COLLÈGE DE FRANCE 1530

Chaire Innovation technologique
Liliane Bettencourt 2021-2022

Énergie solaire photovoltaïque et transition énergétique

Fondation Bettencourt Schueller
Reconnue d'utilité publique depuis 1987

Mercredi 23 février 2022

Les technologies couches minces (aSi,CdTe,CIGS,GaAs)

Daniel LINCOT

Procédés plasma à basse température pour le dépôt de couches minces de silicium: de l'amorphe au cristallin

Pere ROCA I CABARROCAS

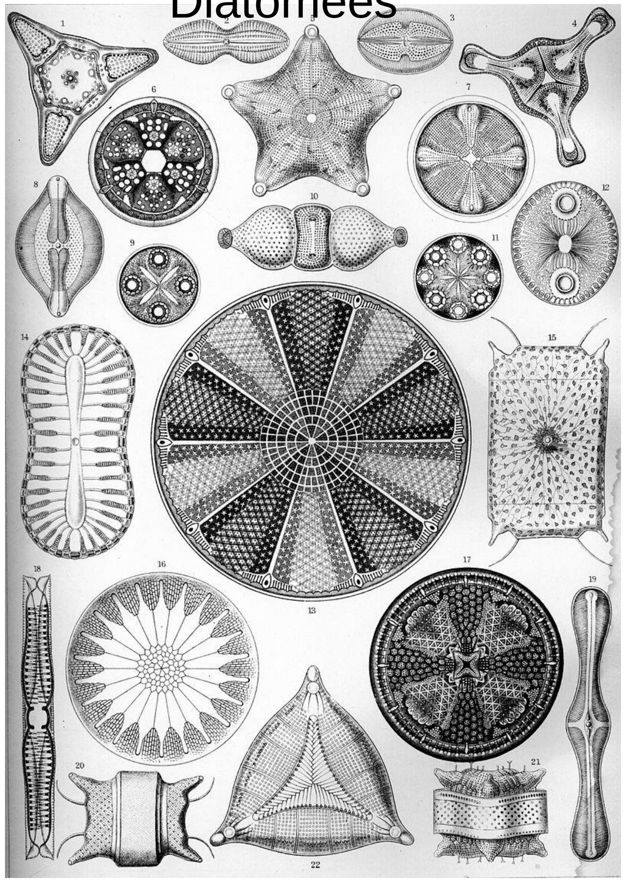
daniel.lincot@cnrs.fr

Sources de SiO_2

Origine biologique
Diatomées

Quartz - Mine de La Gardette, Le Bourg-d'Oisans, Isère France (13 × 13 cm).

Grande mer de sable en Egypte
(72 000 km²)



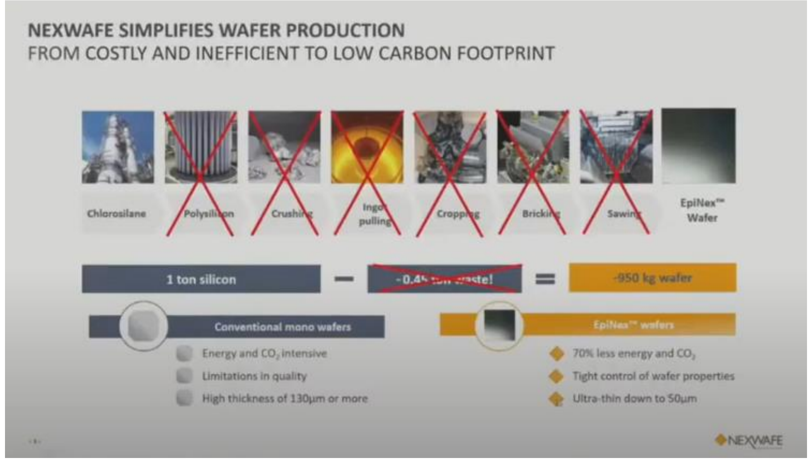
Phytoplancton

Voir : https://www.college-de-france.fr/site/jacques-livage/inaugural-lecture-2002-01-17.htm

Sources: Wikipedia

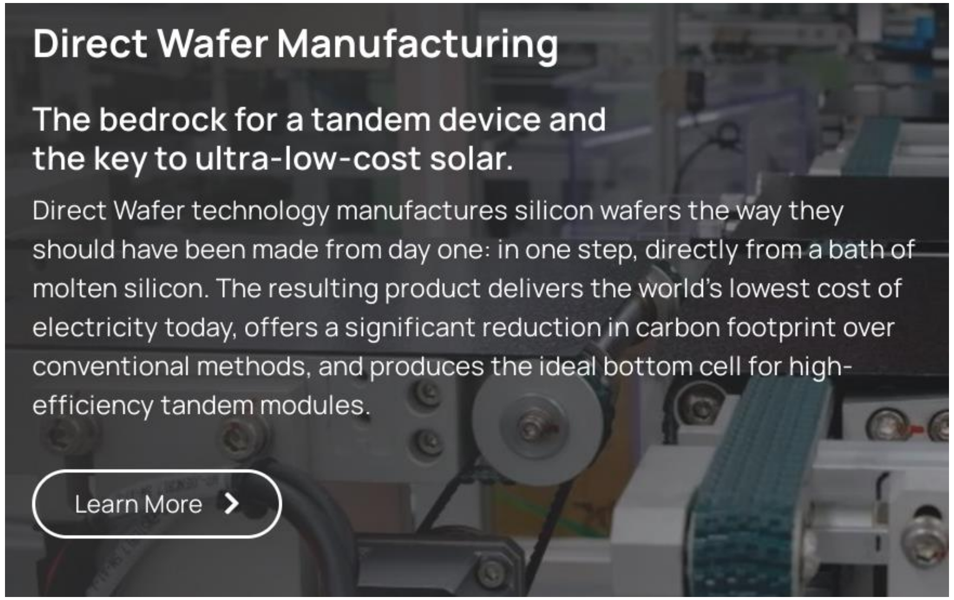
Technologies silicium sans sciage ?

A partir du trichlorosilane



Start up Nexwafe (Fraunhofer)
https://www.nexwafe.com/epinex-process

Coulage direct



https://cubicpv.com/technology/

Autres : tirage de rubans à partir de bains fondus…*

A. Goetzberger et al, Solar Energy Materials and Solar Cells 74(2002)1

La réutilisation des plaquettes de qualité électronique

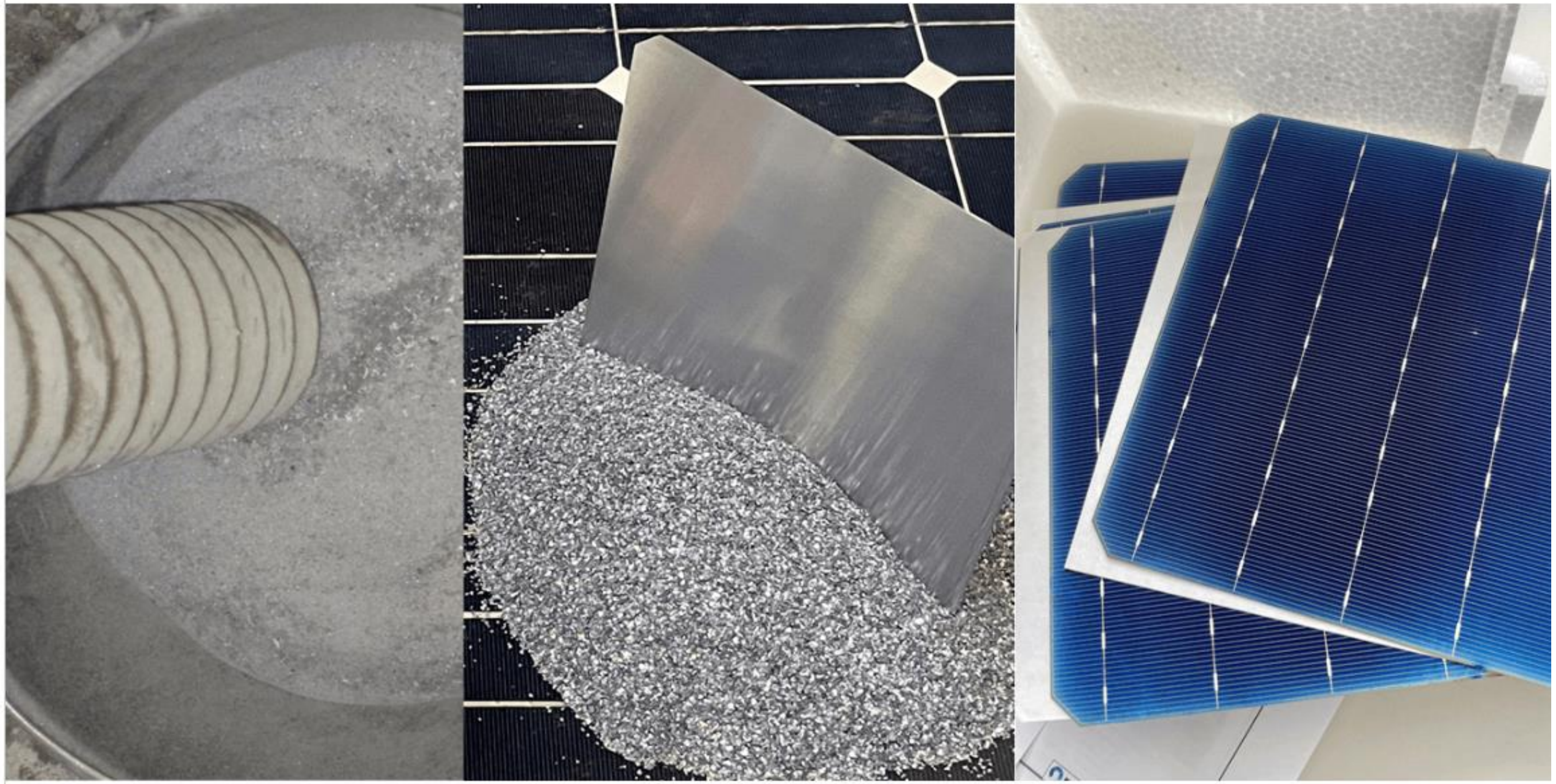
FRAUNHOFER INSTITUTE FOR SOLAR ENERGY SYSTEMS ISE

PRESS RELEASE

PRESS RELEASE
February 7, 2022 || Page 1 | 4

PERC Solar Cells from 100 Percent Recycled Silicon

Around ten thousand tons of silicon in discarded photovoltaic modules end up on the recycling market annually in Germany. This figure will rise to several hundred thousand tons per year by 2029. Currently, the aluminum, glass and copper of the discarded modules are reprocessed, however, the silicon solar cells are not. In order to be able to reuse the silicon, researchers from the Fraunhofer Center for Silicon Photovoltaics CSP and the Fraunhofer Institute for Solar Energy Systems ISE together with the largest German recycling company for PV modules, Reiling GmbH & Co. KG, have developed a solution, in which the silicon in the discarded modules was recycled on an industrial scale and reused to produce new PERC solar cells.



By-products of the treatment process at Reiling GmbH, from which the solar cell fragments are separated and collected (left). Purified silicon and wafers made from 100% recycled silicon (middle). PERC solar cells made

© Fraunhofer ISE

https://www.ise.fraunhofer.de/en/press-media/press-releases/2022/solar-cells-from-recycled-silicon.html

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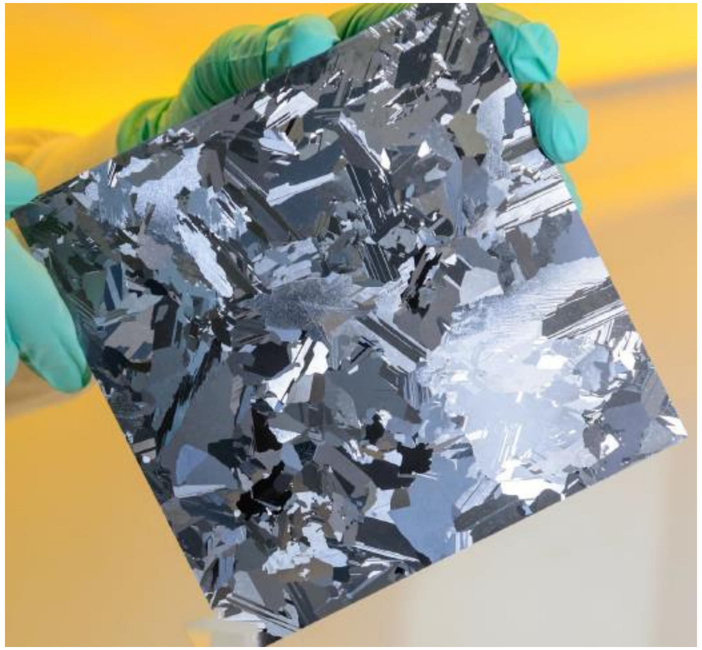
Pourquoi des couches minces ?

- Plaquettes ou « Wafer » → Silicium cristallin : 100 -180 microns
- Couches minces : 0,5- 3 microns



→Economie de matière
→Procédés de fabrication
→Interconnection
→Légèreté, flexibilité
→Nouveaux marchés

Conditions
→ Performances conservées
→ Maturité
→ Stabilité dans le temps
→ Différenciation marché
→Coût

Critère différentiation produit

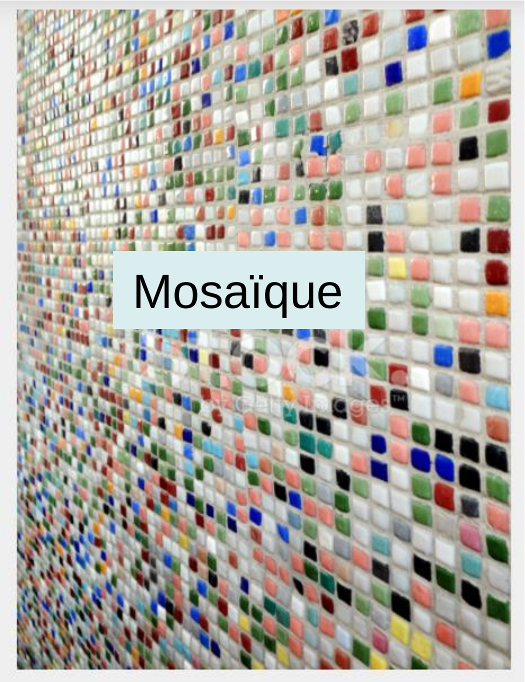
Module silicium amorphe monobloc (3-4 m^2)

Module CIGS flexible (FLISOM)

24th European PV Conference Valencia (2008) Photo J. Wanegue

Passage de technologies de découpe à des technologies de revêtement

Propriétés
de volume



Propriétés
de surface

Sources : le bien public,
Archiexpo, web

Daniel Lincot, Collège de France, 23/02/2022

Exemple des technologies d'affichage

Technologie tubes cathodiques

Ecrans plats

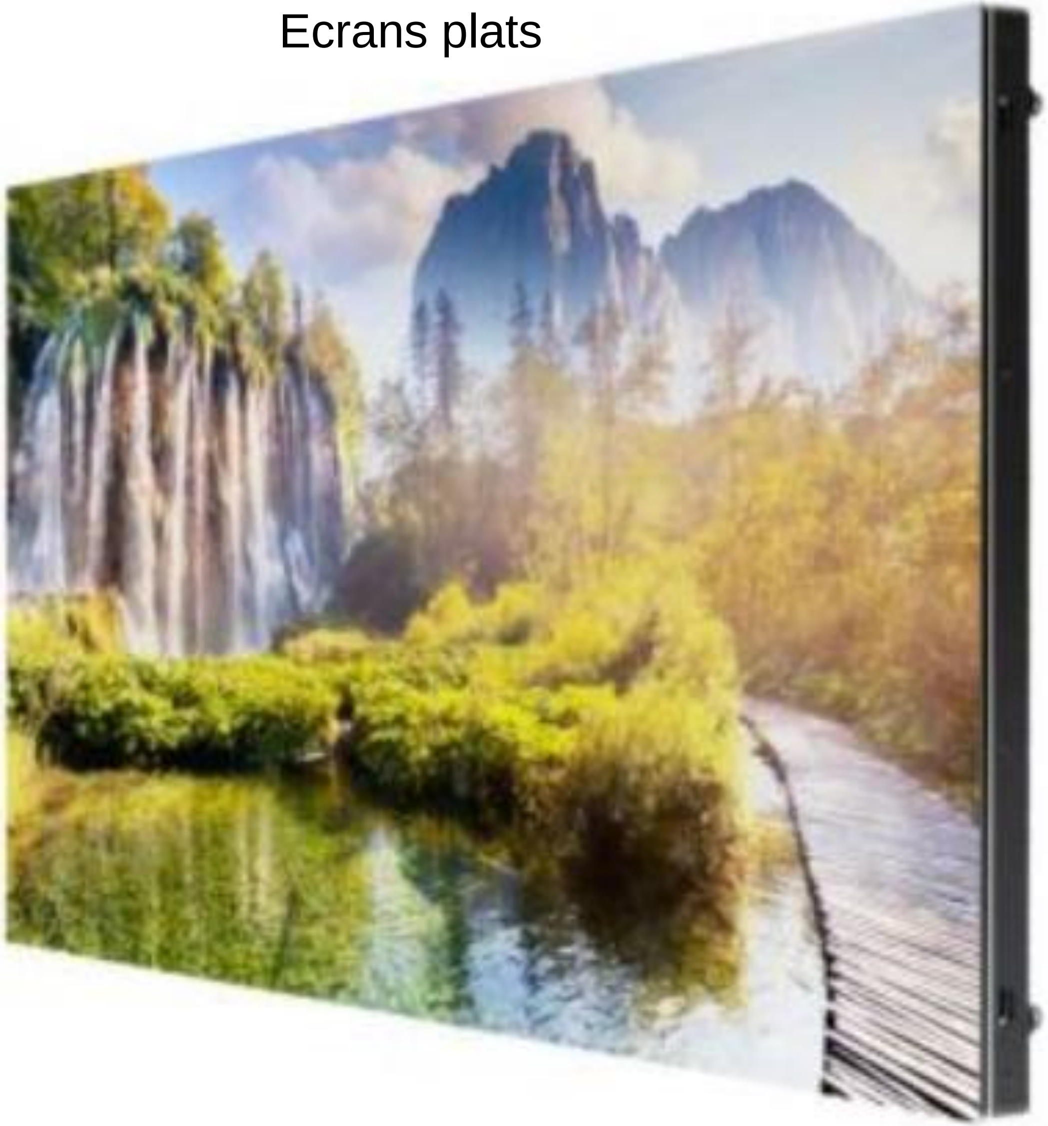
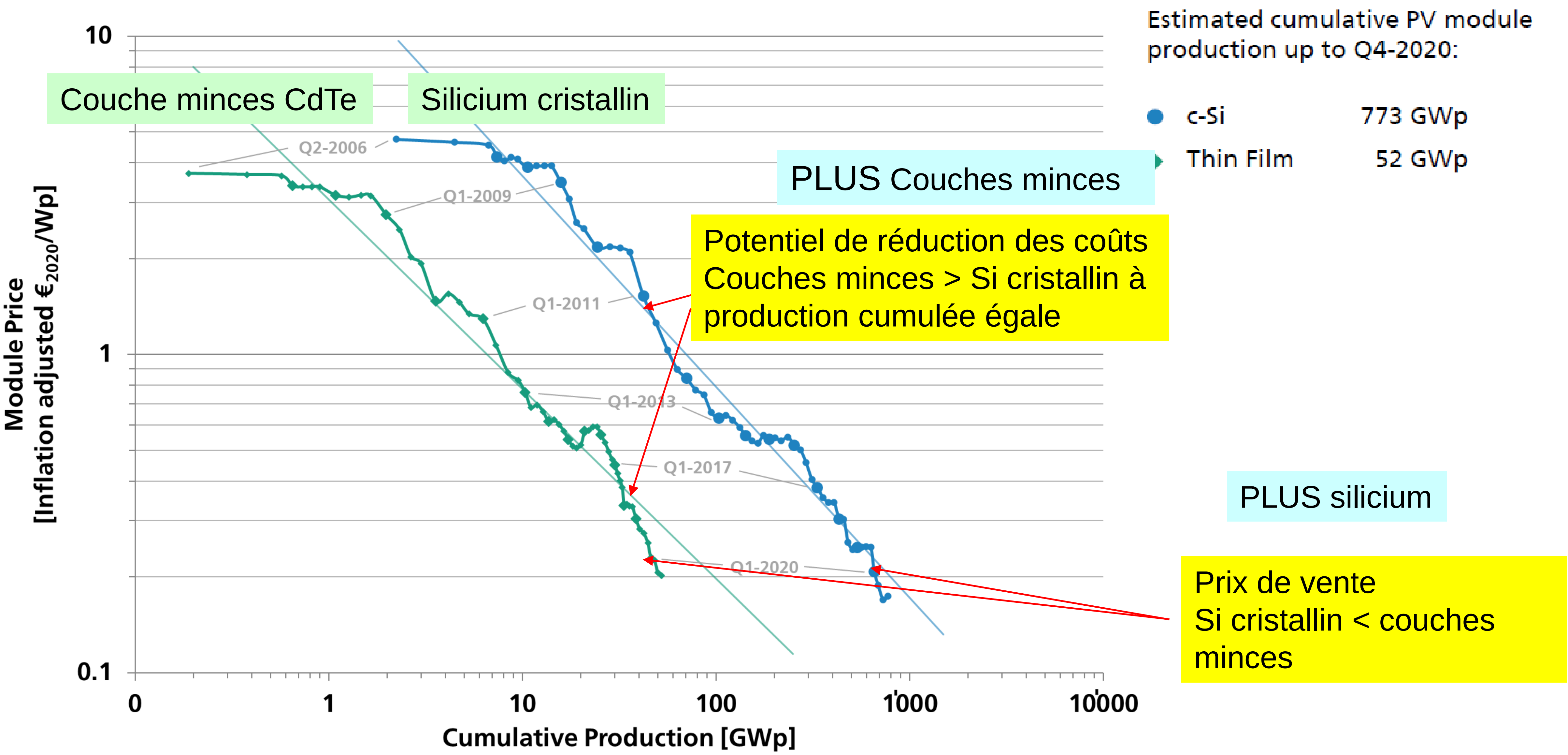


Illustration du paradigme coût-innovation technologique (effet lock in)



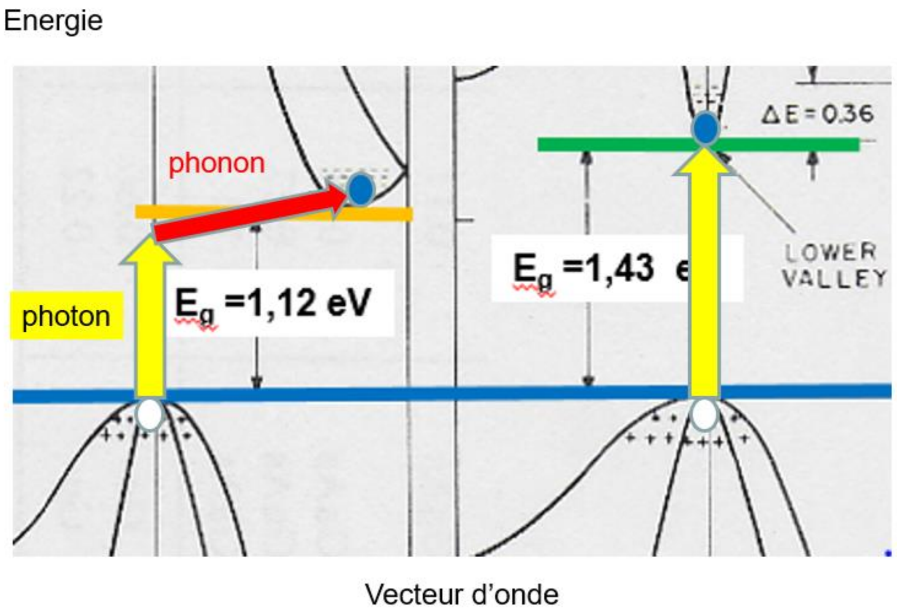
Source : photovoltaic report Fraunhofer, juillet 2021

Critères des propriétés fondamentales

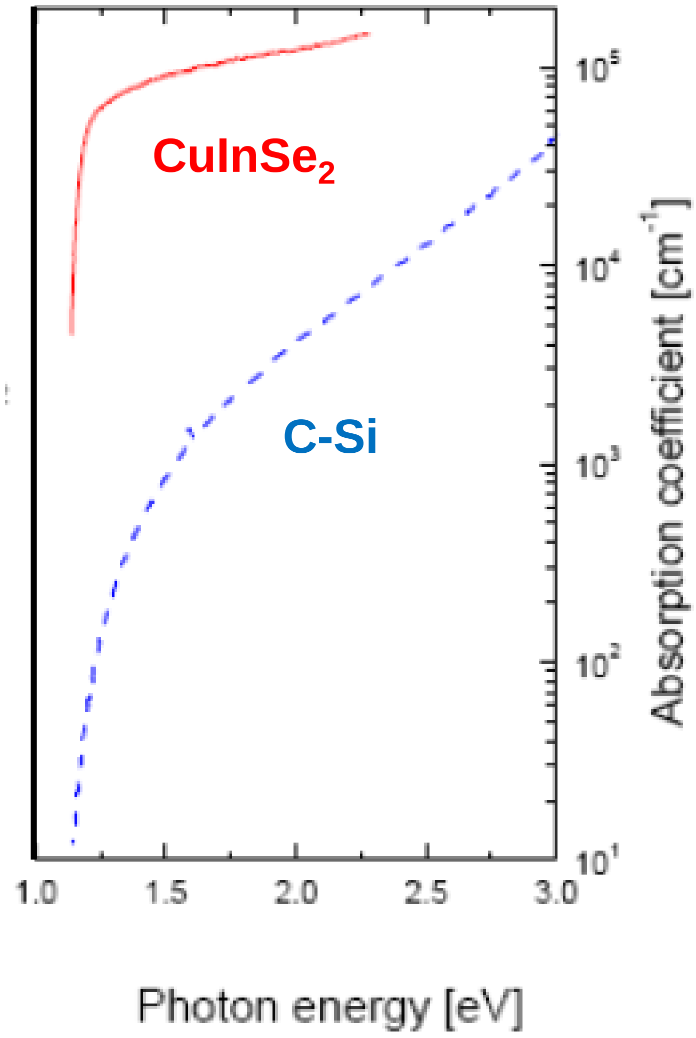
- Propriétés optiques
  - →Bonne absorption de la lumière visible
  - →Coefficients d'absorption élevés ou piégeage optique efficace
- Propriétés électriques
  - → bonne passivation en volume et aux interfaces
  - →jonctions ou hétérojonctions p-n (ou p-i-n) de qualité

Propriétés optiques

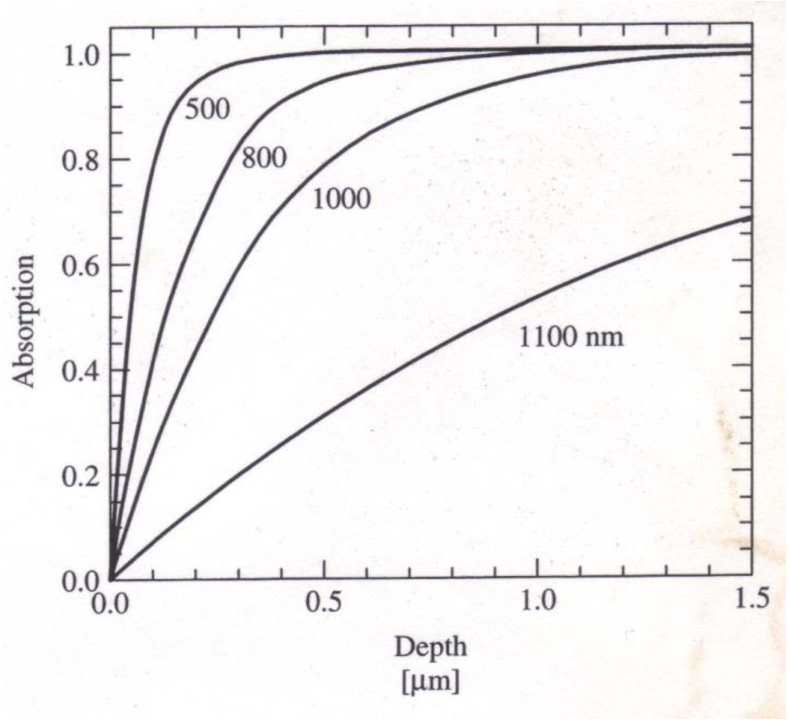
Gap indirect (Si) Gap direct (GaAs)



Coefficients d'absorption



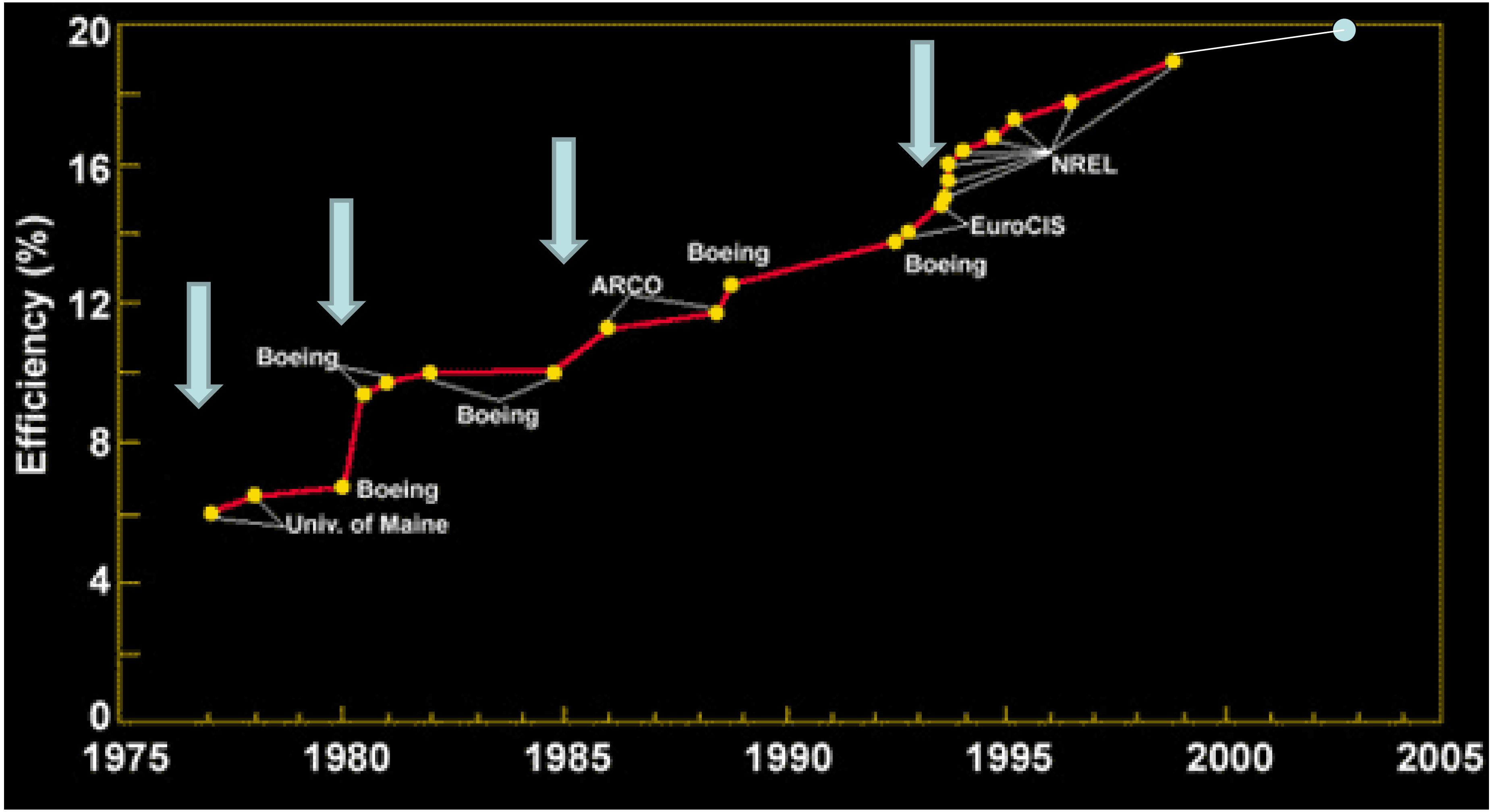
Profondeur de pénétration de la lumière $CuIn_{0,8}Ga_{0,2}Se_2$



Daniel Lincot, Collège de France, 23/02/2022

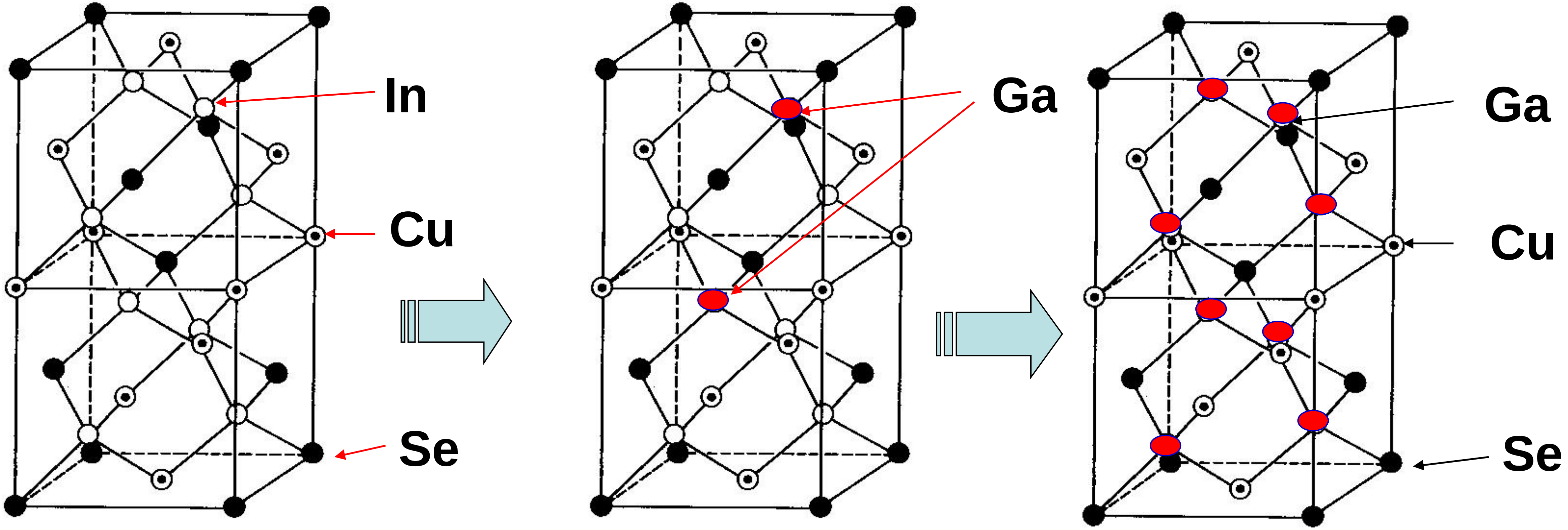
La longue route de la technologie CIGS

2022 : 23,4%



Site Web du National Renewable Energy Laboratory

$CuInSe_2$ $Cu(In,Ga)Se_2$ $CuGaSe_2$

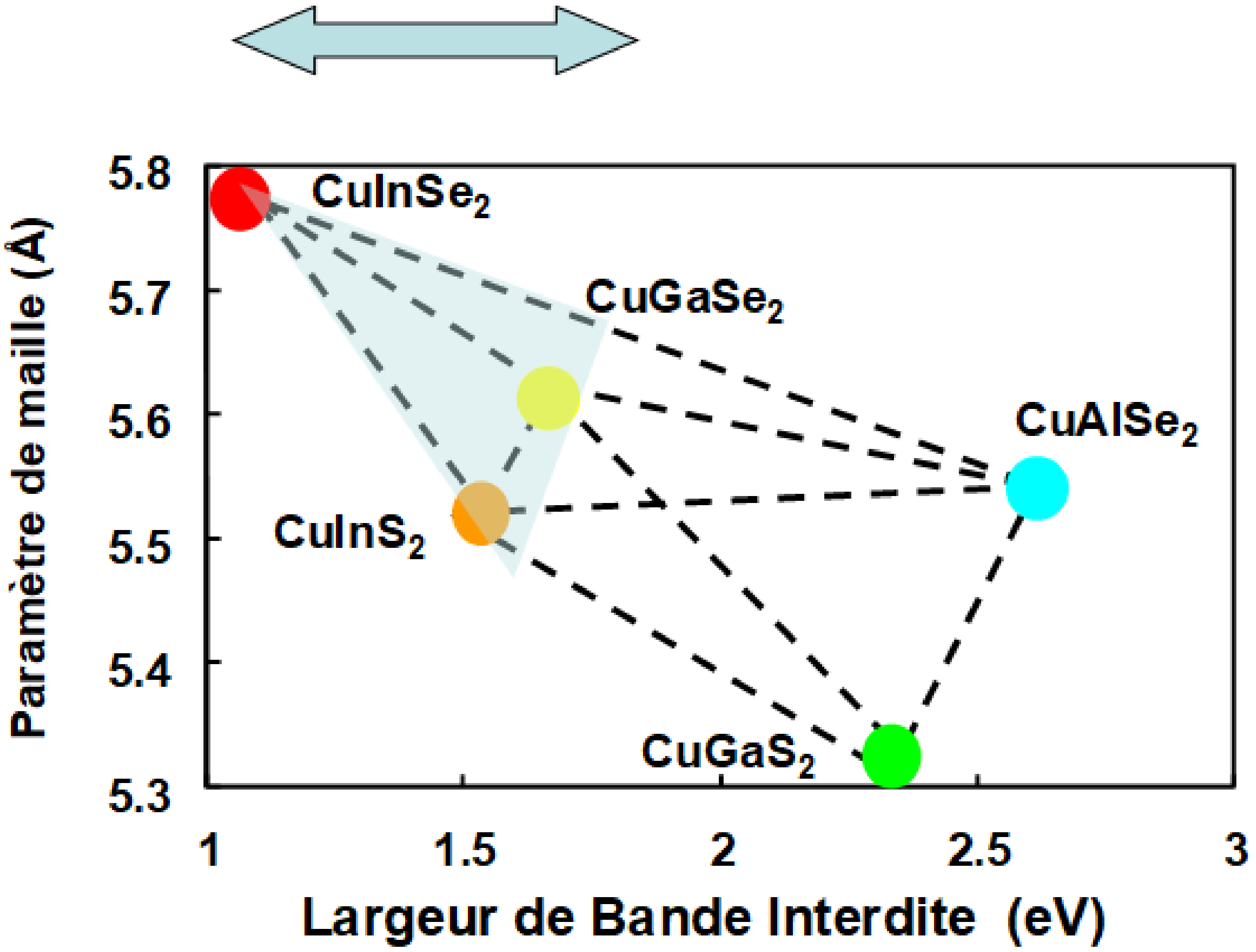


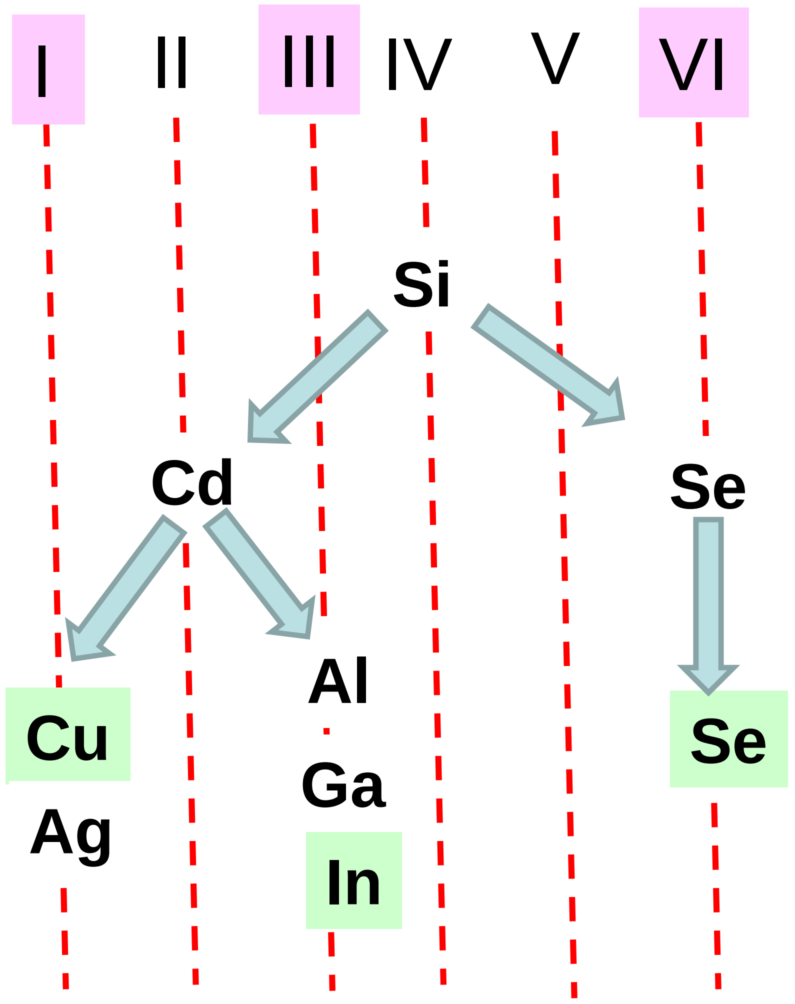
« CIS » 1 eV « CIGS » 1,15 eV « CGS » 1,7 eV

Daniel Lincot, Collège de France, 23/02/2022

Et toute la famille « un-trois-six-deux » : $(Cu,Ag)(In,Ga,Al)(S,Se,Te)_2$

→ Ingénierie de composition, bande interdite, paramètre de maille…

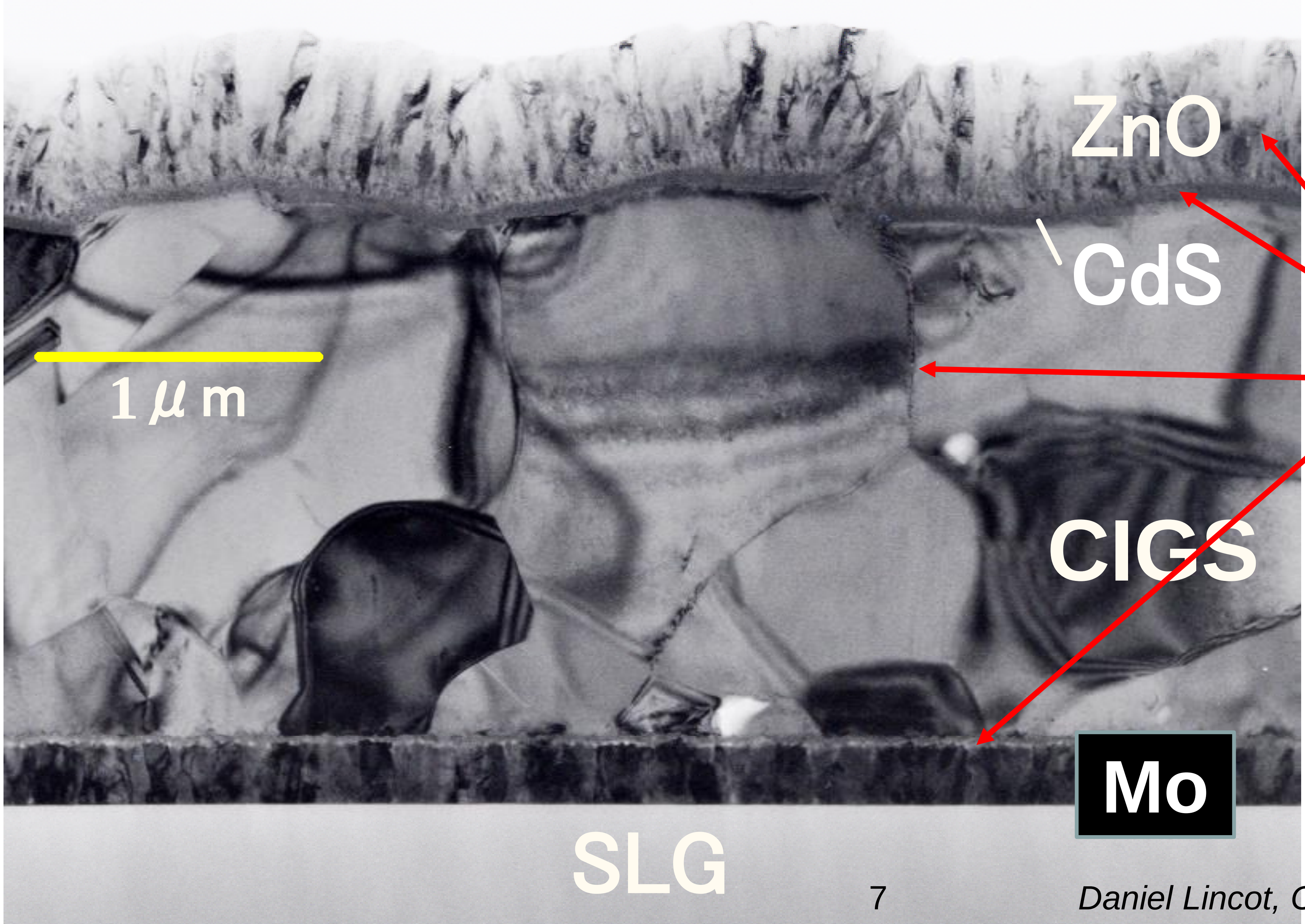




Les champions: $Cu(In,Ga)Se_2$ $Cu(In,Ga)(S,Se)_2$

Daniel Lincot, Collège de France, 23/02/2022

Propriétés électriques et structurales : coupe transverse cellules CIGS (>15% de rendement)



Des défauts structuraux à foison qui devraient condamner la cellule

Microcristaux
Nanocristaux
Joints de grains
Interfaces complexes

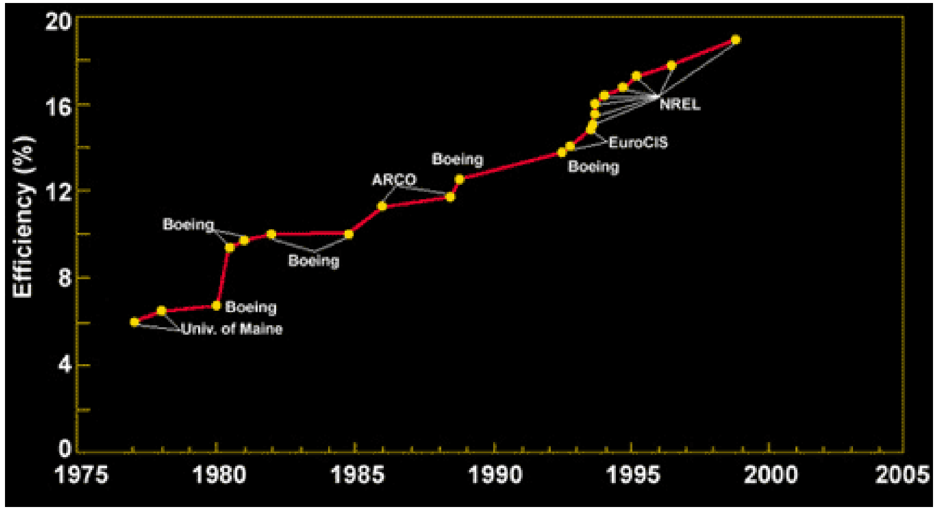
Et pourtant…

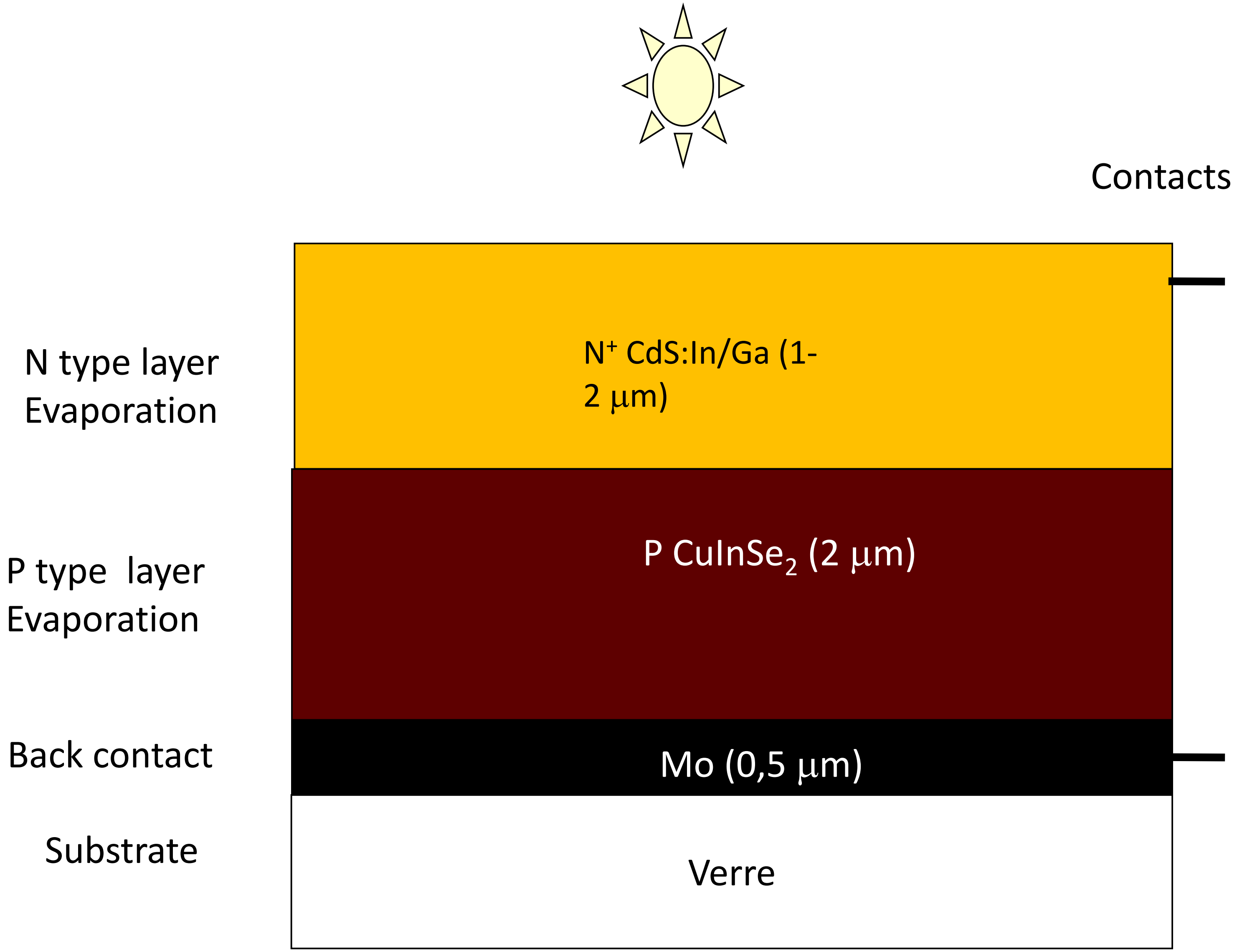
ça marche !

Propriétés de passivation
Structure électronique
Exceptionnelles

<1980

8%

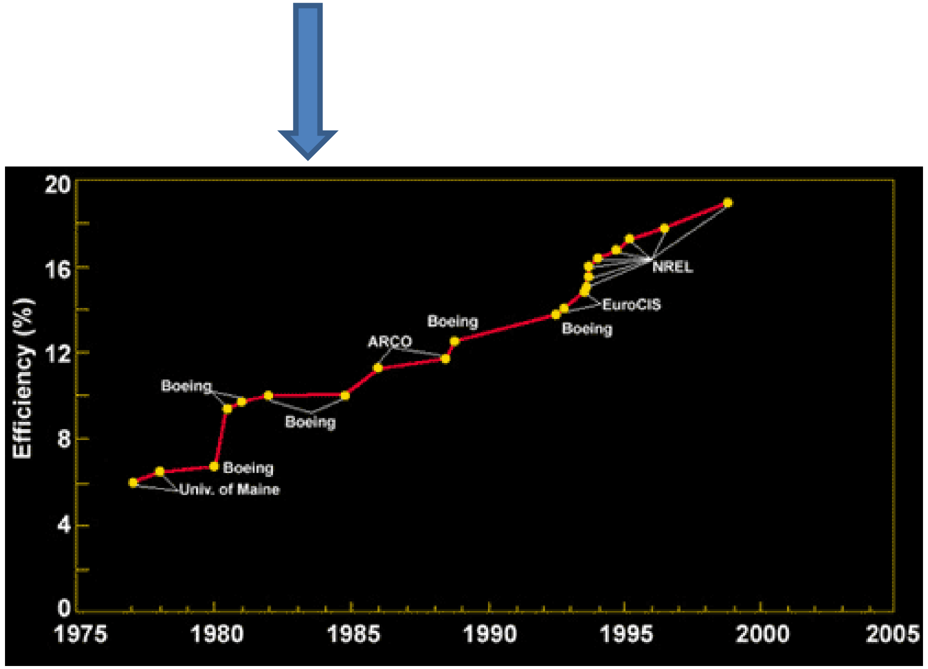


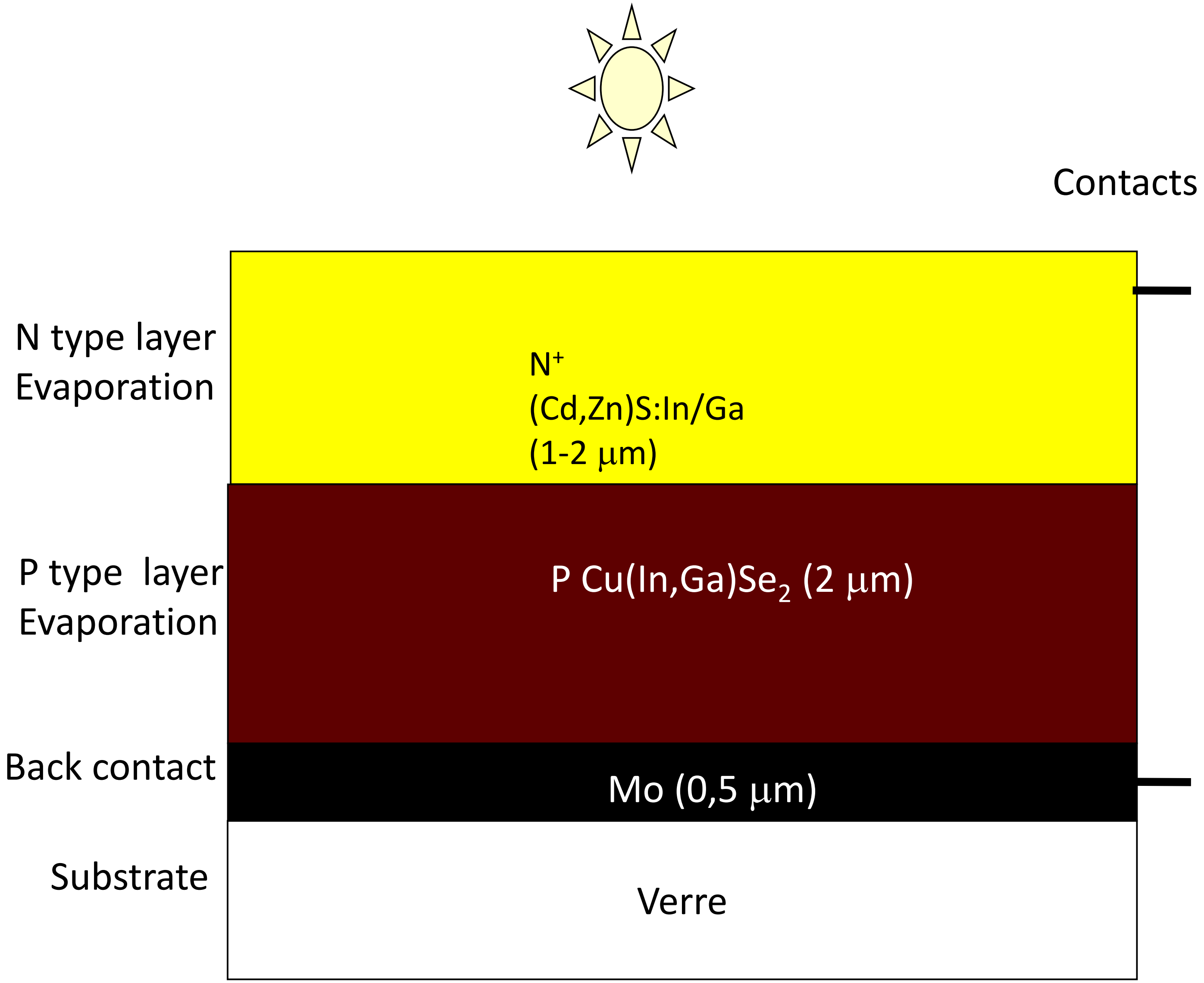


Not to scale

1985

12%





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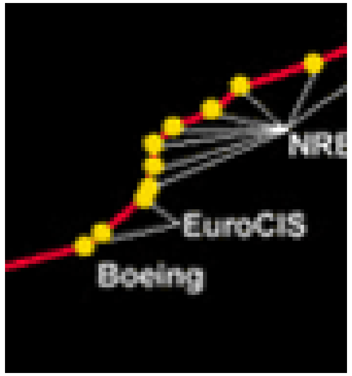
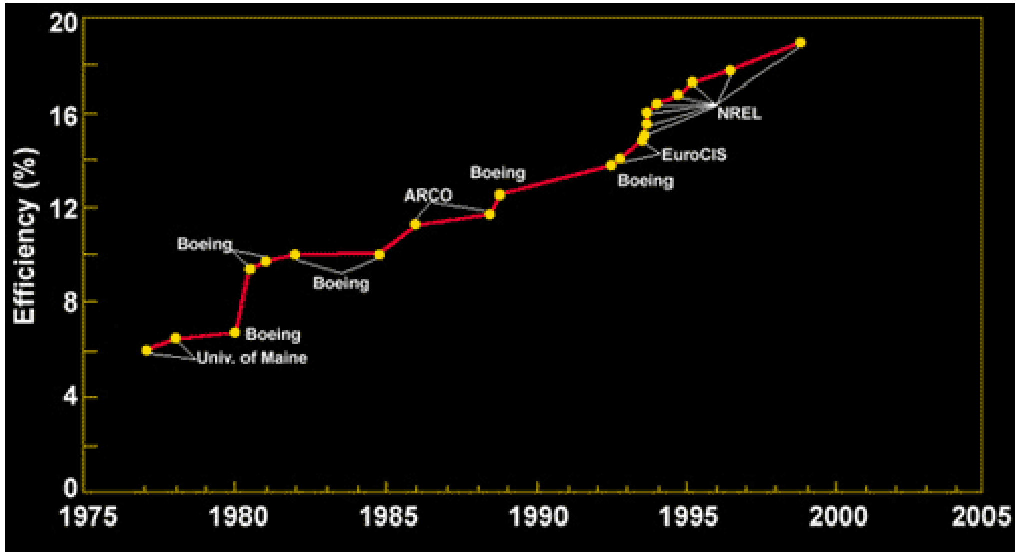
Avancées majeures

1994 15%





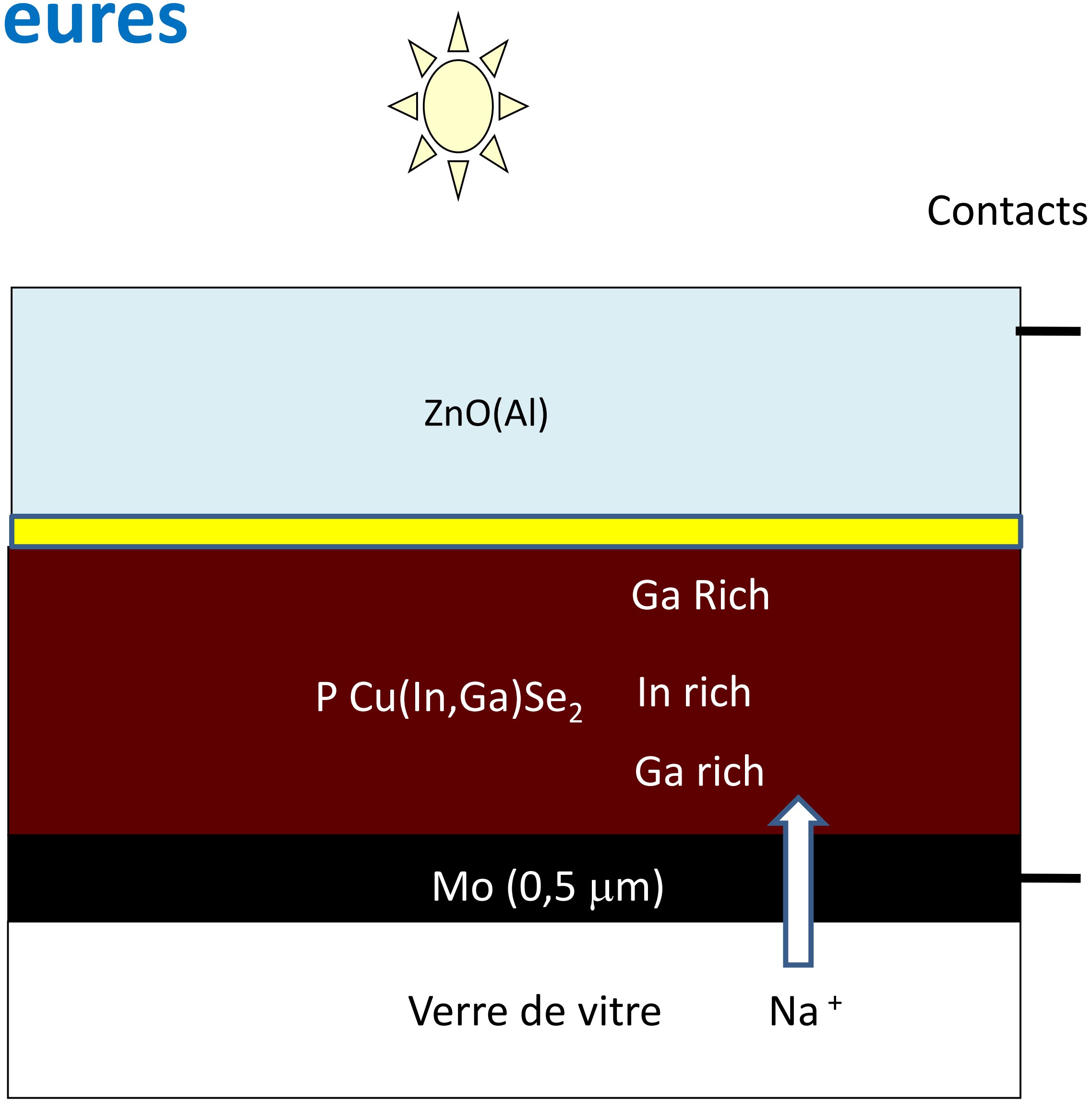
ZnO(Al)
By Sputtering

CdS by
Solution (CBD)

P type layer
By coEvaporation
3 stage process

Back contact

Substrate



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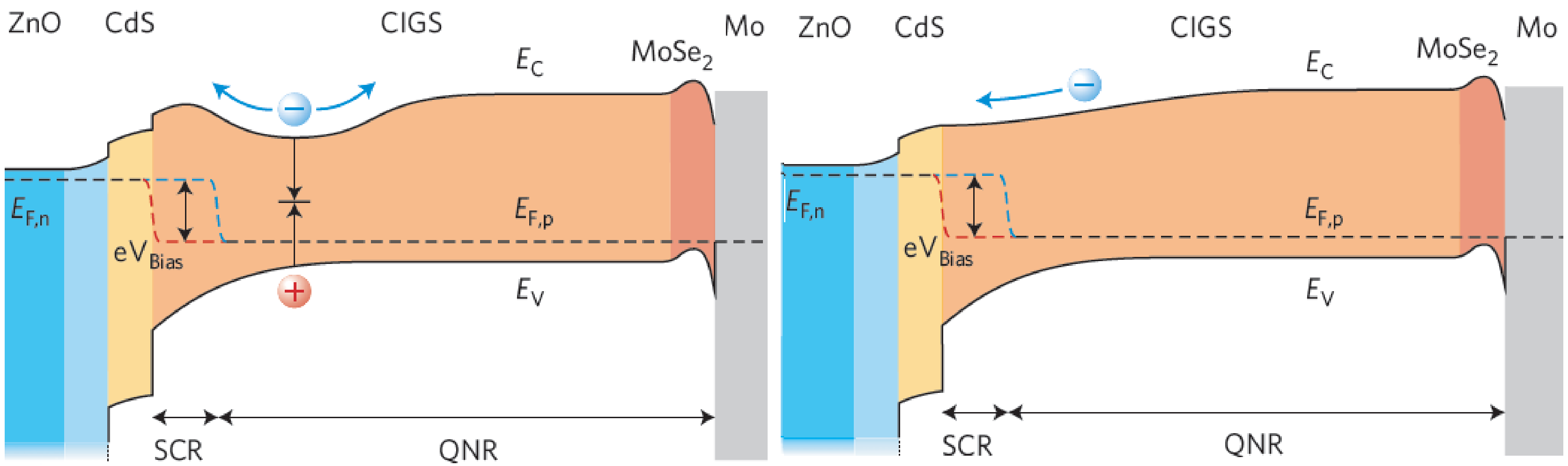
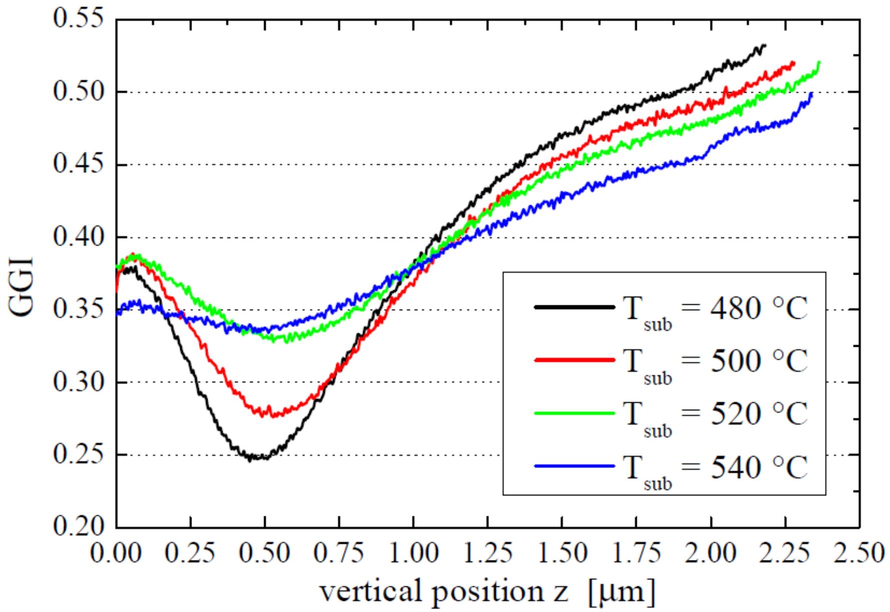
Optimisation des gradients de composition dans la couche de CIGS

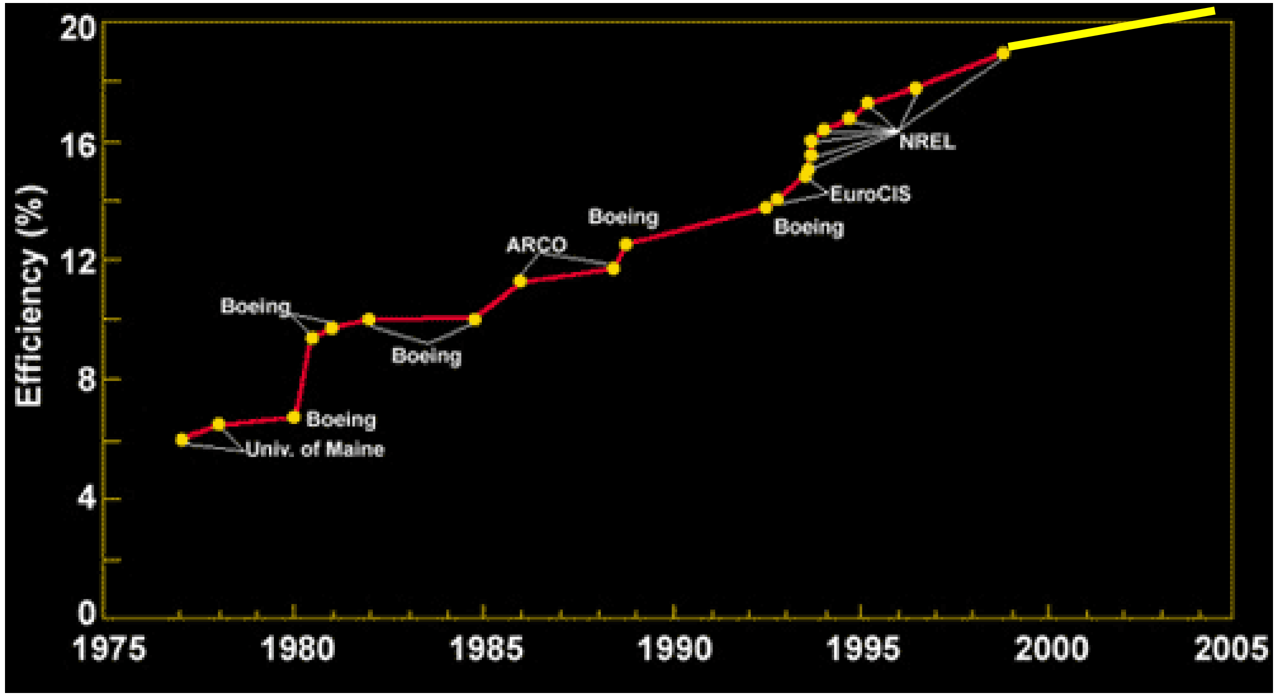


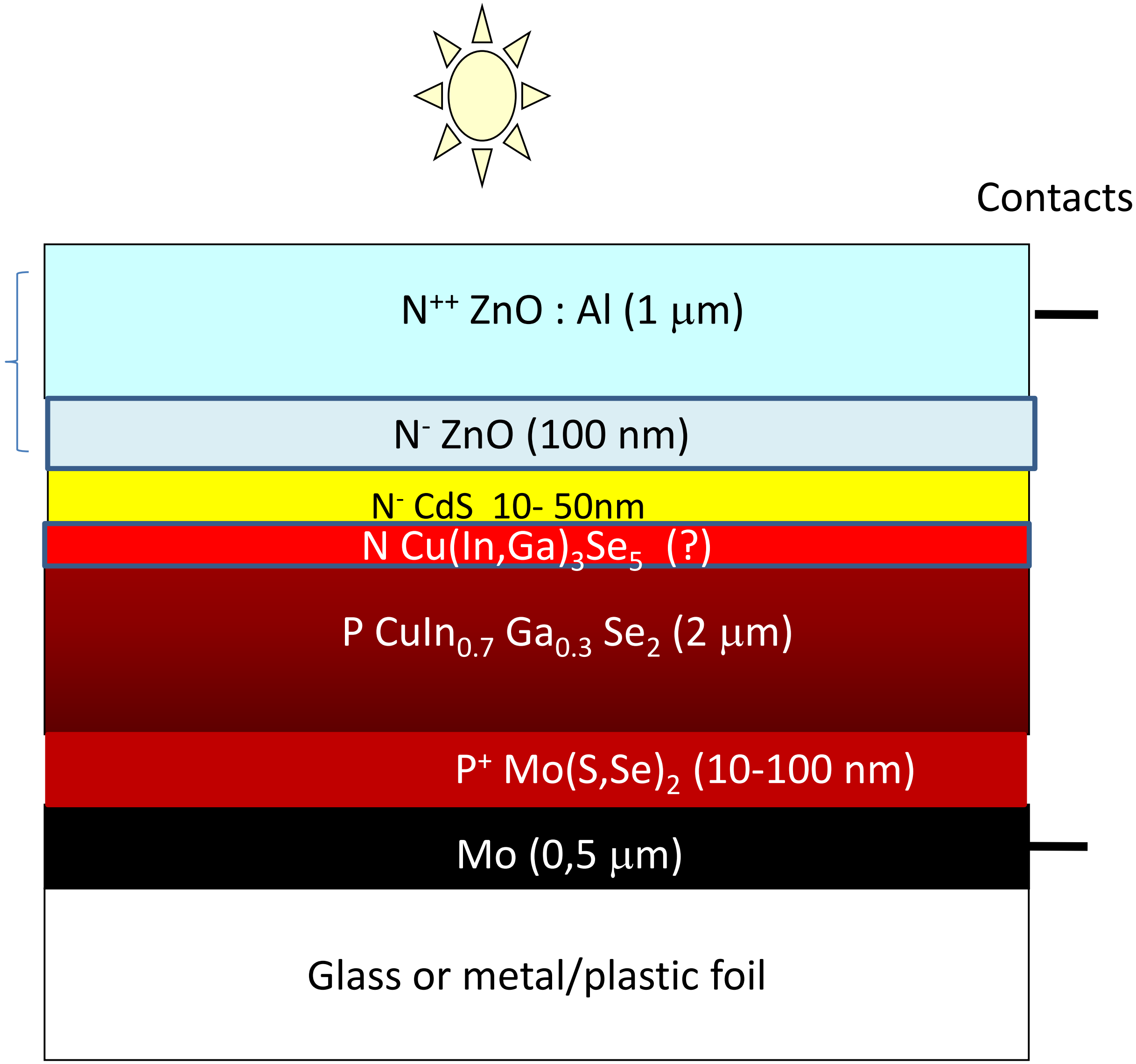


Corrélation avec le rendement de conversion

Daniel Lincot, Collège de France, 23/02/2022

2010
19%

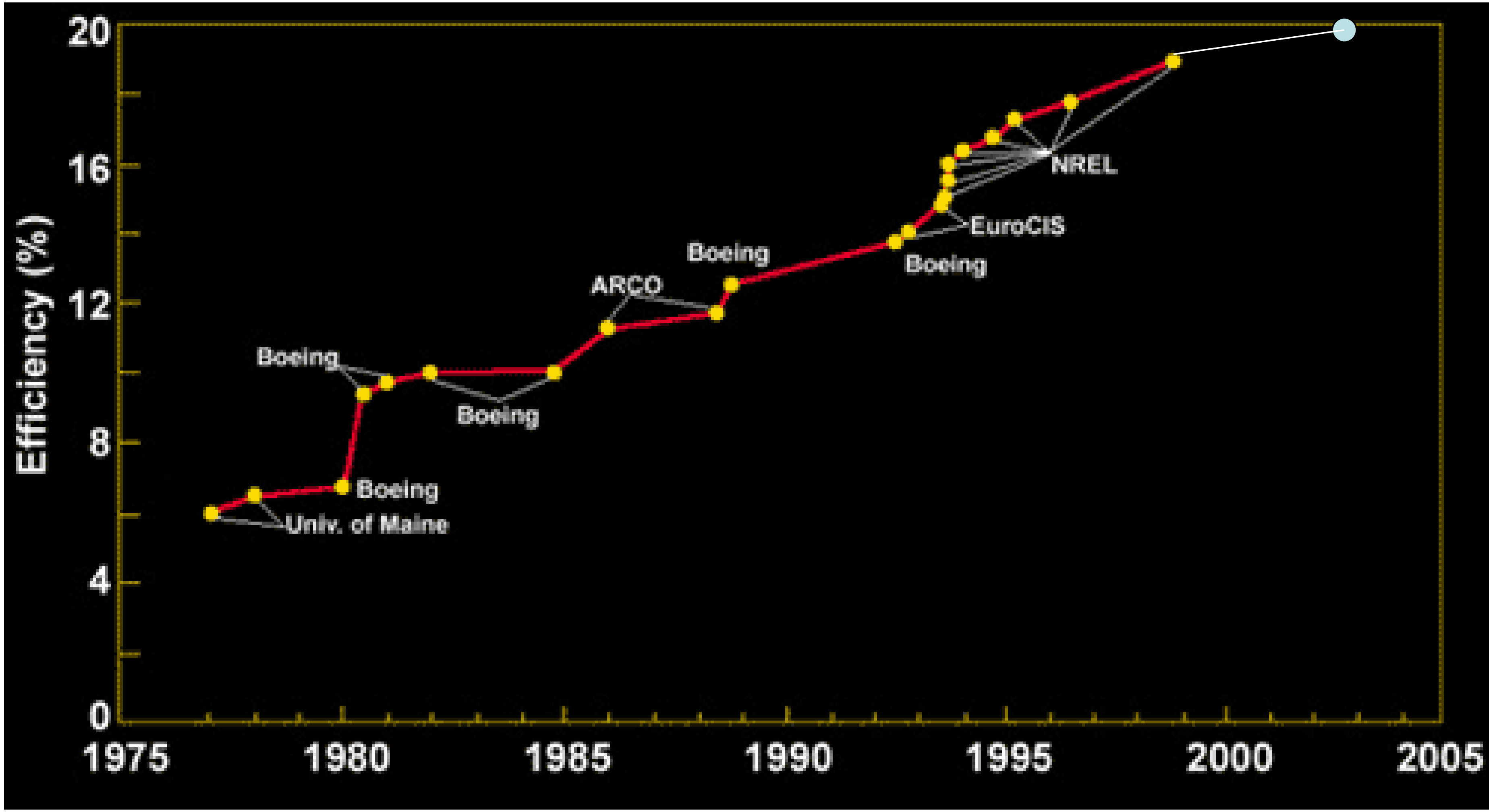




Not to scale

La longue route de la technologie CIGS

2021
23,35 %



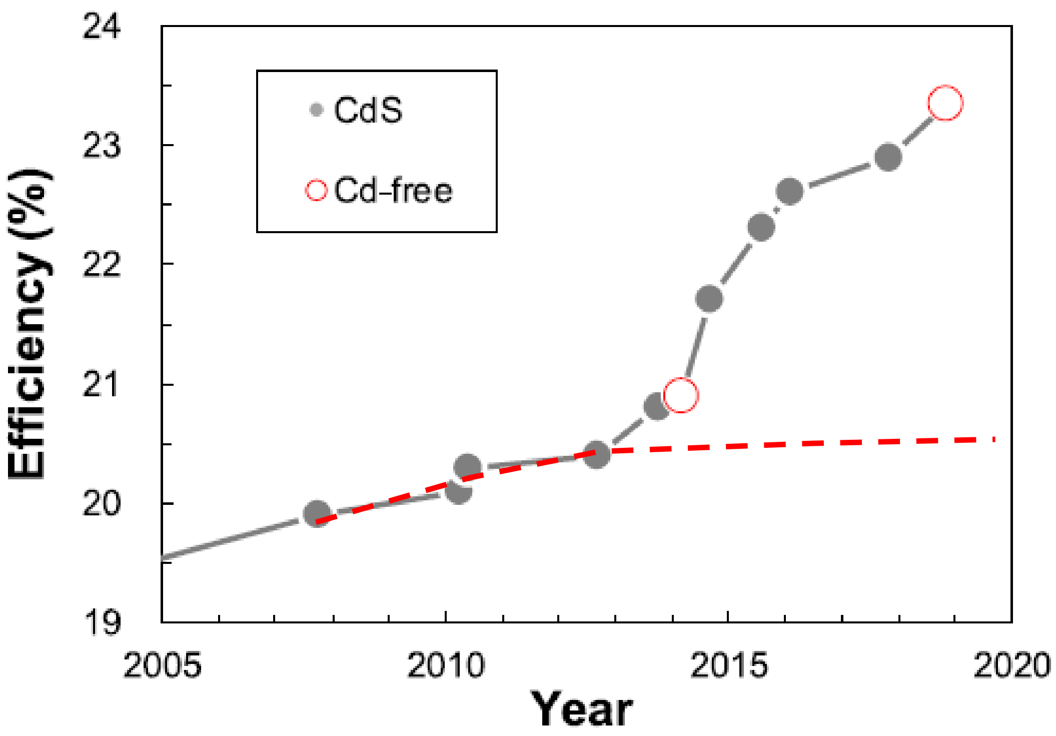
Site Web du National Renewable Energy Laboratory

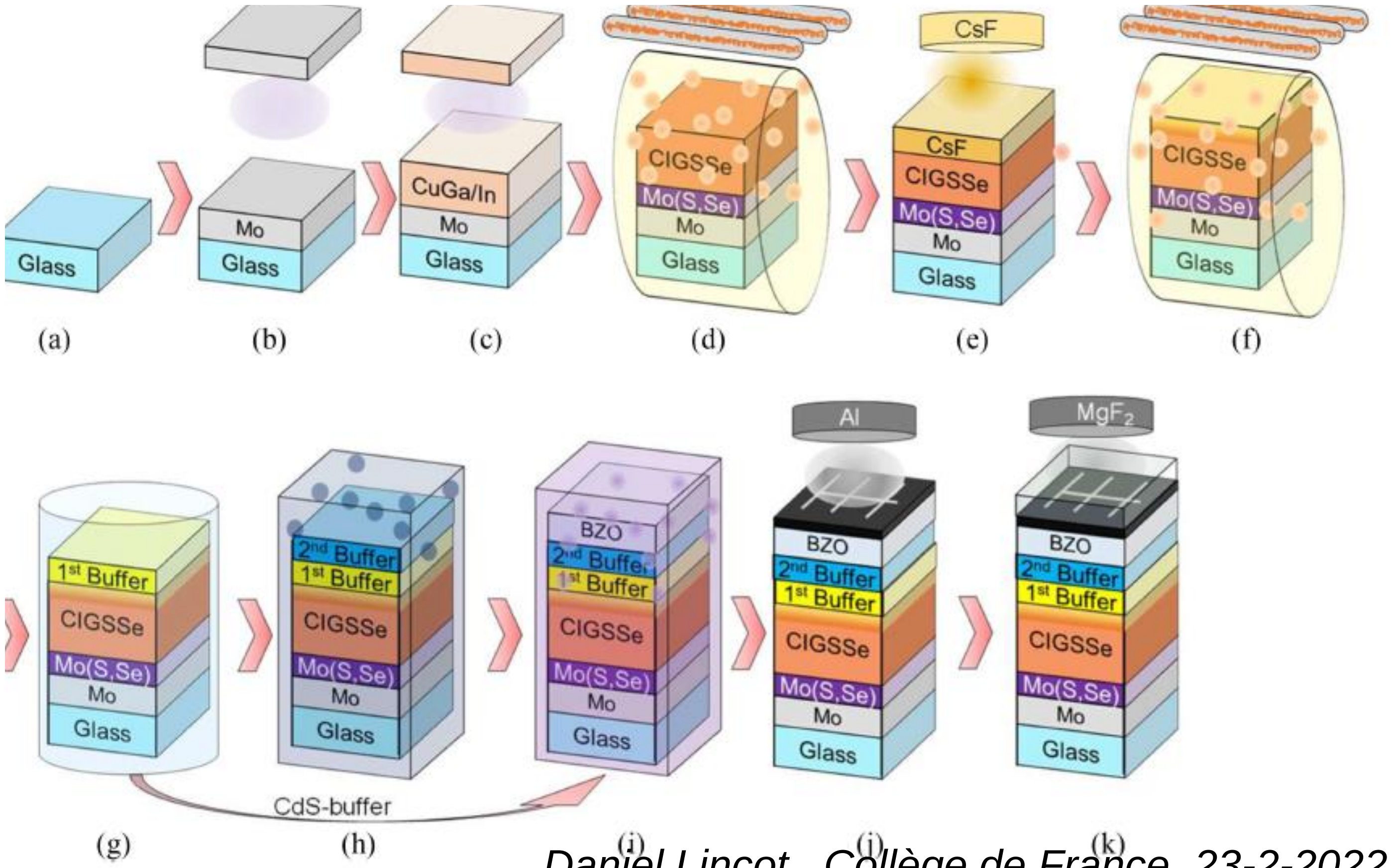
➢ **2015**
→ Ajout alcalins (K,Rb,Cs) en surface
→ Remplacement CdS par Zn(O,S) par CBD

Cd-Free $Cu(In,Ga)(Se,S)_2$ Thin-Film Solar Cell With Record Efficiency of 23.35%

Motoshi Nakamura, Koji Yamaguchi, Yoshinori Kimoto, Yusuke Yasaki, Takuya Kato, and Hiroki Sugimoto

Year	Buffer	Efficiency (%)	V_{oc} (mV)	J_{sc} (mA/cm²)	FF (%)	E_g (eV)	$V_{oc,def}$ (mV)	Test Center
2017	CdS	22.92	746	38.5	79.7	1.13	384	AIST
2019	$Zn(O,S,OH)_x/Zn_{0.8}Mg_{0.2}O$	23.35	734	39.6	80.4	1.08	350	AIST

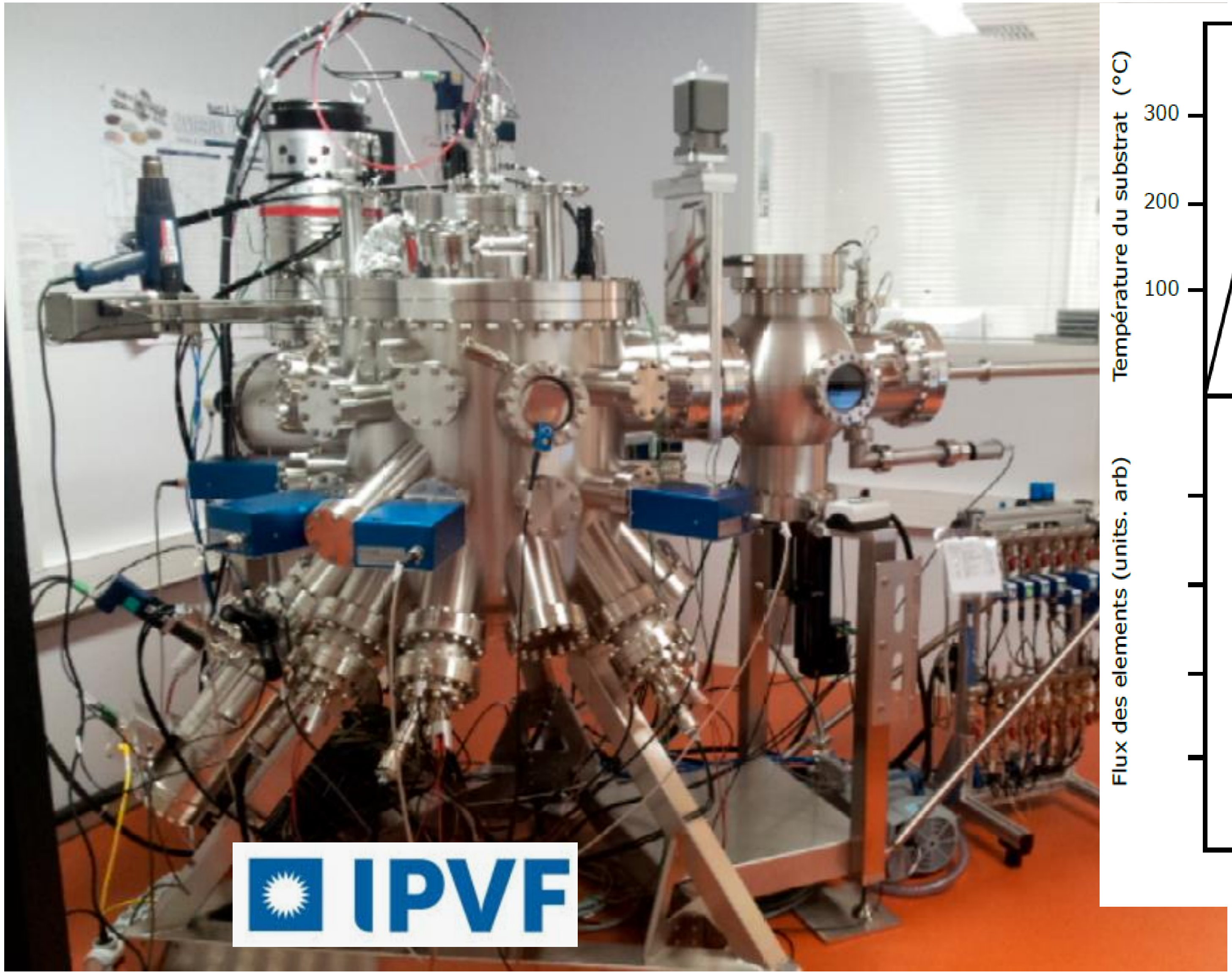


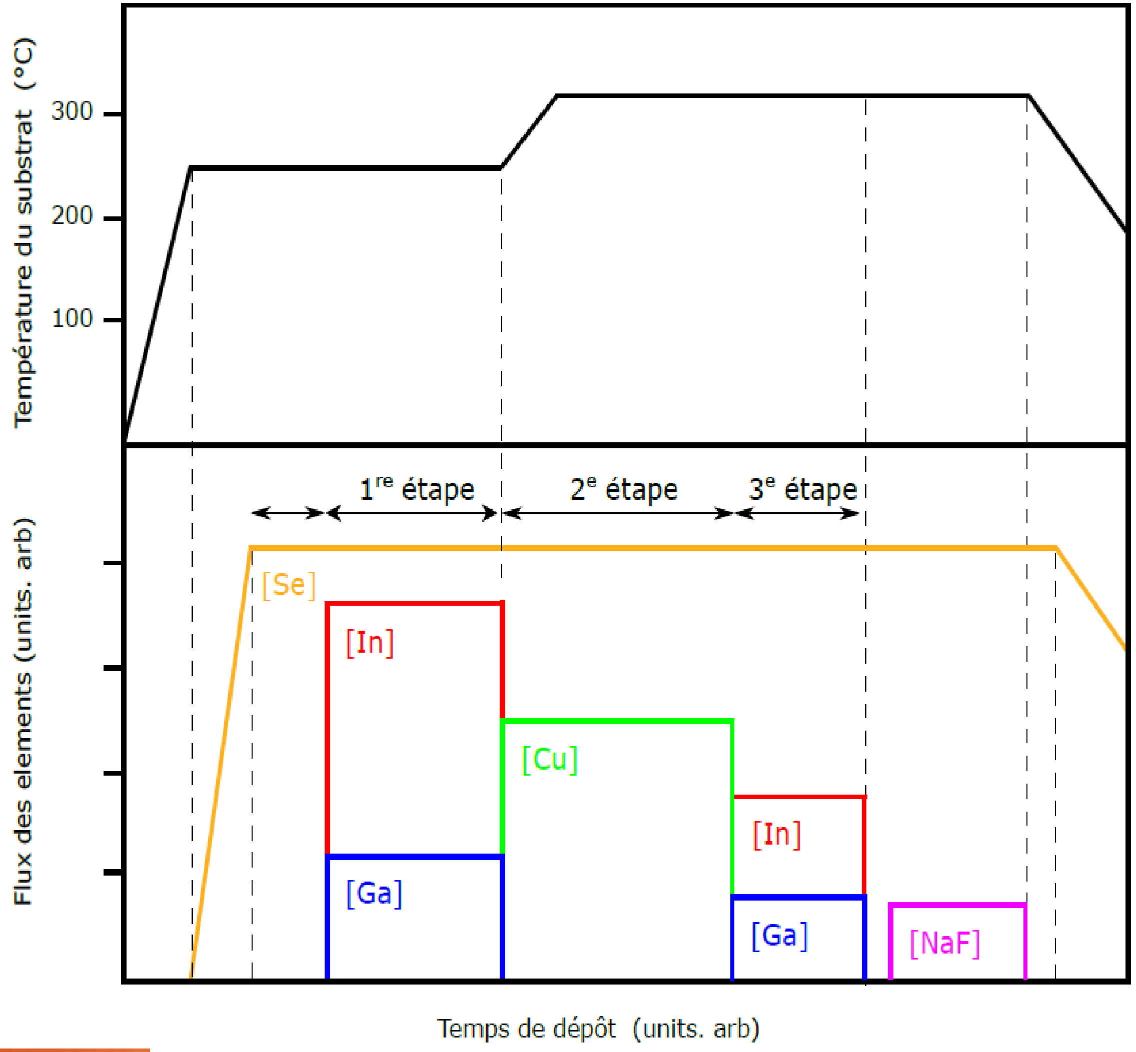


Coévaporation sous ultravide : la méthode « Ferrari »

Sources Cu,In,Ga,Se, NaF,KF… → évaporation thermique (300-1500°C) → dépôt sur verre/Mo (550°C)

Grand contrôle, haute pureté, analogue à l'épitaxie par jets moléculaires (EJM,MBE)

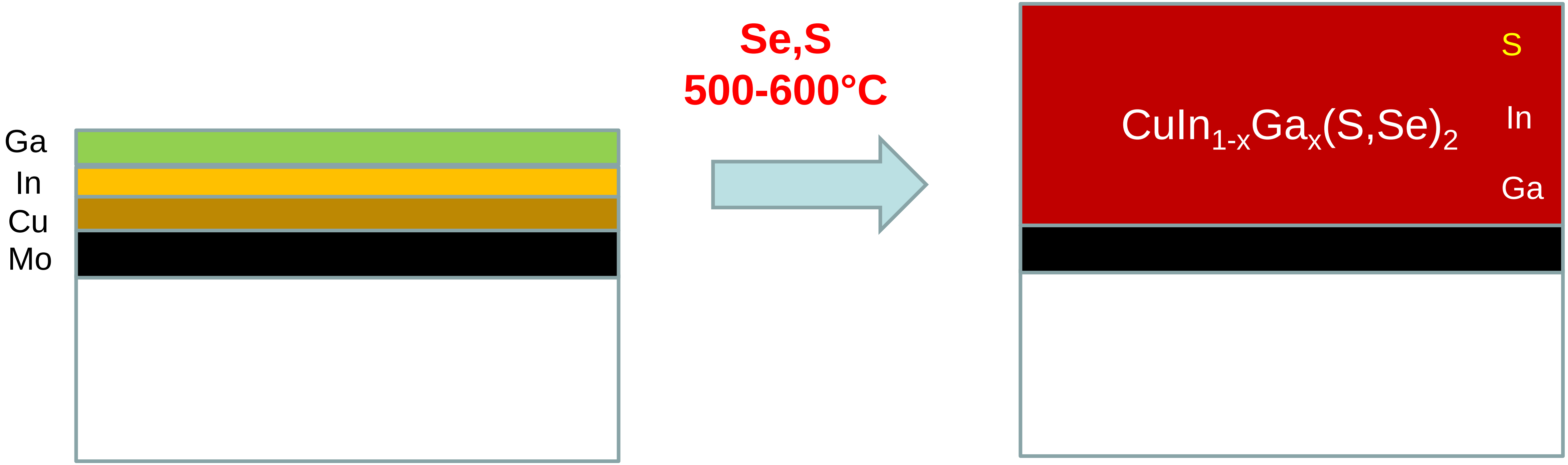




Méthode en deux étapes : procédé « Pizza »

Methode Solar Frontier (23,4 %), Avancis…intérêt industriel (1 GW)

- Dépôt de couches métalliques (Sputtering)
- Sélénisation /sulfuration



Daniel Lincot, Collège de France, 23/02/2022

Experimental results (b): The quaternary system Cu-In-Al-Se

Polycrystalline Phases during the formation of $Cu(In,Al)Se_2$

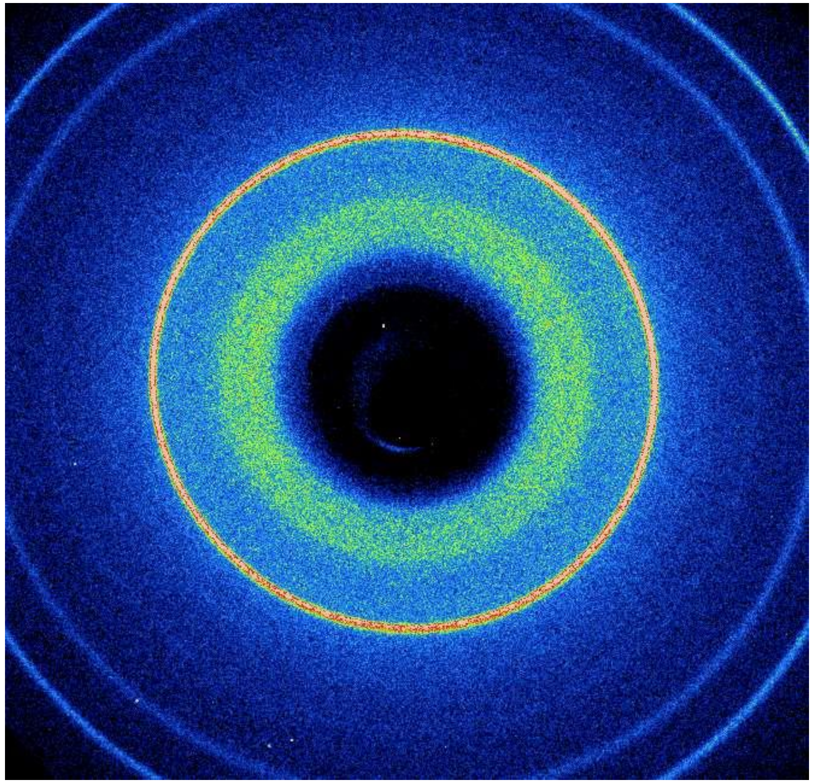
Metals, alloys

Se crystallizes

In melts,
$CuIn_2$ decomposes

Binary selenides

Chalcopyrite



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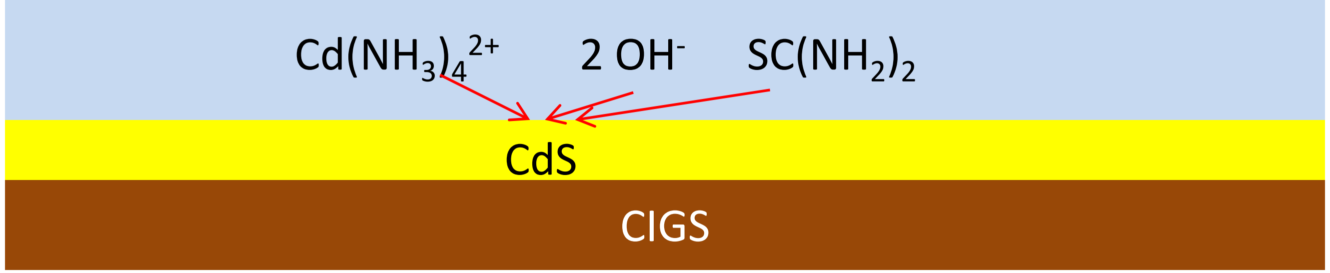
Dépôt chimique en solution (CBD) : analogue CVD en solution

$$M(NH_3)_4^{2+} + SC(NH_2)_2 + 2\,OH^- \rightarrow MS + CN_2H_2 + 2H_2O$$

M= Cd,Zn,Pb….

Contribution majeures CNRS/Chimie Paristech (1991-1994) : CdS,Zn(O,S) puis IRDEP, puis IPVF (→ 2021)

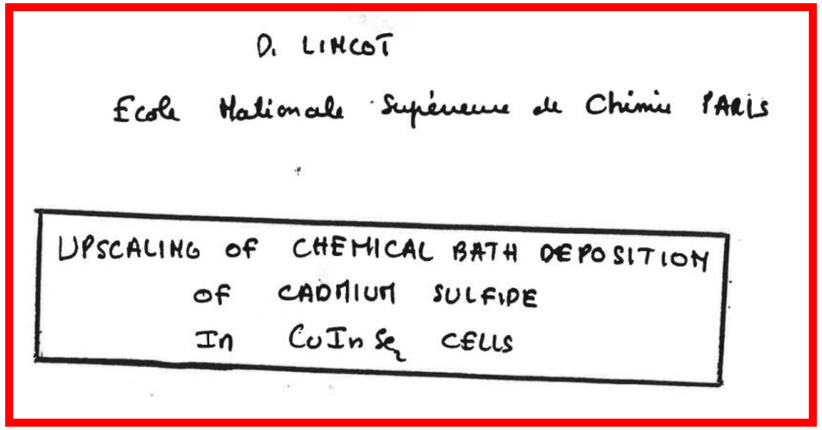
- → Invention réacteur plat oscillant (Eurocis)→ standard industriel
- → Détermination du mécanisme et optimisation



T=60°C
Mileu aqueux
Temps de dépôt 15 min
Dépôt couvrant, épitaxie locale
Excellente homogénéité latérale

La méthode a supplanté les méthodes sous vide
Exemple phare de l’intérêt de la chimie en solution

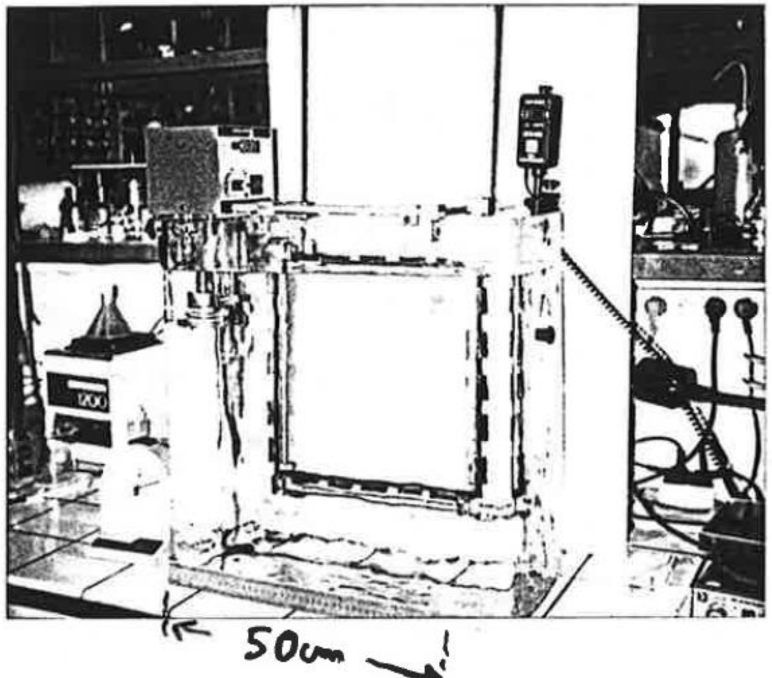
Eurocis Meeting, Naples (1993)


D. LINCOT

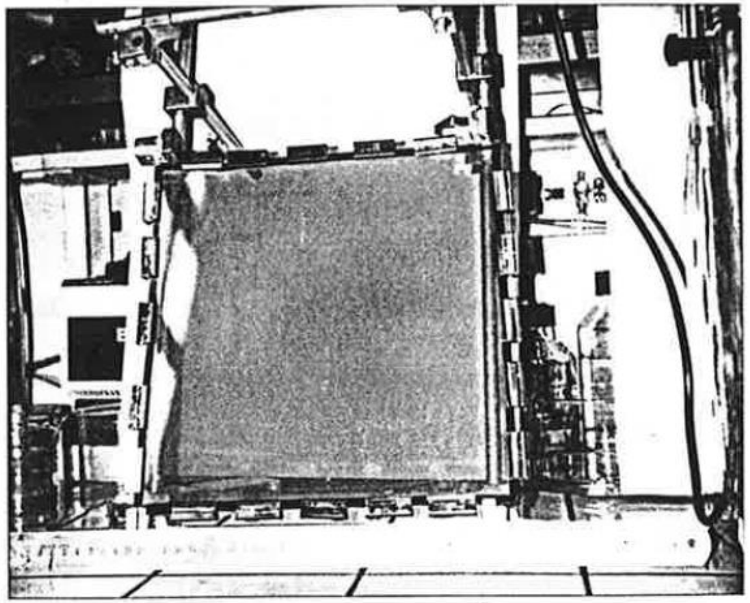
Ecole Nationale Supérieure de Chimie PARIS

UPSCALING OF CHEMICAL BATH DEPOSITION OF CADMIUM SULFIDE IN CuInSe$_2$ CELLS

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

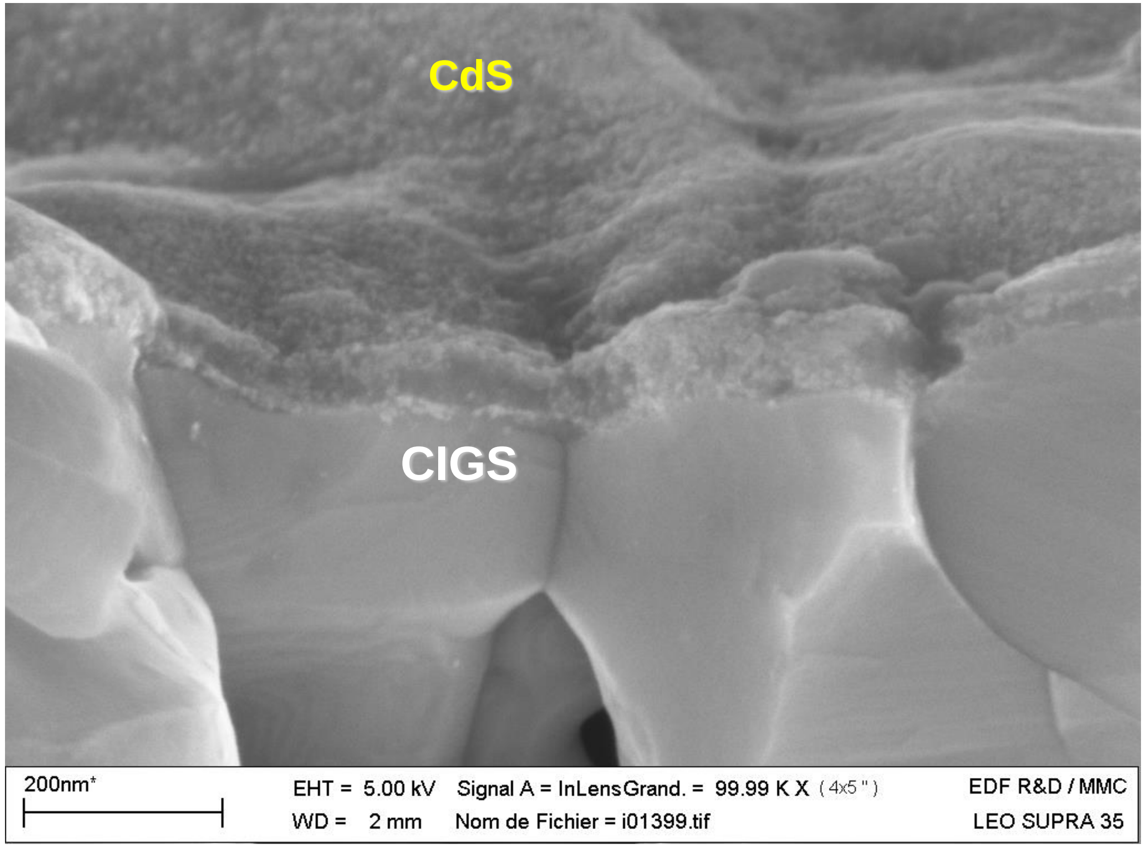


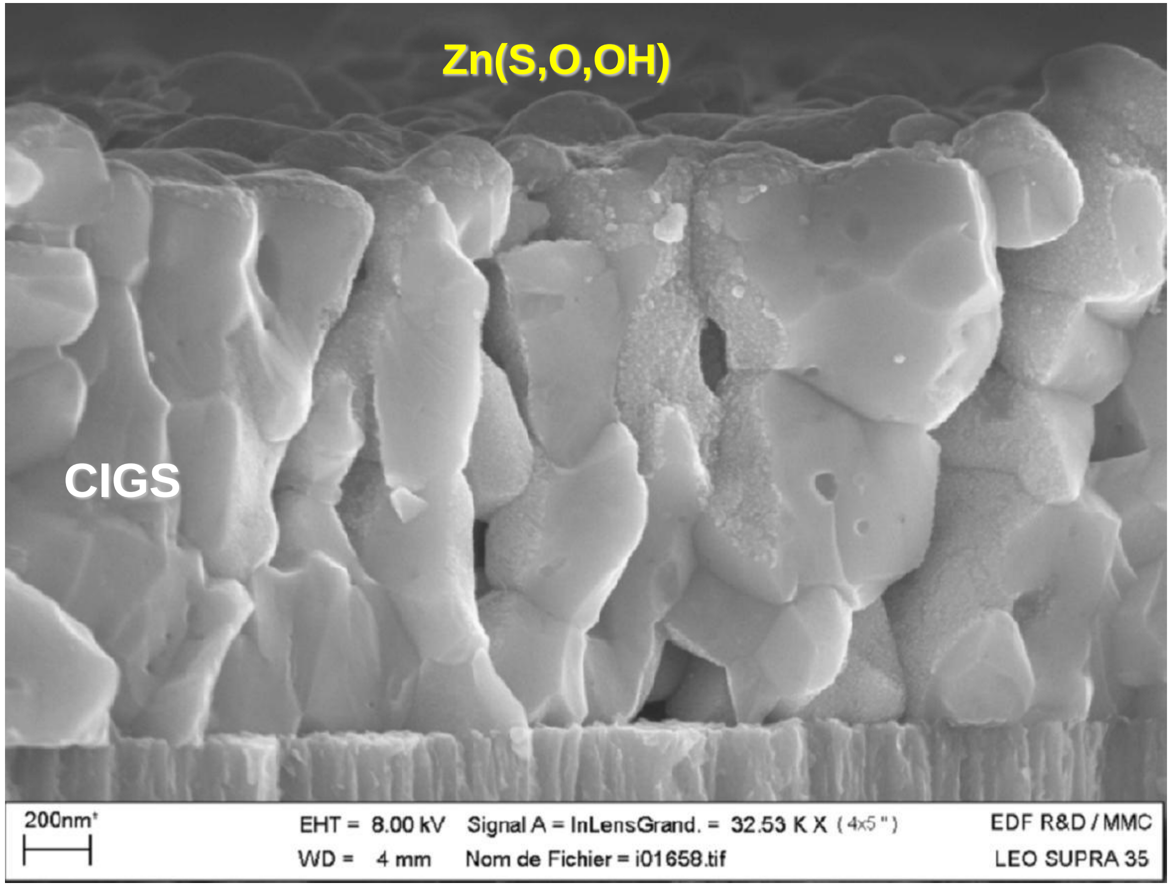
complete reactor, starting conditions for CdS deposition



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


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


Zn(S,O,OH)
CIGS
200nm*
EHT = 8.00 kV
Signal A = InLensGrand. = 32.53 K X (4x5")
EDF R&D / MMC
WD = 4 mm
Nom de Fichier = i01658.tif
LEO SUPRA 35

Growth Mechanism : Ion by Ion surface controlled process

A

Reversible adsorption of cadmium hydroxide species

$$Cd(NH_3)_4^{2+} + 2\,OH^- + Site \underset{k_{-1}^0}{\overset{k_1^0}{\rightleftharpoons}} Cd(OH)_{2ads} + 4\,NH_3$$

B

Formation of a surface complex with thiourea

$$Cd(OH)_{2\,ads} + S{=}C(NH_2)_2 \xrightarrow{k_2^0} [(Cd(S{=}C(NH_2)_2)(OH)_2]^*_{ads}$$

C

Formation of CdS with site regeneration

$$[(Cd(S{=}C(NH_2)_2(OH)_2]^*_{ads} \xrightarrow{k_3^0} CdS + CN_2H_2 + 2H_2O + Site$$

Successive atomic layer controlled growth
Quantitative analytical model established

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
A MEMBER OF THE SINGULUS GROUP
04-2010 - 11

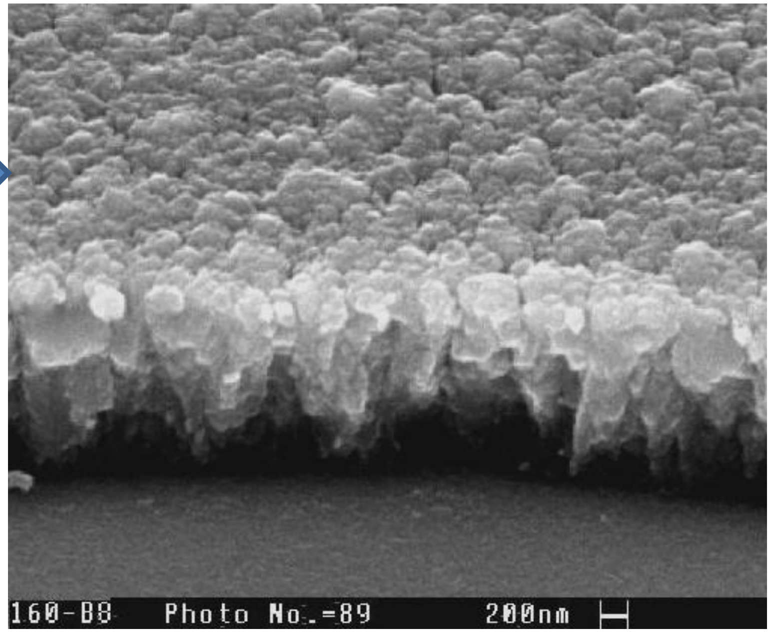
Automated Experimental Setup under production conditions

- Substrate size:
  1200 x 600mm
  600 x 900 mm
  1400 x 1100 mm
- Automated heating
- Automated wobbling (movement)
- Automated dosage

Synthèse électrochimique

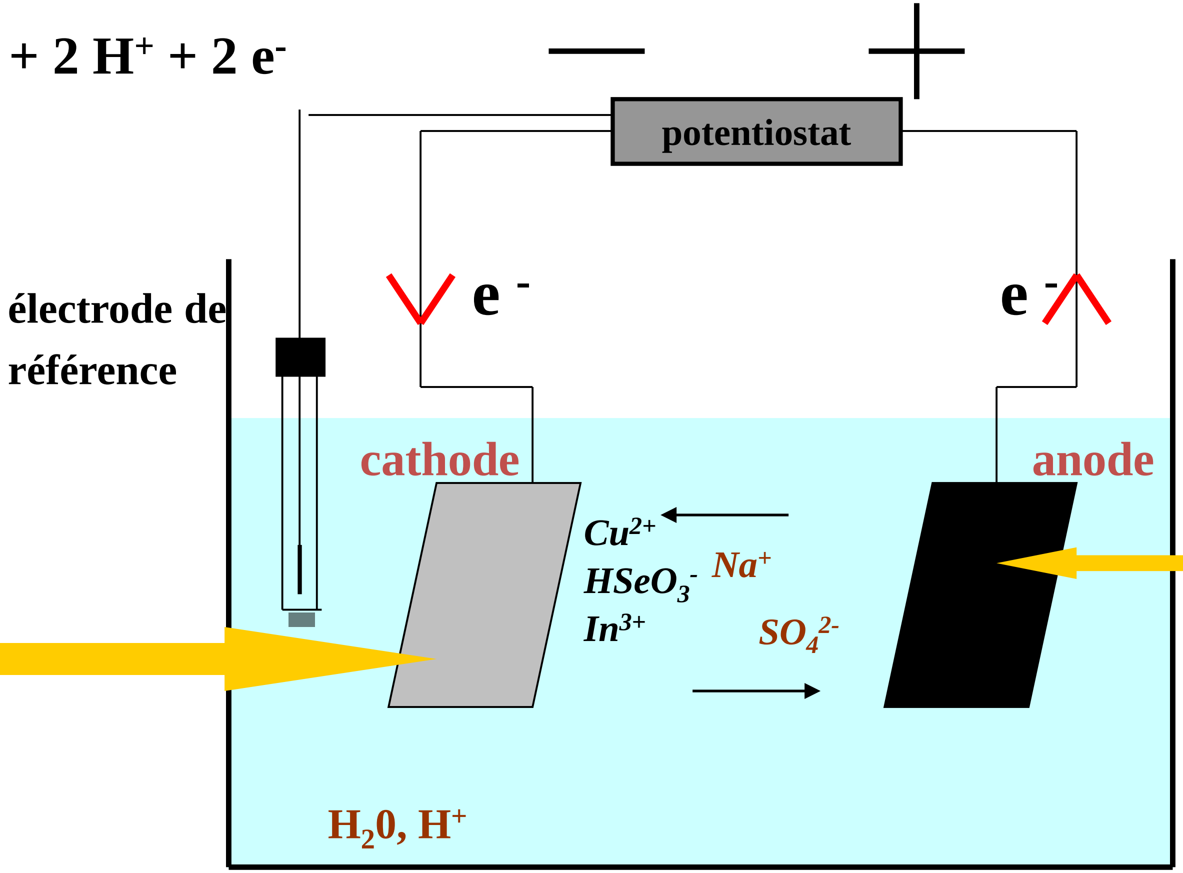
Réaction globale à la cathode

$$Cu^{2+} + In^{3+} + 2HSeO_3^- + 10\ H^+ + 13\ e^- \rightarrow CuInSe_2 + 6\ H_20$$

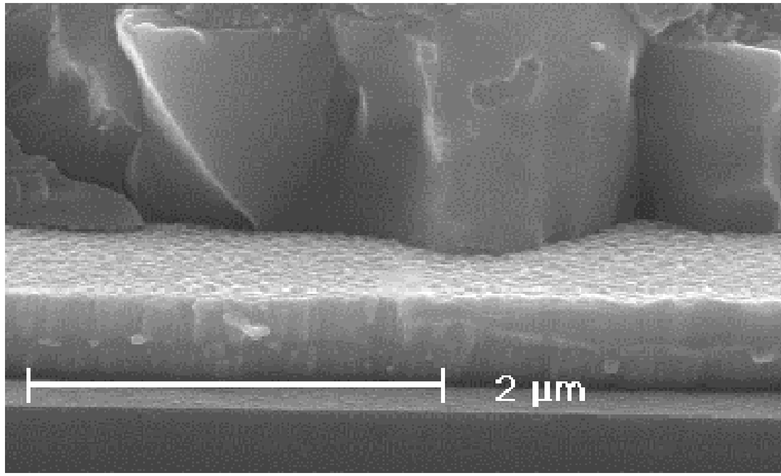


Réaction à l'anode

$$H_2O \rightarrow ½\ O_2 + 2\ H^+ + 2\ e^-$$



Recuit thermique sous P_{atm} sous pression Se ou S



Daniel Lincot, Collège de France, 23/02/2022

Solar Energy 175 (2018) 2–8

An overview on electrodeposited $Cu(In,Ga)(Se,S)_2$ thin films for photovoltaic devices

V. Bermudez

Solar Frontier KK, Technology Division, 123-1 Shimokawairi, Atsugi-shi, Kanawaga 243-0206, Japan

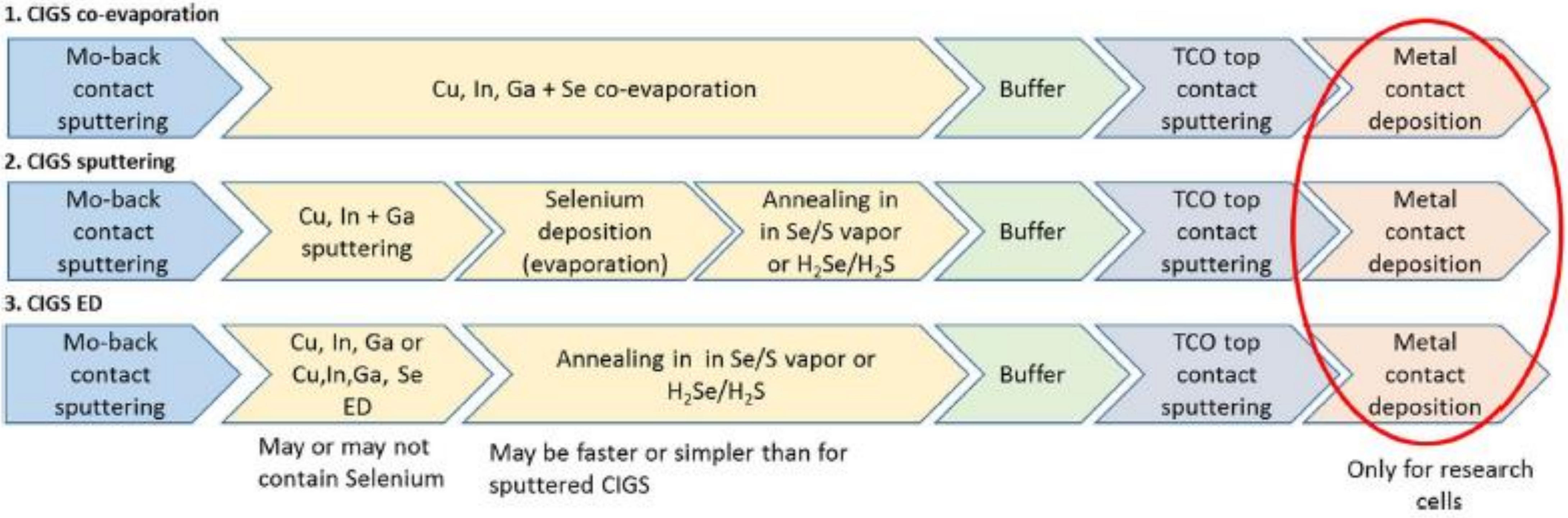
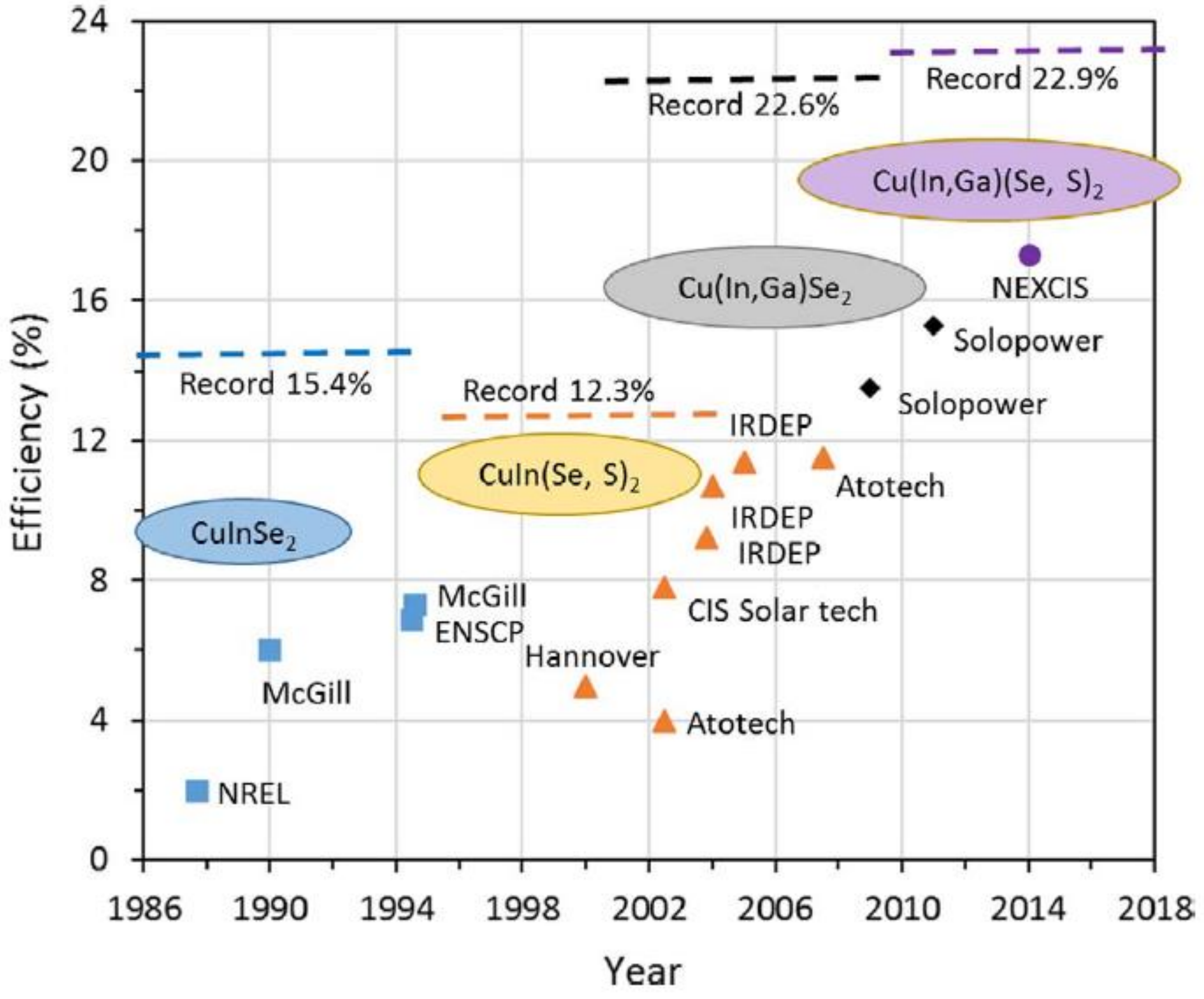


Fig. 1. Main industrial manufacturing processes for CIGS and potential variables.

Daniel Lincot, Collège de France, 23/02/2022

La longue marche de la technologie d'électrolyse vers l'industrialisation



Evolution des rendements record technologie électrochimique

V. Bermudez Solar Energy 175 (2018) 2–8

1994 CNRS-ENSCP (6,4%)

2002 IRDEP (CNRS-EDF-ENSCP) (11,3%)

2014 NEXCIS[sas] (EDF)(17,3%)

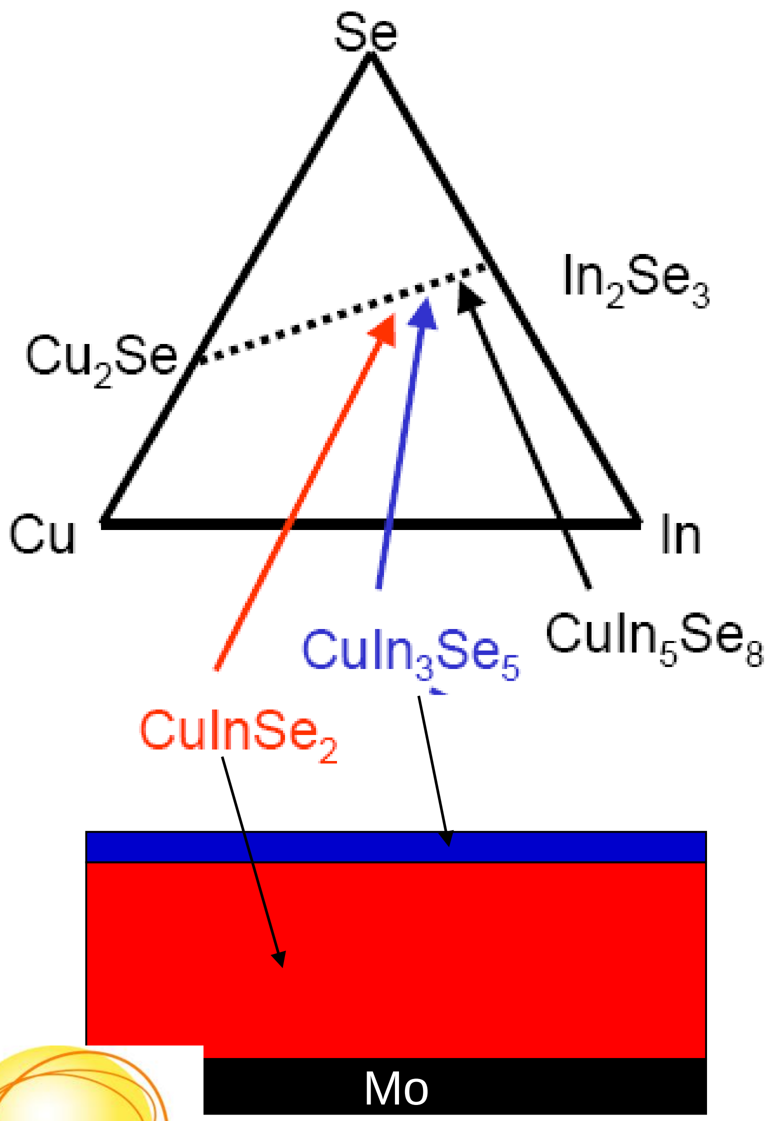
2014 NEXCIS[sas] (EDF) : modules 60x120 cm^2 (14%)

2021 Création de SOY PV[sas] (D. Lincot) <--> IPVF-UPSaclay

Modules flexibles ultralégers par électrolyse

Autre procédé électrochimique industrialisable :
Electrodépôt de ZnO : $Zn^{2+} + ½ O_2 + 2e^- \rightarrow ZnO$
Découverte CNRS-ENSCP 1996
IRDEP 2010

Les secrets du CIGS : Grande tolérance aux écarts à la stoéchiométrie (I)



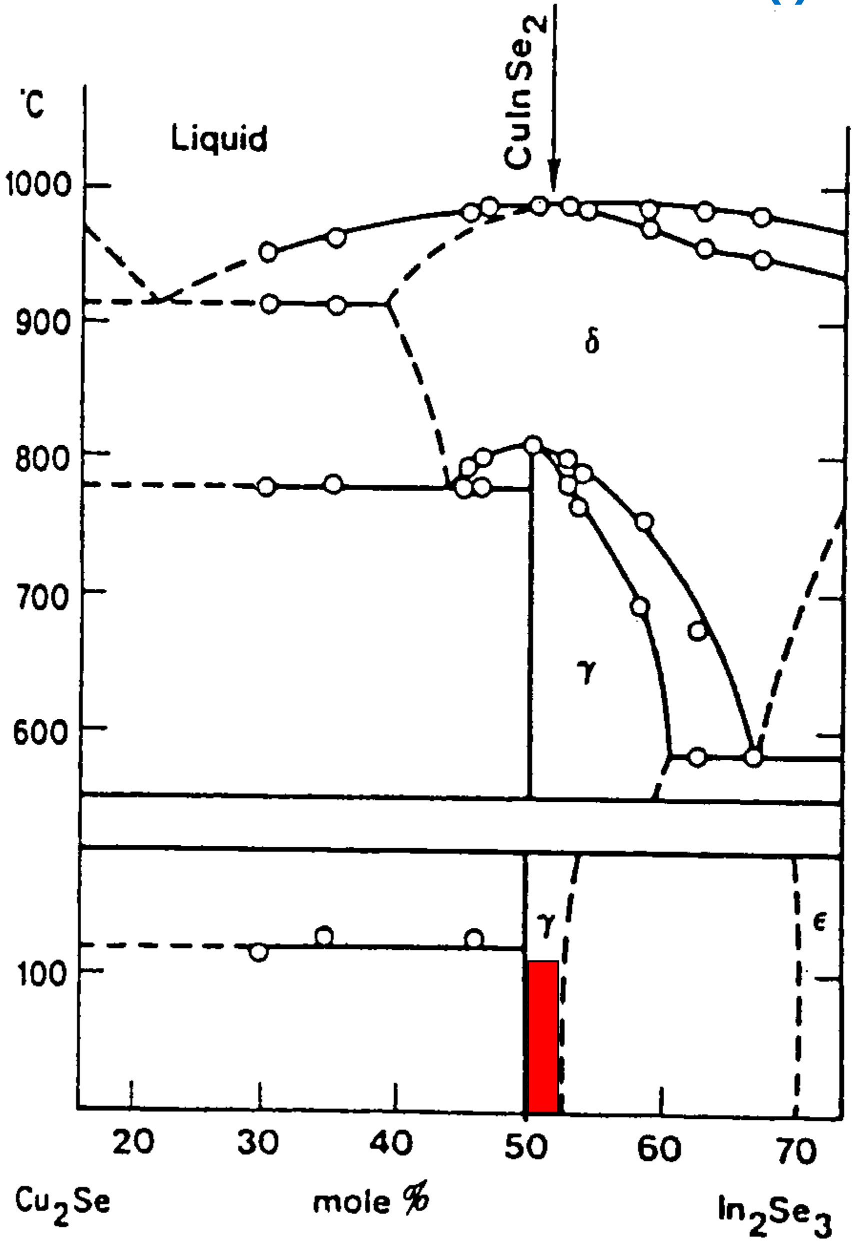
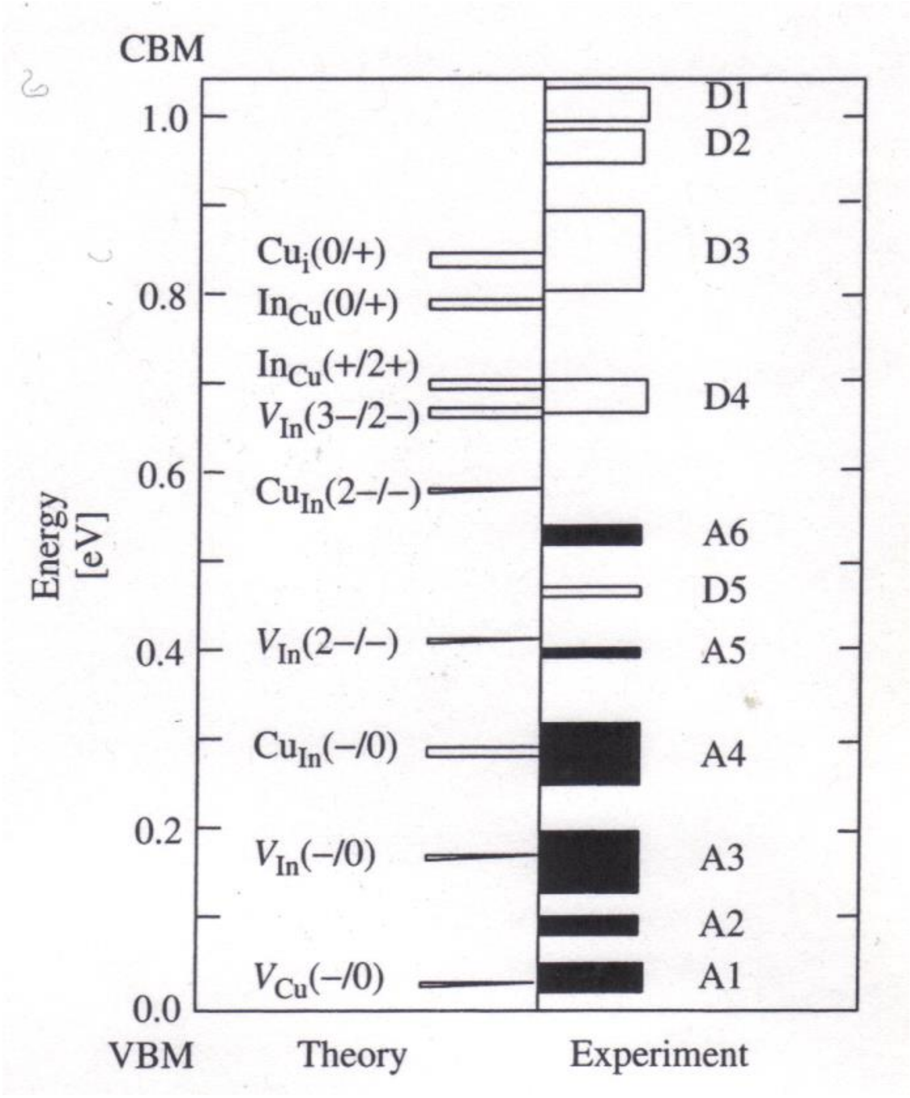


Fig. 3. Pseudo-binary phase diagram of Cu_2Se-In_2Se_3 system.[5)]

Une Chimie des défauts intrinsèques favorable : Phénomènes d'autocompensation



From Zhang et al 1998

Possible extrinsic acceptor : Na_{Cu}

Table 13.2 The most important intrinsic defects for device-quality $CuInSe_2$

Defect	Energy position	Type
V_{Cu}	$E_V + 0.03$ eV	Shallow acceptor
In_{Cu}	$E_C - 0.25$ eV	Compensating donor
V_{Se}		Compensating donor
Cu_{In}	$E_V + 0.29$ eV	Recombination center

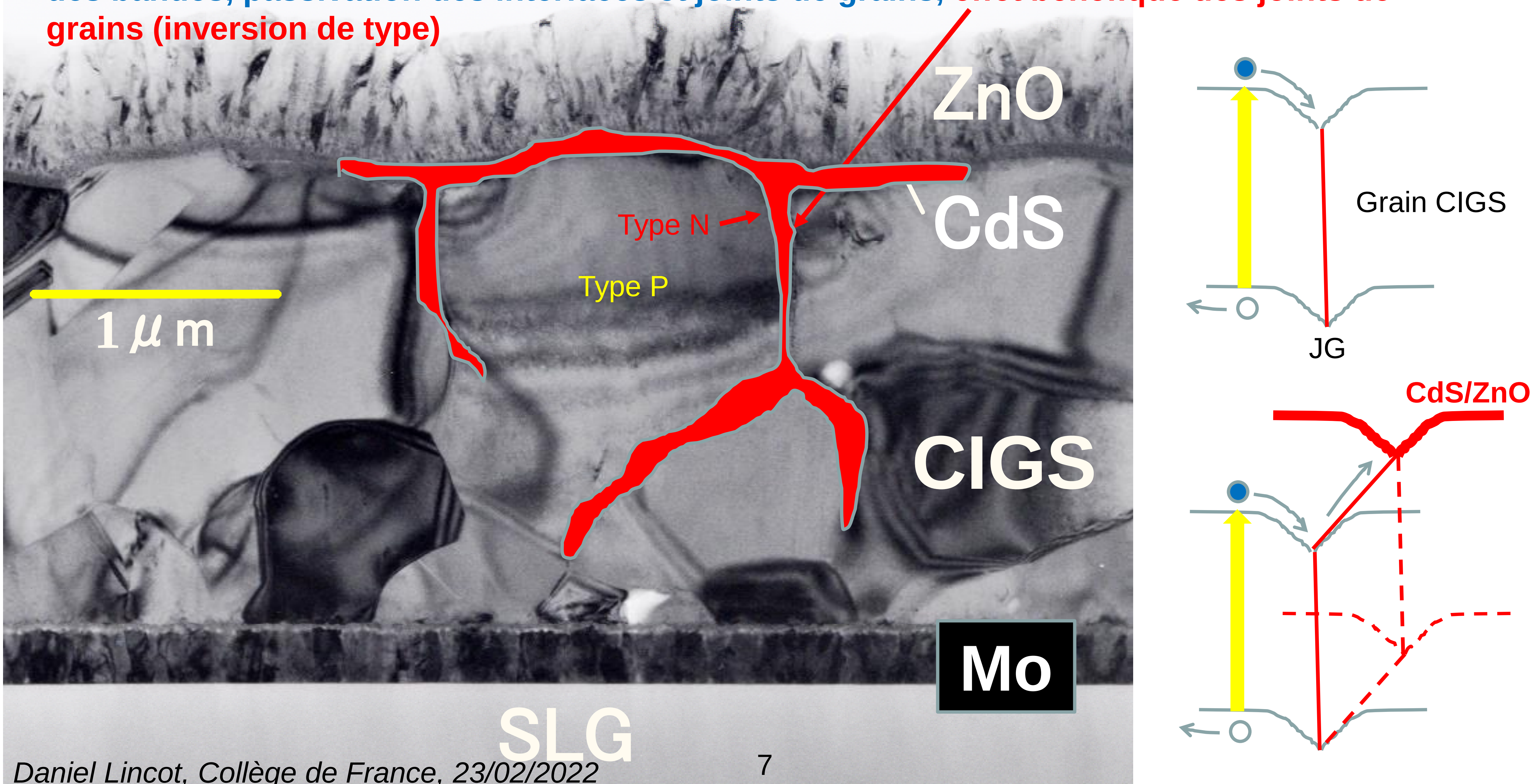
Defect complexes :
Low formation energies

(Cu_{In},In_{Cu}), $(2Cu_i,Cu_{In})$, $(2V_{Cu},In_{Cu})$

no electronic transition in BG
Accomodates In excess
Precludes the formation
of ordered vacancy compounds
CuIn3Se5, CuIn5Se8

W. Shafarman and L. Stolt, CIGS Solar cells
in Handbook of PV Science and Engineering (2003)

Interprétations fondamentales : augmentation des durées de vie dans le CIGS, adaptation des bandes, passivation des interfaces et joints de grains, effet bénéfique des joints de grains (inversion de type)



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Review on incorporation of alkali elements and their effects in $Cu(In,Ga)Se_2$ solar cells

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[c] Key Laboratory of Advanced Materials (MOE), School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

Table 1
The record efficiency CIGS solar cells treated by alkali-fluoride post-deposition treatment (PDT) and corresponding photovoltaic parameters in recent years.

Institutions	Year	PDT	Voc (mV)	Jsc (mA/cm^2)	FF (%)	Eff. (%)	Ref.
EMPA	2013	NaF + KF	736	35.1	78.9	20.4	[4]
ZSW	2014	KF	757	34.8	79.1	20.8	[5]
Solar Frontier	2014	KF	686	39.9	76.4	20.9	[6]
Solibro	2014	KF	757	35.7	77.6	21.0	[7]
ZSW	2014	RbF	746	36.6	79.3	21.7	[8]
Solar Frontier	2015	KF	722	39.4	78.2	22.3	[9]
ZSW	2016	RbF	741	37.8	80.6	22.6	[10]
Solar Frontier	2018	CsF	746	38.5	79.7	22.9	[11]
Solar Frontier	2019	CsF	734	39.6	80.4	23.35	[12]

*EMPA: Swiss Federal Laboratories for Materials Science and Technology.
ZSW: Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg.

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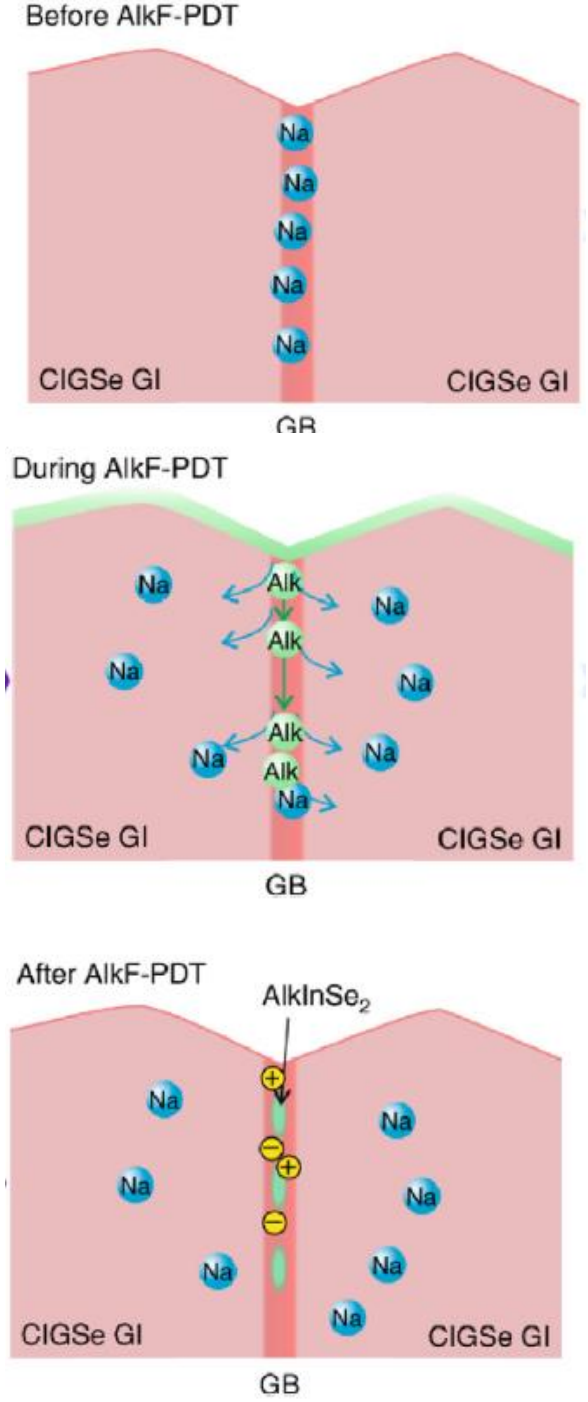

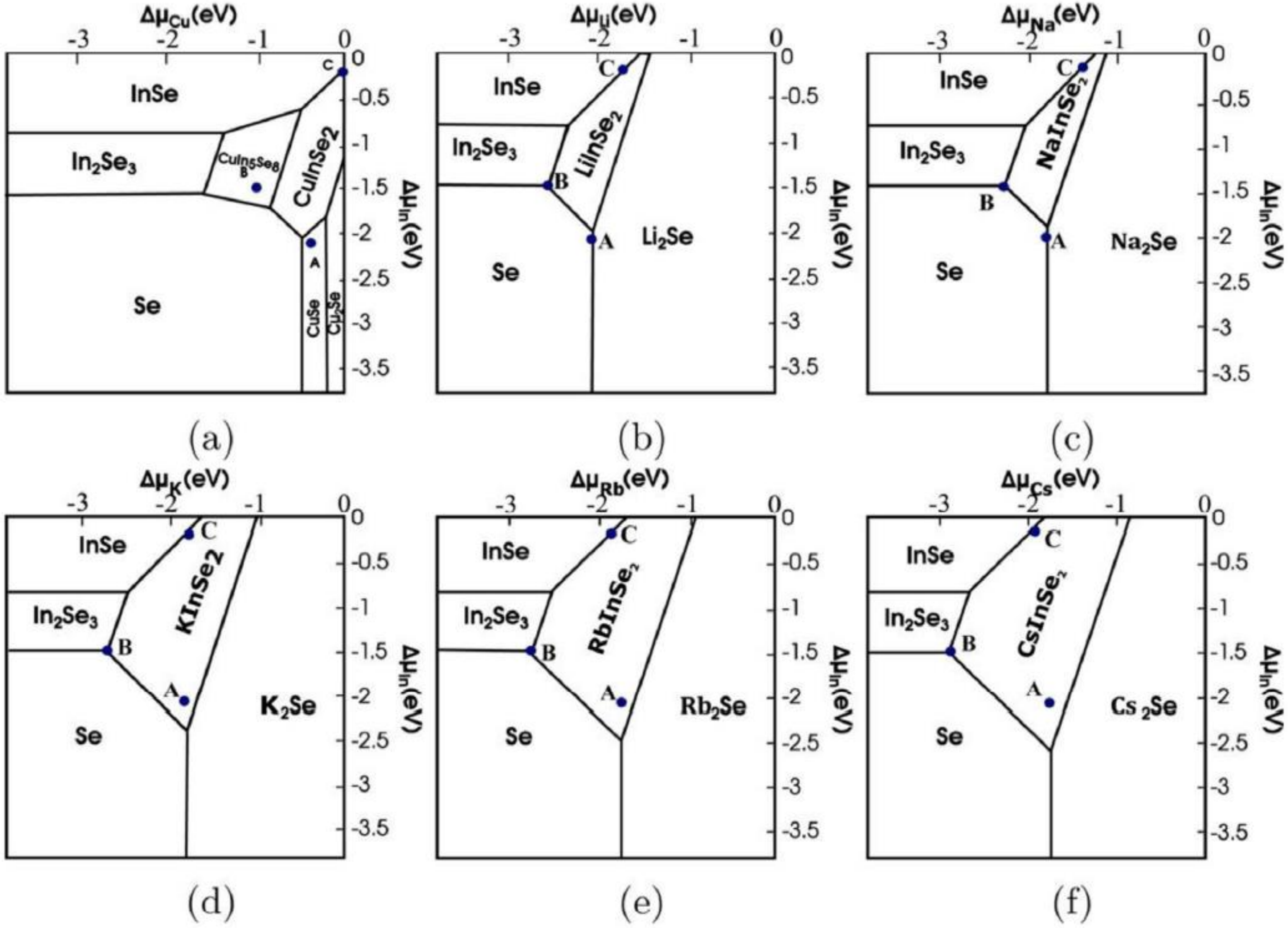

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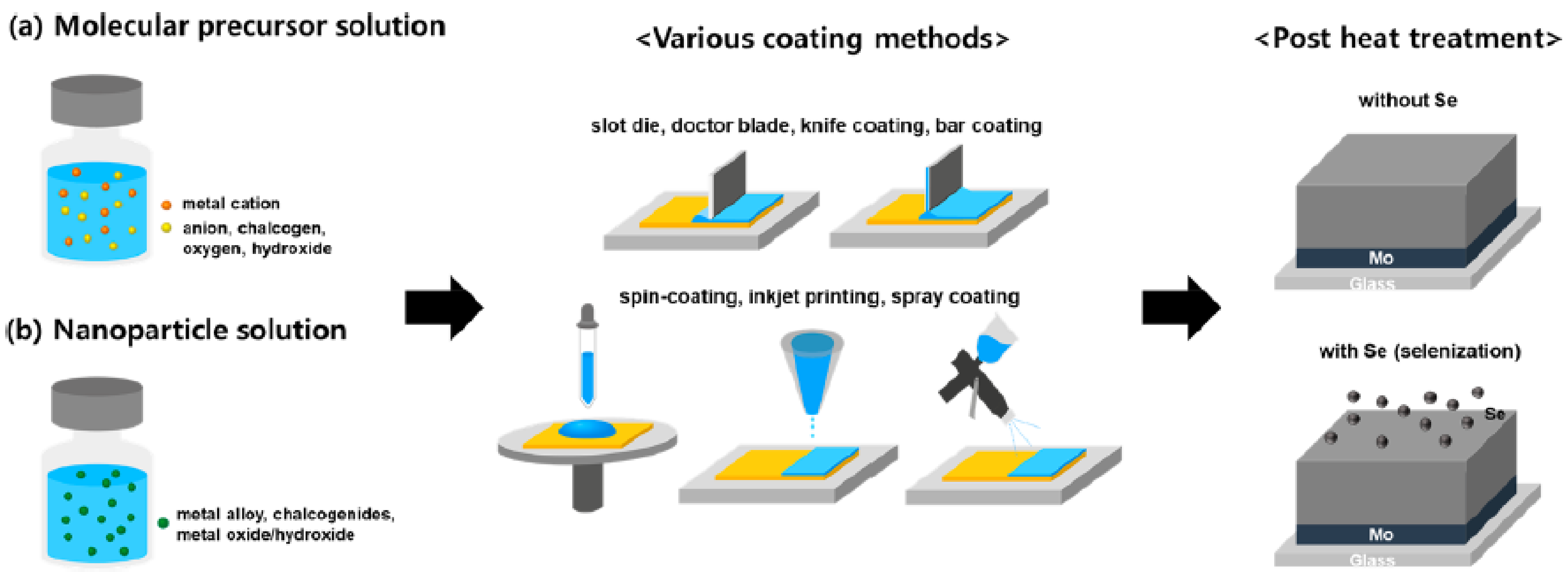
Procédés en solution → Vers l'imprimerie

Impact of Absorber Layer Morphology on Photovoltaic Properties in Solution-Processed Chalcopyrite Solar Cells

Joo-Hyun Kim,[§] Soohyun Bae,[§] and Byoung Koun Min*

Cite This: *ACS Appl. Mater. Interfaces* 2021, 13, 34–47 Read Online

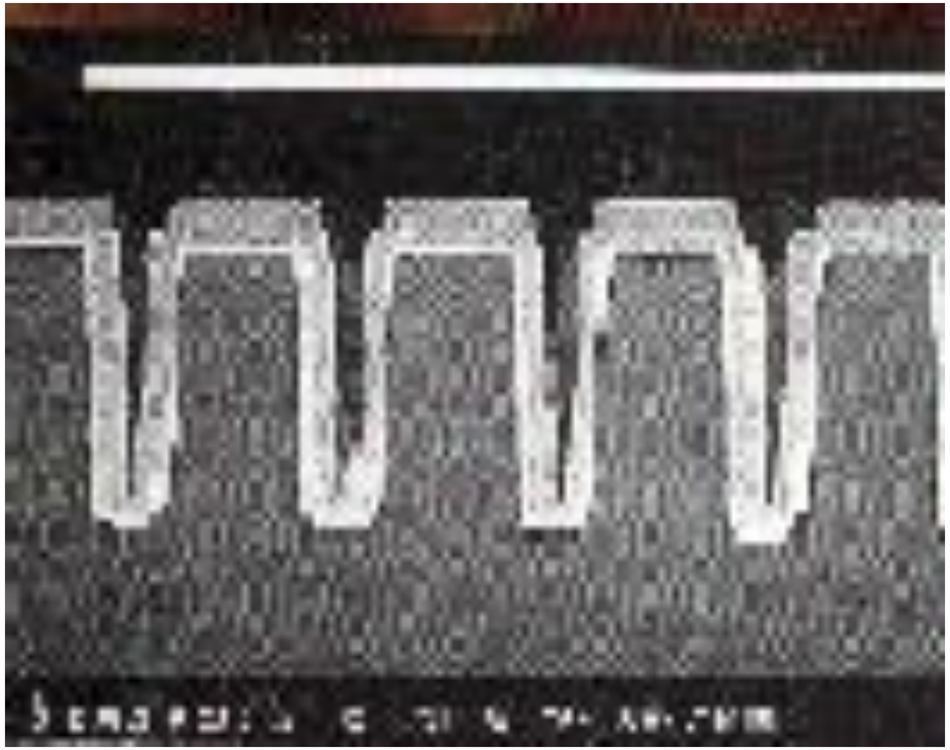
Record : 17,3 %



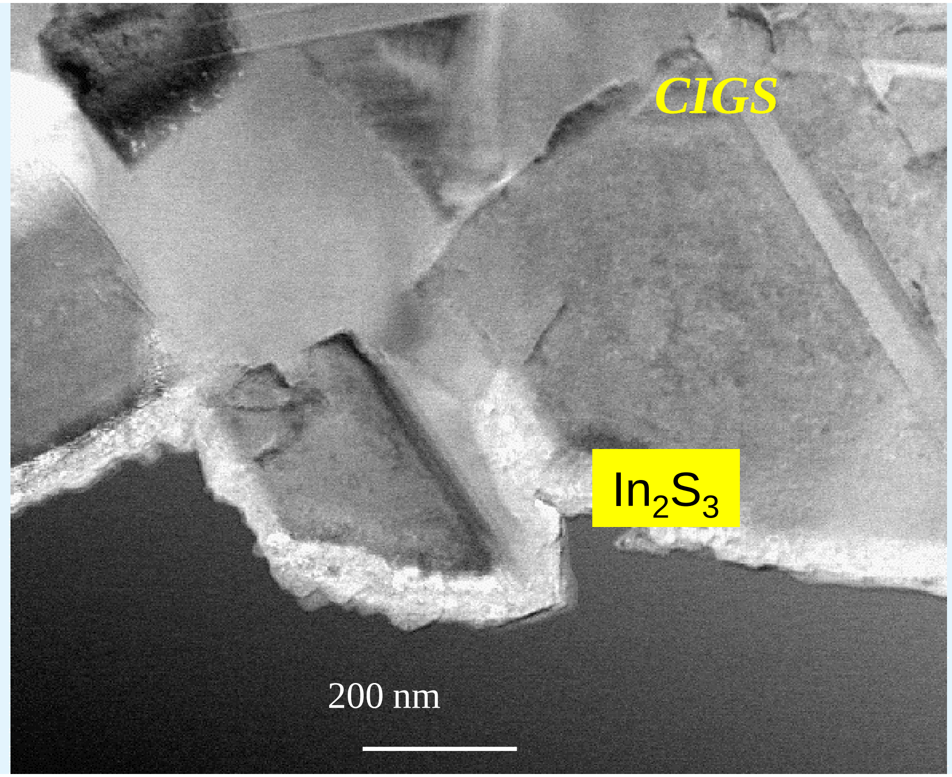
Dépôt alterné en phase gazeuse (Atomic Layer Deposition –ALD)

Basse température, conforme, contrôle monocouche atomique

Microélectronique



Photovoltaïque (sulfures, oxydes…)



CNRS-ENSCP
IRDEP
IPVF

N. Naghavi,
F. Donsanti
N. Schneider
D. Coutancier

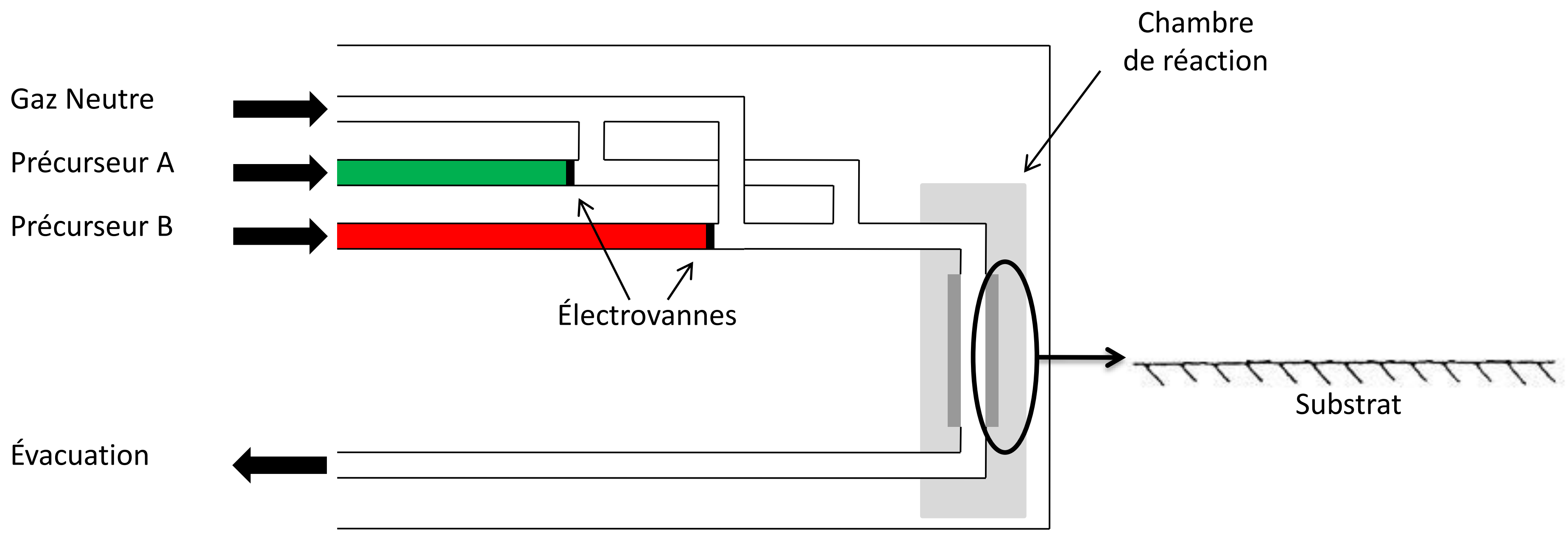
Daniel Lincot, Collège de France, 23/02/2022

Dépôt chimique par flux alternés en phase gazeuse (ALCVD)

Exemple A = $Zn(C_2H_5)_2$, $In(CH_3)_3$
B= H_2O, H_2S

Principe :

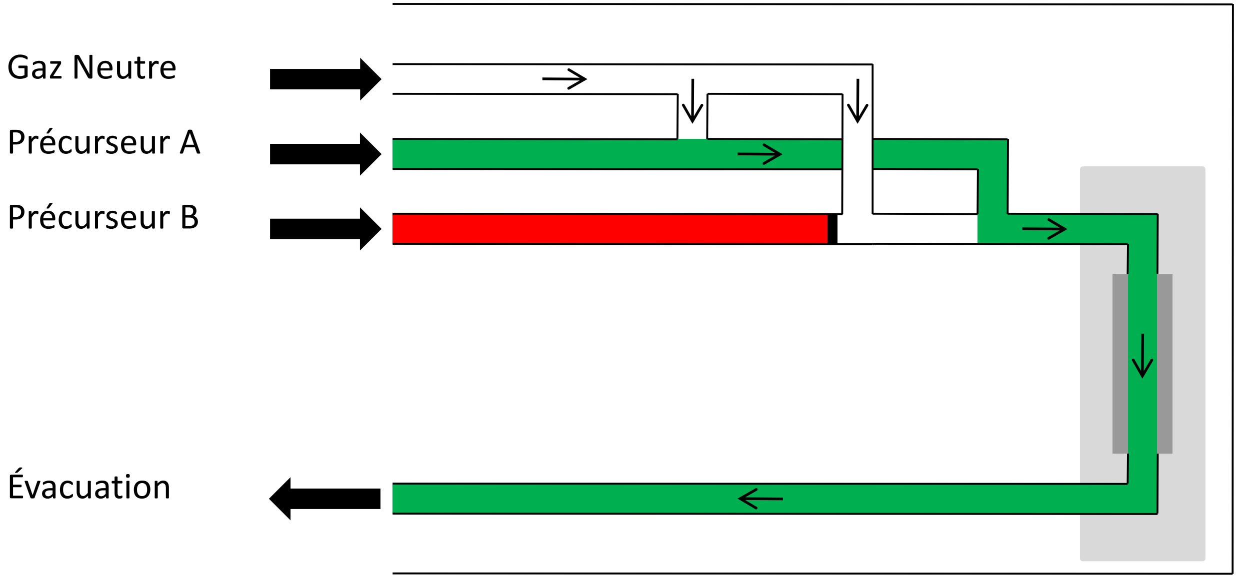
Dépôt découpé en cycles de 4 étapes

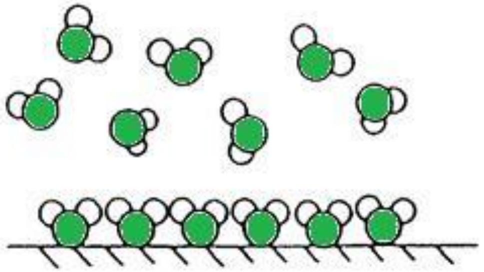


Dépôt chimique par flux alternés en phase gazeuse (ALCVD)

Principe :

Étape 1 : Pulse de précurseur A



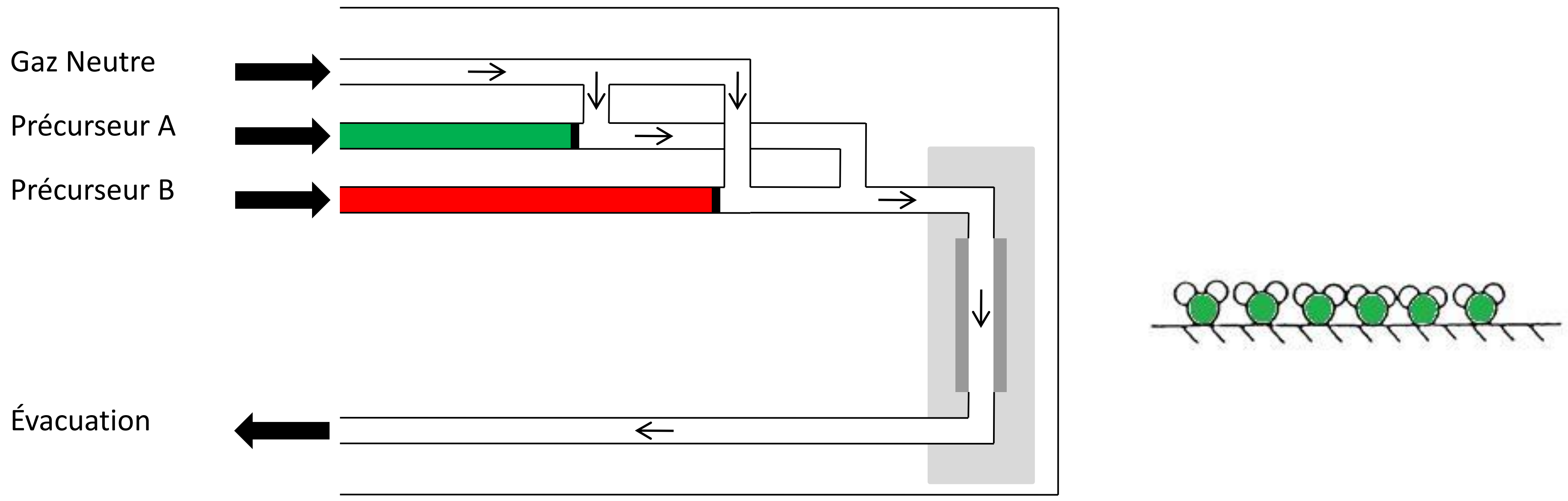


Adsorption en surface du substrat

Dépôt chimique par flux alternés en phase gazeuse (ALCVD)

Principe :

Étape 2 : Purge



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Dépôt chimique par flux alternés en phase gazeuse (ALCVD)

Principe :

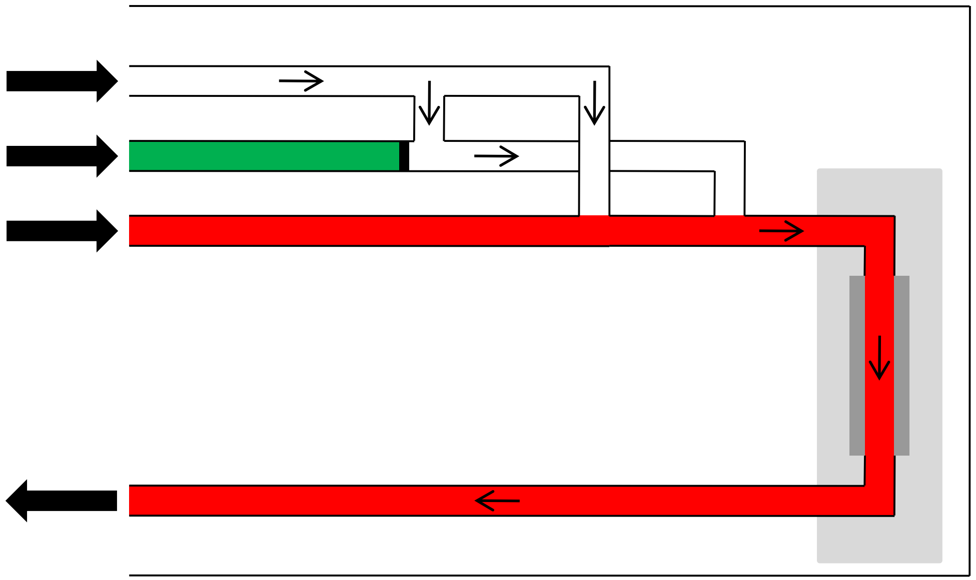
Étape 3 : Pulse de précurseur B

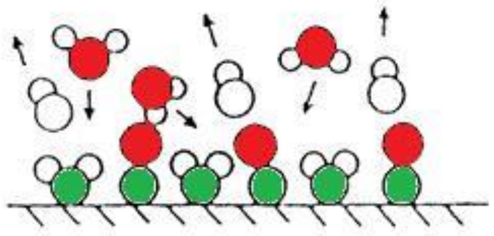
Gaz Neutre

Précurseur A

Précurseur B

Évacuation





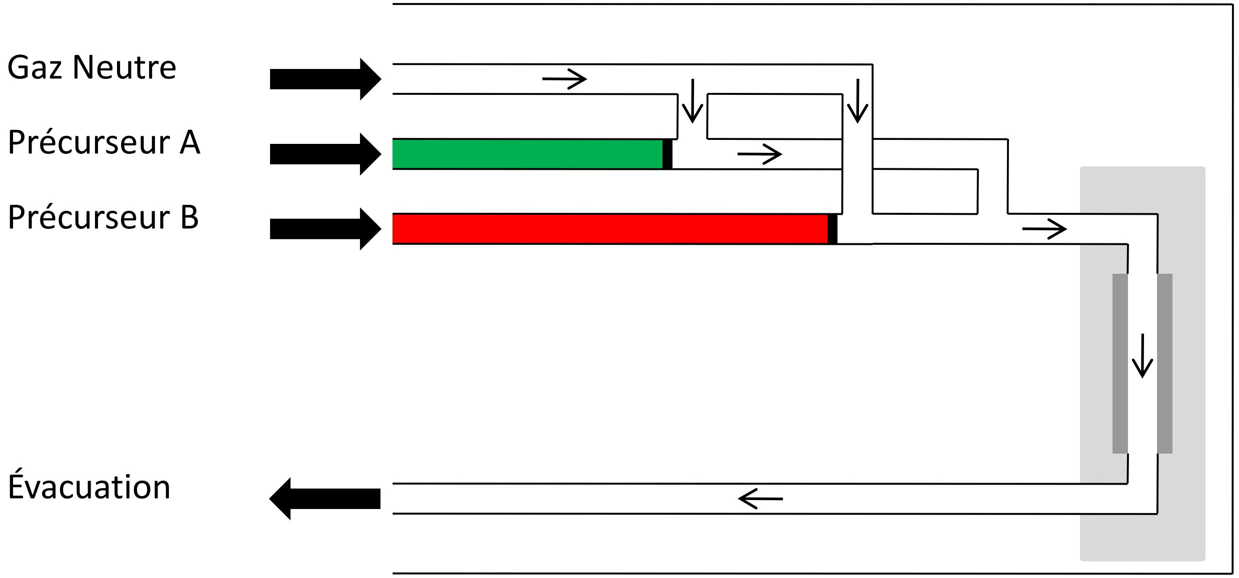
Réaction

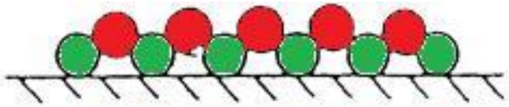
Formation du composé AB

Dépôt chimique par flux alternés en phase gazeuse (ALCVD)

→ Et on recommence :
→ tricoter des matériaux à l'échelle atomique

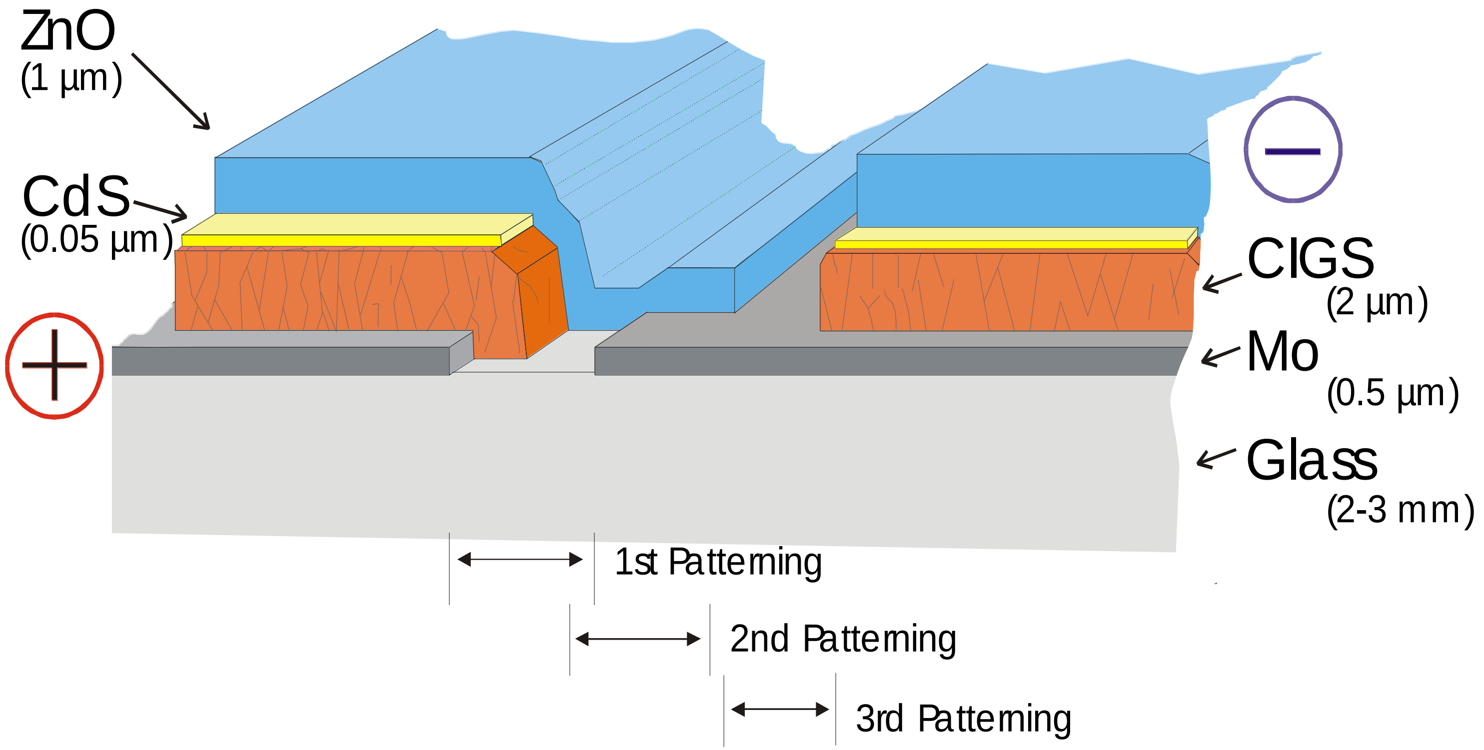
Étape 4 : Purge





En fin de cycle, on obtient théoriquement le dépôt d'une monocouche de matériau.

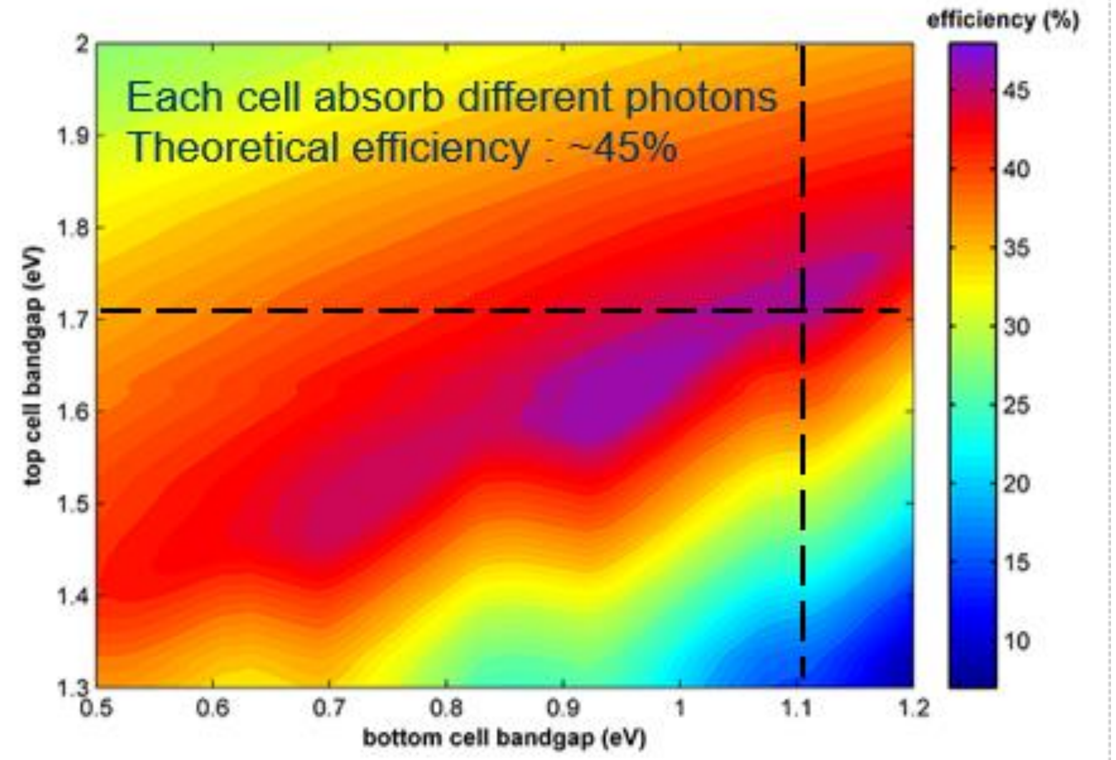
Les modules couches minces : une connectique originale

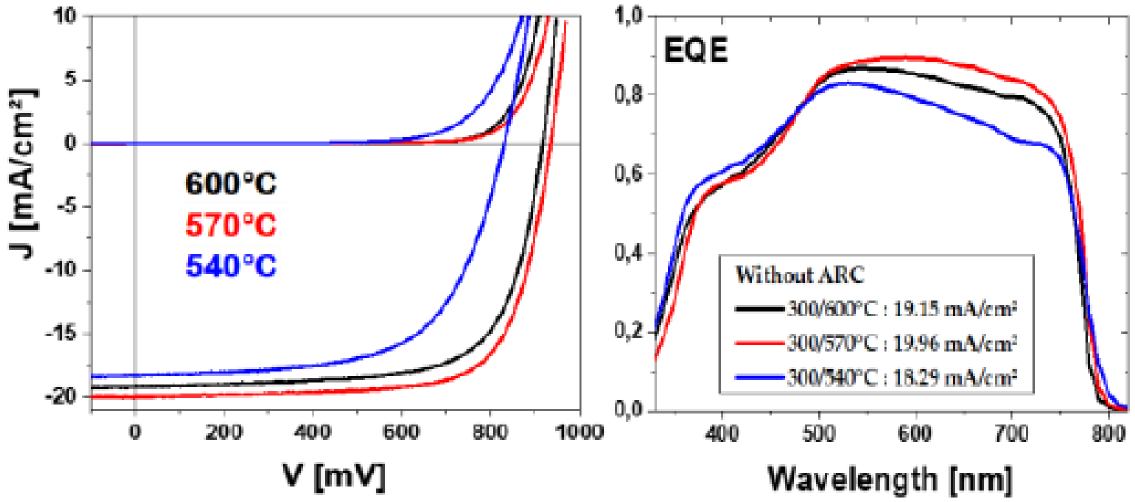


HICIS. HWS 11/07/02

Nouveaux développements

Cellules $CuInGaS_2$ à grande bande interdite (1,6-1,7 eV) pour cellules tandem Si-CIGS



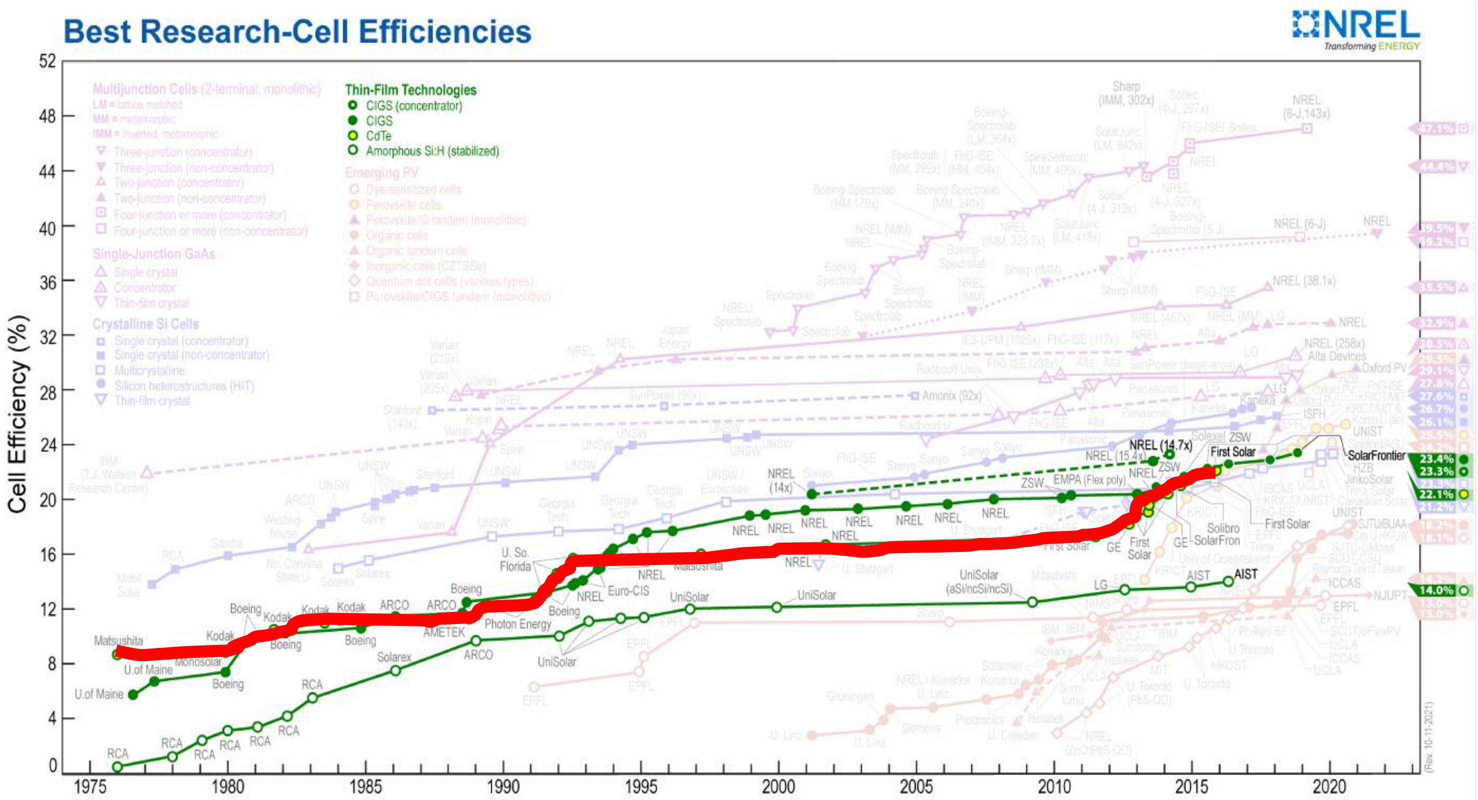


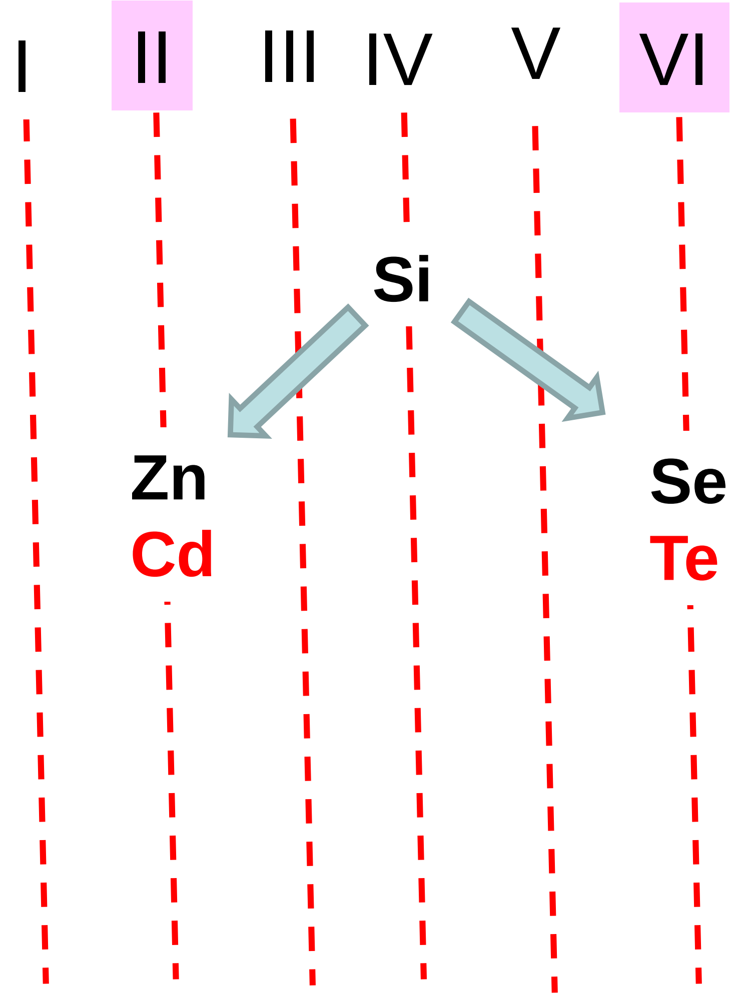
T_m	V_{oc} [mV]	J_{sc} [mA/cm²]	FF [%]	Eff [%]	qV_{oc} (T -> 0 K)
540°C	831	18.3	62.5	9.5	1.45 eV
570°C	935	20.0	72.2	13.5	1.65 eV
600°C	917	19.2	66.0	12.3	1.58 eV

N. Barreau et al., IEEE (2021)
Projet IPVF, ANR EPCIS

La technologie CdTe : les « Deux-Six »

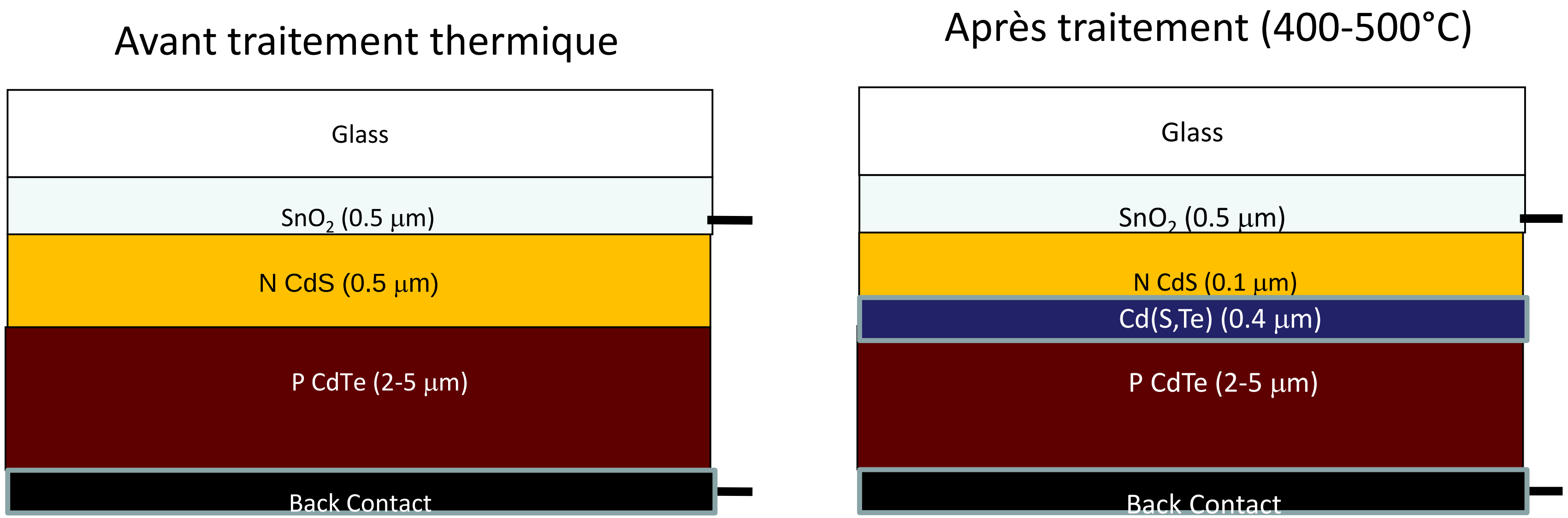
Du « bout de bois » (1978- D. Lincot) à 22,1 %





Un succès industriel éclatant ! FIRST SOLAR

Les cellules solaires CdTe : principe de base



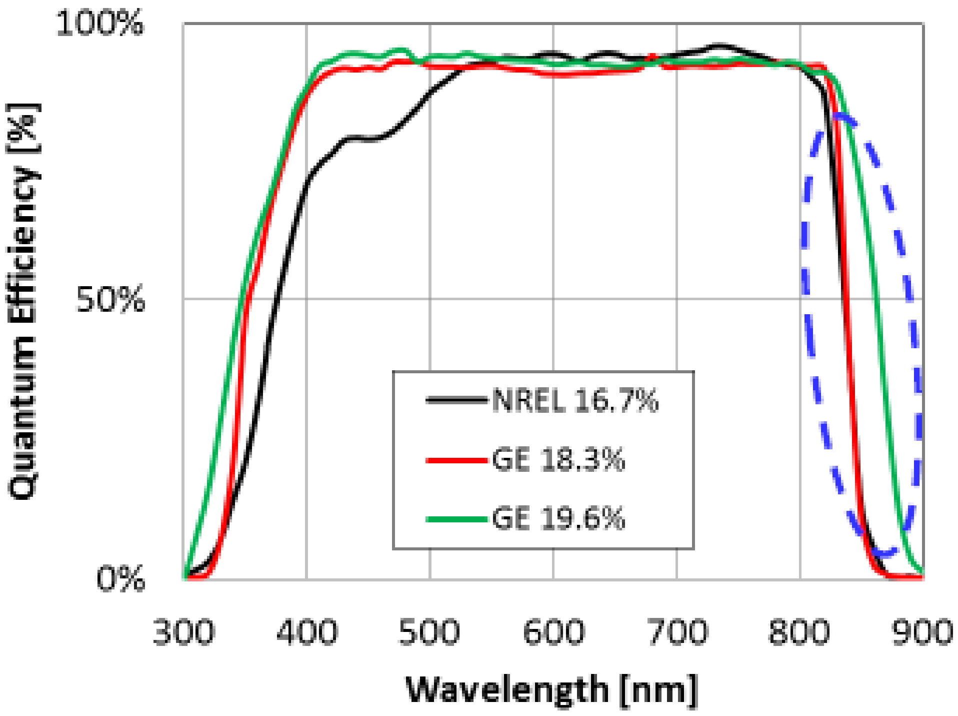
Des secrets gardés bien longtemps :
traitement au Chlorure de cadmium → frittage, passivation des défauts dans CdTe

Une physico-chime proche de celle du CIGS : tolérance au défauts
dopage intrinsèque, phénomènes d'autocompensation…

Evolution des réponses spectrales

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

(Cd,Zn)S
Gap augmente



Cd(S,Te)
Gap diminue

(Cd,Zn)Te
(Cd,Mg)Te
Gap augmente

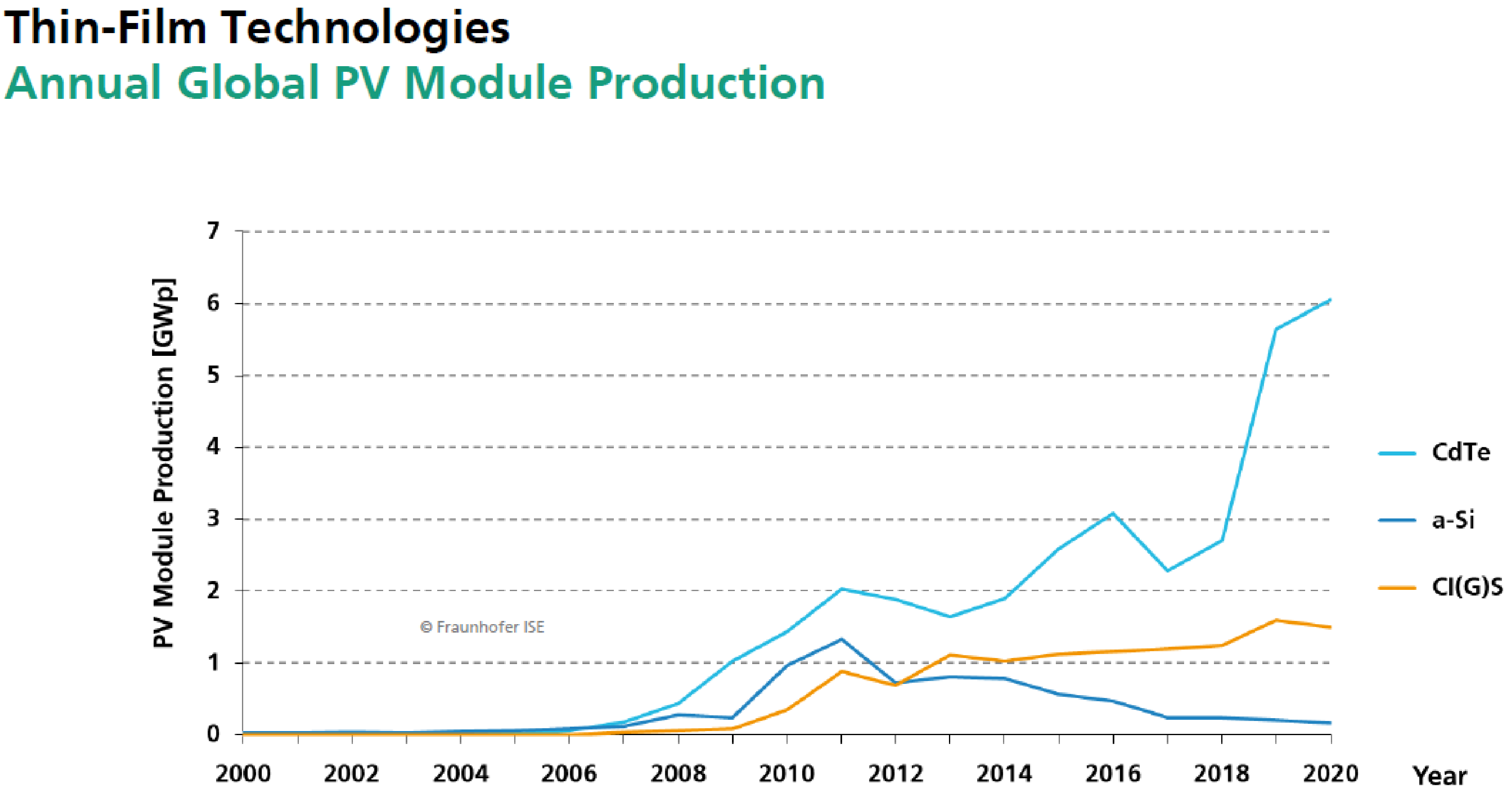
+ Graded band gap in CdTe

2015 : 22,1 %

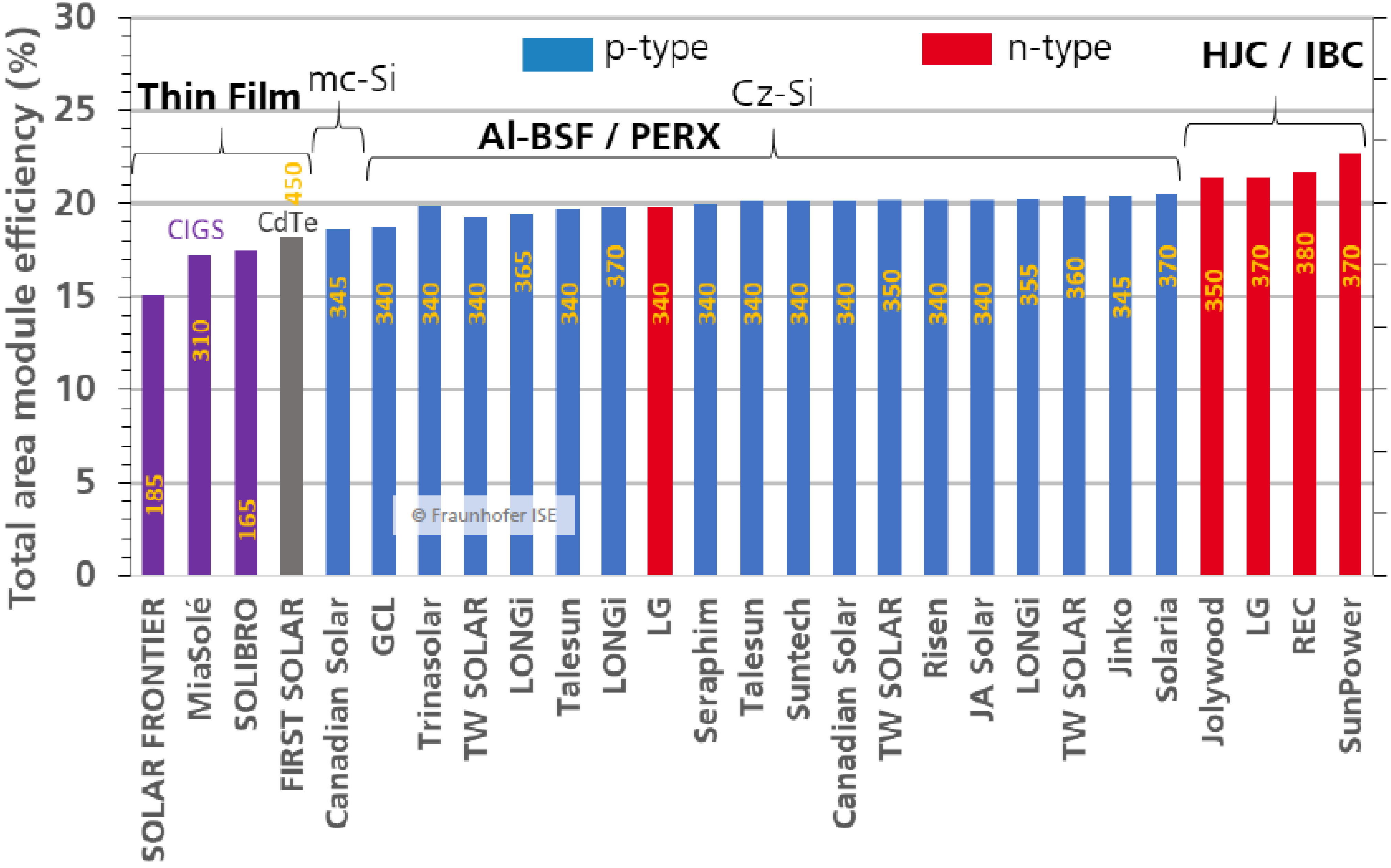
Daniel Lincot, Collège de France, 23/02/2022

https://www.firstsolar.com/

Evolution du marché pour les technologies couches minces



Performances des modules PV commerciaux



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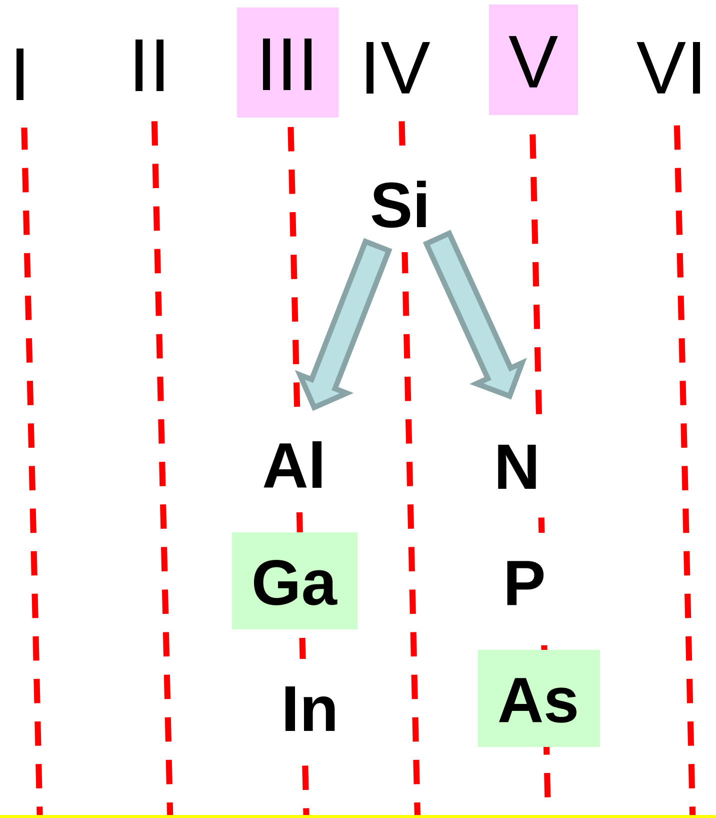
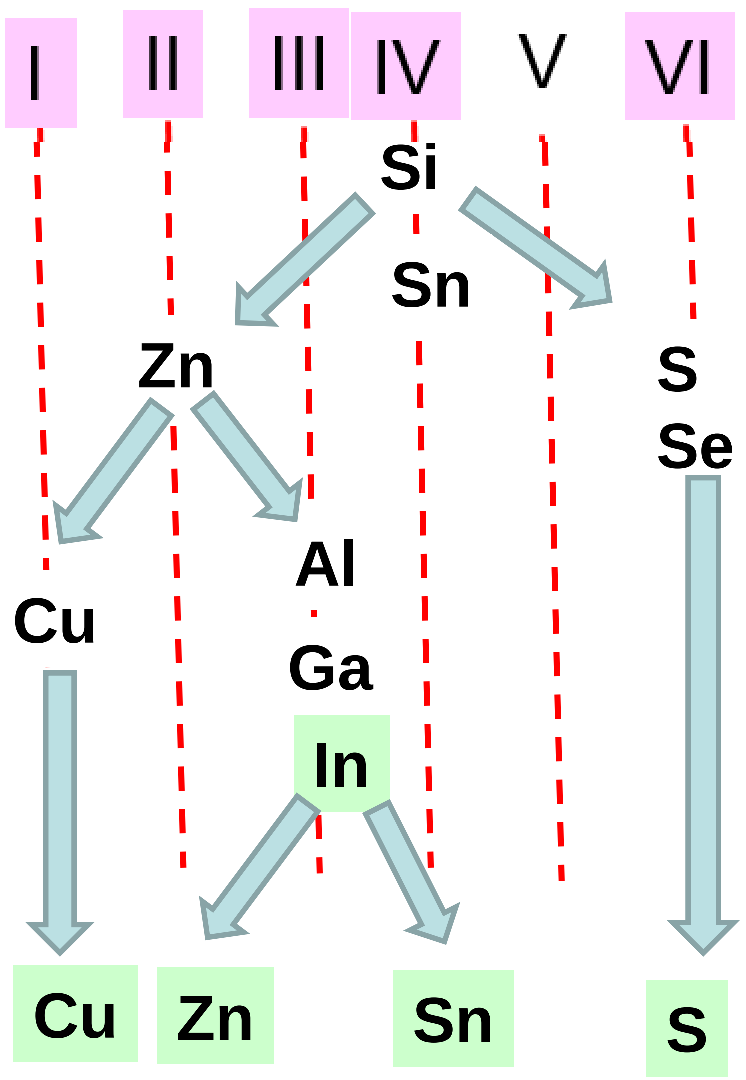
Autres technologies couches minces inorganiques

Les « trois Cinq » :
les « Ferrari du photovoltaïque »



Excellentes performances (28,9%)
Mais…très sensible aux défauts !
→ Croissance épitaxique par MBE ou CVD
→ Rôle de l'ionicité des liaisons plus faible ?

Les KESTERITES : CZTS



$Cu_2ZnSn(S,Se)_4$
1 eV à1,5 eV

Futur du CIGS ?

Rendements encore faibles : 12%

Mais : éléments abondants
Non toxiques

Physicochimie très complexe…

En cours d'évolution

Multiples autres possibilités

« Materials genomics »

De la complexité nait la simplicité

Transparents annexes

Analyse de cycle de vie technologie CIGS : cas de l'Indium

L'indium est à l'opposé du silicium : il est rare et critique,
pourtant sous forme de couches minces sont utilisation est possible, voir l'étude ci dessous

CIGS Thin Film Photovoltaics for EU's prosperity, energy transition and enabling net zero emission targets

Indium production in Europe is sufficient for more than 100 GW per year PV production with potential to meet TW challenges in a cost effective manner

Coordinated developments are essential for industrialisation and applications of CIGS PV

EU can reach a leading position in future markets

Source: https://cigs-pv.net
Contact: E-Mail: info@cigs-pv.net

IPVF Joint Research Unit, HZB Helmholtz Zentrum Berlin, uni.lu Université du Luxembourg, brgm, ZSW, imec, Empa, INL, Uppsala Universitet, Columbia University in the City of New York

https://cigs-pv.net/wortpresse/wp-content/uploads/2021/07/Indium_Availability_for_CIGS_thin-film_solar_cells_in_Europe.pdf

pv magazine

Indium supply not an issue for CIGS industry

Scientists Ayodhya Tiwari and Daniel Lincot recently spoke to **pv magazine** about the future of copper indium gallium selenide solar tech, which could play a key role in providing flexible, lightweight products in the building-integrated PV segment.

AUGUST 11, 2021 EMILIANO BELLINI

MODULES & UPSTREAM MANUFACTURING | TECHNOLOGY AND R&D | EUROPE

https://www.pv-magazine.com/2021/08/11/indium-supply-not-an-issue-for-cigs-industry/