



“Escalamiento de celdas solares de CdTe” – proyecto SENER, Sustentabilidad Energética

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Outline

* Introduction

- PV potential & actual scenario
- Solar cells-basics
- CdTe perspectives

* R & D activities

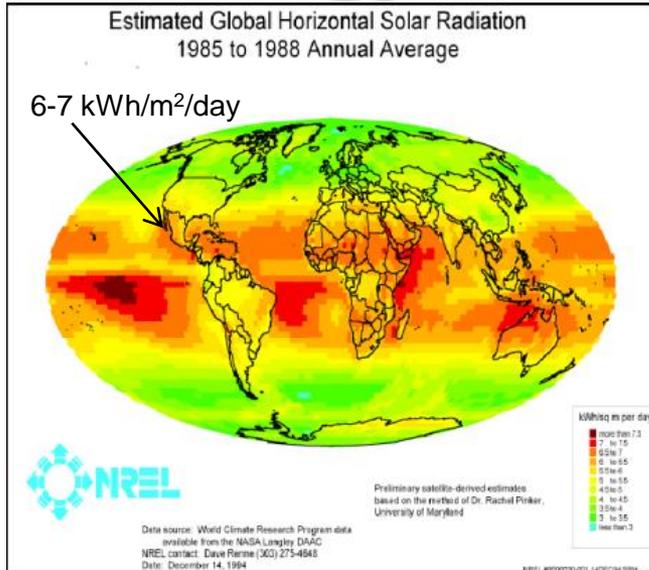
- CdTe/CdS devices

* CdTe issues

* Scale up for CdTe

- CSS process
- Prototype CSS pilot plant for batch processing

PV- a technology to harness Solar Energy



- Earth receives approximately 200,000 TW solar power
- Energy receiving each day is equivalent to the petroleum reserves of the world.
- **600TW can be utilized**
- **With 10% efficiency, 60TW on-shore production**
- **With 10% land use this will translate into 6TW**
- A temporary problem - cost



Portugal, 52,000 panels
11 MW capacidad



Courtesy: N.G. Dhere, FSEC, Florida

Energy is BIG business

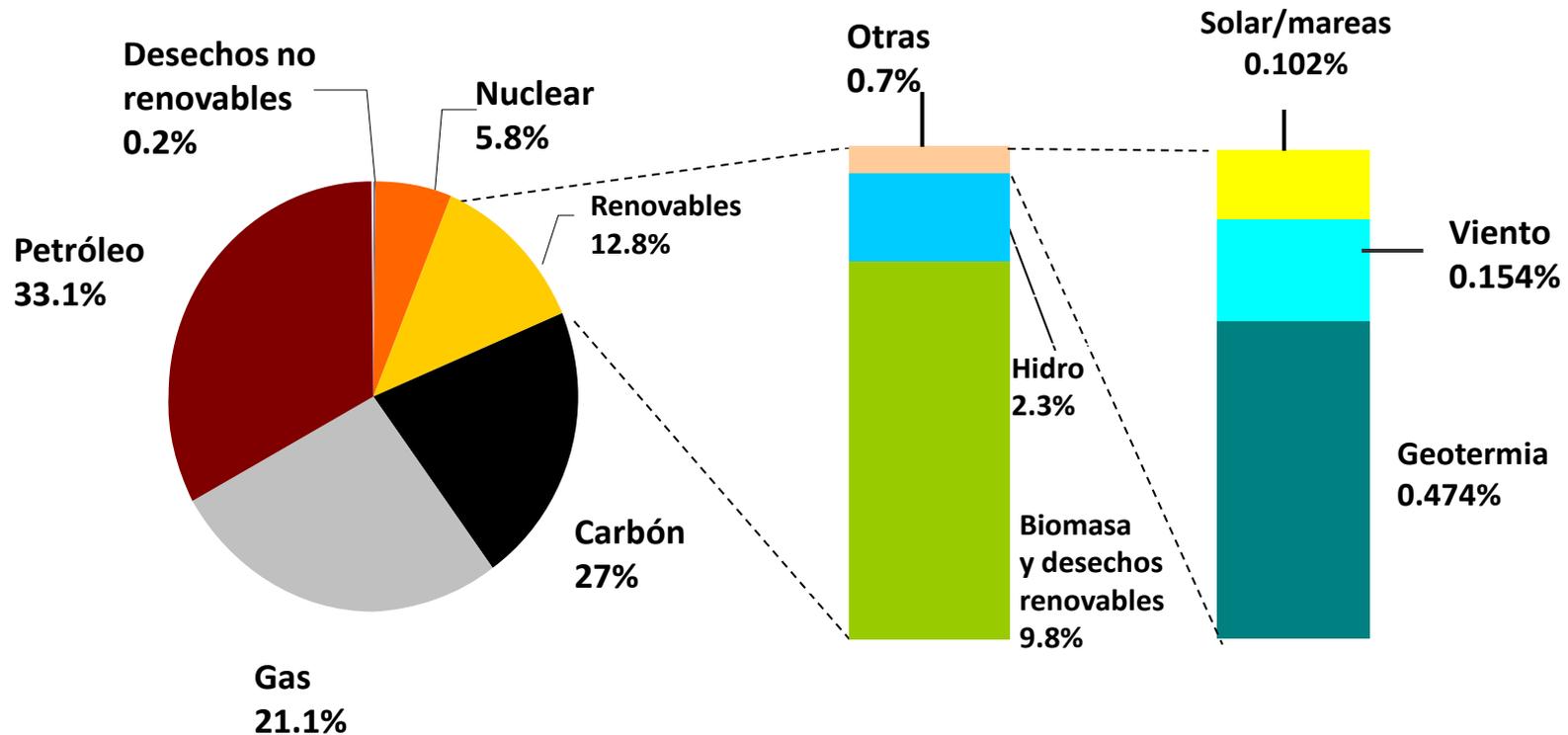
Global Annual dollar outlays-

Energy	4T\$
Agriculture	2T\$
Defense	1T\$ (US- 0.5T\$)

Courtesy- Tim Ellison (Energy Conversion Devices Inc.), 2006

Consumo de energía primaria mundial 2008

12,264 Mtoe

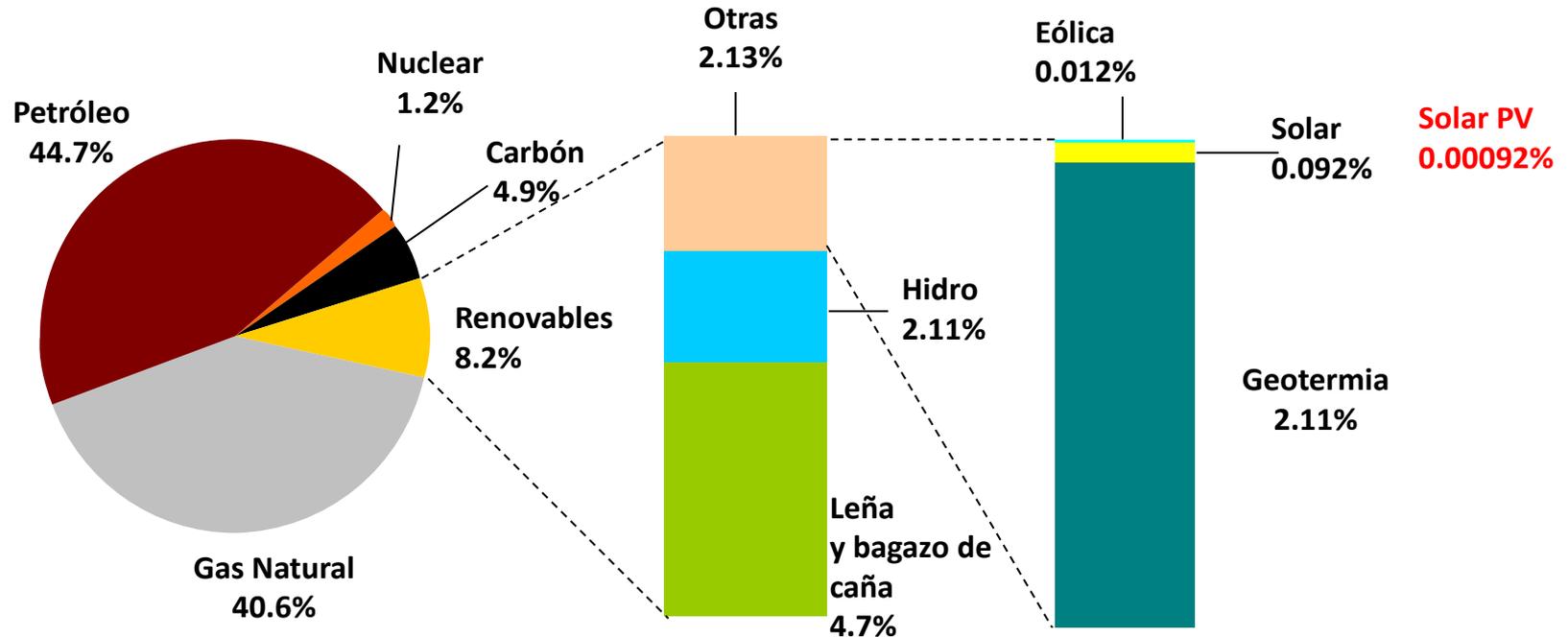


Fuente: IEA (2010), Renewables Information 2010.

Courtesy- Genice Grande, CIE

Consumo de energía primaria en México 2009

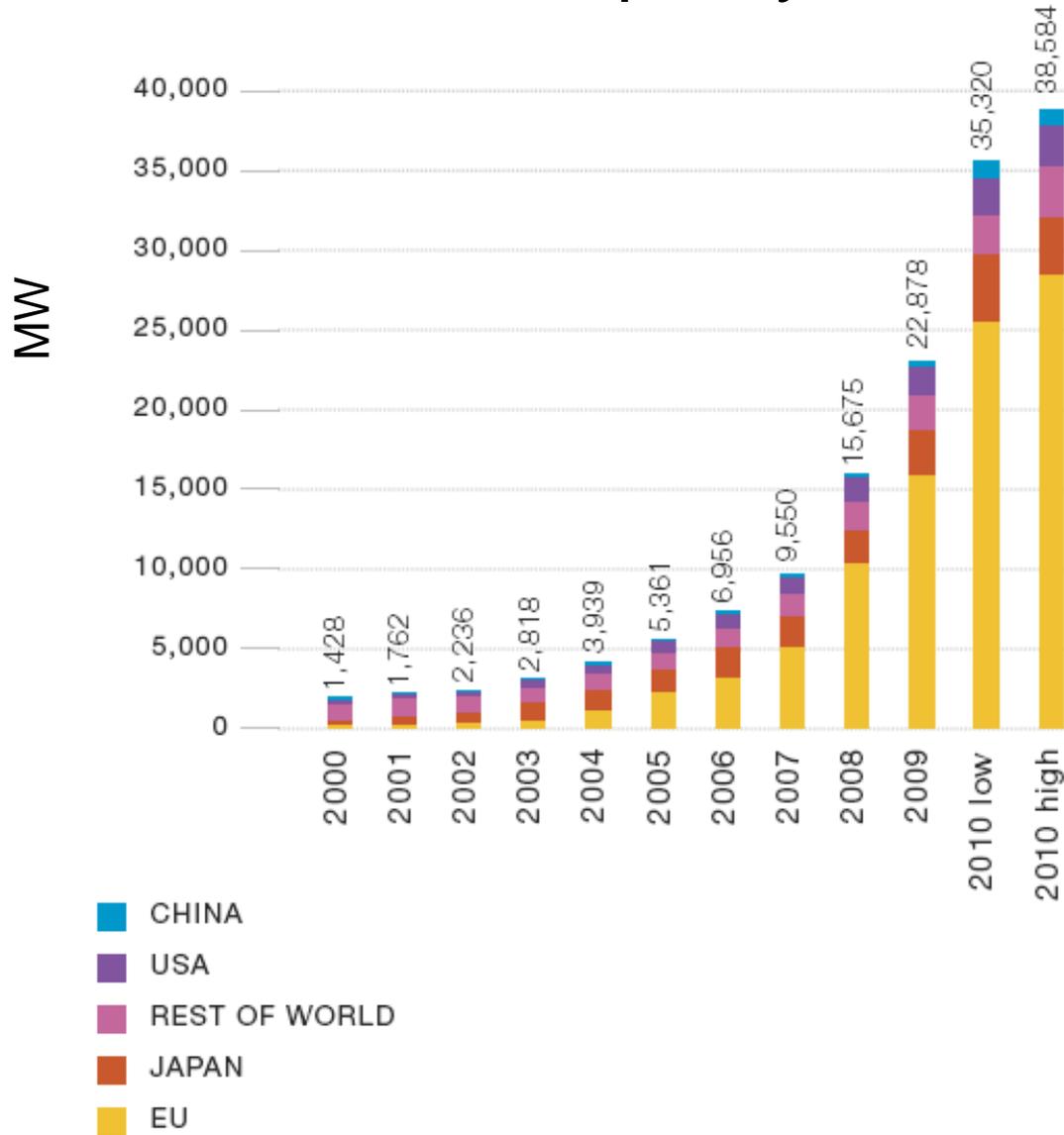
7,361 PJ



Fuente: SENER (2010), Balance Nacional de Energía 2009.

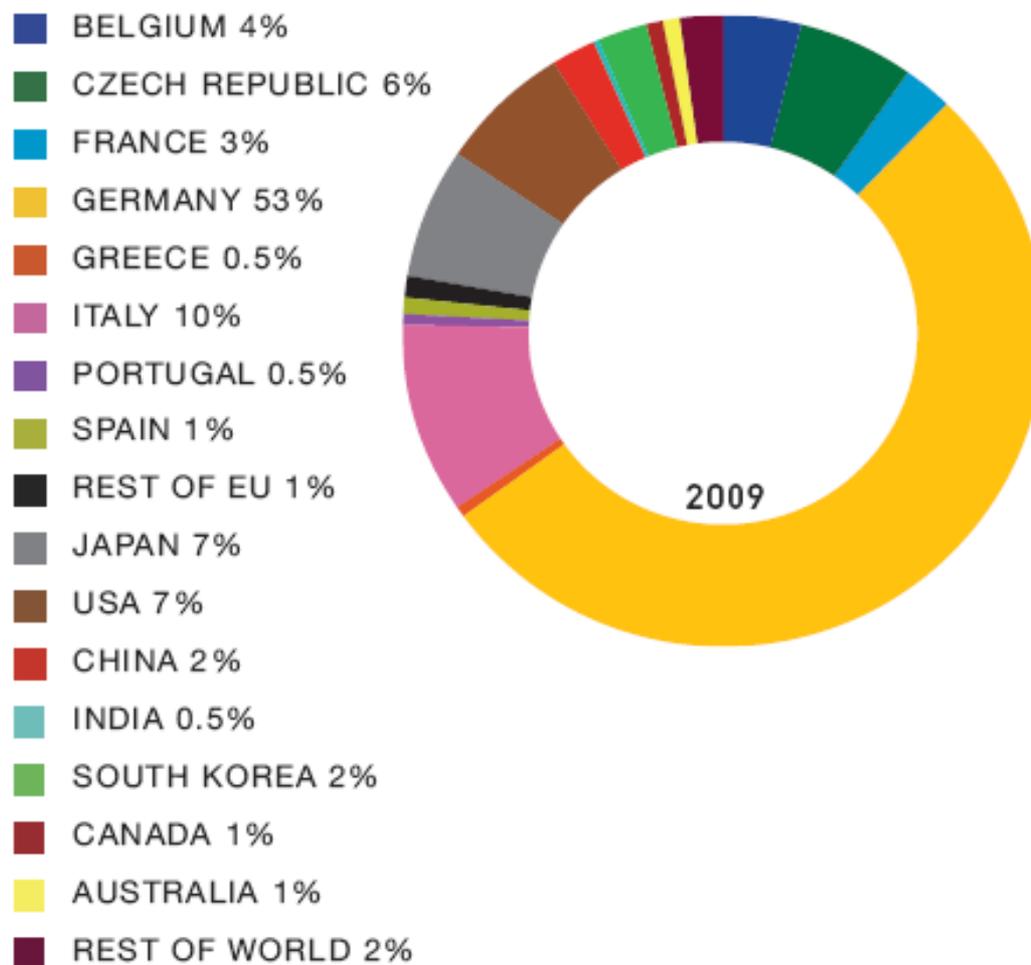
Courtesy- Genice Grande, CIE

PV installed capacity-Global



source: Global Market Outlook for Photovoltaics until 2014, EPIA, May 2010.

THE WORLD PV MARKET IN 2009



source: EPIA.

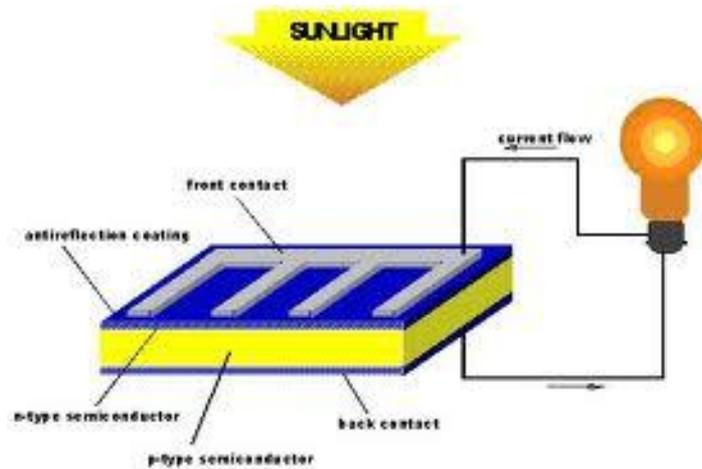
World PV Production 2009

World PV Production in 2009 by technologies

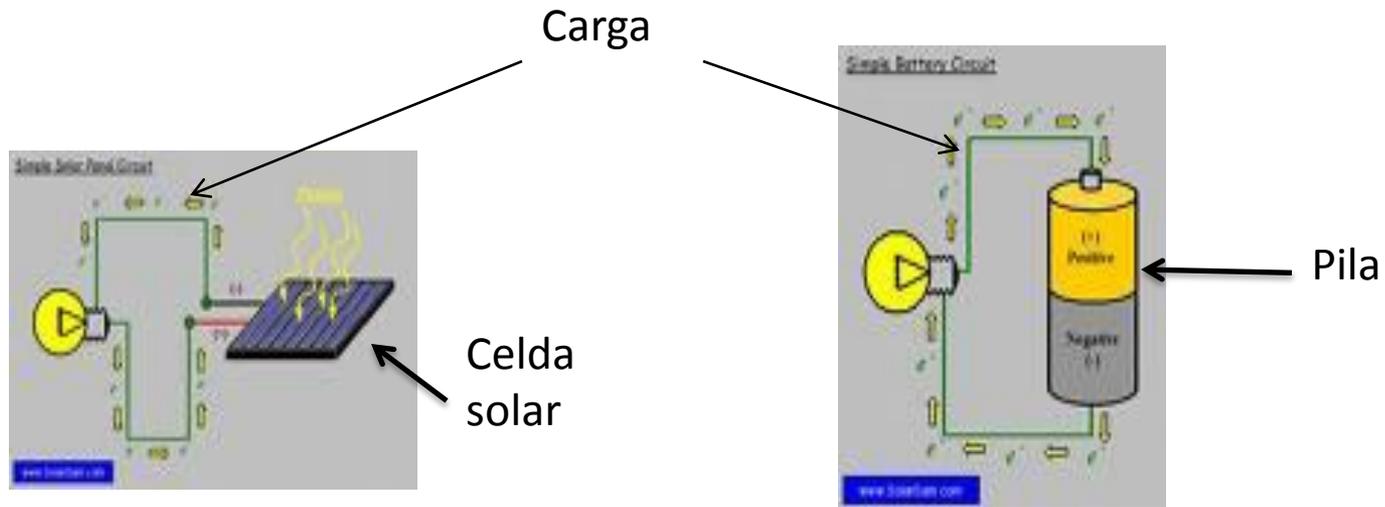
- c-Si: 8.678 GW 81%
- a-Si:H: 796 MW 7%
- CdTe: 1.019 GW 10% (2010 data >1.5GW)
- CIGS: 166 MW

Courtesy: N.G. Dhere, FSEC, Florida

Solar cells-basics

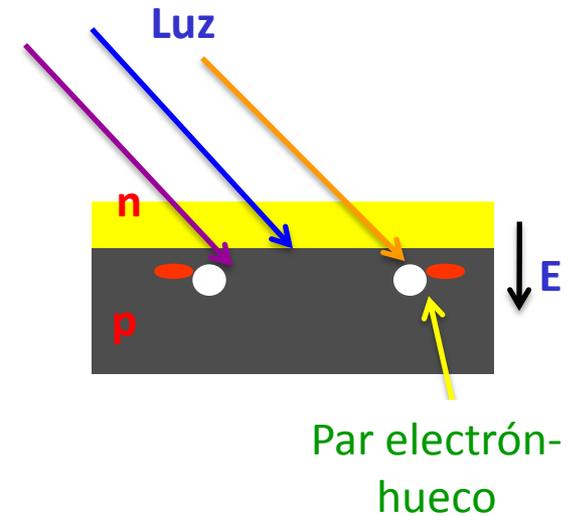
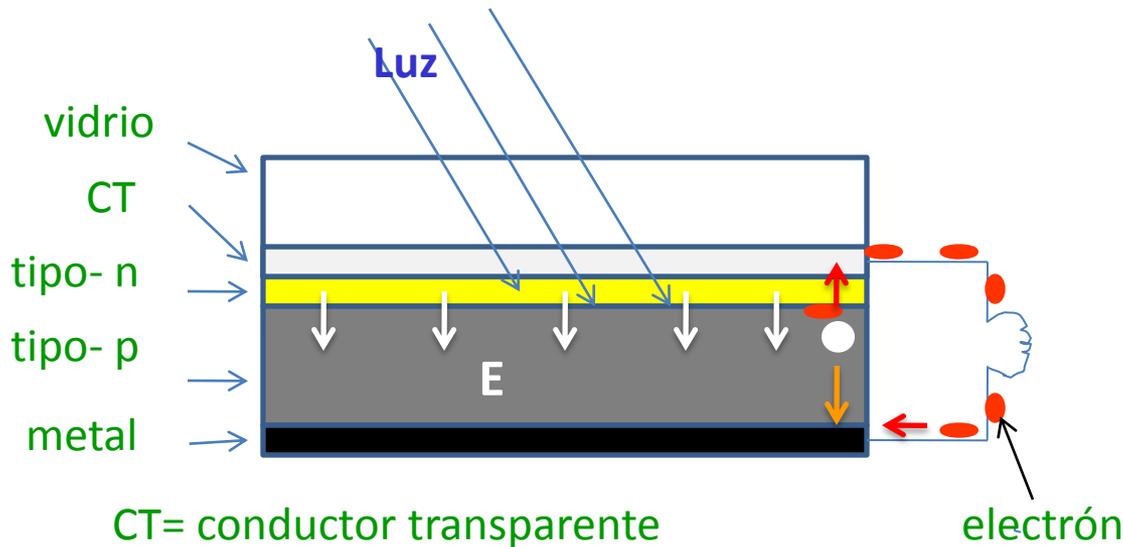


¿Qué son las celdas solares?

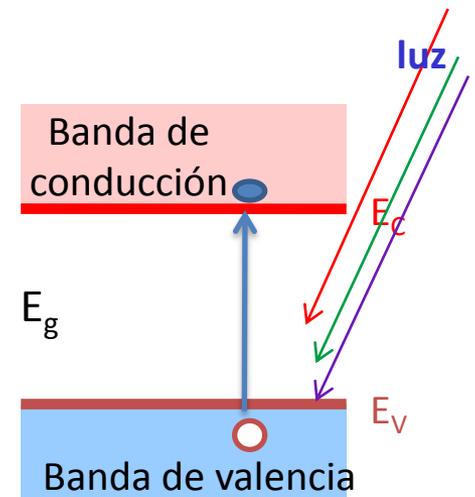


La celda solar es un pila que trabaja con el SOL

Esquema de una celda solar

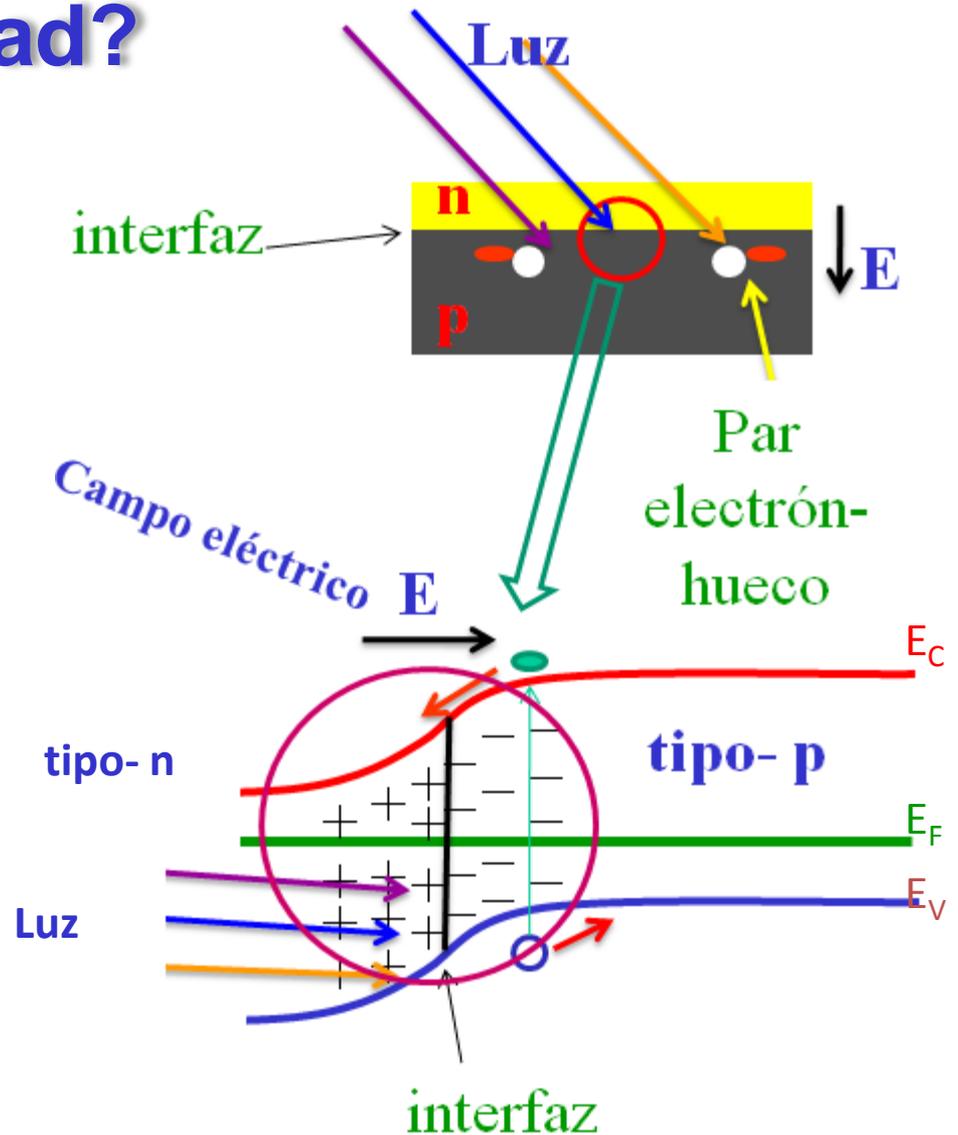


Los electrón-hueco pares generados en el campo eléctrico del unión p-n va mover en direcciones opuestas. Así creando una corriente.



¿Como una celda solar produce la electricidad?

Los par electrón-huecos son separado por campo eléctrico existe en el interfaz, y permitiendo un flujo de electrones en el circuito externo



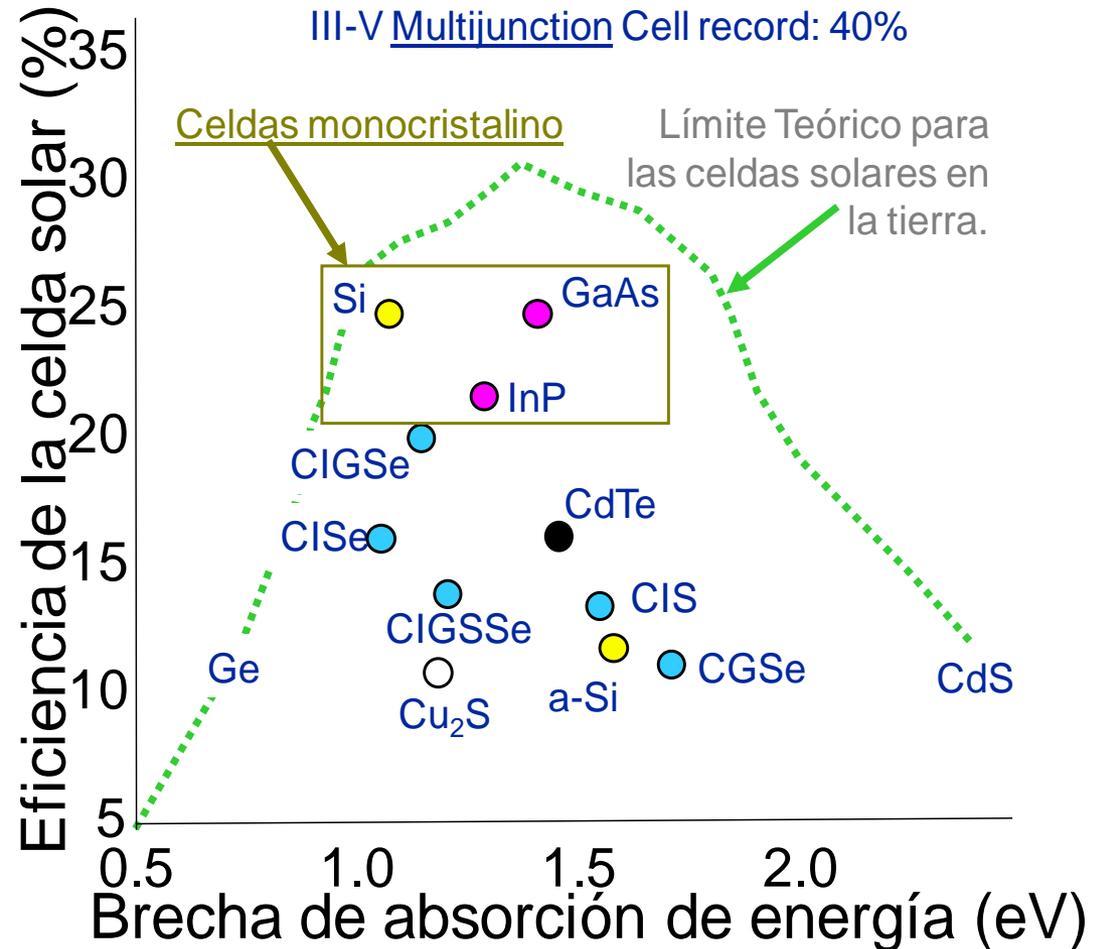
Eficiencia teórico vs. actual

Celdas solares de unión simple

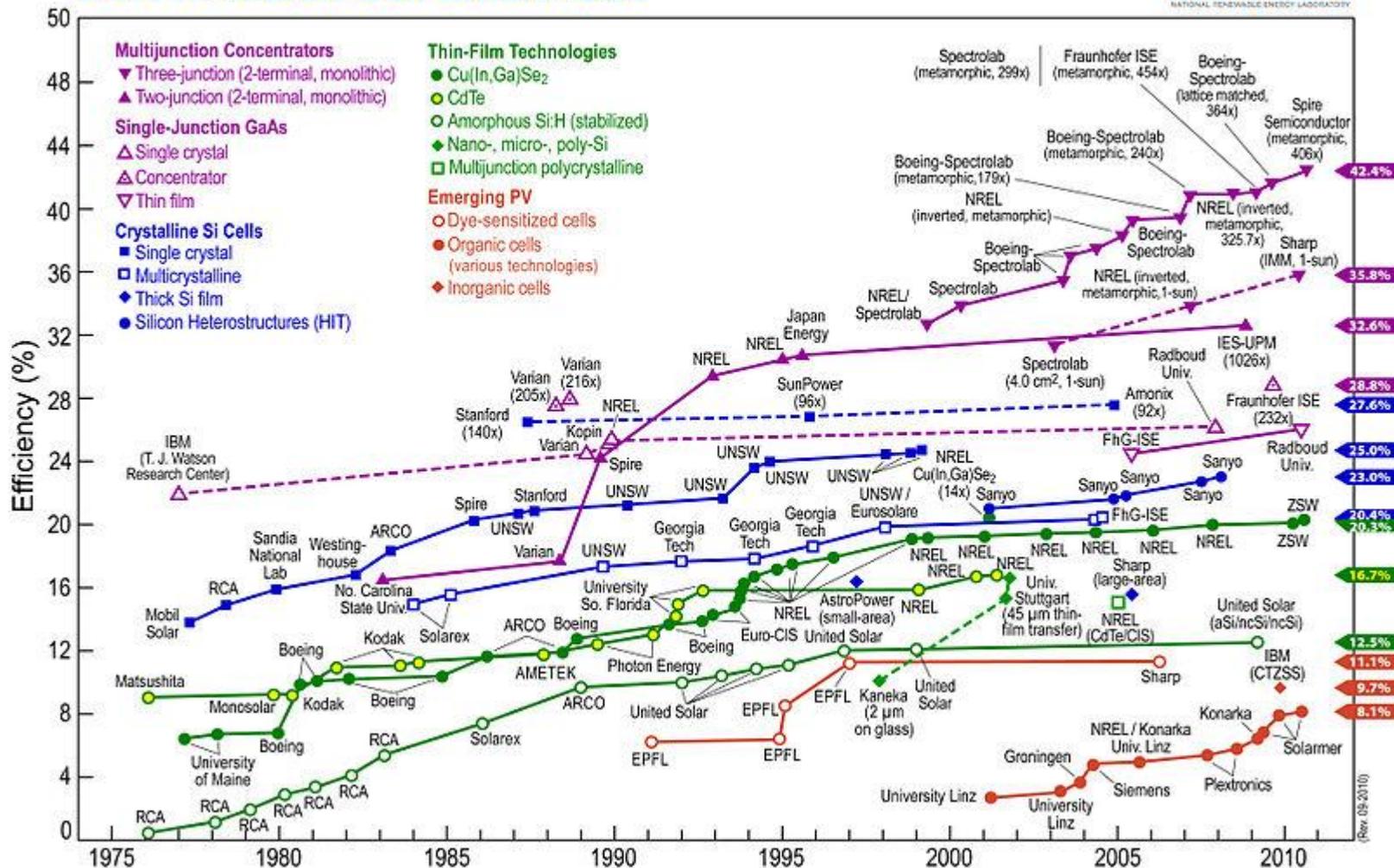
- Si-Silicio
- Compuestos del III-V
- Calcogenuros -CuIn

El Si y el GaAs están cerca de su límite teórico.

Courtesy- Angus Rockett, uiuc



Best Research-Cell Efficiencies



(Rev. 09-2010)



CdTe perspectives

Three Thin-Film PV Technologies & its Strengths

	Demonstrated Efficiency	Production Advantage	Materials Abundance/ Low Toxicity
a-Si			Strength
CdTe		Strength	
CIGS	Strength		

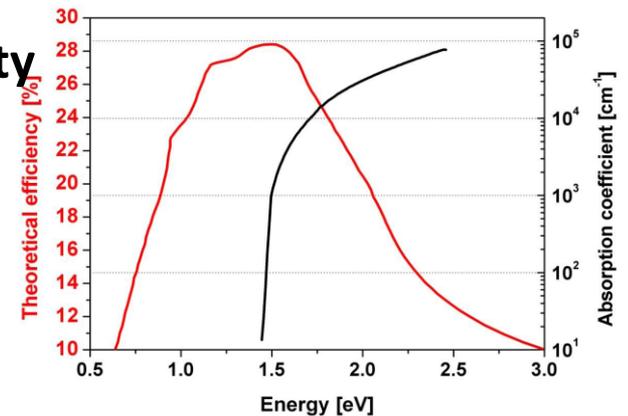
Each technology has different advantages.

Its not clear which (if any) advantage will yield a long-term product advantage.

Courtesy: Miguel Contreras, NREL

Some benefits of CdTe

- High α ; 1 μ CdTe absorbs >92% of the photons with $h\nu > E_g$
- Less than 2% of the equivalent semiconductor Si is required
- 1.45eV close to the ideal band gap for high efficiency
- A stable binary compound which can be deposited by more than 5 large volume manufacturing methods
- Simple manufacturing procedures-high reproducibility
- A low-temperature coefficient making it tolerable to higher module temp.



Estado actual

- Eficiencia record
16.5% (NREL)
- Tecnología
comercializado



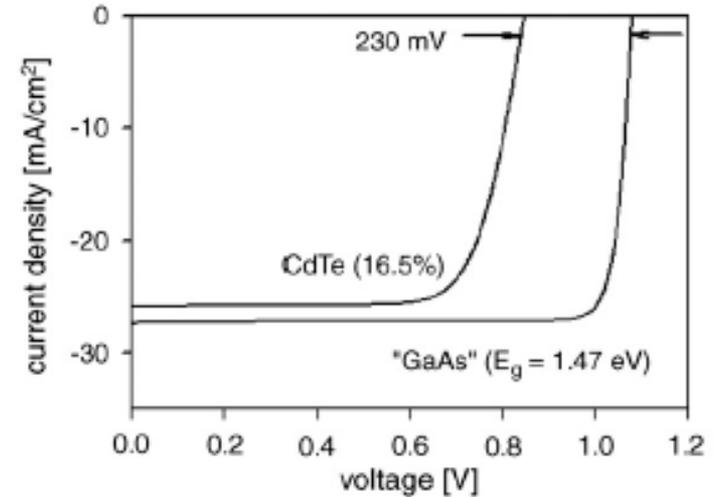
How well CdTe will do ?

-an ambitious and challenging prediction

If the CdTe voltage deficit is reduced with the same current and fill-factor, CdTe cells would achieve more than 20% efficiency.

Reason for the low voltage of CdTe cells is a combination of low carrier density ($\sim 10^{14} \text{ cm}^{-3}$) and low absorber lifetime (generally below 1 ns).

With 10^{17} cm^{-3} carrier density, efficiency can be 22%

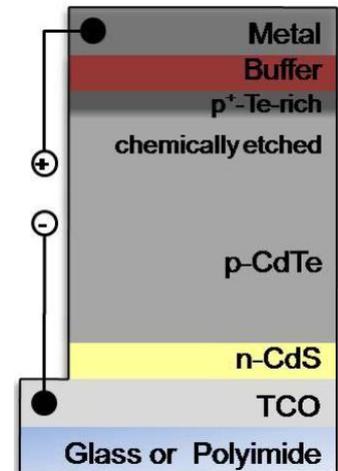


Comparison of record CdTe cell with GaAs adjusted for band gap.

James Sites et al. (Colorado State Uni.)
Thin Solid Films 515 (2007) 6099–6102

Challenges

- Reduce self-compensation effect of CdTe to **increase acceptor concentration**
- **Reduce CdTe layer thickness** to increase raw material yield
- Formation of low resistive and stable **back contact**
- Reducing CdS thickness to **increase blue response**



Some CdTe PV Companies

First Solar, OH	1.4 GW in 2010
Abound Solar, CO	200 mW by 2011
Antec Solar, Germany	
Solar Fields, OH/Calyxo (Germany)	
Primestar Solar, CO	
WK (Willard & Kelsey) Solar Group, OH	
CANRON, NY (and Canada)	
Solexant, CA	
Arendi, Italy	
Advanced Solar Power, China	
Xunlight26. OH	
Wakonda, MA	

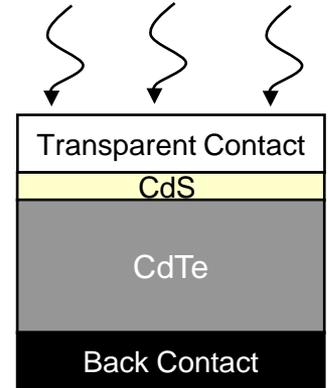
Courtesy- Miguel Contreras, NREL

R & D activities at CIE-UNAM

Programa de CdTe en CIE

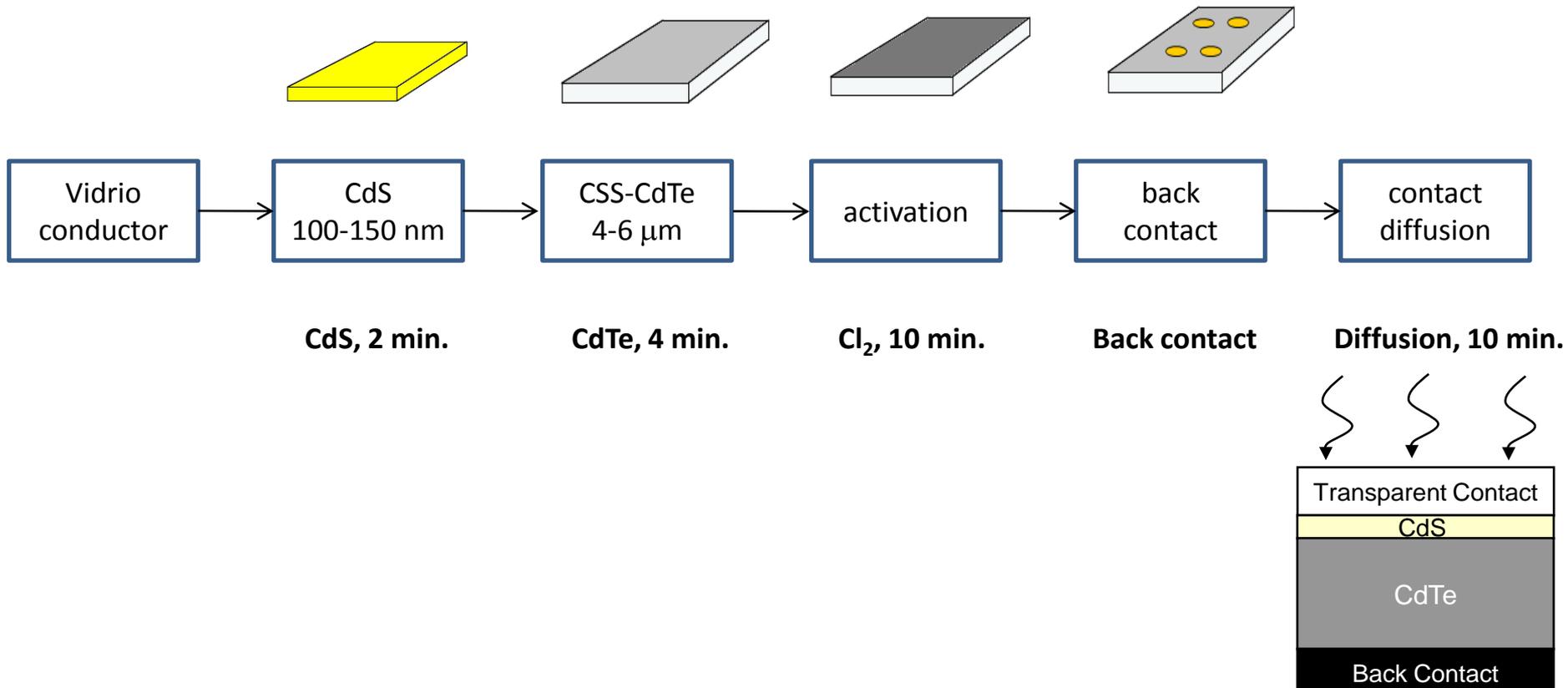
Metas:-

- Desarrollar celdas de alta eficiencia
- Desarrollar tecnologías de sistemas
- Desarrollar nuevas materiales
- Innovación y transferencia de tecnología
- Mayor Academia-industria relación y Promover una industria PV nacional



Programa de CdTe en CIE- Device fabrication steps

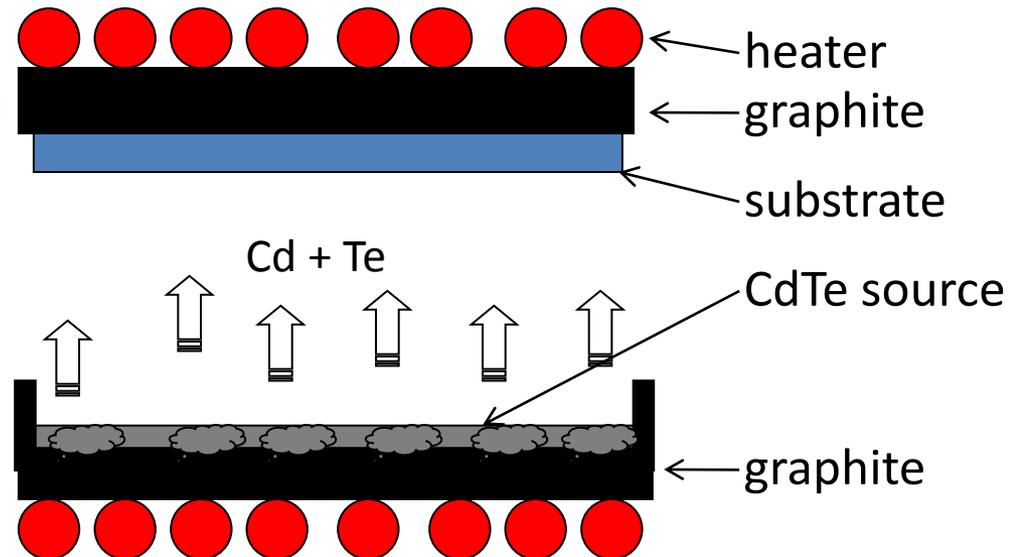
All-CSS process: CdS, CdTe, CdCl₂



CSS process

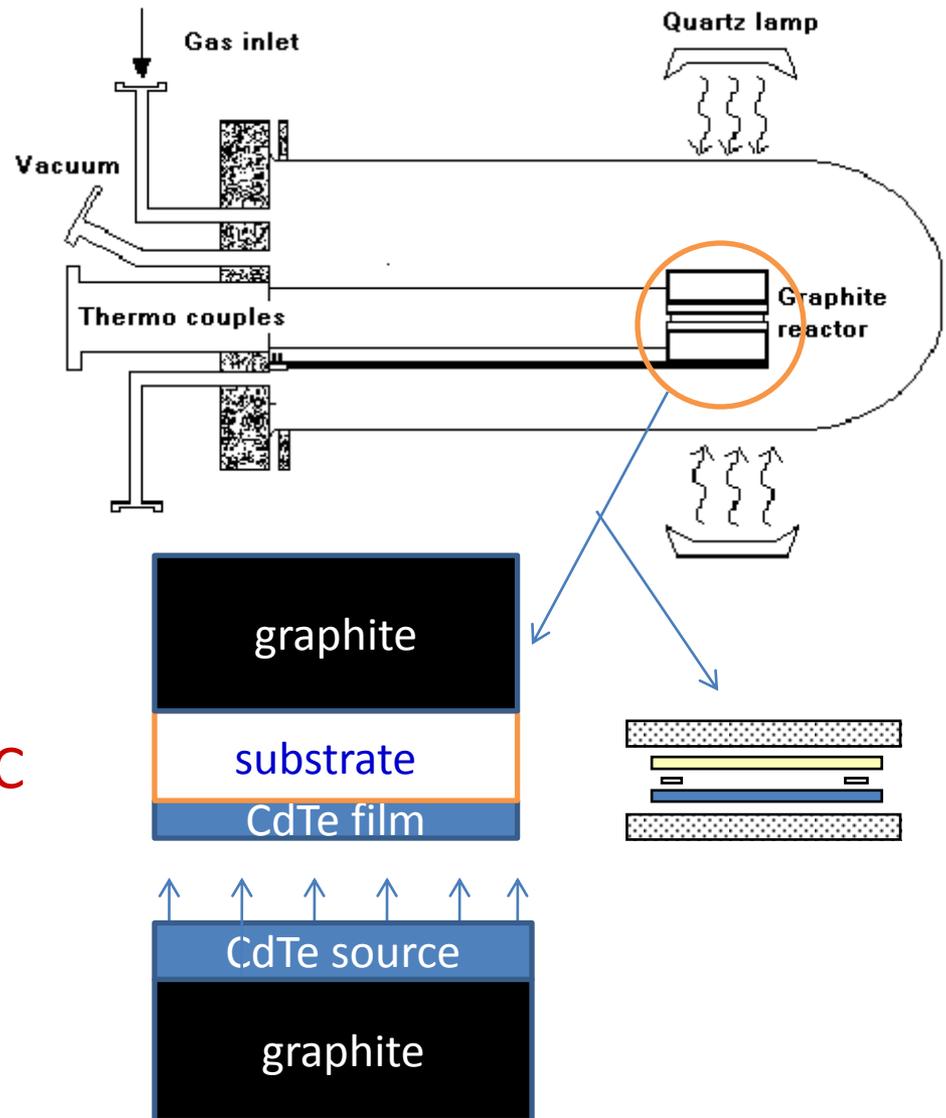
Sublimation- transforms directly from solid to vapor phase

- Escalable
- Alta tasa de deposito; 1-2 $\mu\text{m/s}$
- Less defect densities (near-thermal equilibrium process)
- Mayor eficiencia
- Low vacuum requirements
- Less maintenance
- All-CSS: CdS, CdTe, CdCl₂
- Easy integration in a production line



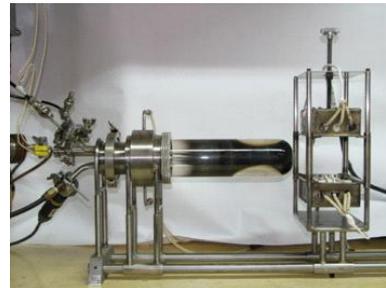
Laboratory scale CSS system

- Ambient: Ar (He)/O₂
- Pressure: 1-20 mbar
- Temp. of source: 600- 700 °C
- Temp. of substrate: 500 - 650 °C



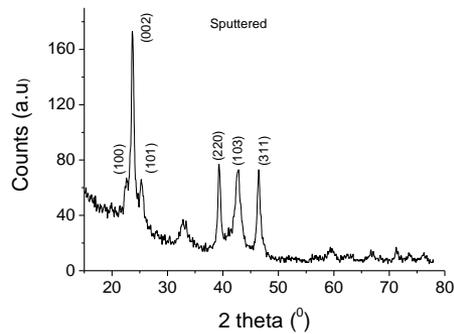
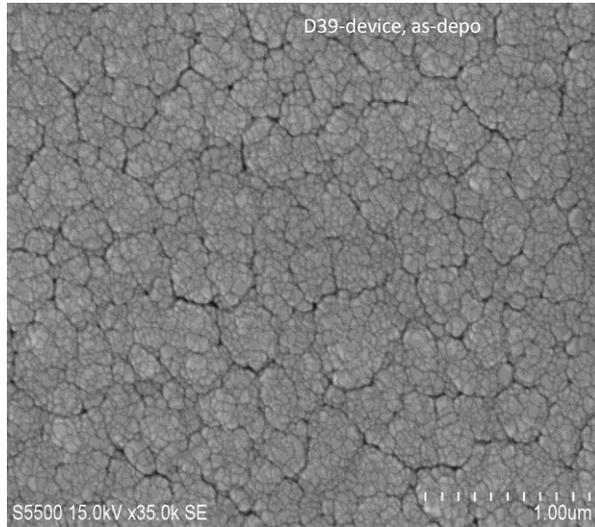
Thin Film processing capabilities

- **CSS**; CdTe & CdS
- **Sputtering**; CdTe & CdS
- **Co-evaporation**; Semiconductor alloys



Sputtered vs. CSS CdTe films: recrystallization

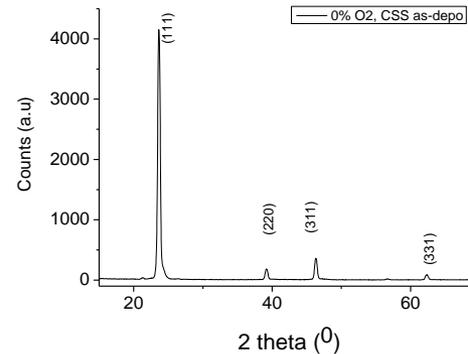
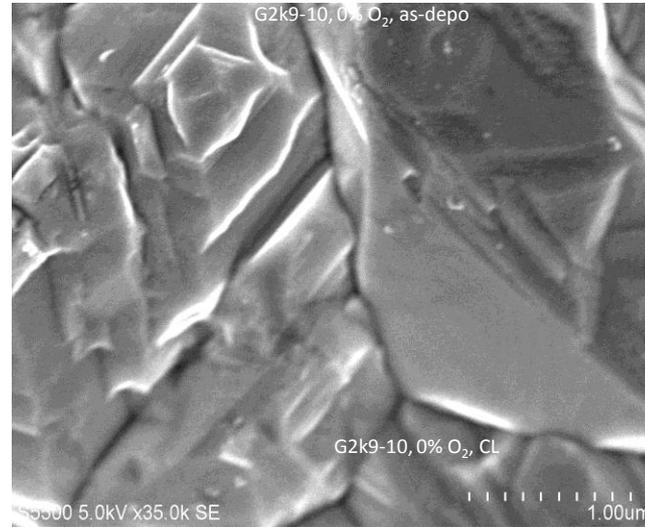
Sputtered



Film deposition @ $\approx 0.03 \mu\text{m}/\text{min}$

Process temp. 250 °C

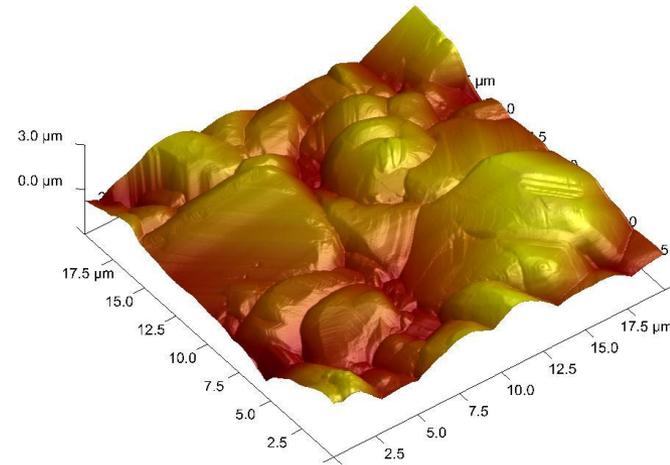
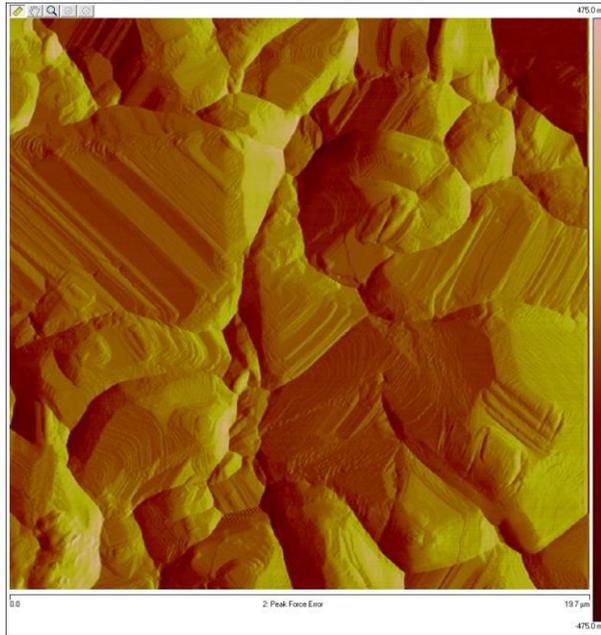
CSS deposited



Film deposition @ $\approx 1 \mu\text{m}/\text{min}$

Process temp. 600 °C

AFM topography of CSS CdTe film

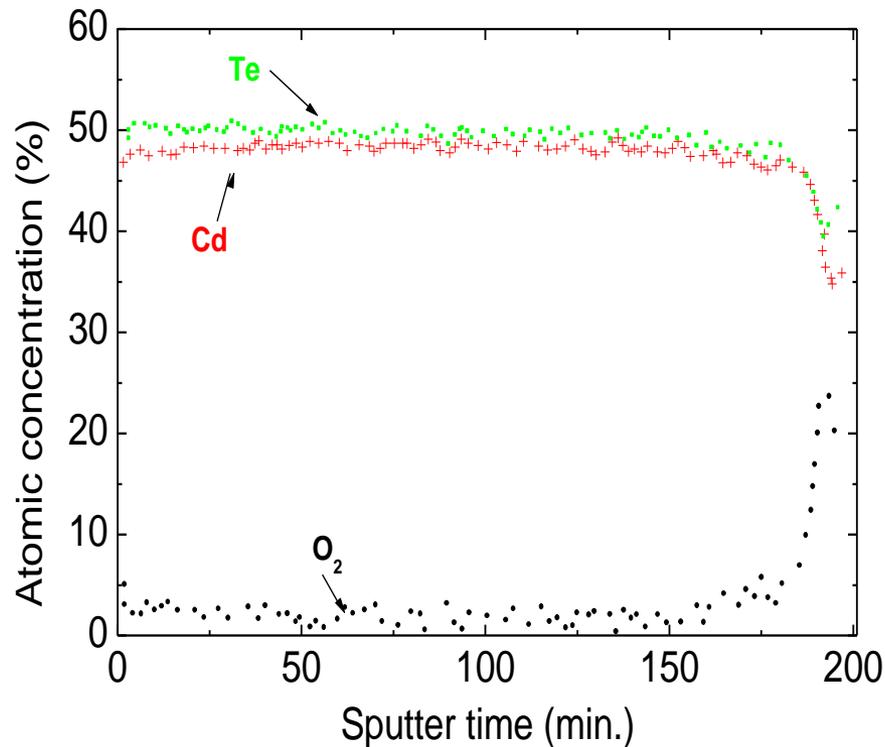


- Void-free (?) grain boundaries
- Large clusters of grains

AUGER depth profile

CSS- CdTe, on Mo substrate

He/O₂ = 80/50



- Rich in Te, typical of p-type
- Constant stoichiometry throughout the thickness
- Oxygen incorporated during CSS process

CdTe/CdS devices

parameters that can affect your device

-Glass cleaning

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-Process temperature

-Ramping

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-Process gas

-Pressure

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-CdS layer

-CdTe formation conditions- role of O₂

-Junction activation

-Amount of Cl

-Duration

-Back contacts

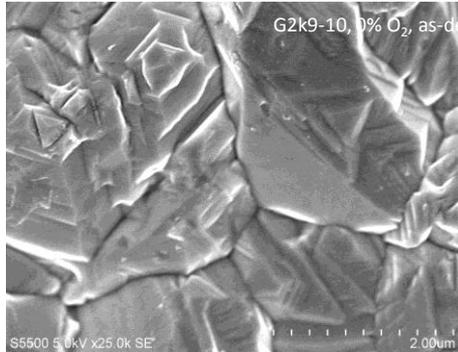
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- AR coating

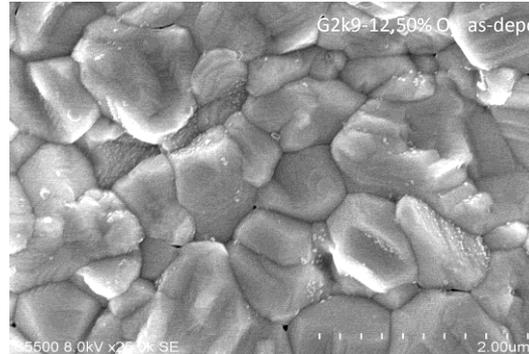
(i) Influence of O₂ in CSS chamber

As-deposited films

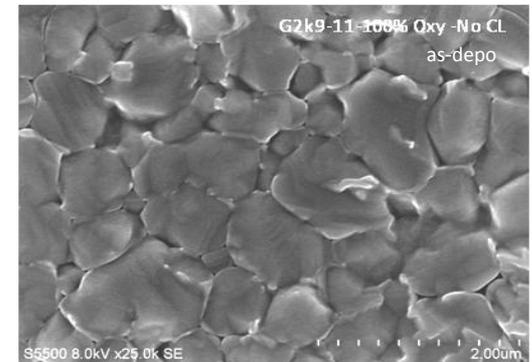
O₂ = 0%



O₂ = 50%



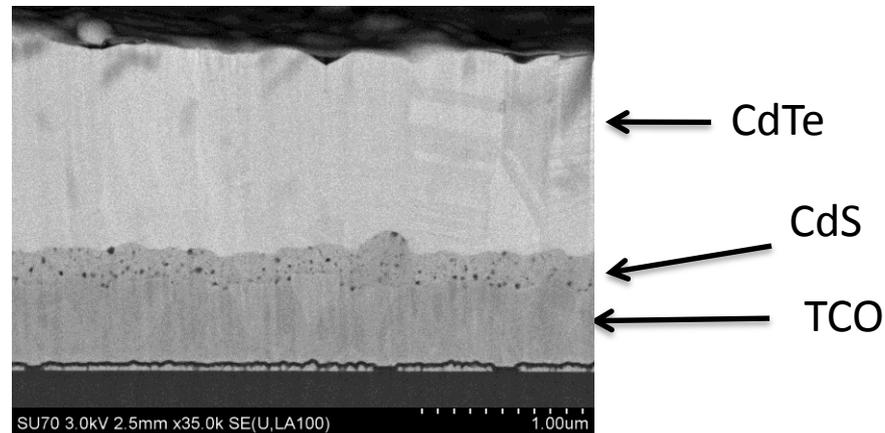
O₂ = 100%



Grain size → ≈ 2 μm

≈ 0.85 μm

≈ 0.88 μm

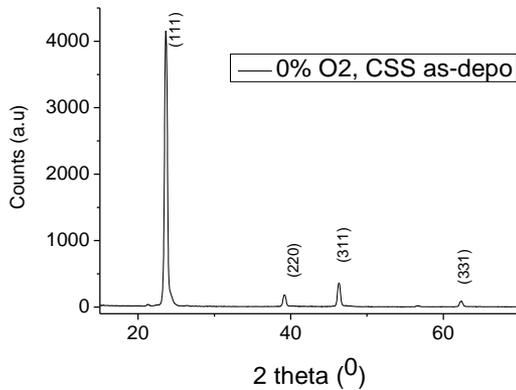


The CdTe nucleation sites increases with O₂, resulting in lower growth rate, small grains, and more compact film.

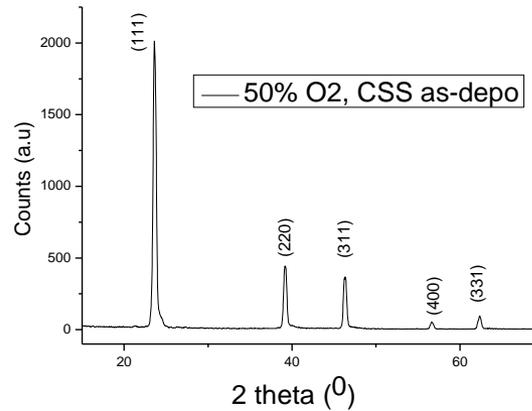
Influence of O₂ in CSS chamber

As-deposited films

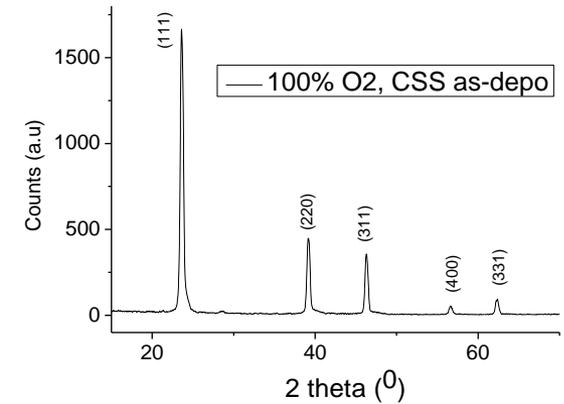
O₂ = 0%



O₂ = 50%



O₂ = 100%



In O₂ environment, films grow with less preference for a direction

Junction:- O₂ in CSS chamber & “S”, “Te” diffusion

Some known facts:

- Grain boundary diffusion can be retarded by oxygen annealing
- Interdiffusion depends on O₂ level in the CdS film, in low O₂ films “S” diffusion is significant, leading to thinning of CdS film.
- When CdS is annealed in O₂, both “S” and “Te” diffusion is controlled
- Consumption of CdS lead to TCO/CdTe junction
- CBD CdS film has less thinning compared to CSS and sputtered films: CBD film has more O₂, received from the bath
- CBD CdS devices has superior performance than non-CBD CdS film devices

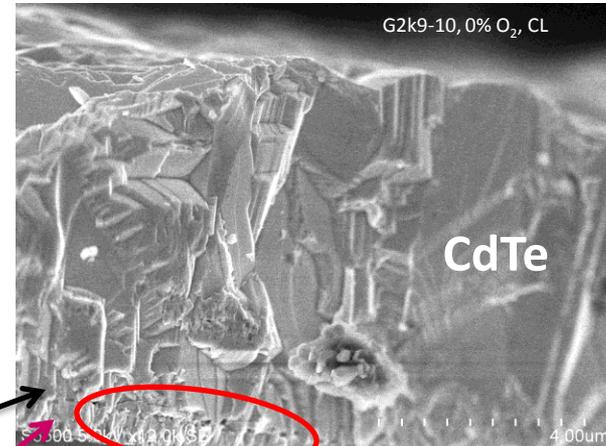
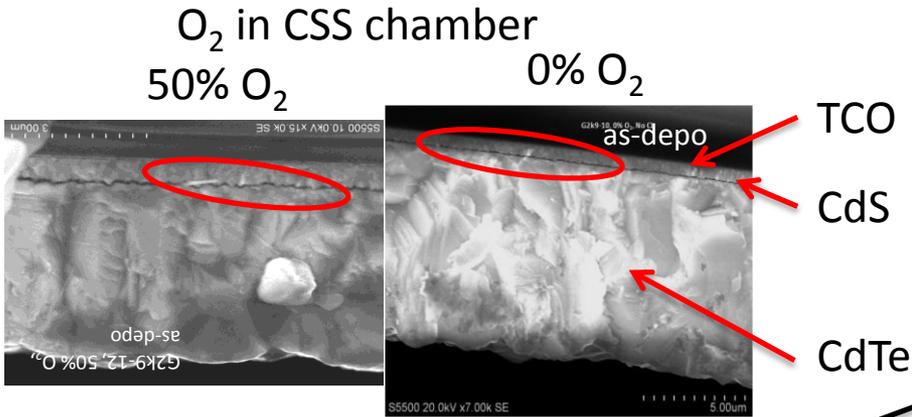
[1] D. S. Albin, et al.; Prog. Photo:Research & Appl. 10 (2002) 309

[2] D. S. Albin, et al.; AIP Conf Proc. 394 (1996) 665

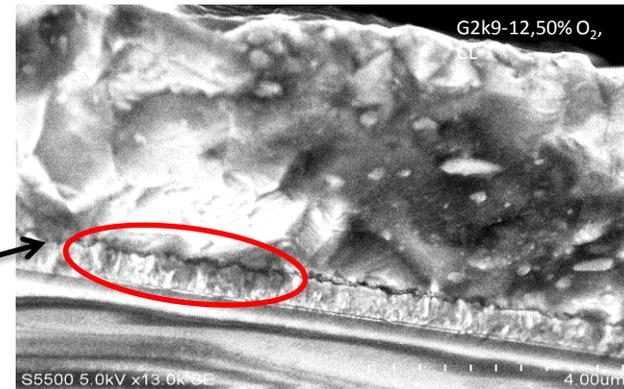
O₂ in CSS chamber & CdS consumption

Tec 7/CdS/CdTe

CdCl₂ @390 C, CdTe in 0% O₂



CdCl₂ @390 C, CdTe in 50% O₂



CdS consumed in 0% O₂ case, consumption is not uniform, lateral non-uniformities at the interface.

However CdS almost retained in 50% O₂ case.

CBD-CdS, no pre-treatments for the CdS film. O₂ level mentioned corresponds to CdTe deposition

Junction- O₂ annealing of CdS and interface diffusion

Short & long wavelength QE

Short λ :

-shallow CdS absorption edge for both, significant for as-deposited case
-less response at 580-650 nm for as-depo. case

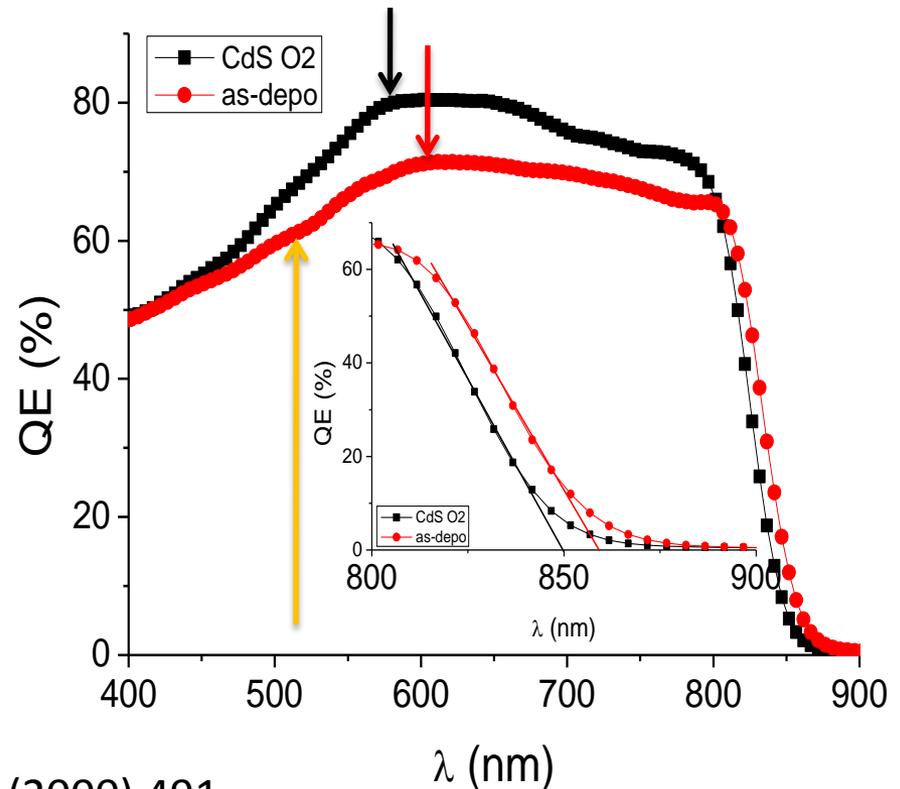
Evidence of Te diffusion, lowering E_g ;
CdS_{1-x}Te_x

Long λ :

-Shift in absorption edge for as-depo. case

Evidence of "S" diffusion to CdTe,
lowering E_g ; CdTe_{1-y}S_y

CdS film annealed in O₂ at 450 C for 45 min
CSS CdTe @ 600 C, He/O₂ = 2/8

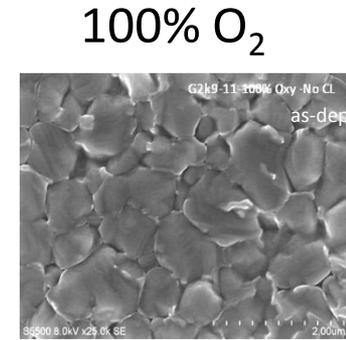
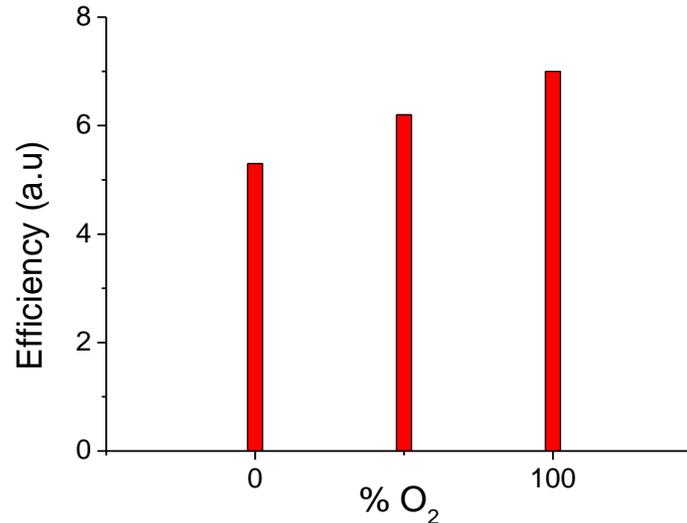
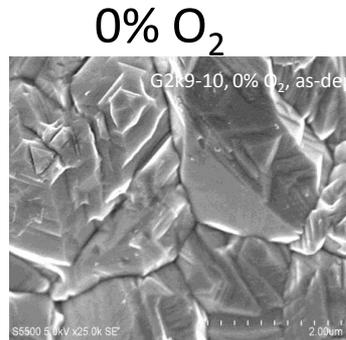


[1] X. Wu, Solar Energy 77 (2004) 803

[2] B.E. McCandless, et al.; Proc. 28th IEEE PVSC (2000) 491

Efficiency vs. O₂ in CSS chamber

→ Tec 7/CBD-CdS/CSS-CdTe/(Cu-Au); CdS: 100-120 nm, CdTe: ≈ 5μm, (Cu-Au): ≈ (3-30)nm



On an average 20 % increase in efficiency

- Passivation of CdTe grain boundaries (trade off with grain size)
- Increased carrier concentration
- Reduced resistivity
- Minimum interdiffusion, CdS/CdTe heterojunction

More or less same difference observed in the case of CdS annealed in O₂ prior to CdTe deposition

(ii) Junction activation

Most crucial step in device fabrication: -vapor chloride treatment at temperatures in the range 400 °C

-Increased p-type doping due to formation of an acceptor complex ($\text{Cl}^- + \text{V}_{\text{cd}}$)

* high voltage

-Low series resistance

* high current

-Modification of band gap states

* compensation

-Recrystallization leading to grain growth and modification of grain boundaries

* reduced shunting

-Spatial junction uniformity and alloying

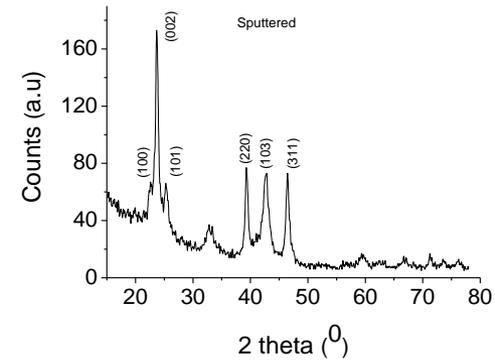
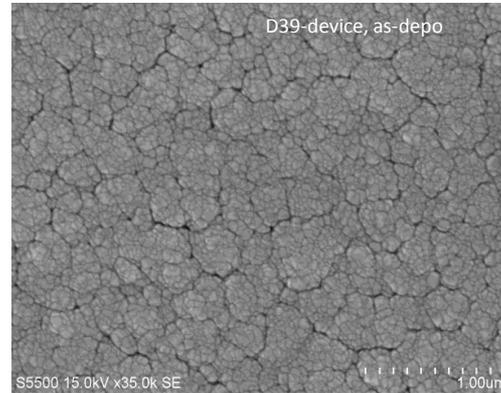
* High yield

-Excess Cl can form compensating donors (Cl_{Te}), damaging the cell

Sputtered-CdTe: effect of chloride treatments

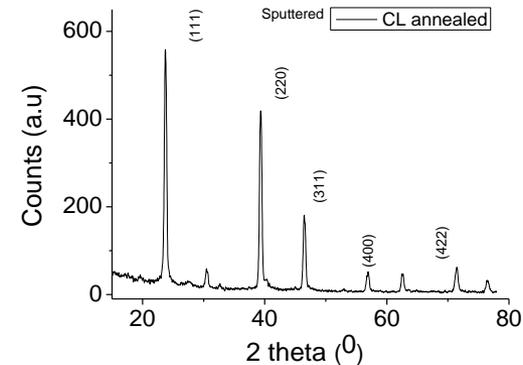
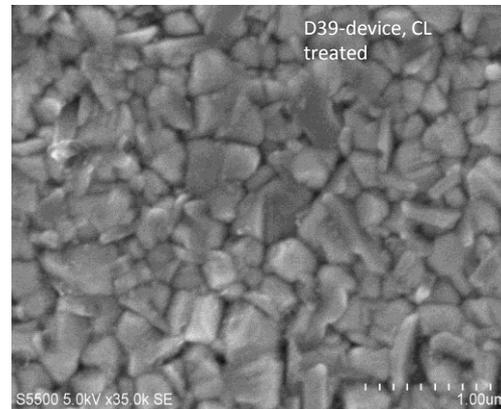
Grains- 50 nm

As-deposited



Grains- 200 nm

Chloride annealed

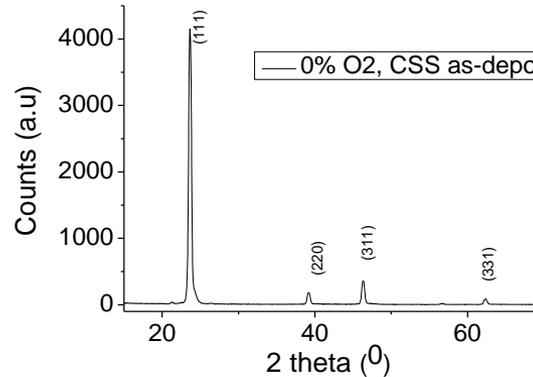
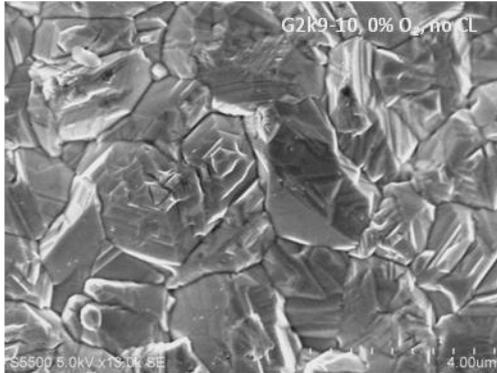


Process temp. 200-250 $^{\circ}$ C

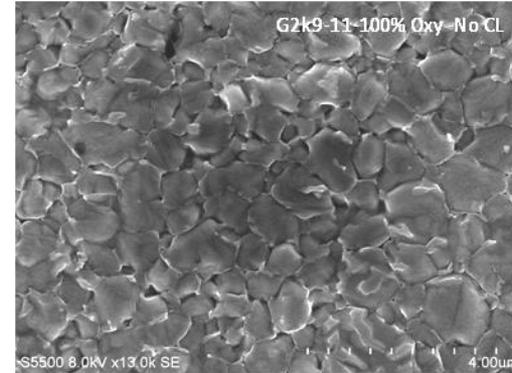
- Recrystallization evident
- Grain growth significant

CSS-CdTe: effect of chloride treatments

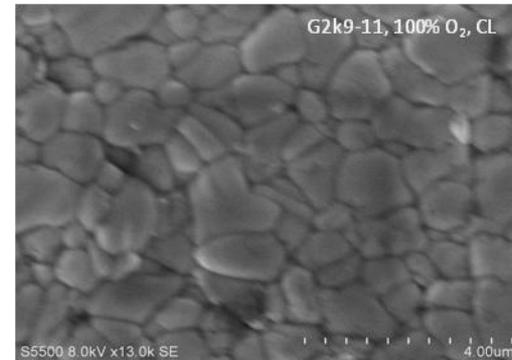
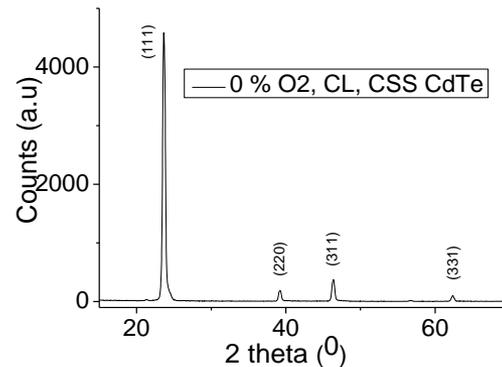
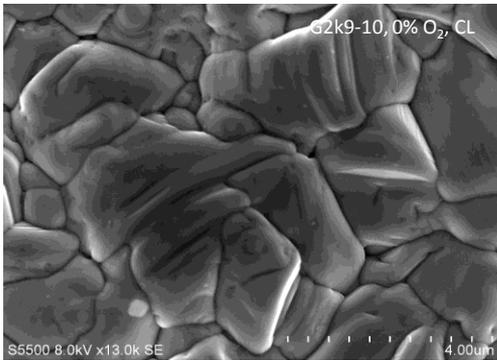
$O_2 = 0\%$



$O_2 = 100\%$



as-deposited



vapor chloride annealed

$$N_A = 3.5 \times 10^{13} \text{ cm}^{-3}$$

$$N_A = 1.9 \times 10^{14} \text{ cm}^{-3}$$

Recrystallization happens in all cases; Grain size remains more or less same

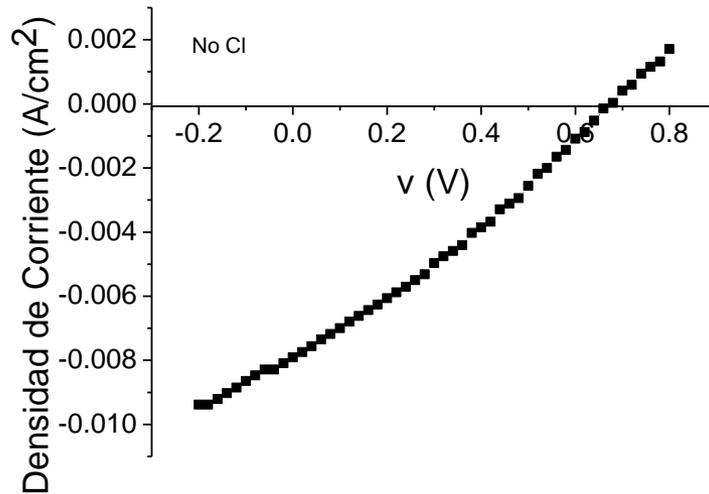
Chloride annealing do not reverse the O_2 effect:

For films deposited at higher temp, the surface energy is already minimum, hence no secondary recrystallization. Same can happen with the presence of native oxides *

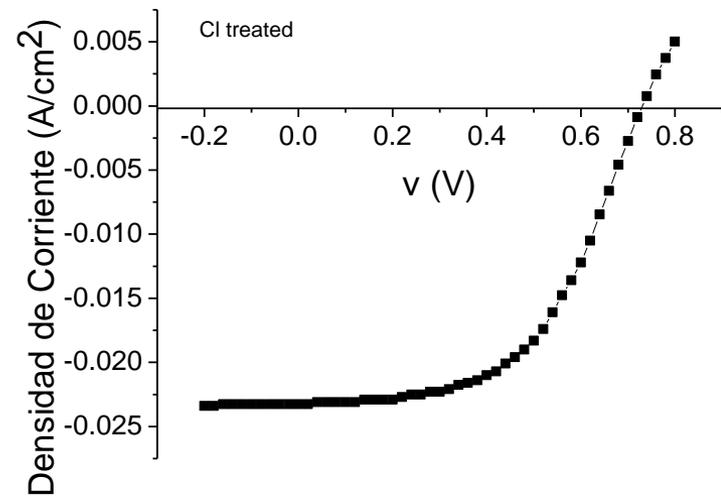
* B. E. McCandles & J.R. Sites; "Cadmium Telluride Solar Cells", Handbook of Photovoltaic Science & Engineering, John Wiley & Sons, 2003

Chloride treatments- effect on device performance

Device **without** Cl treatment



Device **with** Cl treatment

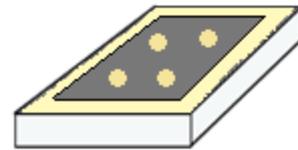
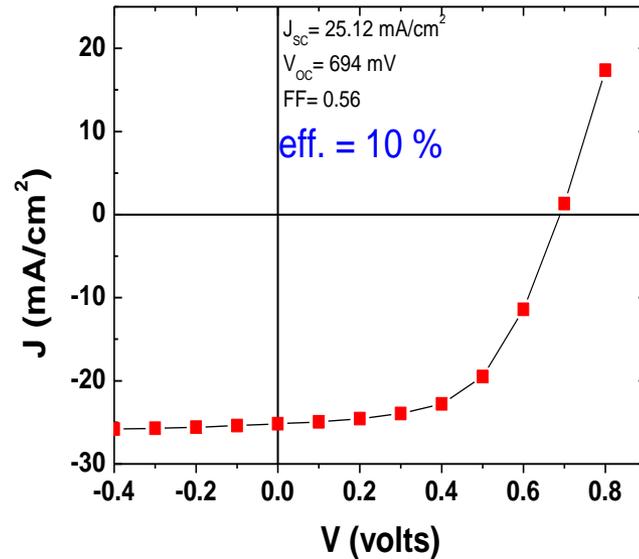


- Higher FF
- Higher J_{sc}

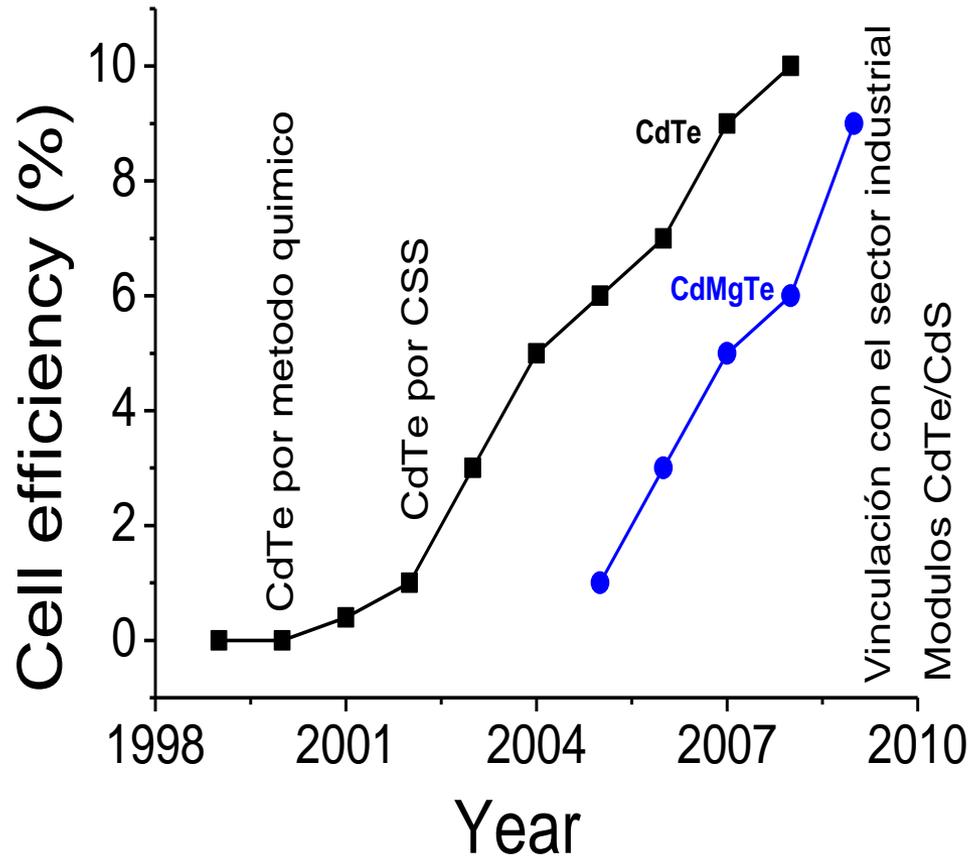
Small area CdTe/CdS cell

Tec 7/CBD-CdS/CSS-CdTe/(Cu-Au)

- No HRT
- No CdTe etching, contact applied directly
- No antireflection coating
- Tec 7 substrate, low transmittance



Our Antecedentes in CdTe Technology



CdTe toxicity issues

How much cadmium (Cd) is encapsulated in CdTe modules?

- CdTe layer contains 3 to 9 g/m²
- CdS contains less than 1 g/m²

Both elemental materials (Cd & Te) are produced as byproducts of mining processes (primarily zinc mining and copper refining) and **present in quantities to support multi-GWs of annual production**

<http://www.nrel.gov/pv/cdte>

- Anderson, B. A. (2000). "Materials availability for large-scale thin film photovoltaics." *Progress in Photovoltaics*, 8, pp. 61-76.
- Zweibel, K. (1999). "Issues in thin film PV manufacturing cost reduction." *Solar Energy Materials and Solar Cells*, 59, pp. 1-18.

Does CdTe pose health risk ?

- CdTe is more stable and less soluble than elemental Cd and therefore is likely to be much less toxic.
- The vapor pressure of CdTe at ambient conditions is zero. therefore, it is impossible for vapors or dust to be generated when using PV modules.
- Exposure of pieces of CdTe PV modules to flame temperatures from 760 to 1100°C illustrated that CdTe diffuses into glass, rather than being released into the atmosphere.

<http://www.nrel.gov/pv/cdte>

<http://www.firstsolar.com/en/CdTe.php>

Does CdTe pose health risk ?-

Reports from Europe

"During standard operation of CdTe PV systems, there are no cadmium emissions - to air, to water, or to soil..... Accordingly, large-scale deployment of CdTe PV can be considered safe to human health and the environment." **French Ministry of Ecology, Energy, Sustainable Development and the Sea. It concluded that, 2009**

"....CdTe used in PV is in an environmental stable form that does not leak into the environment during normal use or foreseeable accidents...."; **Joint Research Center and moderated by the German Environment Ministry**

<http://www.firstsolar.com/en/CdTe.php>

Does CdTe pose health risk?

- The trace amounts of cadmium in a thin-film PV module do not approach toxic levels.
- A rechargeable nickel cadmium battery contains about 2,500 times more cadmium per kilowatt-hour than does a CdTe module.
- The cadmium found in PV modules is inert and sealed better than the cadmium found in NiCd batteries.

<http://www.nrel.gov/pv/cdte>

What are the sources of Cd exposure to humans?

Sources and Relative Contributions of Cd exposure to Humans (data from Europe)	
Phosphate fertilizers	41.3 %
Fossil fuel combustion	22.0 %
Iron and steel production	16.7 %
Natural sources	8.0 %
Non-ferrous metals	6.3 %
Cement production	2.5 %
Cadmium products	2.5 %
Incineration	1.0 %

Environmental Resources Limited (ERL), (February 1990). Evaluation of the **Sources of Human and Environmental Contamination by Cadmium**. Prepared for the Commission of the European Community, Directorate General for Environment, Consumer Protection and Nuclear Safety, London.

“Escalamiento de celdas solares de CdTe” – proyecto SENER

Aprobado:- octubre 2009

Firma de Convenio:- Febrero 2011

Periodo de proyecto:- 2011-2013

“Escalamiento de celdas solares de CdTe”

Objetivo del proyecto:

Optimización de varios procesamientos involucrados en el desarrollo de heteroestructuras **fotovoltaicas de CdTe/CdS** para alcanzar uniformidad de las películas y una eficiencia arriba de 8% **en área mayor que 100 cm².**

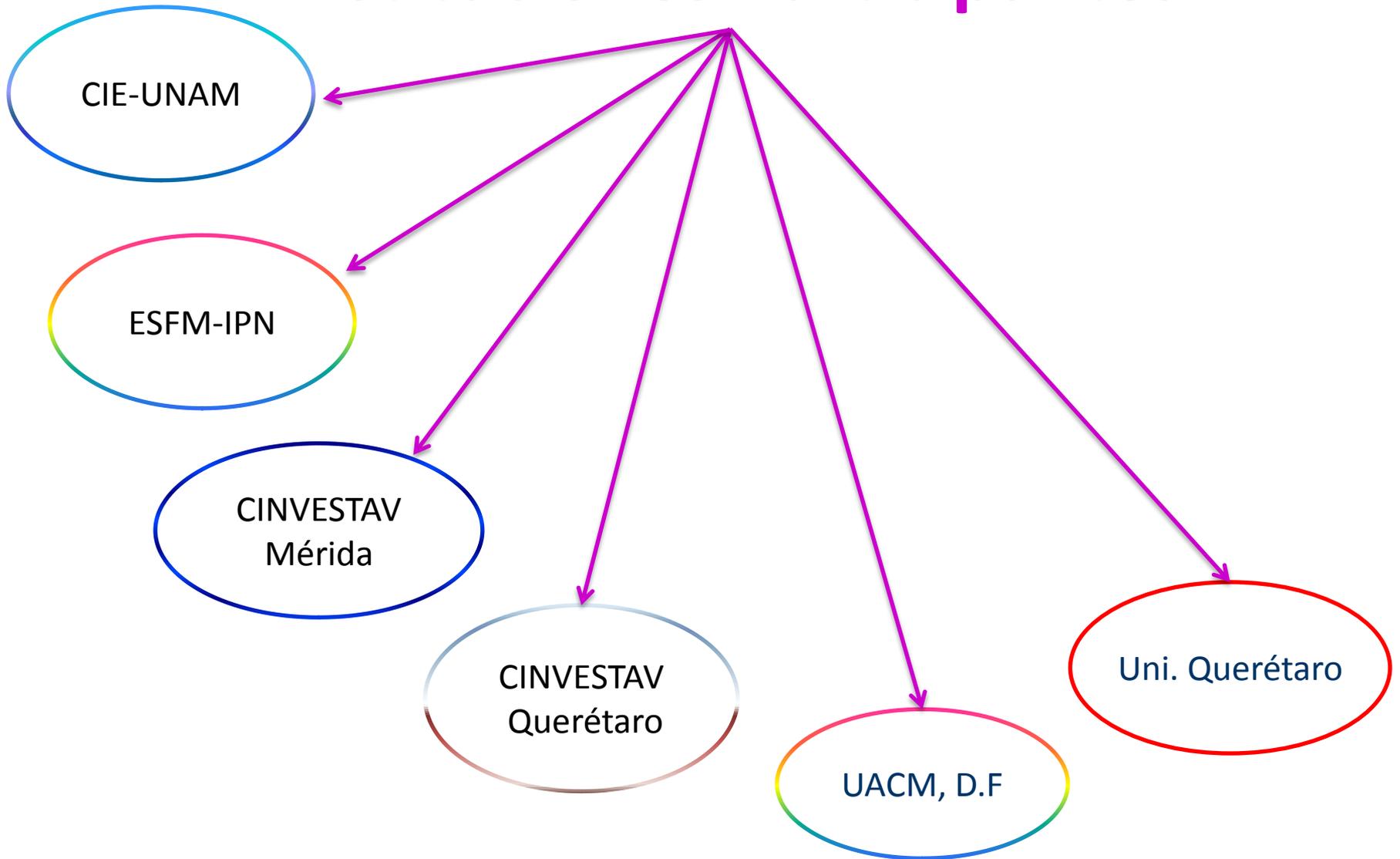
Resultados Esperados

- (i) Prototipo de mini-módulos de CdTe/CdS rayada por láser y interconectada, con un eficiencia arriba de 8%.
- (ii) Transferencia tecnología de procesamiento de módulos fotovoltaicas de CdTe/CdS a sector industrial.
- (iii) Vinculación con sector industrial y un impulso para el creación de industria fotovoltaica nacional.
- (iv) Desarrollo de recursos humanos a nivel posgrado
- (v) Integración de varios grupos nacionales en el tema de celdas solares
- (vi) Creación de infraestructura

Transferencia de la tecnología- un reto

- En México, no hay una industria propio de fotovoltaico
- Existe algunos fabricas/maquiladoras
- Existe instituciones con conocimiento en prototipos
 - CIE-UNAM
 - ESFM-IPN
 - CINVESTAV

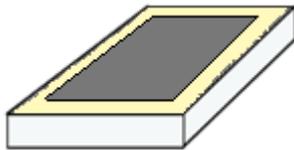
Instituciones Participantes



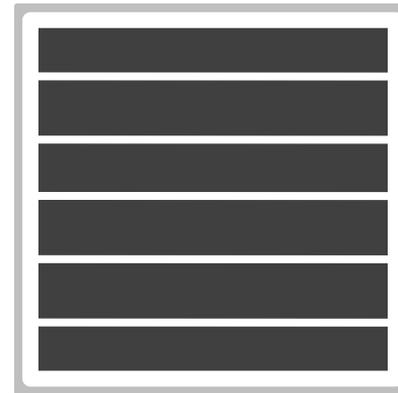
Transferencia tecnológica y vinculación con sector productivo

Metas en corto y mediano plazo

Celda (4 cm²)

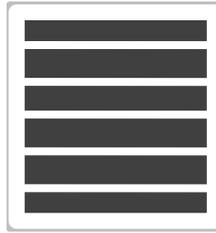


Módulo (100 cm²)



Celdas rayada y interconectada

Aplicaciones de Mini-módulos



Módulo



Aplicaciones



mini cargador



semáforos



Lámparas de calle



sensor

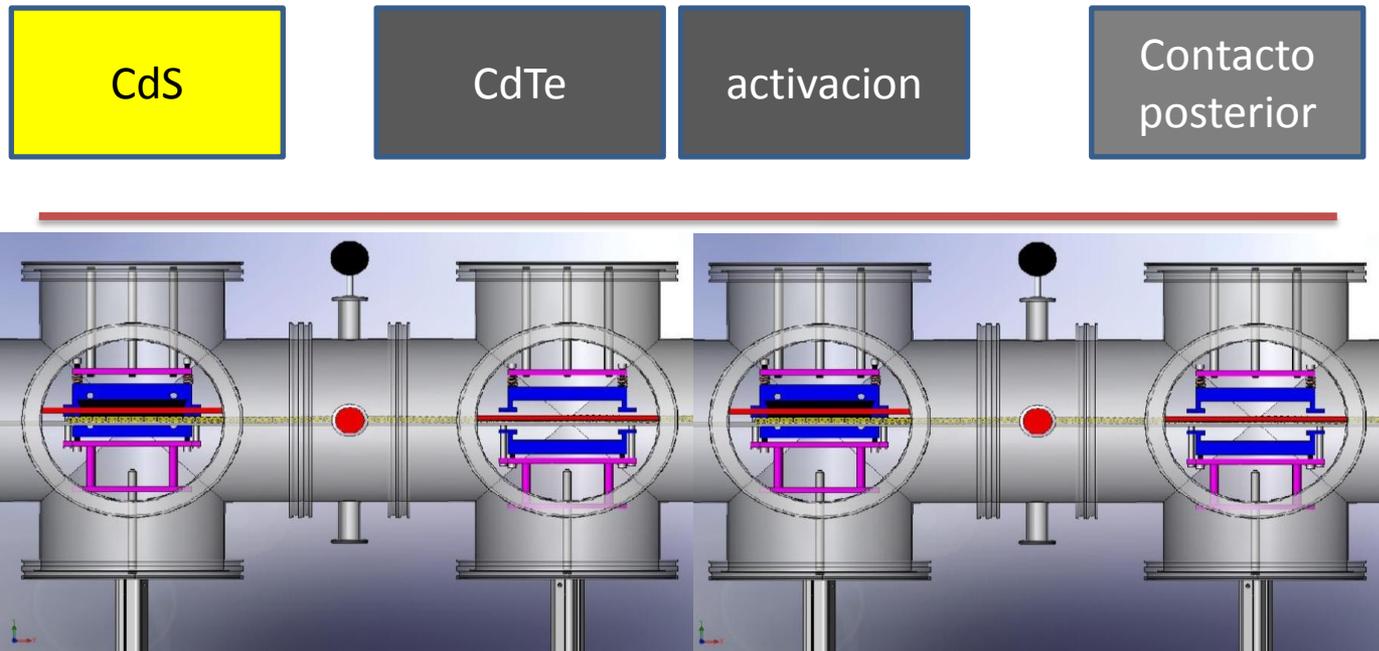


casa solar

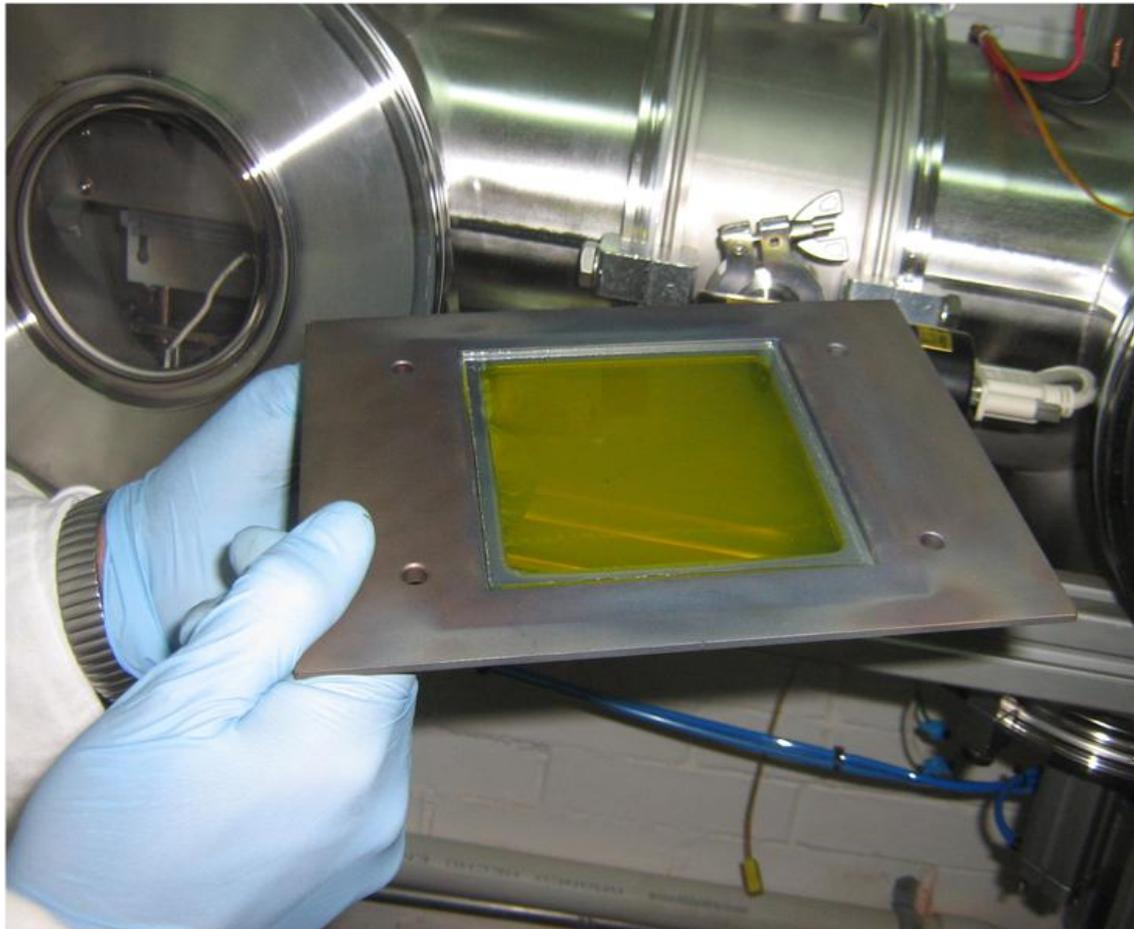
Planta piloto

- Batch processing,
- Low vacuum, low cost systems
- All-dry process, material utilization, high efficiency
- Easy scale up

- todo un proceso: CSS



Película de CdS en área 100 cm², depositado en la planta piloto (primera prueba)



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thank you

