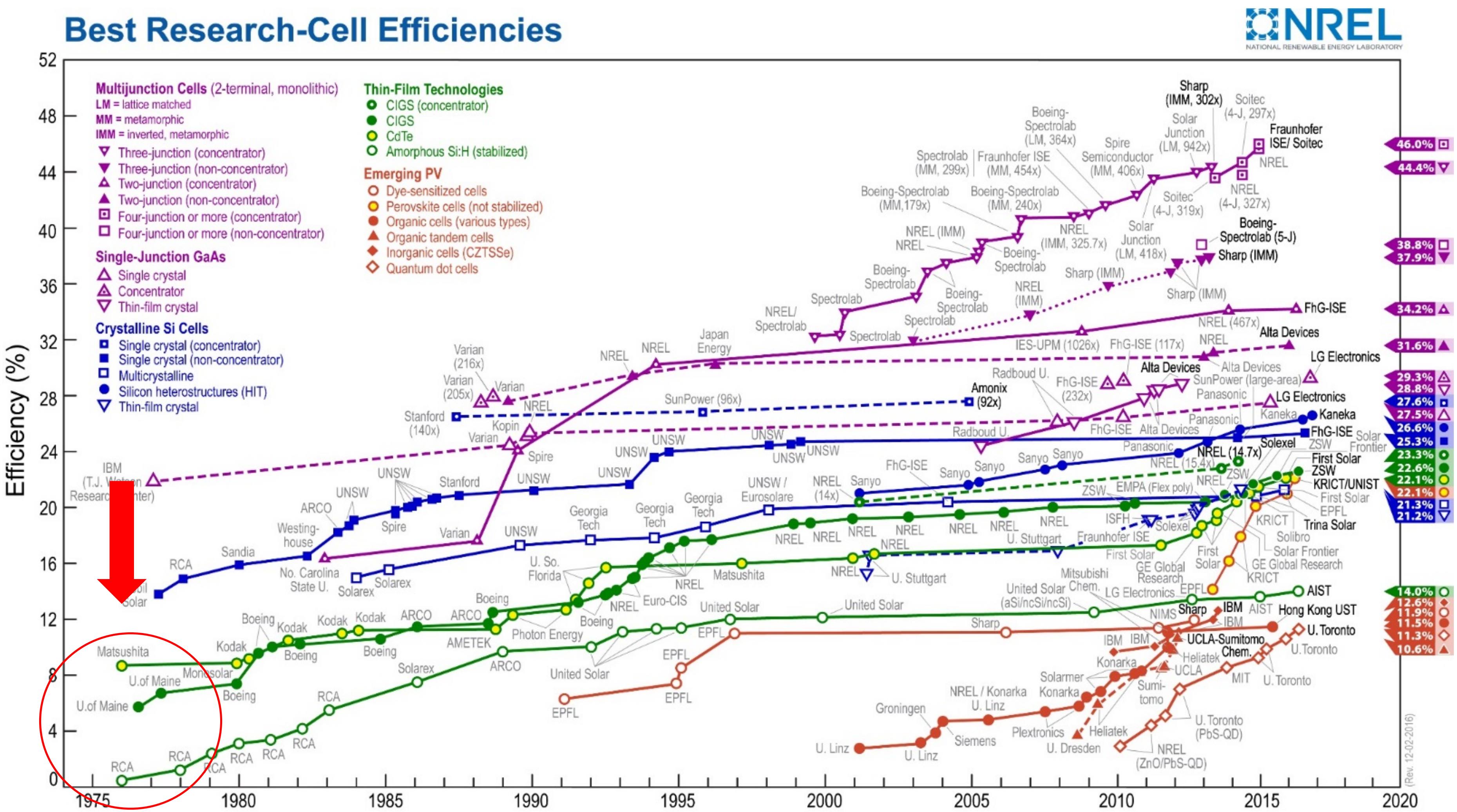
- metallization of the kapton substrate by silk screening of a silver paste,
- evaporation of the CdS, N type layer in an evaporation chamber
- conversion of the superficial CdS layer into a Cu_2S, p type layer by dipping in a cuprous ions solution
- deposition of a collecting grid by an electroplating process,
- encapsulation by thermo setting of a clear plastic sheet.

5.5 % efficiency

Up to 10 % in 1980

But thermodynamically unstable
Abandoned for CIGS

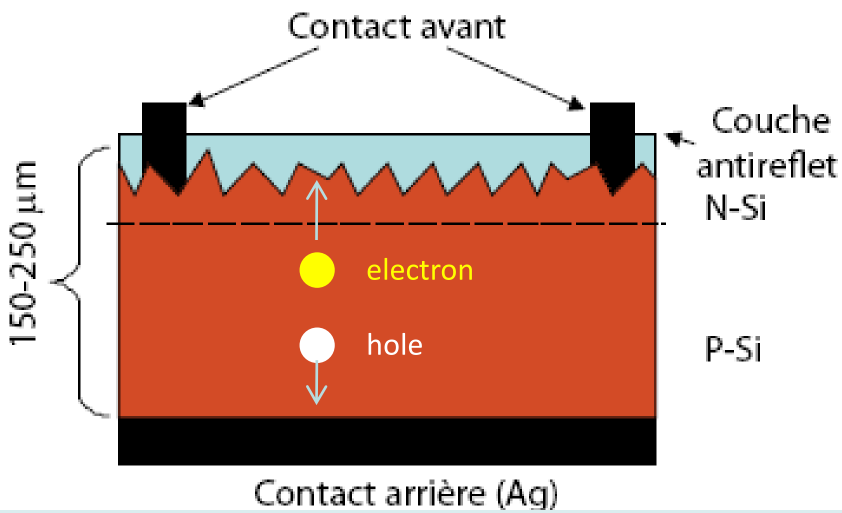
1975 The emergence of inorganic thin film solar cells : CdTe, CIGS, aSi



2016

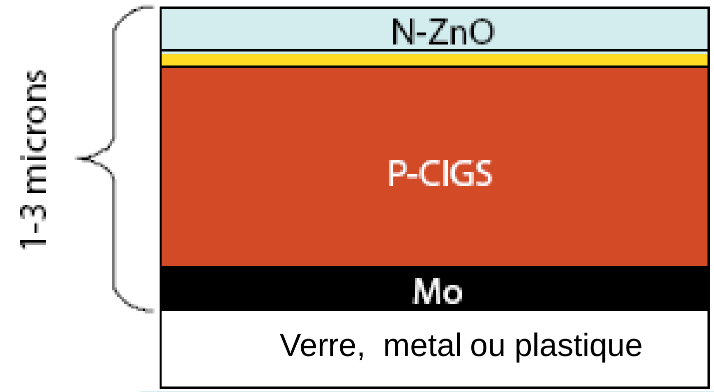
Wafer based versus thin film Technologies

Cellule au silicium cristallin

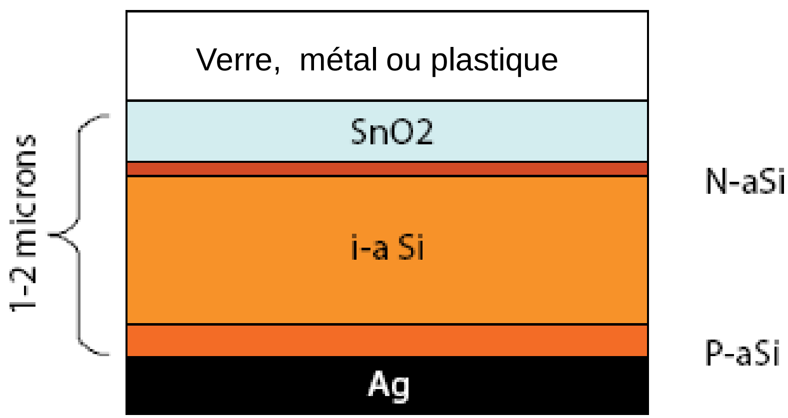


Max Cell : 26,6% % single crystal
21.6% polycrystal

Cellule au $Cu(In,Ga)Se_2$

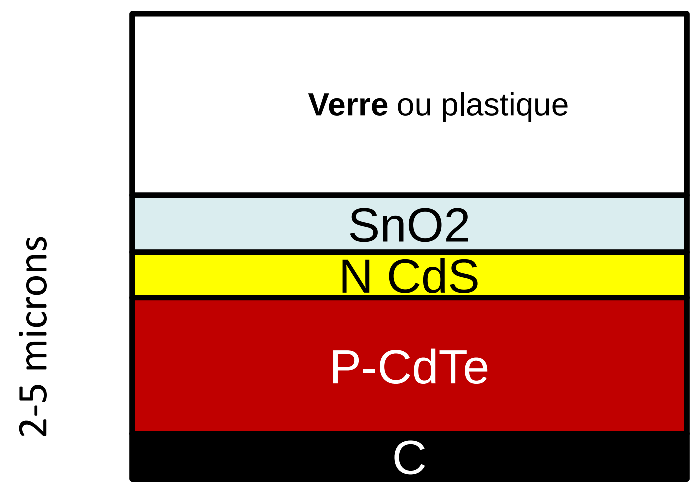


Max Cell : 22,6% %



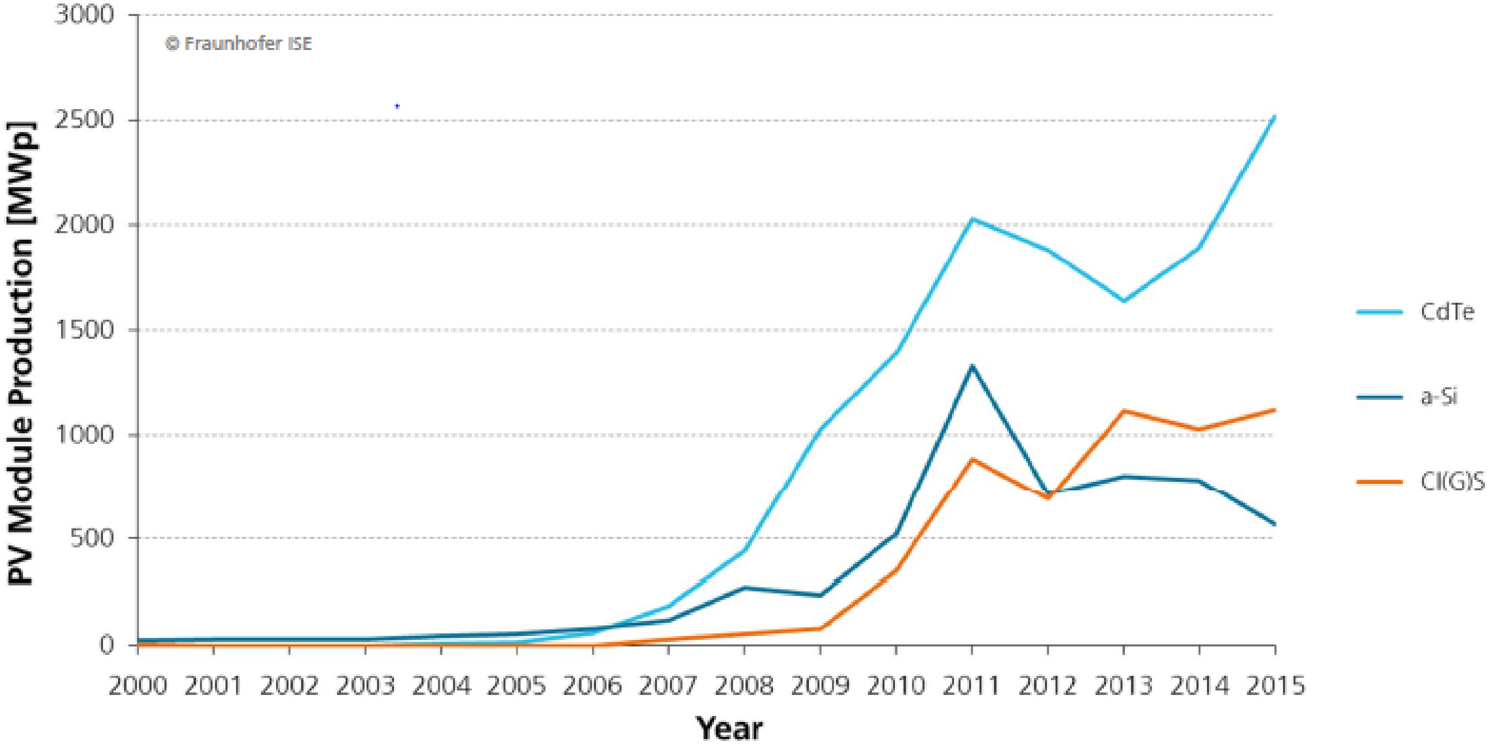
Max Cell : 14%

Cadmium Telluride



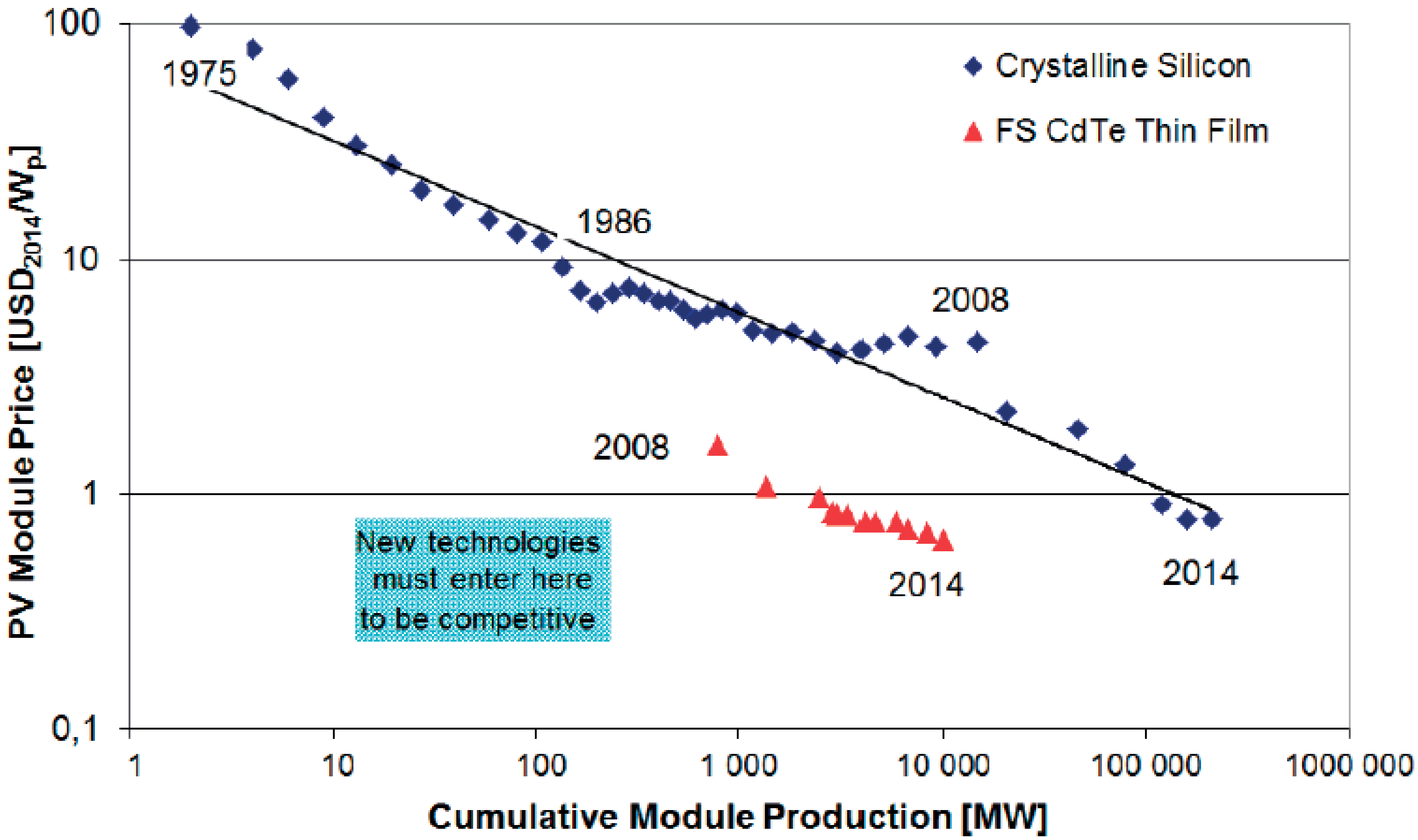
Max Cell : 22,1%

Thin-Film Technologies:
Annual Global PV Module Production

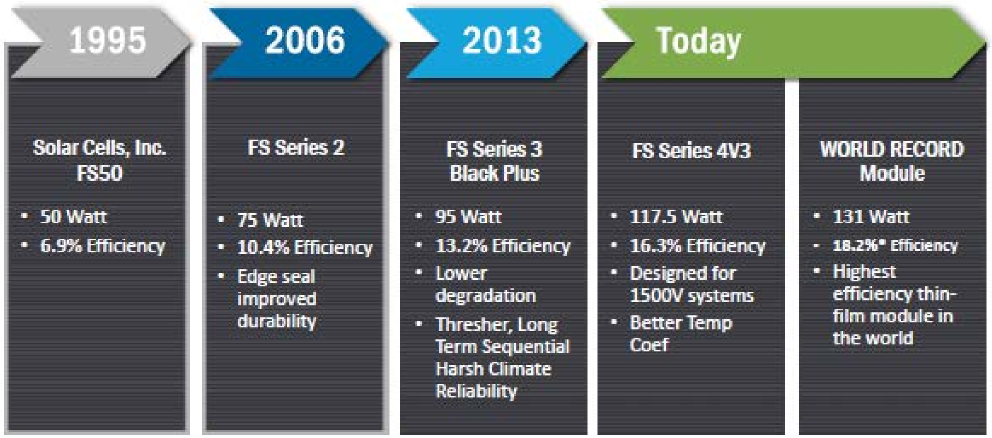


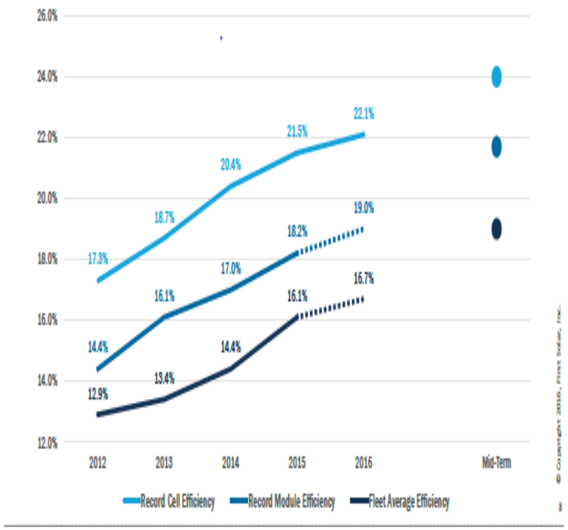
Fraunhofer ISE

PV Status report 2014



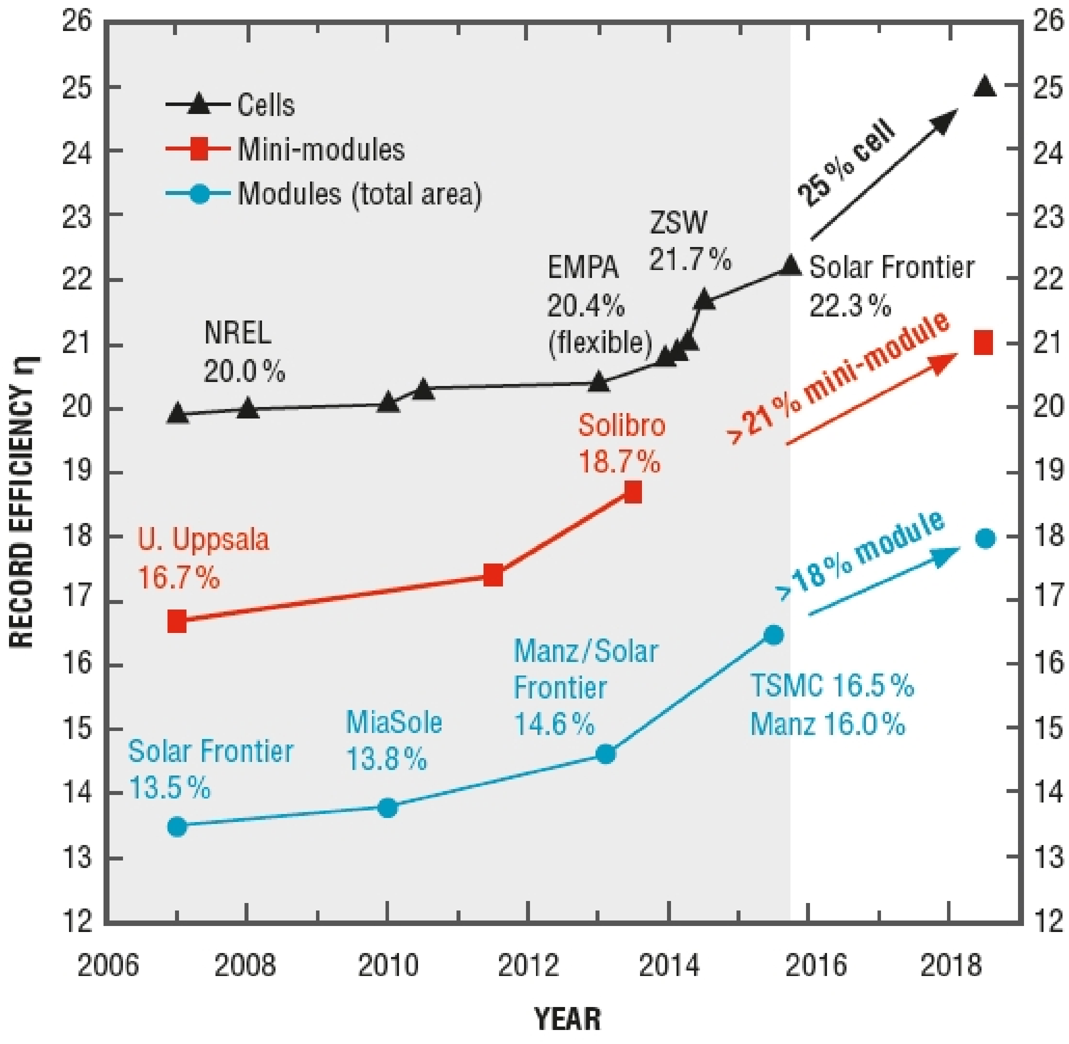
Road map for CdTe conversion efficiencies





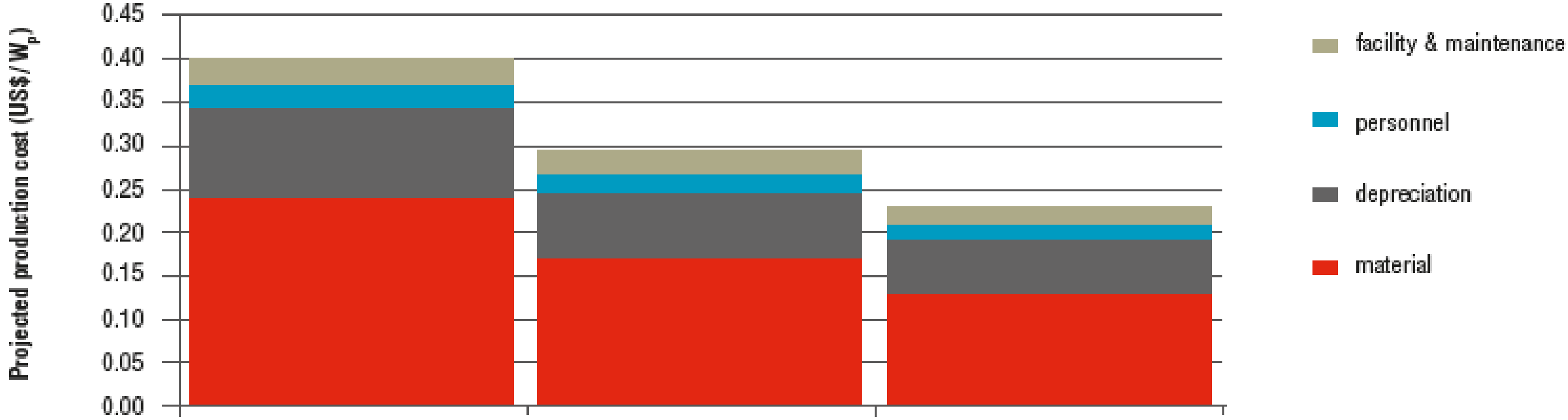
First Solar Web site

Road map for CIGS Conversion efficiencies



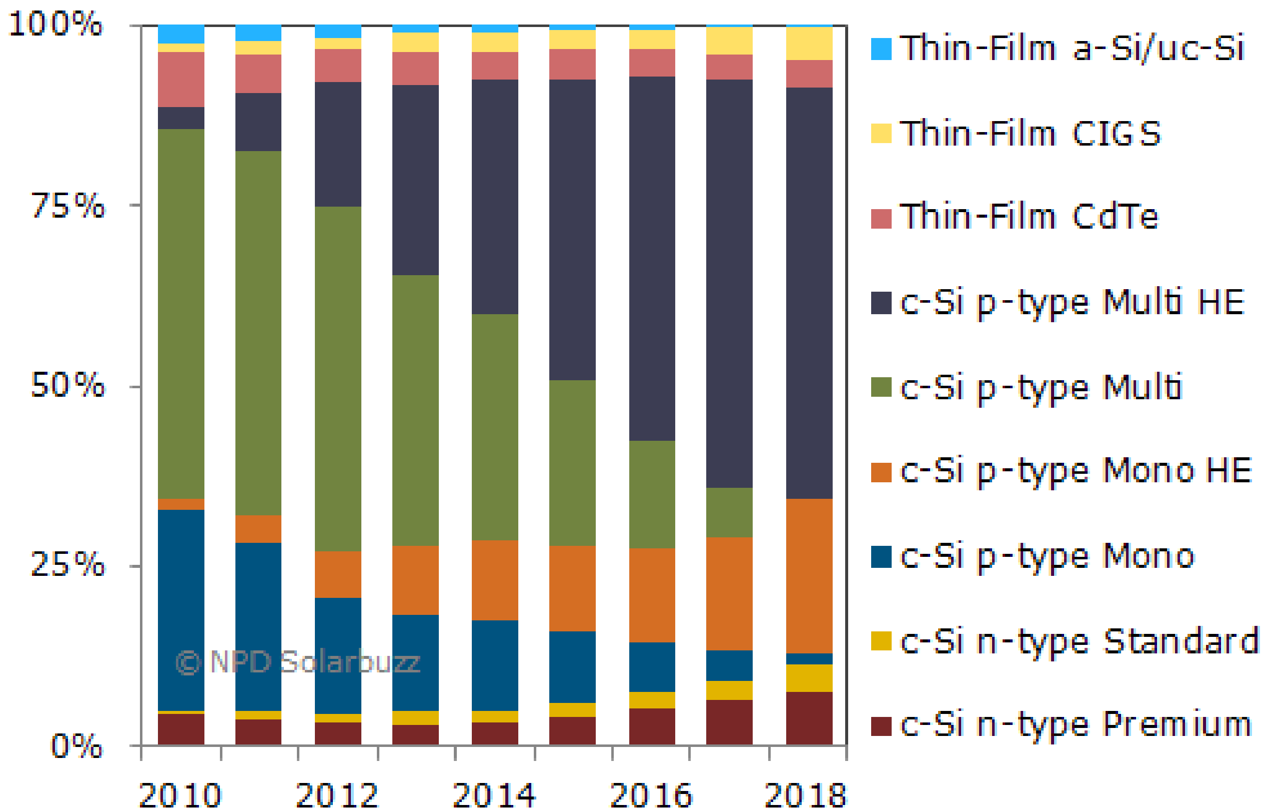
http://cigs-pv.net

CIGS on glass is on the market at the industrial level
(Solar Frontier, Solibro, Manz, Avancis…)



	Present fab	Next gen fab	Upgrade & scale next gen fab
Capacity	150 MW$_p$/a	250–500 MW$_p$/a	500–1000 MW$_p$/a
Average efficiency	14.3 %	16 %	18 %
Reductions versus present fab		material -20 % capex -20 %	material -30 % capex -30 % f&m -20 %

Fig. 3: Projected CIGS production cost using presently available technology and leveraging further cost reduction potential

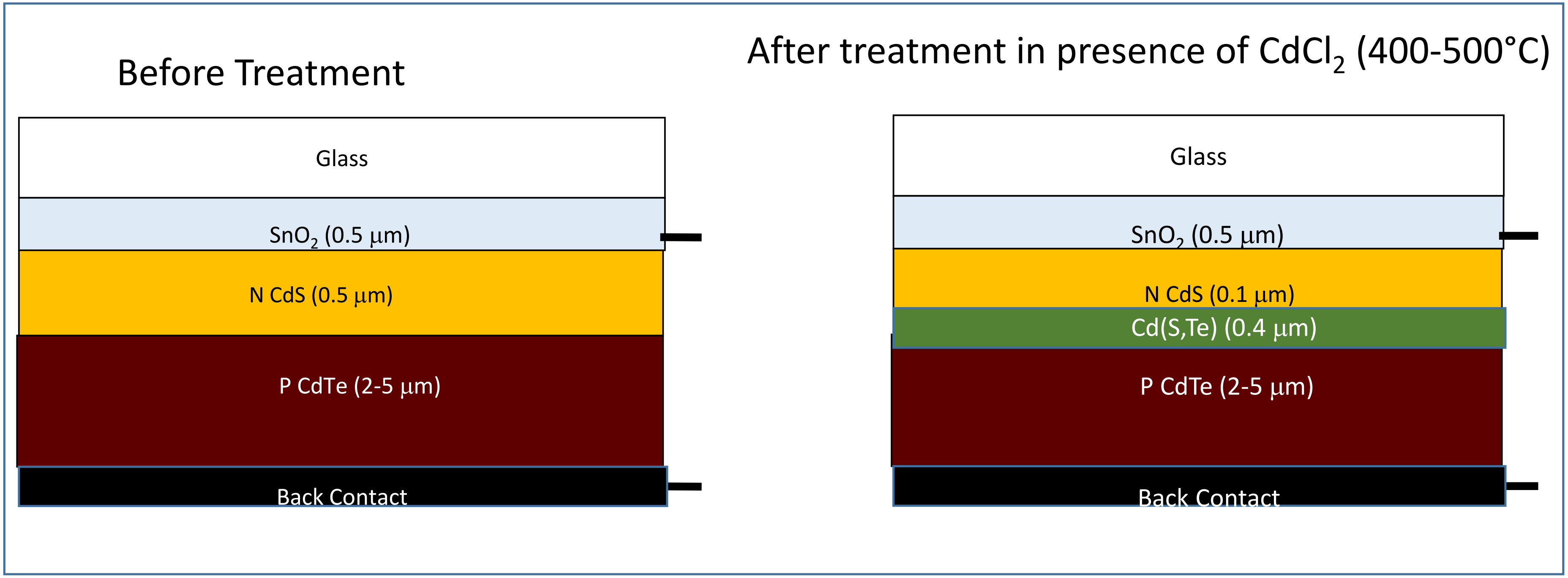


Source: NPD Solarbuzz *PV Technology Roadmap*, September 2014

An *evolutionnary* view of technological progress in thin film solar cells

let’s take a trip through scientific breakthroughts along the « *ages* »

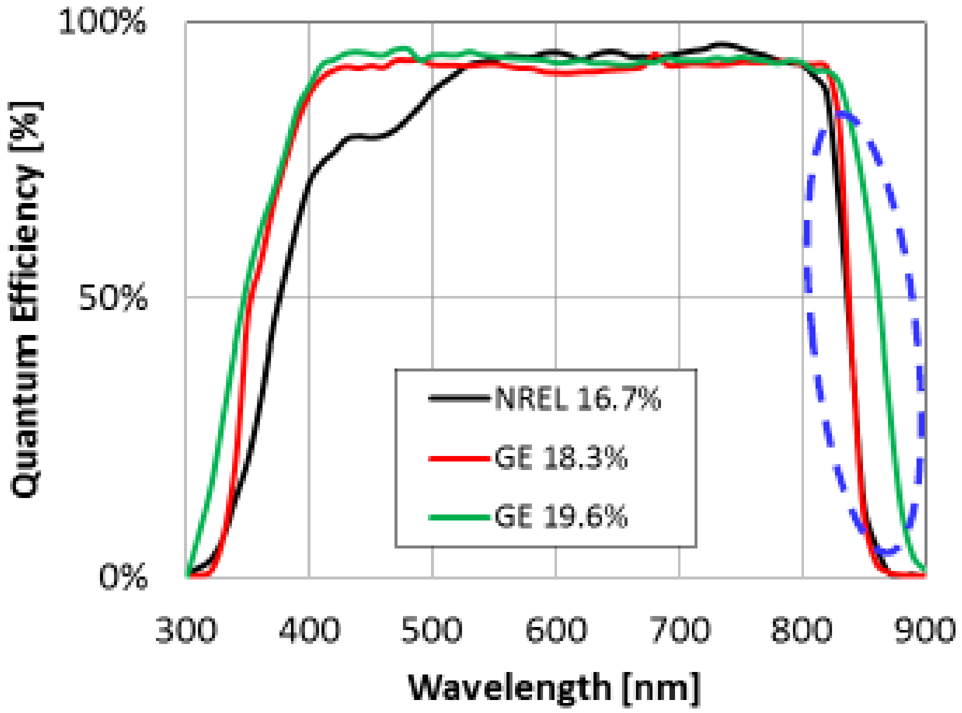
CdTe solar cells : From 6% to 22 % : a succession of progresses in materials science



Scientific breakthroughts : example of spectral responses

New TCO
CdSnO3
CdZnO3
Zn-In-O
Ga-Zn-O

(Cd,Zn)S
Higher Gap



+ Graded band gap
in CdTe

Cd(S,Te)
Lower gap

(Cd,Zn)Te
(Cd,Mg)Te
Higher gap

2015 : 22,1 %

Simpler : Not so simple !

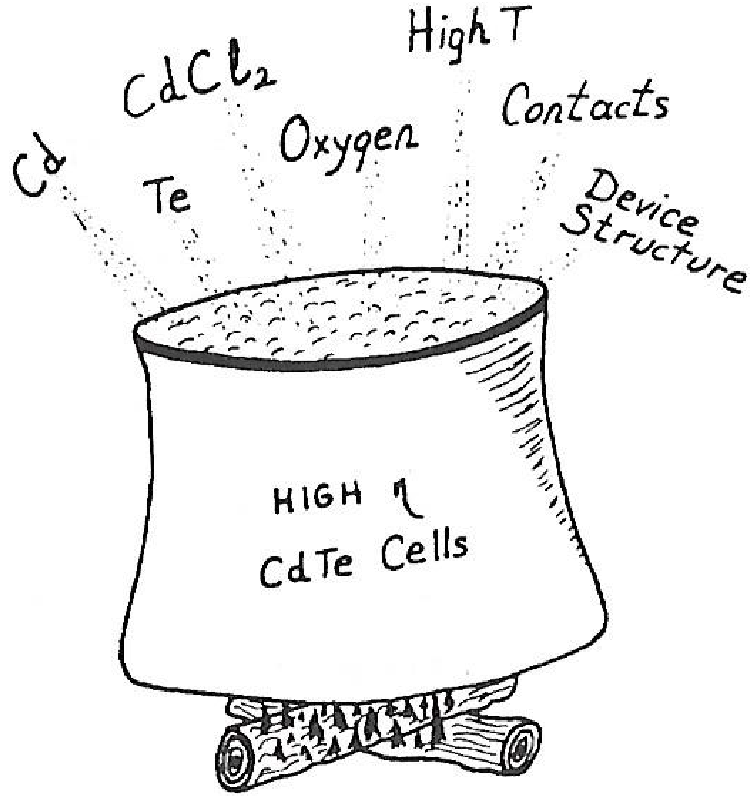
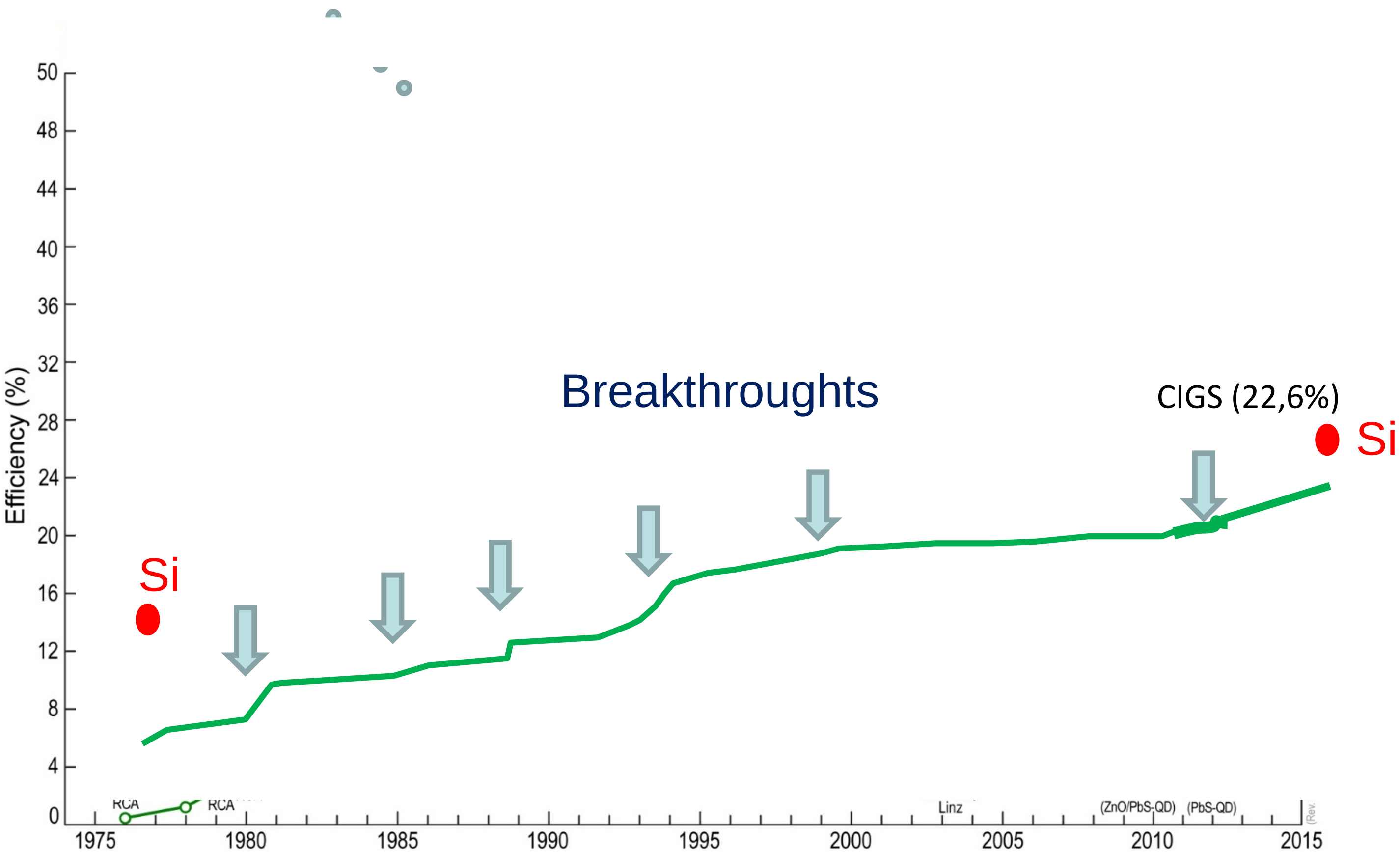


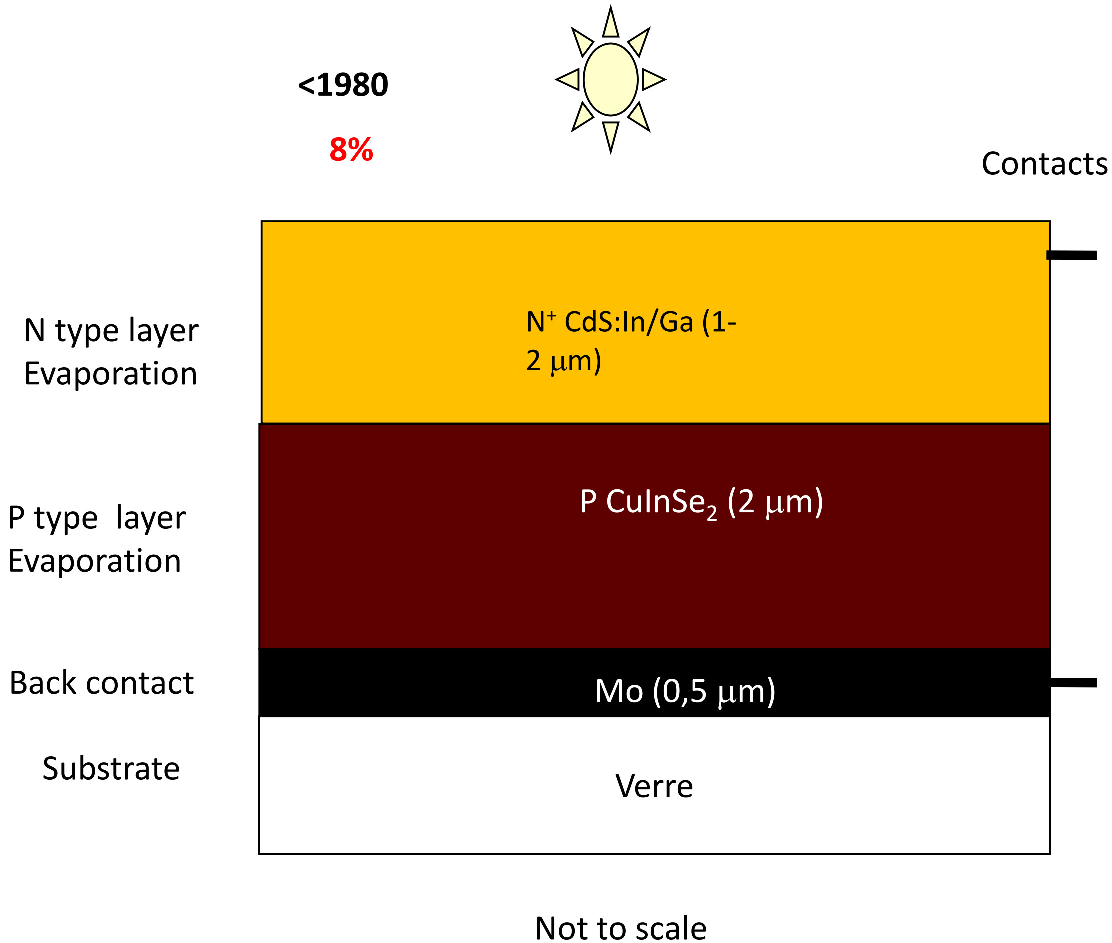
Fig. 5.11. A general recipe for the preparation of high efficiency thin film CdTe solar cells. (Reprinted with permission from B. M. Basol, *International Journal of Solar Energy*, **12**, 25 (1992). Copyright 1992, Harwood Academic Publisher, Langhorne, PA.)

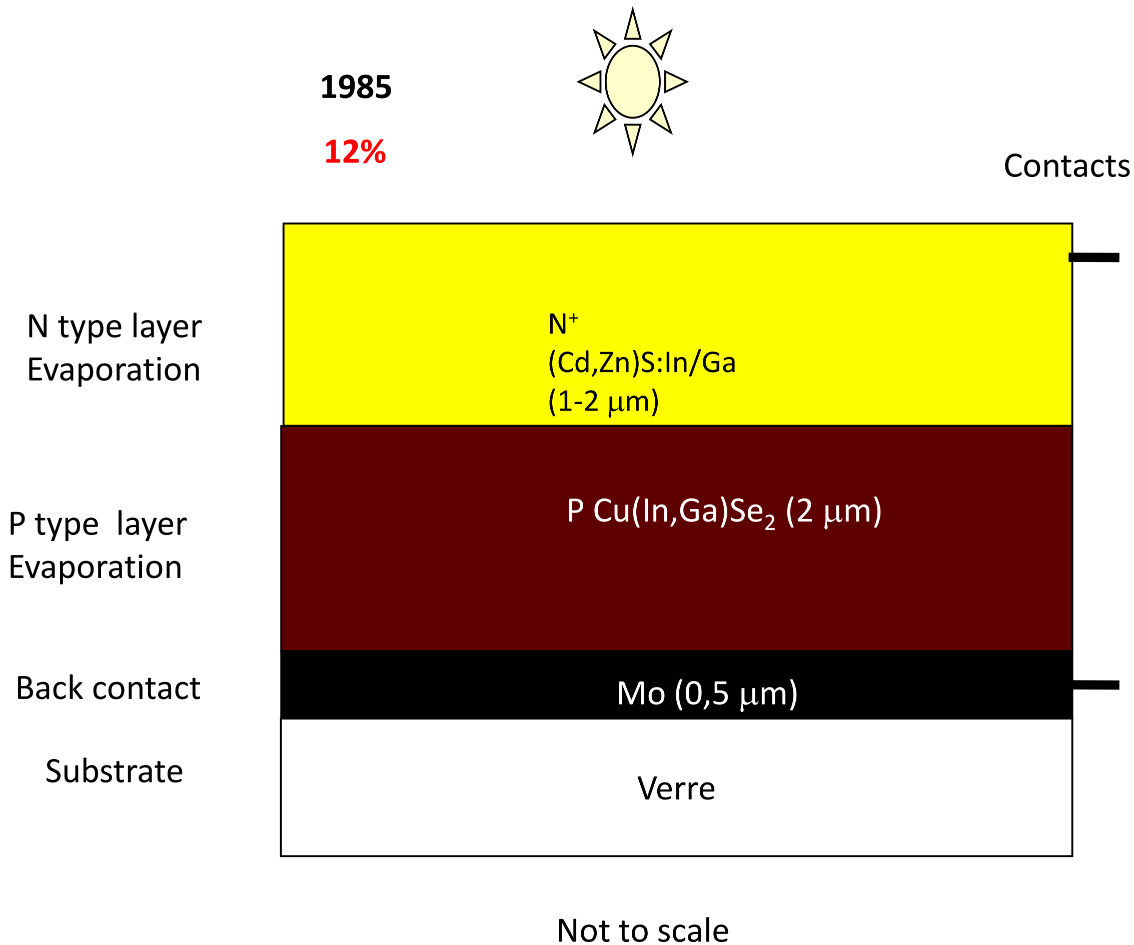
Second exemple :

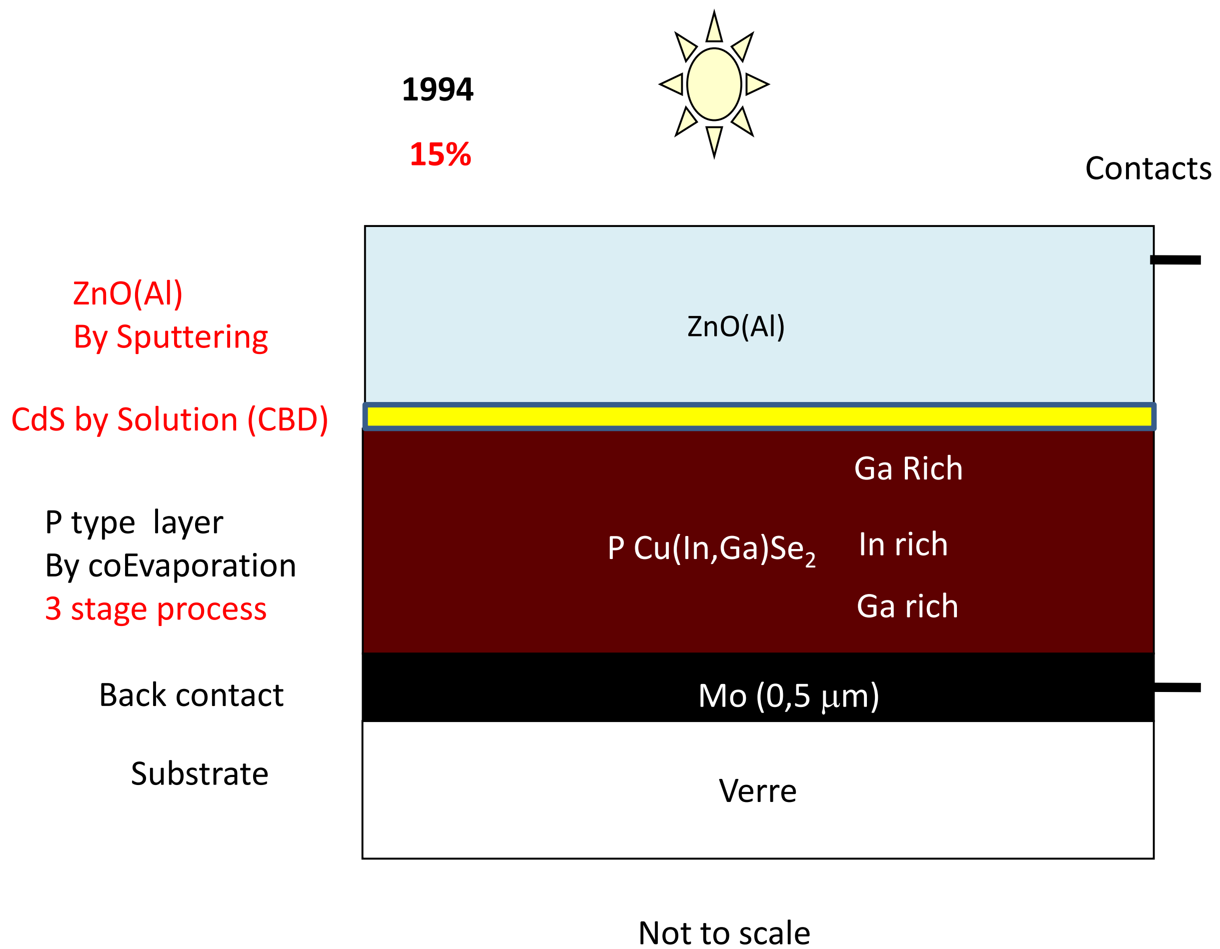
CIGS solar cells $Cu(In,Ga)Se_2$

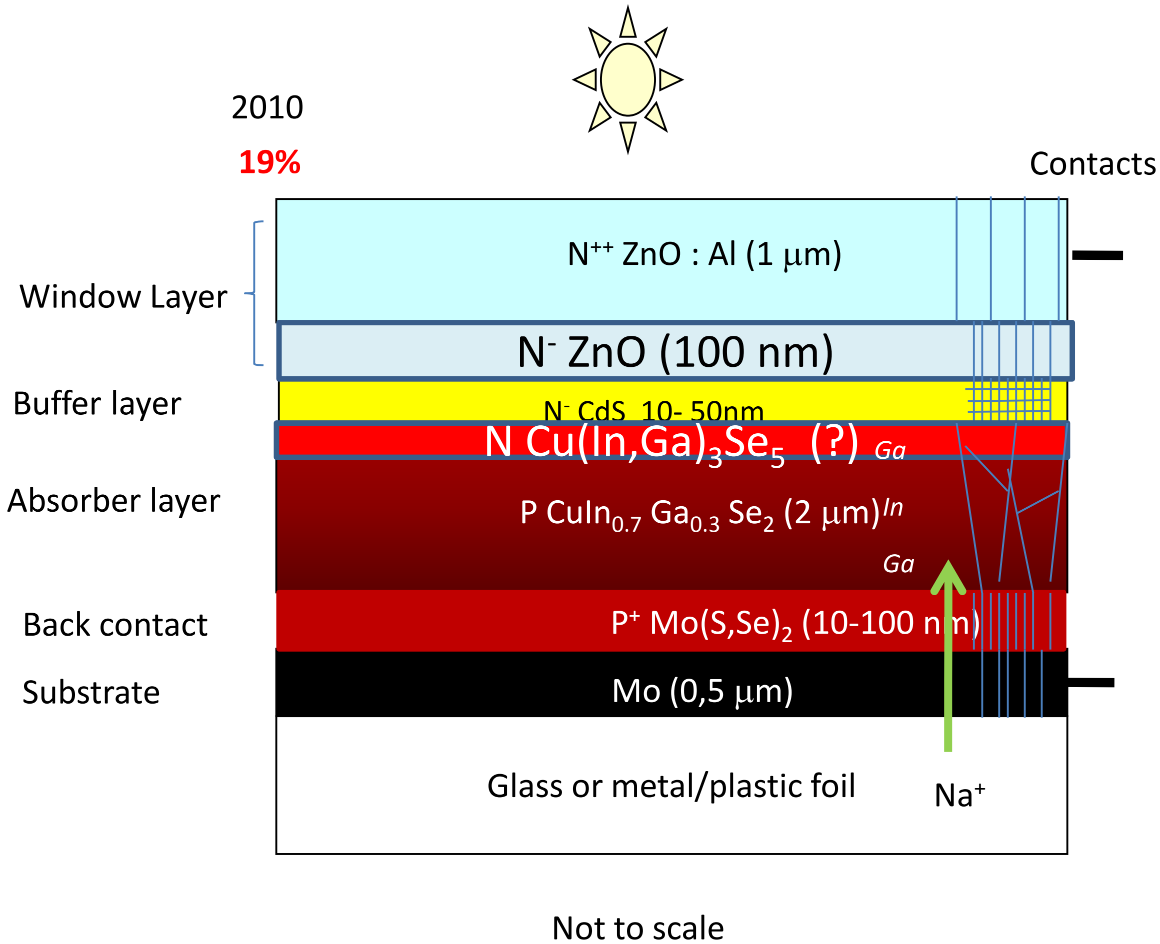
Historical evolution of record efficiencies of CIGS solar cells

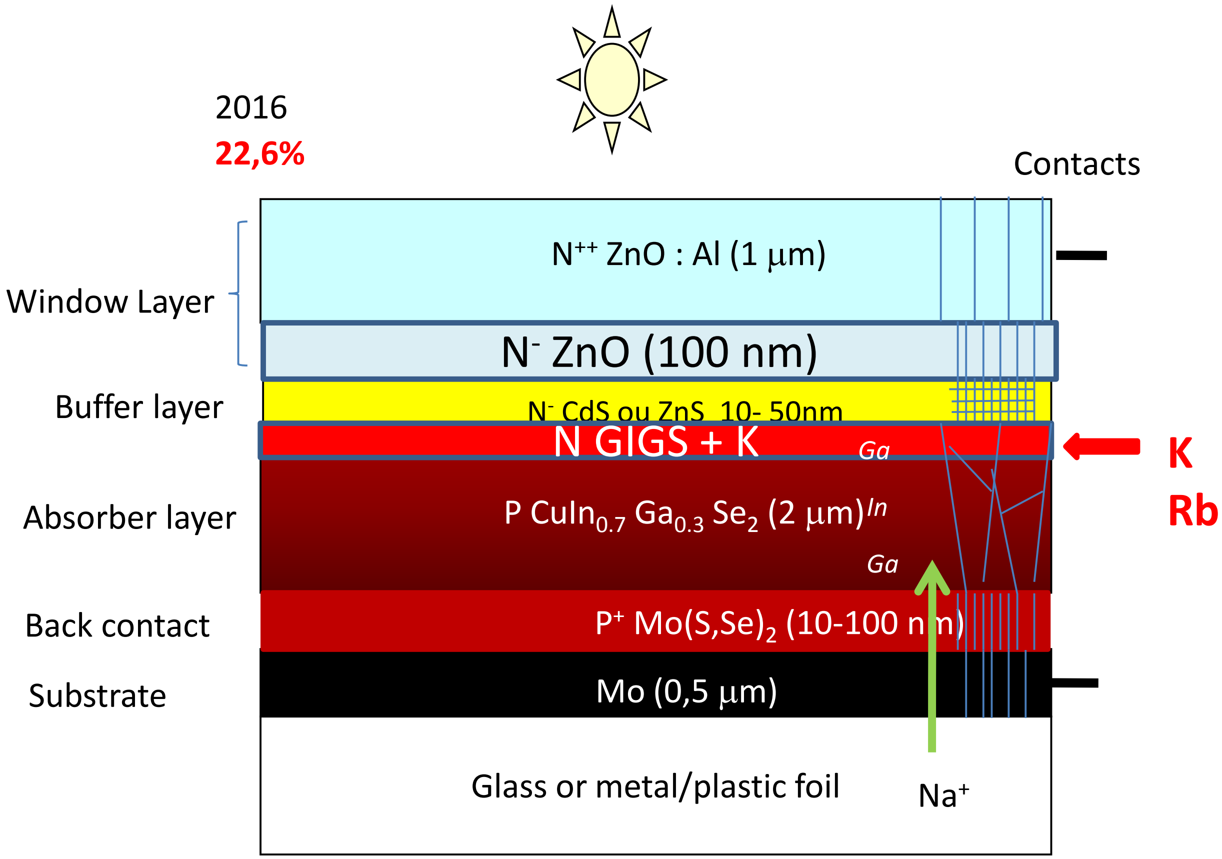



<1980
8%
Contacts
N type layer
Evaporation
N+ CdS:In/Ga (1-2 μm)
P type layer
Evaporation
P CuInSe2 (2 μm)
Back contact
Mo (0,5 μm)
Substrate
Verre
Not to scale


1985
12%
Contacts
N type layer
Evaporation
N+
(Cd,Zn)S:In/Ga
(1-2 µm)
P type layer
Evaporation
P Cu(In,Ga)Se2 (2 µm)
Back contact
Mo (0,5 µm)
Substrate
Verre
Not to scale


1994
15%
Contacts
ZnO(Al)
By Sputtering
ZnO(Al)
CdS by Solution (CBD)
Ga Rich
P type layer
By coEvaporation
3 stage process
P Cu(In,Ga)Se$_2$
In rich
Ga rich
Back contact
Mo (0,5 µm)
Substrate
Verre
Not to scale


2010
19%
Contacts
Window Layer
N^{++} ZnO : Al (1 μm)
N^{-} ZnO (100 nm)
Buffer layer
N^{-} CdS 10- 50nm
N $Cu(In,Ga)_3Se_5$ (?)
Ga
Absorber layer
P $CuIn_{0.7}Ga_{0.3}Se_2$ (2 μm)
In
Ga
Back contact
P^{+} $Mo(S,Se)_2$ (10-100 nm)
Substrate
Mo (0,5 μm)
Glass or metal/plastic foil
Na^{+}
Not to scale


2016
22,6%
Contacts
Window Layer
N++ ZnO : Al (1 µm)
N- ZnO (100 nm)
Buffer layer
N- CdS ou ZnS 10- 50nm
N GIGS + K
Ga
K
Rb
Absorber layer
P CuIn0.7 Ga0.3 Se2 (2 µm)
In
Ga
Back contact
P+ Mo(S,Se)2 (10-100 nm)
Substrate
Mo (0,5 µm)
Glass or metal/plastic foil
Na+

Not to scale

P. Jackson, Rapid research Letters, July 2016

Table 1 List of former and current ZSW record results and the PDT-methods applied.

PDT	η (%)	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	date of publication
N/A	20.3*	740	35.4	77.5	01/2011 [13]
KF	20.8*	757	34.8	79.1	02/2014 [10]
RbF	21.7*	746	36.6	79.3	12/2014 [14]
RbF	22.0*	744	36.7	80.5	03/2016 [15]
RbF	22.6*	741	37.8	80.6	this work

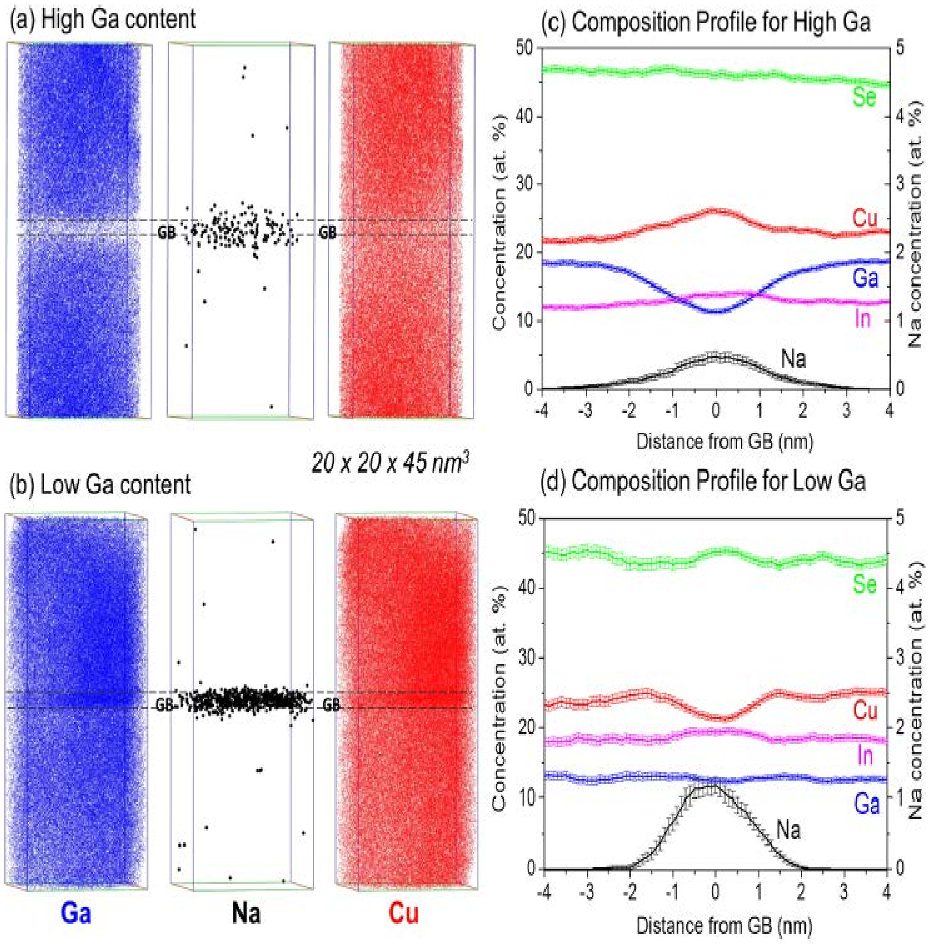
* Independently certified by Fraunhofer ISE.

K or Rb repeal Cu from the surface → K(In,Ga)Se2

A fantastic area for multidisciplanary fundamental research studies

Many discoveries preceed their interpretation !

Exemple I : Role of sodium analyzed by Atomic Probe Tomography
Effect at grain boundaries, change the composition of Ga,In,Cu

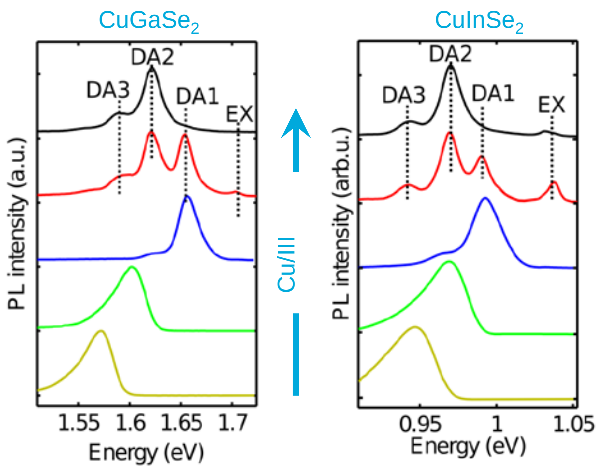


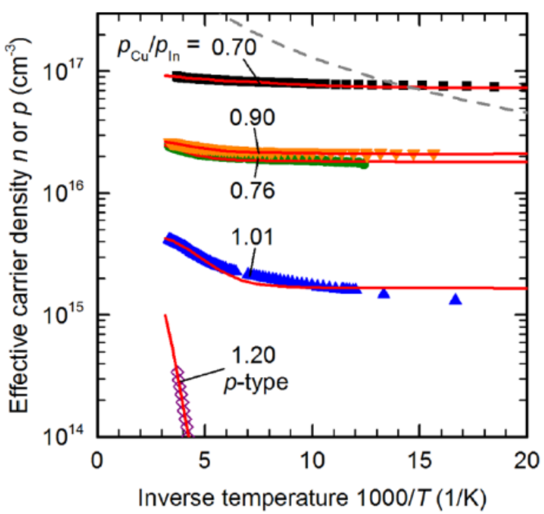
A. Raghawanshi et al. Applied Physics Letters 105, 013902 (2014)

Defects in $Cu(InGa)Se_2$

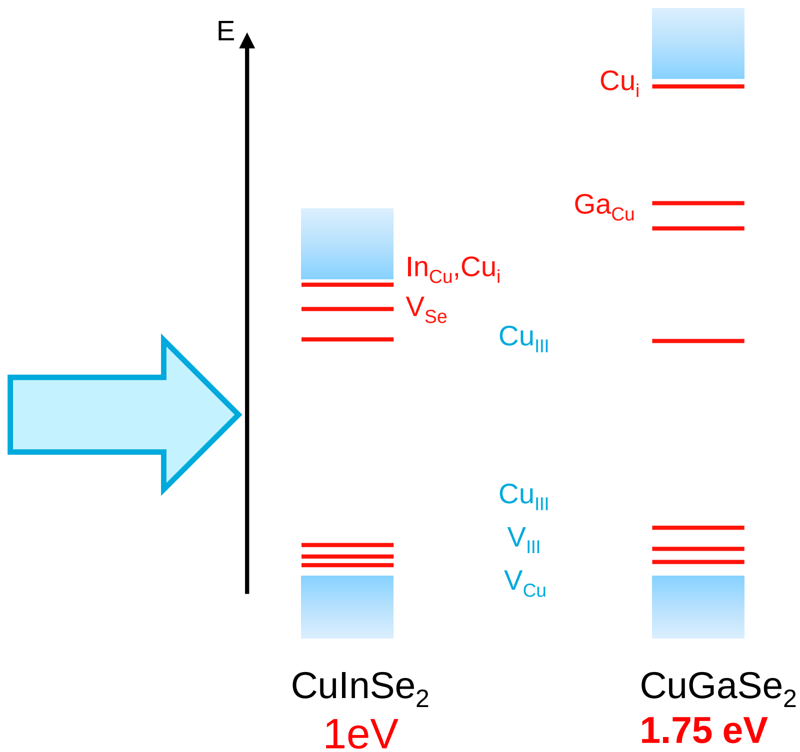
⇒ science based innovation for solar cells

Optical and electrical spectroscopy:





Answer to fundamental question
Why the efficiency of
wide band gap CIGS
Lower than expected



Back to the ultralight, flexible Dream

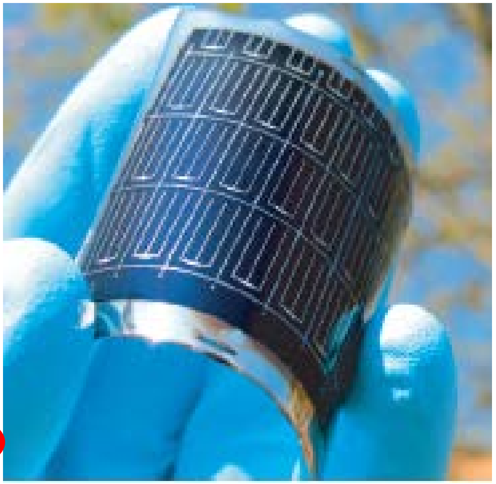
The andeavour of a new area for Thin Film CIGS Photovoltaics

2011

nature materials

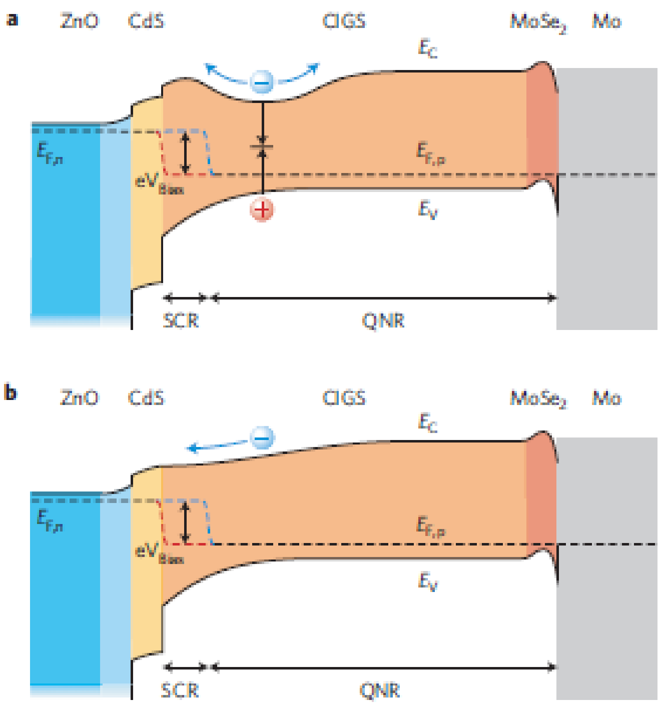
LETTERS

PUBLISHED ONLINE: 18 SEPTEMBER 2011 | DOI: 10.1038/NMAT3122

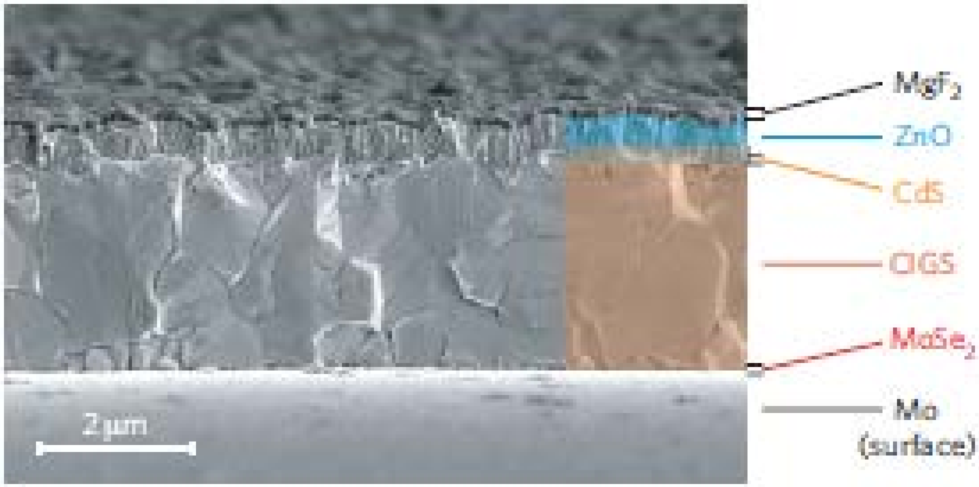


Highly efficient Cu(In,Ga)Se_2 solar cells grown on flexible polymer films

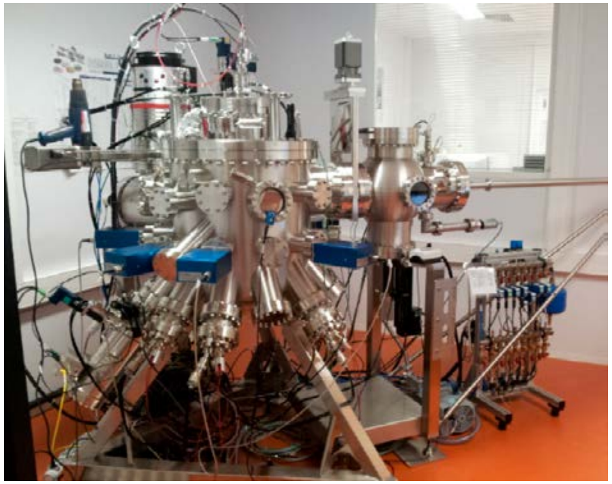
Adrian Chirilă[1]*†, Stephan Buecheler[1], Fabian Pianezzi[1], Patrick Bloesch[1], Christina Gretener[1], Alexander R. Uhl[1], Carolin Fella[1], Lukas Kranz[1], Julian Perrenoud[1], Sieghard Seyrling[1], Rajneesh Verma[1], Shiro Nishiwaki[1], Yaroslav E. Romanyuk[1], Gerhard Bilger[2] and Ayodhya N. Tiwari[1]

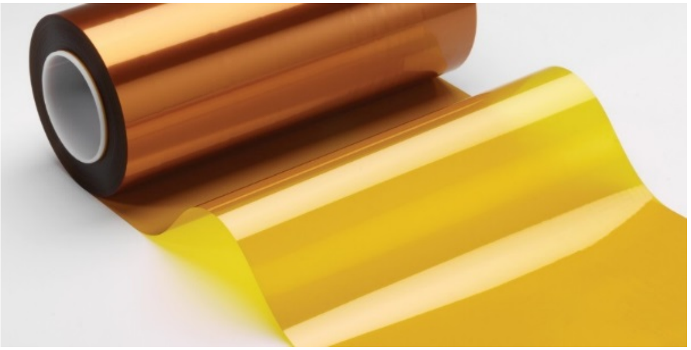


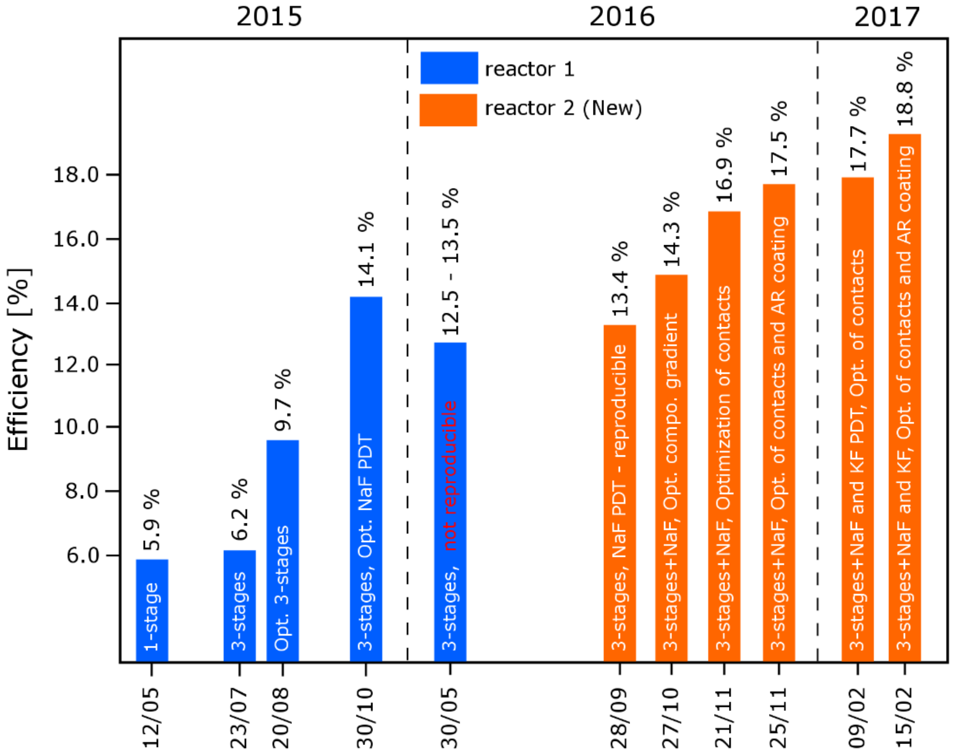
Record 20.3%

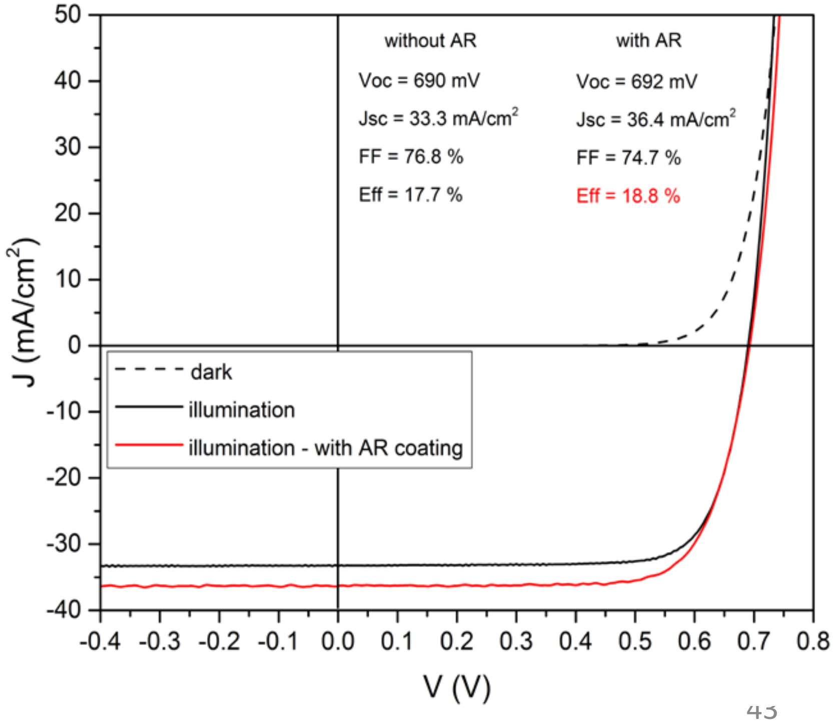


2016 IRDEP-IPVF Project on polymer CIGS solar cells

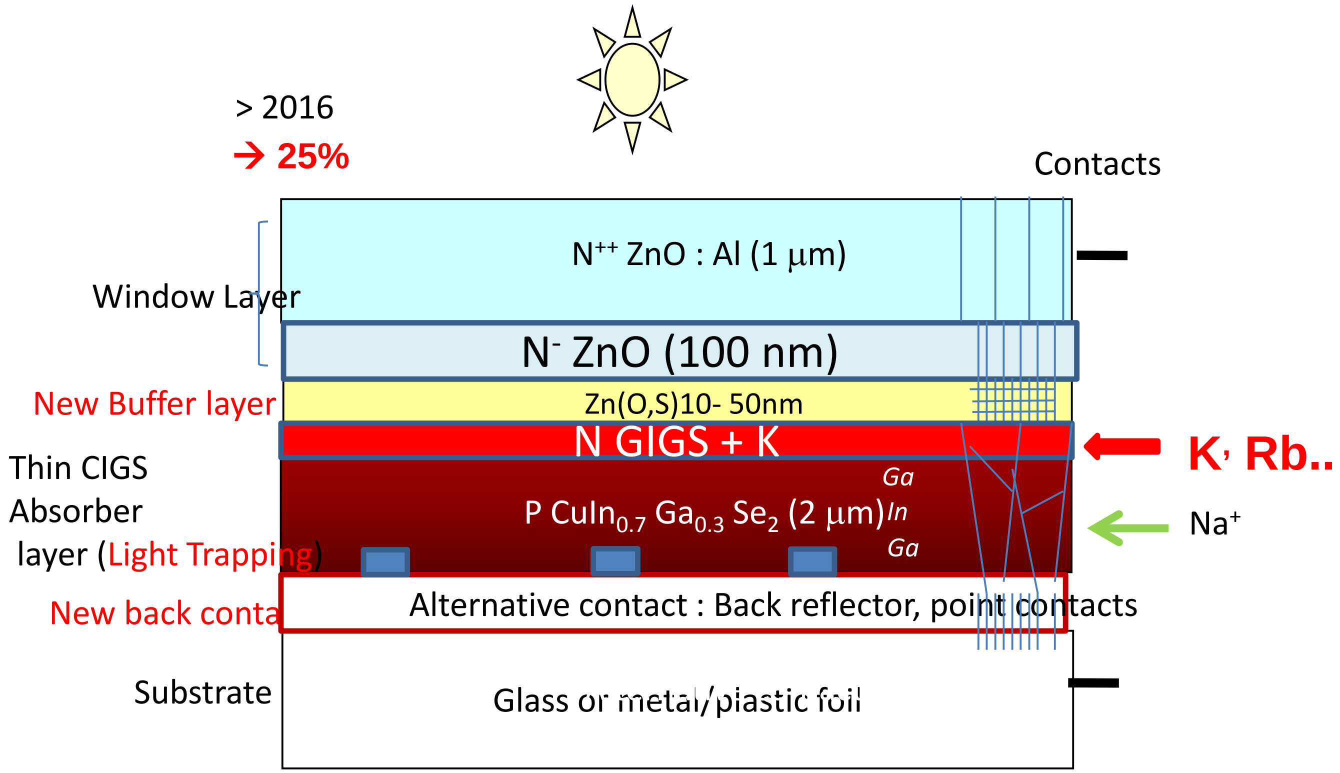








Next step of the evolution : towards 25% CIGS solar cells ?



Not to scale

Research places : Sweden (M. Edoff's Group), HZB, France

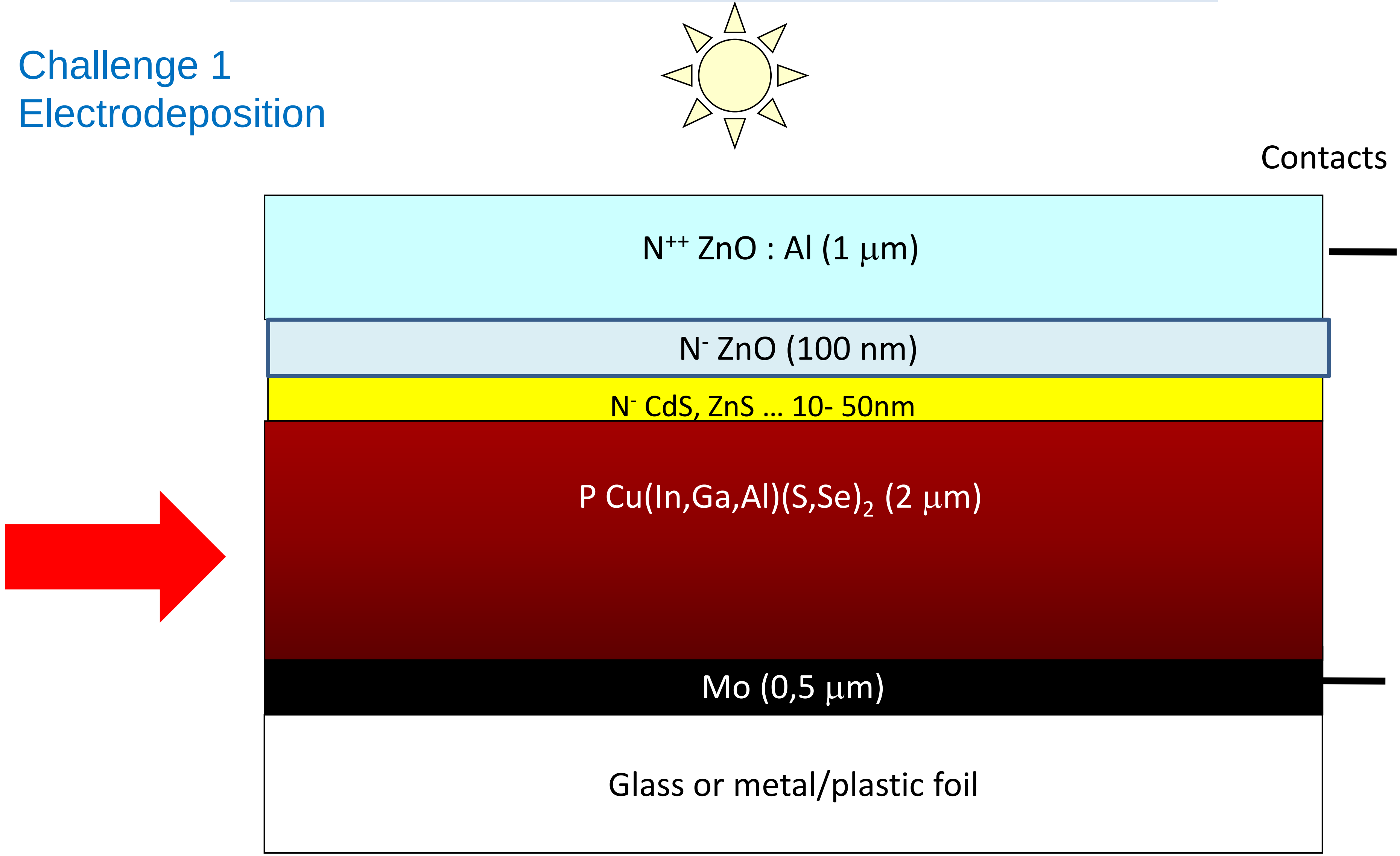
The low cost dream

Atmospheric methods :
Printing,
Electrodeposition,
solution deposition

alternative to High Vacuum Methods

Solution deposition for cost reduction : CIGS thin film solar cells

Challenge 1
Electrodeposition

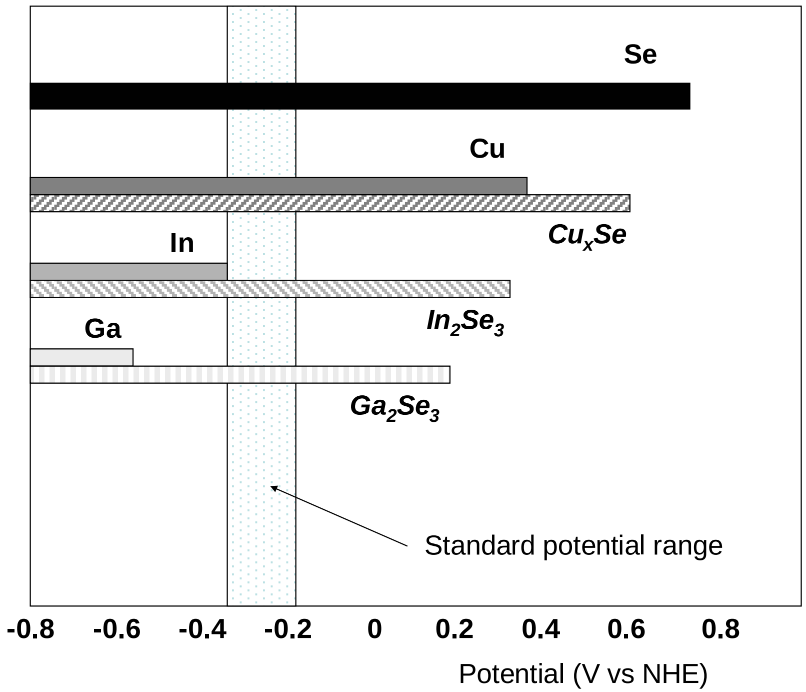


*** In substitution to vacuum methods**

From Lab to industry : The case of electrodeposition of CIGS

Ideal one step electrodeposition reaction :

$$Cu^{2+} + (1\text{-}x)In^{3+} + xGa^{3+} + 2HSeO_3^- + 10\ H^+ + 13\ e^- \rightarrow CuIn_{1-x}Ga_xSe_2 + 6\ H_20$$



1988-1994 – Laboratory studies

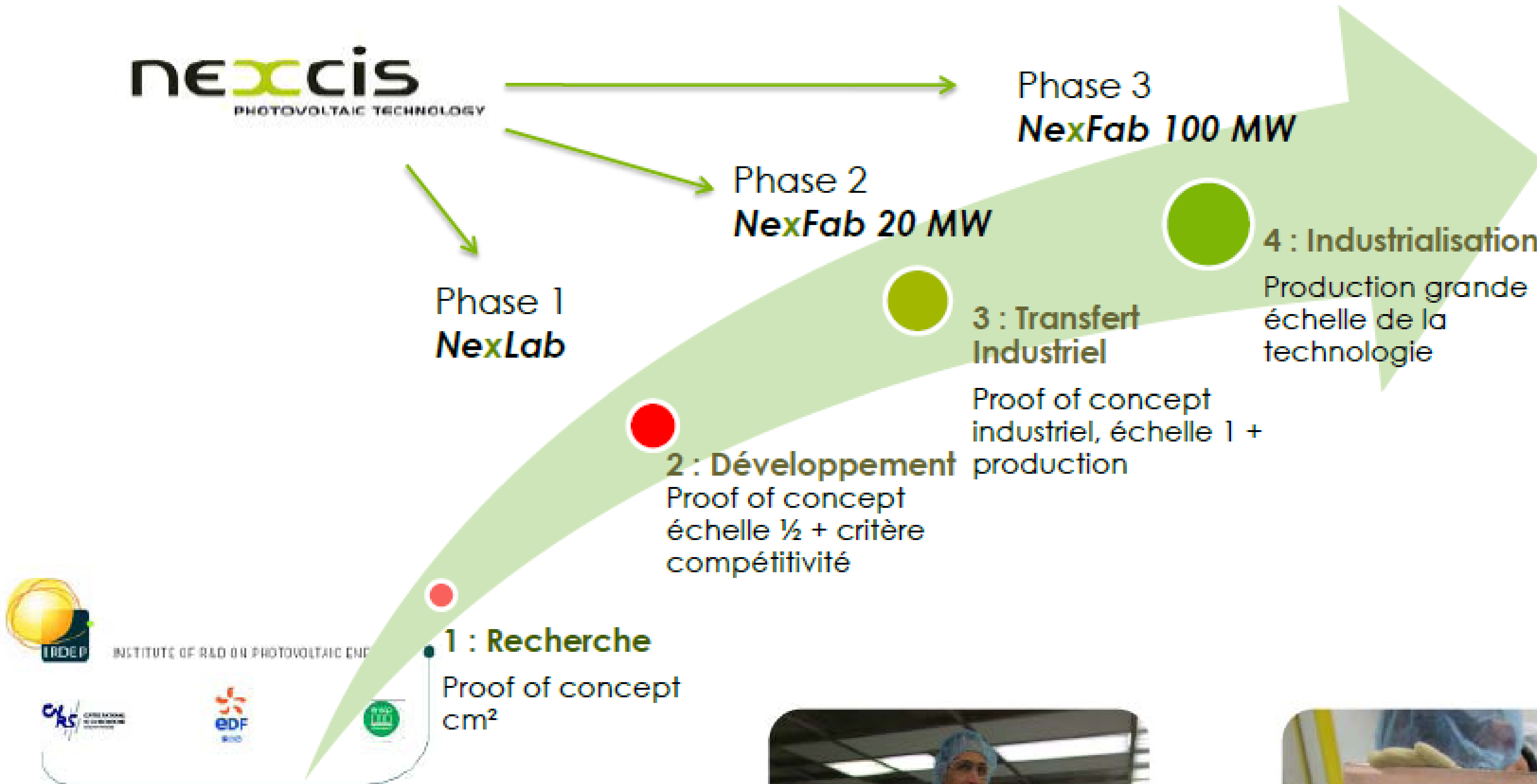
1994- World record 6,4% on < 1 cm^2

1998 – Partner ship with EDF : The CIS by electrodeposition project (CISEL)

2003 - Nouveau record mondial (11.5 % 2003 < 1 cm^2

2009 – Creation de NEXCIS –spin off

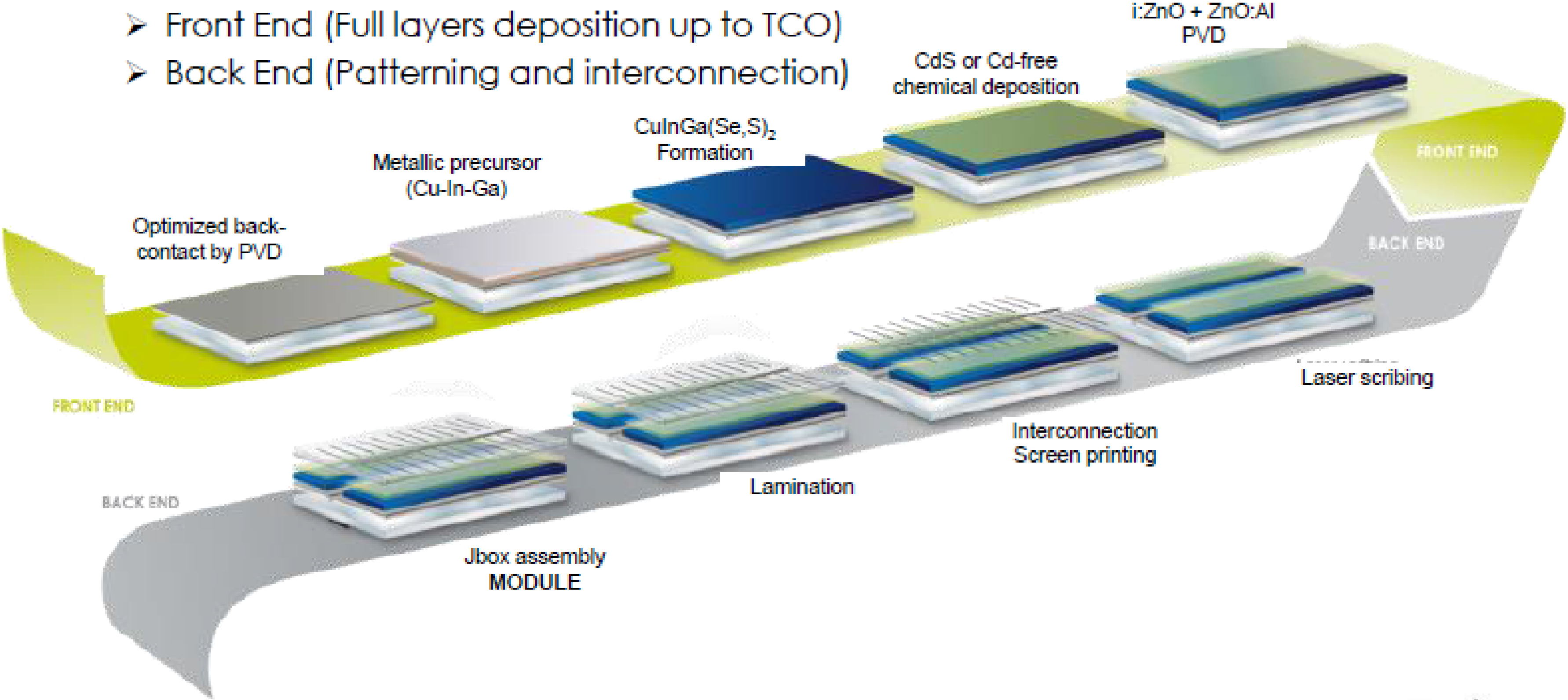
2009 → **2015** *Failure to enter the market*



2015

- 2-step process for CIGS :
  - electrodeposition of a metallic precursor on optimized back-contact
  - Atmospheric thermal treatment under S and Se atmosphere

- Production line separated between:
  - Front End (Full layers deposition up to TCO)
  - Back End (Patterning and interconnection)

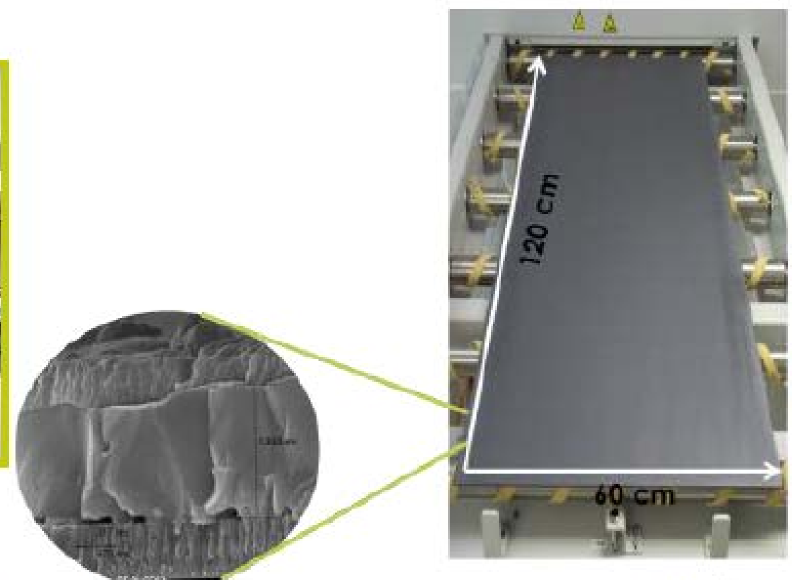


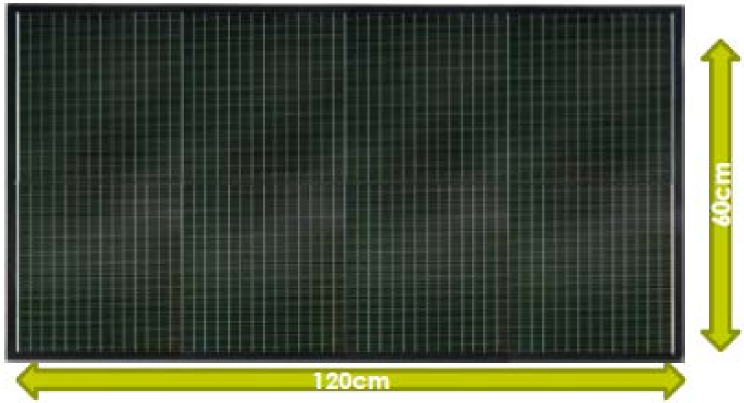
A Pre-industrial 60x120cm² line to demonstrate process capability

Continuous in-line electrodeposition of 60x120cm² plates

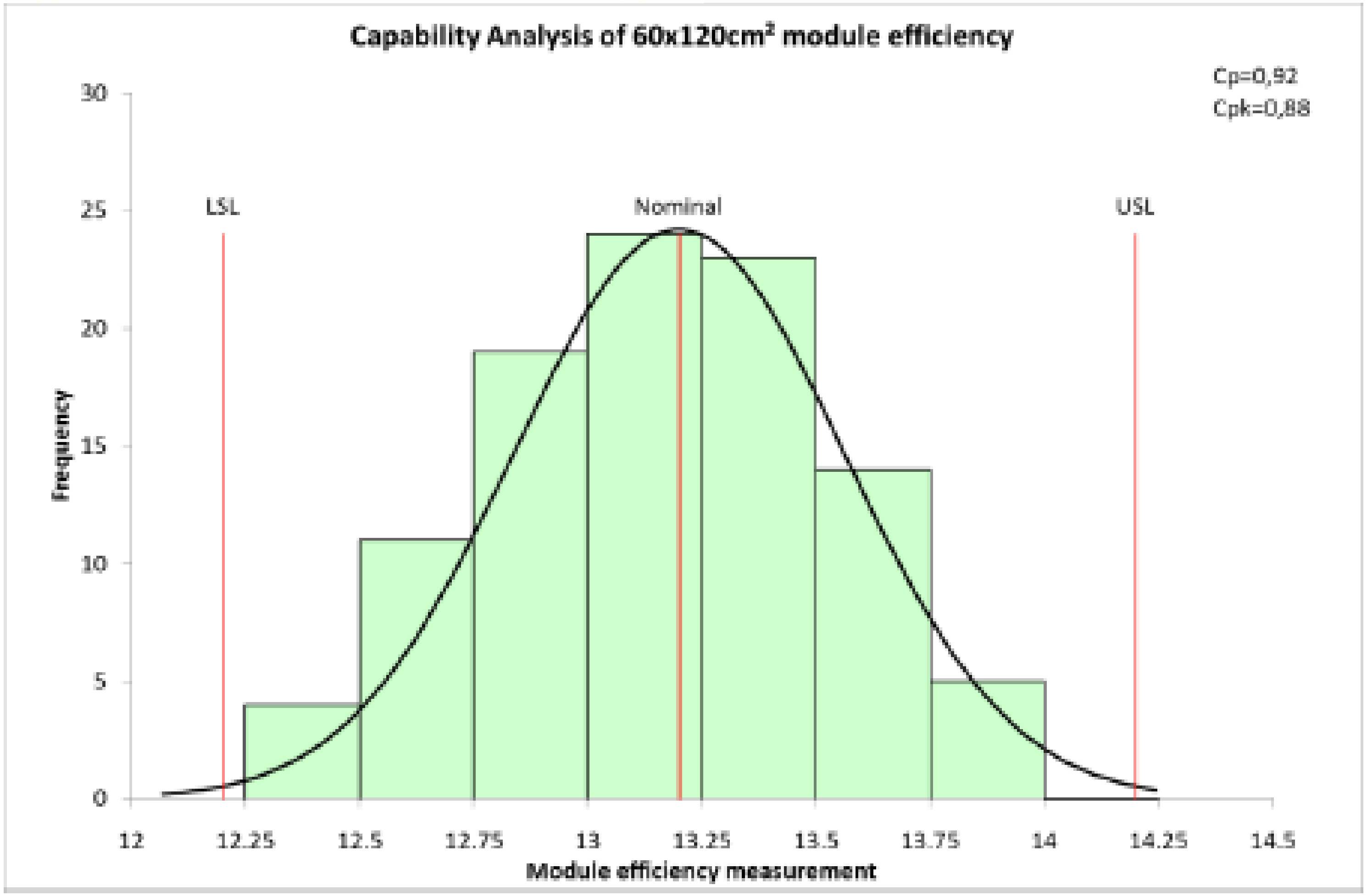
60x120 cm²

NEXCIS Thermal treatment equipment for hydride-free CIGSSe formation

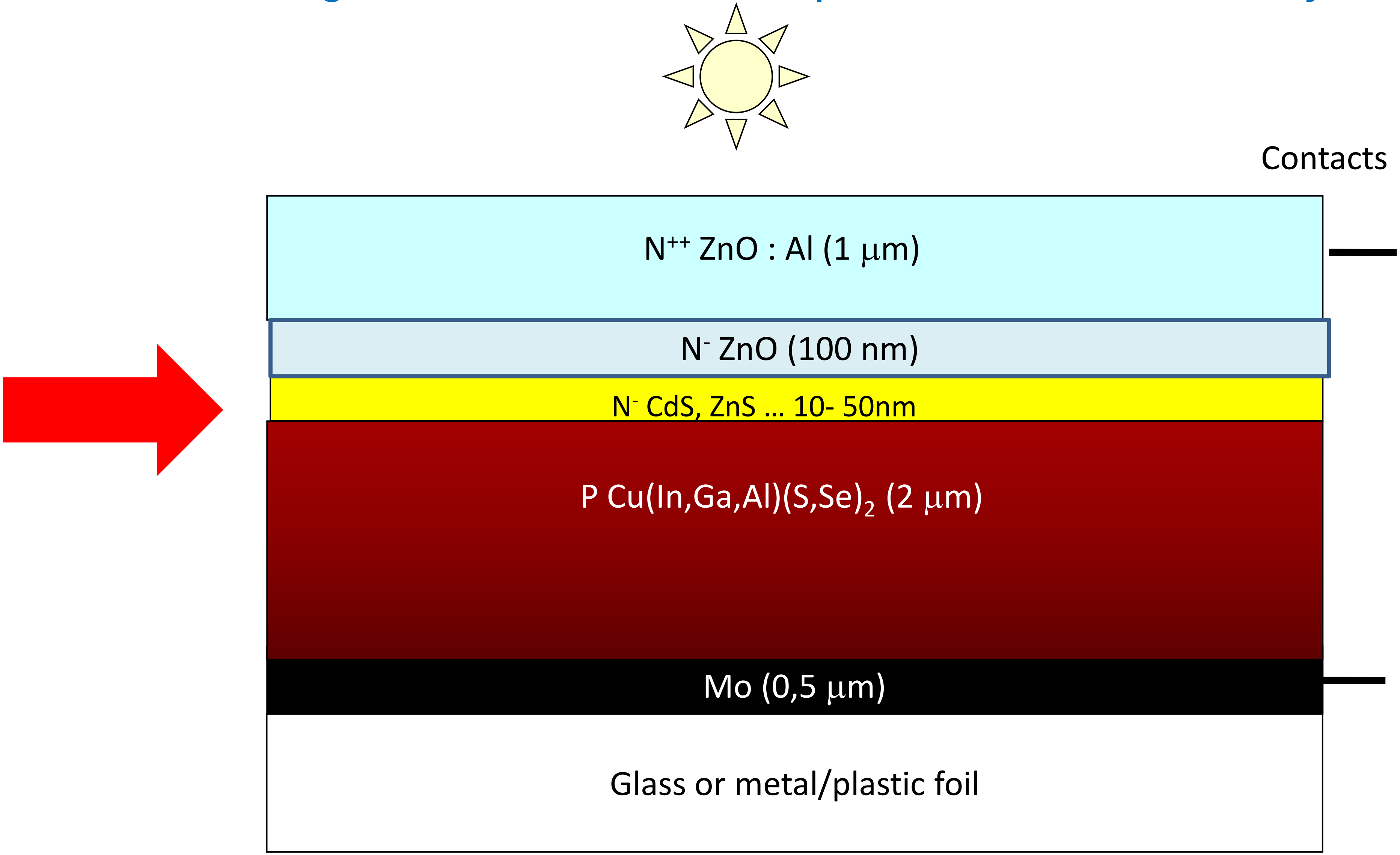




Champion module : 14%
World class results
Champion cell : 17.3%



1989 Challenge 2 Chemical Bath Deposition of the Buffer layer

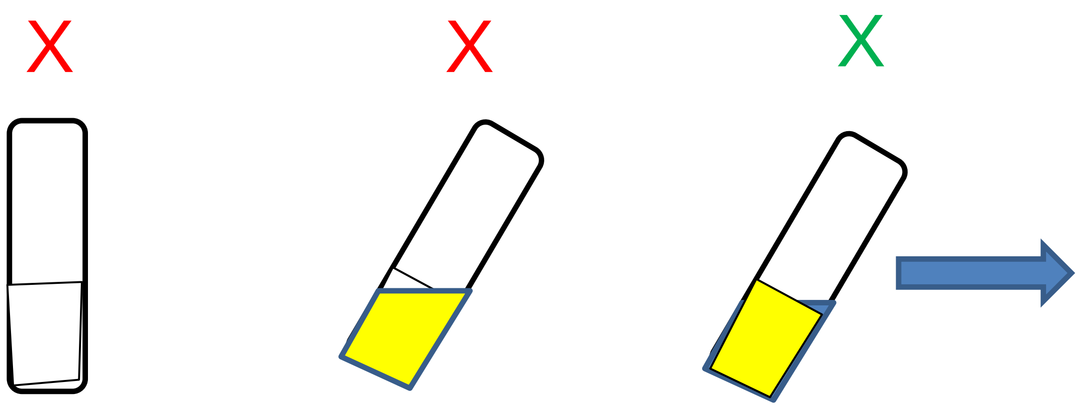


*** In substitution to vacuum methods**

First systematic growth Mechanism studies

1989 : Systematic studies with « baker breaking » → Cd-TU-NH3-pH

$$Cd(NH_3)_4^{2+} + SC(NH_2)_2 + 2\ OH^- \rightarrow CdS + CH_2N_2 + 4NH_3 + 2H_2O$$



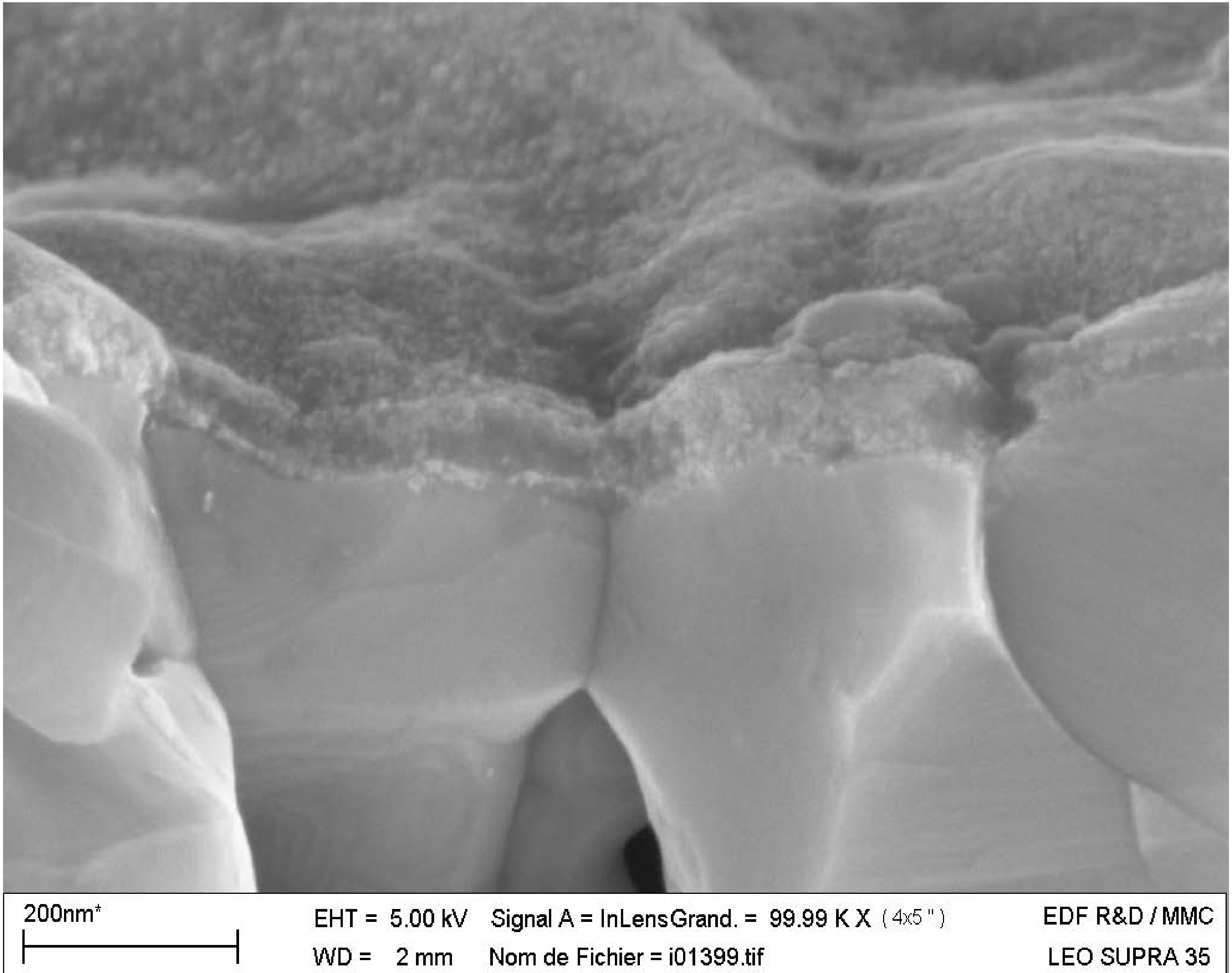
No reaction

Homogeneous reaction

Heterogeneous reaction

Optical properties
Reaction Yeald
Structure

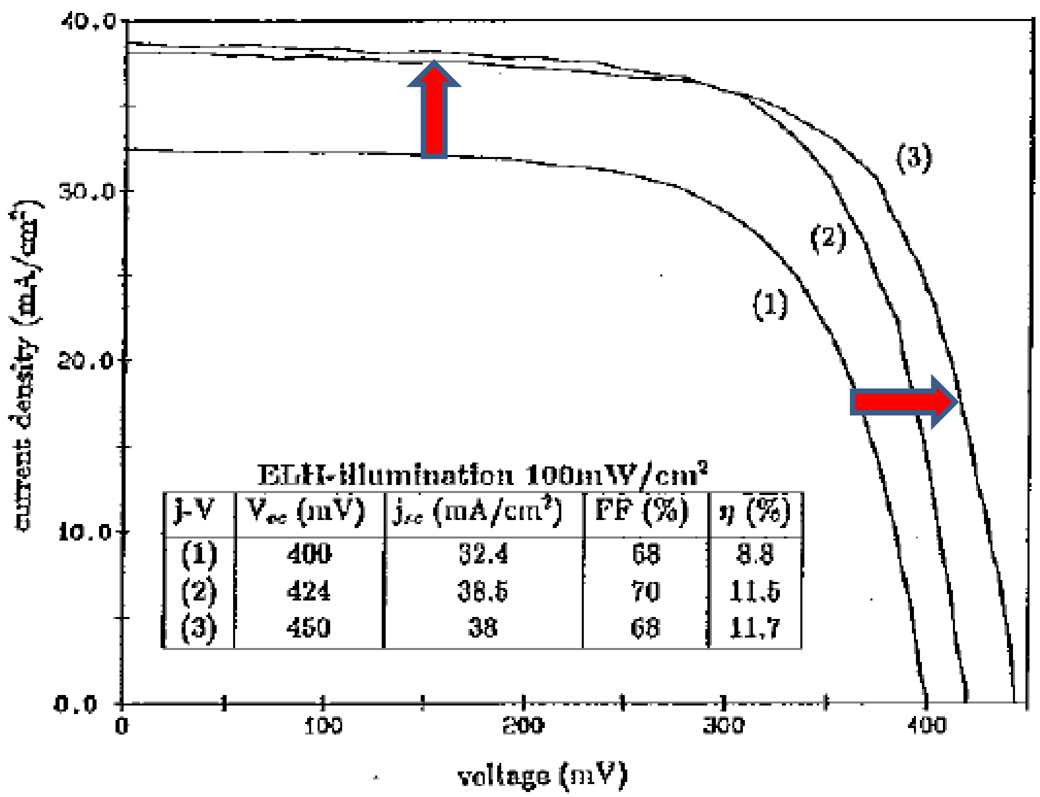
Zone of convenient bath composition


200nm*
EHT = 5.00 kV
Signal A = InLens
Grand. = 99.99 K X (4x5 ")
WD = 2 mm
Nom de Fichier = i01399.tif
EDF R&D / MMC
LEO SUPRA 35

1991

The breakthrough

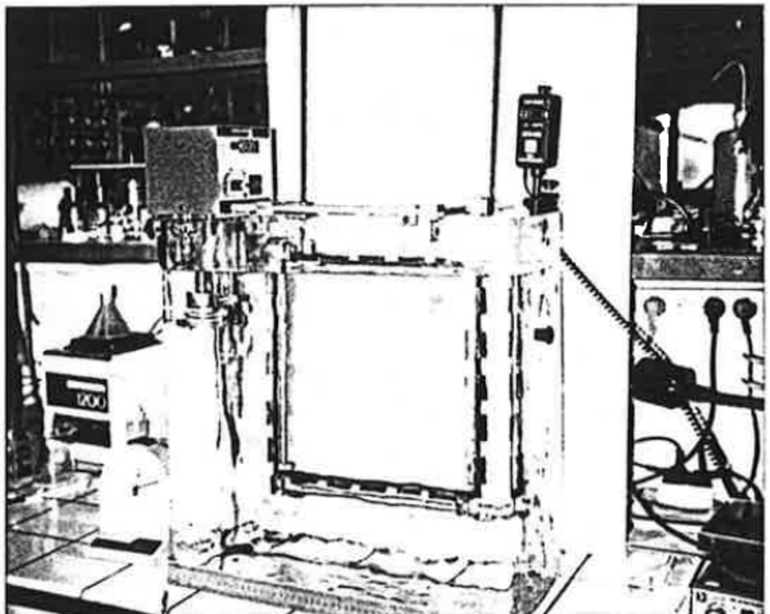
EUPVSEC, Lisbon, 1991



j-V	V_{oc} (mV)	j_{sc} (mA/cm²)	FF (%)	η (%)
(1)	400	32.4	68	8.8
(2)	424	38.5	70	11.5
(3)	450	38	68	11.7

Fig. 5: j-V characteristics of a $Cd_{0.85}Zn_{0.15}S$-$CuInSe_2$ standard device (1) and corresponding ZnO-CdS-$CuInSe_2$ devices with either Sulfate-based (2) or Iodid-based (3) CBD-CdS

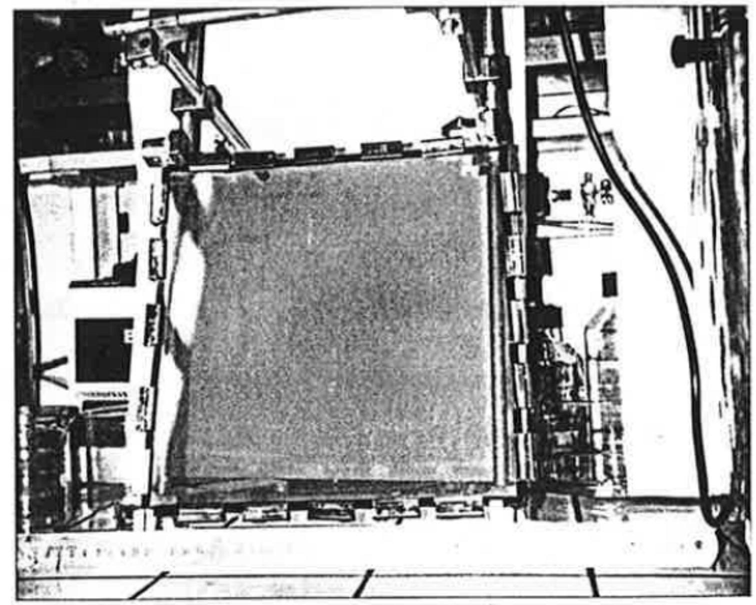
Demonstration of the Upscaling with 2D flat reactor
EUROCIS MEETING, Paris Sept. 1994



50cm

complete reactor, starting conditions for CdS deposition

Story



processed substrates, in their holder out of the bath.

Short Story : The glass plates were coming from the nearby window glass workshop,
The separator was made of telephon electric cables,
The clemps were bought from an art shop nearby,
The large volume water bath was hired from a colleague at ENSCP working on alguea Culture

2016 : Oscilating horizontal single plate has become an industrial standard For CBD deposition

CBD Equipment Technologies – R&D Fully automated Exp.-Set Up

STANGL
Semiconductor Equipment AG
04-2010 - 11

Automated Experimental Setup under production conditions

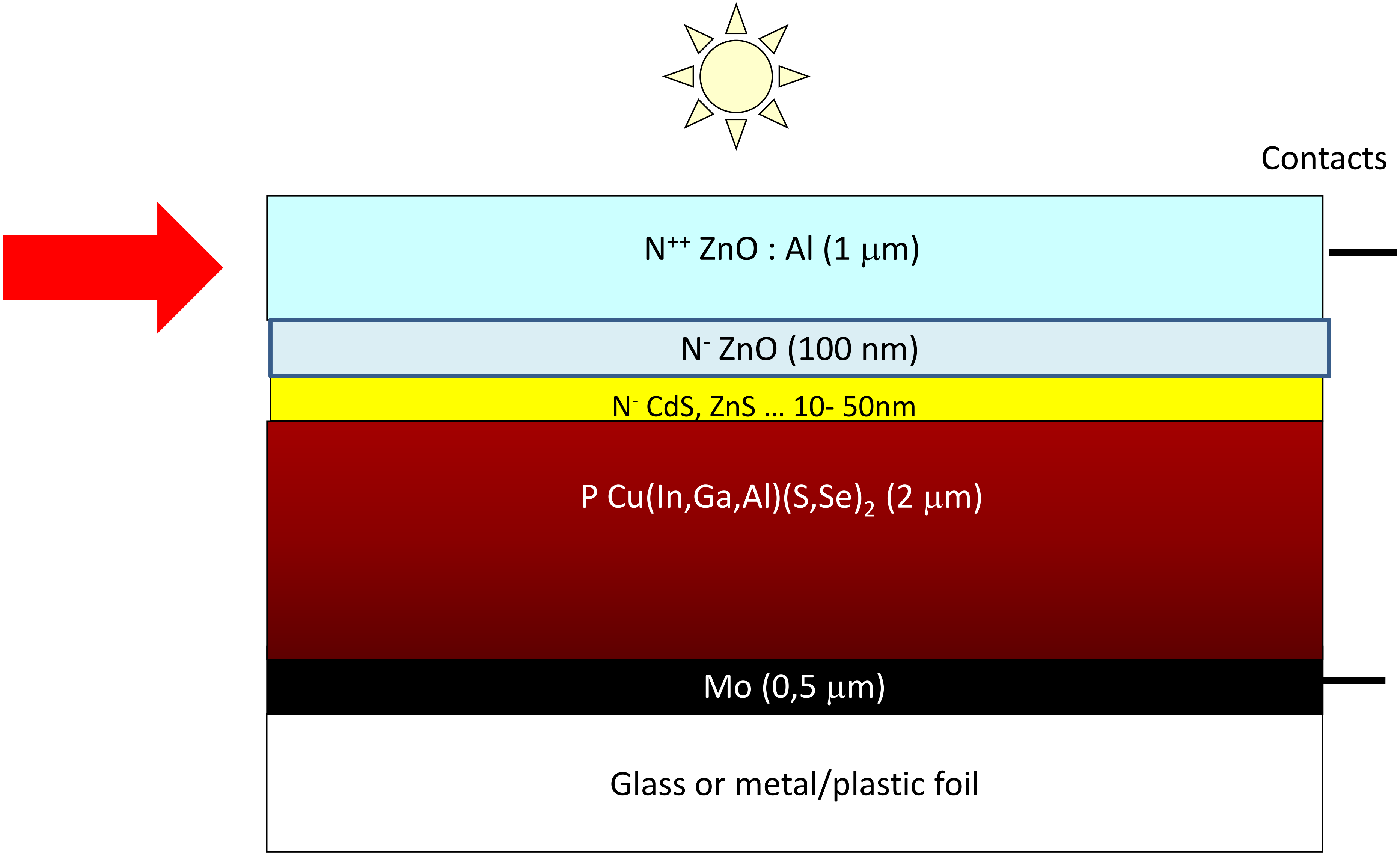
- Substrate size:
  1200 x 600mm
  600 x 900 mm
  1400 x 1100 mm

- Automated heating
- Automated wobbling (movement)
- Automated dosage

D. Lincot, 2nd May 2016, EMRS

1992

Challenge 3: ZnO by electrodeposition



From the idea (1992) to the application (2015)

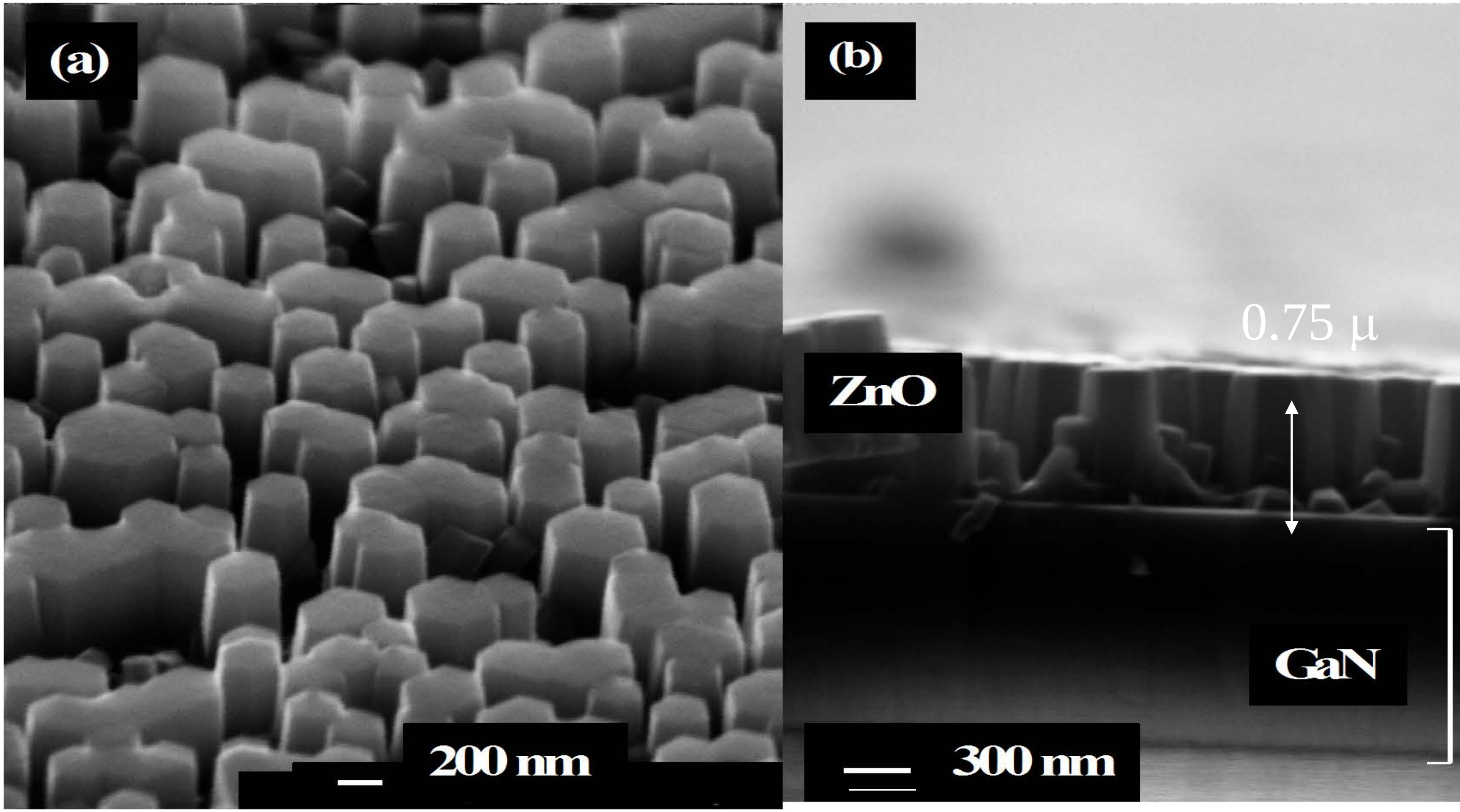
$$Zn^{2+} + \frac{1}{2}O_2 + 2e^- \rightarrow ZnO \qquad E_0 = 0.93\ V/NHE$$

1993 – It works

– $ZnCl_2$: 10^{-4} - 10^{-2} M
– Oxygen : 10^{-5} - 10^{-3} M
– Temperature: 50 - 90°C
– Potential: -1 V to - 1.4 V vs MSE

Electrodeposition on GaN :

84°C, E=-1.4 V/MSE, t=4000s, 22% O_2 , Zn (II) 5.10^{-3} M



PAUPORTE, T., LINCOT, D., Heteroepitaxial electrodeposition of zinc oxide films on gallium nitride, Appl. Phys. Lett., 75 (1999) 3817-3819

2015

SCIENTIFIC REPORTS | 5 : 8961 | DOI: 10.1038/srep08961

SCIENTIFIC REPORTS

OPEN

SUBJECT AREAS:
SOLAR CELLS
SEMICONDUCTORS

Received
2 November 2014

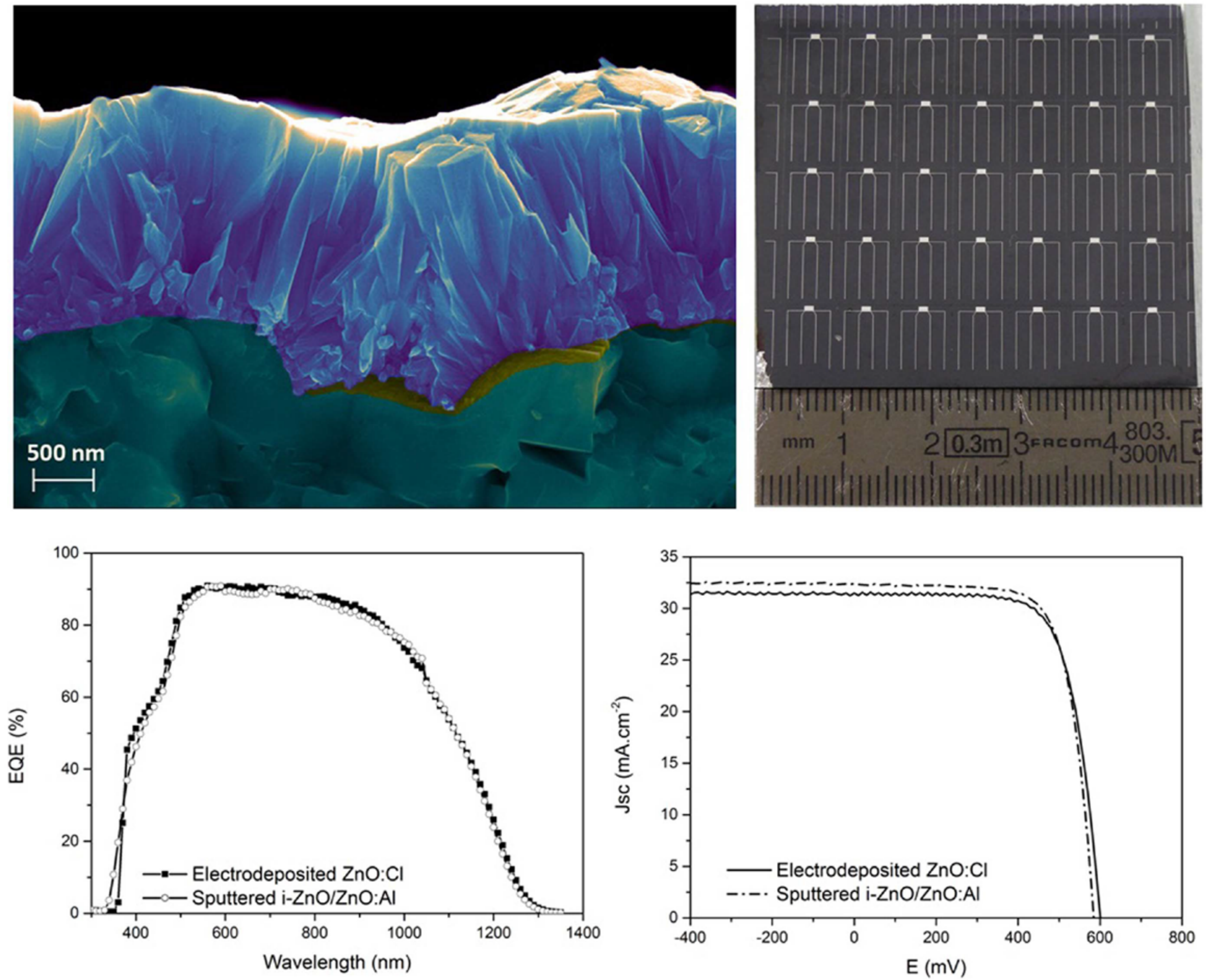
Accepted
9 February 2015

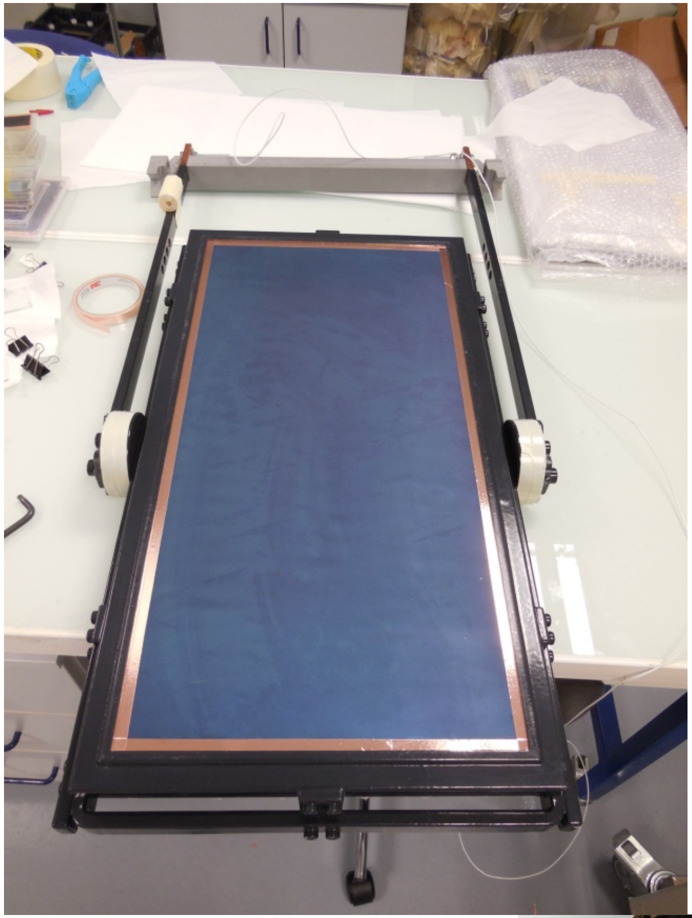
Published
10 March 2015

Electrodeposition of ZnO window layer for an all-atmospheric fabrication process of chalcogenide solar cell

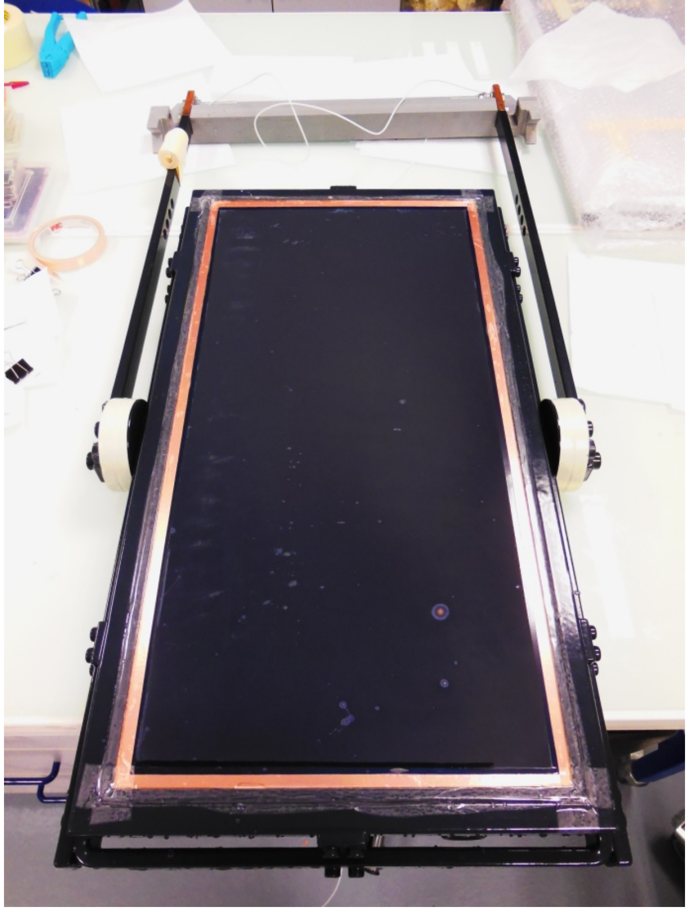
Fabien Tsin[1,3], Amélie Venerosy[2,3], Julien Vidal[1,3], Stéphane Collin[4], Johnny Clatot[1,3], Laurent Lombez[2,3], Myriam Paire[1,3], Stephan Borensztajn[2,3], Cédric Broussillou[5], Pierre Philippe Grand[5], Salvador Jaime[5], Daniel Lincot[2,3] & Jean Rousset[1,3]

[1]EDF R&D, 6 quai Watier, 78400 Chatou Cedex, France, [2]CNRS, 6 quai Watier, 78400 Chatou Cedex, France, [3]IRDEP, Institute of Research and Development on Photovoltaic Energy, UMR 7174 CNRS EDF Chimie ParisTech, 6 quai Watier, 78400 Chatou Cedex, France, [4]LPN, Laboratoire for Photonics and Nanostructures, UPR 20 CNRS, Route de Nozay, 91460 Marcoussis, France, [5]NEXCIS Photovoltaic Technology, 13790 Rousset, France.


500 nm
mm 1 2 0.3m 3 FRCOM 4 803. 300M 5
EQE (%)
Wavelength (nm)
Electrodeposited ZnO:Cl
Sputtered i-ZnO/ZnO:Al
Jsc (mA.cm^{-2})
E (mV)
Electrodeposited ZnO:Cl
Sputtered i-ZnO/ZnO:Al



Starting industrial Transfert (2015)



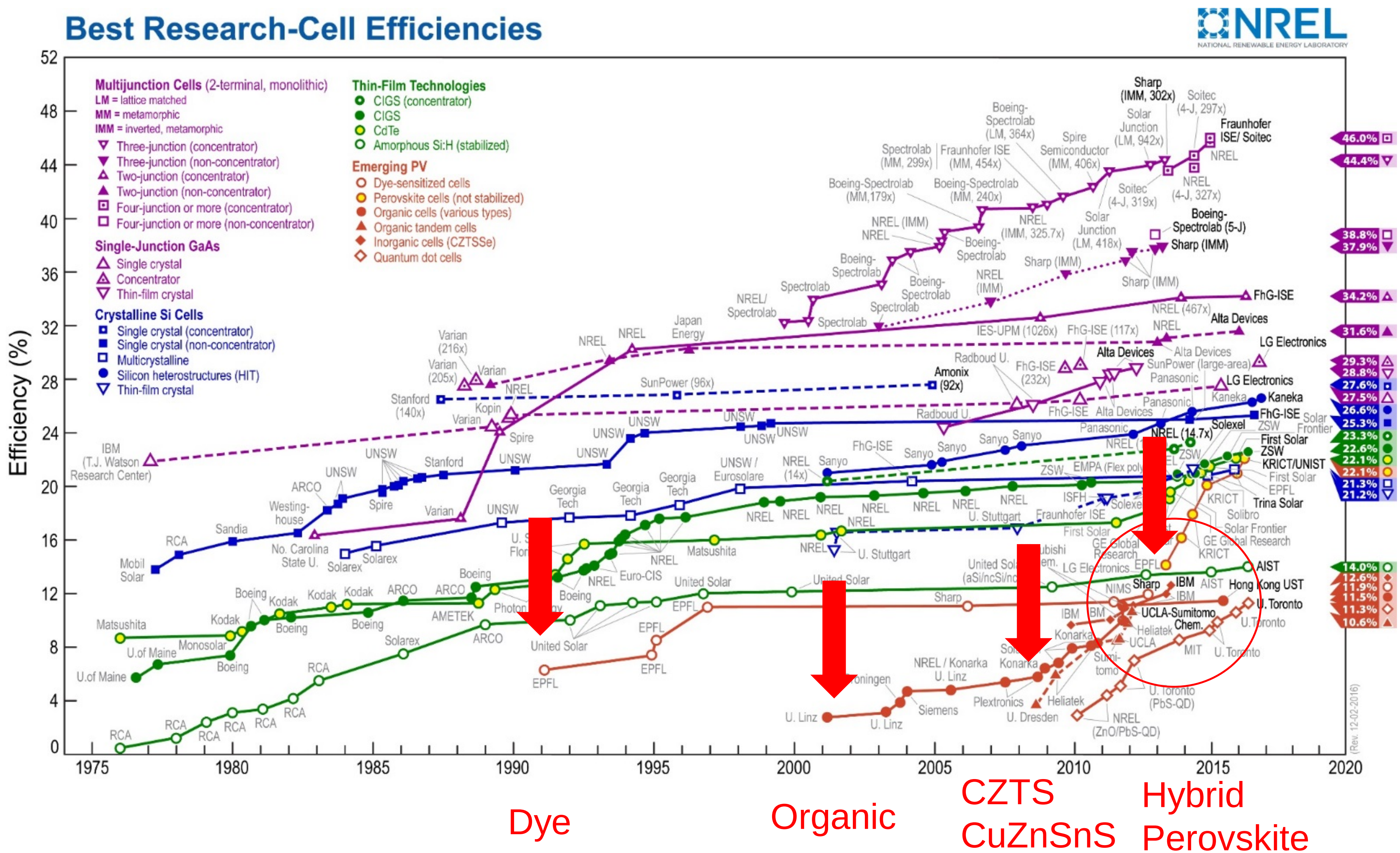
Fabien TSIN
Docorant

New concepts, new thin film technologies

↓

Dye cells, Organic, Perovkites

The emergence of new thin film solar cells : Dye Cells, Hybrid, Perovkite



The irruption of Perovskite solar cells

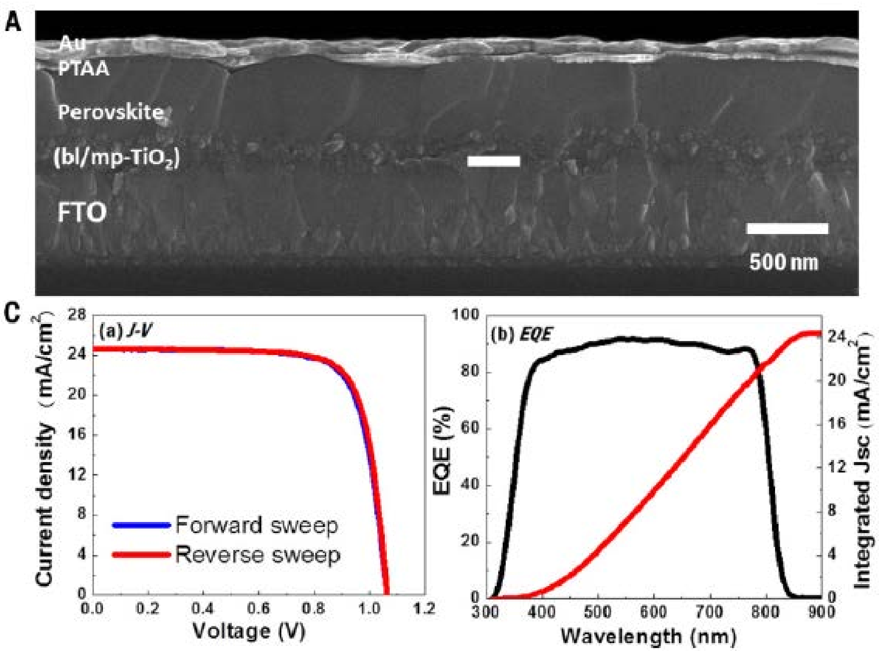
2015

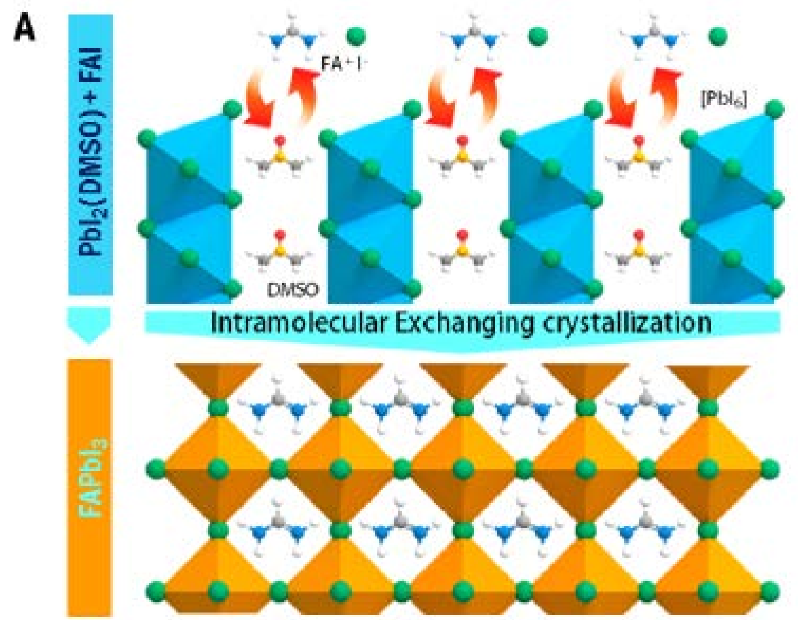
Record efficiency 22. 1%

Sciencexpress

High-performance photovoltaic perovskite layers fabricated through intramolecular exchange

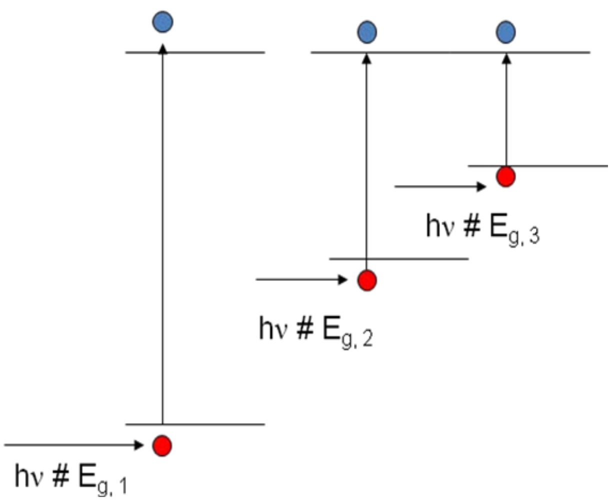
Woon Seok Yang,[1*] Jun Hong Noh,[1*] Nam Joong Jeon,[1] Young Chan Kim,[1] Seungchan Ryu,[1] Jangwon Seo,[1] Sang Il Seok[1,2†]

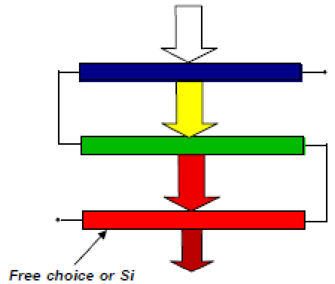


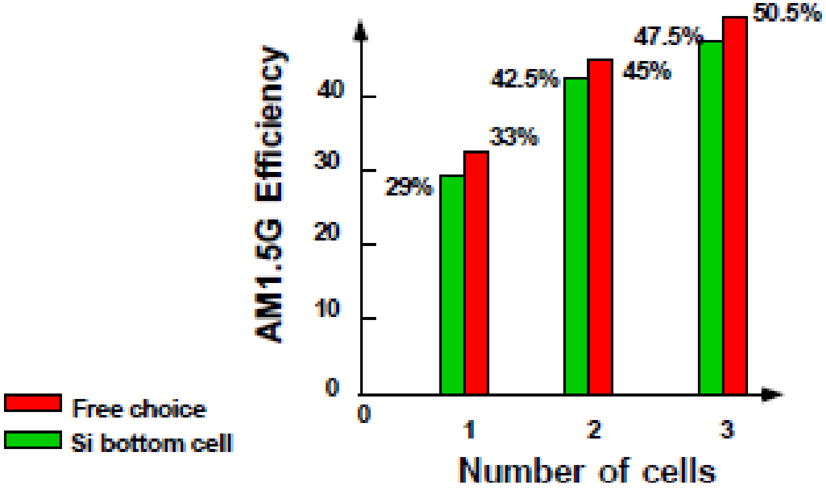


Sciencexpress / sciencemag.org/content/early/recent / 21 May 2015 / Page 1 / 10.1126/science.aaa9272

Un concept établi : les multijonctions

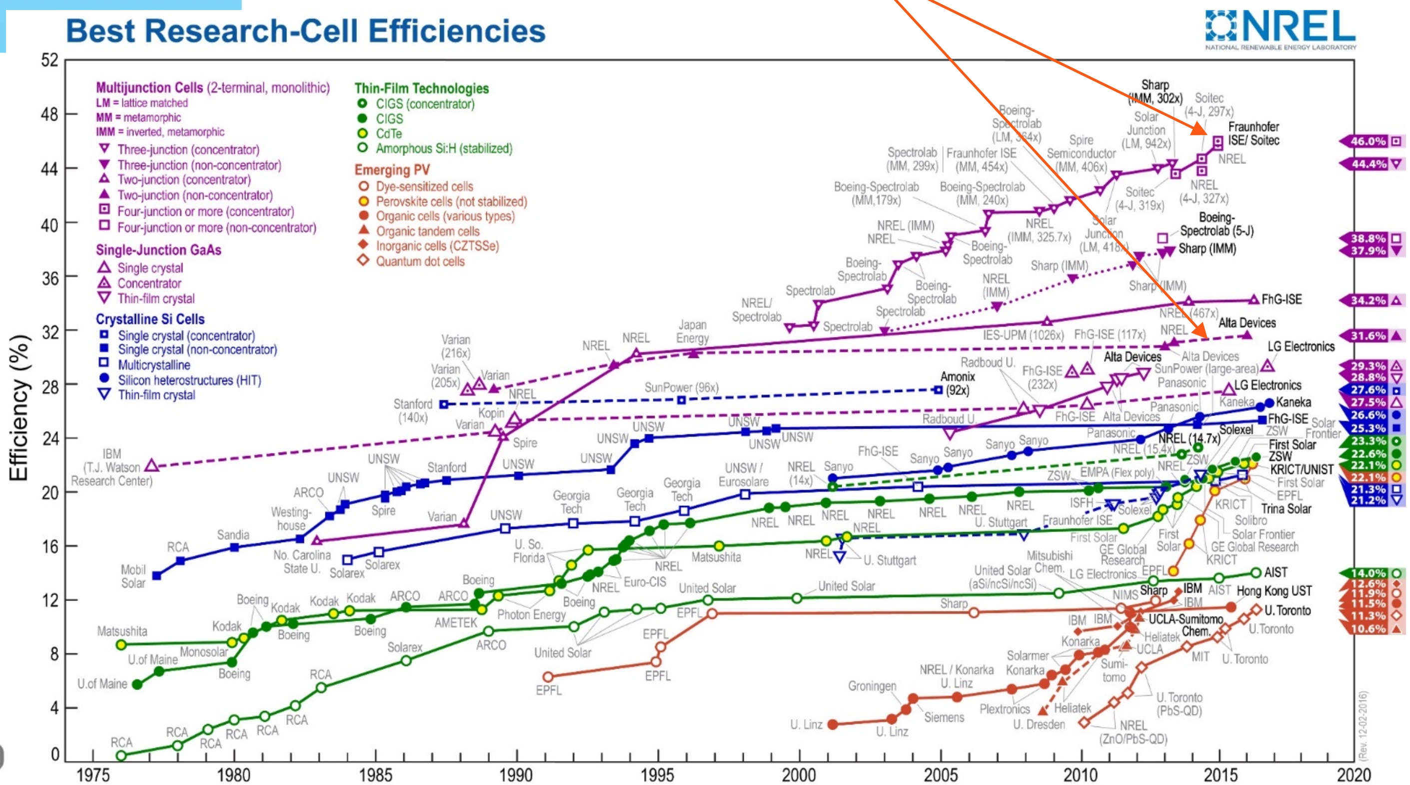






Daniel Lincot : Séminaire L'énergie solaire : Energie du futur ? Collège de France 21/04/2017

La voie des multijonctions



Record jonction tandem : Si-GaInP 31,4 % (EPFL-NREL)

D'ILE-D

L'initiative 30-30-30

IPVF
INSTITUT PHOTOVOLTAÏQUE D'ILE-DE-FRANCE

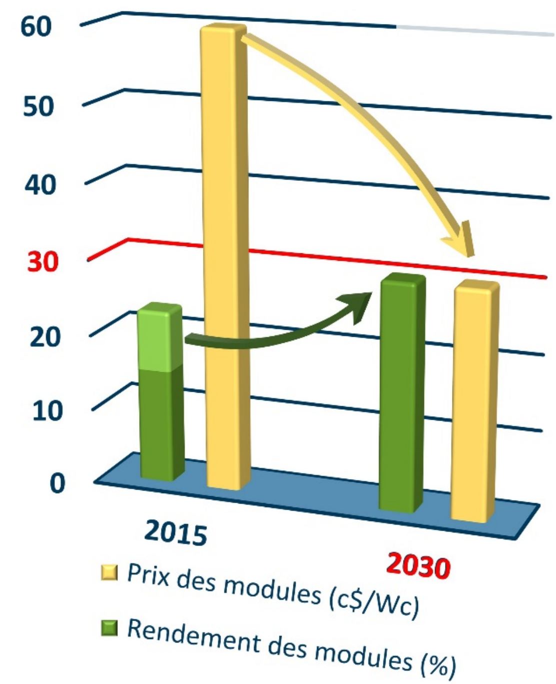
Un point de passage partagé avec des représentants des plus grands centres de recherche internationaux :

Vers des **modules photovoltaïques avec**

un rendement
> 30%

pour un prix
< 30 c$/Wc

à l'horizon
2030



UNE INITIATIVE SUPPORTÉE PAR ...

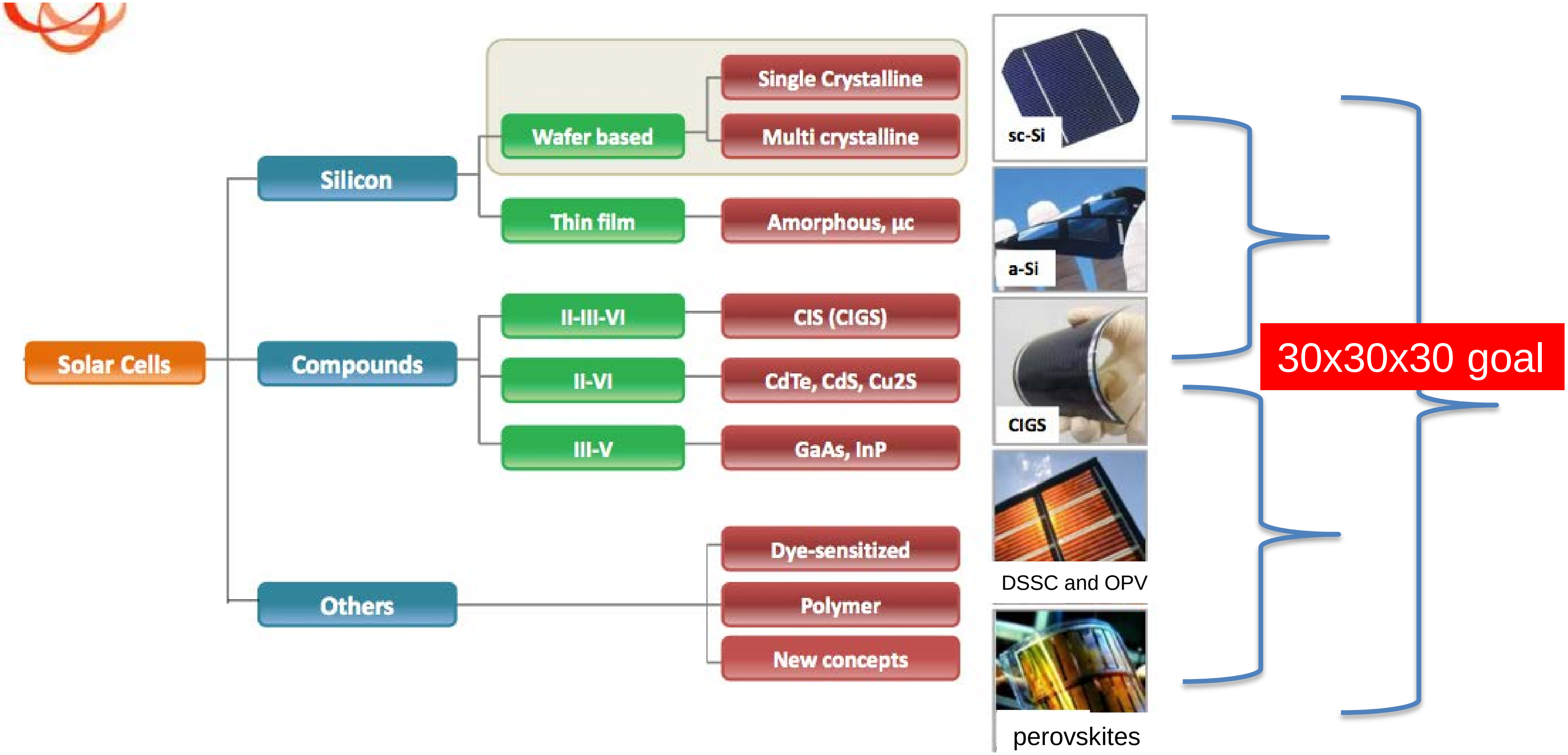
Jean-François MINSTER IPVF	**Michael GRAETZEL** EPFL	**Andreas BETT** Fraunhofer ISE	**Marika EDOFF** Uppsala University	**Christophe BALLIF** EPFL
Michael POWALLA ZSW	**Philippe MALBRANCHE** INES	**Yoshita OKADA** RCAST, NextPV	**Jean-François GUILLEMOLES** CNRS, NextPV	**Alex FREUNDLICH** University of Huston
Accord par e-mail :	**Martin GREEN** UNSW	**Jeff POORTMANS** IMEC	**Wim C. SINKE** ECN	**Ayodha N. TIWARI** EMPA, EPFL

PARIS2015 COP21·CMP11

New paradigm for photovoltaics

SQ limit
Differentiation process

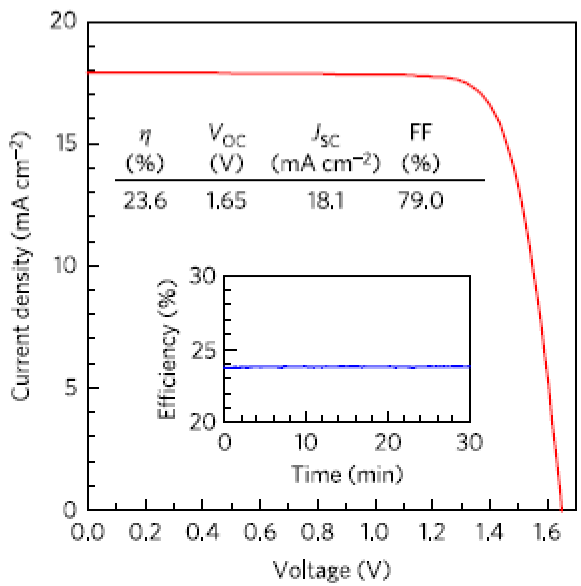
Post SQ Limit : 30-40-50%
Convergence process

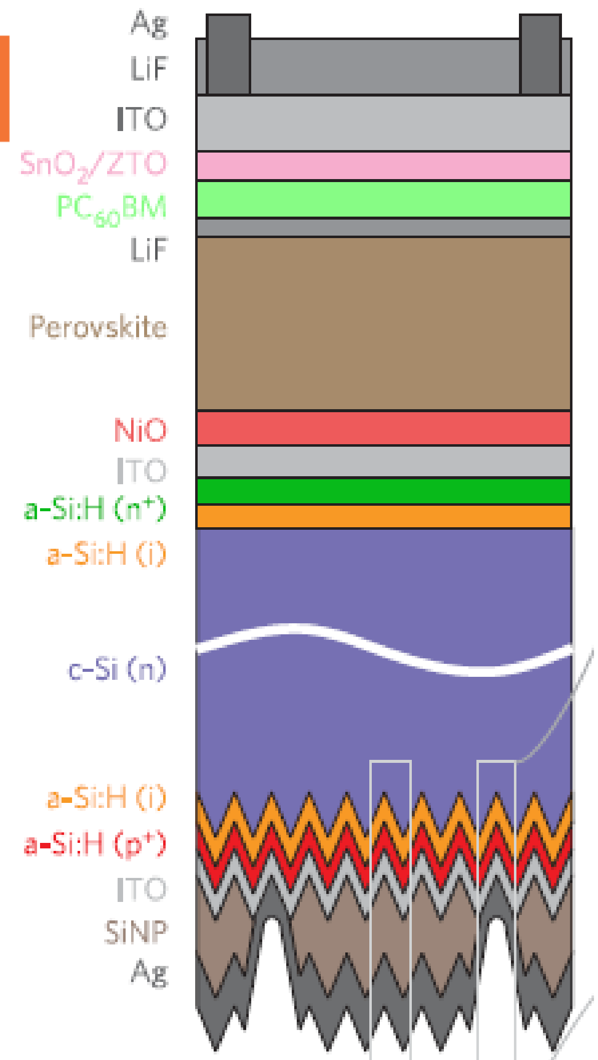


nature energy
ARTICLES
PUBLISHED: 17 FEBRUARY 2017 | VOLUME: 2 | ARTICLE NUMBER: 17009

23.6%-efficient monolithic perovskite/silicon tandem solar cells with improved stability

Kevin A. Bush[1†], Axel F. Palmstrom[1†], Zhengshan J. Yu[2†], Mathieu Boccard[2], Rongrong Cheacharoen[1], Jonathan P. Mailoa[3], David P. McMeekin[4], Robert L. Z. Hoye[3], Colin D. Bailie[1], Tomas Leijtens[1], Ian Marius Peters[3], Maxmillian C. Minichetti[1], Nicholas Rolston[1], Rohit Prasanna[1], Sarah Sofia[3], Duncan Harwood[5], Wen Ma[6], Farhad Moghadam[6], Henry J. Snaith[4], Tonio Buonassisi[3], Zachary C. H





Other approaches : Si-III/V, CIGS/Perovskite

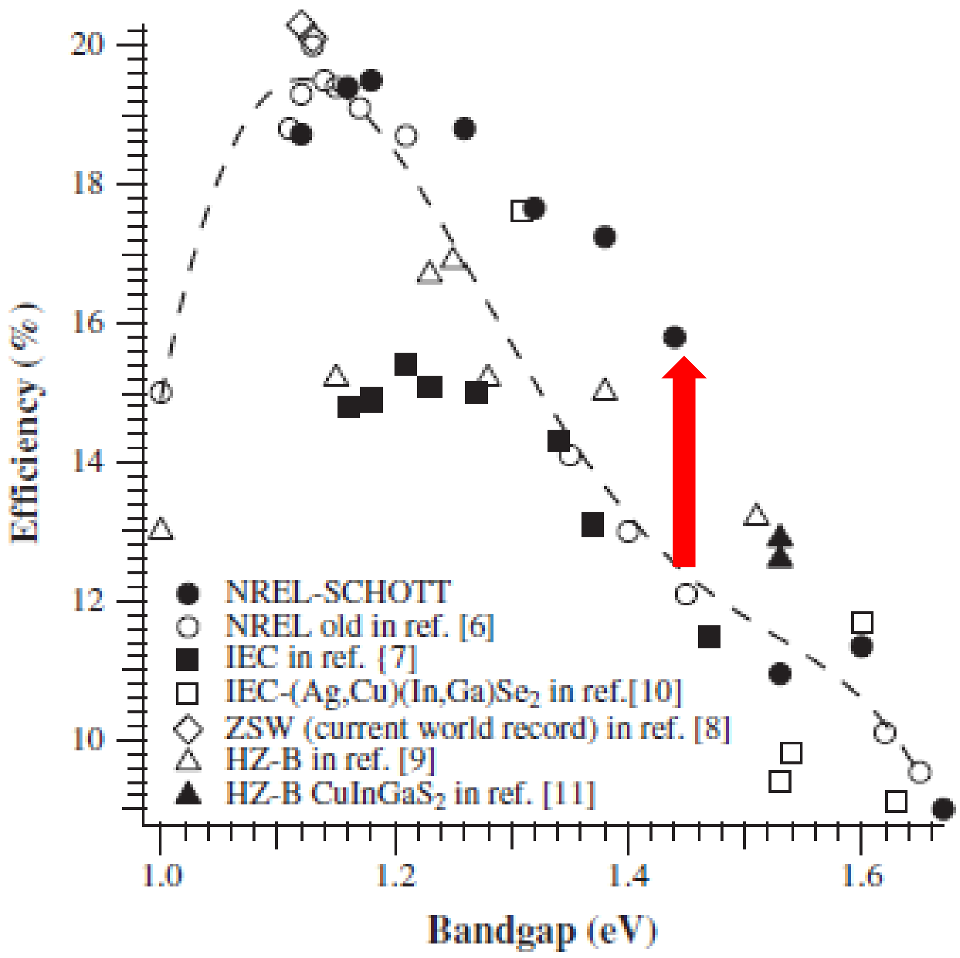
TOP CELL : Thin Film Solar Cells

2012 Progress in Photovoltaics → **The CIGS Option for top cell**

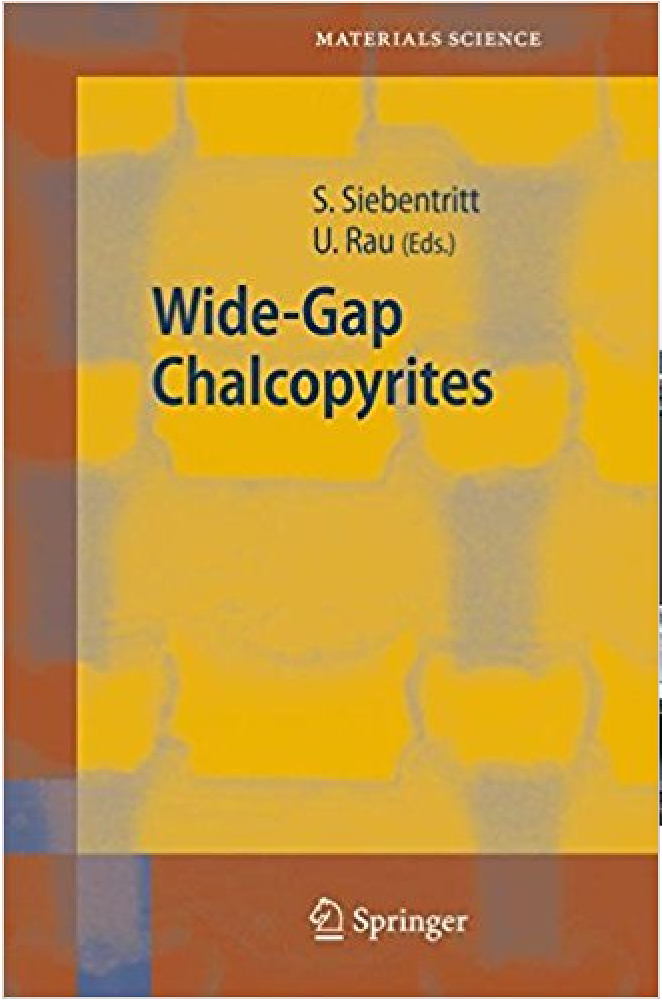
Wide bandgap $Cu(In,Ga)Se_2$ solar cells with improved energy conversion efficiency

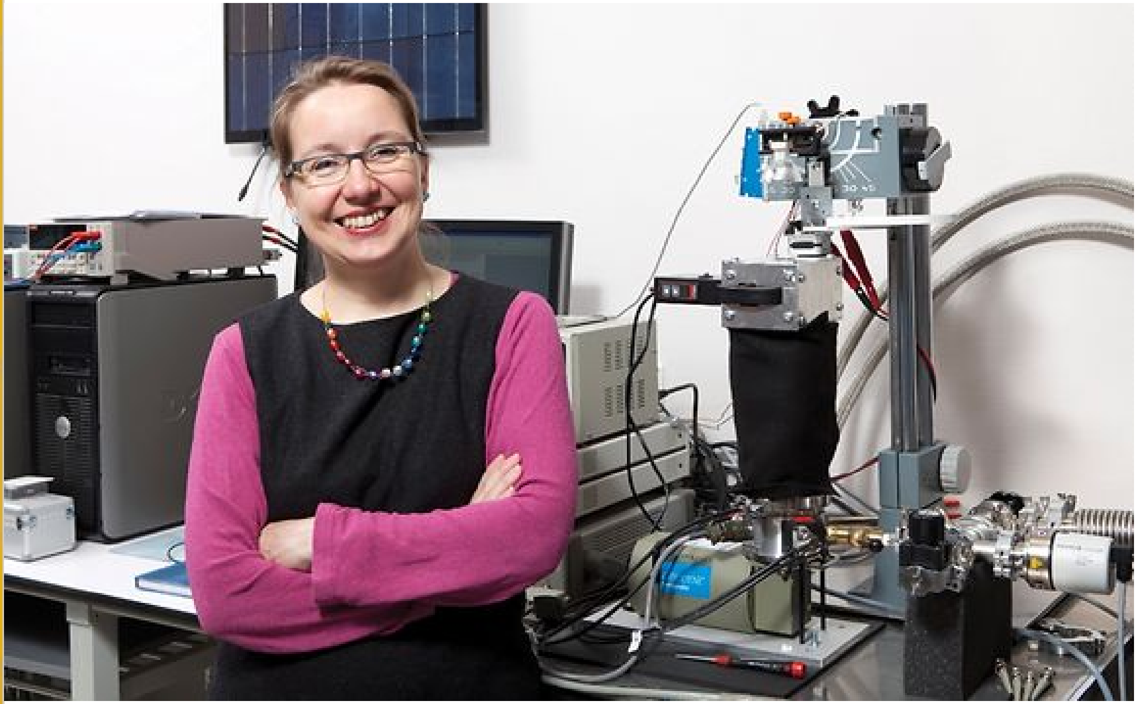
Miguel A. Contreras[1]*, Lorelle M. Mansfield[1], Brian Egaas[1], Jian Li[1], Manuel Romero[1], Rommel Noufi[1], Eveline Rudiger-Voigt[2] and Wolfgang Mannstadt[2]

[1] National Renewable Energy Laboratory, Golden, CO, USA
[2] Schott AG, Mainz, Germany



Wide Bandgap Chalcopyrites/Chalcogenides

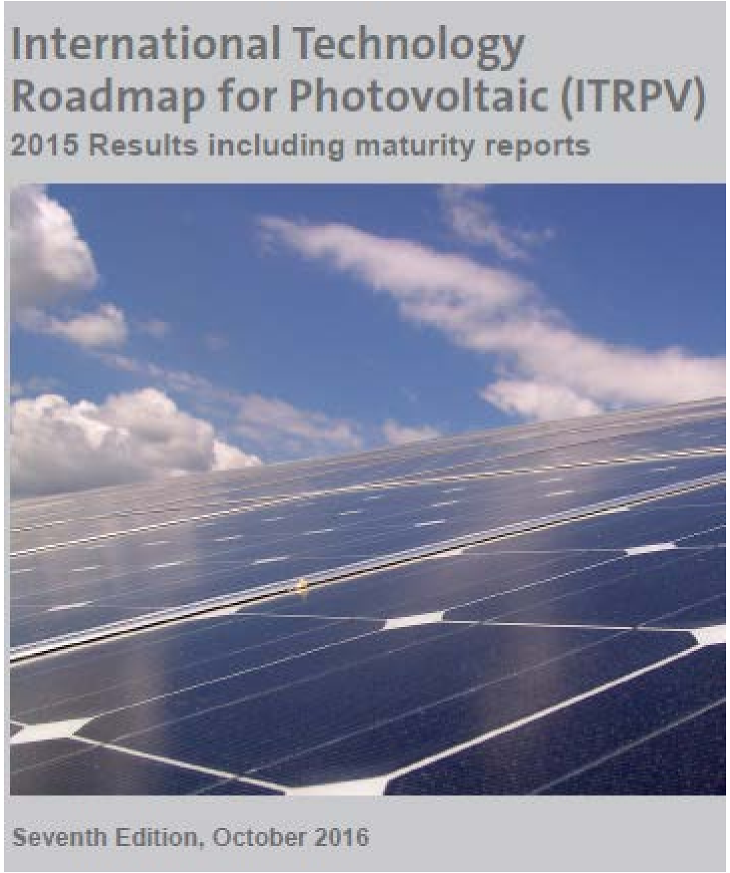




Breakthrough needed

Thanks : A. Tiwari

Photovoltaics : There is plenty of room ahead for thin film technologies !



1 we are here
2 we go there

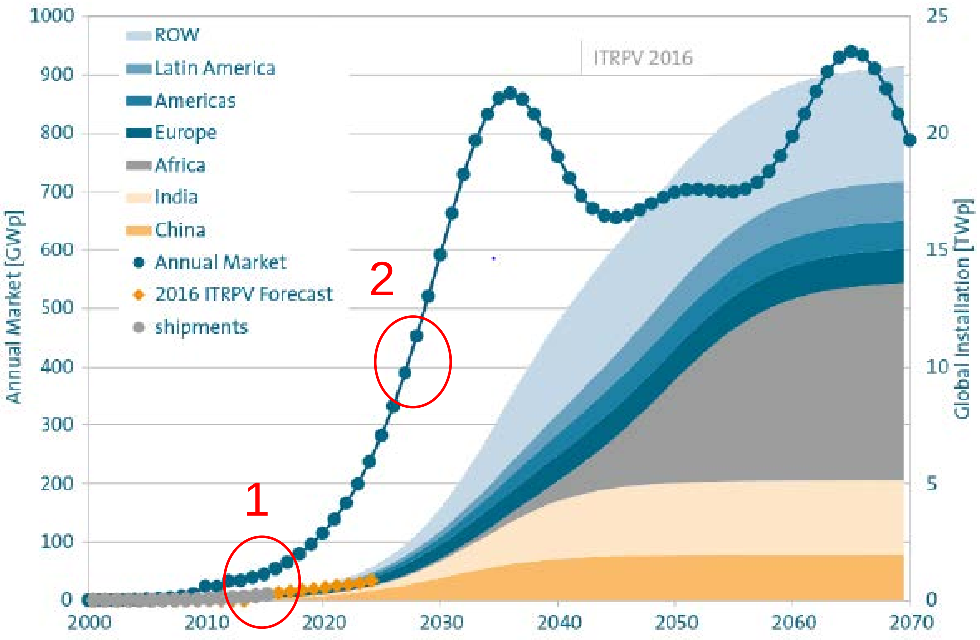


Fig. 48: Cumulative installed module power calculated with a logistic growth approximation for Scenario 2, assuming 23 TWp installed PV module power in 2070 (see Table 2).