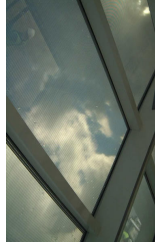
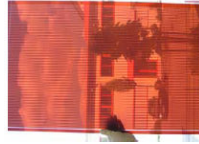
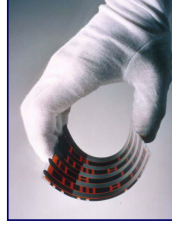


Advances in Thin Film Silicon Photovoltaics



Lucia Vittoria Mercaldo
*ENEA - Portici Research Center
Photovoltaic Technologies Section*

NIS Colloquium, Torino June 23, 2008

ENEA R&D medium-long term activities

- **Concentration photovoltaics**
- **Silicon thin film PV technology**
- **III generation approaches and organic devices**



**ENEA
Portici
Research
Center**

Thin film Si research group & projects

Head of PV Technologies Section

Carlo Privato

Researchers:

Maria Luisa Addonizio
Marco Della Noce
Paola Delli Veneri
Lucia V. Mercaldo

Research fellows:

Iurie Usatii
Claudia Diletto

Ph.D. Students:

Emilia Esposito
Luigi Fusco

Ongoing Projects:

- **Fotoenergia (MIUR)** [Partners: ENEA (coordinator), CESI Ricerche, University of Parma, Ferrara, Bologna and Napoli “Federico II”]
- **Agreement ENEA - Fondazione Tronchetti-Provera**

Proposals:

Sun_to_Grid Project (“Industria 2015”, with ST Microelectronics as proponent)

Outline

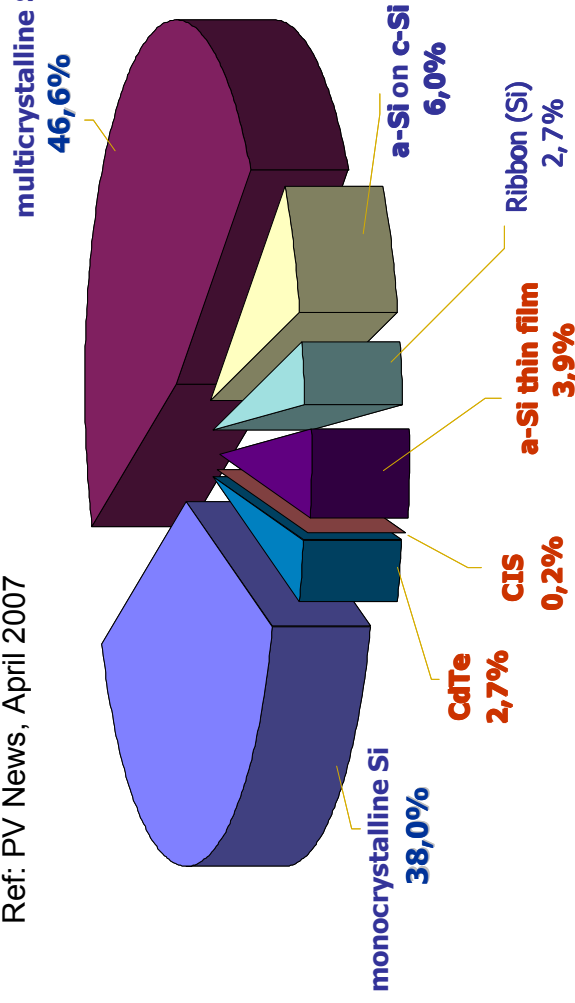
- PV market overview
- Advantages of thin film Si PV
- State of the art on thin film Si solar cells
- R&D activity in ENEA (Portici Research Center)
 - TCO development
 - Micromorph devices
 - Solar cells on polimeric substrate
 - III generation approaches



*ENEA
Portici
Research
Center
Kaneka installations*

Photovoltaic production by technology

Ref: PV News, April 2007

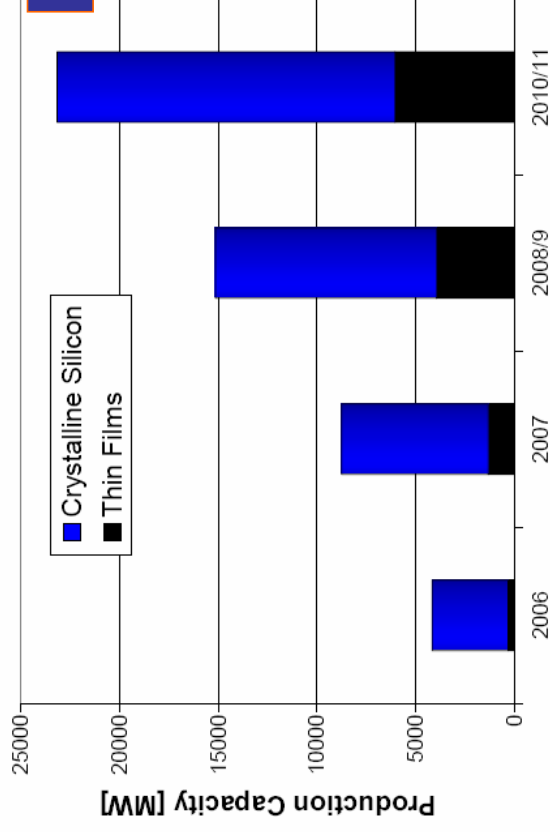


Nowadays PV production is dominated by **crystalline silicon modules** (in different forms), which represent above **90% of the market**.

Up to now the main advantage of this technology was that complete production lines could be bought, installed and be up and producing within a relatively short time-frame (low-risk placement with high expectations for return on investments).

However, the ongoing shortage of Si wafer feed stock will be a bottleneck for sustaining the present growth rate for c-Si based PV!

A chance for thin film PV



Announced Capacity Increase

Source:

PV Status Report 2007

Arnulf Jäger-Waldau

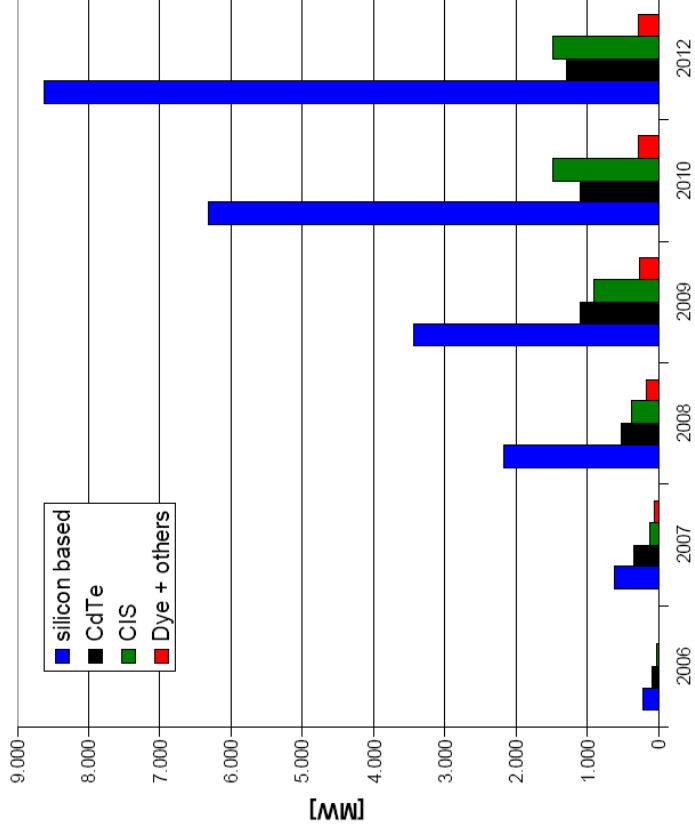
European Commission
Joint Research Centre
Institute for Environment
and Sustainability

Should the announced increases be realised, total production capacities will then stand at 23 GW by the end of this decade, of which 6 GW could be thin films.

BOOM or BUBBLE?

Announced Production Capacities by Technology

Equally competitive technologies are amorphous/micromorph Silicon, CdTe and Cu(In,Ga)(S,Se)₂ thin films. In addition Dye-cells are getting ready to enter the market.



Thin Film Industries:
more than 130 companies
in the world
68 companies are silicon based

The reason is probably that
12 to 13 companies offer
“turn-key” systems.

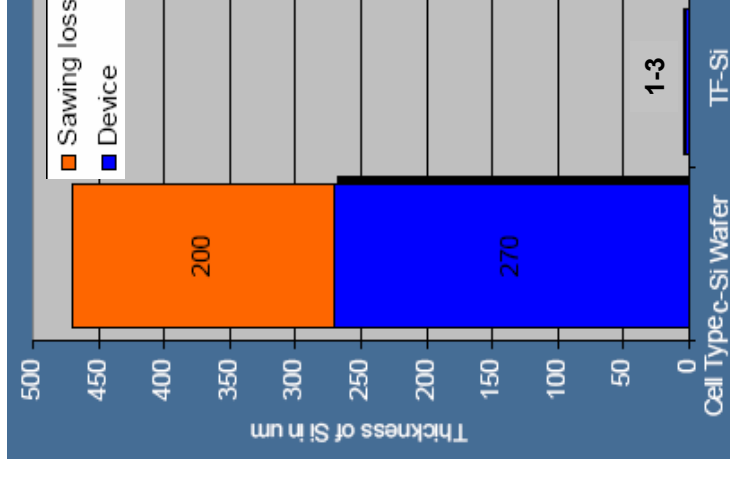
Recent news in Italy:
agreement between **ENEL**
and Sharp on joint studies
on triple junction thin film PV

Source: Waldau, PV Status Report 2007

Advantages of thin film Si technology

Silicon band gap (1.1 eV) is almost optimum to make a single junction solar converter. In addition Si is the most abundant mineral on Earth and its disposal does not create any pollution problem.

a-Si thin films absorb sunlight better than c-Si, and can be made at low temperature on low-cost substrates (glass, metal foils, and plastics).



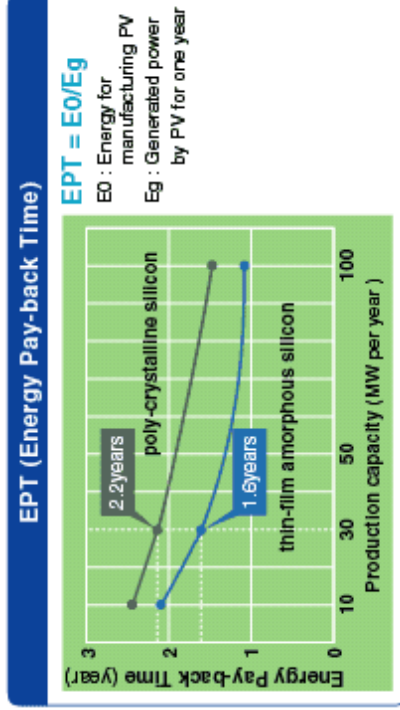
✓ **Reduction of the active material.**

✓ **Reduction of production costs.**

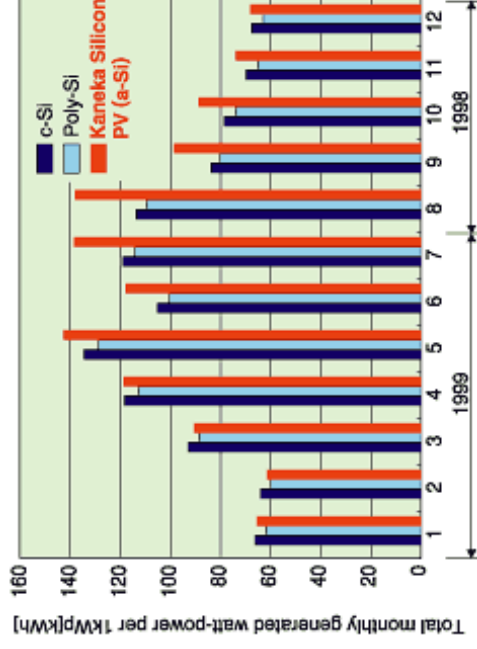
Outdoor performance and energy payback time

Source: <http://www.pv.kaneka.co.jp/why/>

Good outdoor performance in terms of generated power, especially at higher ambient temperature, even when compared to the best c-Si modules.



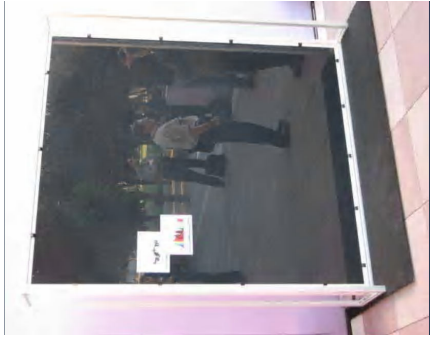
● Comparison of total generated watt-power per month among various materials



EPT is the time to "pay back" the energy used in the PV module manufacture by its own power generation.

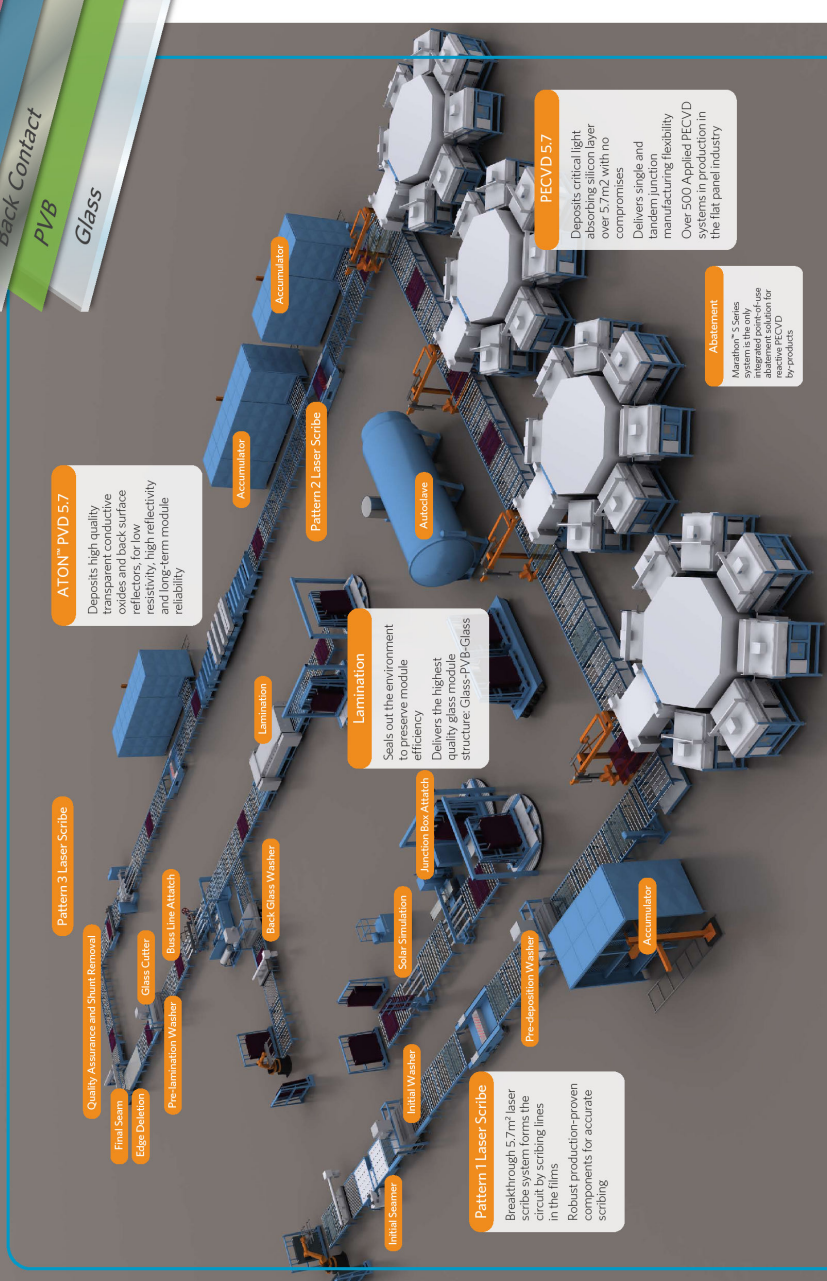
Deposition Processes on large area for high production volumes

oerlikon
solar



Applied SunFab™ Thin Film Production Line Tandem Junction

Glass
TCO
a-Si
μc-Si
Back Contact
PVB
Glass



ATON™ PVD 5:7
Deposits high quality transparent conductive oxides and back surface reflectors, for low resistivity, high reflectivity and long-term module reliability

Pattern 3 Laser Scribe
Quality Assurance and Shunt Removal
Final Seam
Edge Detection
Pre-lamination Washer
Glass Cycler
Bus Line Attach

Accumulator

Pattern 2 Laser Scribe

Lamination
Seals out the environment to preserve module efficiency
Delivers the highest quality glass module structure, Glass-PVB-Glass

Junction Box Attach

Pattern 1 Laser Scribe
Breakthrough 5.7mm laser circuitry scribe module circuit by scribing lines in the films.
Robust production-proven components for accurate scribing

PECVD 5:7
Deposits critical light absorbing silicon layer over 5.7mm with no compromises
Delivers single and tandem junction manufacturing flexibility
Over 500 Applied PECVD systems in production in the flat panel industry

Abatement
Marathon™ S Series integrated point-of-use abatement solution for TCO by products

Applied SunFab Automation Software

Applied SunFab Service

Applied SunFab™

Go Big. The new standard: 5.7m²

Applied's technology, global support and extensive manufacturing know-how deliver solutions for lowest cost per watt.

1.4m²

The Applied SunFab line produces modules nearly four times larger than conventional modules on the market.

4x larger

5.7m²

2.2m
2.6m



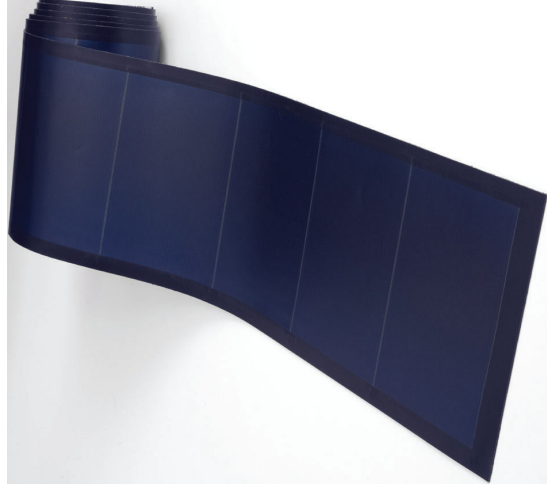
ACCELERATING
SOLAR



Products can be made lightweight and flexible

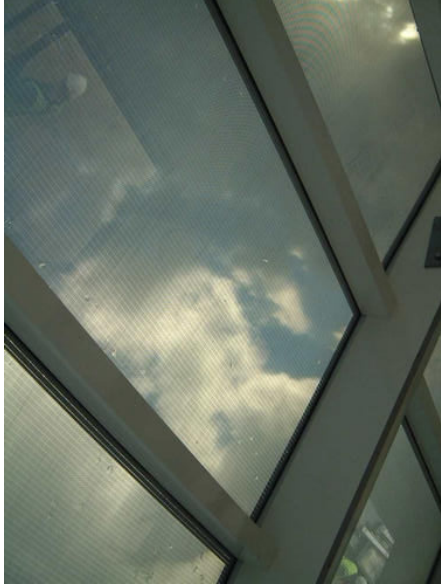


 **flexcell**



UNI-SOLAR

See-through products are available



КАПЕКА

SHARP

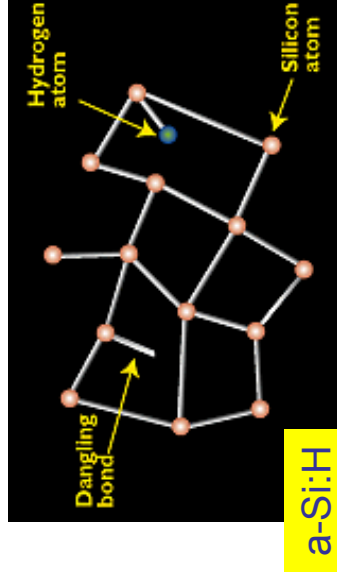
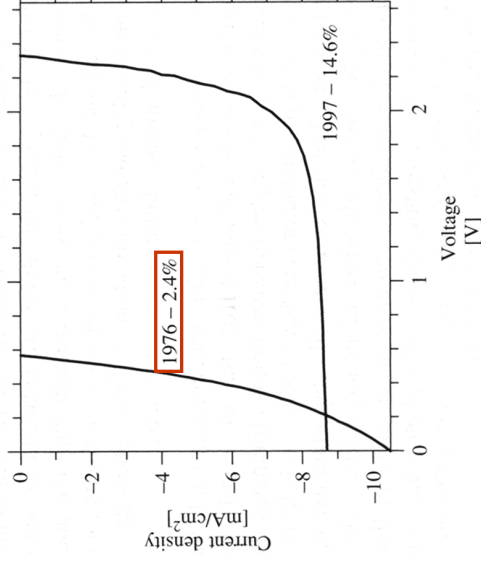
Potentiality to allow a large diffusion of PV in architecture



Brief history (1)

1976: Carson and Wroski report on the first a-Si:H solar cell.

1980: Schott Solar starts a-Si:H solar cell production on glass, followed by Sanyo in 1982.



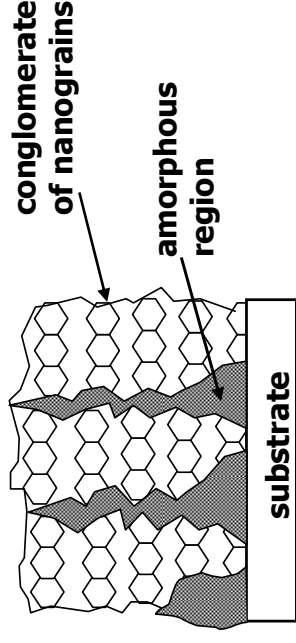
There are two major issues:

- lower efficiency with respect to c-Si,
- stability problems (light induced efficiency reduction due to metastable defect creation in the material. Saturation after ~ 1000 h)

Brief history (2)

1994: First $\mu\text{c-Si:H}$ and micromorph tandem solar cell realized at IMT - University of Neuchatel (Switzerland).

Versatile complex material containing micrometer sized conglomerates of nanograins (~20-30nm) in amorphous tissue.



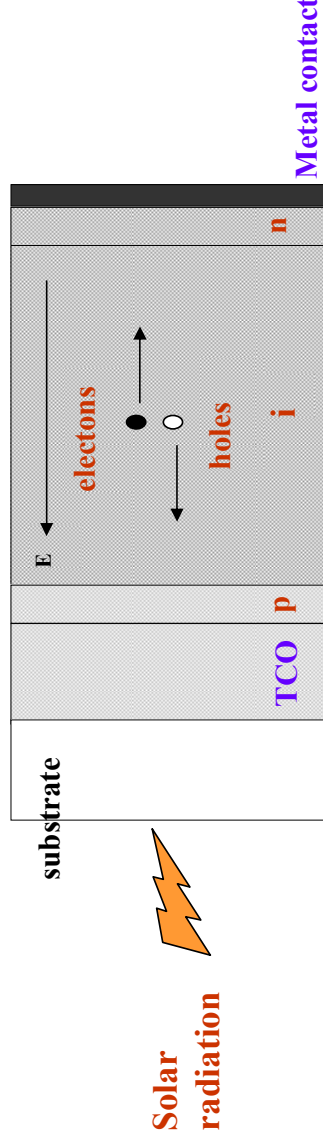
$\mu\text{c-si:H}$ has some interesting peculiarities: {
☺ Better stability to light soaking
☺ Long wavelength response

1996: United Solar starts a-Si:H solar cell production on flexible substrates.

1999: Kaneka demonstrates first micromorph module.

Thin film silicon solar cells

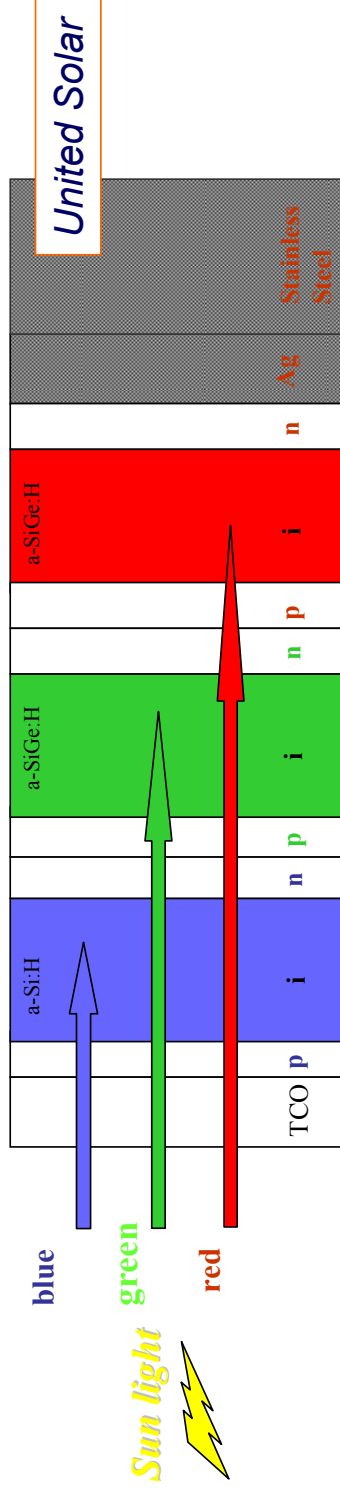
p-i-n or n-i-p junctions



- ✓ Sun light enters through the p layer which is called window layer
- ✓ The intrinsic layer is the active material
- ✓ The photocarriers are swept away by the built-in electric field to the n-type and p-type layers.

Amorphous silicon multijunction solar cells

Series of cells using materials with different energy gap devoted to absorb different parts of the solar spectrum



The "spectrum splitting" determines higher efficiency with respect to the single junction.

Due to thinner active layer in each junction the light soaking effect is reduced.

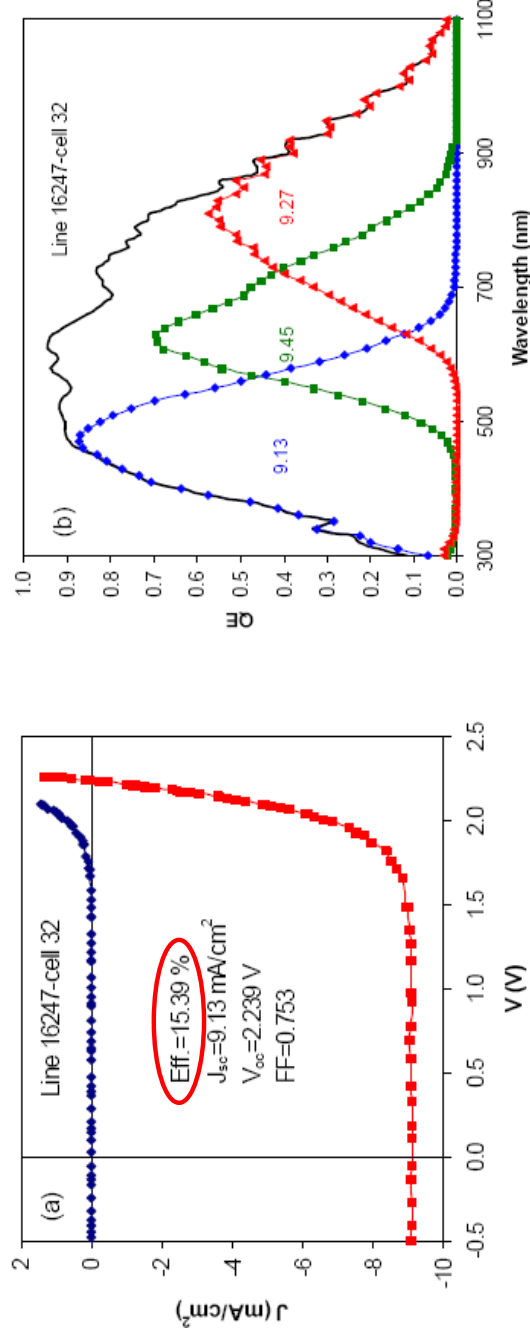
Record on initial efficiency

CORRELATION OF CURRENT MISMATCH AND FILL FACTOR IN AMORPHOUS AND NANOCRYSTALLINE SILICON BASED HIGH EFFICIENCY MULTI-JUNCTION SOLAR CELLS

Baolie Yan, Guozhen Yue, Jeffrey Yang, and Subhendu Guha
United Solar Ovonic LC, 1100 West Maple Road, Troy, Michigan

IEEE 2008

a-Si:H/a-SiGe:H/nc-Si:H triple-junction solar cells



active-area: 0.25 cm²

State of the art at lab scale

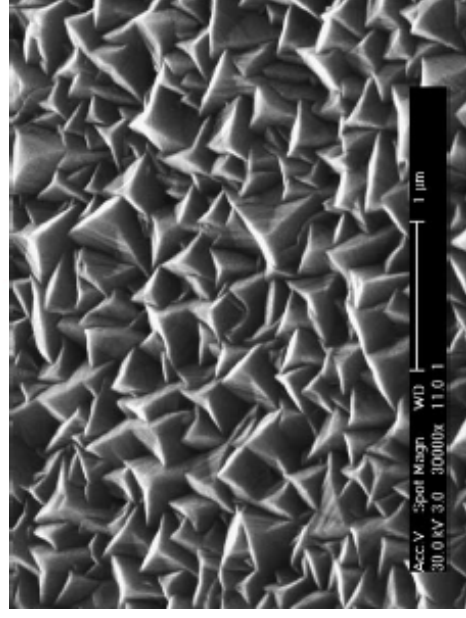
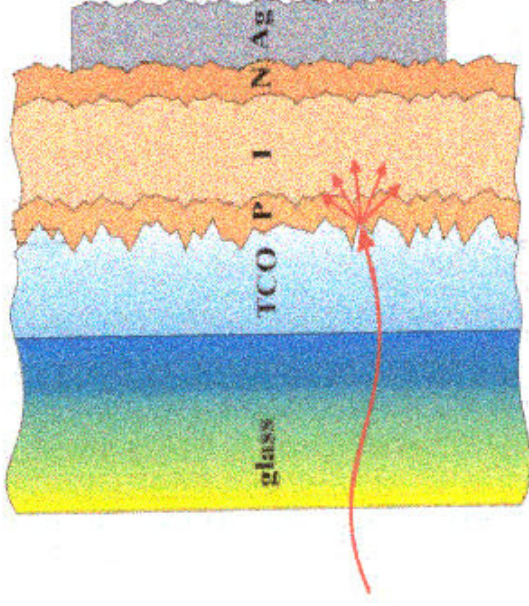
Cell structure	Area (cm ²)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	Efficiency (%)	Laboratory
a-Si	0.25	0.965	14.36	0.672	9.3 Stab.	United Solar
a-Si/a-SiGe/a-SiGe	0.25	2.30	8.11	0.697	13.0 Stab.	United solar
μC-Si	1	0.545	25.7	0.70	9.8 Not stab.	IPV Jülich
a-Si/ μC-Si	0.25	1.284	13.5	0.692	11.0 Stab.	Neuchâtel

ENEА activities on thin film silicon solar cells

- ✓ **Development of transparent and conductive oxide (TCO) films**
- ✓ **Tandem “micromorph” solar cells**
- ✓ **Solar cells on polymeric substrates**
- ✓ **Third generation approaches**

Light trapping issues

The use of a rough transparent conductive oxide (TCO) layer is essential in order to increase the efficiency of thin film solar cells.



Requirements for high-quality TCO:

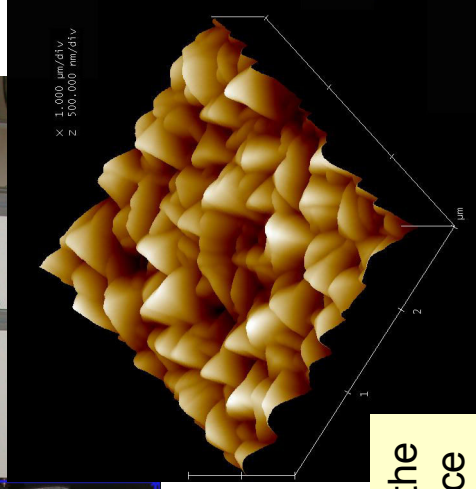
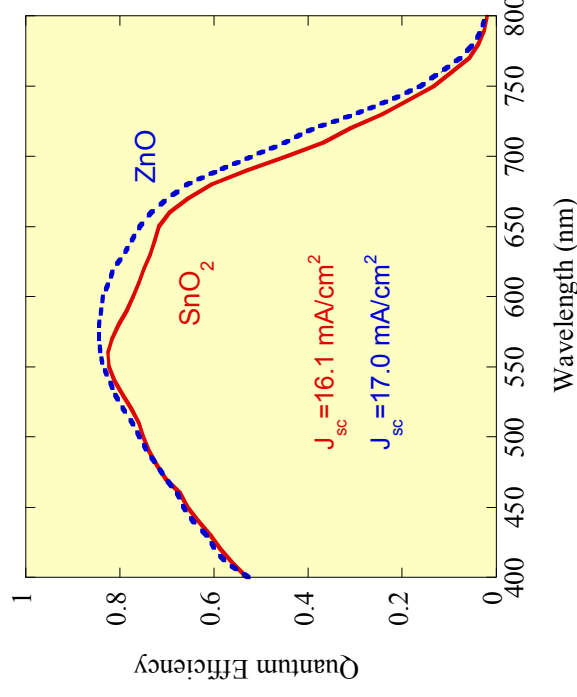
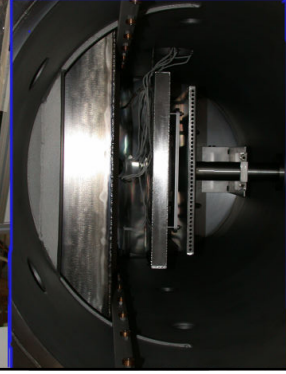
- ✓ High electrical conductivity
- ✓ High transparency
- ✓ High light-scattering ability (haze ratio)
 $H = T_{\text{diffuse}} / T_{\text{total}}$

Transparent and conductive oxide (TCO)

Development of a customized LP-MOCVD system to deposit ZnO textured films on large area substrates (30x30cm²)



Deposition system



AFM image of the textured surface

The texturing produces a good light-trapping effect

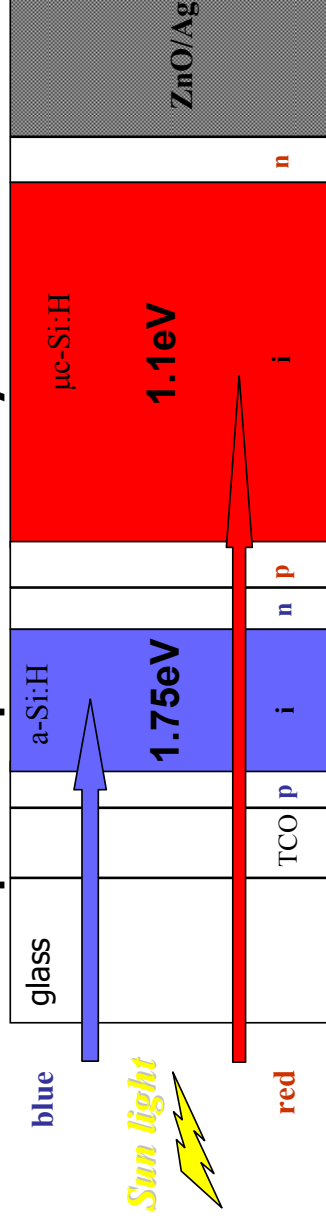
Enea results: LP-MOCVD ZnO

- Textured material on 30 x 30 cm² area.
- Growth rate > 28 Å/sec.
- Good thickness uniformity ($\pm 5\%$).
- Good electrical properties
(Resistivity = $1 \times 10^{-3} \Omega \text{ cm}$, Mobility = 32 cm²/Vs).
- High transparency (> 82 %).

Next step: industrial scale-up

Micromorph tandem solar cells

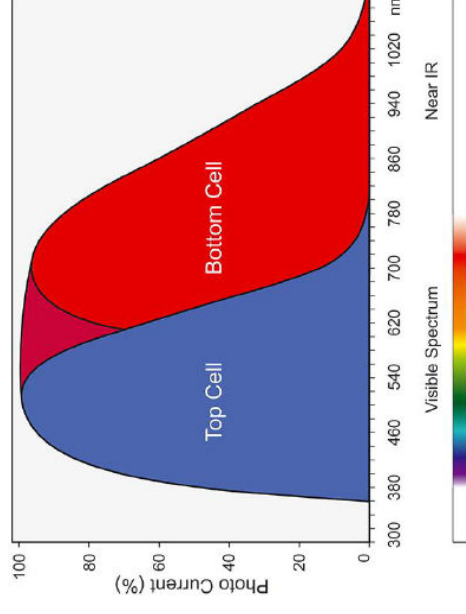
Amorphous top cell + microcrystalline bottom cell



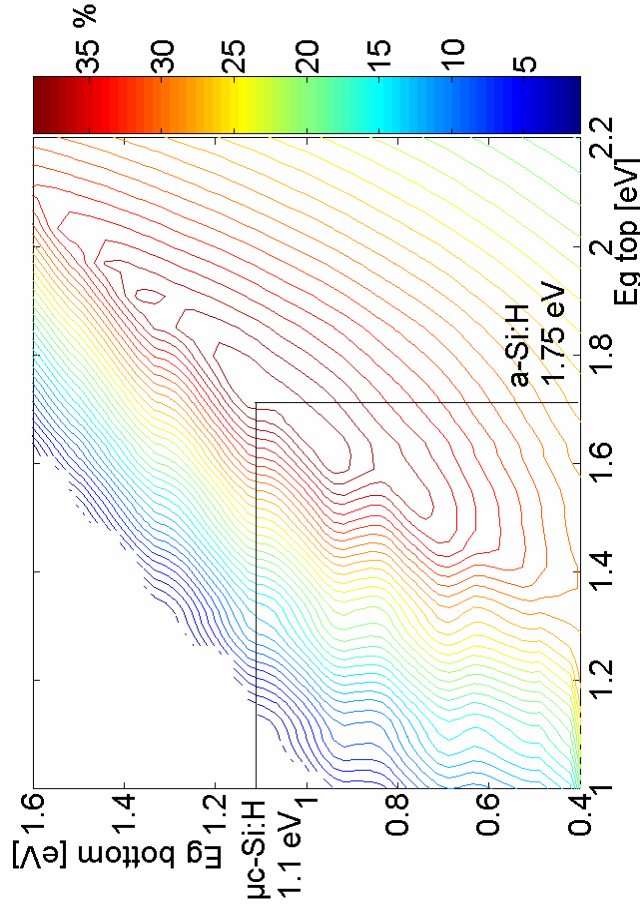
Advantages:

- ✓ The light-induced degradation typical of a-Si is effectively reduced
- ✓ Better utilization of the solar spectrum: the spectral sensitivity of the device is enlarged towards the near-infrared region

☺ Elimination of costly germanium gas from the multijunction fabrication process



Maximum efficiency plot for tandem cells



Gaps of $\mu\text{c-Si:H}$ (1.1 eV) and a-Si:H (1.75 eV) form an almost ideal combination.

Upper efficiency limit for **micro-morph tandem** cell:

$\eta > 30\%$

F. Meillaud et al., Sol. Energy Mater. Sol. Cells 90, 2952 (2006).

Courtesy of Prof. A. Shah, Univ. Neuchatel (Switzerland)

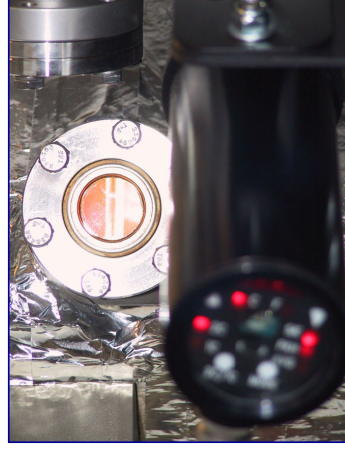
Still very far from upper limit → Research is needed!

Trends in current thin film technology

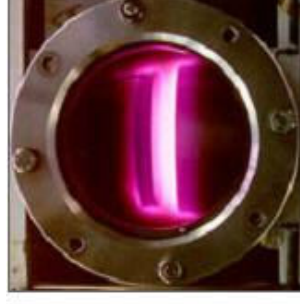
Fairly "thick" ($> 1\mu\text{m}$) microcrystalline (slowly deposited) absorber layers are needed!

Development of faster deposition techniques:

☞ Hot Wire CVD
(HW CVD)



☞ Very High Frequency PECVD
(VHF PECVD)

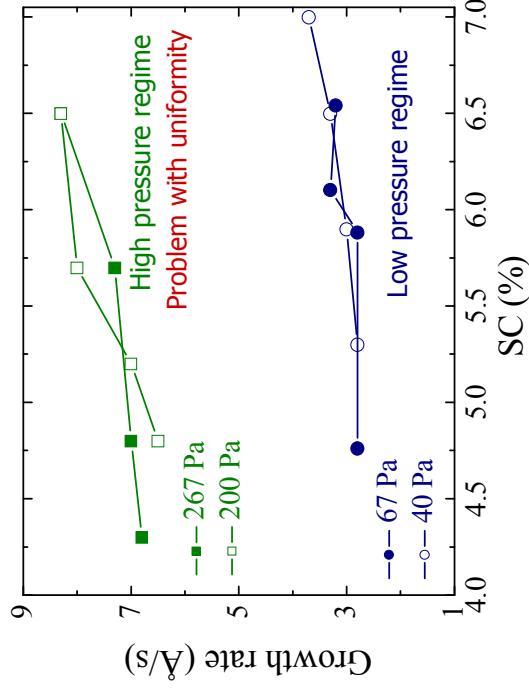


Microcrystalline Si ($\mu\text{-Si:H}$) in ENEA

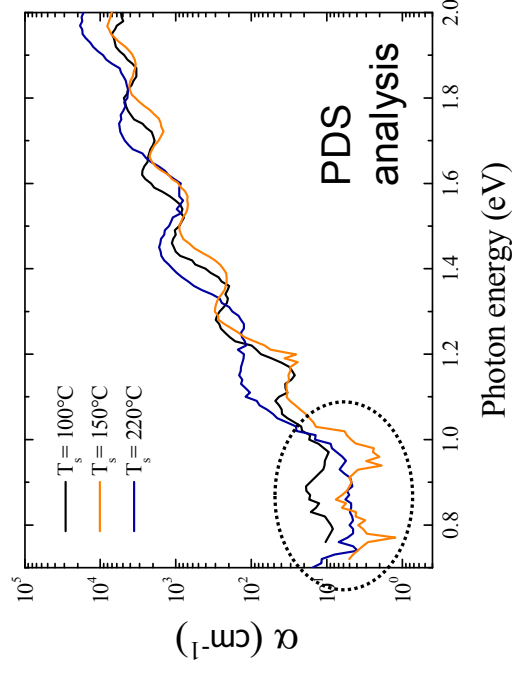


**Technique : VHF PECVD at 100 MHz
gas mixture SiH_4 and H_2**

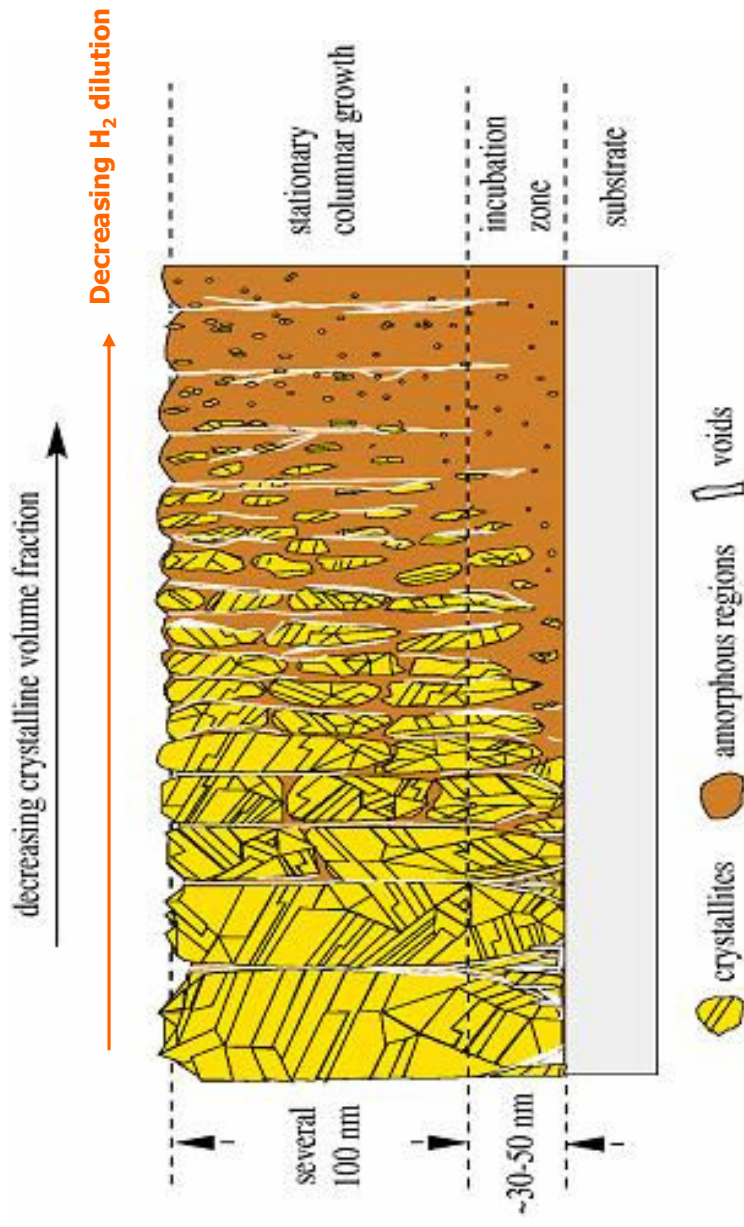
Deposition temperature = 150°C



Delli Veneri, Mercaldo, Privato, Ren. Energy 33, 42 (2008)



Hydrogen dilution effect on $\mu\text{c-Si:H}$

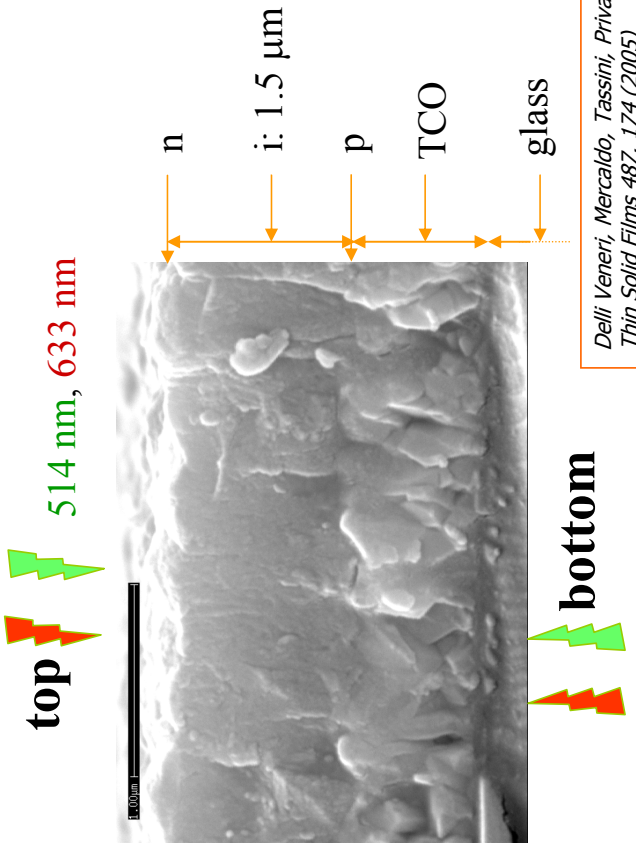


The crystalline volume content of the films can be varied depending on the deposition conditions.

Depth- dependant micro-Raman analysis

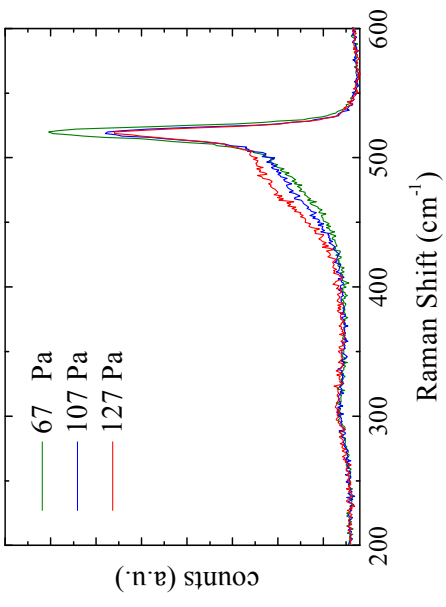
180 nm |
700 nm |
700 nm |
180 nm |

Less ordered structure in the first stages of the deposition

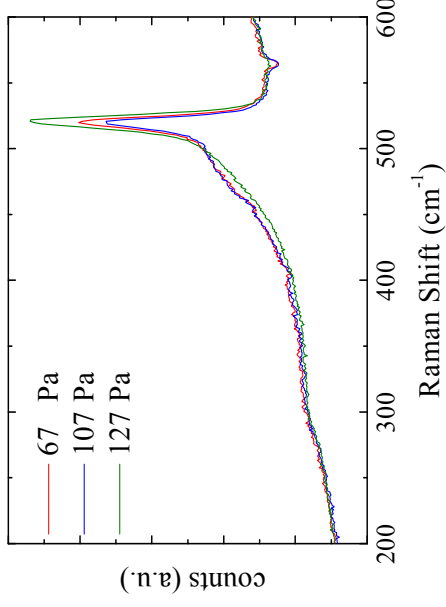


Delli Veneri, Mercaldo, Tassini, Privato, Thin Solid Films 487, 174 (2005)

Top illumination, 633 nm excitation light

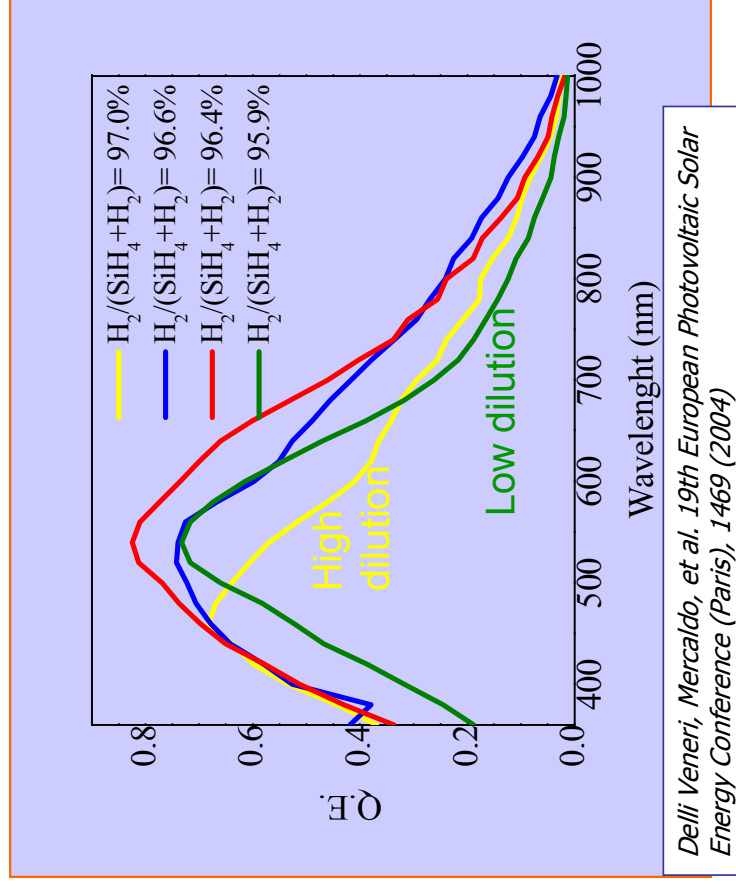


Bottom illumination, 633 nm excitation light



Hydrogen dilution effect on $\mu\text{c-Si:H}$ cells

Efficiency is maximized when using $\mu\text{c-Si:H}$ grown in the amorphous-to-crystalline transition region.



High H_2 dilution:

“too crystalline” material \rightarrow
 \rightarrow low absorption coefficient.

Low H_2 dilution:

Low quality material with
large amorphous content.

Intermediate dilution:

Optimal spectral response

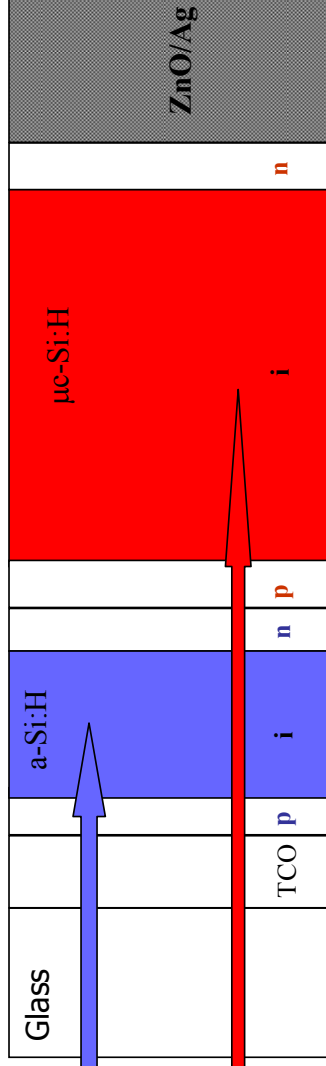
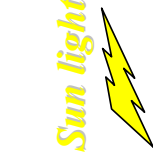
Best $\mu\text{c-Si:H}$ material
for solar cells:
crystallinity fraction
around 50 - 70%

Effect of bottom cell on tandem device

Substrate: Asahi U-type

Cell Area: 1 cm x 1 cm

blue



Top Cell:

p a-SiC:H thickness: 7 nm

i a-Si:H thickness: 270 nm

n $\mu\text{c-Si:H}$ thickness: 30 nm

Back contact:

ZnO/Ag

Bottom Cell:

p $\mu\text{c-Si:H}$ thickness: 30 nm

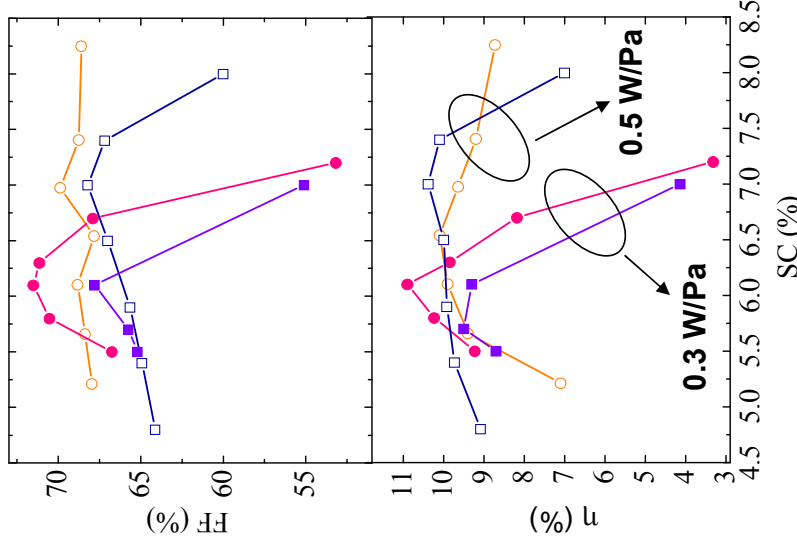
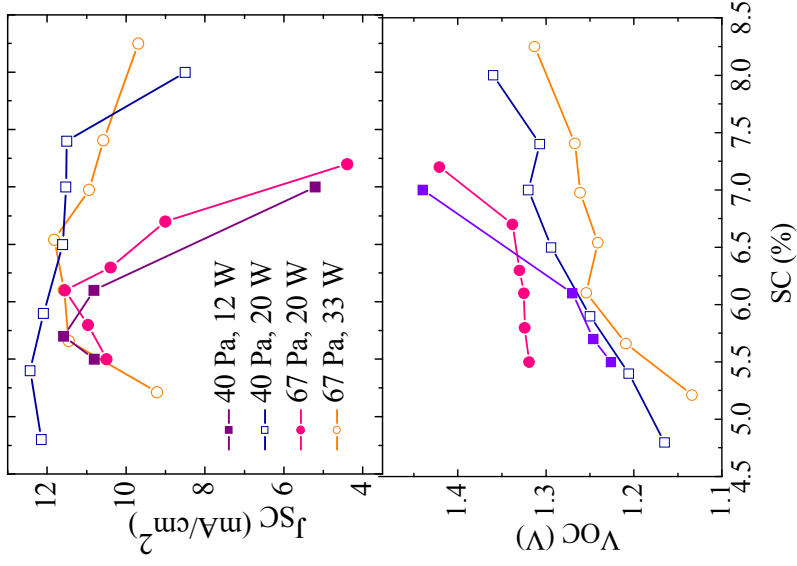
i $\mu\text{c-Si:H}$ thickness: 1.5 μm

n $\mu\text{c-Si:H}$ thickness: 40 nm

Different deposition conditions for i layer explored

When fabricating a micromorph tandem solar cell, the basic problem is combining a high-current but low-voltage microcrystalline cell with a low current but high-voltage amorphous cell.

Micromorph tandem devices



*Delli Veneri,
Mercaldo, et al.
Journal Non-Cryst.
Solids 354, 2478
(2008).*

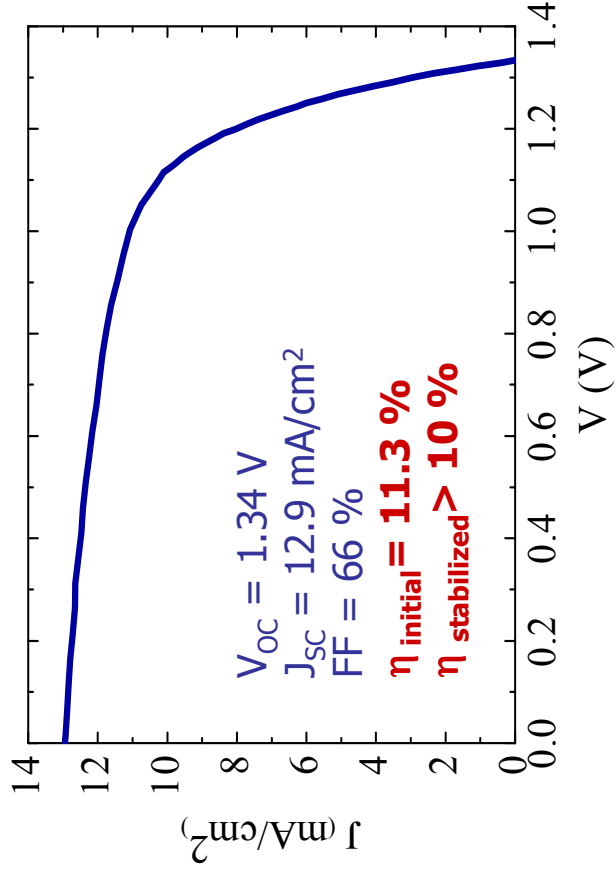
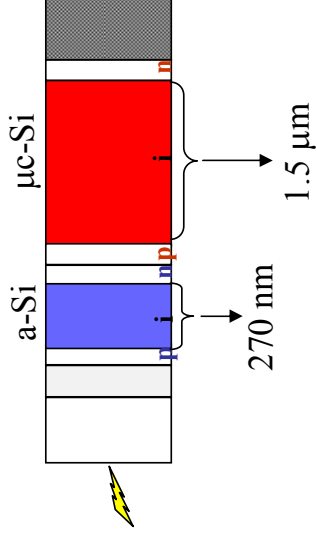
At high power to pressure ratio (0.5 W/Pa) high J_{sc} and almost constant FF and η in a wide SC range

The weak dependence on SC makes such deposition regime very interesting for industrial application.

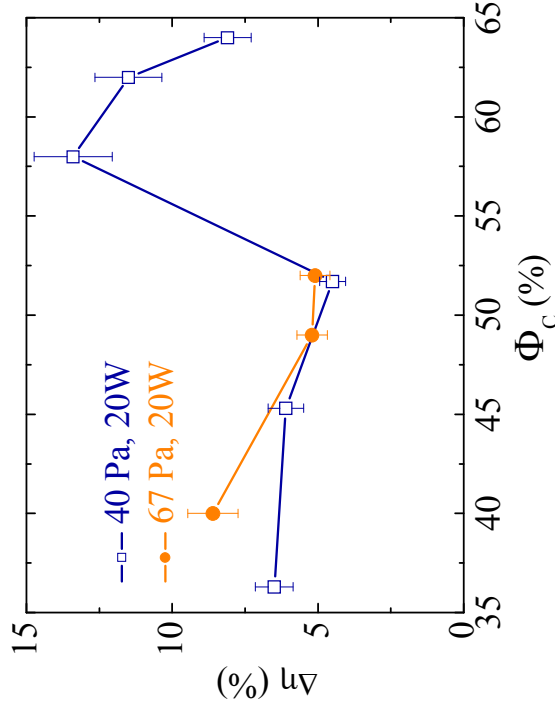


Best efficiency

Technique: VHF PECVD at 100 MHz
Deposition temperature = 150°C
Low power to pressure ratio = 0.3 W/Pa
Substrate: Glass/SnO₂ Asahi U-type
Area: 1 cm X 1 cm



Stability of tandem devices



Experimental:
200 hours of light-soaking at open-circuit under solar simulator (AM 1.5)

Relative efficiency loss
 $\Delta\eta = (\eta_{\text{initial}} - \eta_{\text{degraded}}) / \eta_{\text{initial}} \sim 5 - 13 \%$
depending on the crystalline phase fraction in the $\mu\text{-Si}$ bottom layer

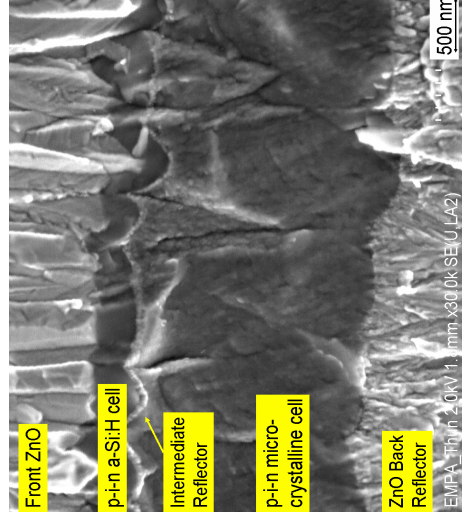
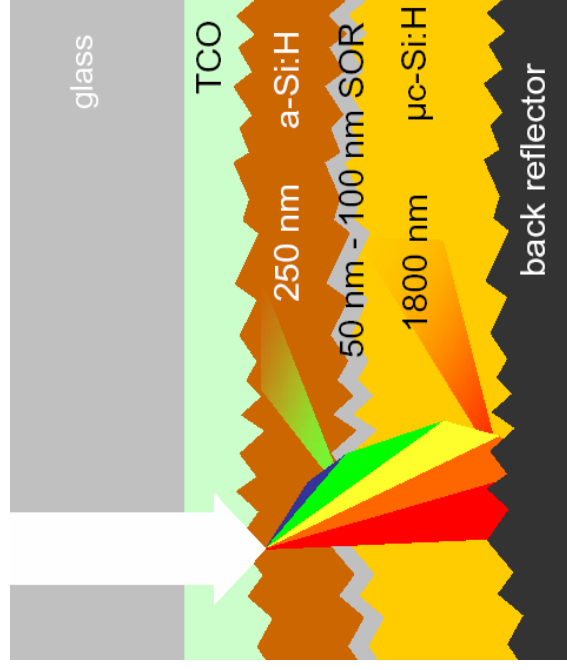
The large $\Delta\eta$ measured for the series deposited at 40Pa for $\Phi_c > 58\%$ can be due to a current mismatch, with the amorphous top cell limiting the output value.

Due to better stability of the microcrystalline component, a tandem device with a bottom cell limited current mismatch is preferable in order to reduce the light-induced degradation effect.

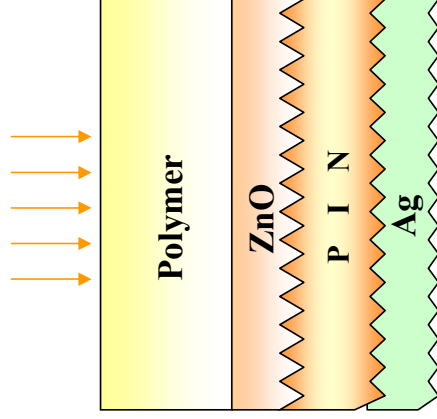
Delli Veneri, Mercardo, et al, Journal Non-Cryst. Solids 354, 2478 (2008).

Intermediate reflector

Using an appropriate material as intermediate reflector in between the two component cells, it is possible to enhance the photocurrent of the top cell without increasing the thickness, thus improving also the device stability.

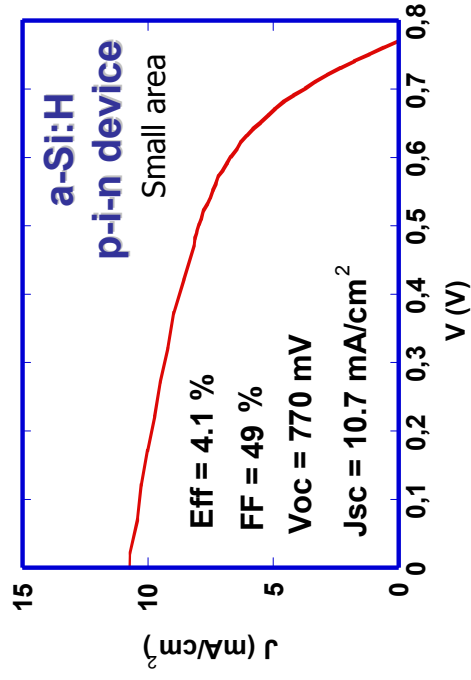
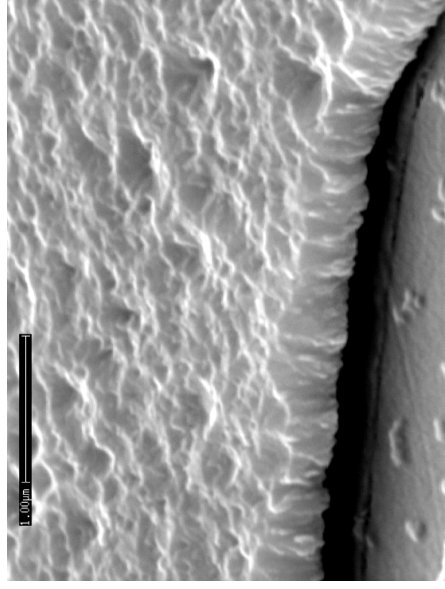


Solar cells on flexible substrate

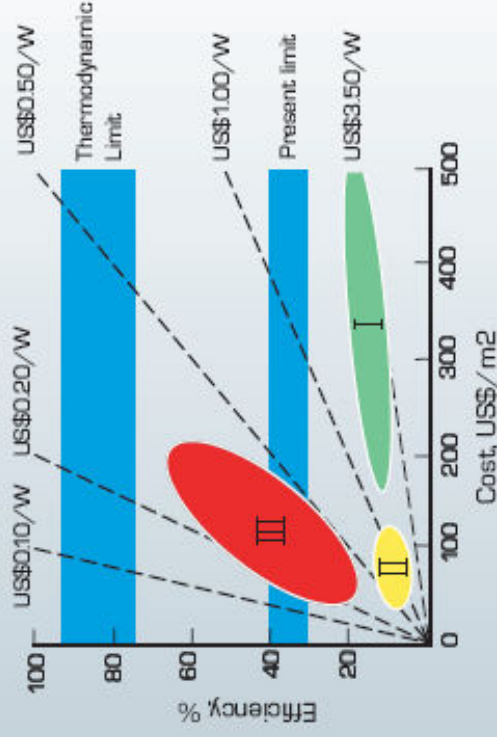


Deposition technique: VHF PECVD at 100 MHz

Substrate: PET/ZnO



III generation photovoltaics

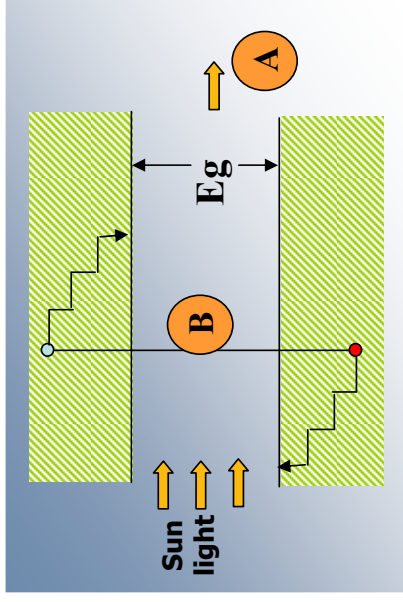


Thin Film Technology (the 2nd Generation PV) has brought the PV field in a new better region of the Cost-Efficiency space

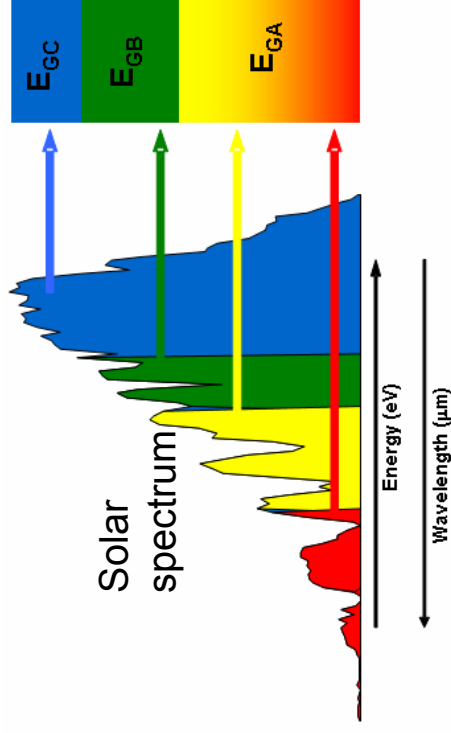
According to the U.S. DoE, for PV becoming an effective solution to the energy problem, the costs should reach the level of **0.33 USD / W**

The new challenge for the technical and scientific community is to develop a **third generation of thin film PV** which follows this much more aggressive slope (0.33 USD / W).

The III generation multijunction approach



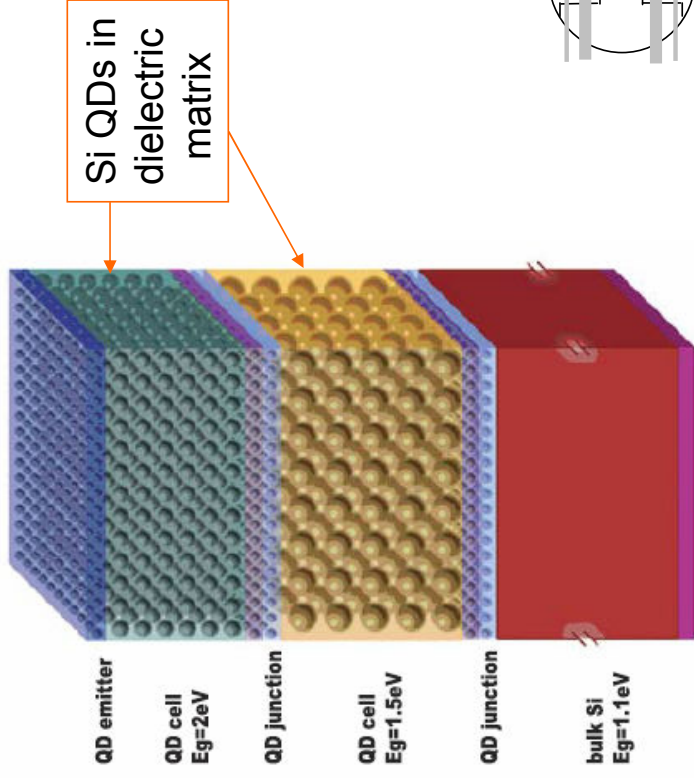
The two most important power loss mechanisms in single bandgap solar cells arise from the inability to absorb photons with energy less than the bandgap **A** and thermalisation of photon energy exceeding the bandgap **B**.



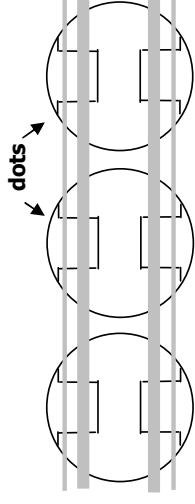
The idea is to engineer new materials with tailored band gap, which absorb photons in a dedicated energy range, by using the **quantum confinement effect**.

All Si quantum dot solar cell

prof. M. Green (UNSW, Australia)



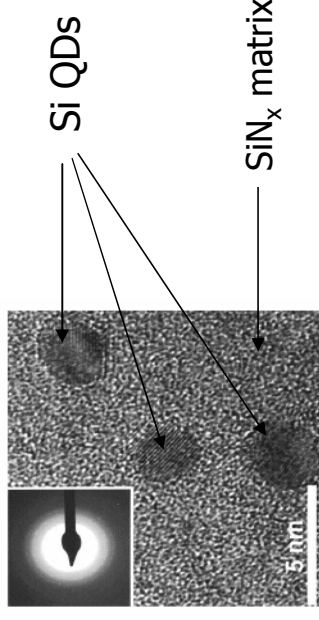
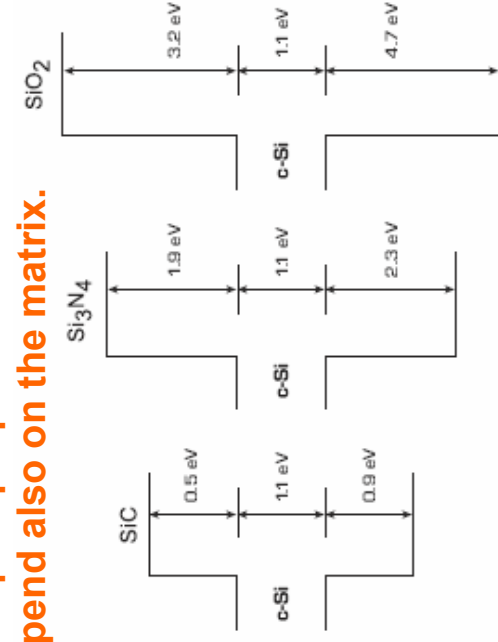
The concept behind this innovative device is the variation of the band gap with the size of quantum dots and the contemporary of higher efficient absorption in the solar spectrum in nanostructures.



Our idea: find a substitute for a-Si:H in thin film tandem devices

PECVD in situ growth of Si QDs in SiN_x

Transport properties will depend also on the matrix.



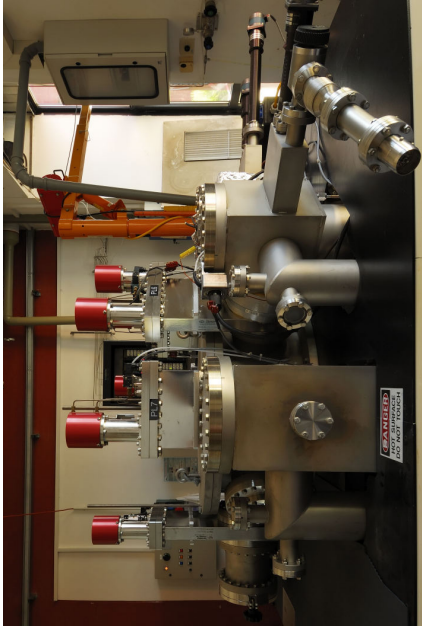
T.-W. Kim et al., *Appl. Phys. Lett.* 88 (2006) 123102

Inhomogeneous growth is promoted in low rate regime by formation of Si dangling bonds acting as nucleation sites.

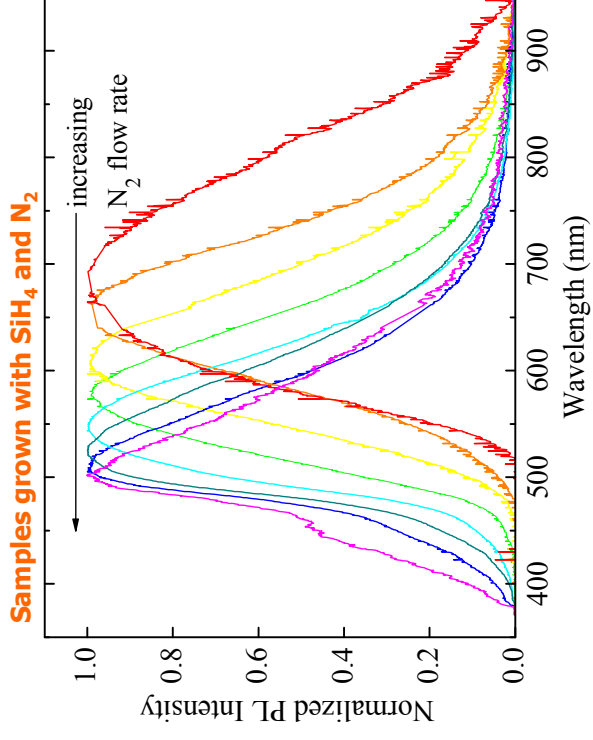
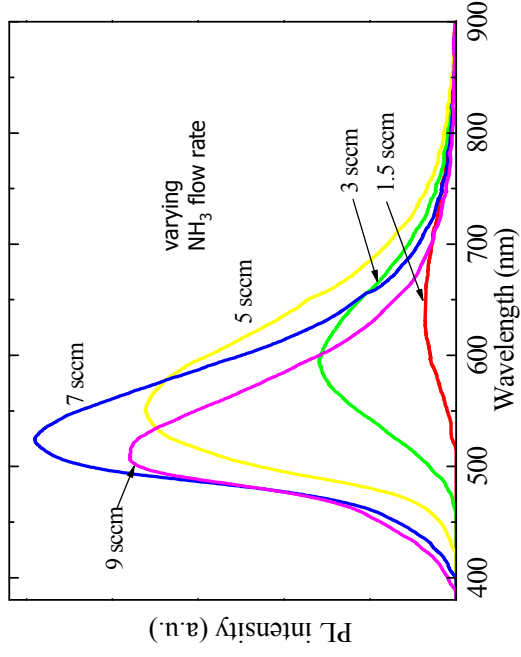
A lower barrier height between adjacent quantum dots, such as with silicon nitride instead of silicon oxide, enhances carrier tunnelling and larger interdot distance can be allowed.

Deposition temperature $\leq 300^\circ\text{C}$
NO POST ANNEALING

ENEА results: room temperature PL

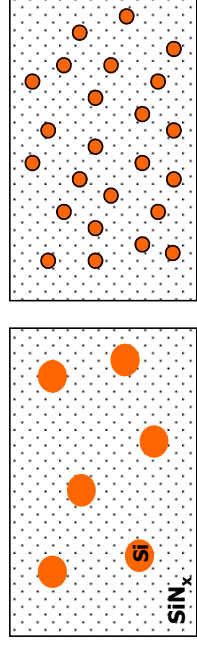


Samples grown with SiH_4 and NH_3 diluted in N_2



Samples grown with SiH_4 and N_2

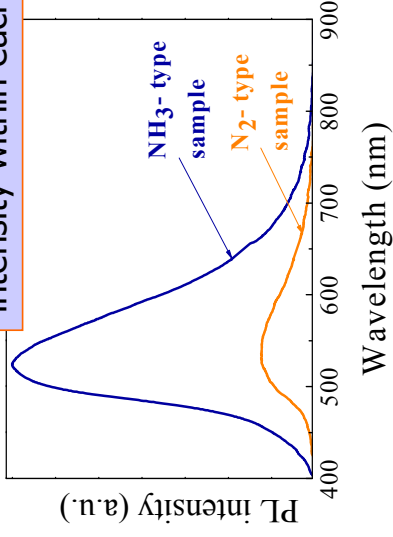
L.V. Mercado et al., submitted to Mat. Science and Engineering B (2 papers).



Increasing N_2 or NH_3 flow rate

ENE A results (2)

Comparison of samples with max PL intensity within each series

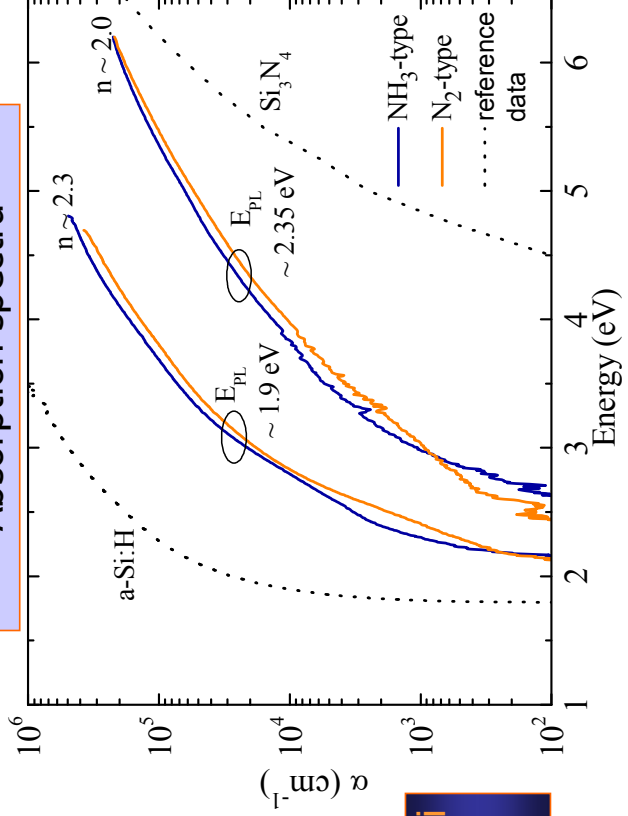


The extra hydrogen available in NH₃ type samples more efficiently passivates nonradiative defect centers at the dot-matrix interface.

L.V. Mercado et al., submitted to Mat. Science and Engineering B

Presence of strongly absorbing Si regions enhances the low energy optical absorption.

Absorption spectra



Thanks for your attention

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ENEA activities on thin film silicon solar cells

- ✓ **Development of transparent and conductive oxide (TCO) films**
- ✓ **Tandem "micromorph" solar cells**
- ✓ **Solar devices on polymeric substrates**
- ✓ **Third generation approaches**

NIS Colloquim, Torino June 23, 2008