The Abdus Salam International Centre for Theoretical Physics

2269-27

Workshop on New Materials for Renewable Energy

17 - 21 October 2011

Novel growth technology for thin film photovoltaics: II-VI semiconductors and TCO

Carlo TALIANI
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Italy


Novel growth
technology for thin film photovoltaics:
II-VI semiconductors and TCO
Carlo Taliani
ISMN - CNR
Bologna
ORGANIC
SPINTRONICS
2SN

Carlo Taliani background

- '70 Chemical physics of aromatic molecules (AM)
- Solid state spectroscopy of AM synonimous of Organic Semiconductors (OSemicon)
- Solid state properties of OSemicon
- '86 High Tc superconductors, growth, PIA, polarons
- '92 first UHV growth of OSemicon
- '90 OLED, FET, OPV developments
- '2001 invention of Organic Spintronics (OS)
- '2003 PPD ablation technique and establishment of OS company
- '2007 II-VI thin film PV growth by PPD at 2SN SpA

- Bologna is a 3000 yr. old town with a large well preserved medieval centre.

- Is the site of the oldest (900yr) University in the world.

Outline

- PV and Grid Parity
- Second Generation Photovoltaics
- Thin Film Growth Technologies

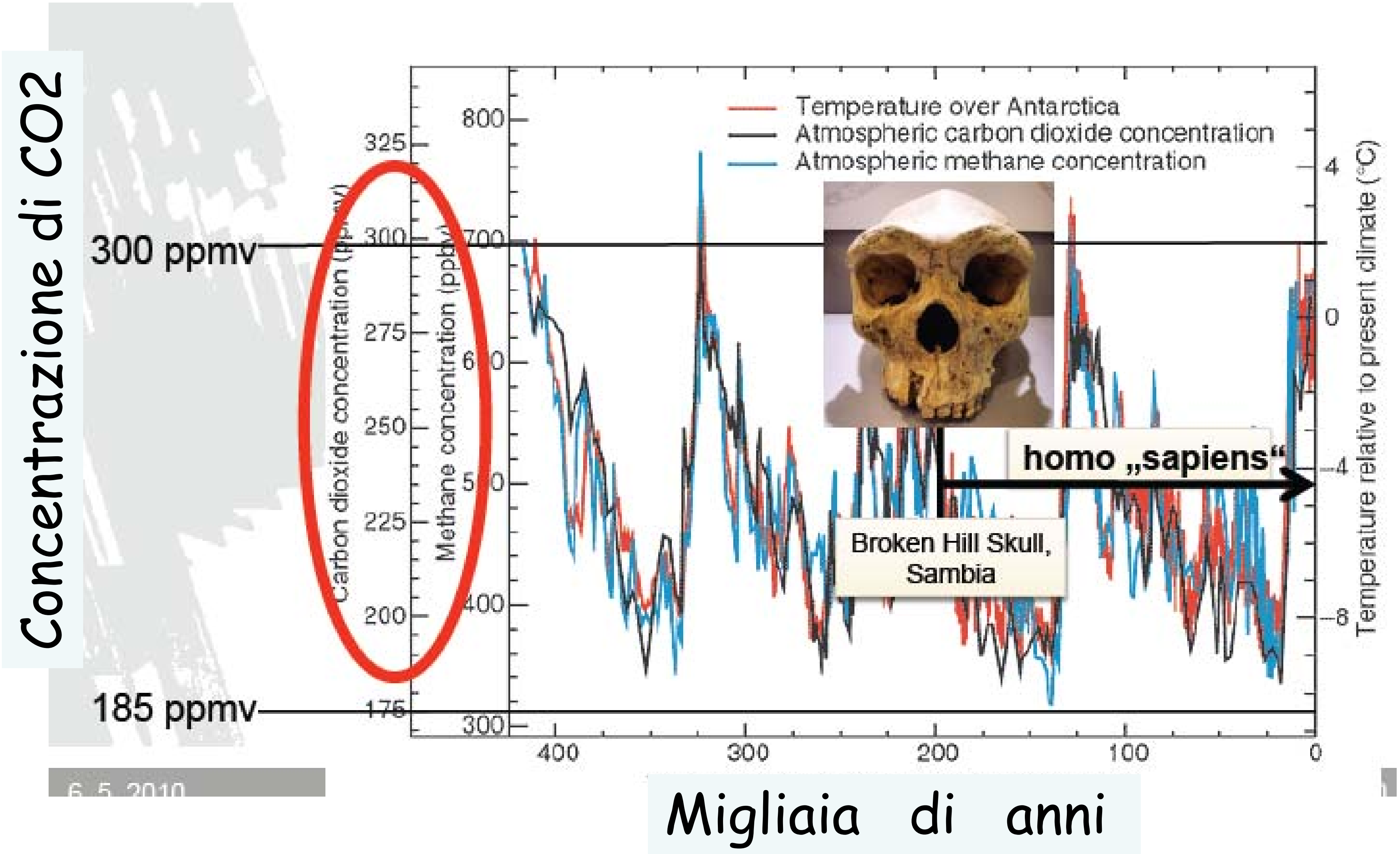
- PPD Ablation
- sustainable thin film deposition process
- environmentally friendly process

- CdTe PV on glass and metal
- integrated in the building structure

- Transparent Conductor
- Trasparency vs Conductivity
- TCO on plastic
- Inverted TOLED by top deposition

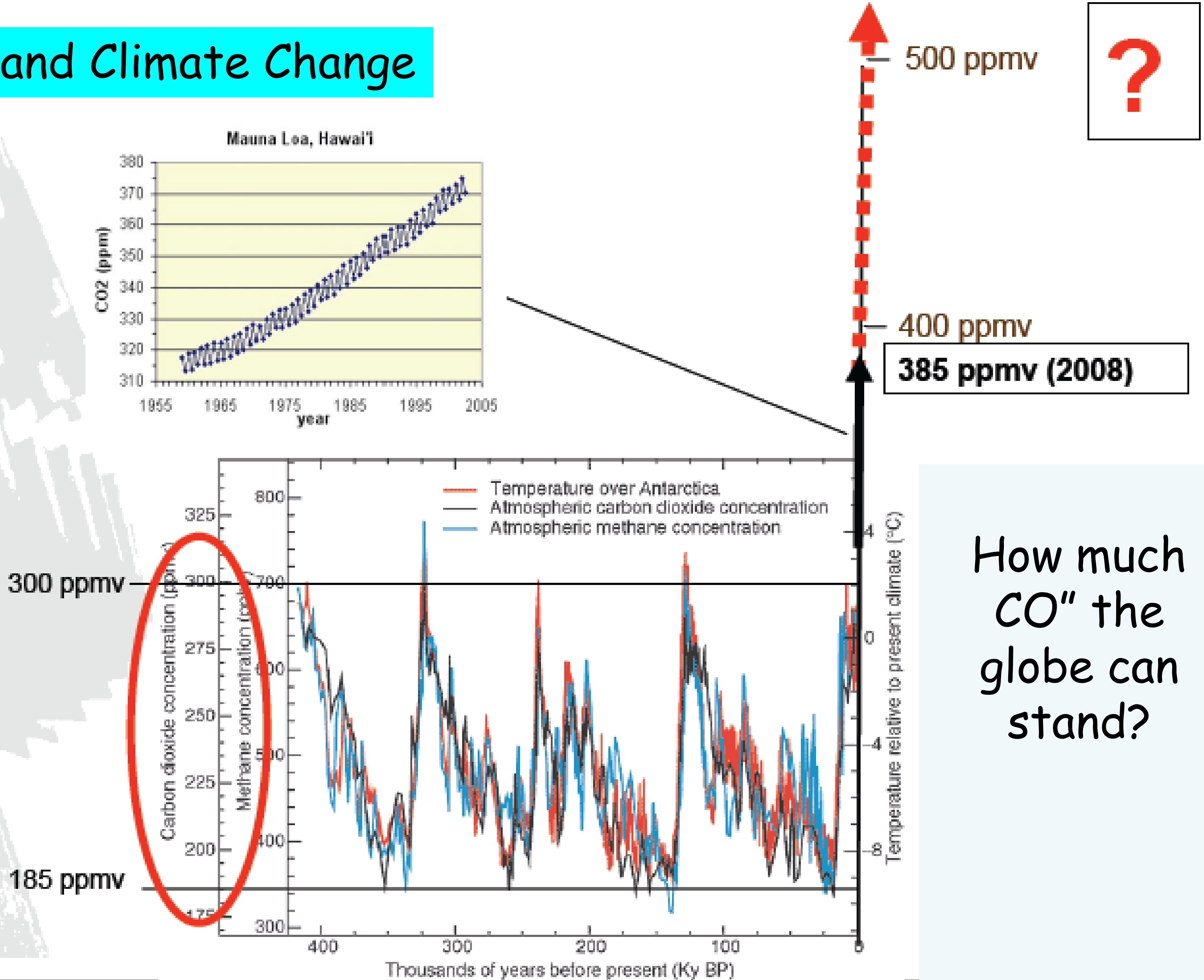
Motivation

Co2 vs time



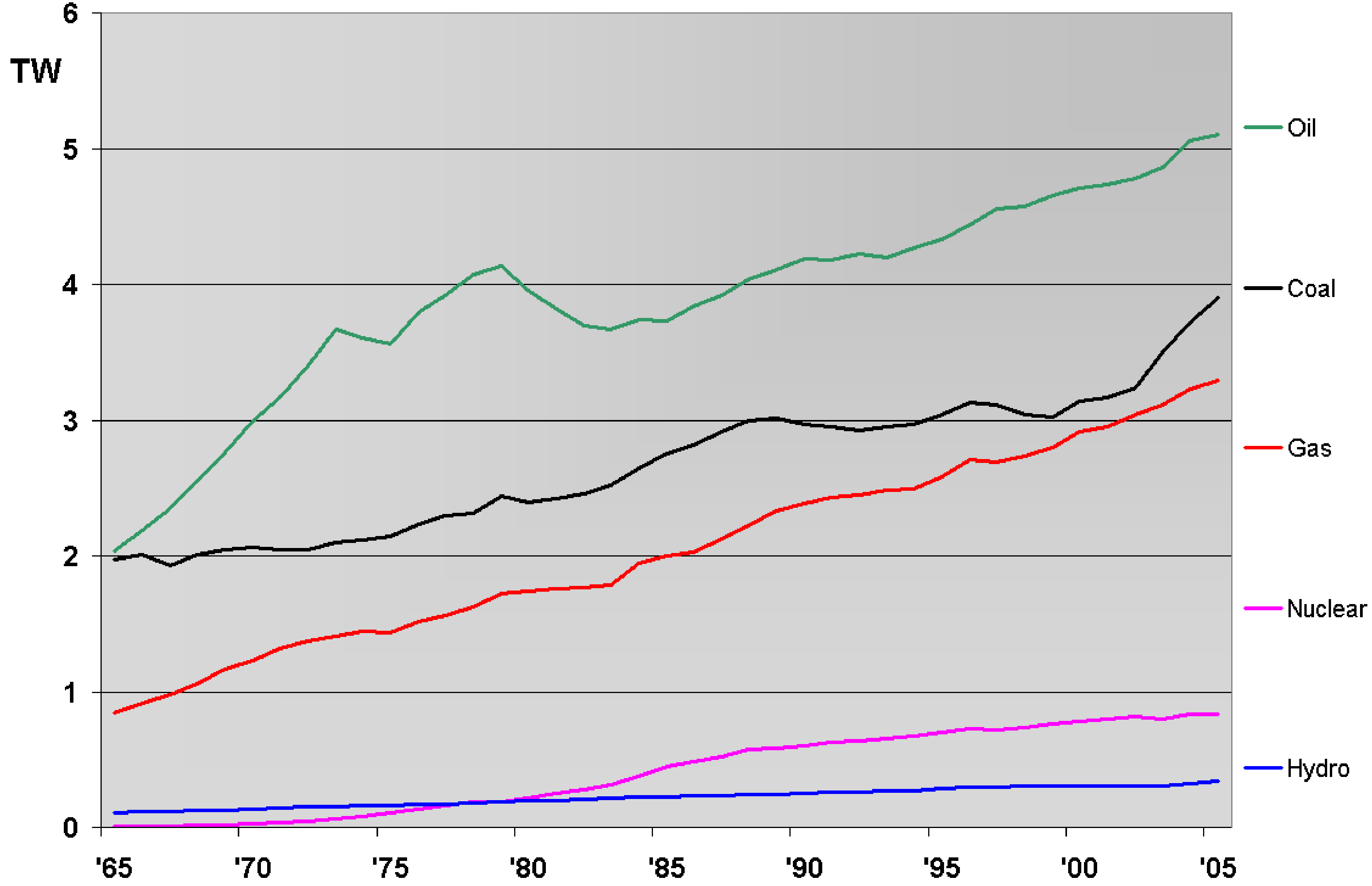
6. 5. 2010

CO2 and Climate Change



How much CO” the globe can stand?

15 TW needed for the world



Need for CO_2-free Power

In order to stabilize our climate we need in 2050 at least

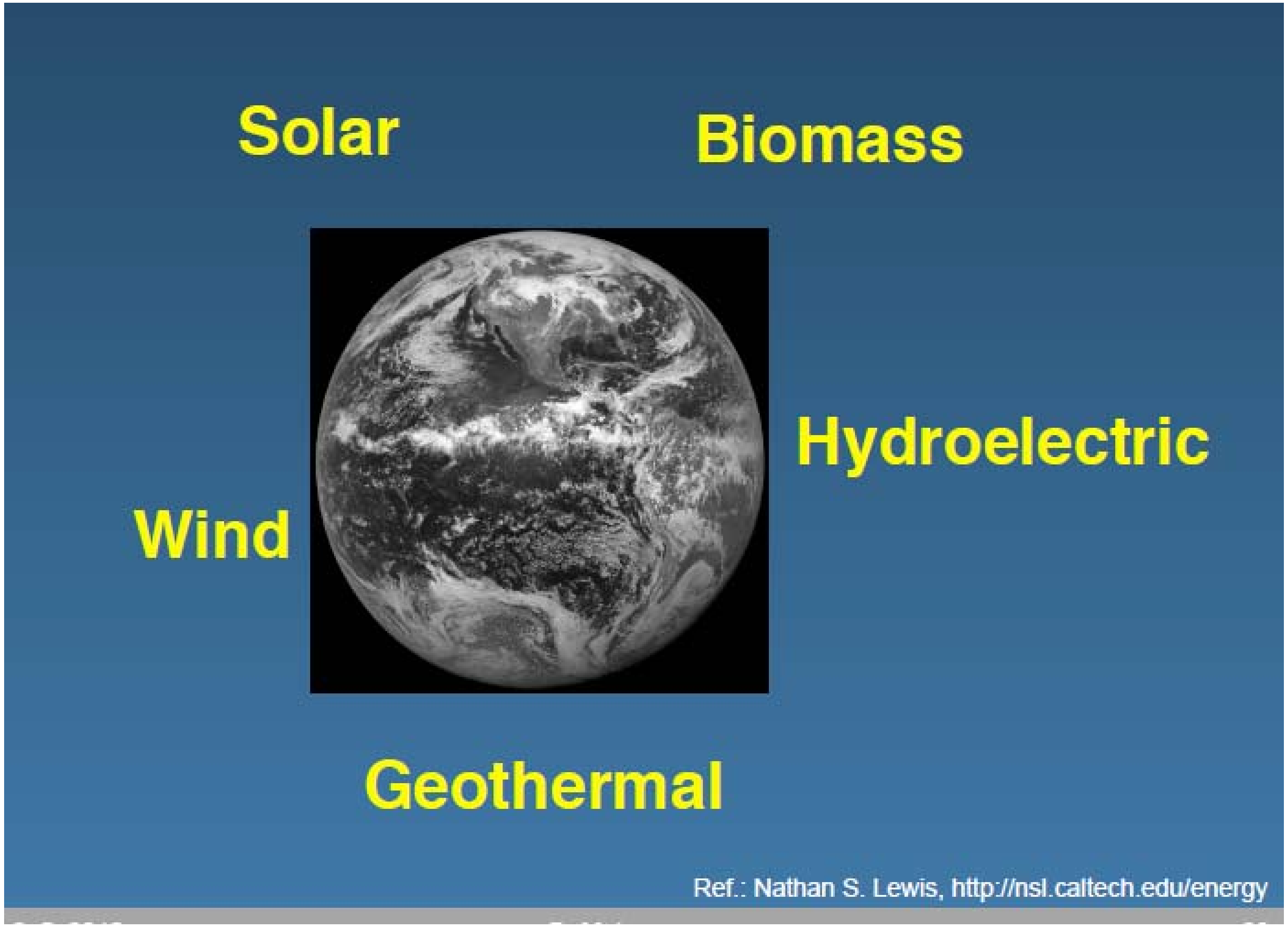
10 TW to 30 TW

of CO_2-free power.

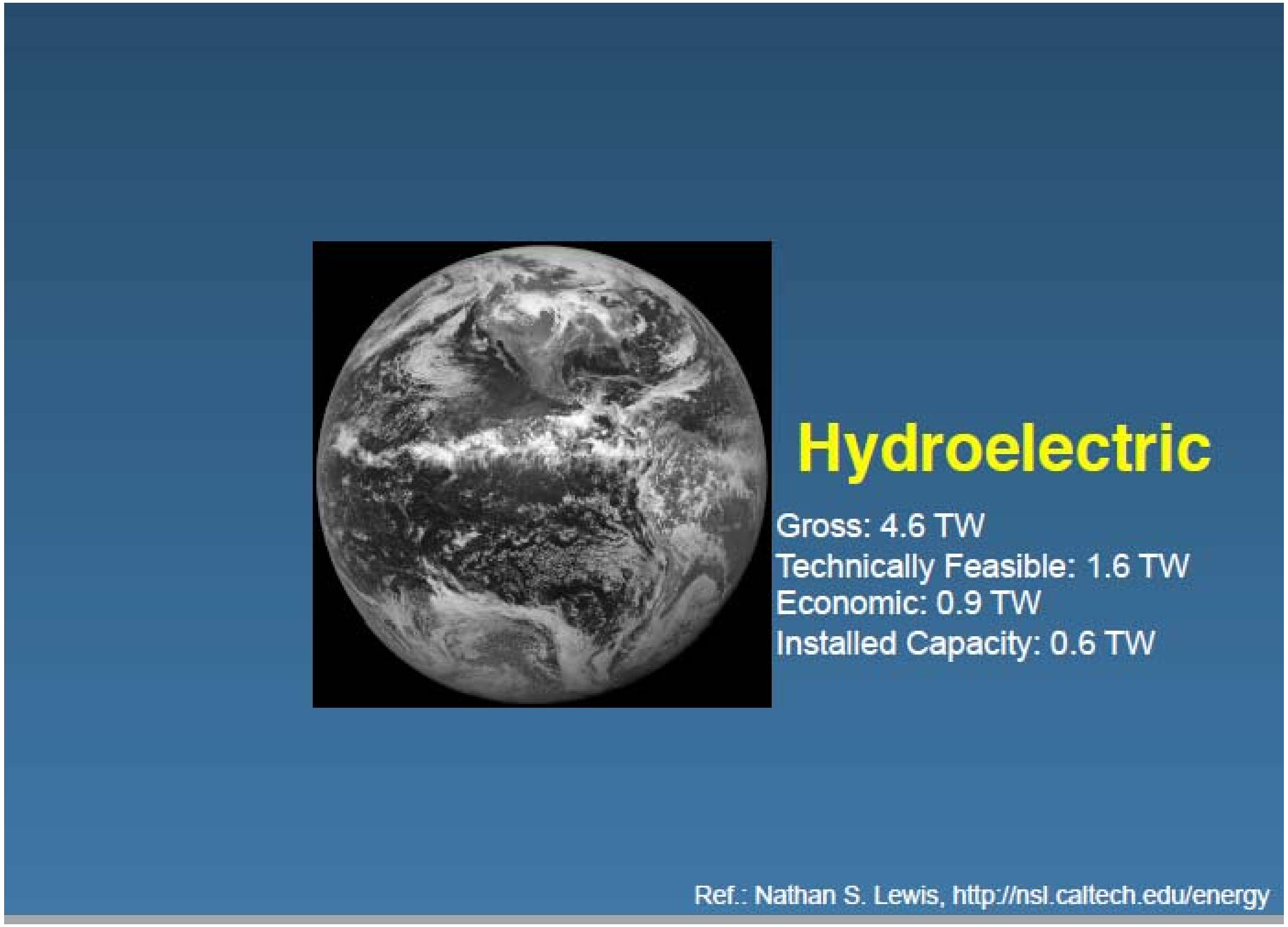
based on extremely optimistic assumptions
and very conservative calculations

Ref.: M. I. Hoffert et al., Nature 319 (1998), 881

Alternatives



Hydro 1,6TW


Hydroelectric
Gross: 4.6 TW
Technically Feasible: 1.6 TW
Economic: 0.9 TW
Installed Capacity: 0.6 TW
Ref.: Nathan S. Lewis, http://nsl.caltech.edu/energy

Geotherm. 11,6TW

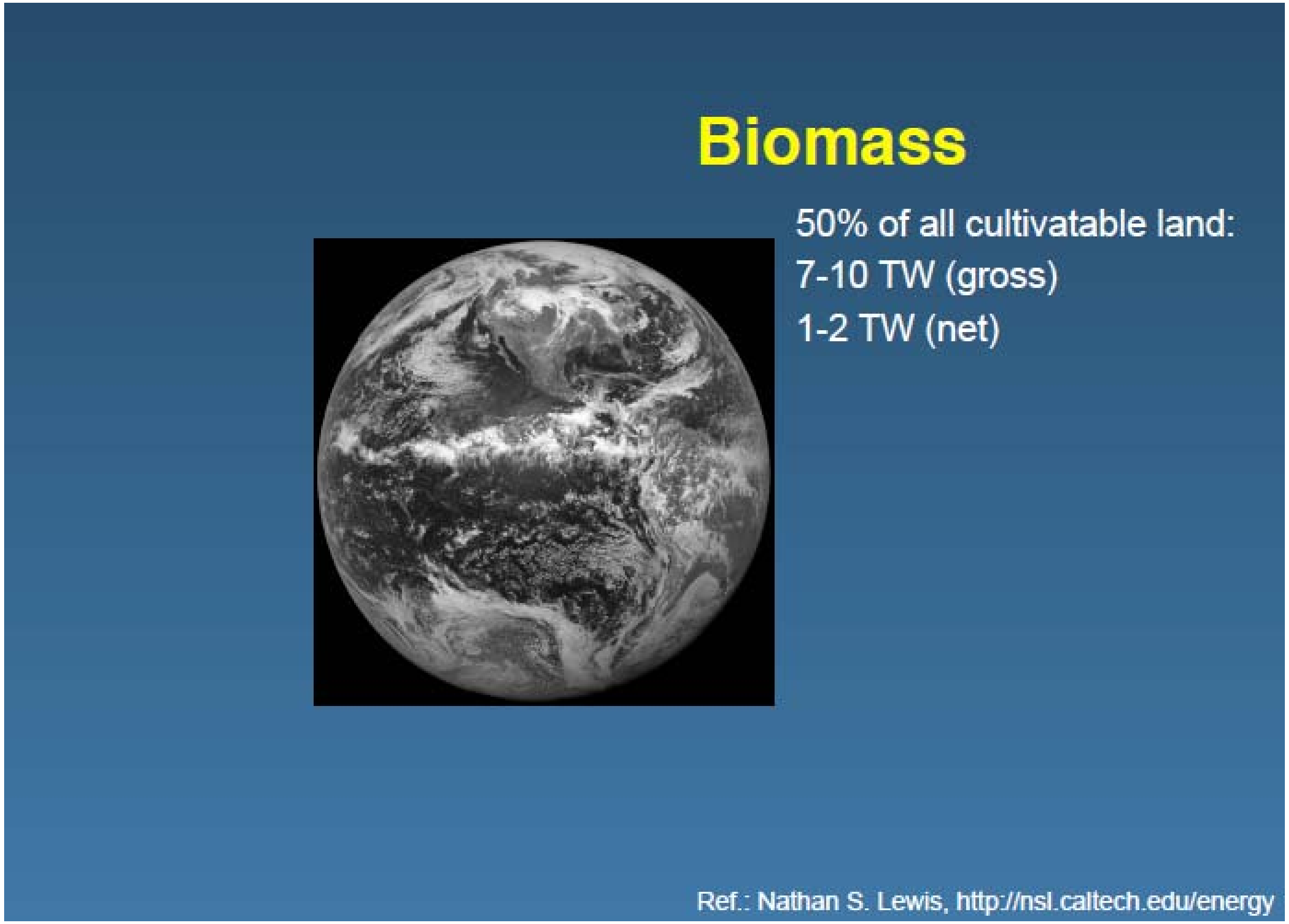
Wind 2 - 3TW

Wind

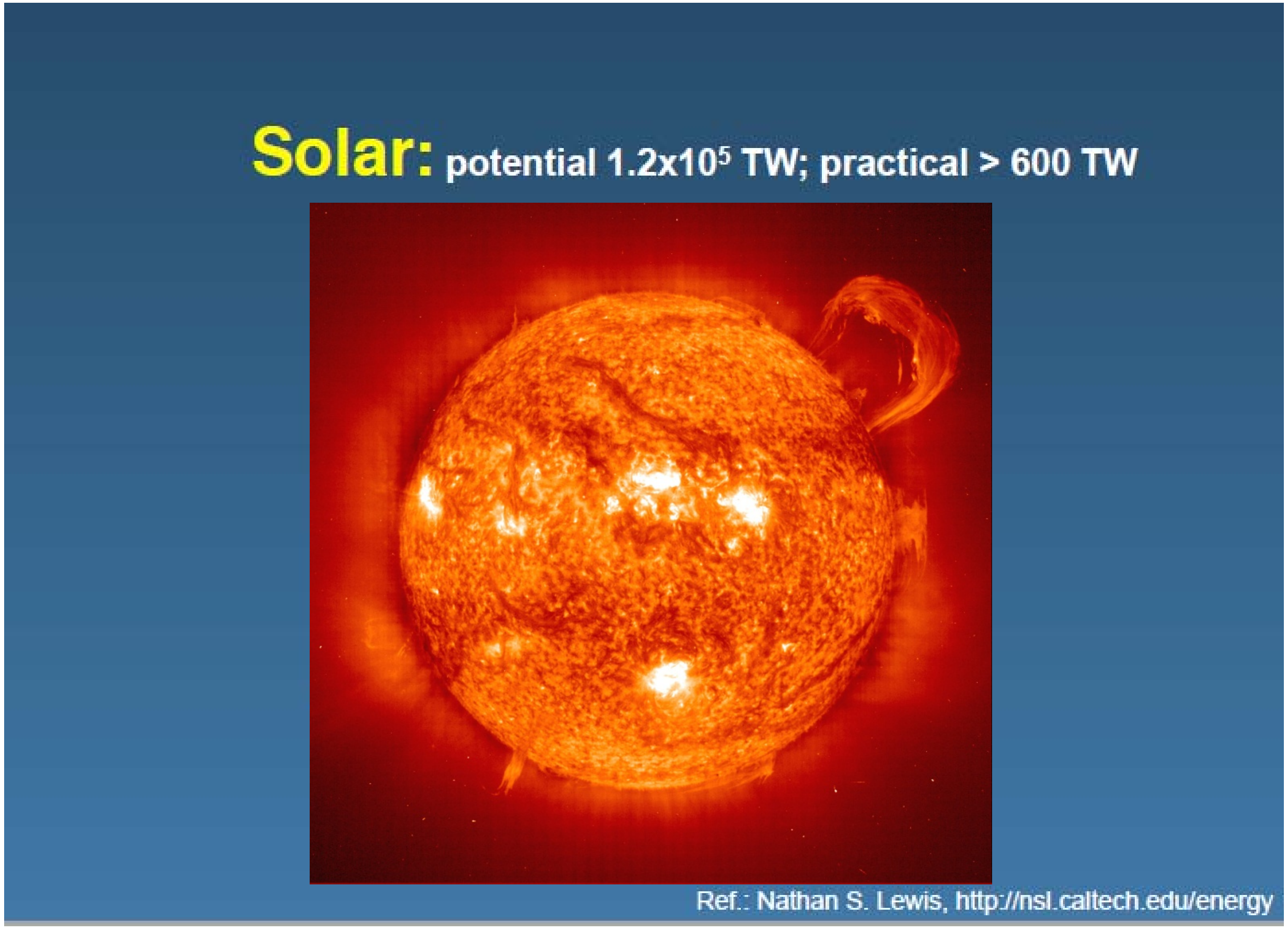
4% Utilization
Class 3 and
Above
2 - 3 TW

Ref.: Nathan S. Lewis, http://nsl.caltech.edu/energy

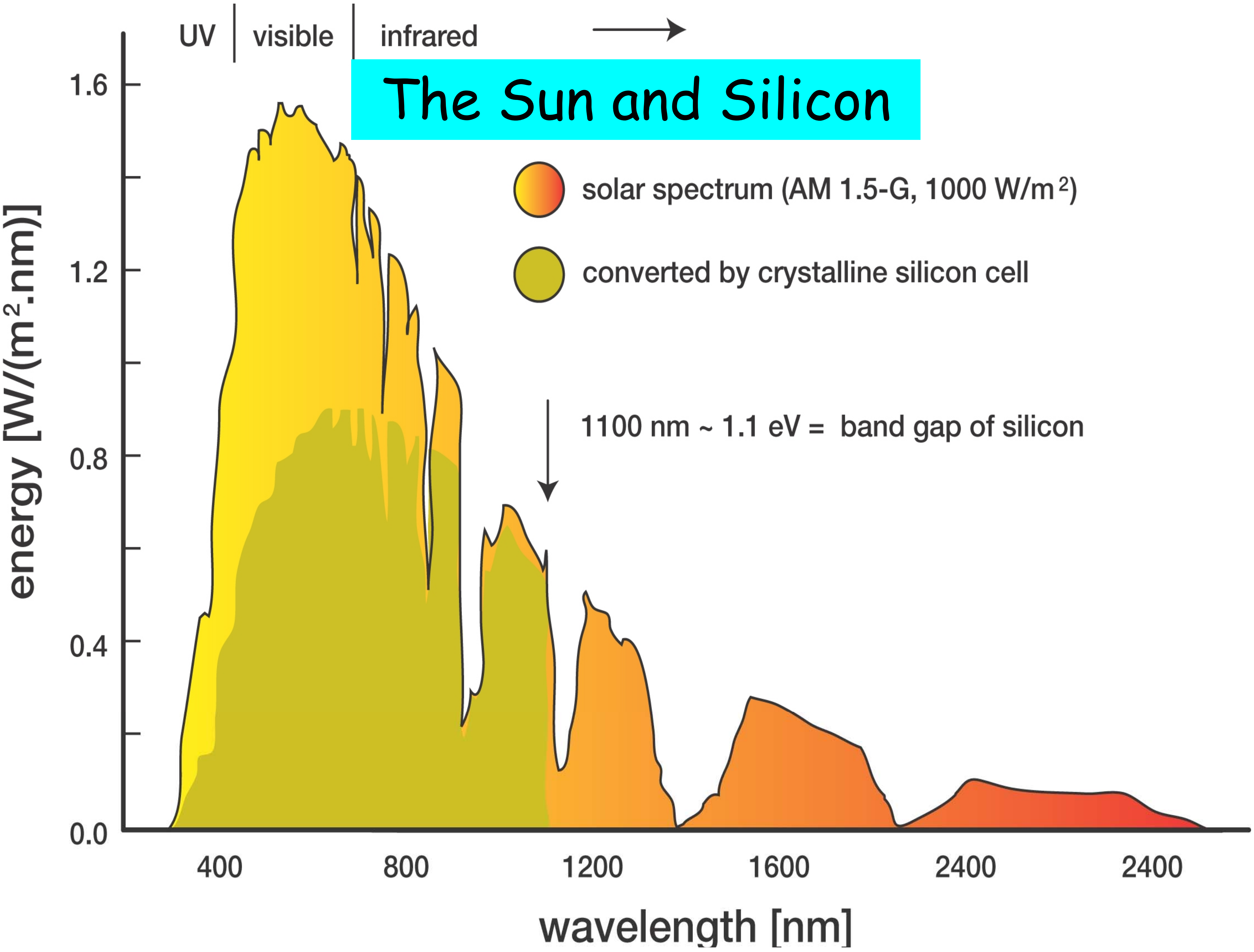
Biomass 1 - 2TW



Solar 600TW

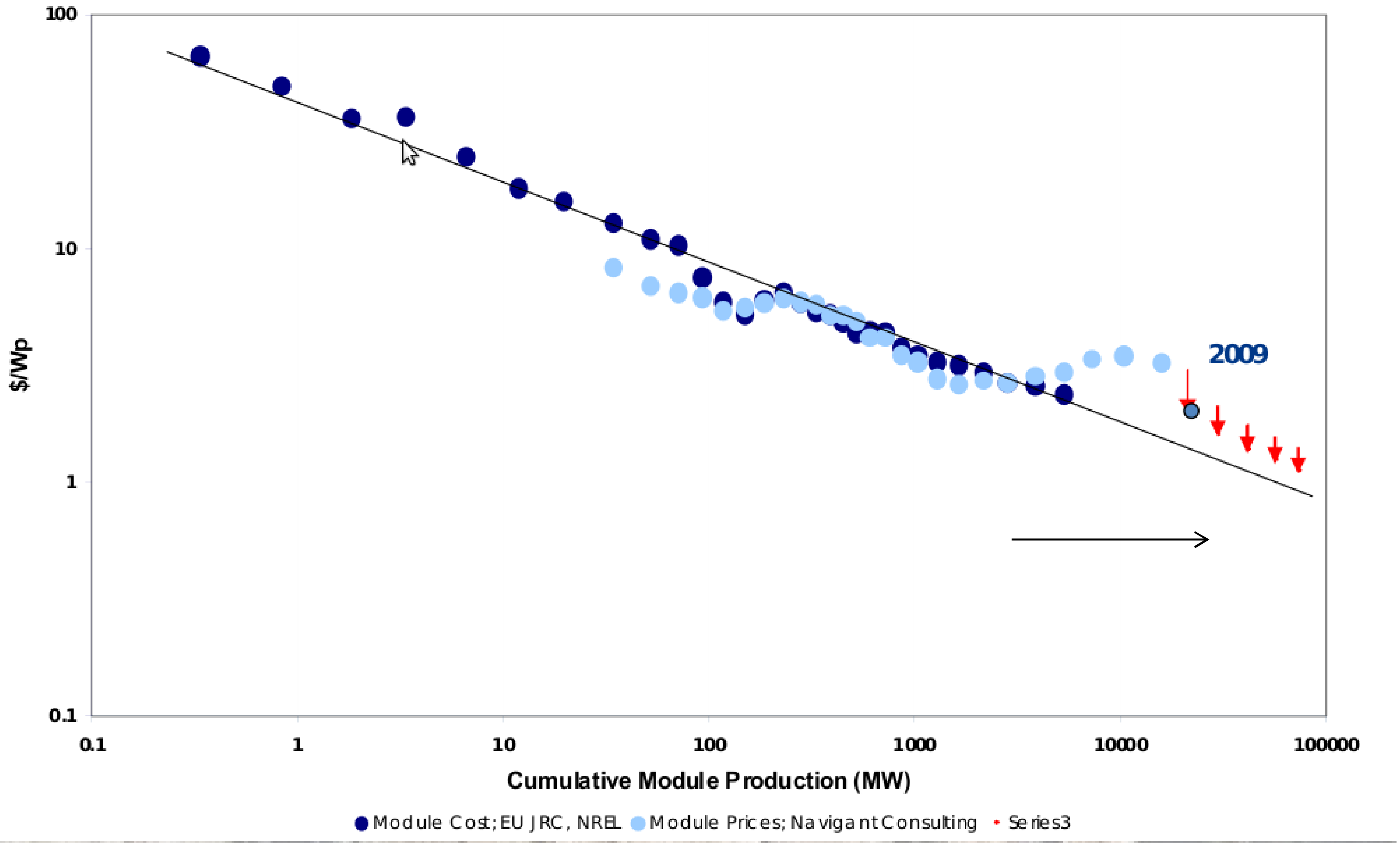

Solar: potential 1.2x10^5 TW; practical > 600 TW
Ref.: Nathan S. Lewis, http://nsl.caltech.edu/energy

The Sun and Silicon



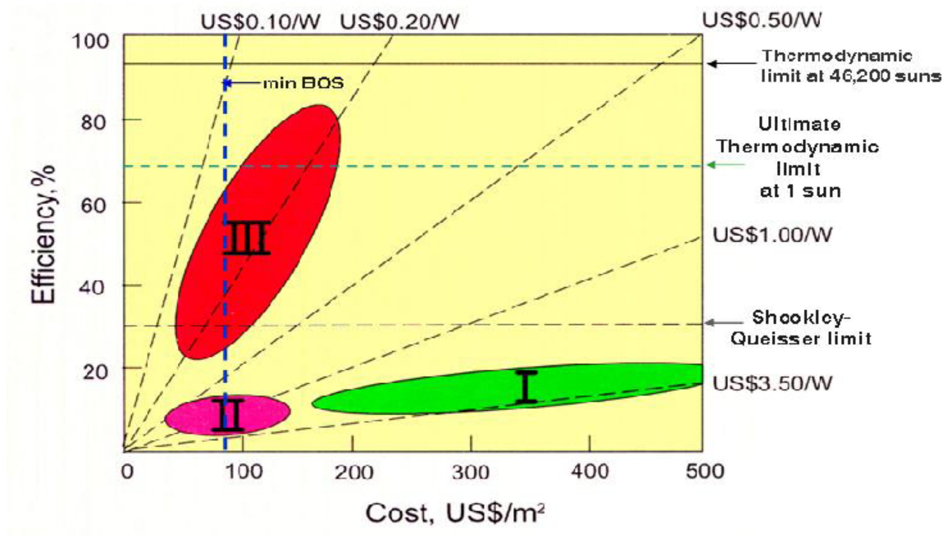
Motivation

PV: learning curve



Development of a novel low cost photovoltaic (PV) technology

- Present cost of PV is unsustainable
- Need to find a low cost (Gen II) PV technology
- Thin films option

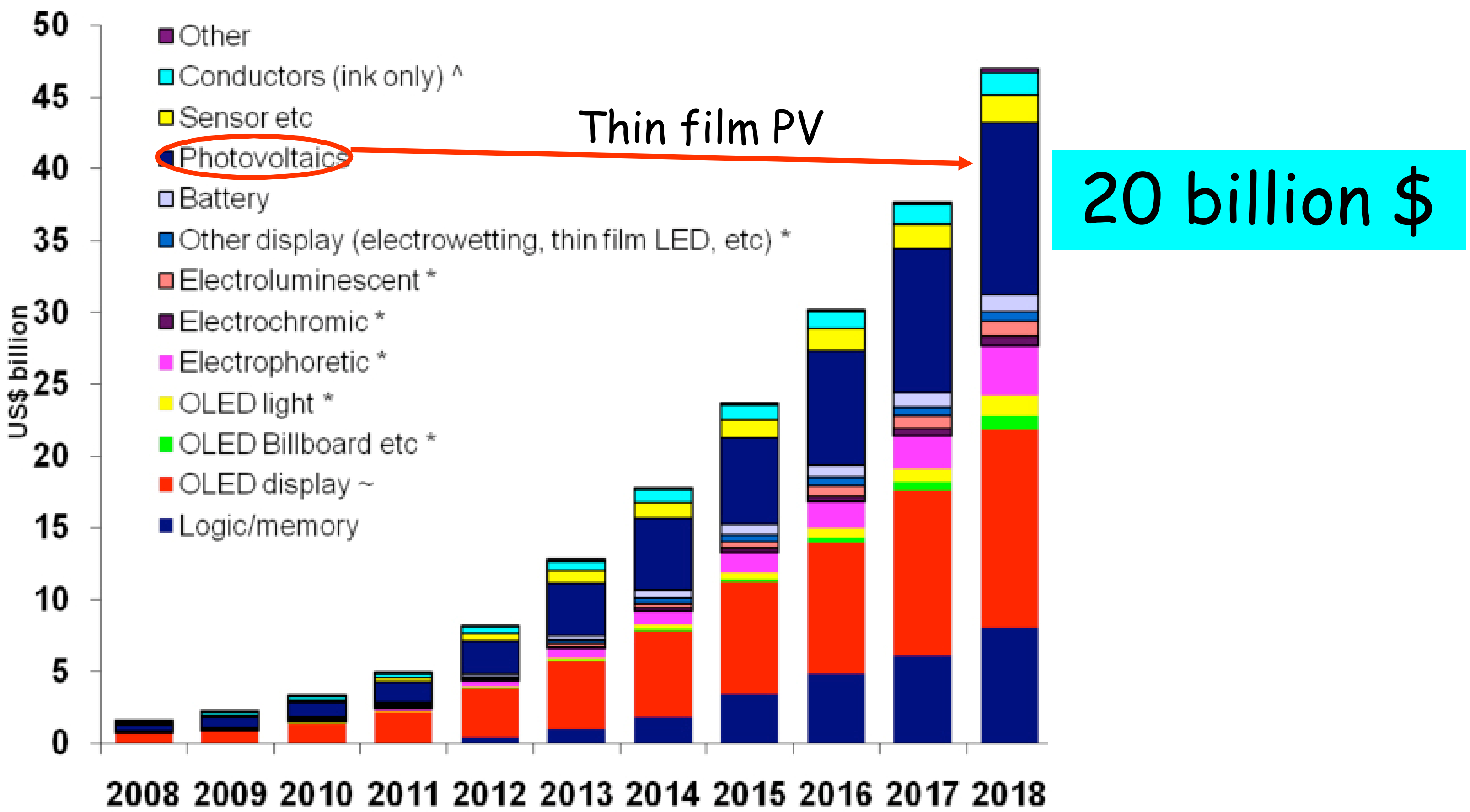


For PV or PEC to provide the full level of C-free energy required for electricity and fuel—solar power cost needs to be ~2 cents/kWh ($0.40/$W_p$).

Gen II Photovoltaic market perspective

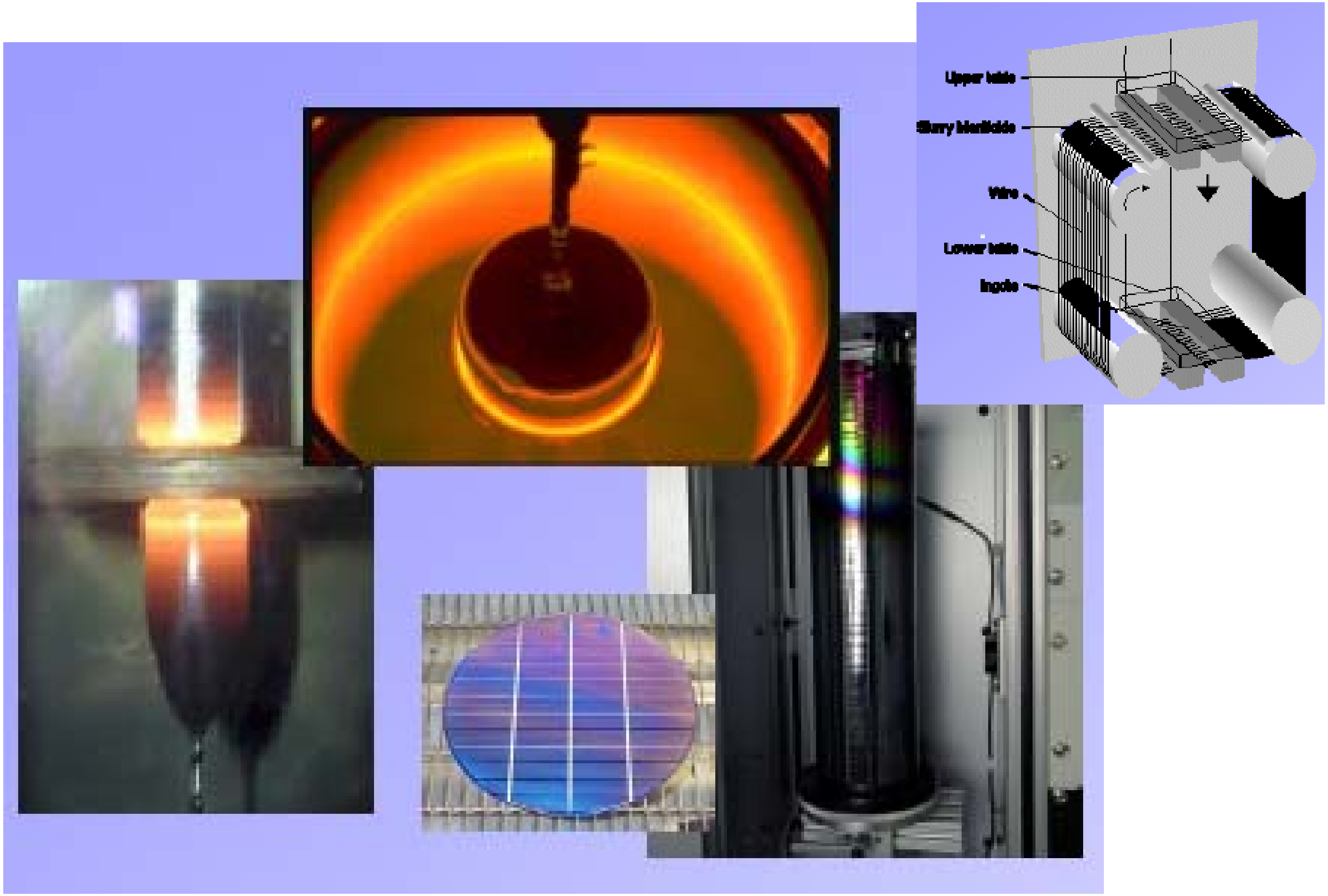
Market size perspective of major new technologies

Thin Film Photovoltaic (bejond conventional silicon technology) represents a 12 bil $ market. (Source IDtechEx)

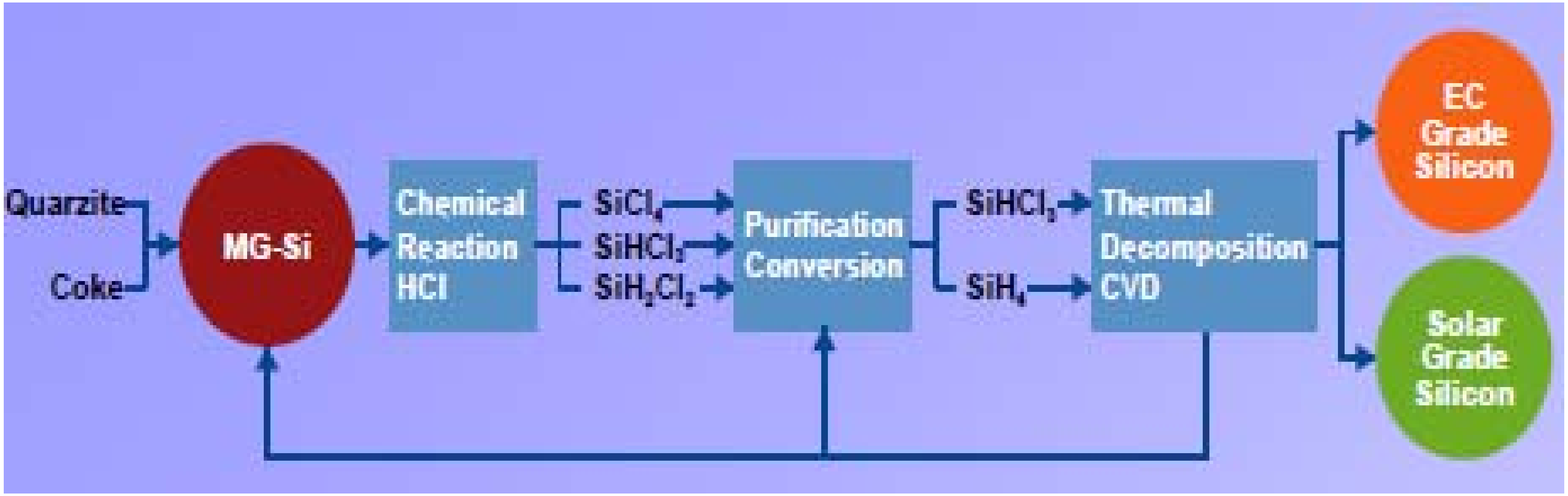


Silicon is not the material for solar

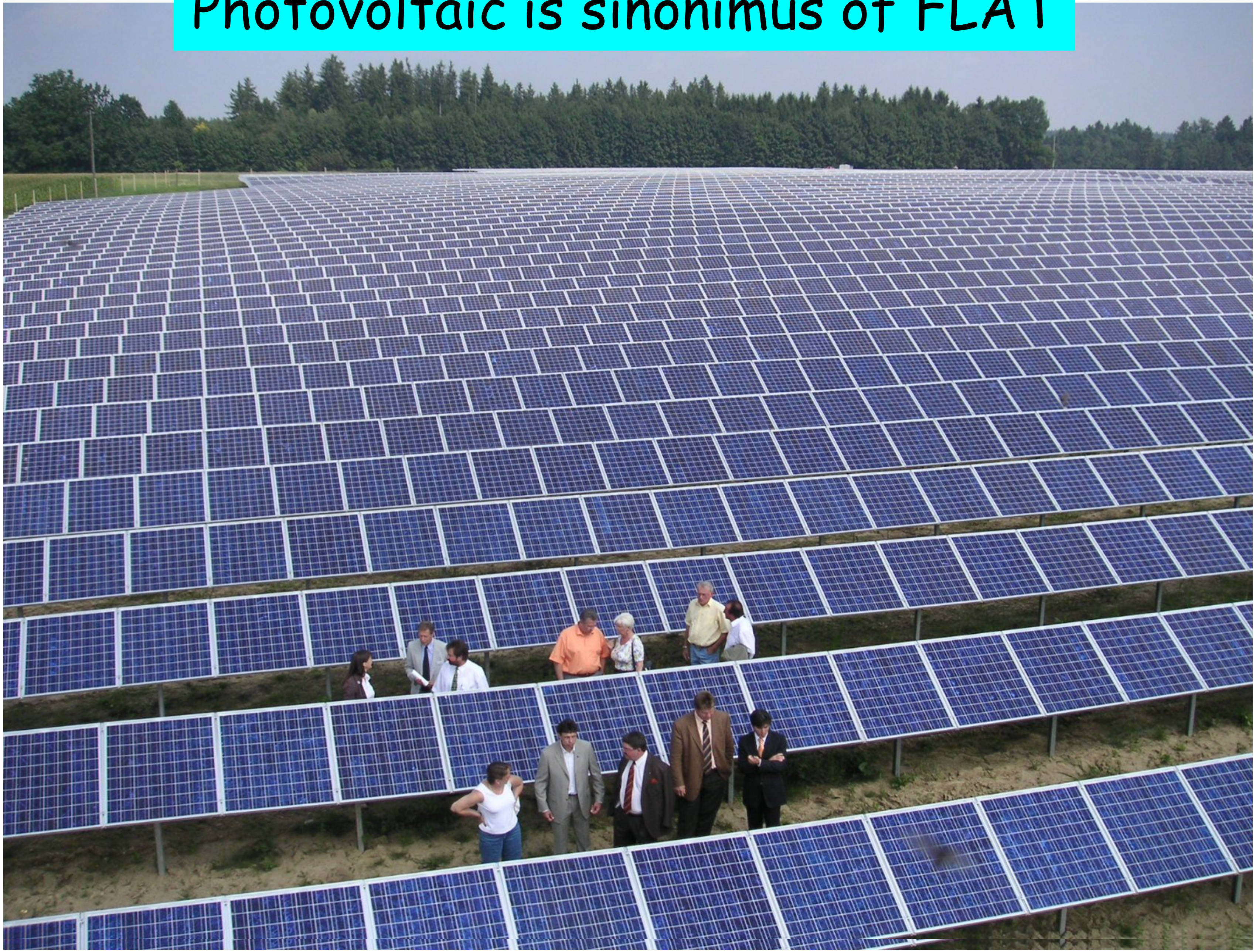
Silicon manufacturing



Silicon manufacturing



Photovoltaic is sinonimus of FLAT



The silicon paradox

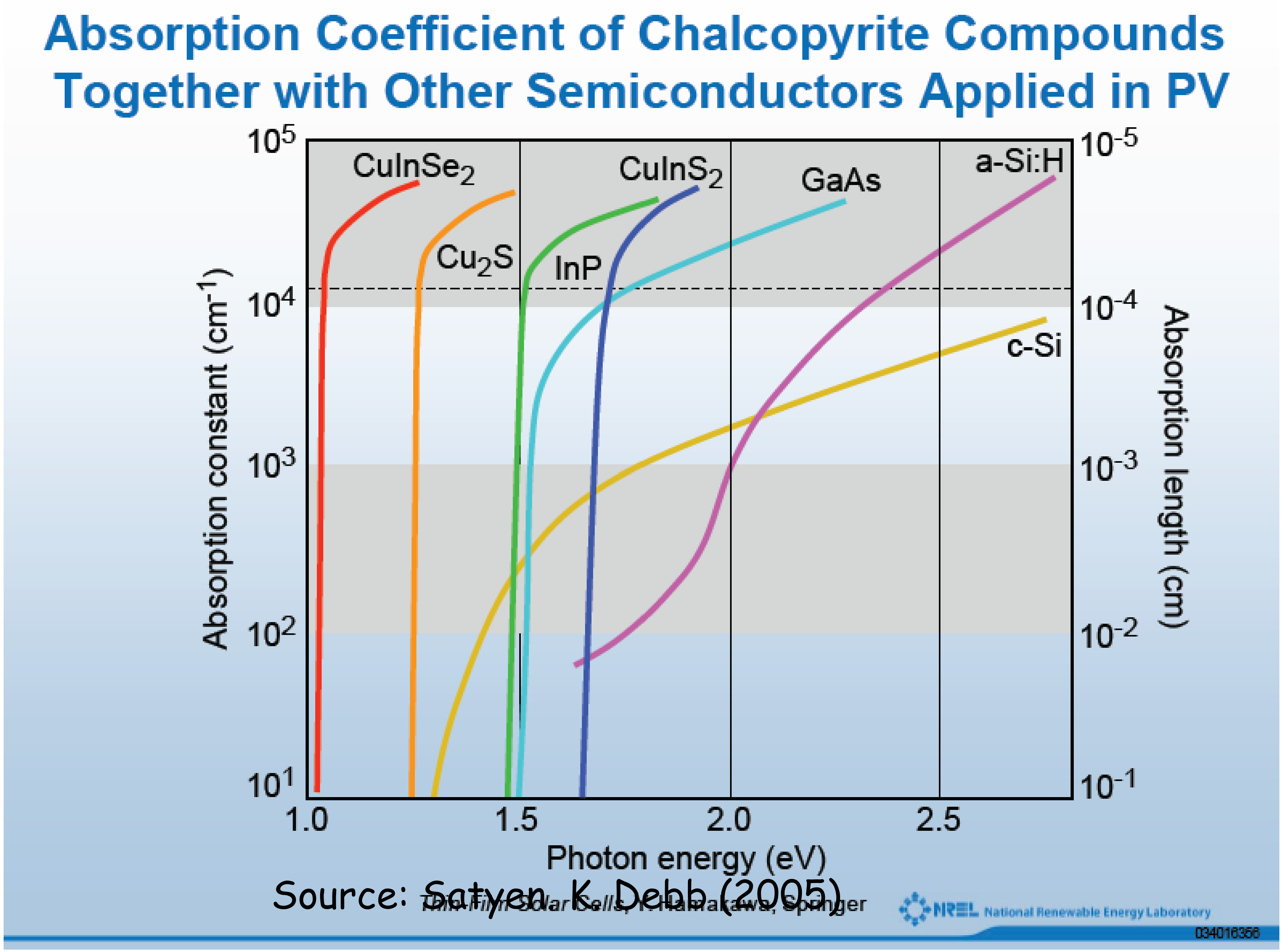
Silicon is not suitable for PV since it is a indirect-gap semiconductor (small absorption cross section).

The cost to make it is determined mainly by the energy required to purify and treat it.

Whichever is the fossile energy cost (grid cost) silicon will follow it.

There is no hope to achieve grid parity with silicon!

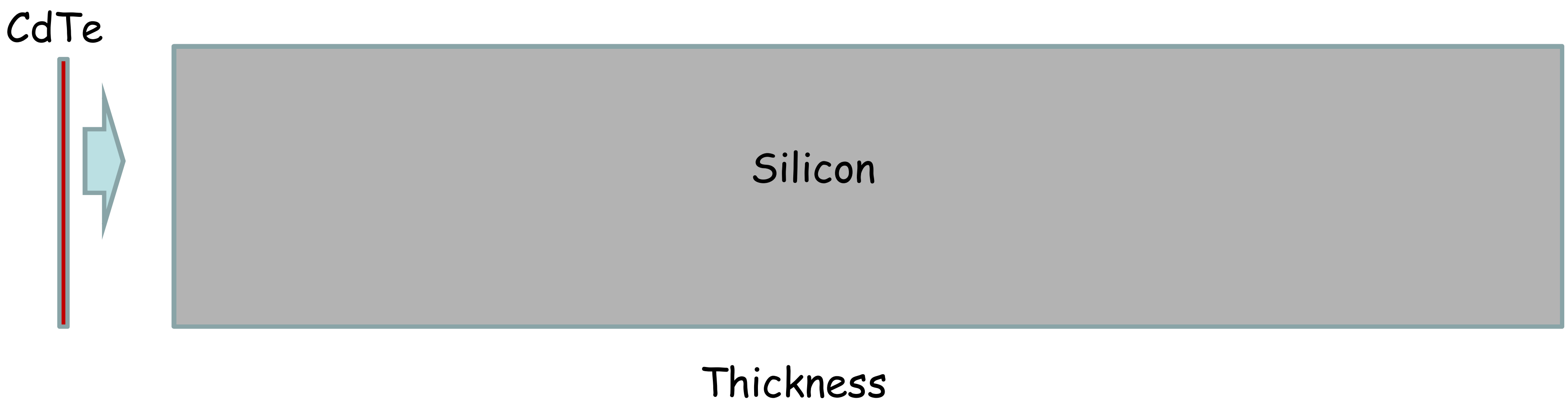
Direct vs Indirect Band Gap



Source: Satyen K. Debb (2005)

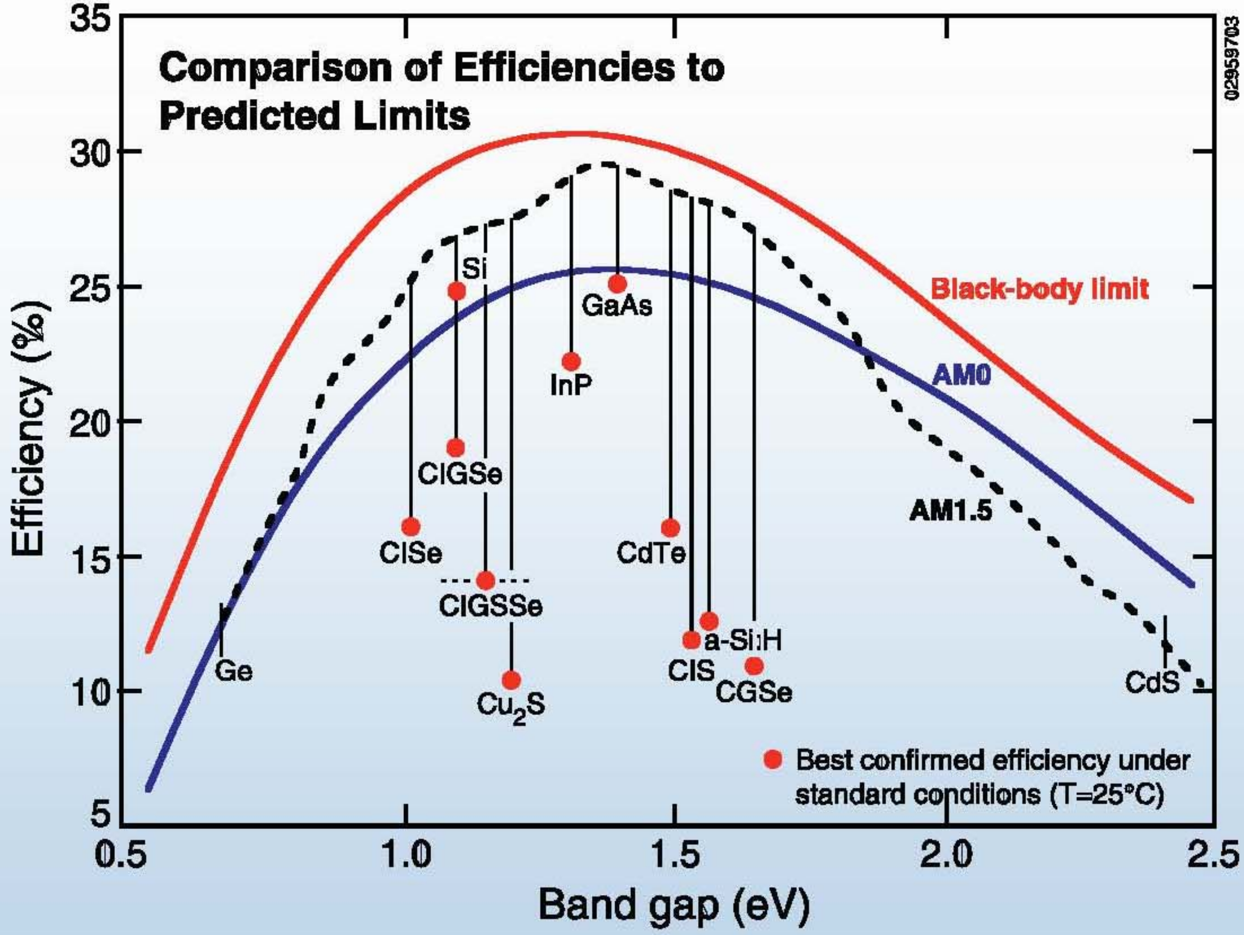
Why CdTe?

1 CdTe is a direct gap semiconductor (i.e. absorbs efficiently sunlight).
one micron thickness is sufficient



The silicon paradox: is a poor absorber because it is an indirect gap semiconductor.

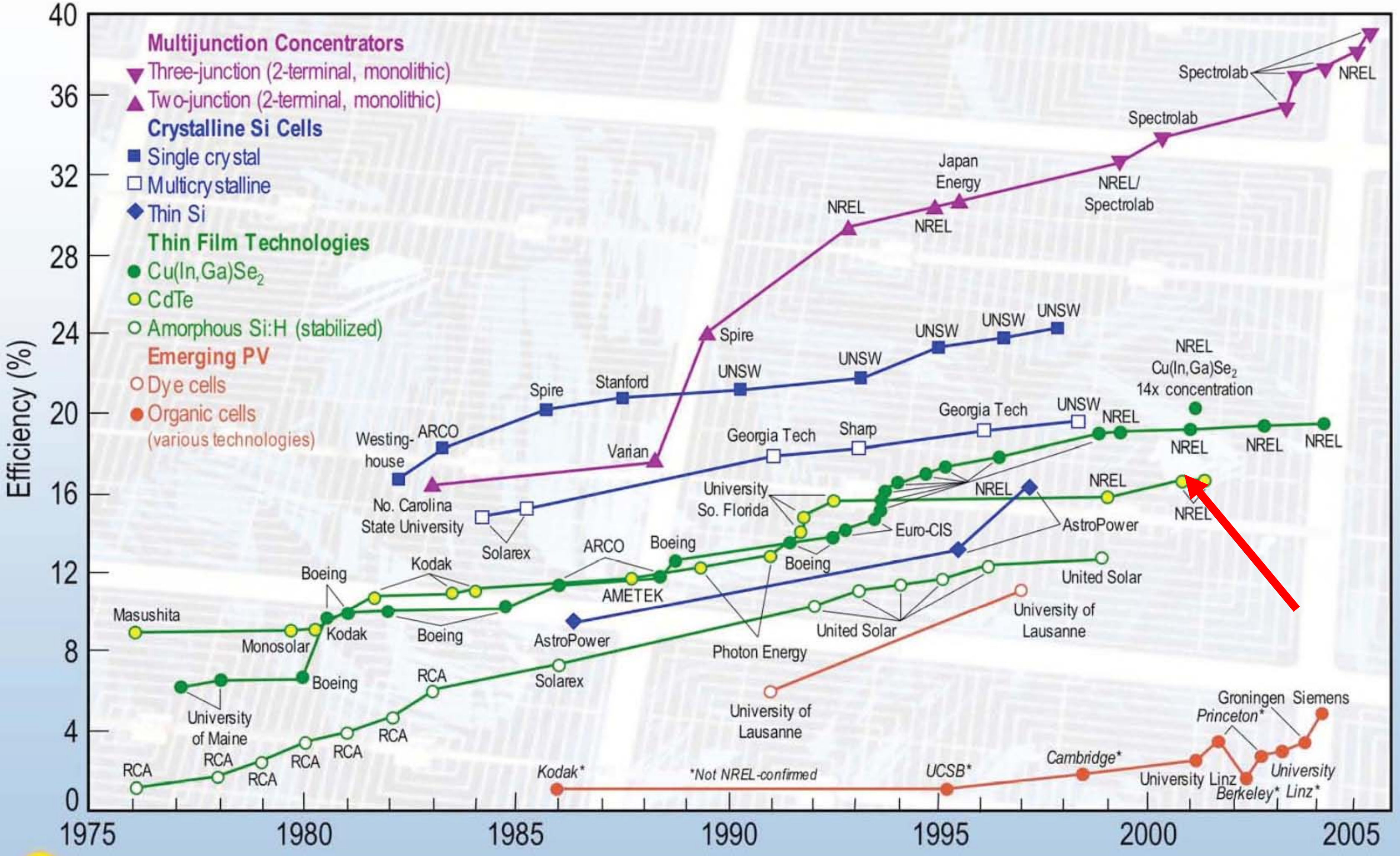
2 In theory the efficiency is in excess of 30%



Calculated AM1.5 efficiencies (dashed line) and AM0 efficiencies (solid line), comparing achieved cell efficiencies (laboratory-best, confirmed) for various technologies

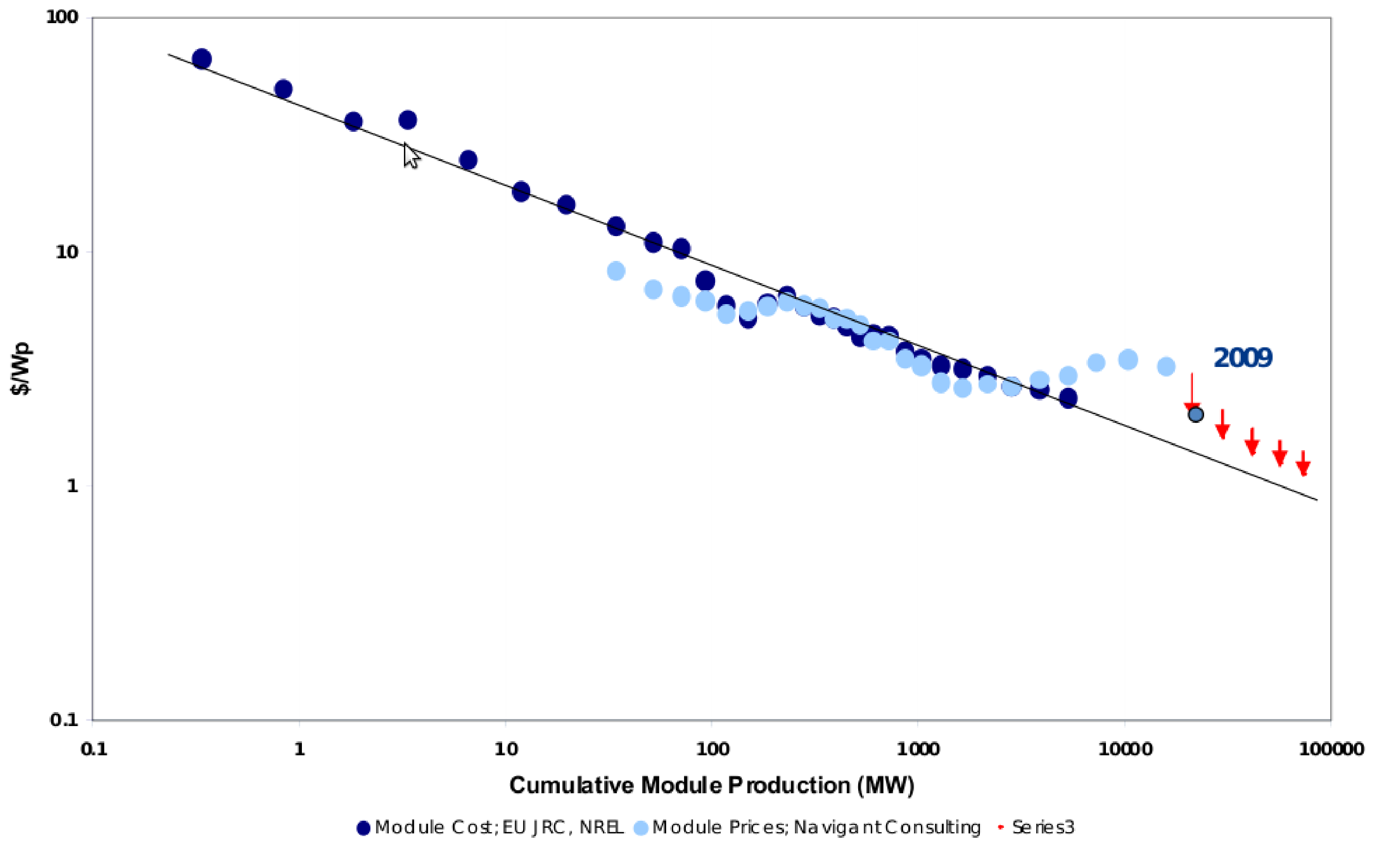
Source: Satyen. K. Debb (2005)

Best Research-Cell Efficiencies



Source: Satyen. K. Debb (2005)

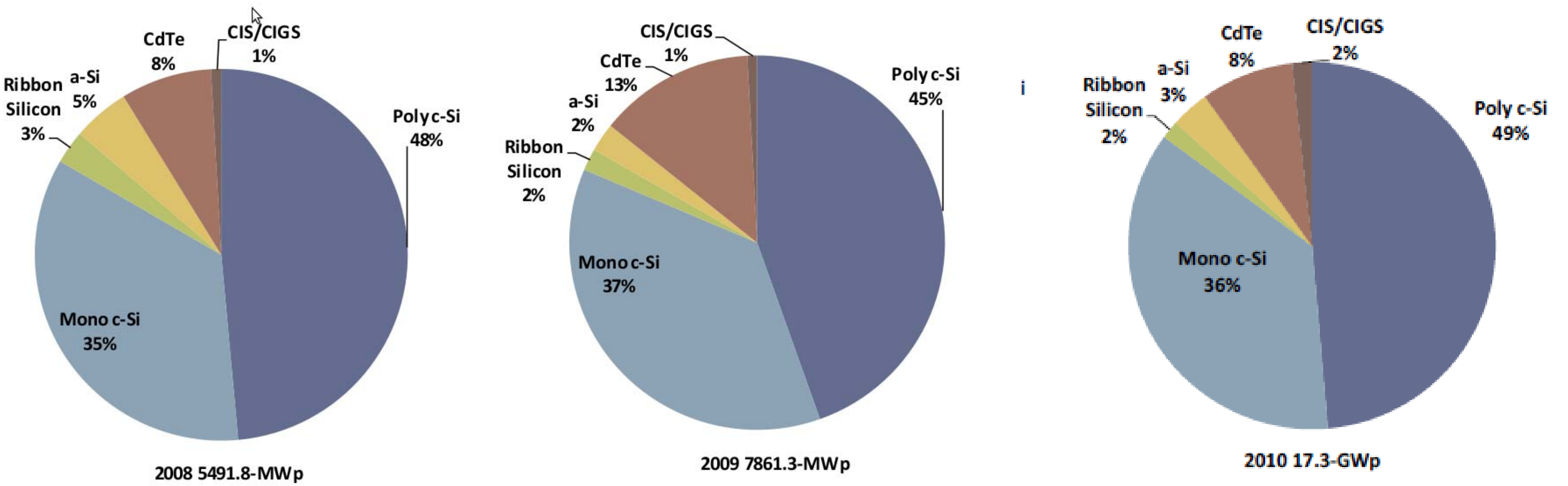
PV: Cost *learning curve*



Production costs and sales prices vs time. See the umbrella effect in 2008 due to over-demand determined by the subsidies determining the entrance of unsustainable technologies.
Source: Navigant Consulting

Technology Market Shares, 2009 and 2010

Thin films held a 17% share of the market for all PV technologies in 2009, and a 13% share of the market in 2010. In 2010, thin film shipments grew by 72% over 2009, with c-Si growing by 129% over 2009.



CdTe : 430 (2008) – 1021 (2009) – 1384 (2010) MW/yr

Thin film PV

Fotovoltaico di seconda generazione

Film sottile

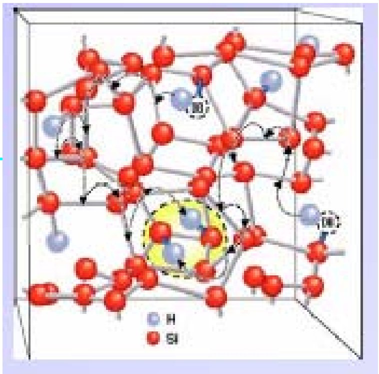
- Poco materiale
- Poca energia, basse temperature..
- Nanotecnologie

Silicio amorfo

CdTe (Tellururo di Cadmio)

CIGS

Fotovoltaico di seconda generazione

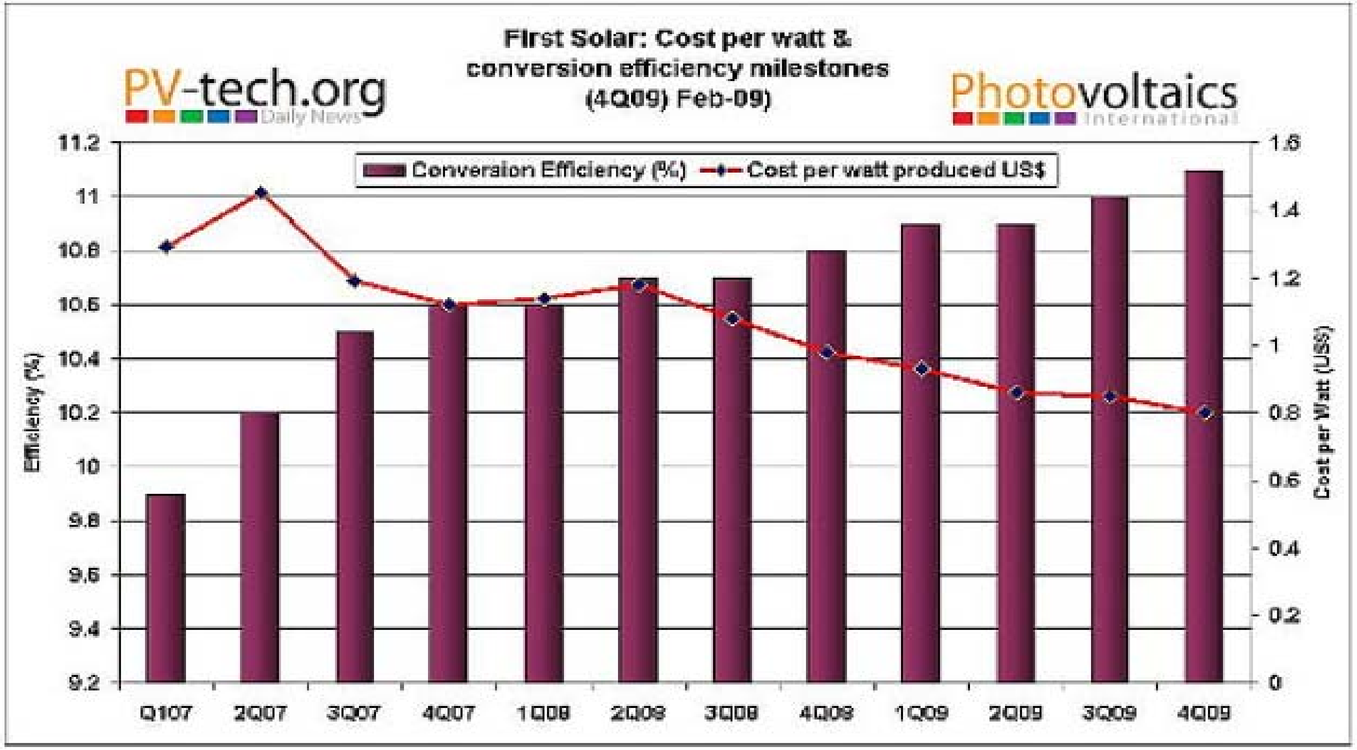


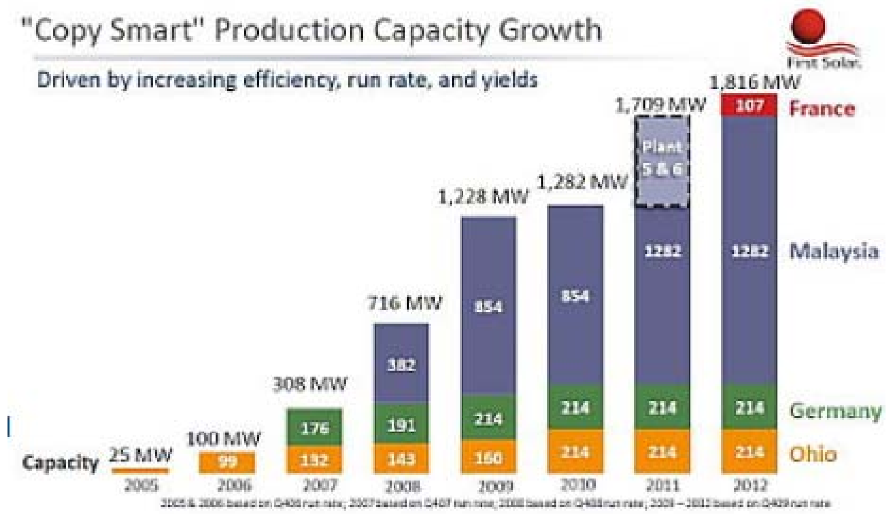
Silicio amorfo : basso rendimento e alti costi

Tellururo di Cadmio: basso costo e crescita impetuosa

CIGS: ancora a livello di sviluppo

The Champion First Solar Case





Our approach

OS and 2SN have developed a new thin film deposition technology characterized by:

- Proprietary IP CdTe process and fabrication
- Low material cost and consumption
- Low installation, mantainence and running costs
- Safe (contained low P) fabrication method
- Shortening time to market by integrating the module into existing CdTe lines
- Suitable for Roll to Roll on metal and plastic foils
- Conformable PV (flexible, building integrated)

Material usage and availability

Table 2 Are There Enough Materials for Energy-significant PV Production?

Technology	Material	World Production (MT/yr)[a]	Materials Required (MT)[a,b]	% of Current Production	Annual Growth Needed (%)
Crystalline silicon	Purified silicon	25,000[b]	130,000	520	3.7[c]
	Silver (grids, cell pads)	20,000	6,000	30	0.53
Thin-film Cu (In, Ga)Se_2 alloys	Indium	250 (by-product)	400	160	2.0[d]
	Selenium	2,200	800	36	0.6[e]
	Gallium	150	70	47	0.9[f]
Thin-film CdTe	Tellurium	450 (2,000 unused by-product)	933	38 (of total, including unused)	2.2
	Cadmium	26,000 (by-product)	8	3	0.06
Thin-film silicon	Germanium	270 (3,200 unused by-product)	40	1 (of total, including unused)	0.7

[a] Necessary production for each type of PV technology to produce 20 GW/yr by 2050
[b] Metric tons
[c] Elemental silicon is not constrained by supply; current production is low because of low demand.
[d] Indium is a by-product of zinc, which has been growing at 3%/yr for 50 years. Indium growth will probably exceed demand because of growth in zinc.
[e] Selenium is a by-product of copper; an increase of only 0.16% per year would keep pace with demand.
[f] Gallium is not constrained by supply; current production is low because of low demand.

The PPD Thin Film Deposition Technology

Pulsed Plasma Deposition: a key enabling technology for thin film fabrication

Carlo Taliani
ISMN e
Organic Spintronics SrL

Presentation to IIT Milan _ june 2011

Outlook

Organic Spintronics and the PPD technology

PPD source improvements and evolution

Applications:

- Transparent conducting oxides (TCO)
  - TCO at low T on PET and org. semicon.
  - Indium free TCO at low T
- Hard coating
  - Oxides on HDPE for implants
  - Diamond Like Carbon (DLC)
- Photovoltaics
  - CdTe/CdS , CIGS,
- Buffer layers
  - CeOx, YSZ, ZrOx, TiOx,..
- Ultra high k (barium strontium titanate – BST)
- Carbides WC, SiC

FROST & SULLIVAN

2008 BEST PRACTICES AWARD

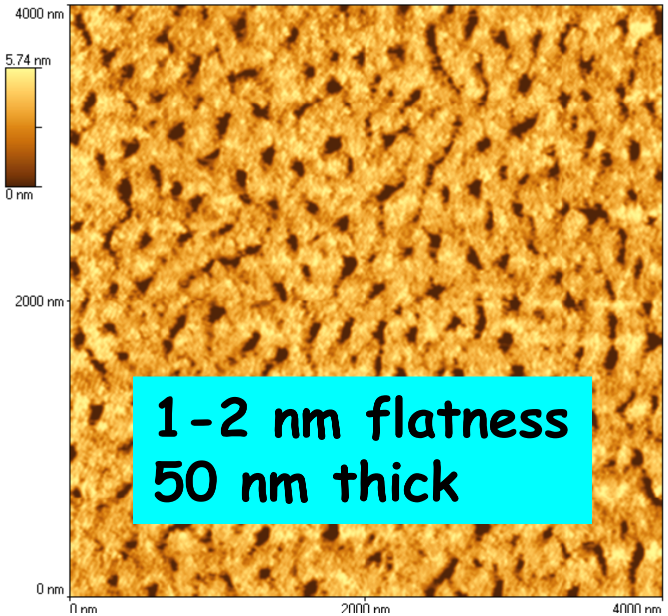
PPD: towards an industrial tool

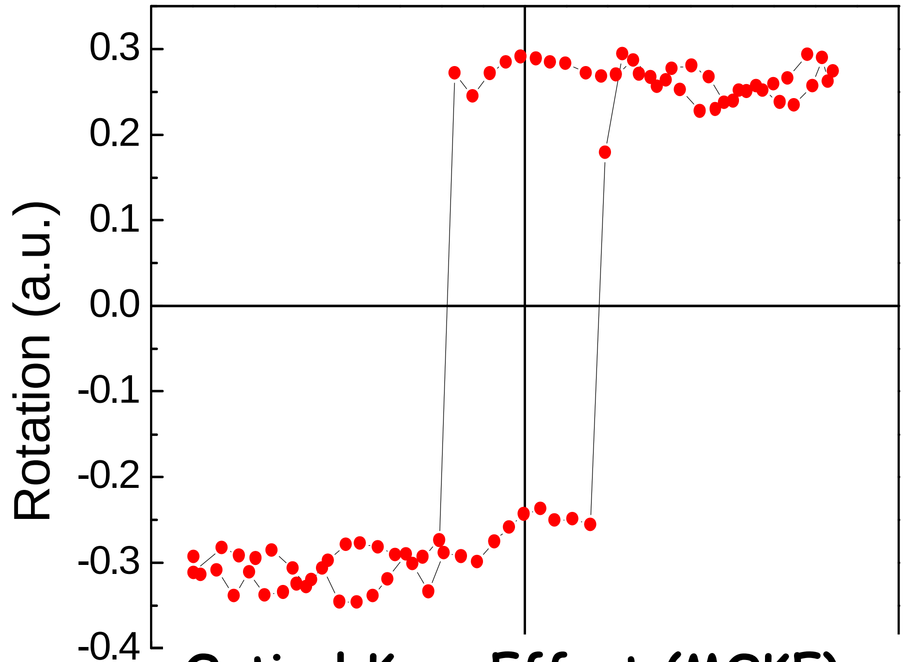
ORGANIC SPINTRONICS

2003: the origins

from research to business

$La_x Sr_{1-x} Mn O_3$ films by PPD deposition on STO





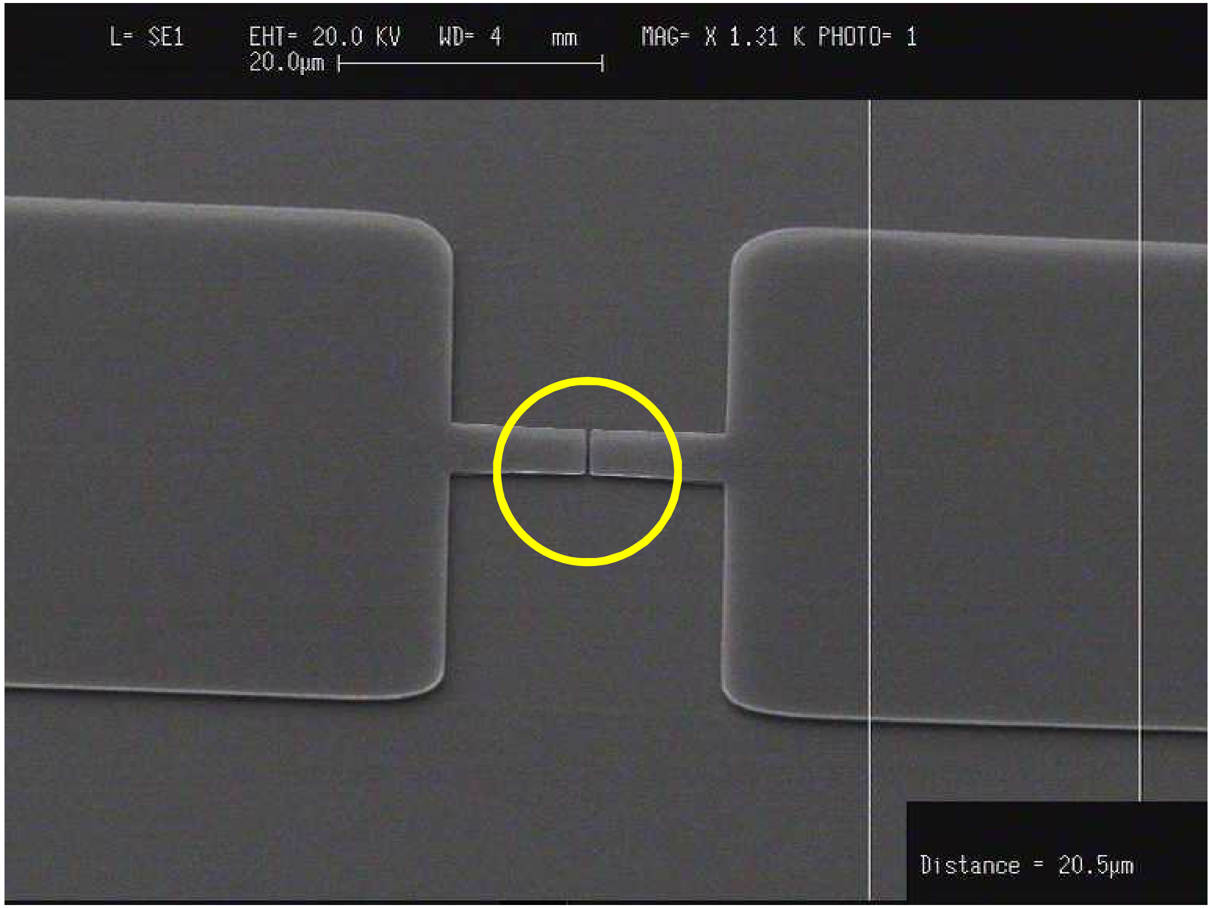
Optical Kerr Effect (MOKE).
In plane field, 20 nm thick

V.A. Dediu, et. 2002

ISMN Institute for Nanostructured Materials CNR Bologna

ORGANIC SPINTRONICS

The first organic spin-valve



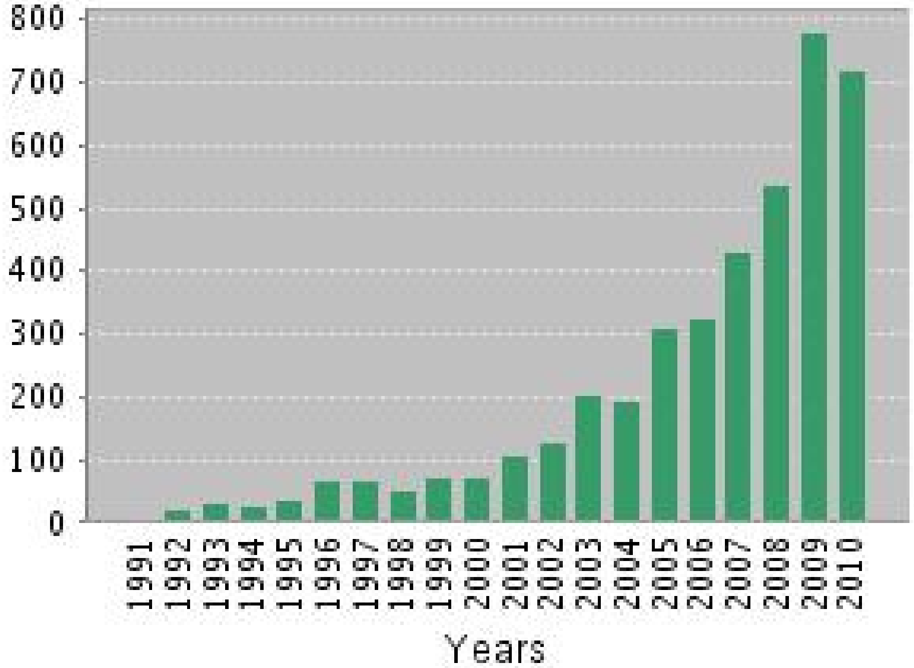
A new field emerged from this paper

ISMN Institute for Nanostructured Materials CNR Bologna

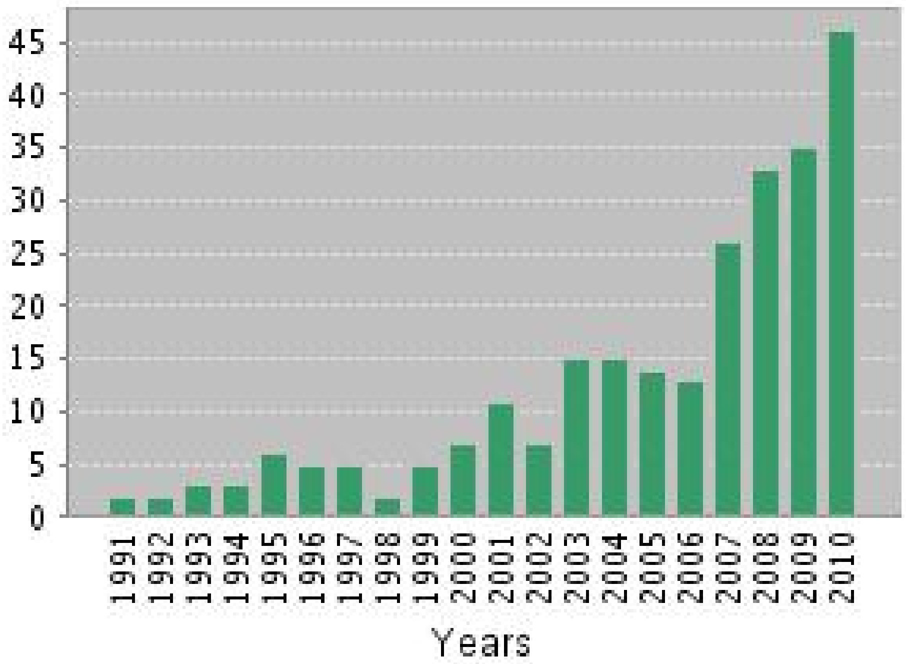
ORGANIC SPINTRONICS

Organic Spintronics:
a new rapidly expanding scientific area

Citations in Each Year



Published Items in Each Year



SpinOS 2007

Workshop on Spintronic Effects in Organic Semiconductors
Bologna Italy 9 September - 11 September 2007

We are pleased to inform you of the Workshop on Spintronic Effects in Organic Semiconductors (**SpinOS 2007**) that will be held at the CNR Campus in **Bologna** from **9 to 11 September 2007**.

The main scope of the **SpinOS 2007** Workshop is to bring together for the first time the international community of scientists working in Organic Spintronics.

The organizers hope to start an intense dialog in the community and to lay the foundations for future regular meetings in the field of both basic research and applications of spin injection and transport in organic semiconductors.

The Conference will include presentations on recent experimental and theoretical results on various spintronic effects in organic semiconductors.

For more details, please visit our website at http://www.spinos.org

Conference chairman

C. Taliani. ISMN-CNR, Bologna

Scientific Advisory Committee (confirmed)

Martin Aeschlimann. Univ. Kaiserslautern
Sasha Alexandrov. Loughborough University
Arthur J. Epstein. Ohio State University
Albert Fert. Unité Mixte CNRS/THALES
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Stefano Sanvito. Trinity College Dublin
Darryl Smith. Los Alamos National Laboratory
Erio Tosatti. SISSA/ICTP
Evgeny Y. Tsymbal. University of Nebraska
Xin Sun. Fudan University
Z. Valy Vardeny. University of Utah
Markus Wohlgenannt. University of Iowa

Program committee

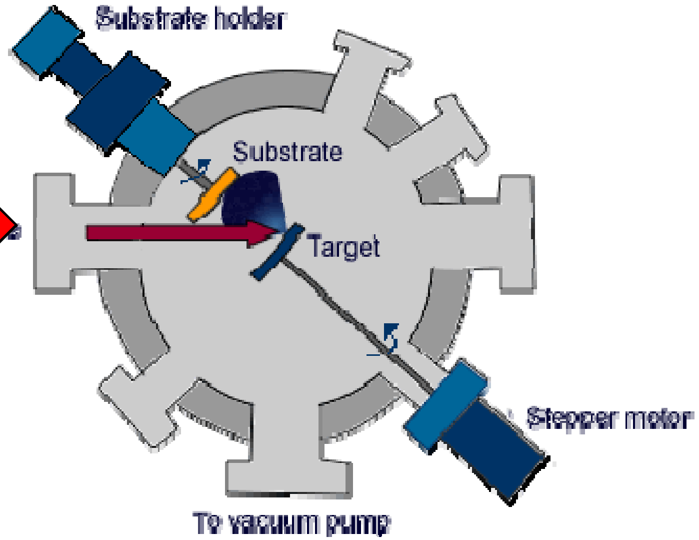
V. Alek Dediu. ISMN-CNR, Bologna
Georg Schmidt. University of Würzburg

We look forward to seeing you at the conference

ORGANIC SPINTRONICS

Pulsed Plasma Deposition by Ablation

100 ns electron beam

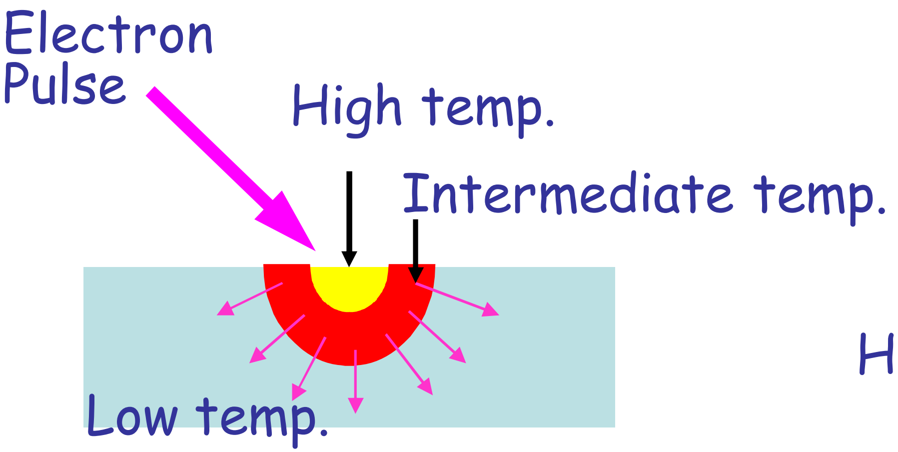


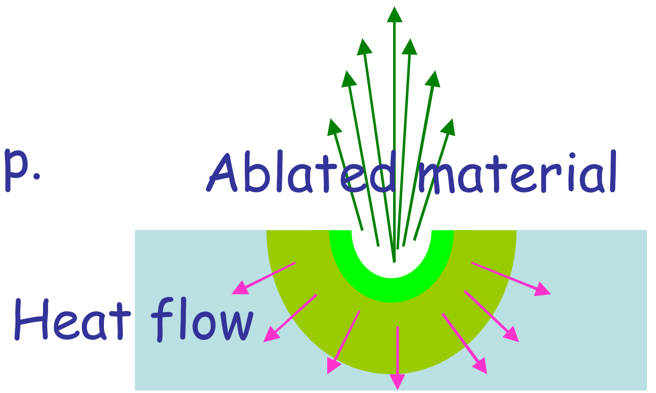
Deposition characteristics:

- Good composition trasfer
- Smooth surface

The ablation process

Ablation below the target surface ejects a fast, dense and fully ionized plasma normal to the surface forming a film on a substrate.

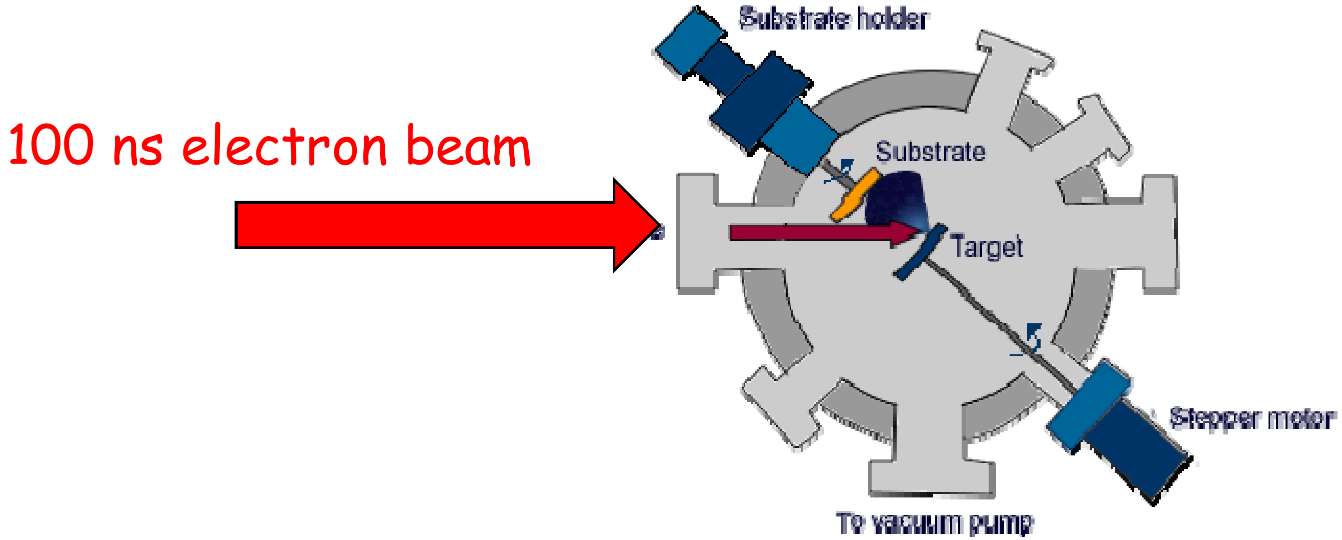




Composition of the substrate is the same of the target

Is a scalable process suitable for industrialization (contrary to Pulsed Laser Deposition)

Pulsed Plasma Deposition by Ablation



Deposition characteristics:

- Good composition trasfer
- Smooth surface
- Good homogeneity
- As in the case of PLD

Advantages:

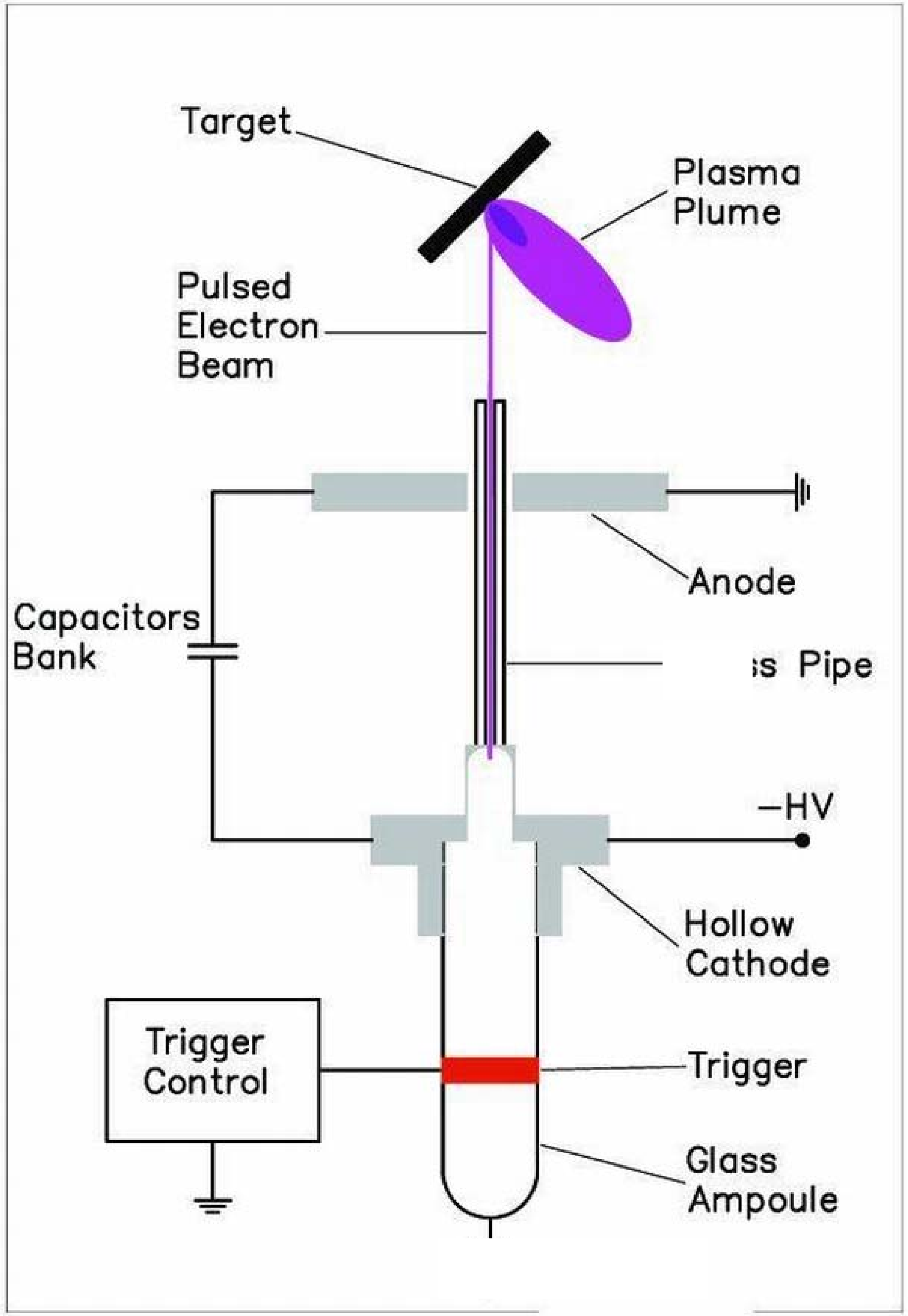
- Low equipment cost
- Low running cost
- Scalable for large area
- Suitable for industrial application

PPD ablation principle

Triggered discharge and accelleration from the hollow cathode to the anode generates a focussed electron beam that interacts with the target.

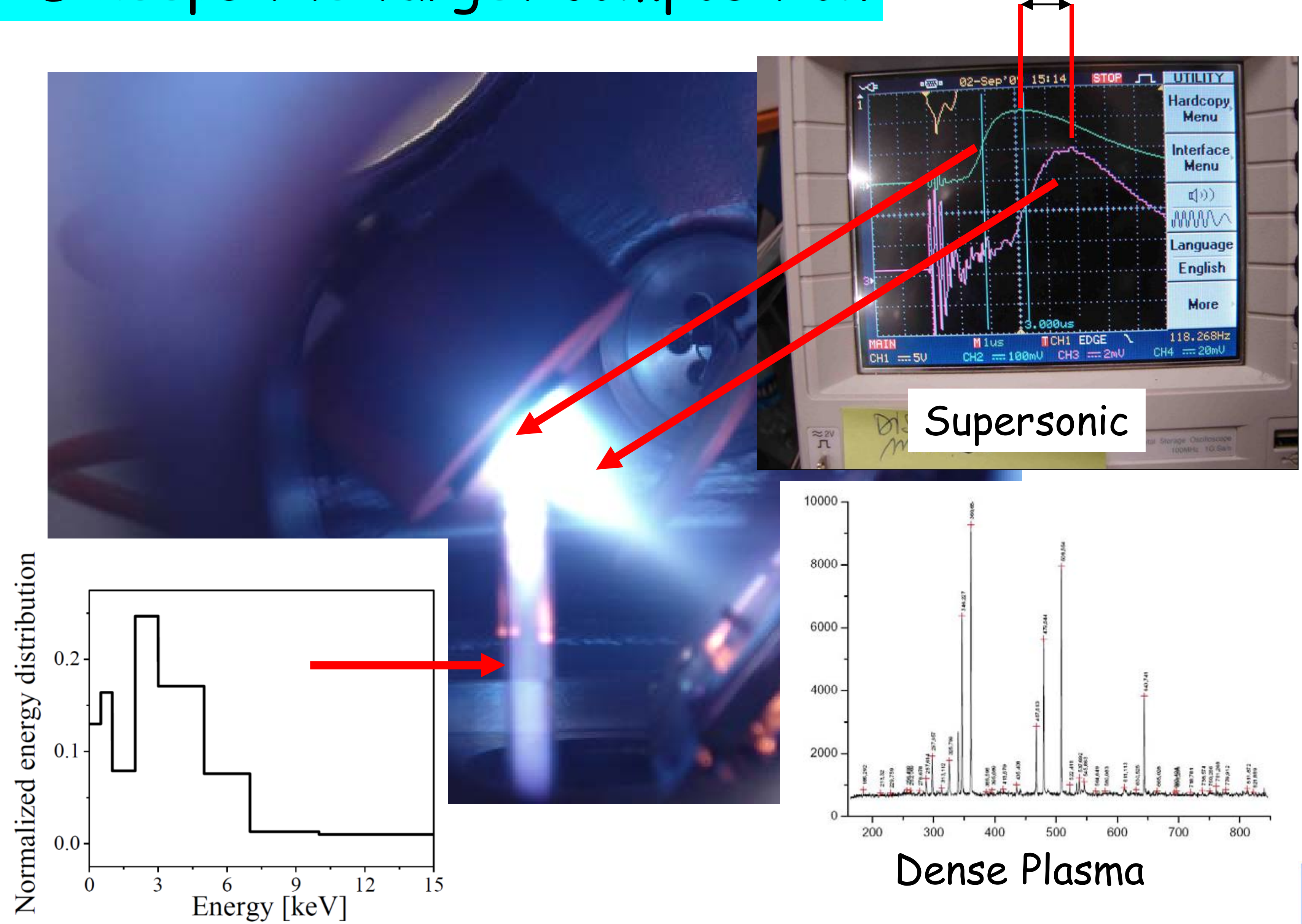
Target material explodes and is ejected forming a supersonic and dense plasma.

- Duration: 100 ns
- Max. energy: > 4J
-Beam size at target: 3 mm^2
(and less by plasma focussing)



PPD keeps the target composition

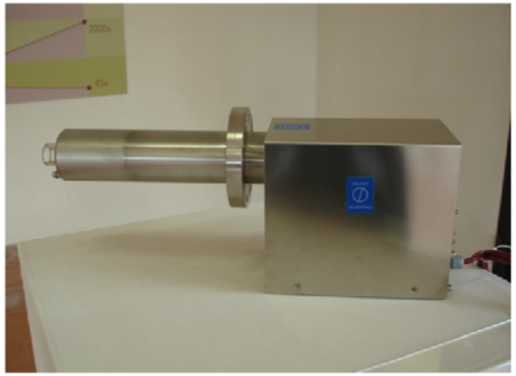
25 mm = 5 Km/s



Electron Energy (J.A.P.,106,73301,(2009))

ORGANIC SPINTRONICS

Evolution of PPD Guns: from GenI to Gen III



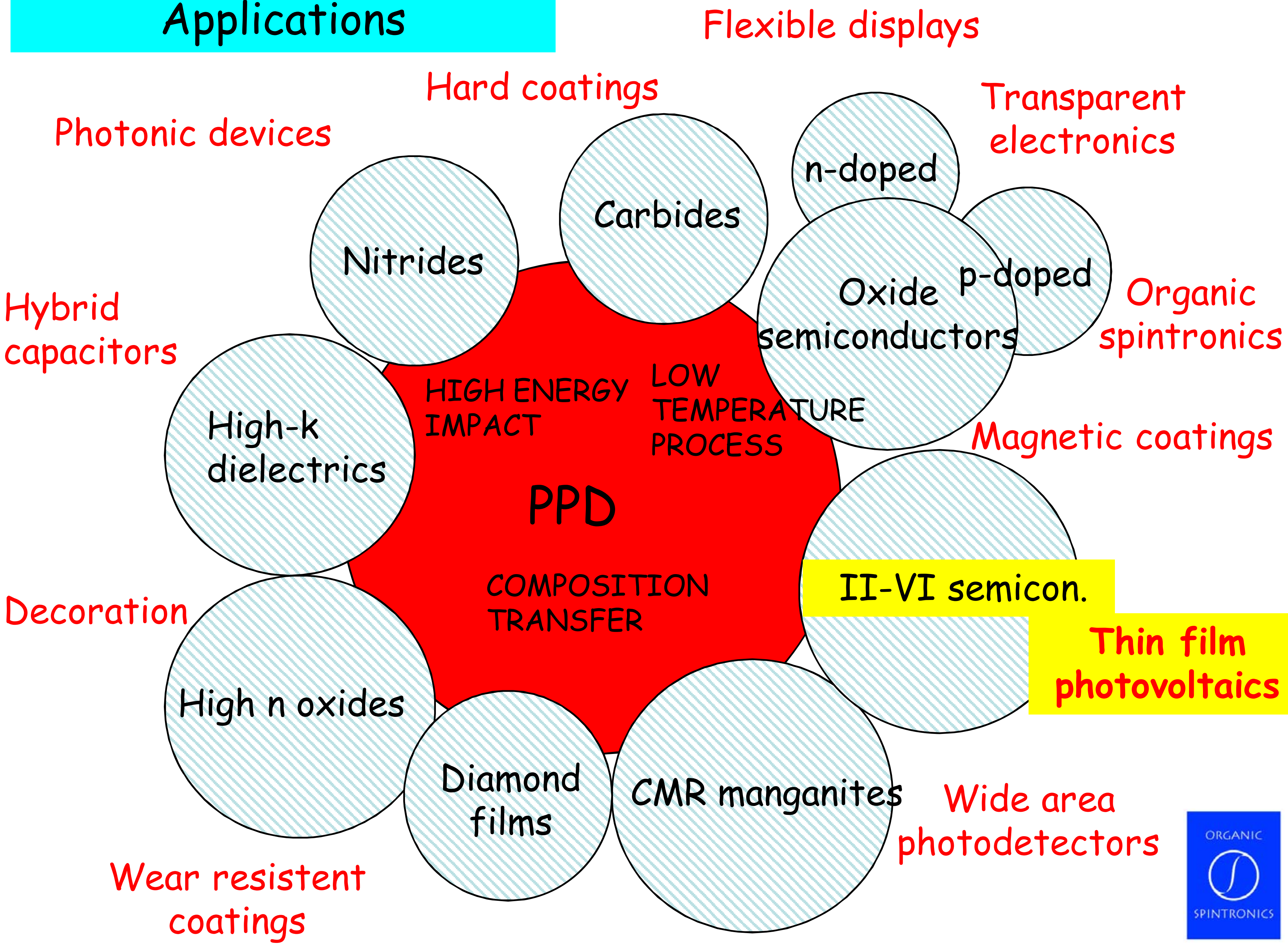
30Hz, 2007

10 Hz, 2005

2 Hz, 2004

ORGANIC SPINTRONICS

Applications



Chalcogenides by the PPD

SIENA SOLAR NANOTECH

A new deposition technology for CdTe, CdS thin film PV

Carlo Taliani, President

2SN in brief

Siena Solar Nanotech (2SN) was born in 2007 as a spin-off of Organic Spintronics , a spin-off of the National Research Council of Italy (CNR). 2SN posses the IP of the process and the PPD technology for II-VI semiconductors

Vision: getting grid parity by depositing CdTe, CdS and TCO by a new thin film deposition technology.

Business: - commercialize thin film deposition PPD equipments for CdTe, CdS and TCO

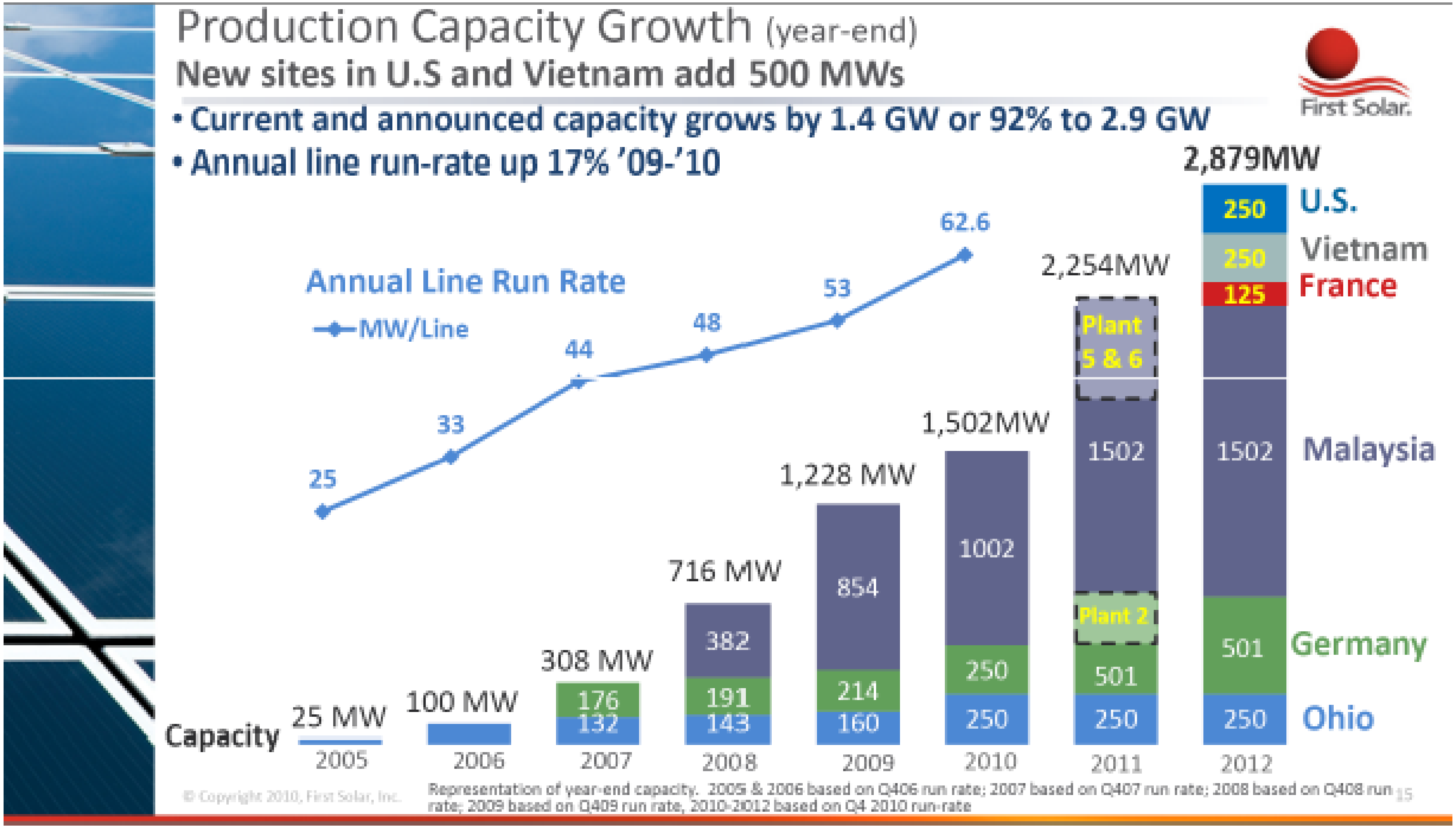
- integrate our PPD technology in traditional flat glass lines

-develop R2R thin film deposition equipments for flexible substrates

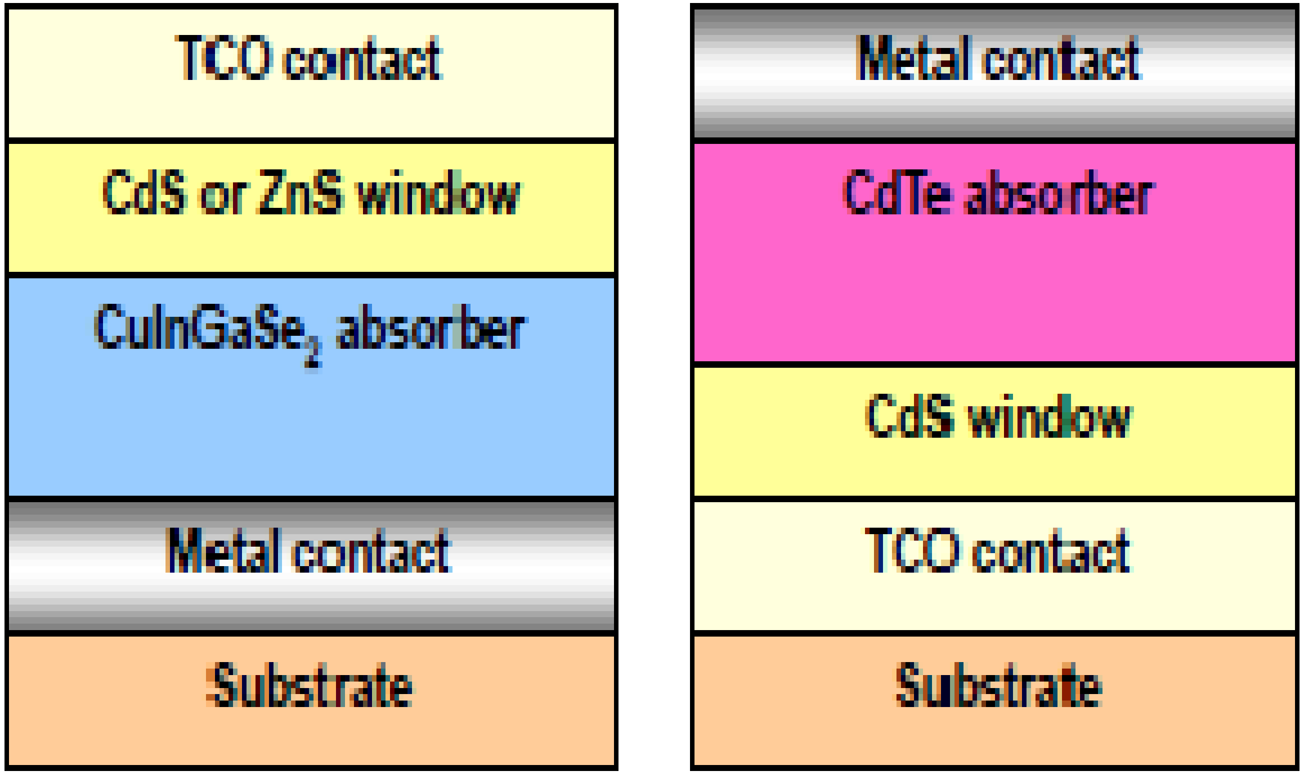
2SN SpA is undergoing to a second round of investment for the development of the 30 cm web pilot equipment

SIENA SOLAR NANOTECH

The CdTe champion



CdTe vs CIS now
Flat vs Flex



Cost reduction factors by the PPD

The PPD technology enables the achievement of grid parity by :

- Reducing material usage
- Increasing deposition rate
- Reducing the thermal budget
- Introducing a safe and sustainable fabrication process
- Improving efficiency
- Implementing a wide area scalable deposition system
- Implementing a Roll to Roll web deposition

2SN SIENA SOLAR NANOTECH

Cost reduction parameters

The PPD technology enables the achievement of grid parity by :

- Reducing material usage
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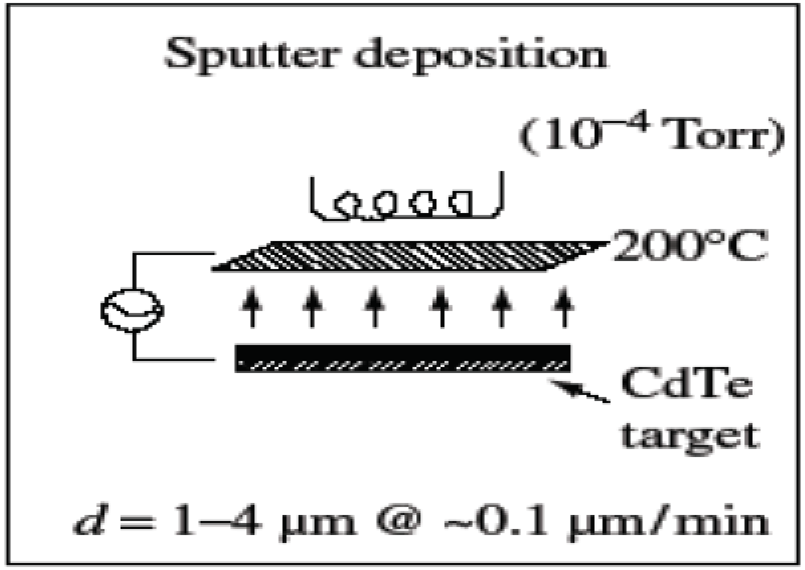
2SN SIENA SOLAR NANOTECH

Thin film fabrication technologies

•Technique	•Species generated	Energy (E)
•Thermal •Flash evaporation •Vapour transport sublimation •Electron gun evaporation •Molecular beam epitaxy	•neutral atoms •molecules	Kinetic E at kT
•Sputtering •DC sputtering (for metals) •RF sputtering (for semiconductors) •Reactive sputtering (for oxides,….)	•neutral atoms •ions	•Plus low electronic E (few eV)
•CVD •mw, thermal, rf activated … •Plasma enhanced CVD •etc	•molecular fragments •ions	•Plus low electronic E (few eV)
•PLD •Nd YAG (IR), excimers lasers (UV)	•neutral atoms •ions •clusters	•Supersonic kin. E and large electronic E

CdTe Thin Film Growth Technologies: 2

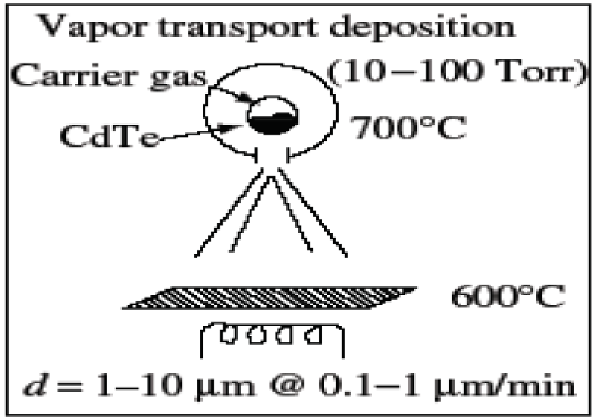


RF sputtering U. of Toledo

Problems:

- Slow
- Homogeneity (thickness)
- No industrial application

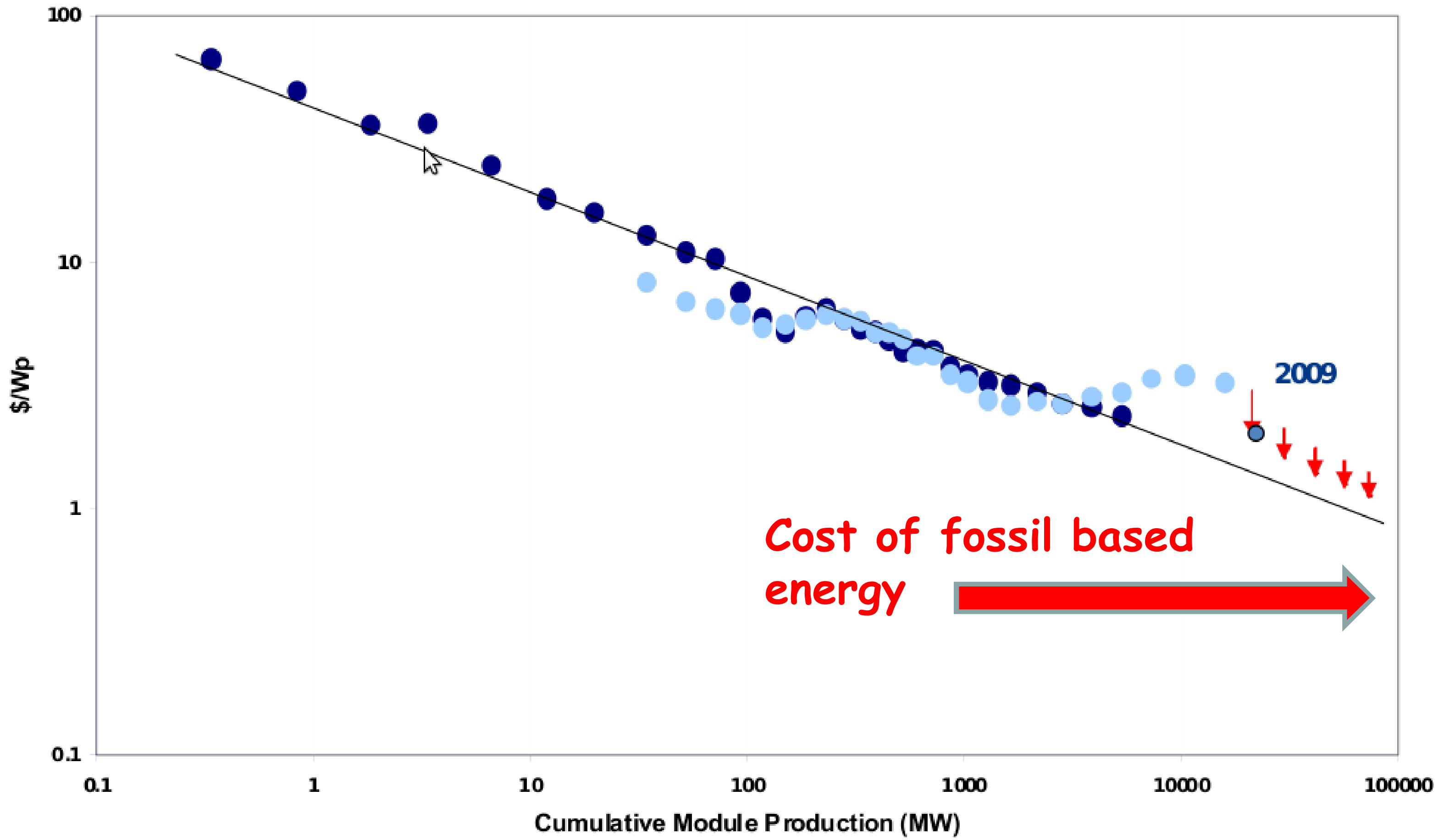
Present CdTe deposition technology by First Solar



- High roughness (thick)
- Hot gases (risky)
- High T (costly)

Source: Satyen. K. Debb (2005)

Our goal: grid parity by chalcogenide thin film photovoltaics



Photovoltaic production costs and sales prices vs time.
Source: Navigant Consulting

We aim at total costs lower than 0.5 €/Wp

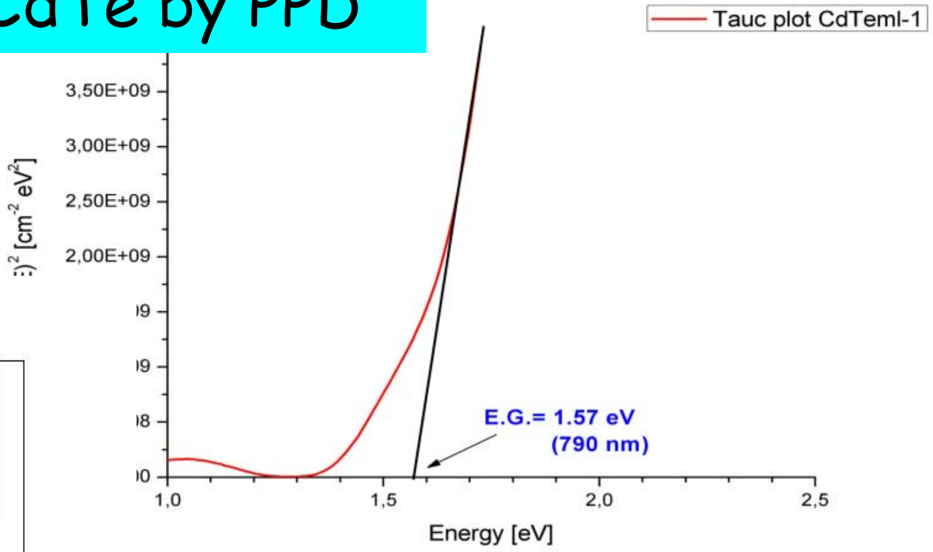
The nature of the challenge!

Technology is the challenge
Relevant issues are: cost & cost

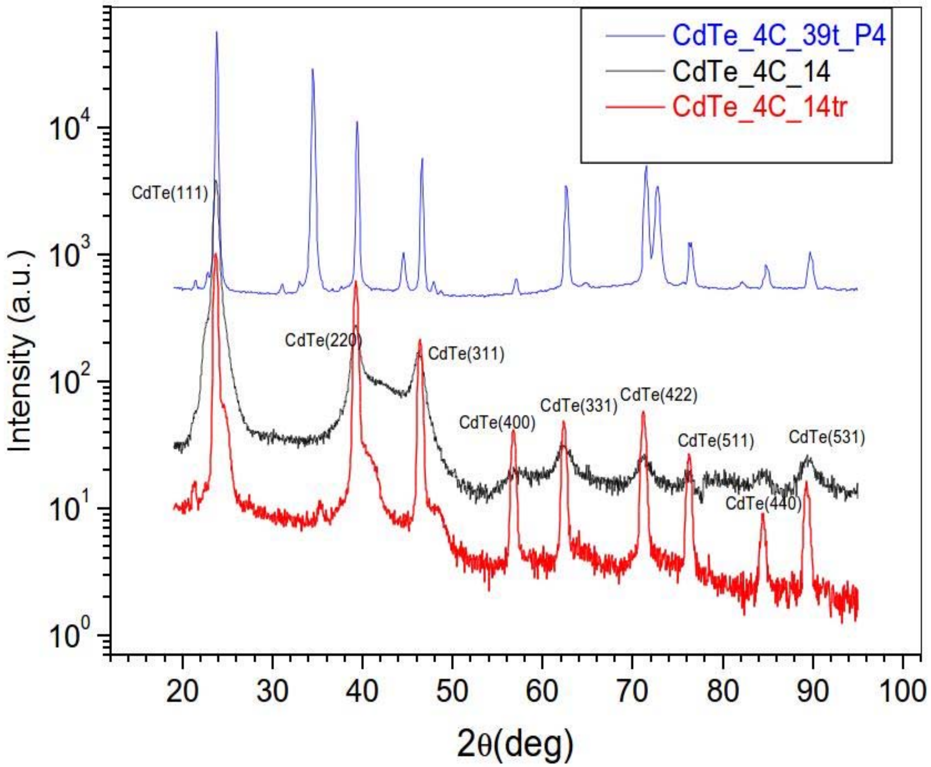
- Reduce material (reduce cost)
- Increase deposition rate (reduce cost)
- Reduce thermal budget (reduce cost)
- Introduce a safer process (reduce cost)
- Improve efficiency (reduce cost/W)
- Implement in line productivity (reduce cost)
- Implement Roll 2 Roll (reduce cost)

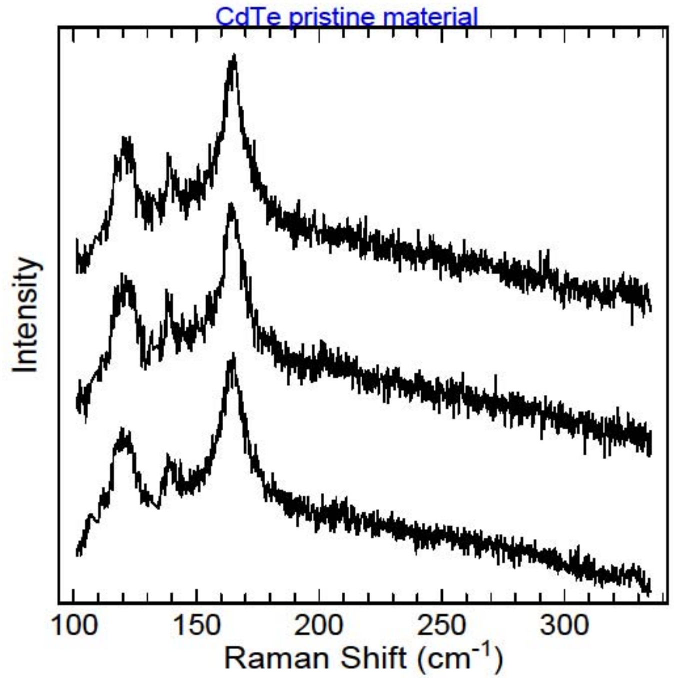
2SN SIENA SOLAR NANOTECH

Pristine CdTe by PPD



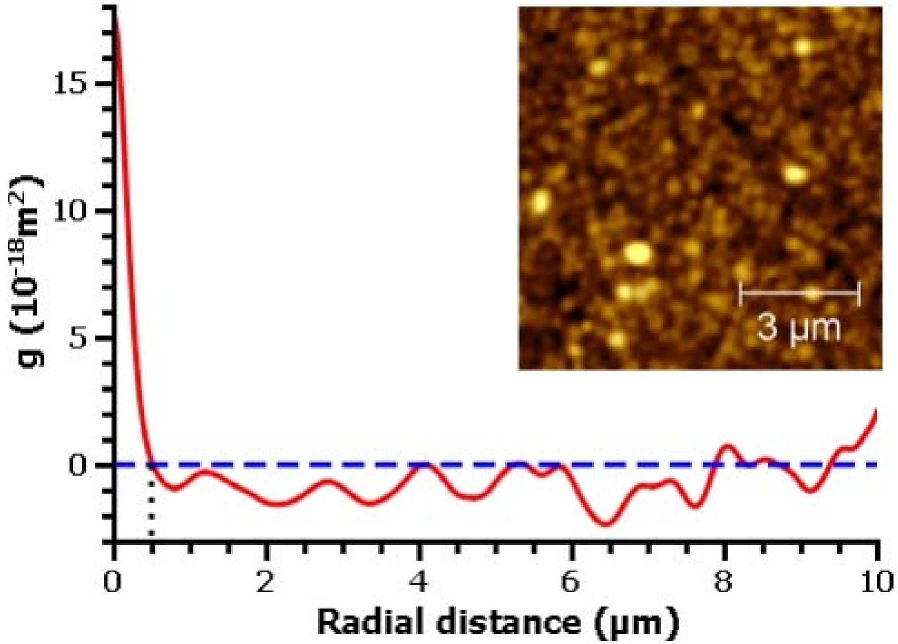
optic geometry: PSA(θ, 2θ) for sample 39, GID for sample 14



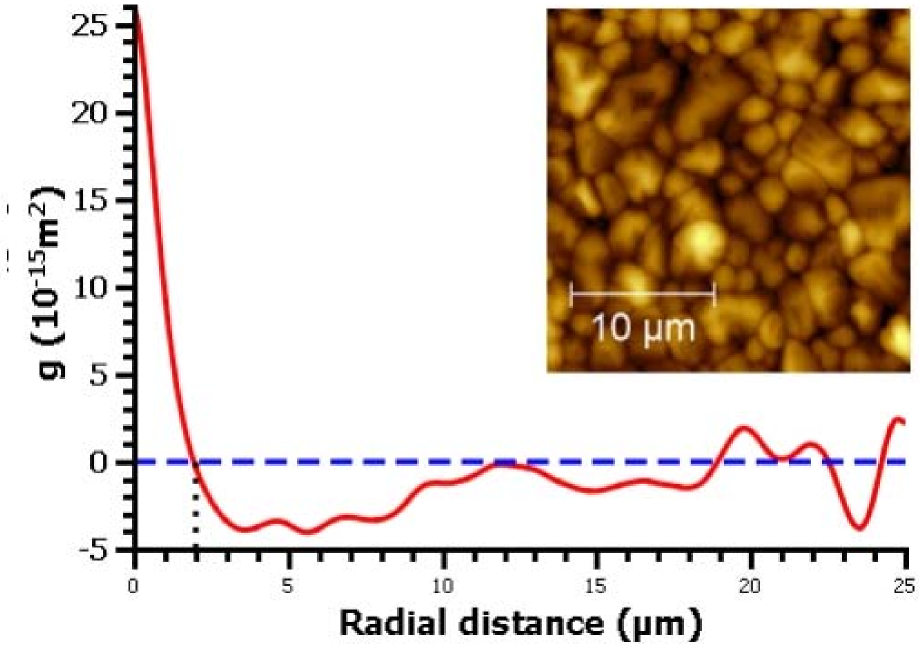


Reducing material usage

The PPD technology enables to make very smooth layers reducing the need to deposit 6-8 μm as in the case of the present CSS and VTD technologies. One μm is sufficient. 8 times less material



CdTe deposited at room temperature
Roughness 4 nm r.m.s (AFM image).



CdTe treated with CdCl2 at 420°C
Roughness 152 nm r.m.s
AFM image.

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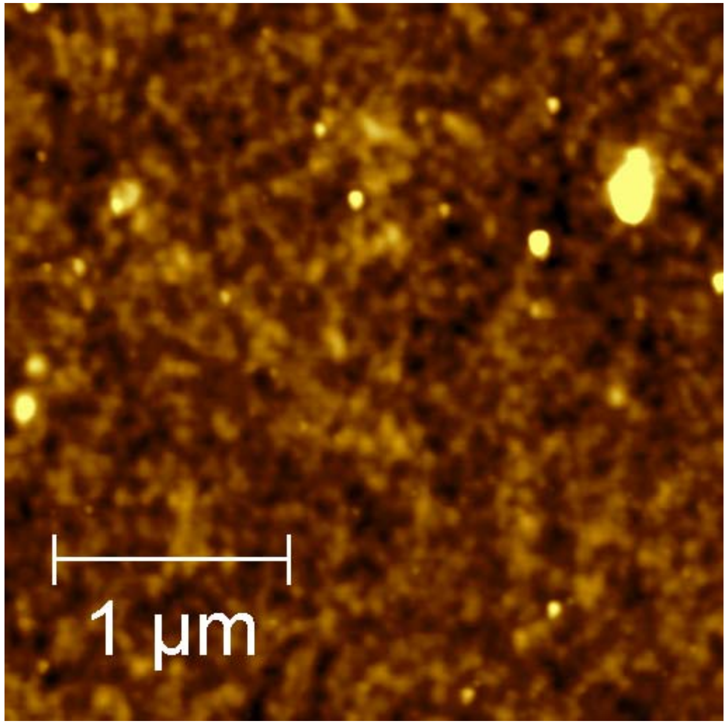
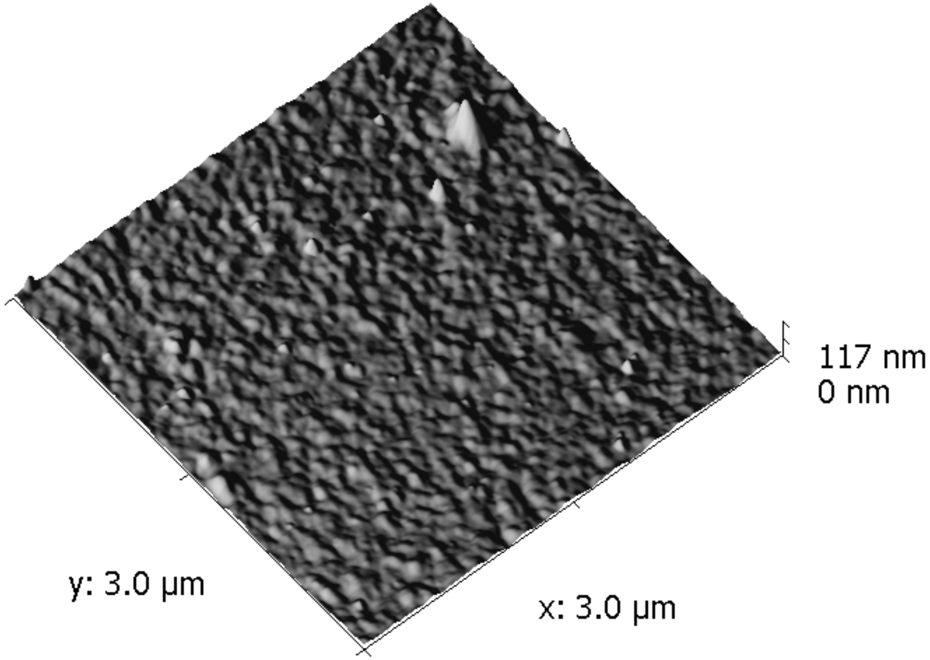
Reducing material usage





Cd S is also deposited at room temperature :
Roughness 4 nm r.m.s . AFM images

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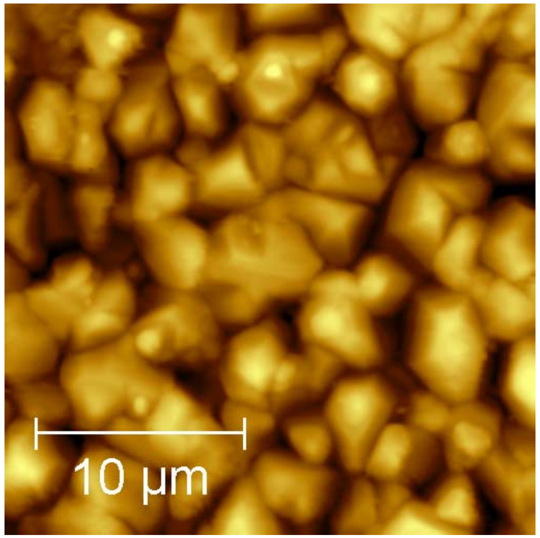
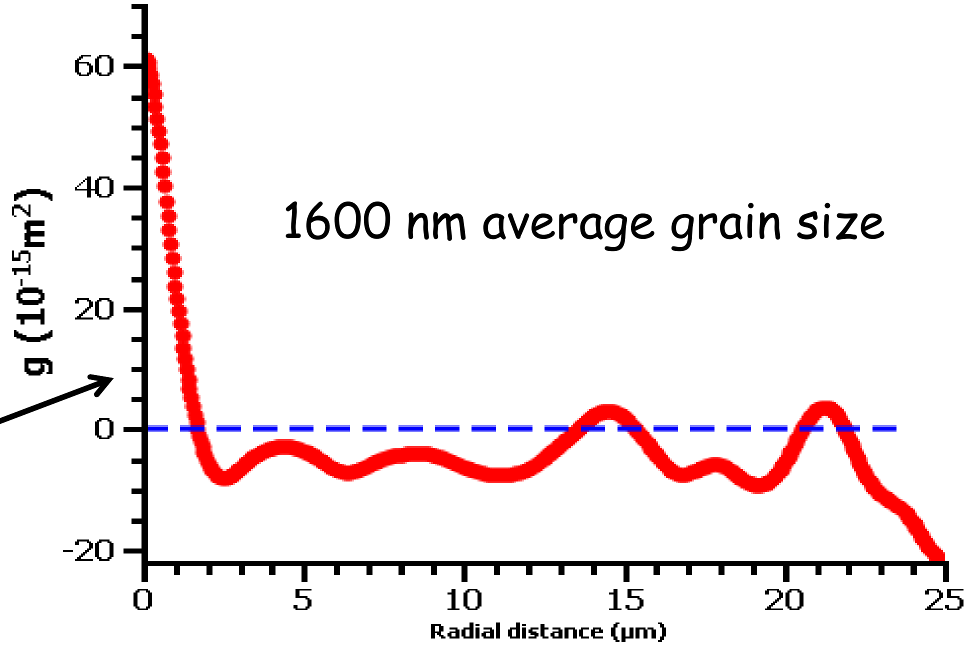
Reducing material usage: comparison with CSS

CdTe made by traditional CSS





Roughness: 1093±44 nm

PPD use less material and does not use gases

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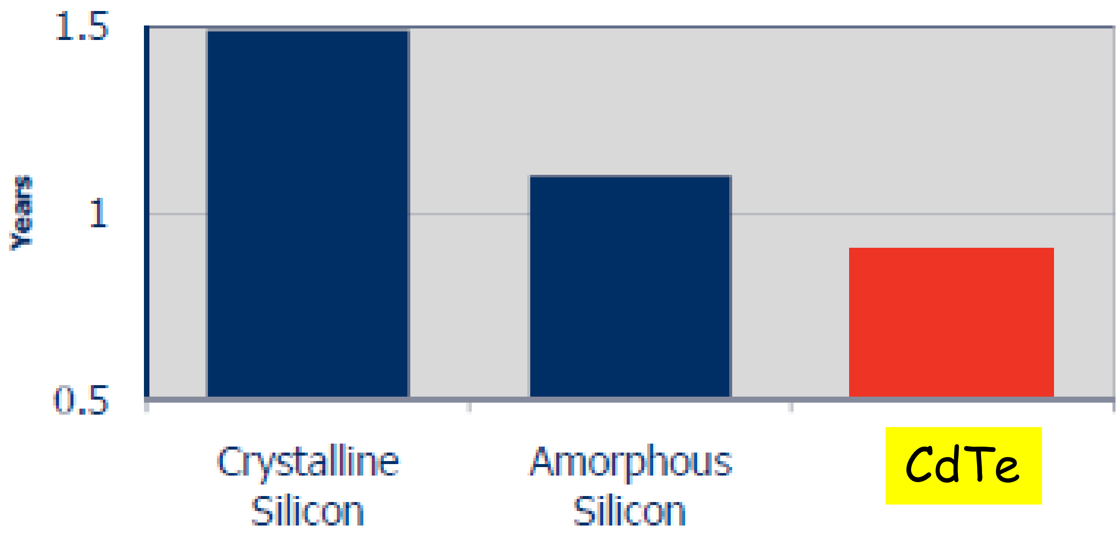
Reducing thermal budget

Energy Payback Time

SOLAR FRONTIER

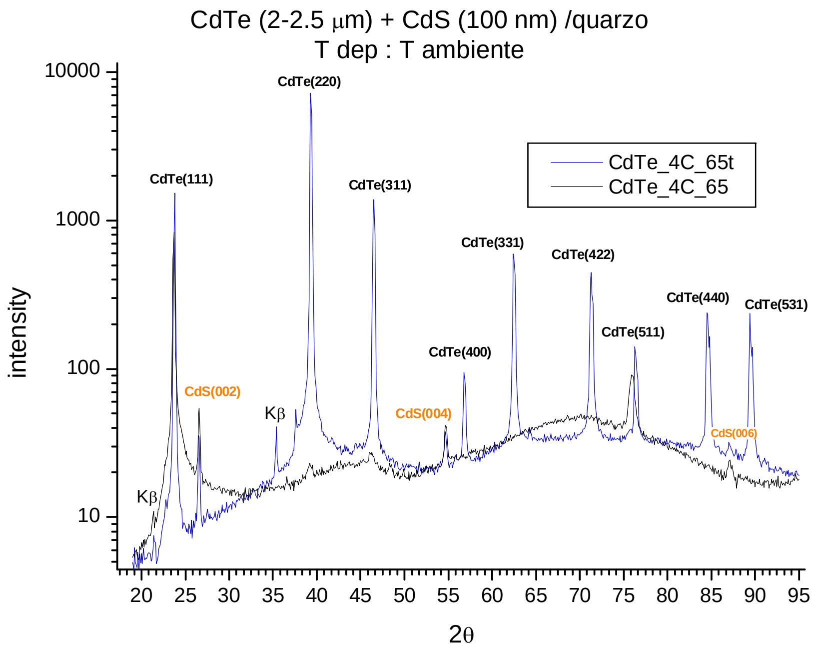


- Energy Payback Time (EPT): the time required for a module to generate the amount of energy spent in its production
- CdTe modules have a faster EPT than conventional silicon

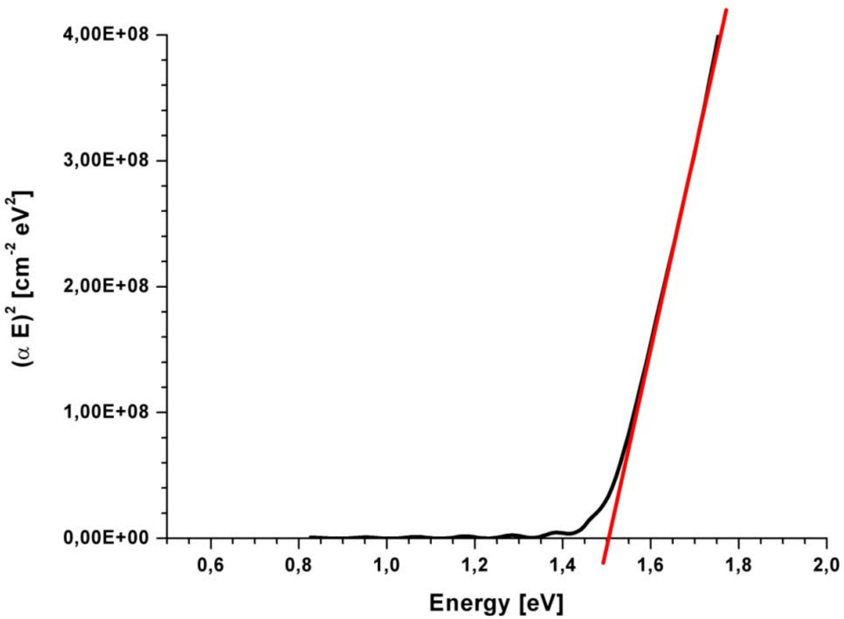
Source: New Energy and Industrial Technology Development Organization (NEDO)

Reducing thermal budget

The PPD technology enables the deposition of excellent quality and cristalline CdTe at room temperature



CdTe and CdS : X ray structures at Room temperature



CdTe energy gap

Increasing deposition rate

The PPD technology allow to reach dep. rates of 300- 400 nm/min. for CdS and 500 – 700 nm/min for CdTe.

CdS	PPD	Sputtering	CBD	CSS
Deposition rate (nm/min)	300-400	50	3	100
Average grain size (nm)	20	50	12-15	5-80
Roughness (nm r.m.s.)	3		5 -120	
Temperature (°C)	RT	200	60 - 85	
Reference	Acharya 2007	Romeo 1998	Choi 98	Ferekides 1998

Ten times faster than conventional CBD and better smoothness

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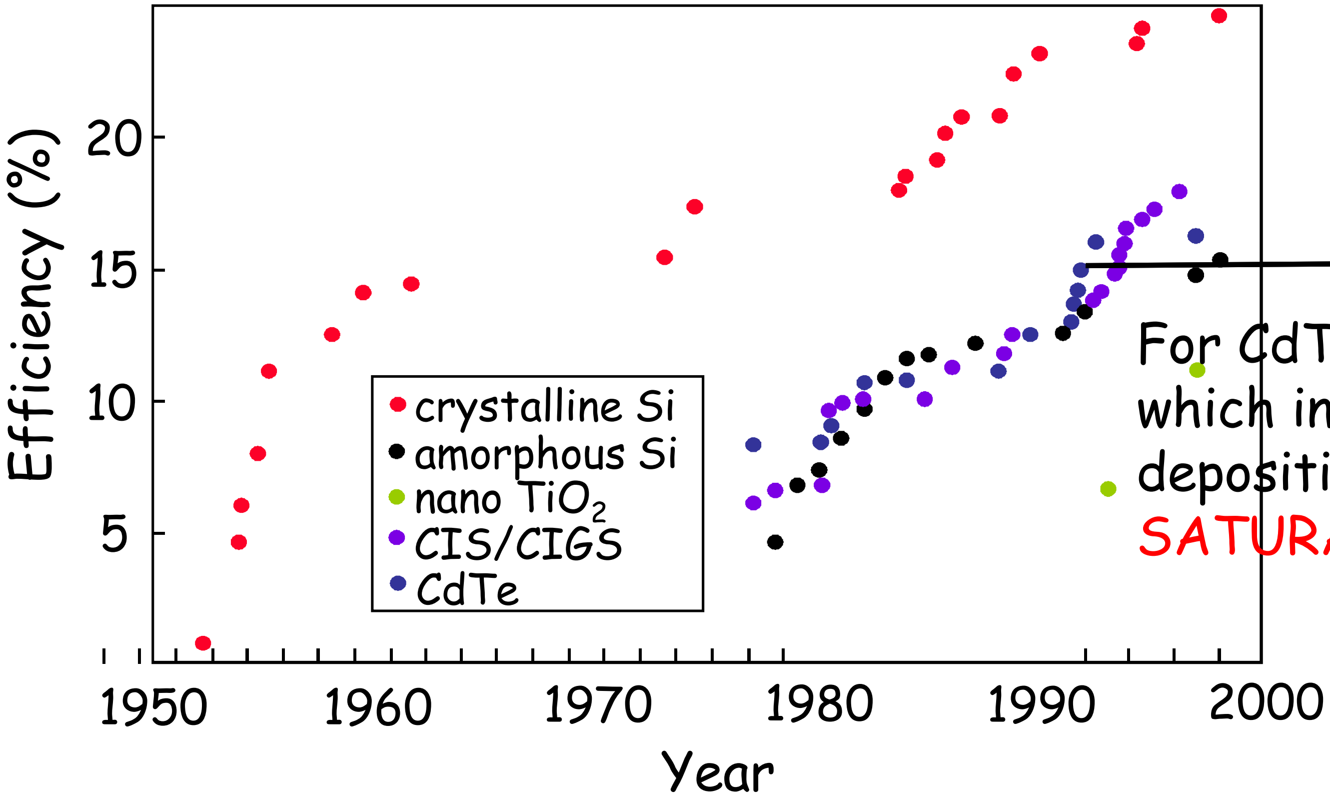
Improving efficiency

The learning curve concept involves the improvement of the quality of materials, processes etc.

Better CdTe and CdS, better interfaces, lower absorption losses, allow to follow the learning curve.



For CdTe there is a plateau which indicates that current deposition technologies are SATURATED

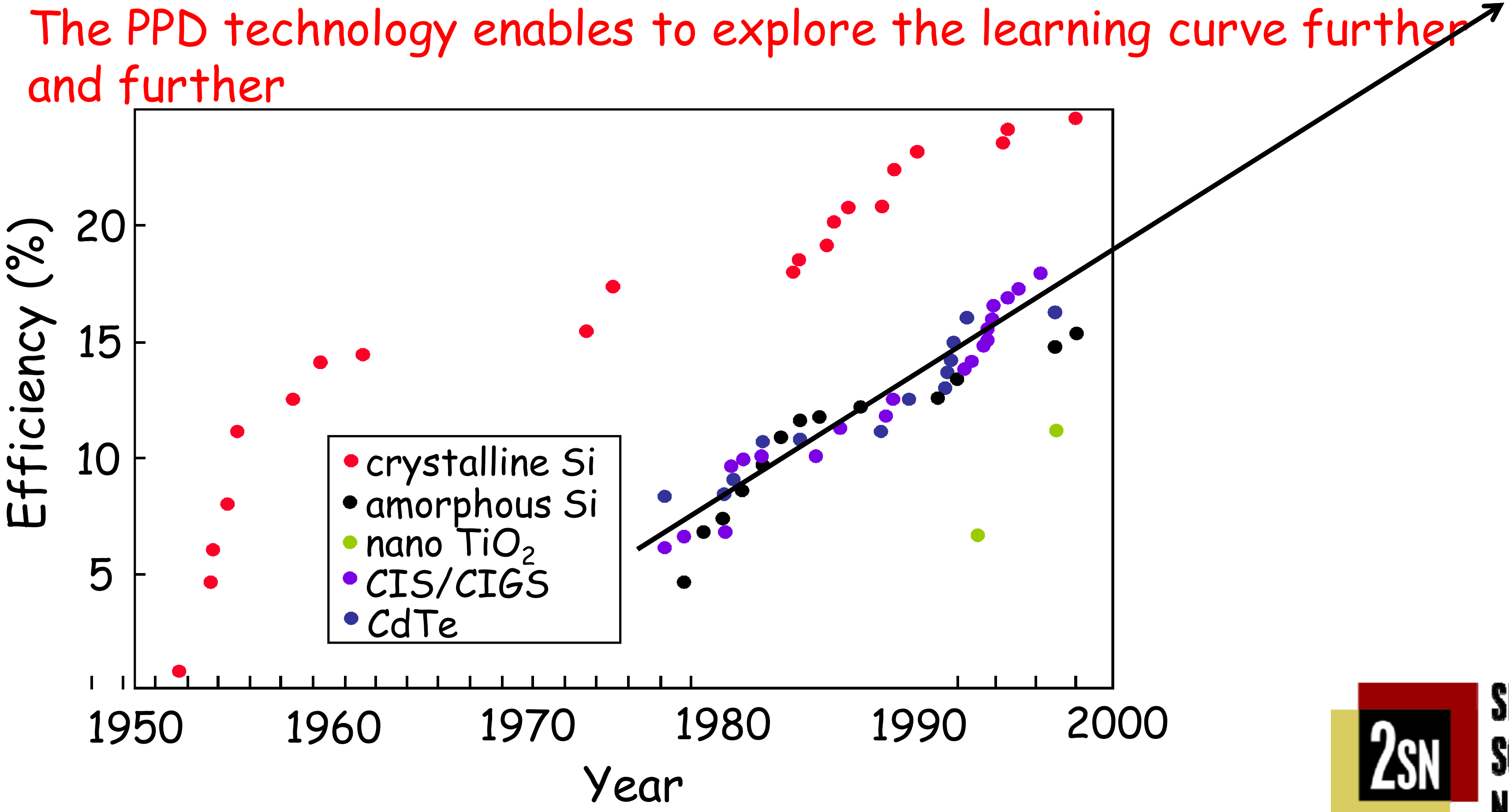
SIENA SOLAR NANOTECH

Improving efficiency

The learning curve concept involves the improvement of the quality of materials, processes etc.

Better CdTe and CdS, better interfaces, lower absorption losses, allow to follow the learning curve.

The PPD technology enables to explore the learning curve further and further



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Safe processing

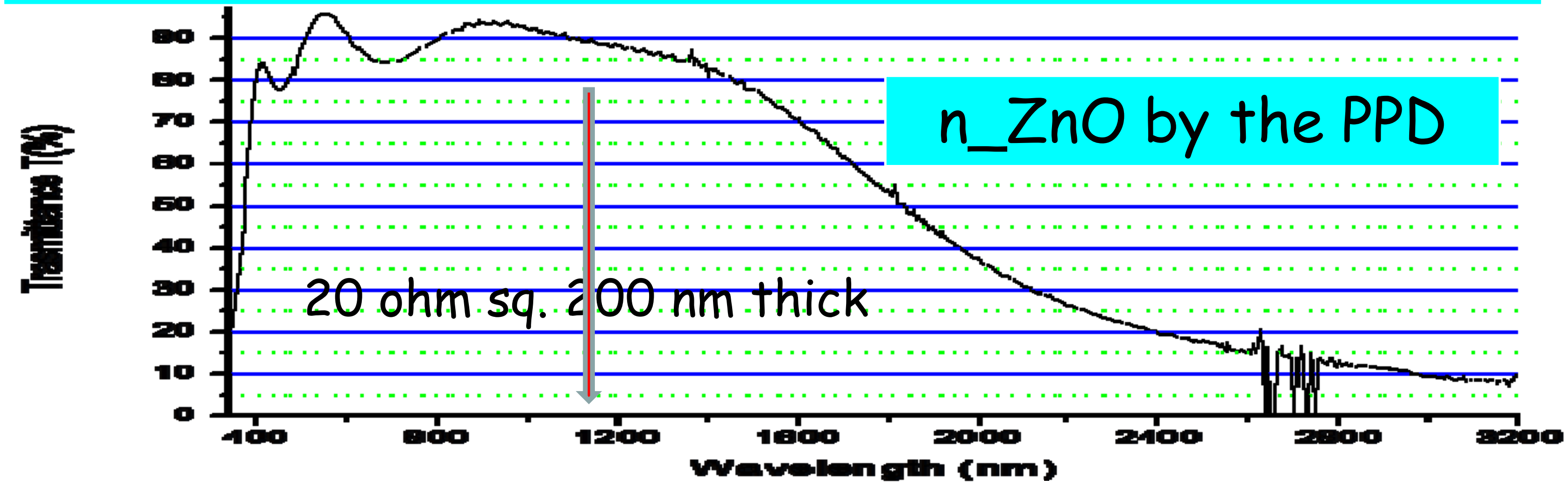
Insoluble high melting point CdTe is trasferred to the substrate in vacuum.

- No exposure to Cd vapour
- No processing gases
- Low temperature process
- Confined environment in vacuum

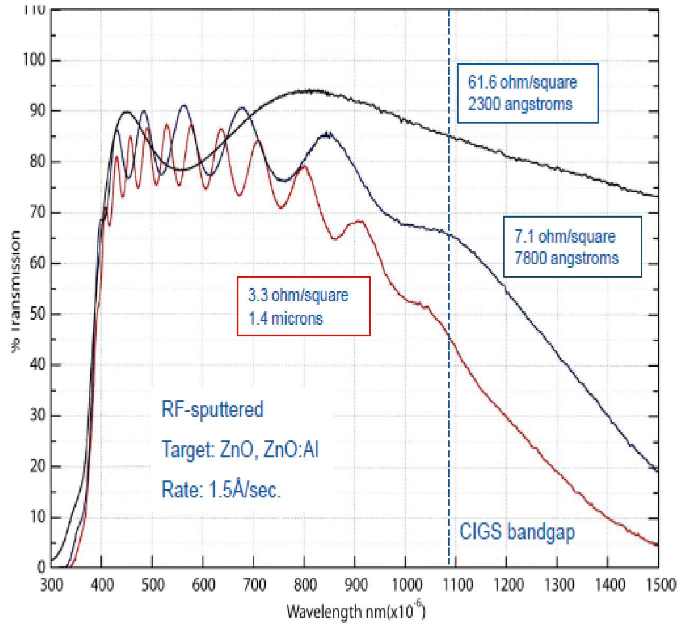
Transparent Conducting Oxides
by the
PPD

Improving efficiency

Excellent near IR T% at Eg CdTe and CIGS



n_ZnO by the PPD



Al_ZnO by sputtering (commercial)

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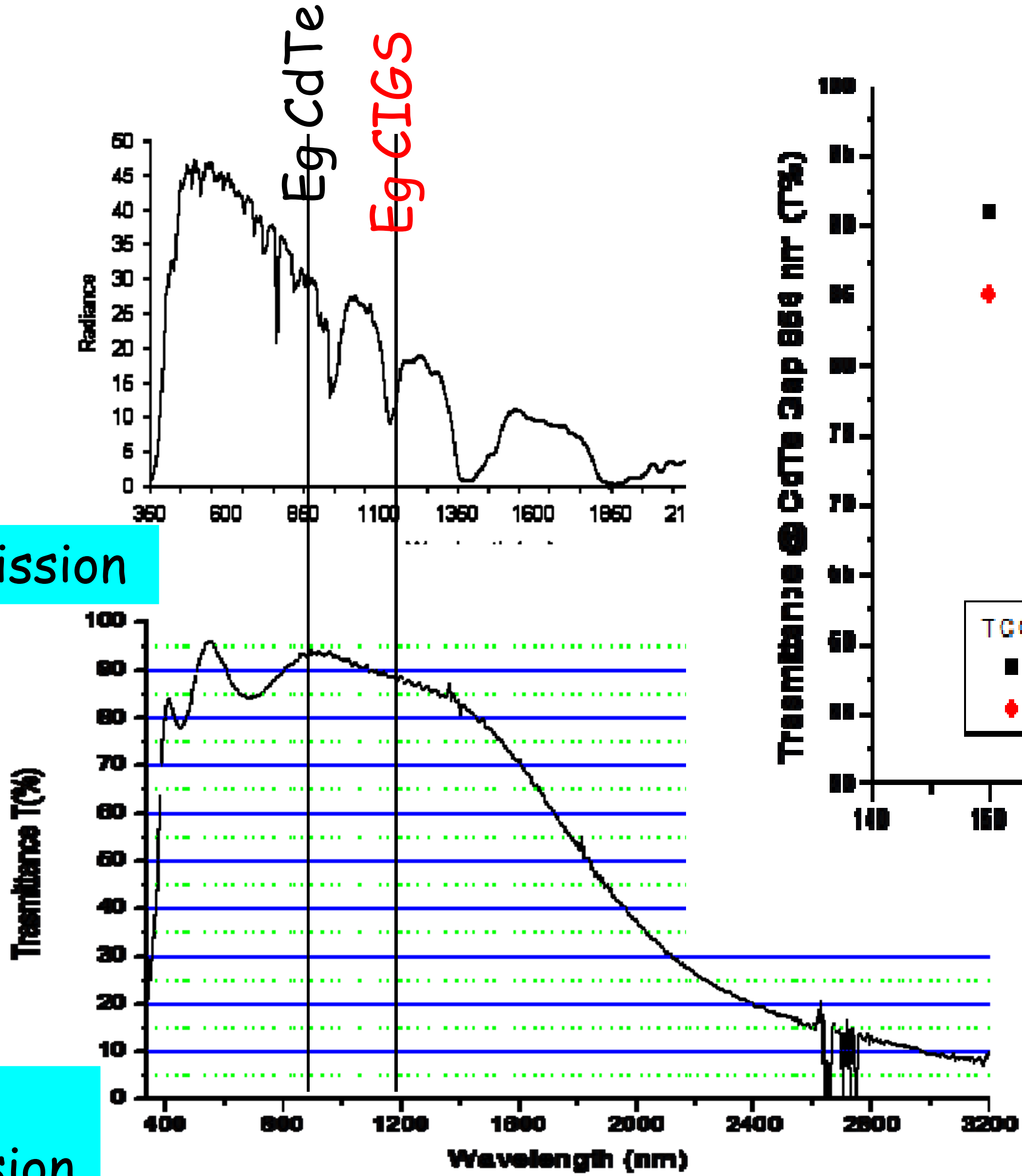
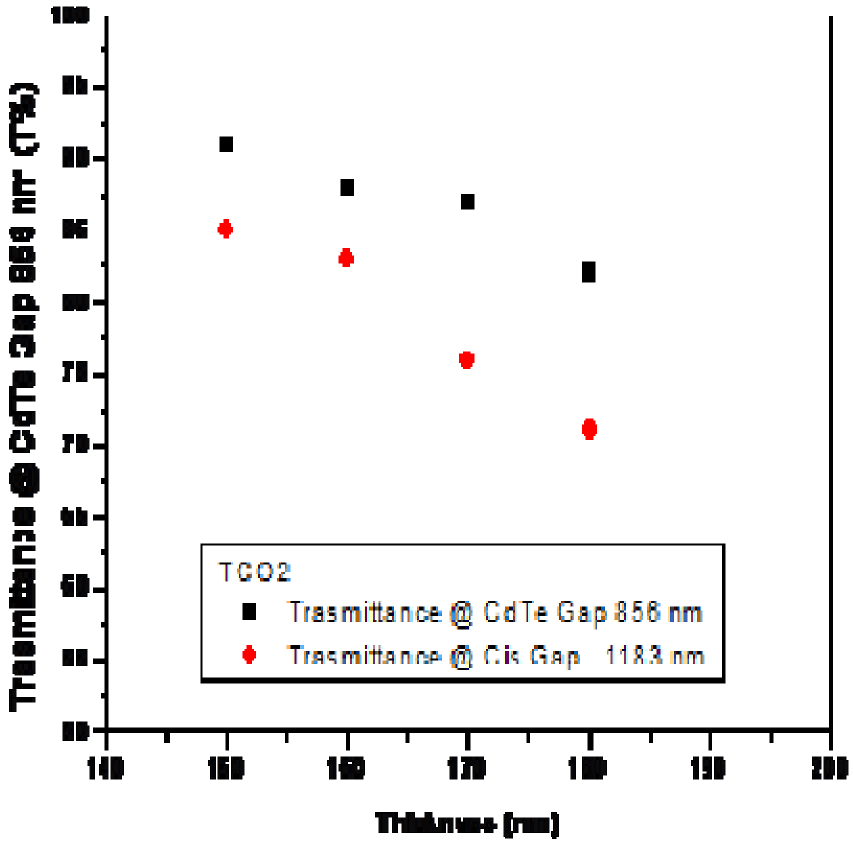
Improving efficiency: lower abs. loses

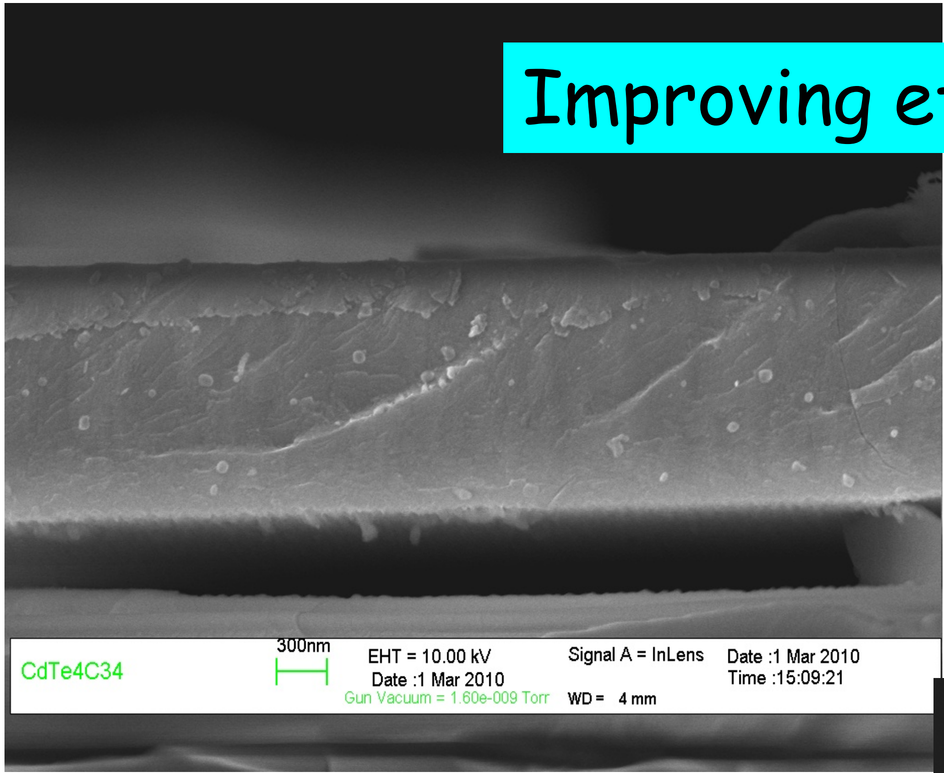


Solar emission

TCO2 transmission



Improving efficiency

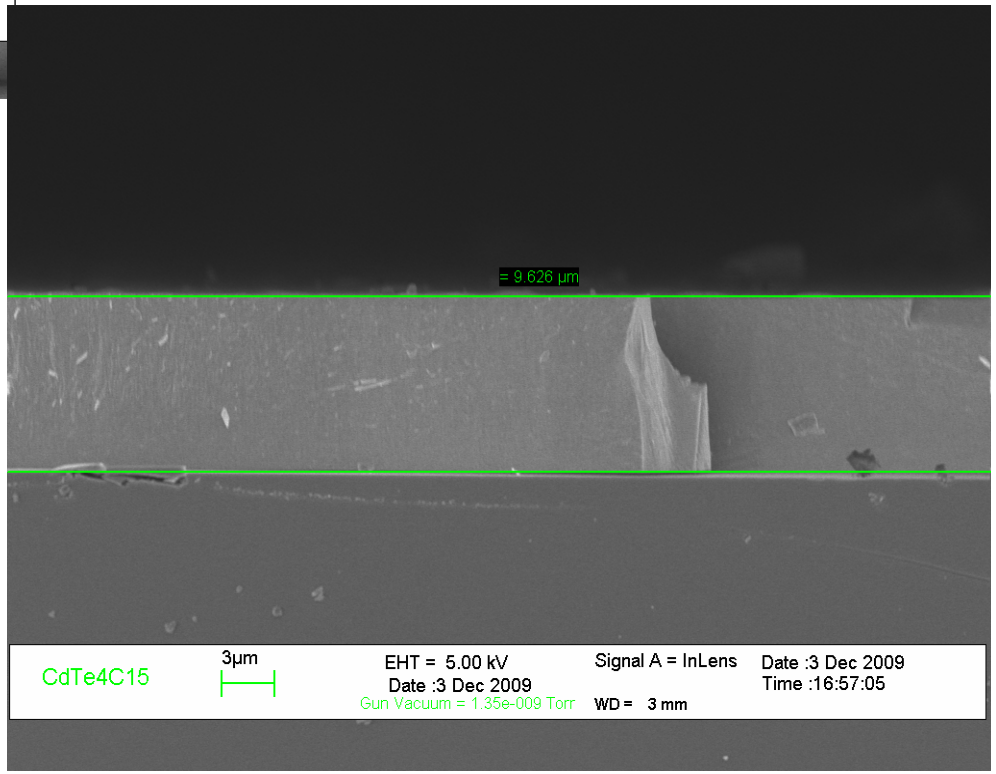


Compact high density pristine CdTe (density equal to crystalline bulk)

Equally possible to deposit on glass or metal (flexible) substrates

i.e.

substrate or superstrate



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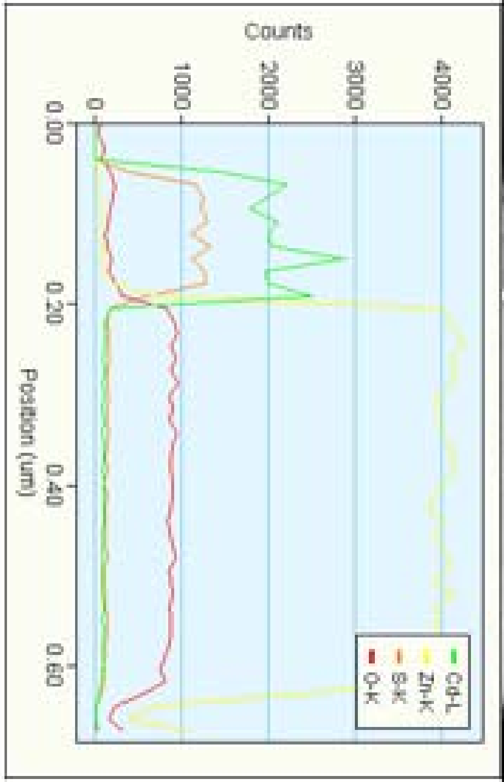
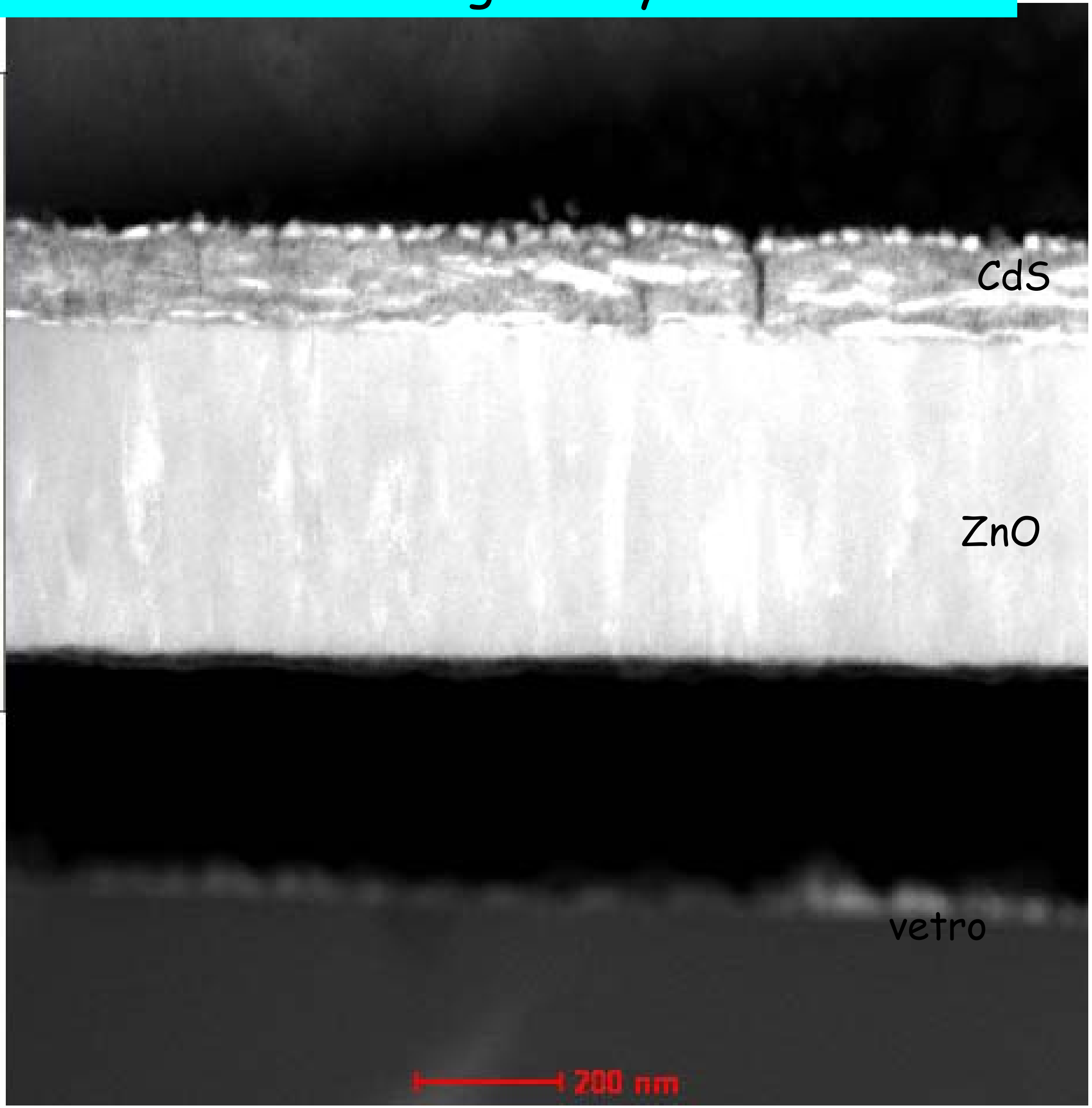
TEM Pristine CdS on ZnO/glass by the PPD



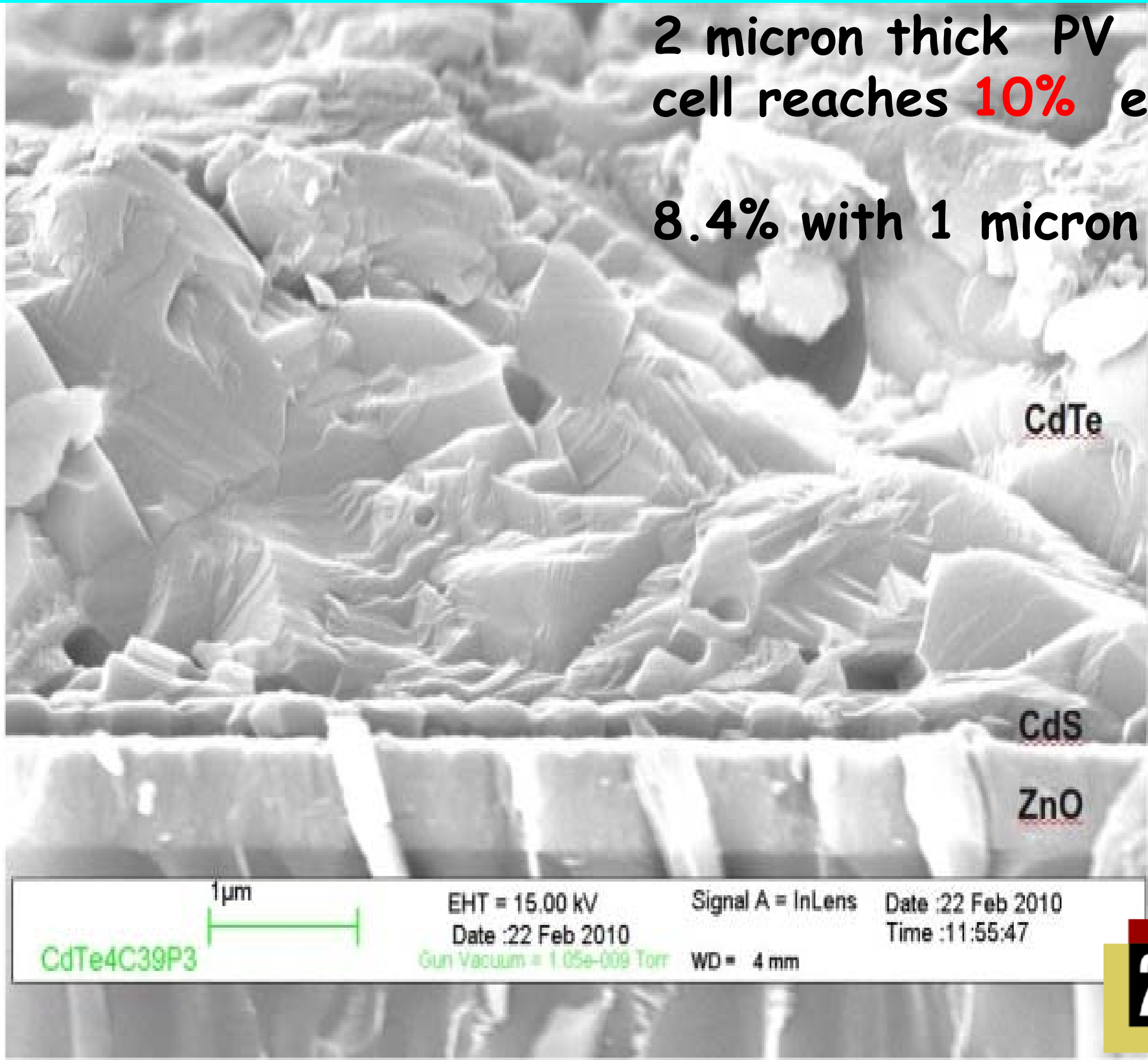


No intermixing of ZnO and CdS

n-ZnO / CdS / CdTe for thin film photovoltaics: fully PPD

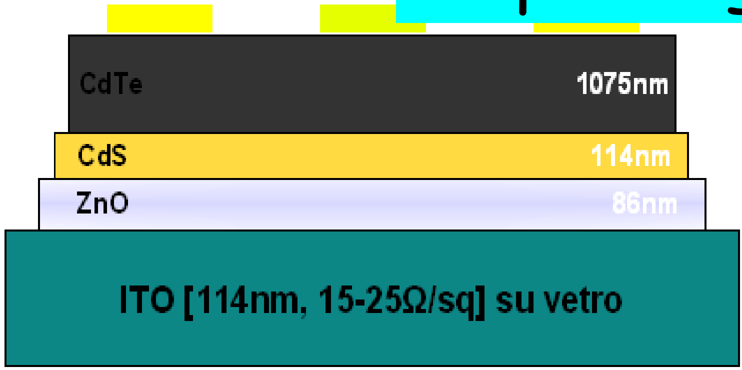
2 micron thick PV cell reaches 10% efficiency

8.4% with 1 micron thick.

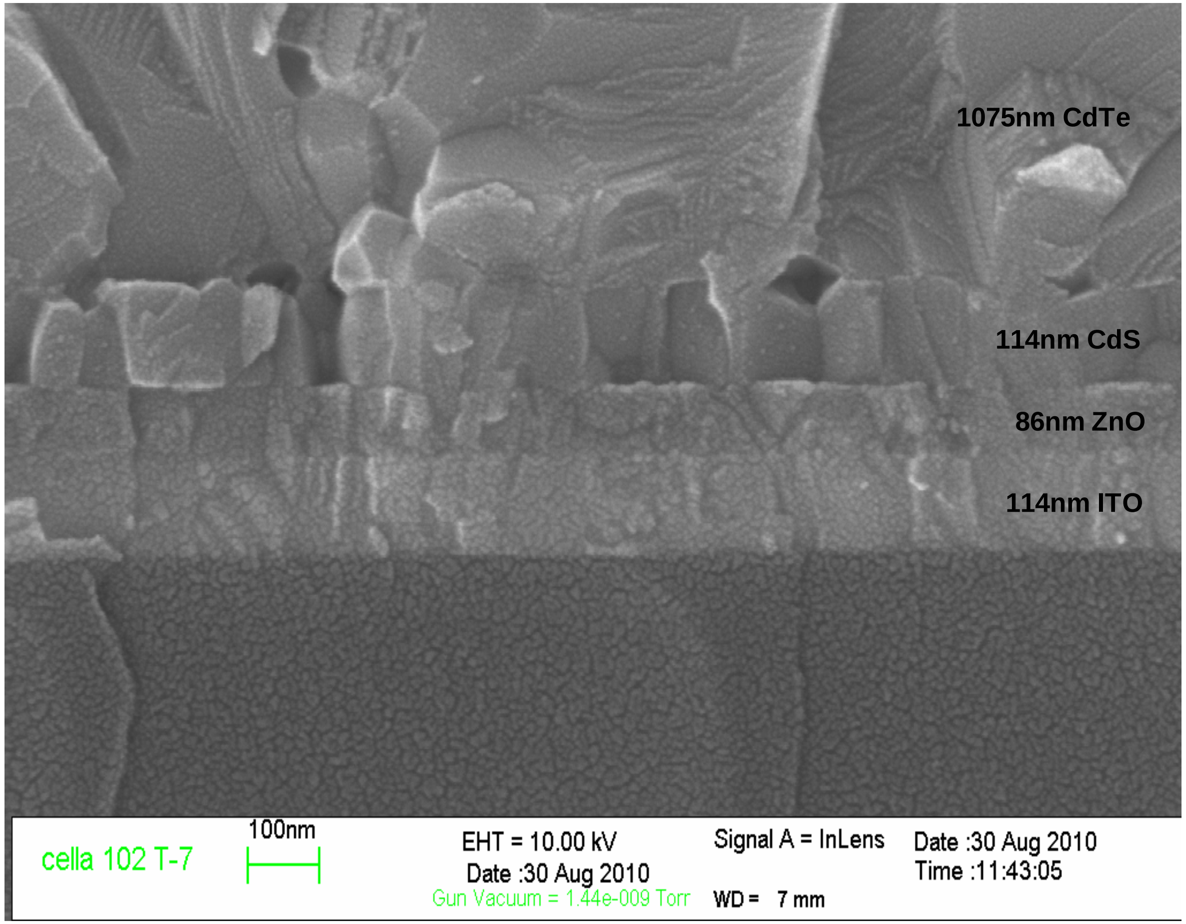


SIENA SOLAR NANOTECH

Improving efficiency



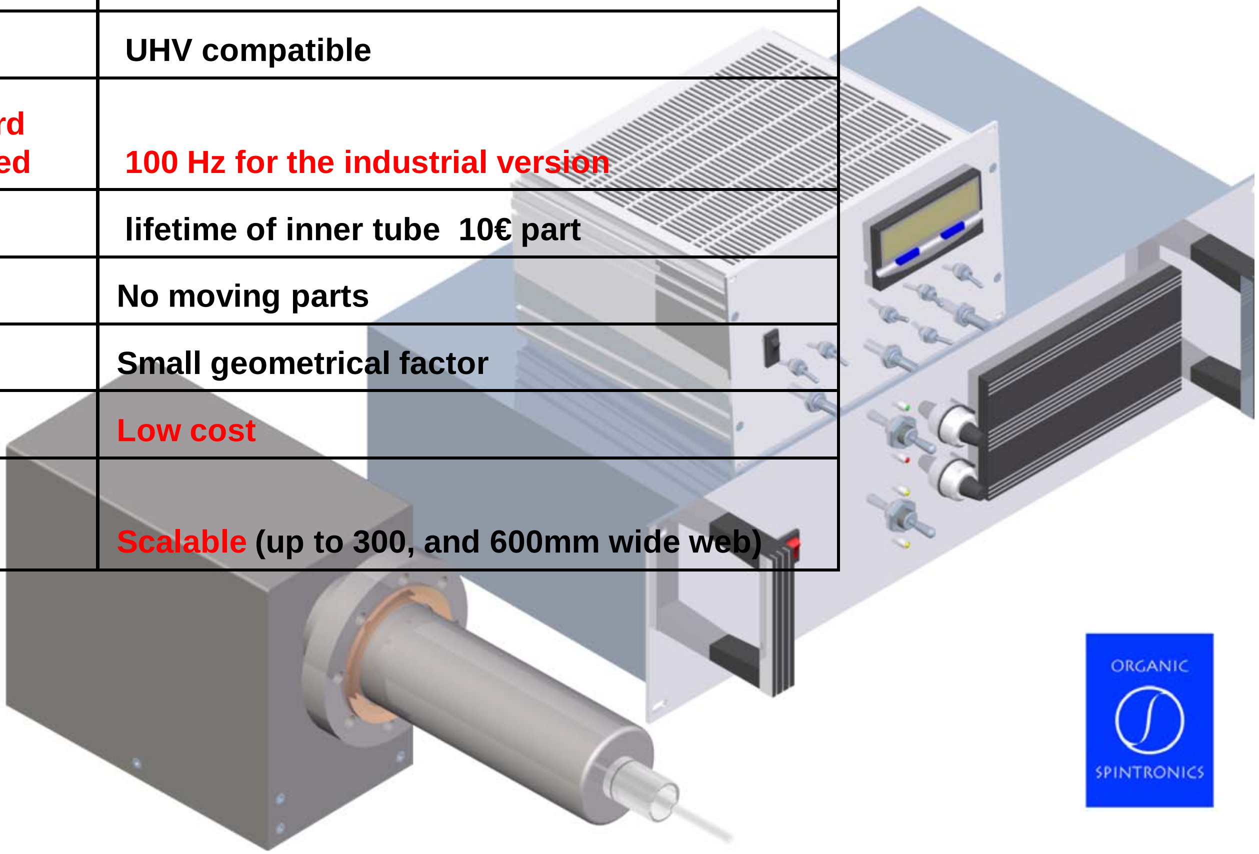
1 micron thich rudimental PV cell reaches 8.4% efficiency.



PPD technology at OS

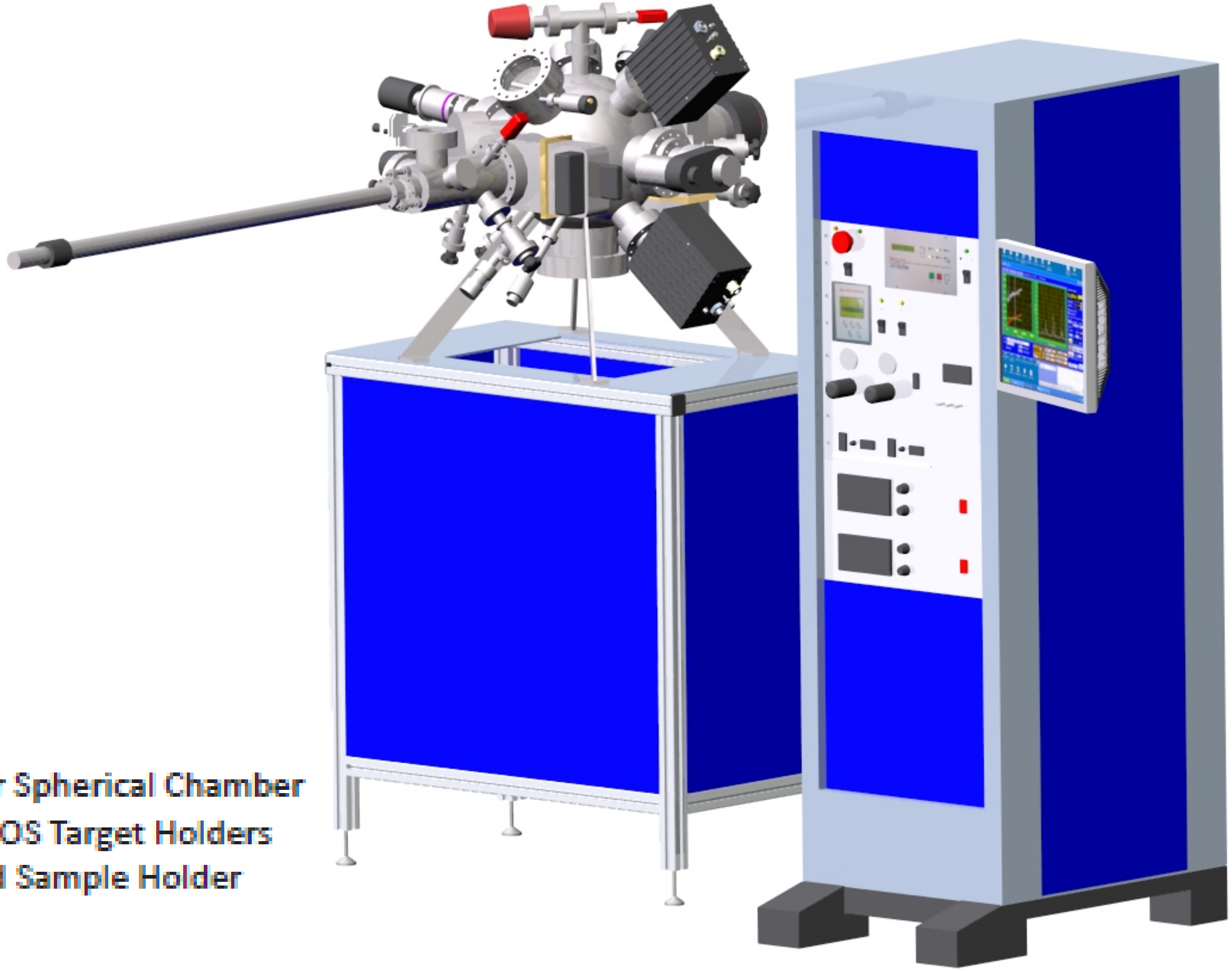
PPD Gen III Gun

Characteristics		Remarks
Deposition rate	50 – 700 nm/min	- depending on target material - one to two orders of magnitude higher than sputtering
Efficiency	> 30%	Power trasferred from discharge to electrons
Bakeable	200°C	Glass metal construction
Mounting	CF 63 UHV	UHV compatible
Repetition rate	15 Hz standard 30 Hz advanced	100 Hz for the industrial version
Lifetime	$>10^9$ shots	lifetime of inner tube 10€ part
Rugged		No moving parts
Compact		Small geometrical factor
manteinance		Low cost
suitable to arrange in a serie		Scalable (up to 300, and 600mm wide web)



PPD Gen III Twin Spark System

PPD systems



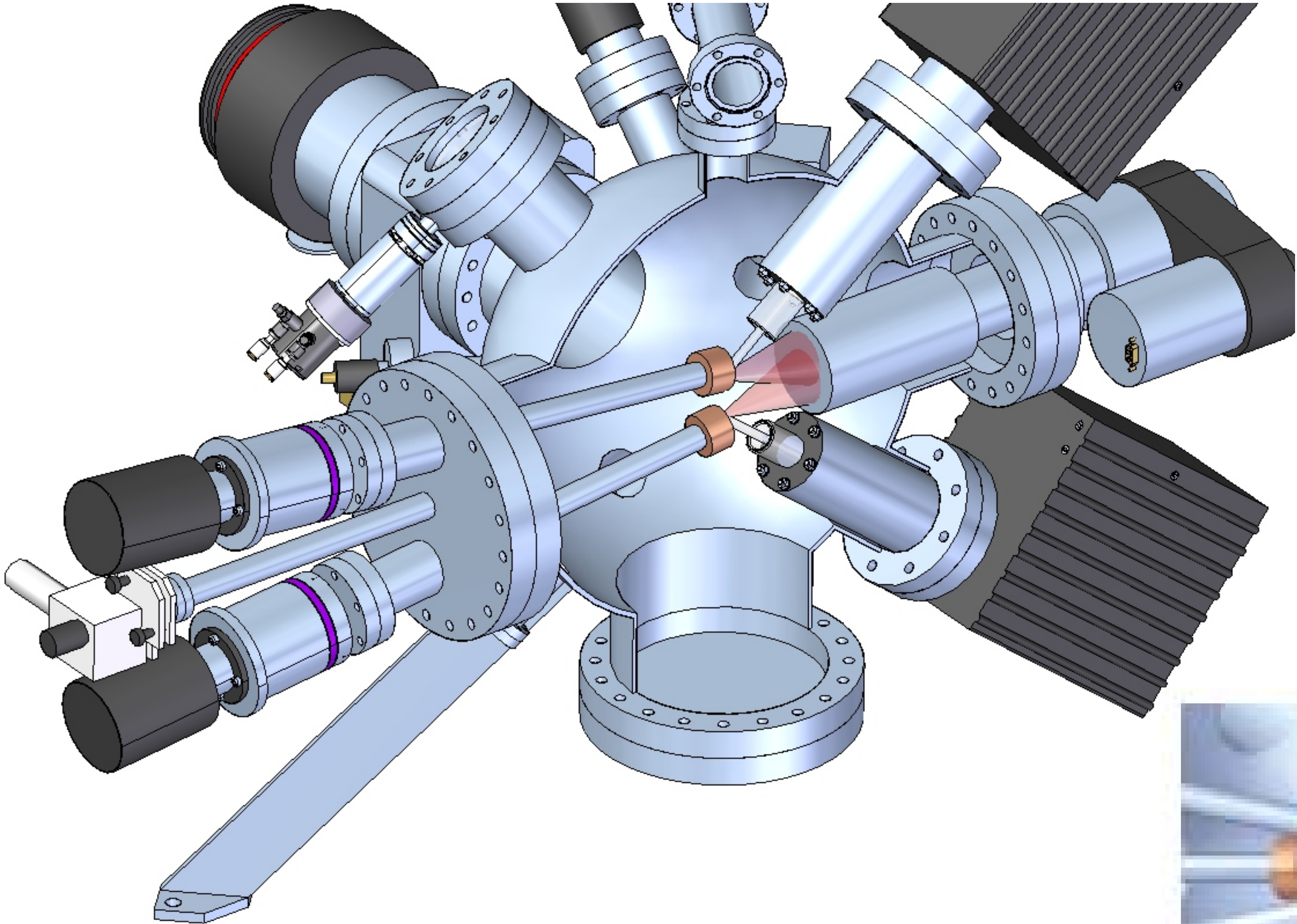
System including:

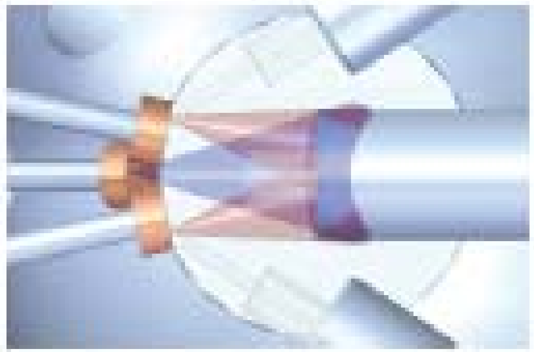
- UHV 350 mm diameter Spherical Chamber
- Up to 3 PPD Guns and OS Target Holders
- 2" diameter OS Heated Sample Holder
- Control Unit

Next: computer controlled growth (thickness and plasma composition)

Adding plumes to achieve wider areas

PPD systems

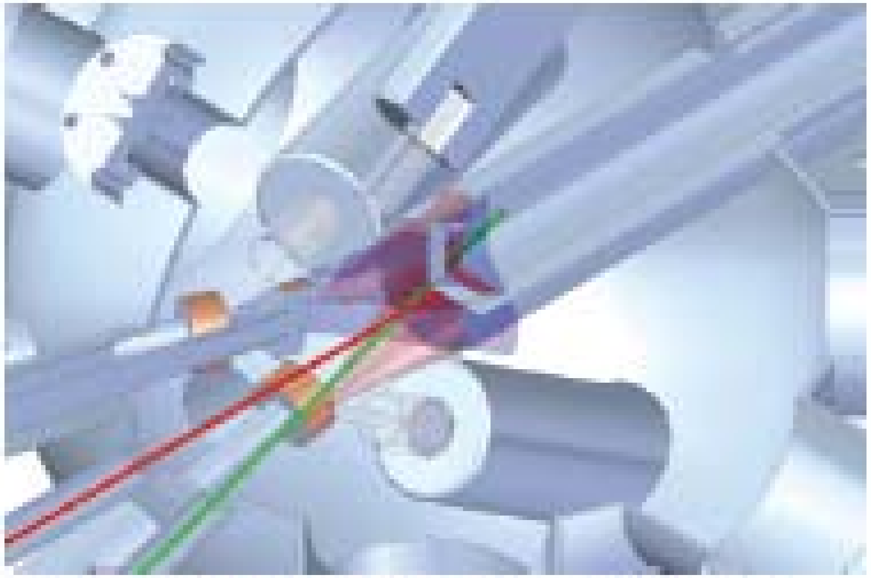




Wide area deposition configuration

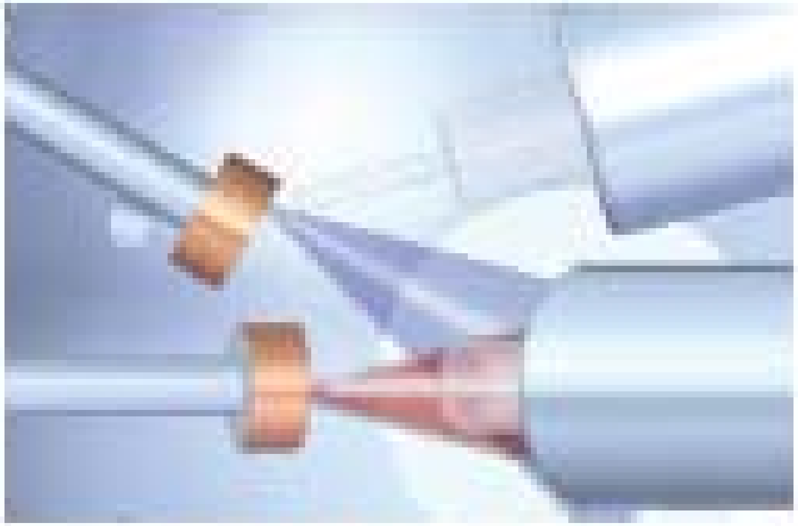
Mixing plumes: towards unconventional doping

PPD systems



Three PPD Gun III guns mounted for:

- Wide area
- NEW 30° plasma´s intersection for innovative *in situ* doping



Mixing plumes
deposition configuration

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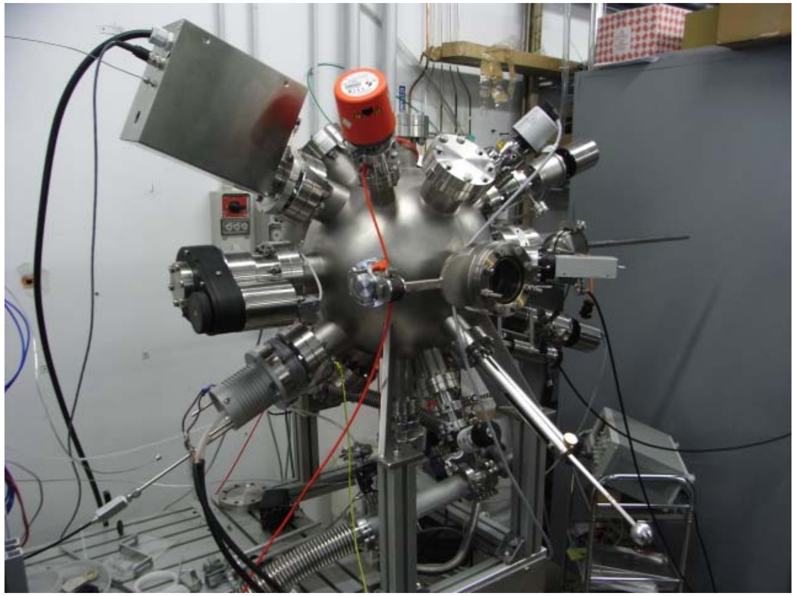
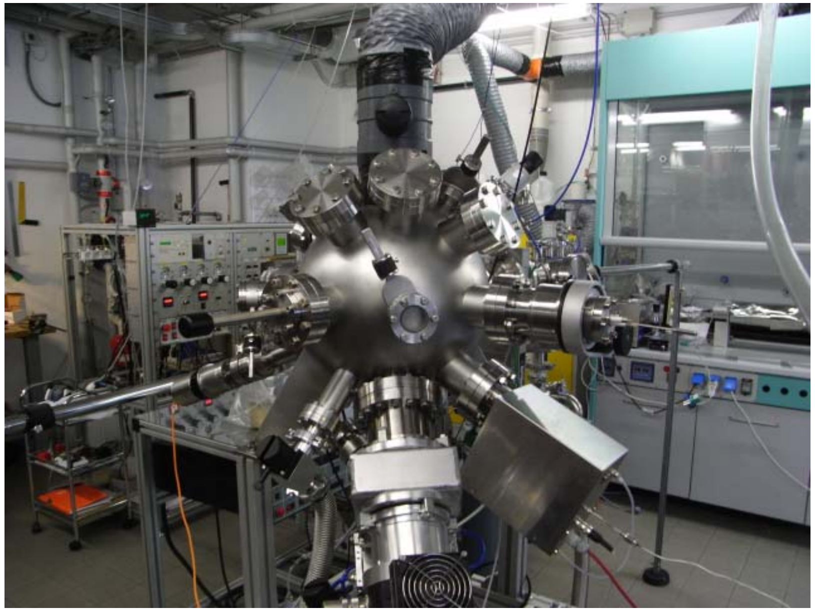
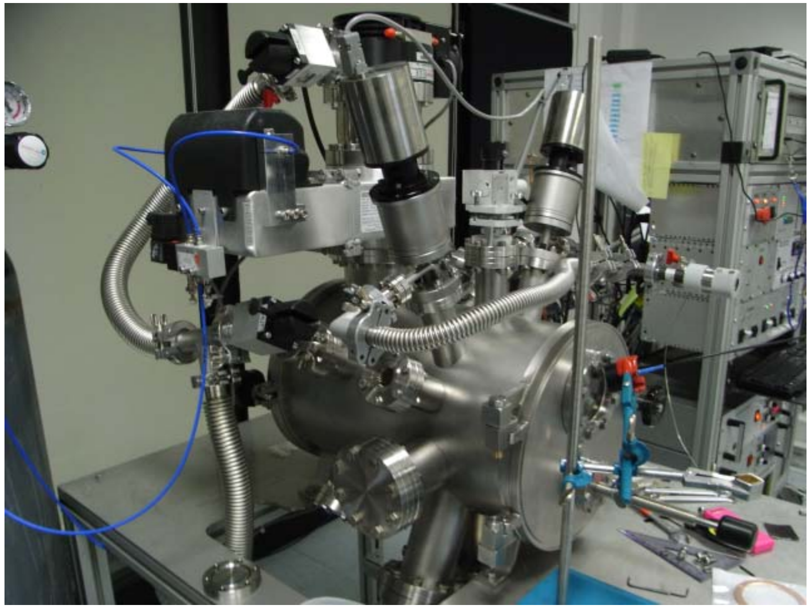
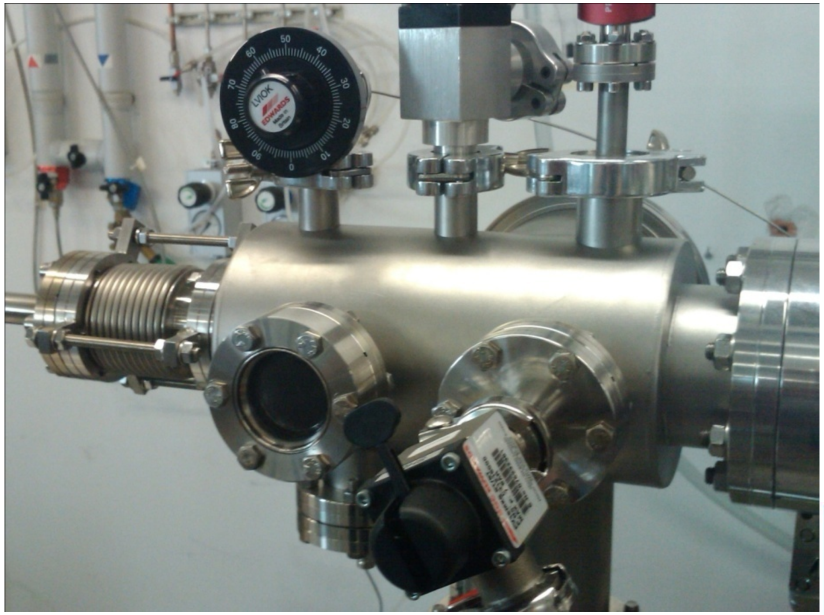
PPD systems (Gen II, III and IV) at OS

PPD systems









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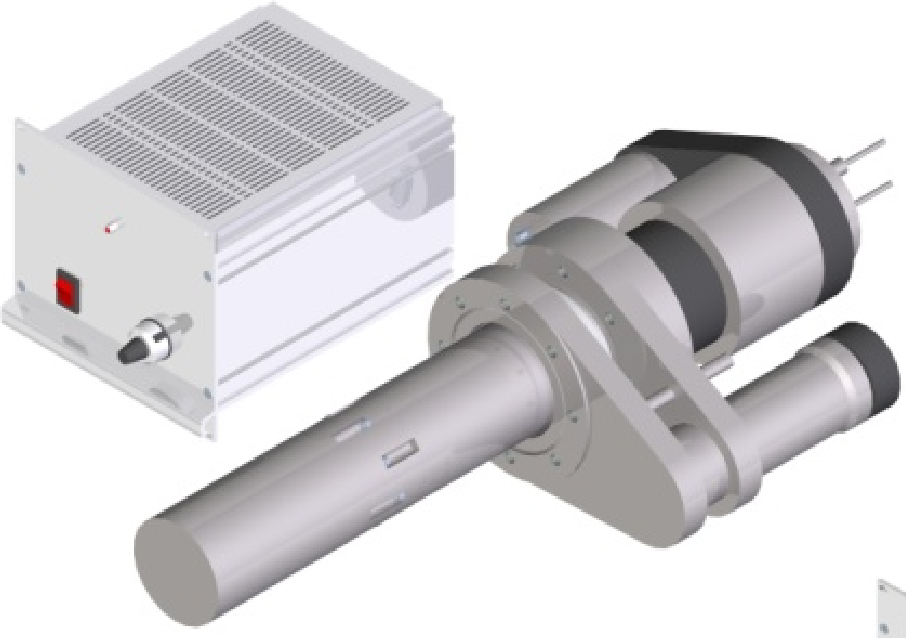
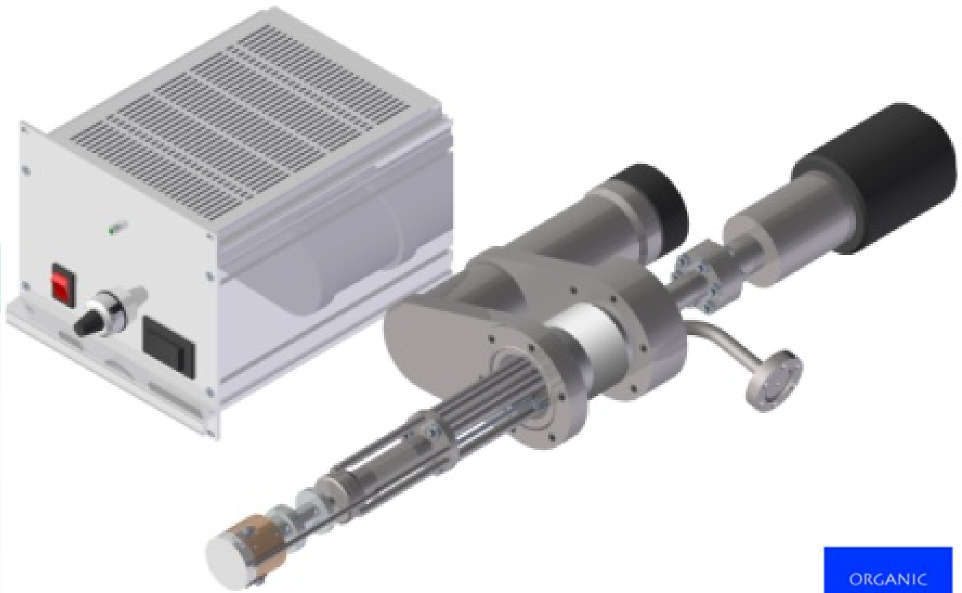
2″ heated sample holder
1.2″ rot. target holder

Accessories



Sample holder	
Sample diameter	up to 2 inches
Max. temperature of sample	900 °C
Magnetic rotation	up to 1 Hz
UHV Mounting (z adjustable)	CF 63 50 mm



Target holder	
Target diameter	Typ. 32 mm
Magnetic rotation	up to 20 Hz
Target tilting (x and y)	up to 5°
UHV mounting (z adjustable)	CF 40 50 mm

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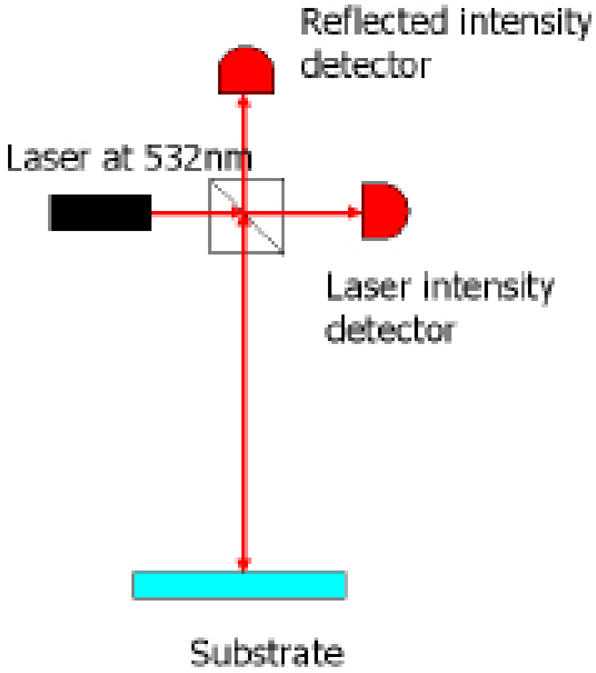
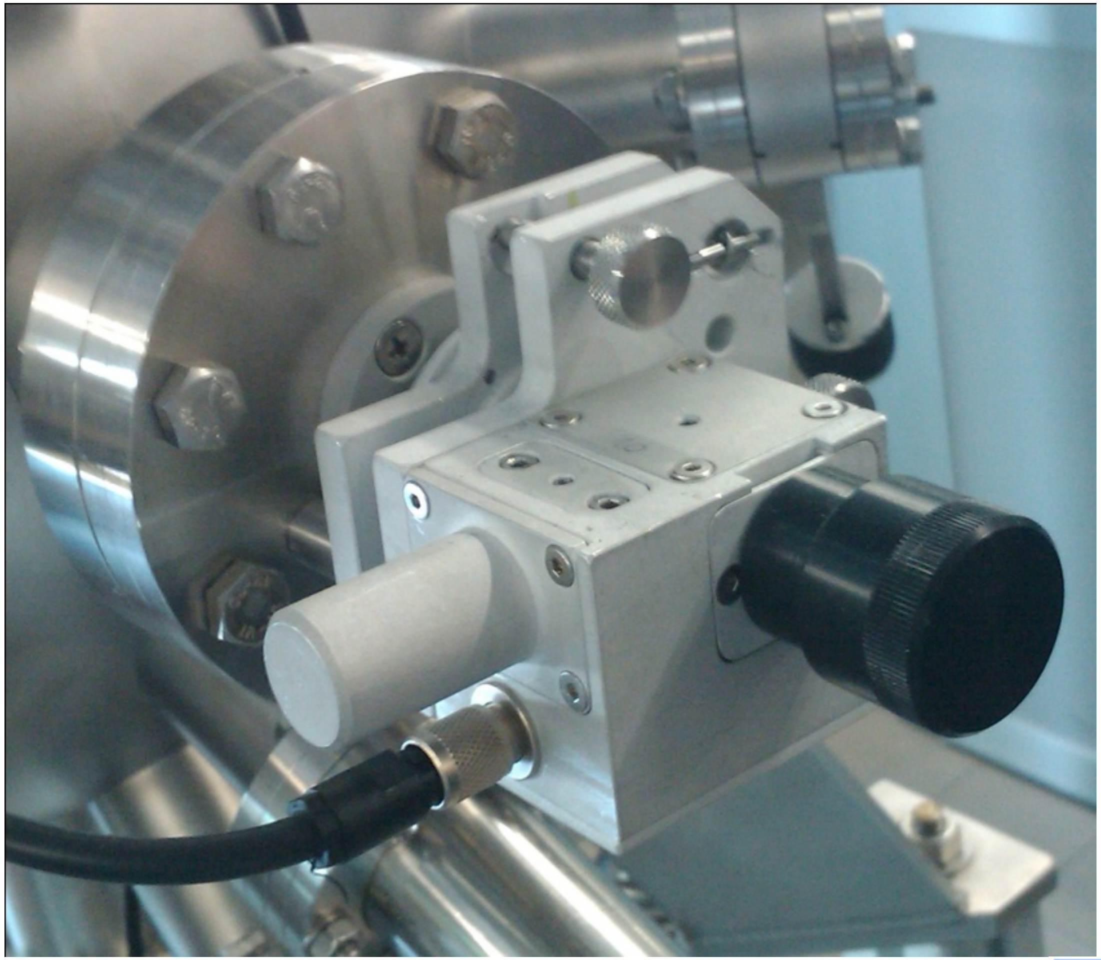
in-situ Laser Thickness Monitor (LTM)

Accessories

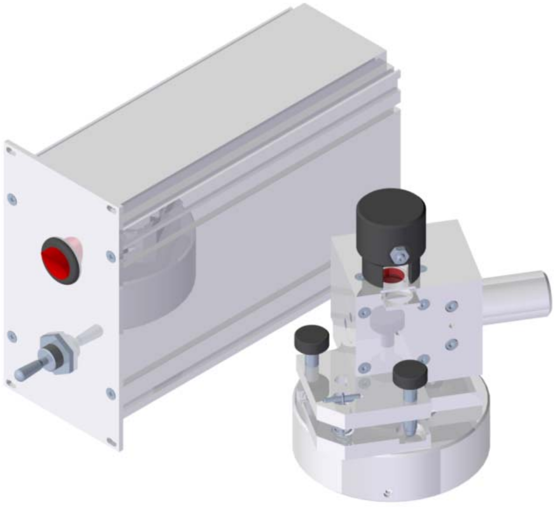




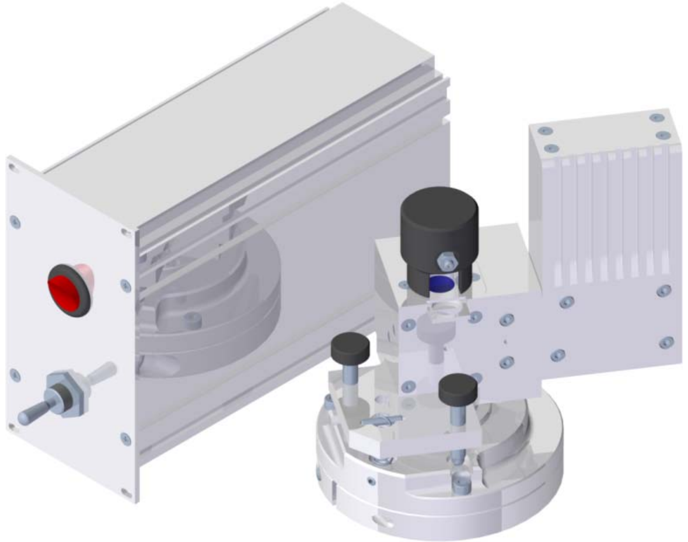
In situ LTM for a wide range of Eg materials

Accessories

LTM standard specification	
Laser frequency	532 nm (or 650, 450 nm)
Laser power	< 5 mW
Thin thickness resolution	Approx. 2 nm



IR (low Eg Materials) LTM specification	
Aligning laser	632 nm
Laser power (@ 632 nm)	2 mW
Measuring laser	830 nm
Laser power (@ 830nm)	< 5 mW
Thin thickness resolution	Approx.2 nm



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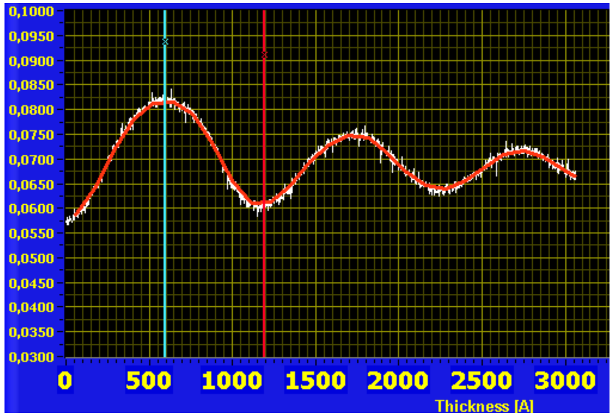
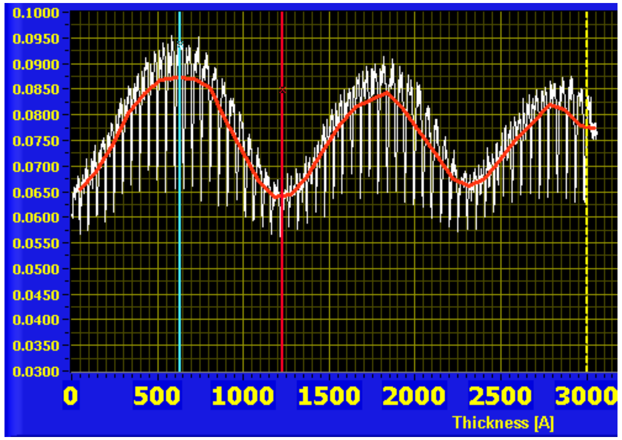
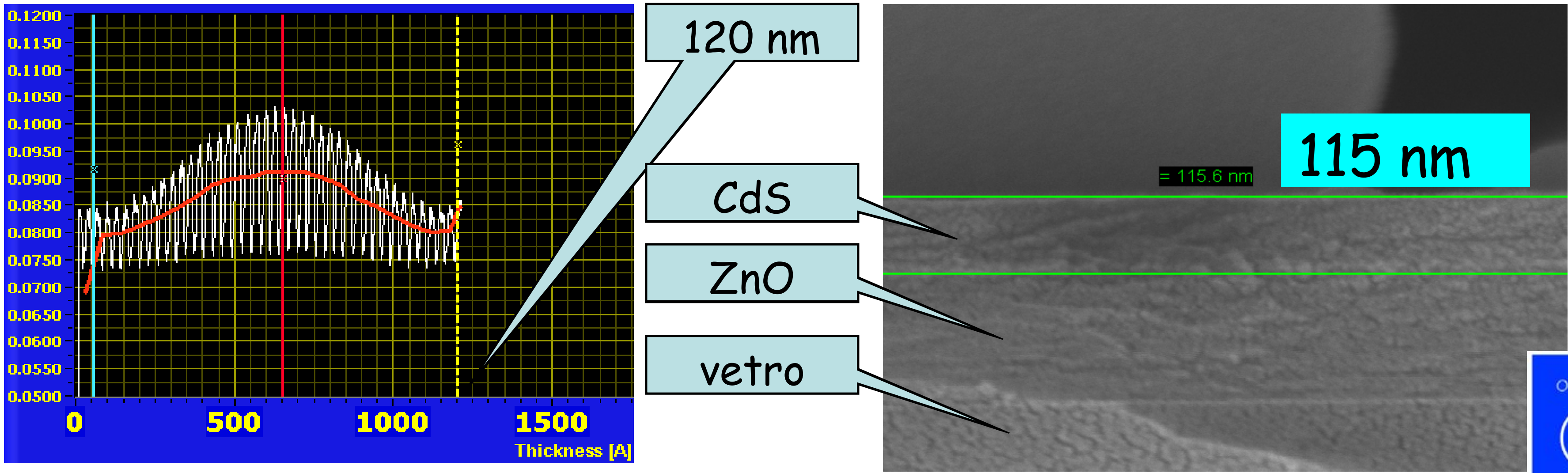
In situ Laser Thickness Monitor (LTM)

Accessories



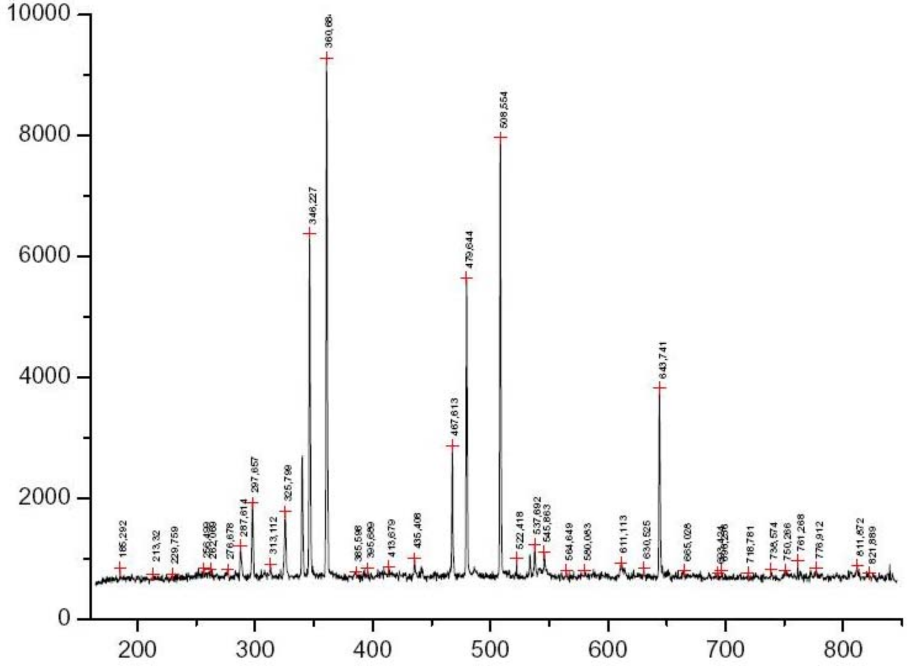


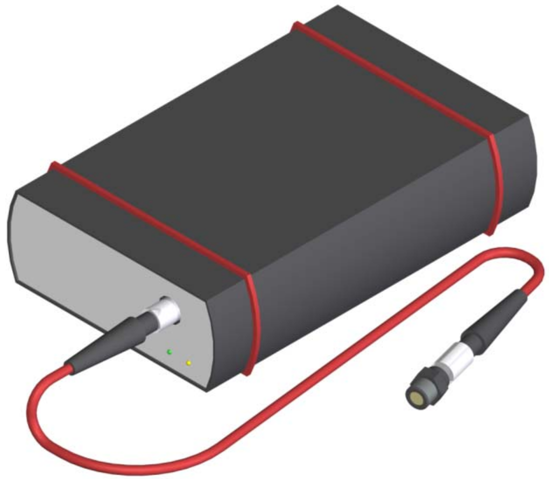
In situ LTM growth of low Eg material (i.e CdS)



PLSP *in situ* spectrometer for composition growth monitoring

Accessories





Plasma emission spectroscopy (i.e. Zn plasma above fig.)
to identify ionized species in the plume and
to measure the plasma temperature and therefore
the deposition conditions during growth

Fabrication parameters are easily reproducible

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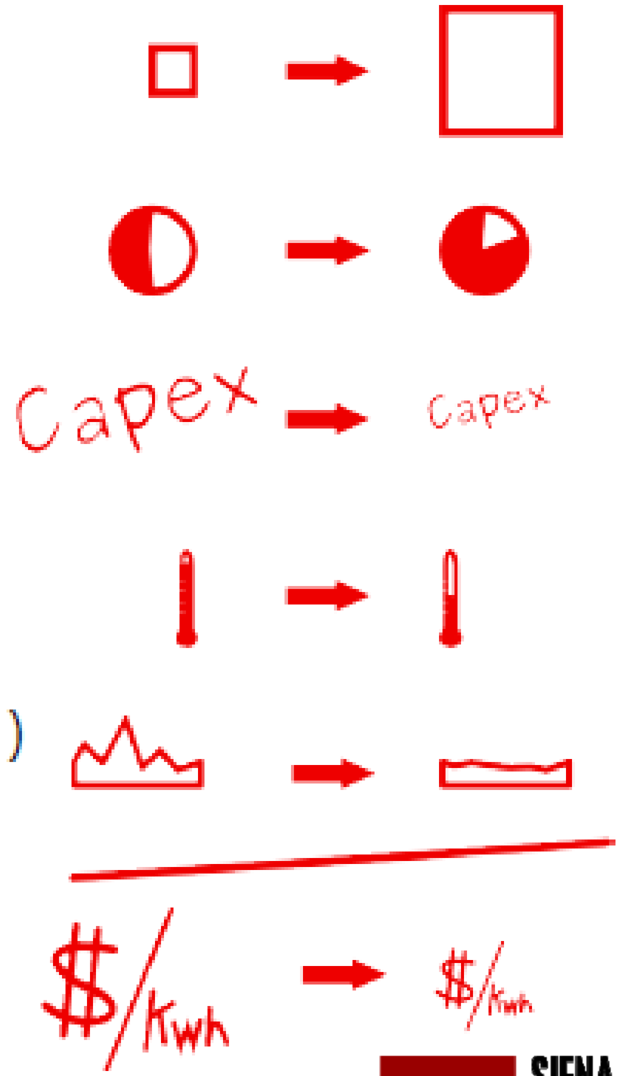
Industrial developments

PPD technology conclusions

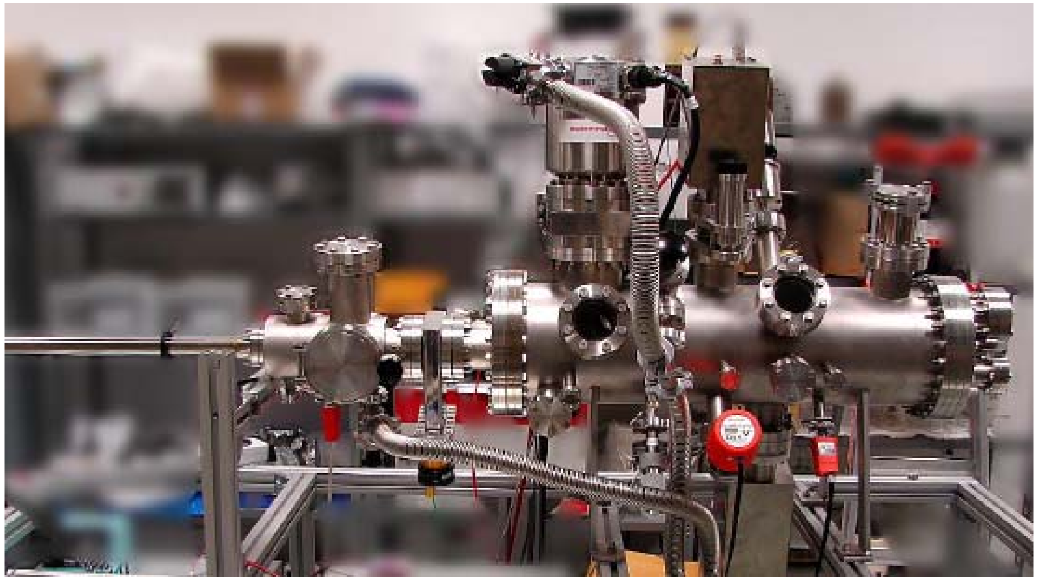
- Wider area
- Increasing deposition rate
- Lower Capex
- Lower thermal budget
- better film quality = efficiency
- Lower costs



SIENA SOLAR NANOTECH

Linear cw PPD

System information	
Base pressure	< 1 x 10-7 mbar
Chamber diameter	DN 200 mm
Chamber length	750 mm
Web size	40 mm
Number of guns	2



A ribbon is fabricated
by a c.w. process
Additive PPD process is proved

Next step is wider web area deposition by multiple PPD guns

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PPD industrial guns: Gen IV 100Hz

Dep.rate:
up to 700 nm/min
depending on materials

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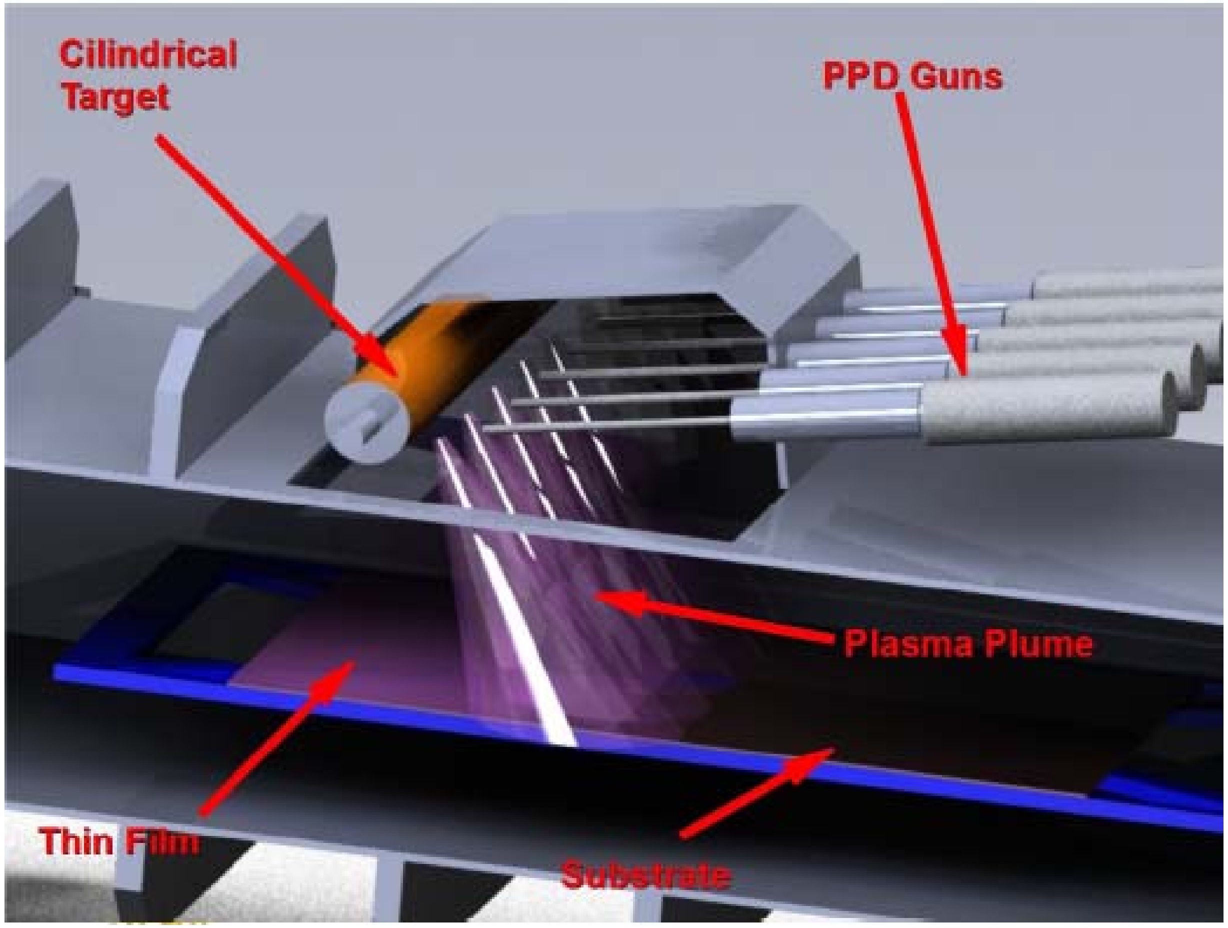
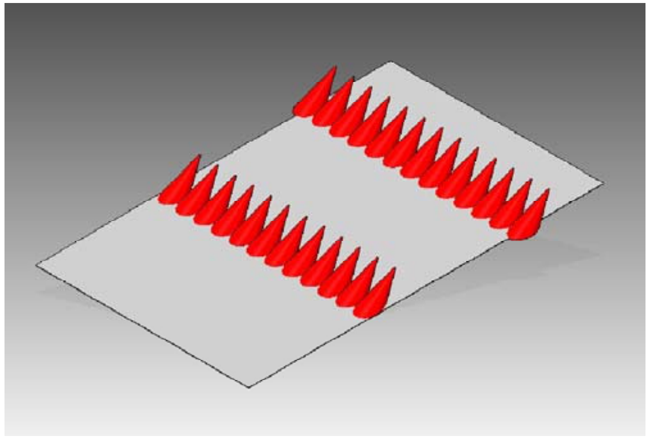
Gen IV at 100 Hz in operation

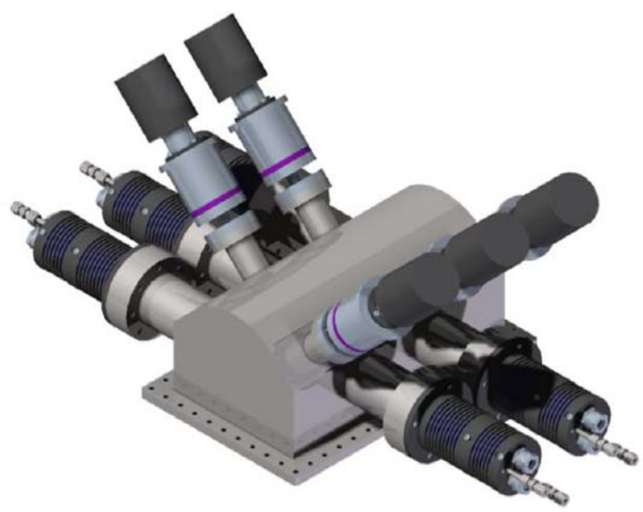
The PPD wide area concept



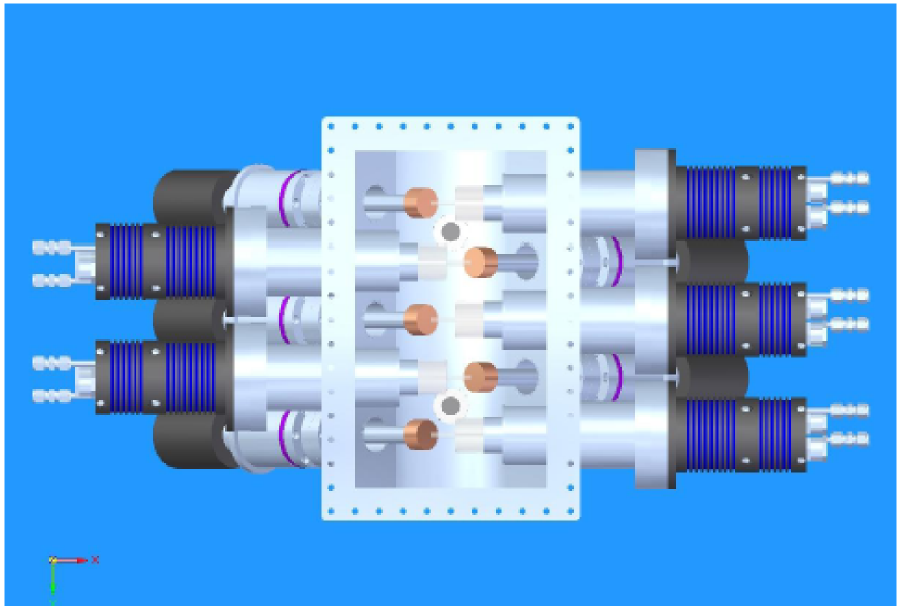


Wide area R2R PPD

300 mm wide R2R modular system for the pilot production unit



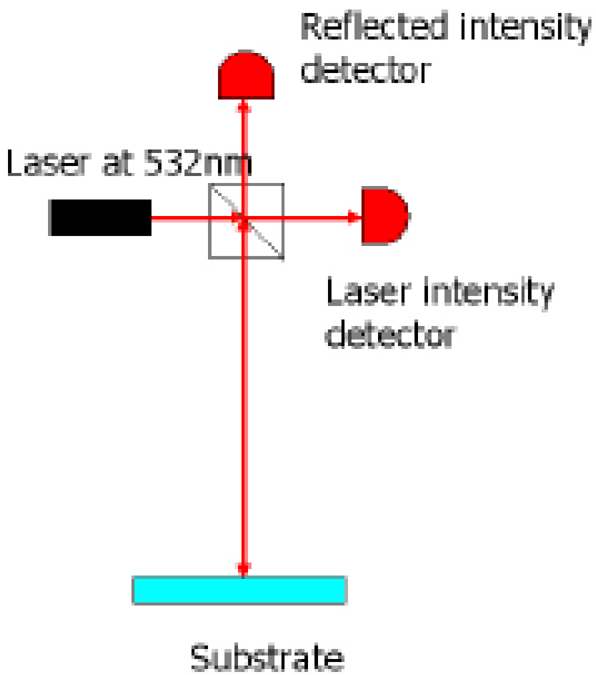
Multiple modules may allow to reach the desired productivity

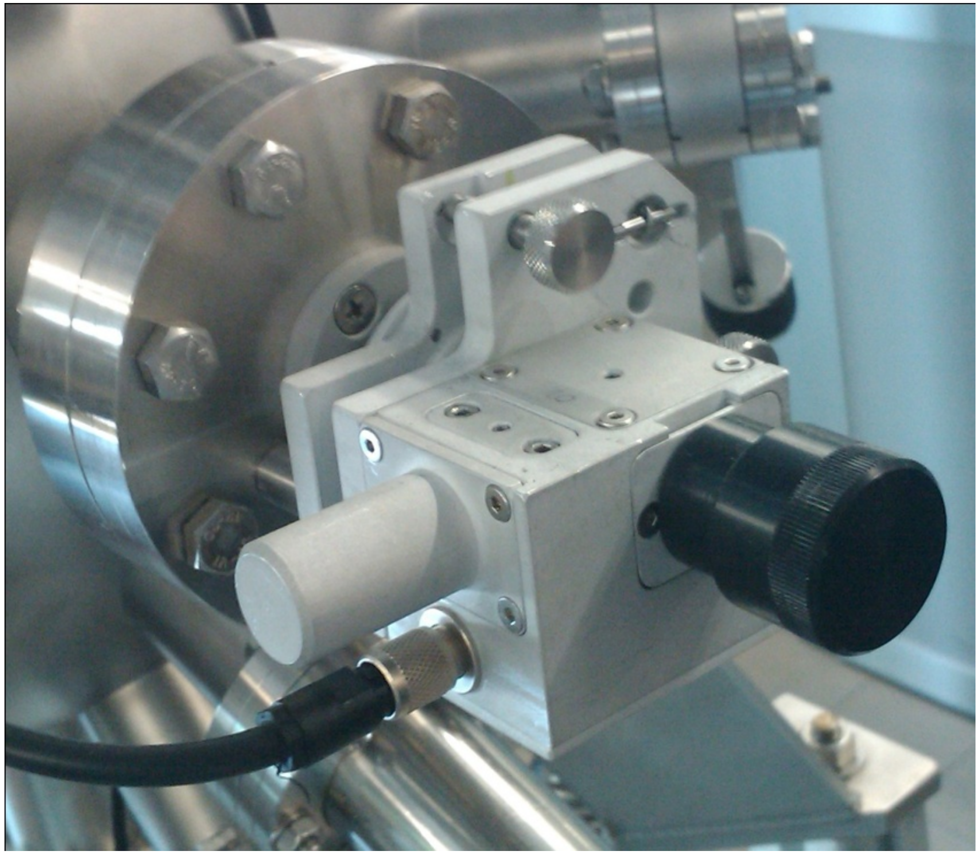


The plasma surface coverage has a gaussian shape and is therefore suitable for homogeneous coverage on wider web sizes

Accessories for the PPD R2R

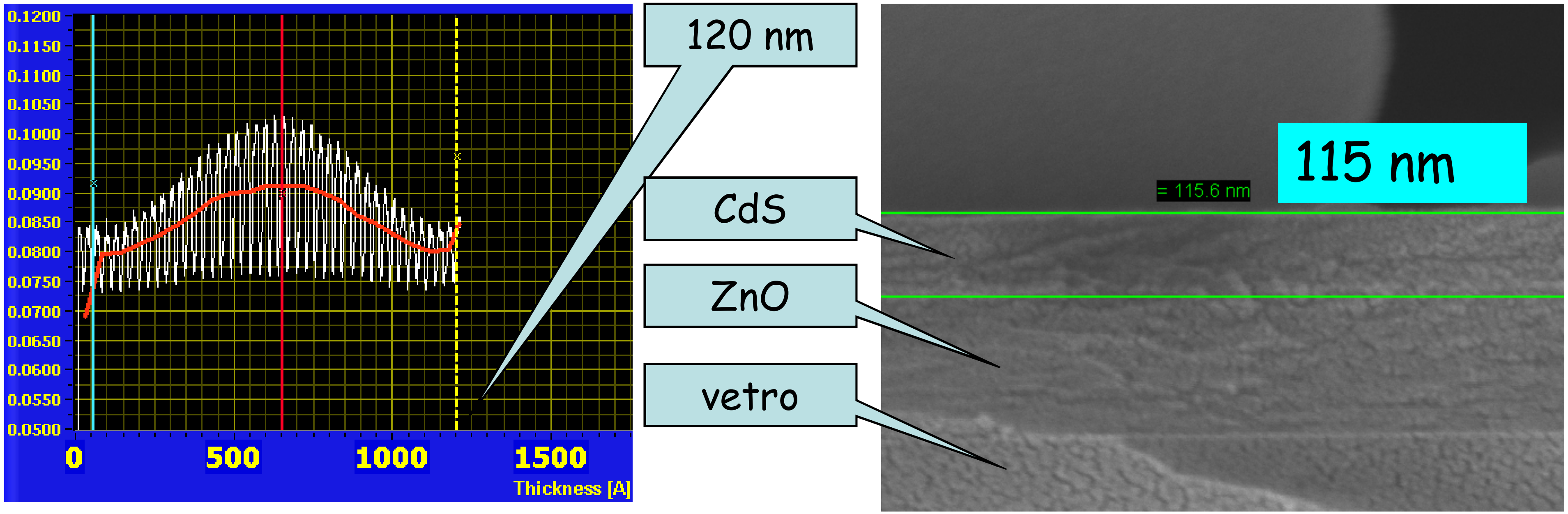
in-situ Laser Thickness Monitor (LTM)





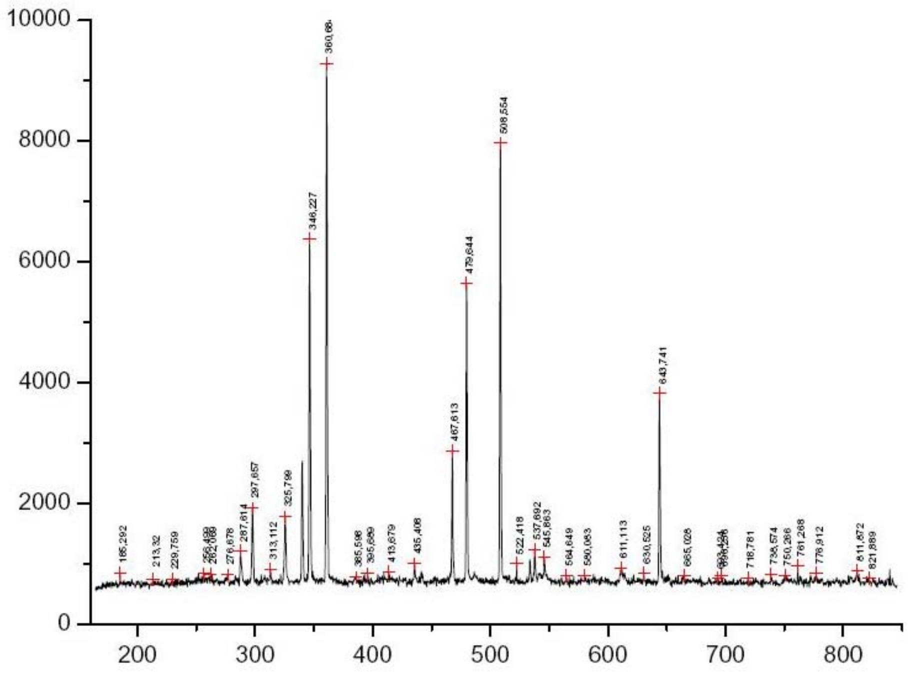
Accessories for the PPD R2R

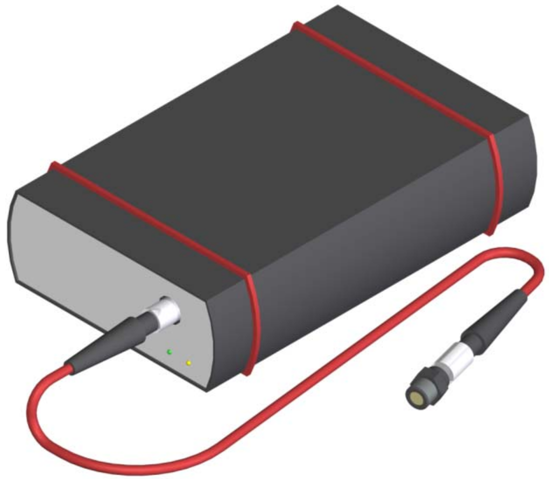
In situ LTM measurement of a low Eg material (i.e CdS)



Accessories for the PPD R2R

PLSP in situ spectrometer for composition growth monitoring





Plasma emission spectroscopy (i.e. Zn plasma above fig.)
to identify ionized species in the plume and
to measure the plasma temperature and therefore
the deposition conditions during growth

Fabrication parameters are easily reproducible

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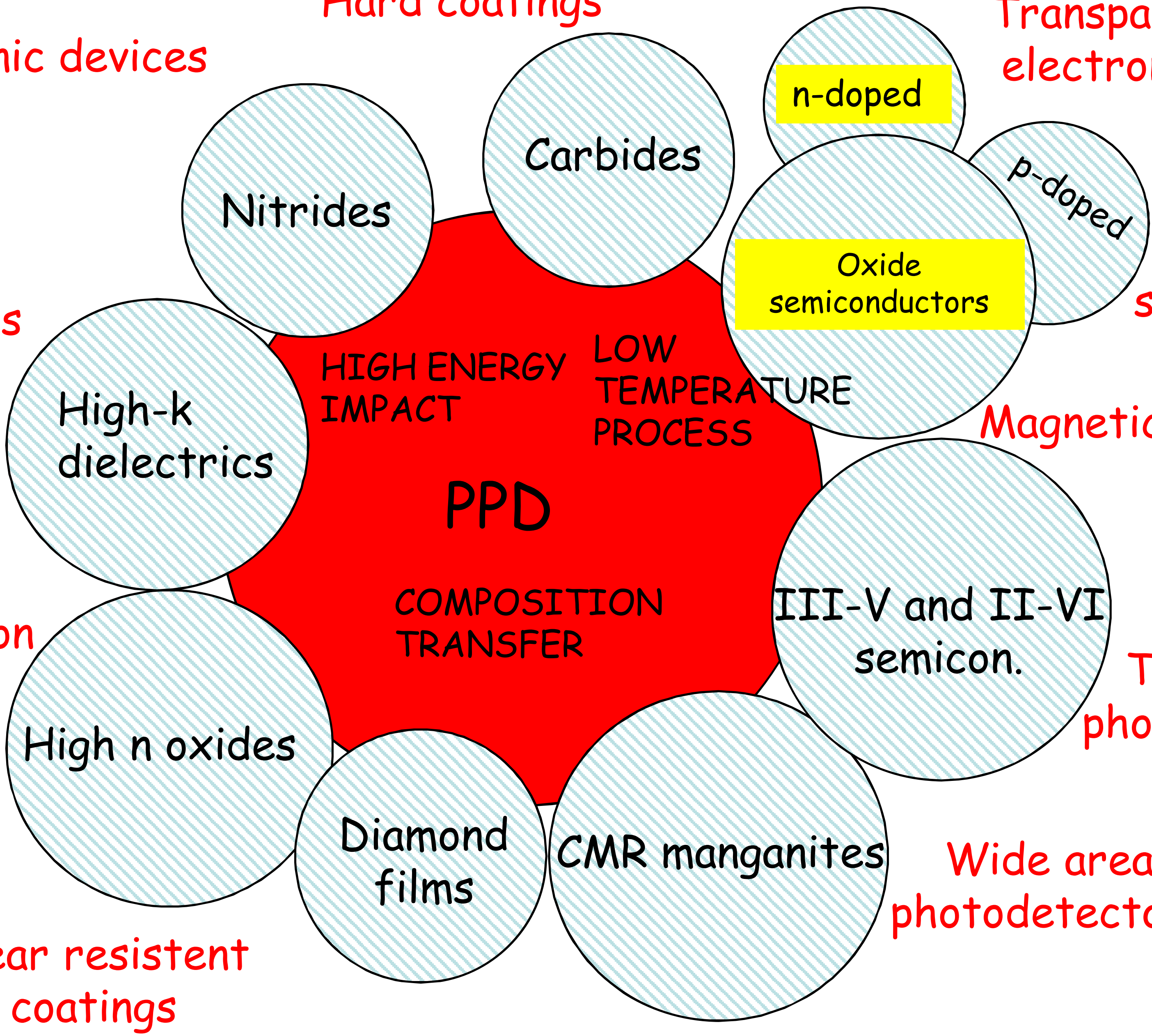
TCO on flexible substrates enabling flexible OPV

i.e. enabling OPV future perspectives !!!

Applications



Oxygen vacancy n doping of TCO

Doping may be achieved either by:

- Substitution (i.e.: tetravalent vs trivalent ions)
- Removal of oxygen (oxygen vacancies)

Substitution (i.e. Sn vs In in ITO) requires heating post-recristallization to overcome the site substitution barrier as in sputtering.

With the PPD process oxygen vacancies are introduced at room temperature

Next generation displays

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Flexible issues

Applications

Flexible electronics
Flexible displays
Flexible photovoltaics
more..

Active materials

Soft matter:
Organic semiconductors
Polymers

Substrates

Plastic substrates:
Lower cost
Good mech. properties

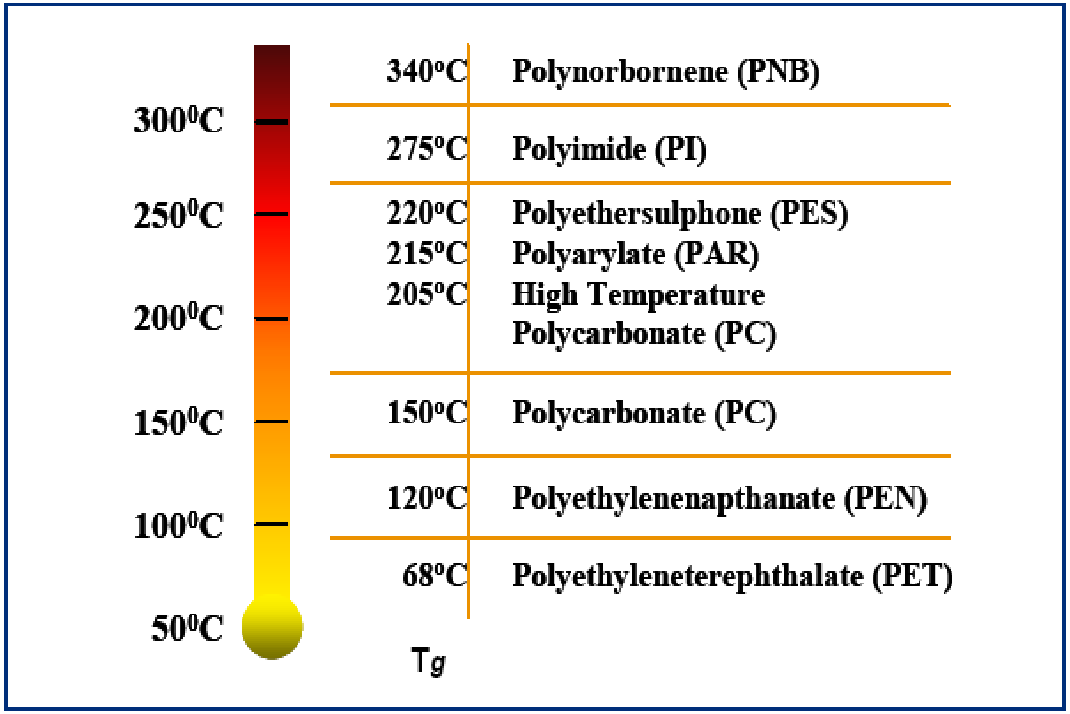
Requirements

TCO at low temperature + Barrier to oxygen and water

TCO: the temperature factor vs substrate

The most appealing plastic substrate is PET for which the processing TCO cannot exceed 80°C (see the inset).

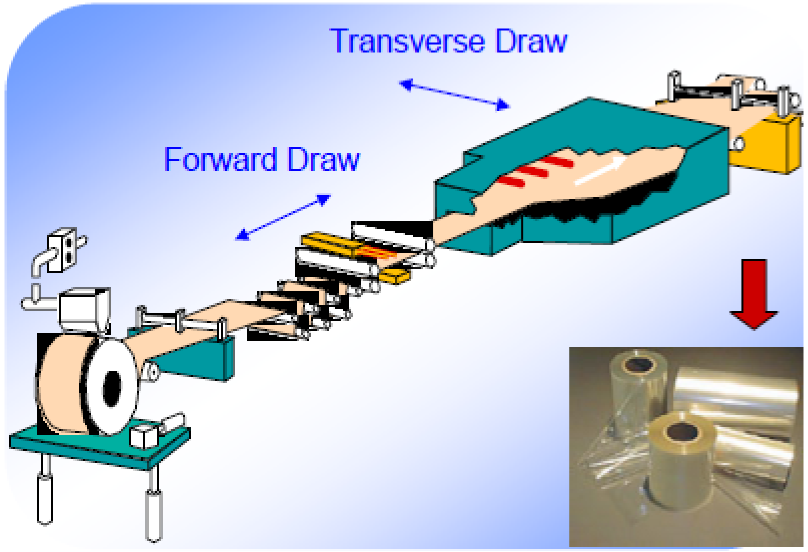
The Pulsed Plasma Deposition technique (PPD) developed by Organic Spintronics is a novel thin film fabrication method that allows to process TCO at room temperature.



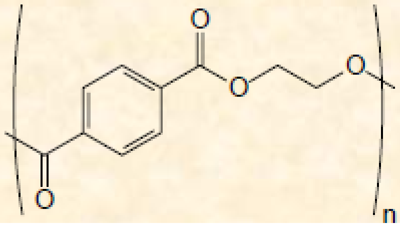
Polyester Film Technology (1)

DuPont Teijin Films

- PET and PEN polyester films
- Biaxially oriented, semi-crystalline
  - High stiffness
  - Dimensional stability
  - Optical transparency
  - Solvent resistance
  - Thickness = 0.5-500 µm

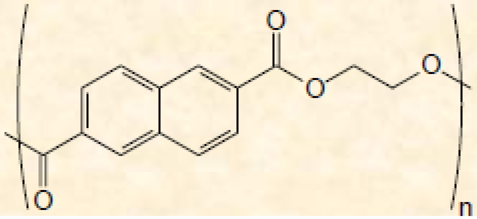


Melinex®, Mylar® and Teijin® Tetoron®
Polyethylene terephthalate (PET)



T_m = 255 °C
T_g = 78 °C

Teonex®
Polyethylene naphthalate (PEN)



T_m = 263 °C
T_g = 120 °C

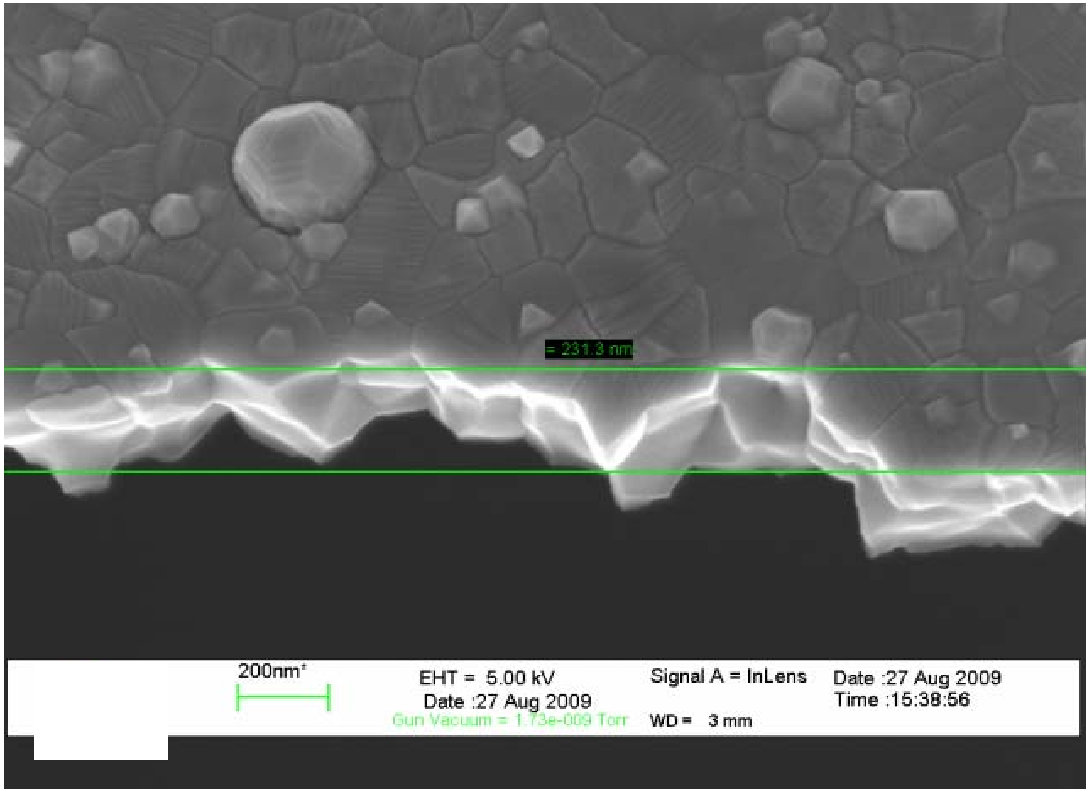
Transparent Conducting Oxide on PET by the PPD at room temperature

RT PPD deposition on plastics: OS Patent pending

Characteristics of n_ ZnO on PET by PPD at room temperature

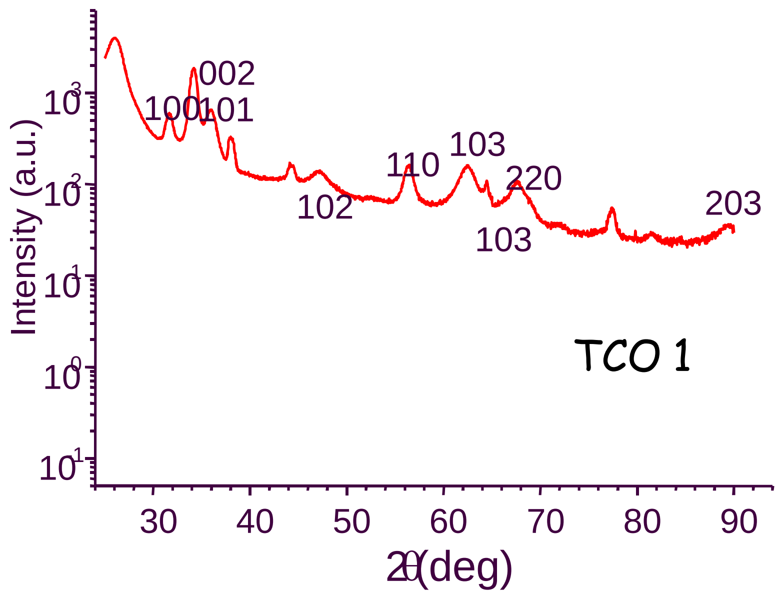
Characteristics	
Substrate	Melinex ST 504 (Du Pont)
Thickness	200 nm
Sheet resistance	Approx. 10 ohm square
Average VIS transmittance (T%)	Higher than 90 T%
Raughness (Rq)	19 nm
Uniformity (with two guns)	8% at 3 sigma

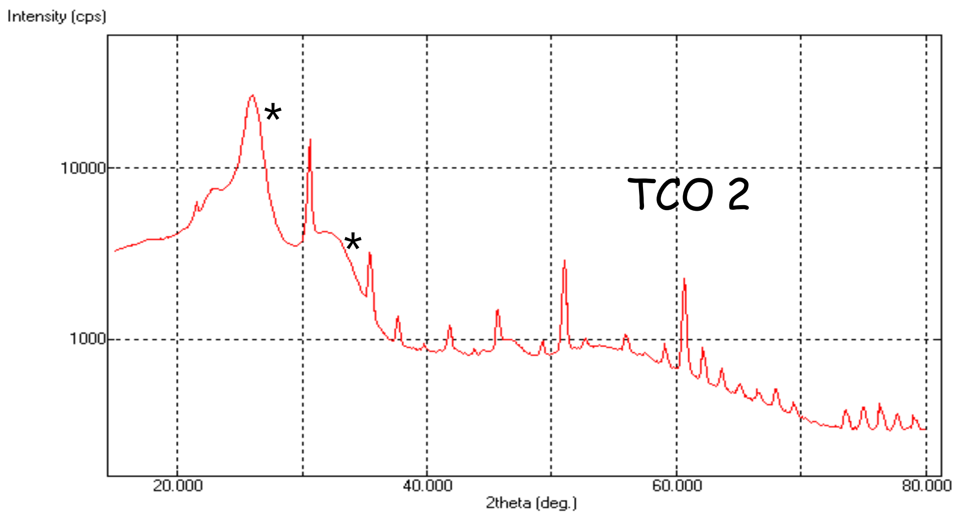
SEM of n-ZnO on PET by the PPD at RT



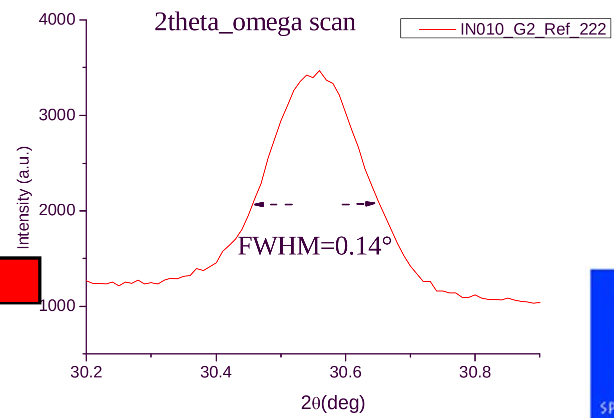
Dense and highly connected cristalline layer from the phase SPM
Excellent conductivity.

High cristallinity at RT growth
XRD grazing incidence





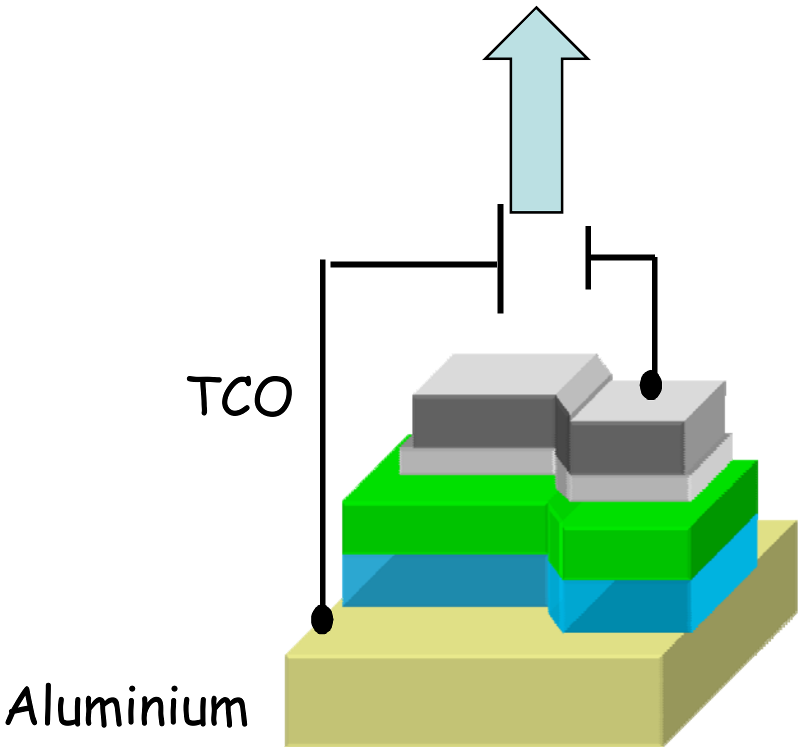
Randomly oriented
Cristallites
Size (LRO) of 65 nm



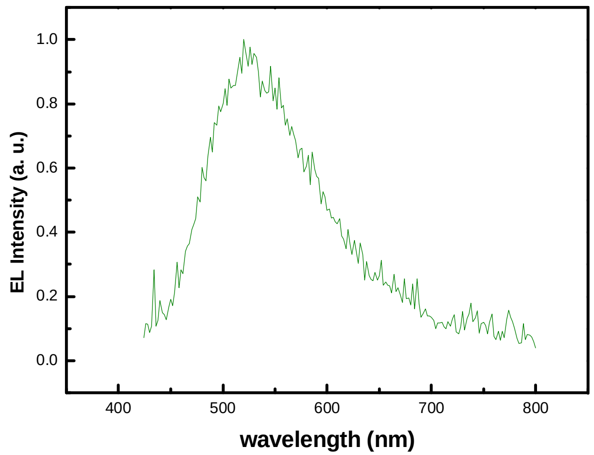
TCO on flexible substrates enabling flexible OLED

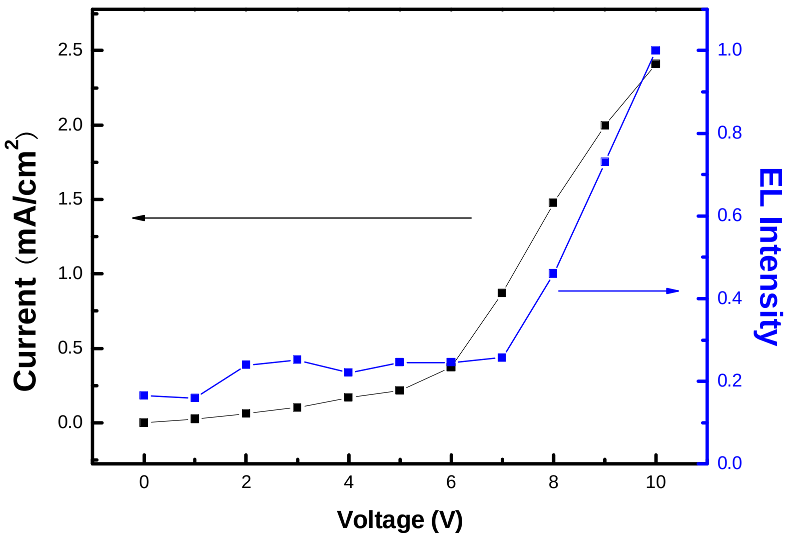
Top emitting OLED
RT TCO (IMO) on Organic Semiconductors

Y. Zhang, E. Lunedei



TCO (IMO) is deposited on top of the organic semiconductor (AlQ3)





Adhesion

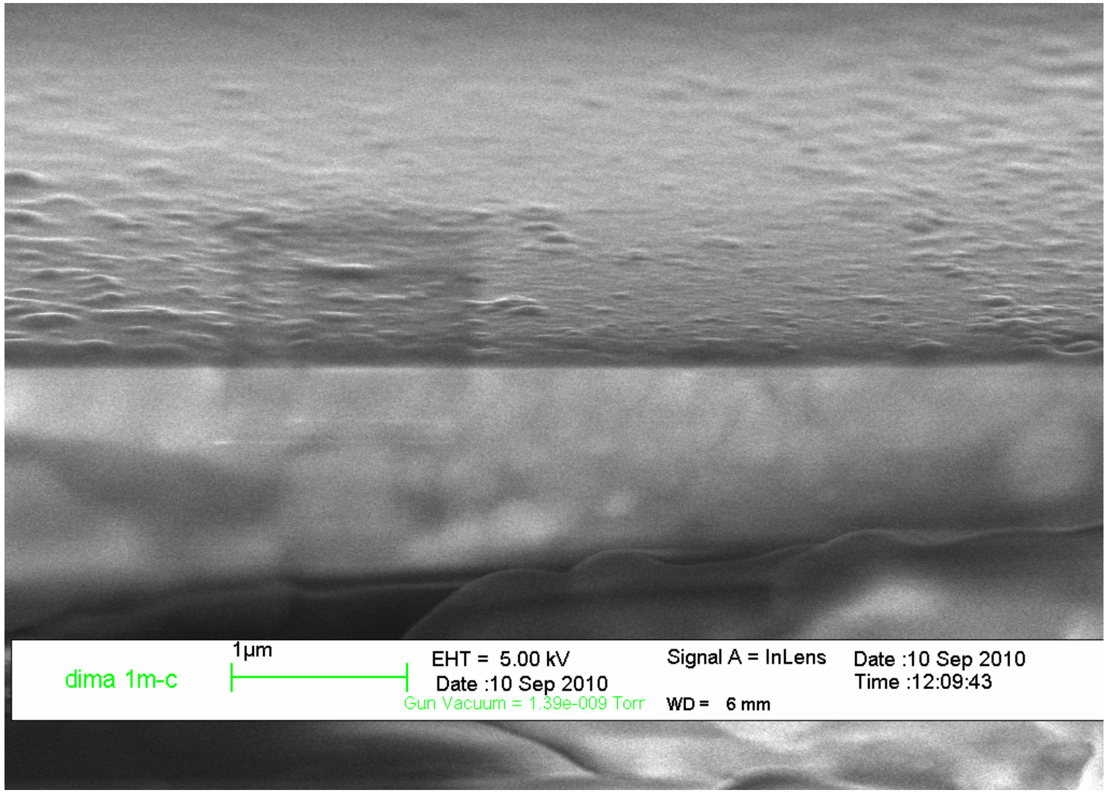
Spec: MIL – M - 13508

Surface of TCO on PET (x500)
After scratching and Peeling
(scratch test)

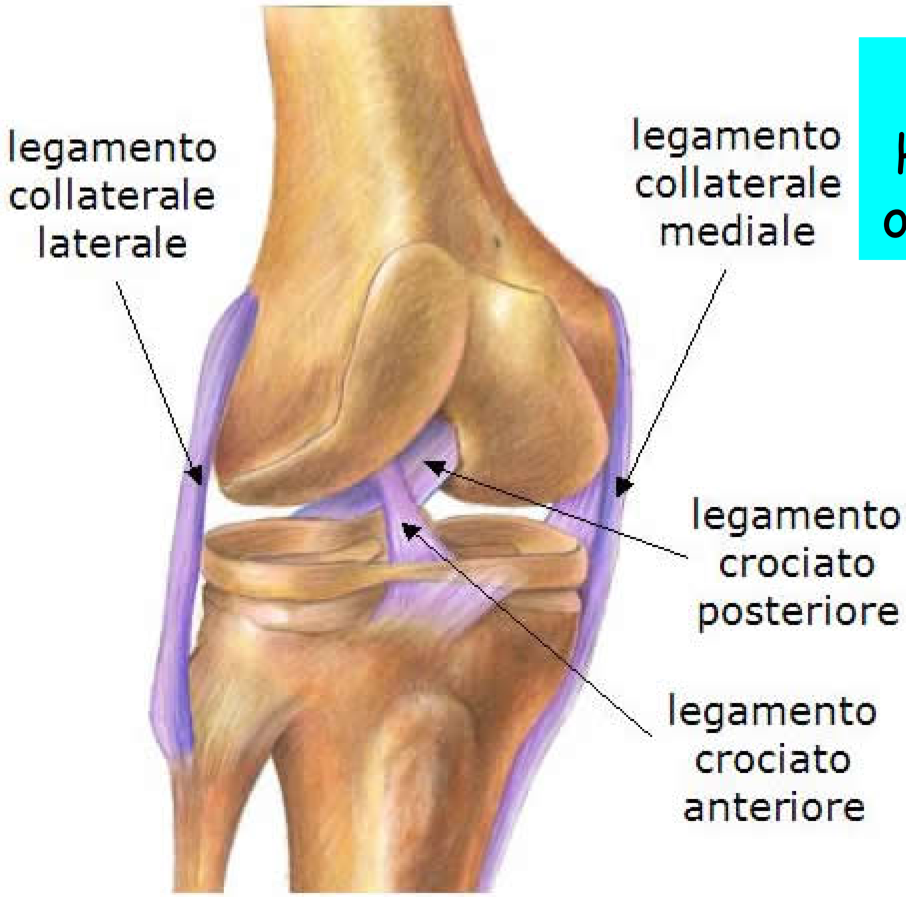
Room Temperature deposition on plastics: Patented

Hard coatings for implants

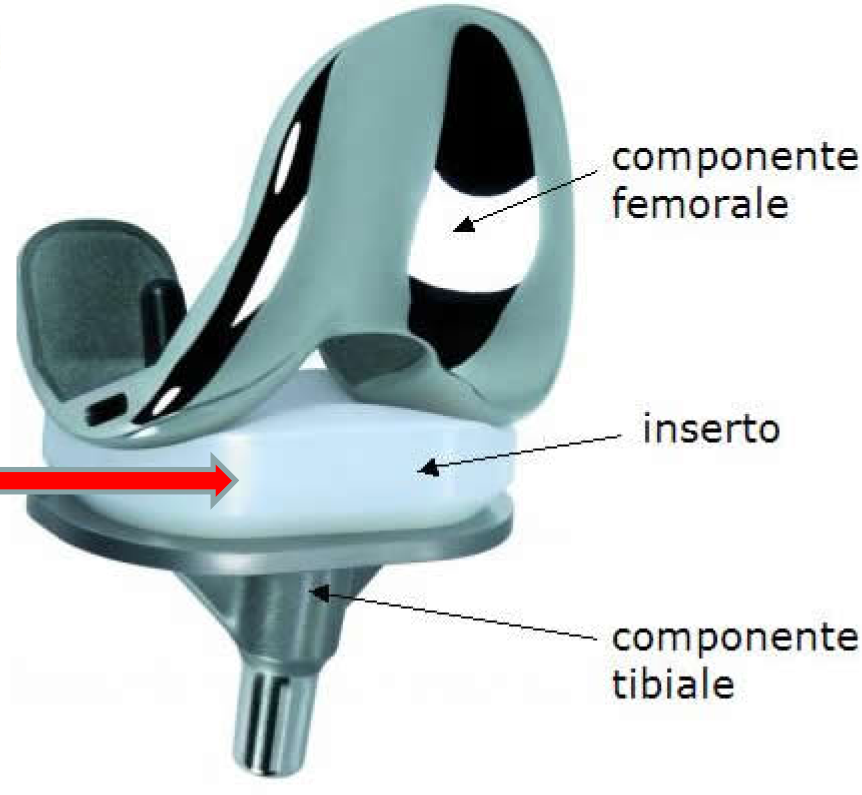
Zirconia (ZrOx) on PET by PPD



Problem:
HDPE insert has a limited lifetime
only 2 may be executed on a patient



Need of a hard coating on HDPE



(immagine concessa da Lima-Lto SpA)

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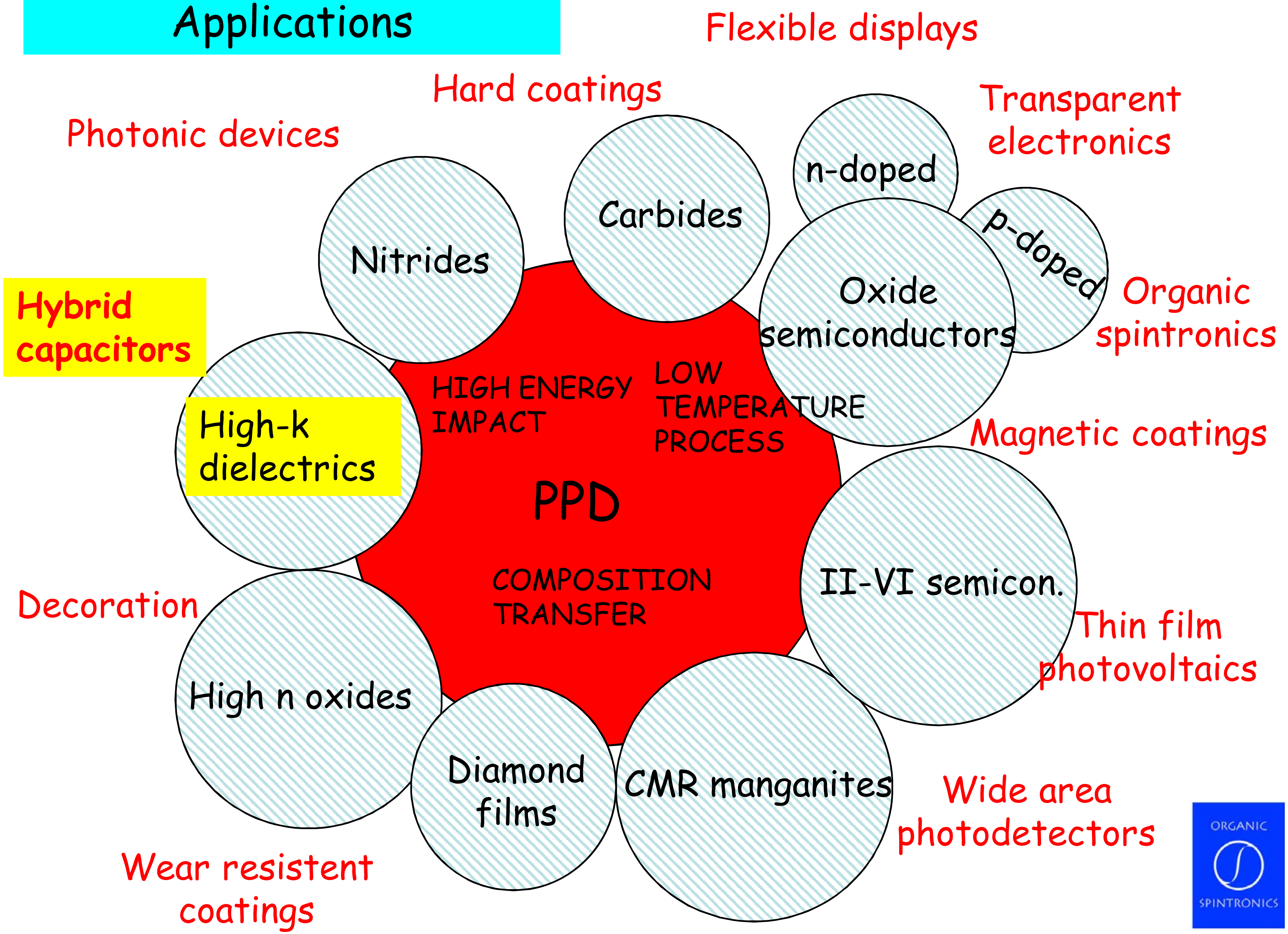
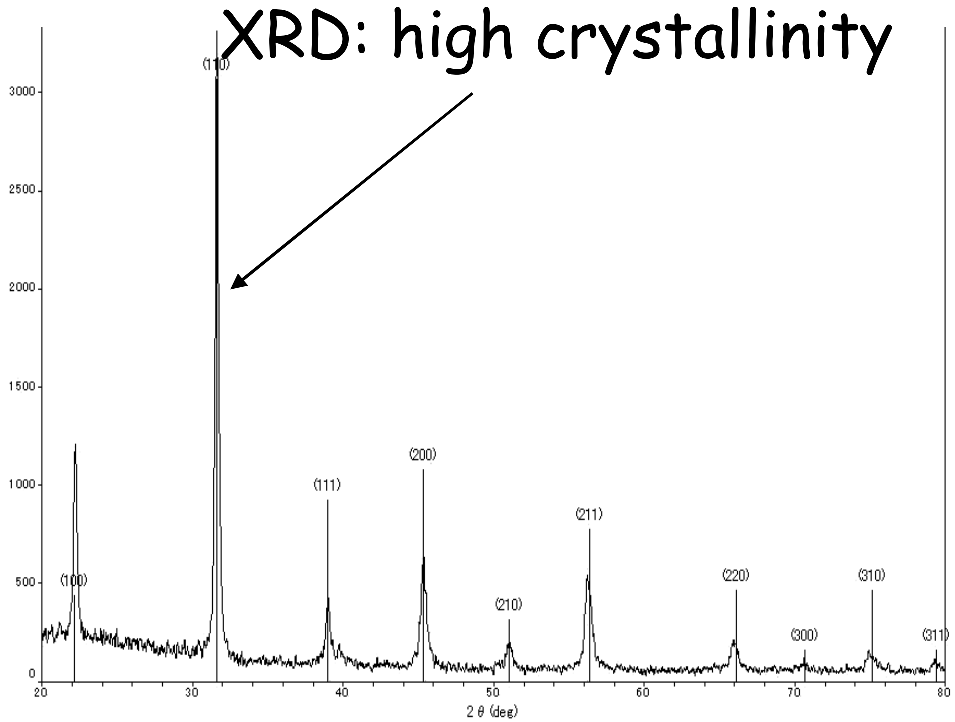
More applications of the PPD

Applications

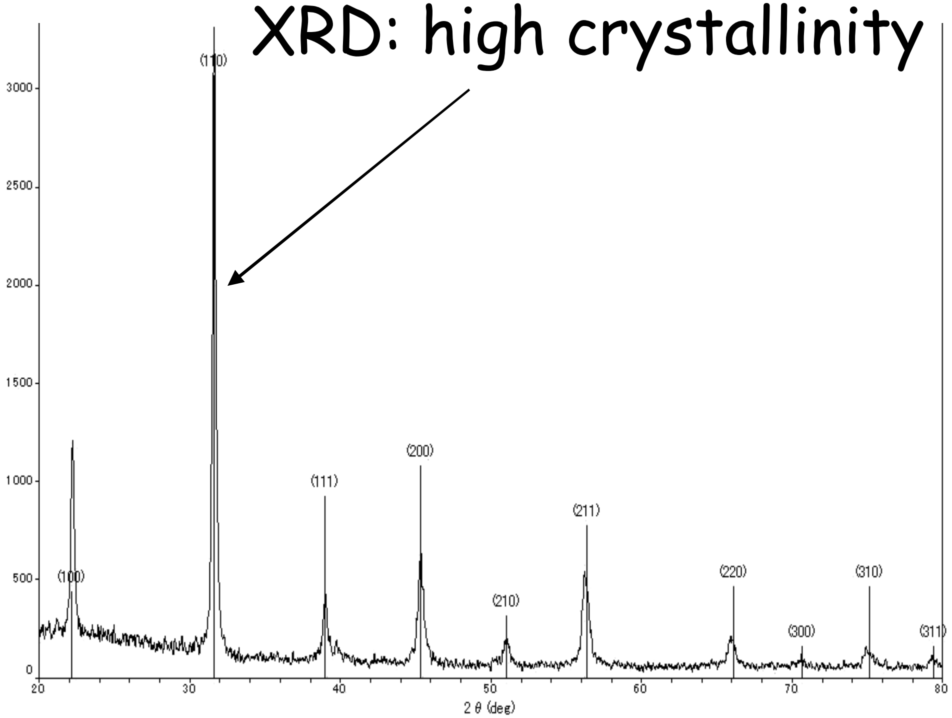


Barium Strontium Titanate (BST) by PPD on sapphire

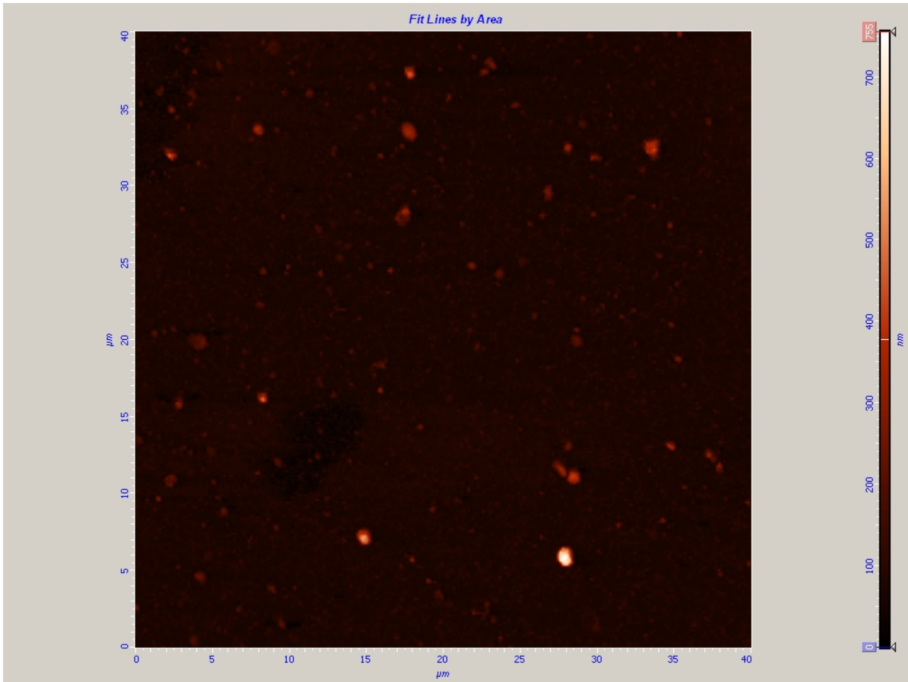


Barium Strontium Titanate (BST) by PPD on sapphire

XRD: high crystallinity

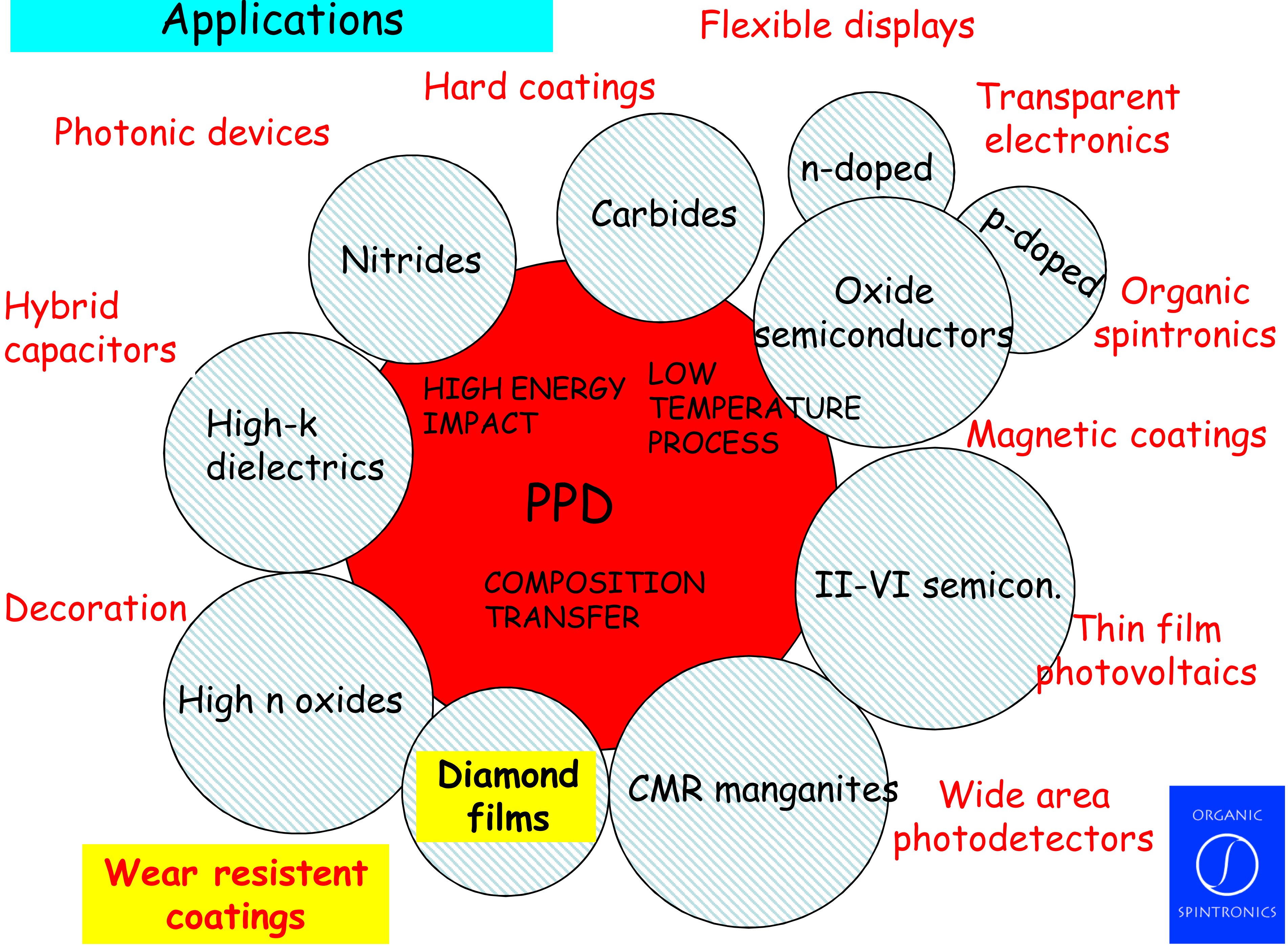


AFM: low roughness

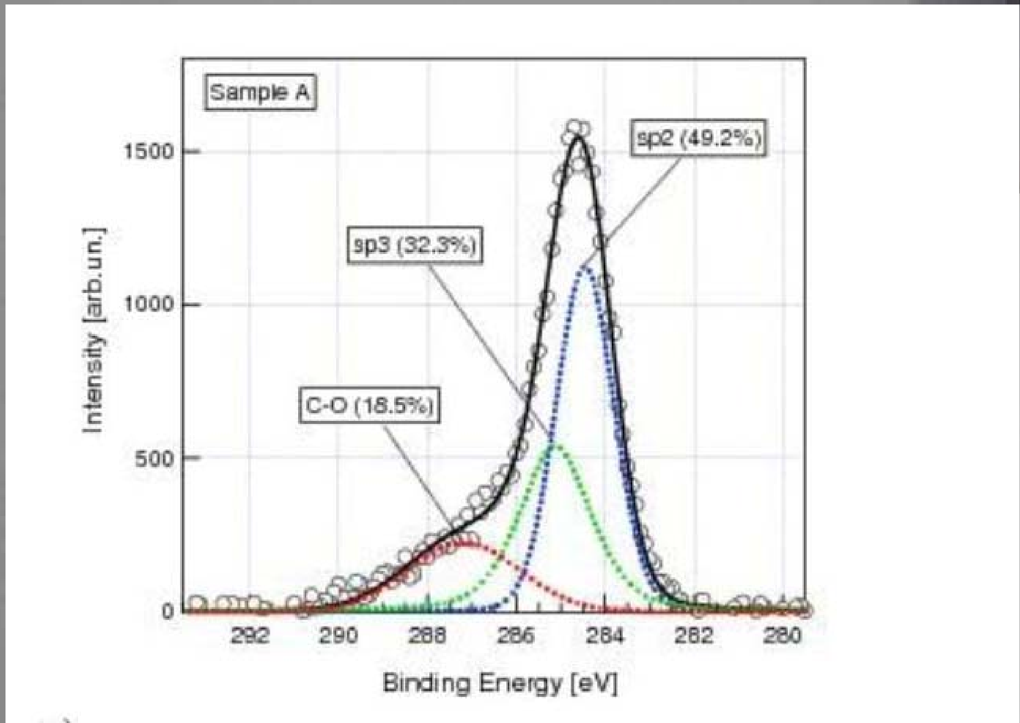


Dielectric constant : 500

Applications



Tetrahedral α carbon by PPD on WC



XPS: 80% sp^3
α carbon

Conclusion

Pulsed Plasma Deposition (PPD) allows to:

- Trasfer of the target composition to the sample
- Fabricate thin films at low temperature

PPD enables the fabrication of:

- Chalcogenide photovoltaic thin films
- Transparent conducting oxides (TCO) at room temperature
- High dielectrics like barium strontium titanate (BST)
- Many more ….

PPD is industrially scalable, efficient and with a high rep. rate

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Team

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