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# "Thin Film Silicon Solar Cells"


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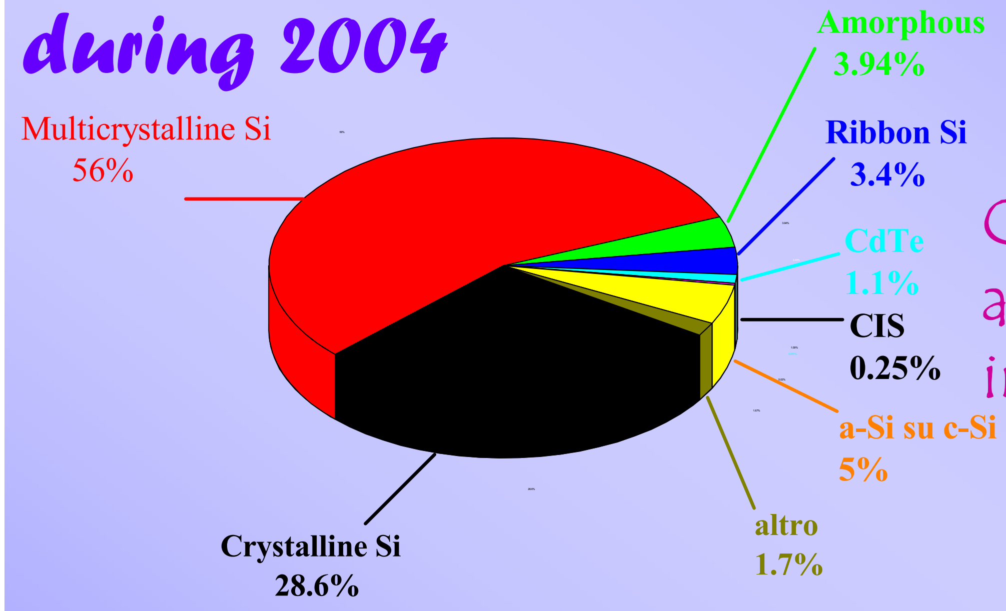
# Thin film Silicon Solar Cells

*Paola Delli Veneri*

**Enea -** ***Research Center***

# Photovoltaic production for different technologies during 2004




Crystalline silicon based solar cells are the most successful in industrial production.

- ☝c-Si based PV industry has mostly benefited from the rejects of the production of integrated circuits
- ☝The scarcity of feed stock will be a bottleneck for sustaining a growth rate of 20-25% up to 2020.

## ….until now….

## …the market of thin film modules has been limited!!

### Why??

The potential cost reduction of thin films has still to be demonstrated.

The solar cell conversion efficiencies are lower in comparison with c-Si devices.

There are technological problems.

## ...but...
## the advantages of thin film technologies...

- ✓ Reduction of the active material.
- ✓ Reduction of production energetic costs.
- ✓ Possibility to fabricate large area modules.
- ✓ Possibility to fabricate modules on flexible substrates.

**Thin film technologies have the potentiality to allow a large diffusion of PV in architecture**

# Technologies State of Art

| Type | Laboratory cell efficiency record (%) | Module efficiency record (%) | Commercial module efficiency (%) |
|---|---|---|---|
| mono Si. | 24.7 | 22.7 | 12-17 |
| multi Si | 20.3 | 15.3 | 11-14 |
| a-Si | 13.0 | 10.4 | 6-7 |
| CdTe | 16.5 | 10.2 | 6-7 |
| $CuInGaSe_2$ | 18.4 | 13.1 | 8 - 11 |

- Lack of adequate industrial/technological experience
- Low production yield
- Production hadards
- Relatively high temperatures (400-500°C)
- raw material availability.

The motivation for developing a high-performance, viable thin-film solar cell technology, based on *silicon*, can be clearly perceived.

✓a-Si multijunction solar cells

✓ Micromorph Solar cells (Tandem a-Si/μc-Si)

# History of amorphous and microcrystalline Si

- ☞The research on non-crystalline and heterogeneous materials has grown over the past 20 years in solid state physics.
- ☞Silicon can be modified from single crystalline state via a two-phase microcrystalline state, to an almost perfectly disordered, amorphous state.
- ☞The technological potential of each form of thin film silicon is tremendous.
- ☞The unique properties of amorphous and microcrystalline silicon, together with the modern technique for preparing thin films over large areas, open many opportunities for semiconductor device applications.

## *Mainly steps*

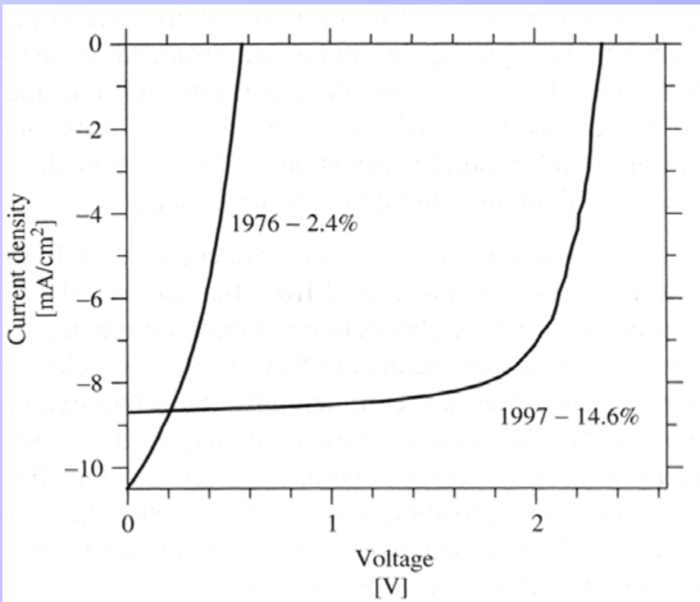
1965: Sterling and Swann report the formation of films of "silicon from silane" in a radio frequency glow dicharge

1969: Chittick et al. found that amorphous silicon deposited by glow discharge had better photoconctuctive properties than that made by traditional techniques, evaporation and sputtering.

1972: Spear and LeComber demonstrated that plasma deposited amorphous material can be made with a low density of states in the band gap.

1975: they demonstrated the material can be doped n-type and p-type by adding phosphine or diborane to the glow discharge gas mixture

## *1976: Carson and Wroski reported a solar cell based on amorphous silicon.*




After several years, it emerged that plasma-deposited amorphous silicon contained a significant percentage of hydrogen atom bonded into material structure.

These H atoms were essential to the improvement of the electronic properties of the material.

The improved form of amorphous material has generally been known as hydrogenated amorphous silicon (a-Si:H)

## *Advantages of amorphous silicon thin films*

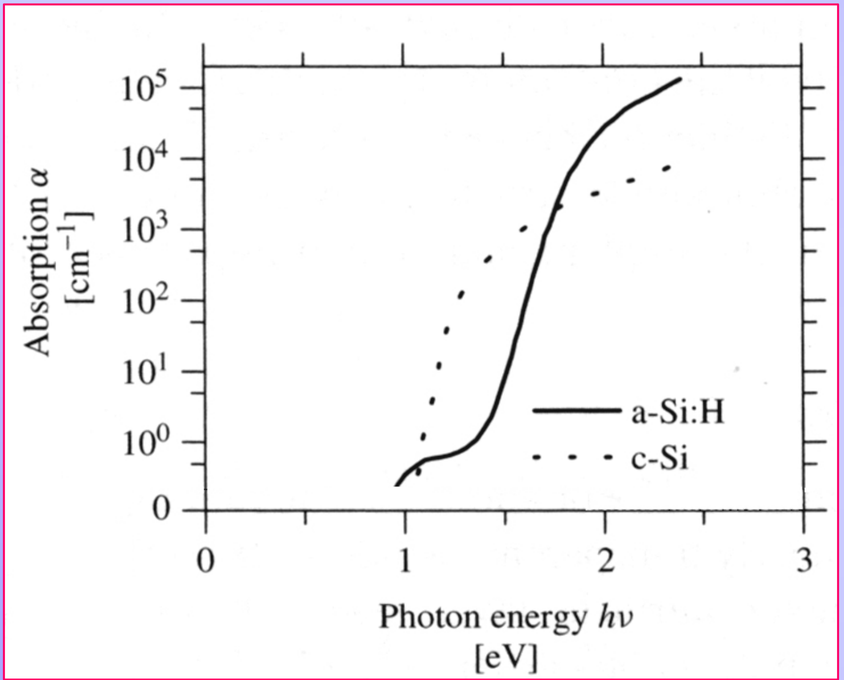
☺ Amorphous silicon has the advantage of being deposited at relatively low substrate temperatures (180–300 °C);

☺ it allows for the use of very low-cost substrates, such as cheaper forms of glass, stainless steel, aluminum, and especially polymers (polyimide, possibly also PET)

☺ It can be deposited on large area substrates with good uniformity

**.....Other advantages....**

Due to different optical properties, solar cells realized with a-Si:H are thinner with respect to devices fabricated with c-Si




✓c-Si energy gap: 1.1eV

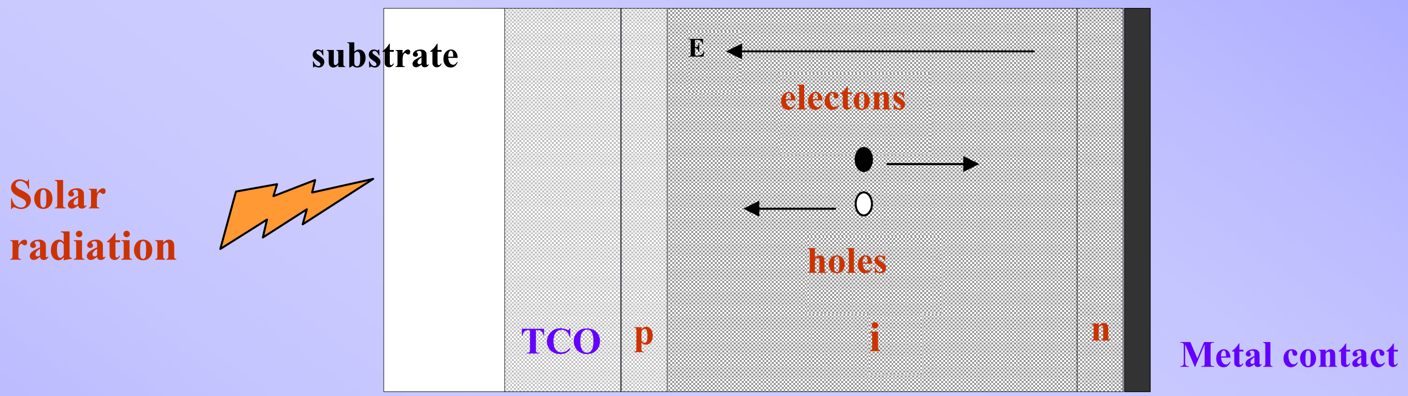
✓a-Si:H energy gap: ~1.75eV

☞Active layer thickness of a-Si solar cells: 200-500 nm

☞Active layer thickness of c-Si solar cells: 200-500 µm

# Amorphous thin silicon solar cells

## p-i-n single junction




- ✓Sun light enter the photodiode 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.

## Criteria for "device quality" intrinsic amorphous films

| *Property* | *Requirement* |
|---|---|
| Dark conductivity | $<1 \times 10^{-10}$ S/cm |
| AM1.5 100mW/cm2 photoconductivity | $>1 \times 10^{-5}$ S/cm |
| Band gap, Tauc | <1.8 eV |
| Absorption coefficient at 400 nm | $\geq 5 \times 10^{5}$ cm$^{-1}$ |
| Activation energy | ~ 0.8 eV |
| Density of dangling bond states | $\leq 1 \times 10^{16}$ cm$^{-3}$ |
| Hydron content | 9-11 at.-% |

## Criteria for doped a-Si:H layers for application in solar cells

| *Property* | *requirement* | |
|---|---|---|
| | *p-type a-Si:H* | *n-type a-Si:H* |
| Conductivity (S/cm) | $> 10^{-5}$ | $> 10^{-3}$ |
| Conductivity for a 20nm thick film (S/cm) | $> 10^{-7}$ | $> 10^{-4}$ |
| Band gap, Tauc (eV) | > 2.0 | >1.75 |
| Activation energy (eV) | < 0.5 | < 0.3 |

## ...problems!!!...

☹ ***Low efficiency***

☹ ***Low stability***

✓ One of the intriguing facets of amorphous silicon solar cells is the significant decline in their efficiency during their first few hundred hours of illumination

✓ This behavior is mostly due to Stabler-Wroski effect. The defect concentration of material increase after light soaking.

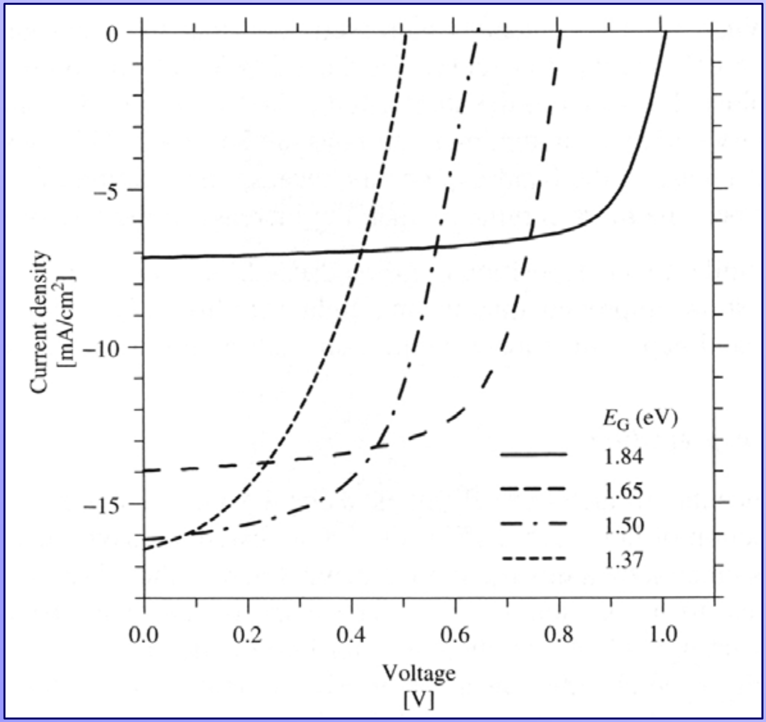
✓ The Stabler-Wroski effect contributes to noticeable variation in the conversion efficiency.

✓ This effect can be partially solved by using thinner intrinsic layers.

## ...To overcome the problems.....
## Amorphous silicon multijunction solar cells

✓ Multijunction solar cells use the concept of spectrum splitting

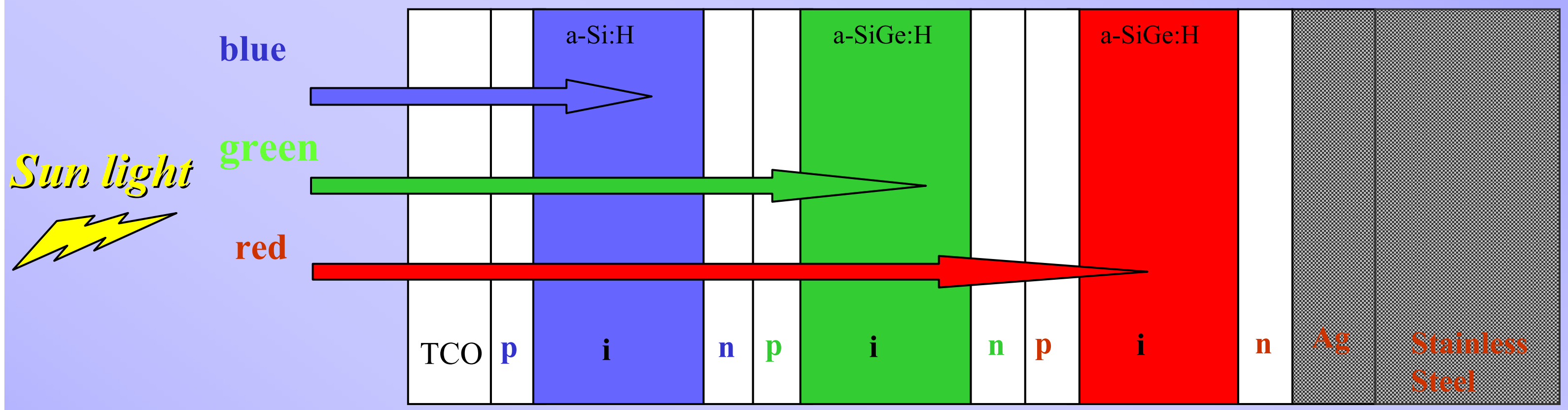
✓ To split the solar spectrum, active materials with different energy gap need to be used.




- **When a-Si is allowed with other elements such as Ge, C, O and N amorphous alloy materials with different band gap can be obtained.**
- **In particular, in the a-SiGe:H alloys the absorption edge is shifted to lower photon energy**

# a-Si multijucionction solar cells

The intrinsic material of different junctions has different energy gap

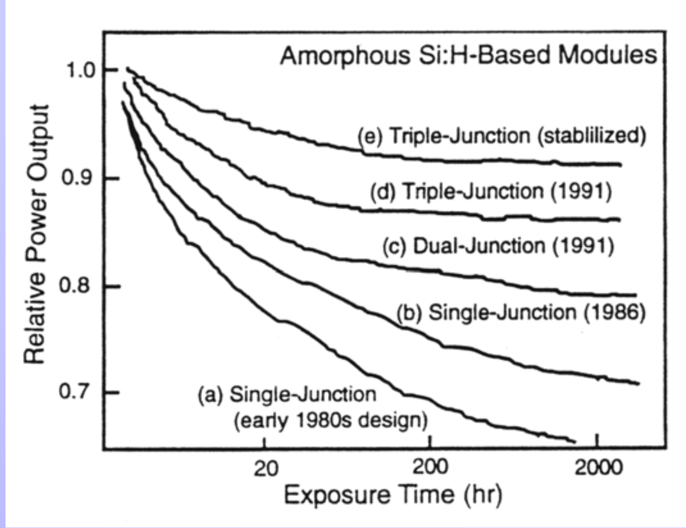



- ☞Top cell absorbs energies larger than 1.8 eV
- ☞Middle cell absorbs energies larger than 1.6 eV
- ☞Bottom cell absorbs energies larger than 1.4 eV

**Triple junction efficiency record: 13% on 0.25 cm$^2$ area**

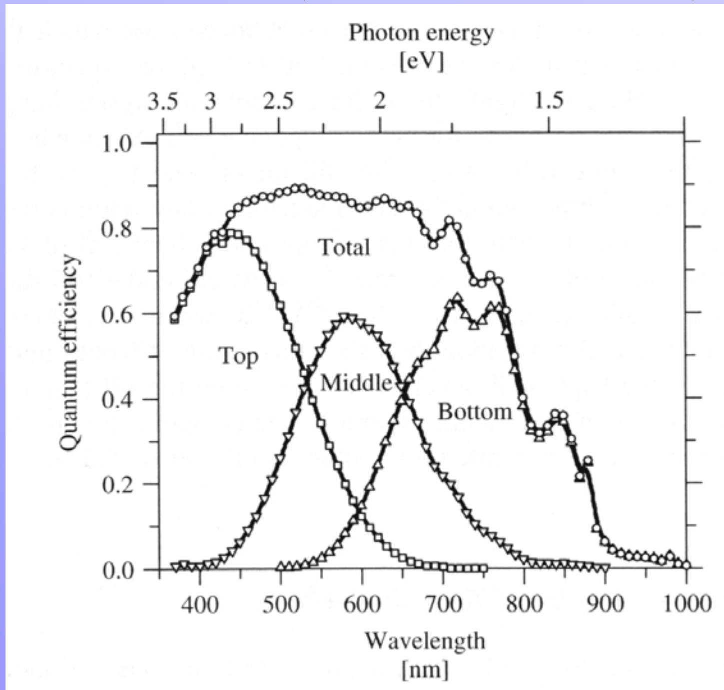
***Yang J. et al., APL, 70, 2977 (United Solar 1997)***

# Advantage of multijunctions




*Kazmerski L.L., Ren.&Sust. En.Rev. 1,Nos.1/2 (1997) 71*

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




Wang W et al., Conf. Rec. 29th IEEE (2002) 1082

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

## New development in thin film silicon:
## Microcrystalline silicon (μc-Si)

*Microcrystalline Si can be defined as a material containing amorphous tissues, crystalline grains (~20-30nm) and grain boundaries*

**Pioneering work was done in 1994 at University of Neuchatel by Meier et al.**

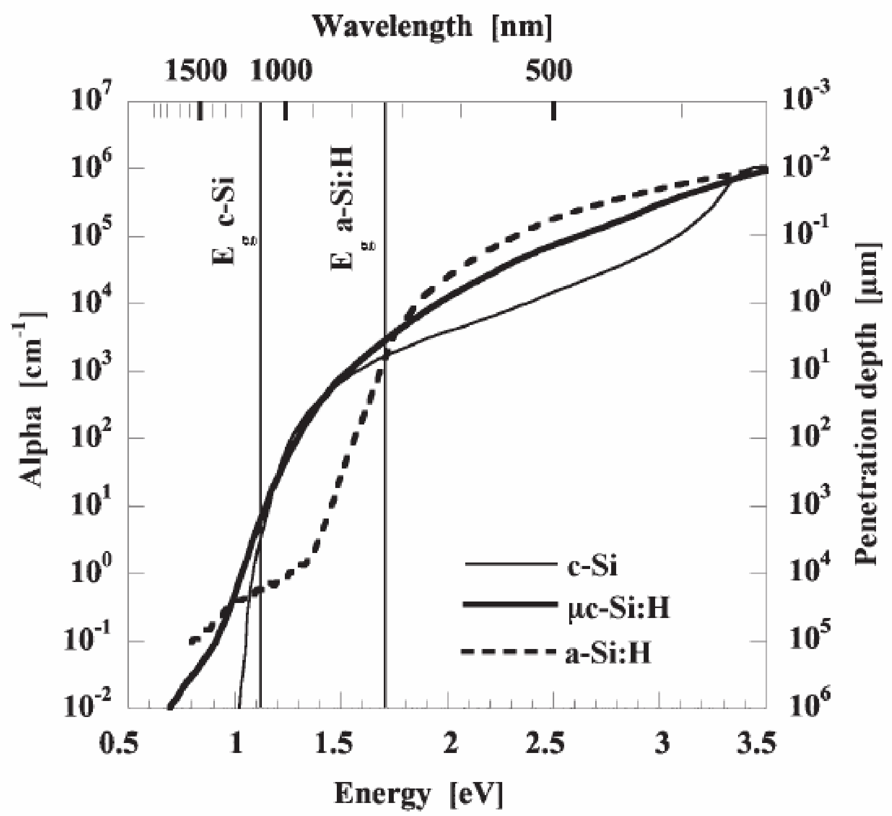
**pin-type μc-Si:H solar cell with stable conversion efficiencies of 4.6% was fabricated.**

The main attention of the cells fabricated with this new type of thin-film absorber material is:

☺ The stability to light soaking;

☺ The long wavelength response.

# *Optical properties of μc-Si:H*




*Poruba A. et al., JAP (88) 2000, 148*

✓The cross-over point between a-Si:H and μc-Si:H is around 1.75 eV.

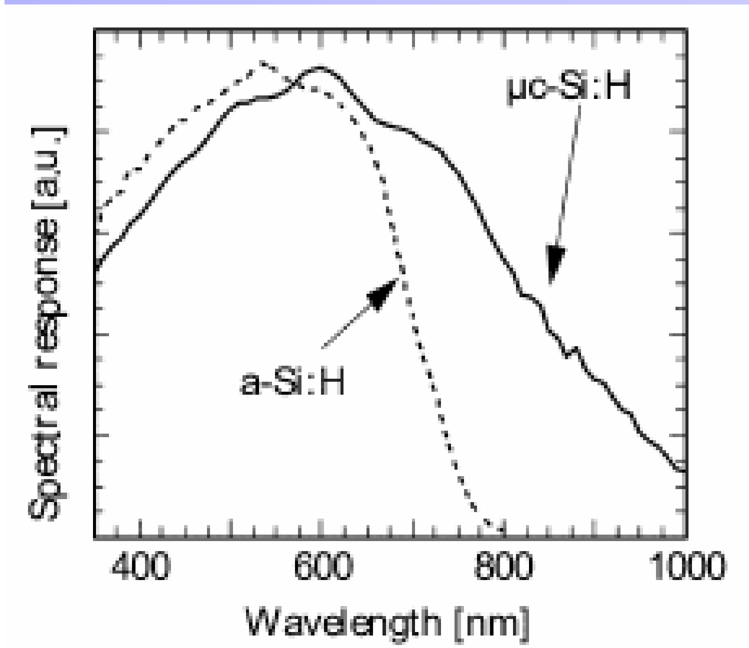
✓For hν > 1.75 eV amorphous layers have a higher value of absorption coefficient and for hν < 1.75 eV, microcrystalline layers have a higher value of α

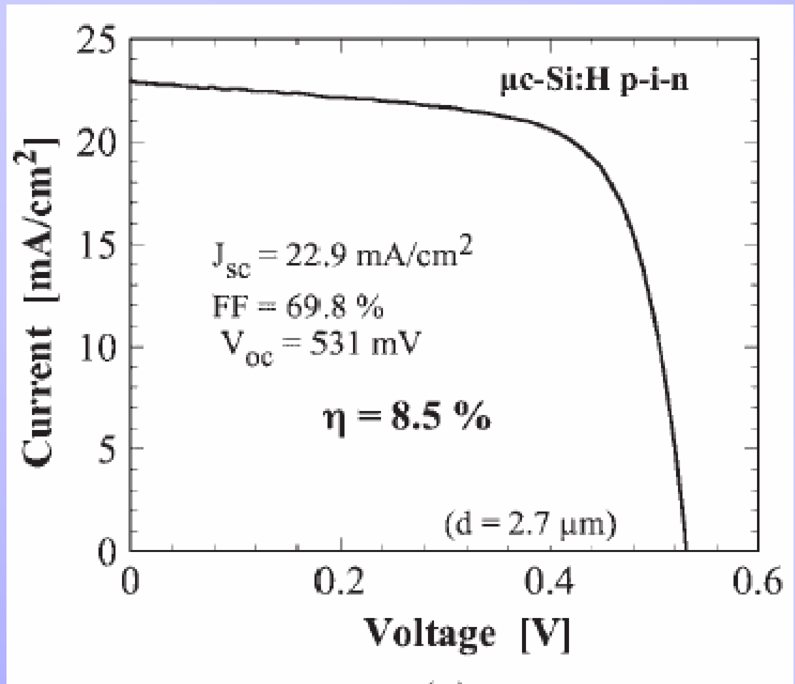
Silicon is a material with an indirect band gap, and, therefore, the absorption coefficient in all forms of crystalline silicon is relatively low.

**1-3 μm thick microcrystalline film needs to absorb the solar radiation**

# Criteria for 'device quality' microcrystalline silicon films

| *Property* | *Requirement* |
|---|---|
| Dark conductivity | <1 x $10^{-7}$S/cm |
| AM1.5 100mW/cm2 photoconductivity | >1.5 x $10^{-5}$ S/cm |
| Band gap | 1.0 – 1.1 eV |
| Absorption coefficient at 0.8 eV | < 1 $cm^{-1}$ |
| Activation energy | 0.5 – 0.57 eV |
| Crystalline fraction | 60 – 70 % |
| Orientation of grains (XRD) | Predominantly (220) |

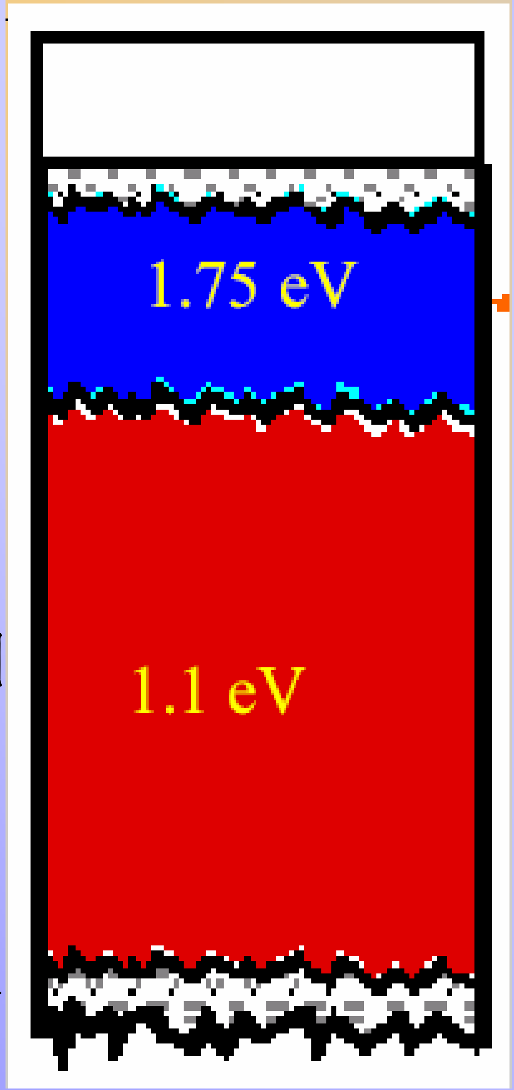


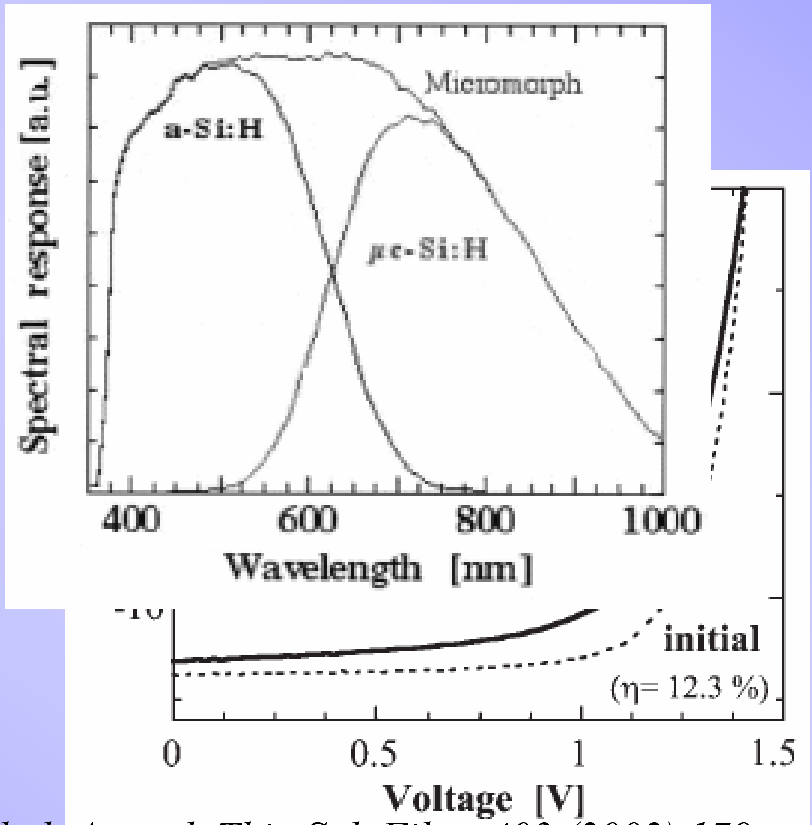

*Meier J et al., Proc. Mat. Res. Soc. Symp. 507 (1998) 139*

...by combining a-Si and μc-Si solar cells....

## *Micromorph tandem solar cells*




Spectral sensitivity of a-Si/μc-Si solar cell




*Shah A. et al. Thin Sol. Films 403 (2002) 179*

# *Advantages/disadvantages of microcrystalline-amorphous tandem solar cells*

☺Better utilization of the solar spectrum (1.75 eV & 1.1 eV band gaps)

☺ Elimination of costly germanium gas from the multijunction fabrication process

☺Better stability against light-induced effects

☹Fairly "thick" (> 1μm) microcrystalline (slowly deposited) absorber layers

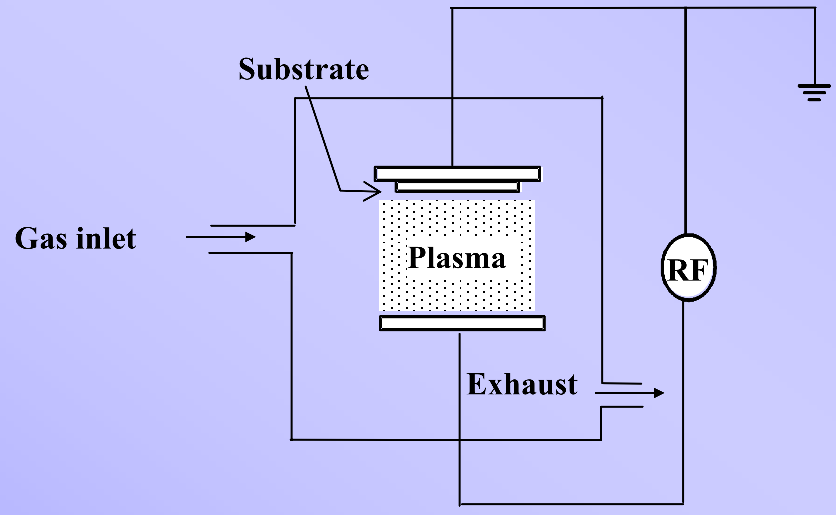
☹ Top cell still unstable

**Crucial point of PV thin film technology:**

## *Deposition technique*

- Chemical vapor deposition (CVD) is the most widely used process for making Si films.
- A source of gas, for example $SiH_4$, is decomposed in several possible ways such as plasma (PECVD), catalysis (Hot-wire CVD), etc.
- In most cases, the source gas is diluted with hydrogen to obtain the microcrystalline Si growth regime, whereas amorphous silicon is generally obtained with pure silane ($SiH_4$).
- The decomposed species after a series of gas phase reactions reach the substrate and deposit.

# Deposition process: PECVD




❖This deposition process is based on electron impact dissociation of a process gas such as silane in a plasma.

❖A low-pressure weakly ionised plasma created between two electrodes contains positive, negative and neutral species (radicals).

❖The powered electrode is called the cathode and the grounded anode electrode is where the substrate is attached for deposition.

✓The positive ions and the radicals reach the substrate and undergo surface reactions during deposition.

✓Radicals are considered to be the main precursors for the growth of both amorphous and microcrystalline silicon.

✓ It is agreed from many reports that $SiH_3$ is the main precursor for the device quality films.

# Deposition process: PECVD

PECVD using 13.56-MHz excitation is the most widley used today in manufacturing of a-Si-based materials.

High quality a-Si:H films are obtained at a growth rate of about 3 Å/s

....problems related to μc-SI:H deposition...

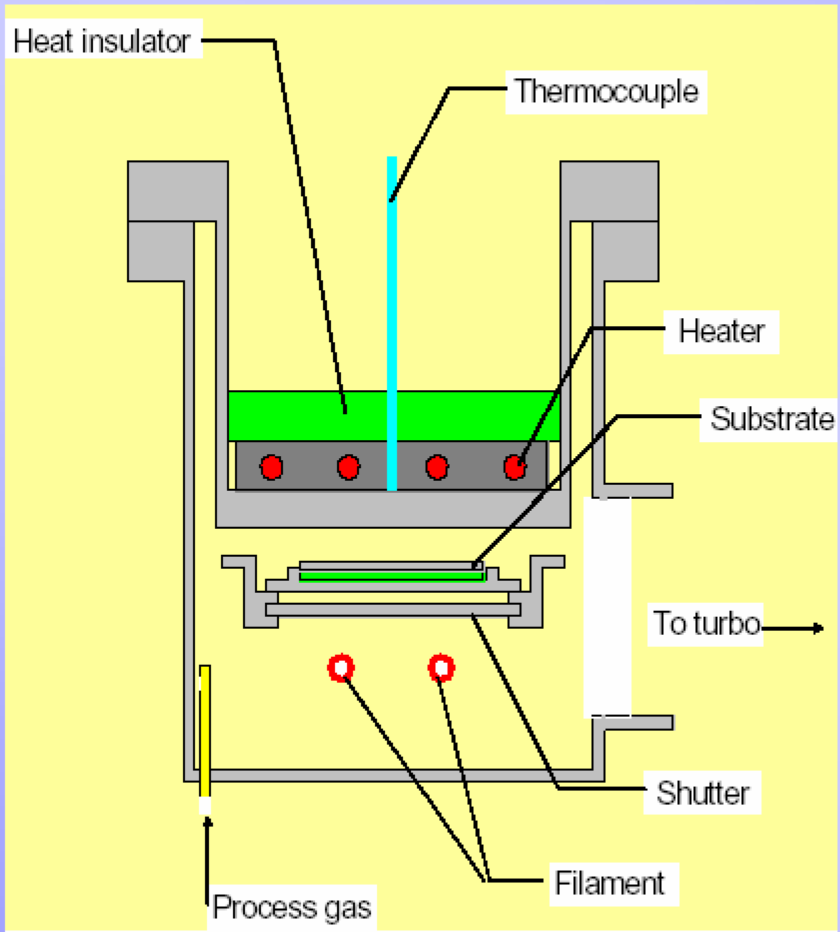
- ☹ **Low growth rate**
- ☹ **Effect of ion bombardment on the growing surface**

Trends in current thin film technology:

***development of faster deposition techniques***

- ☞ Very High Efficiency CVD (VHF CVD)
- ☞ Hot Wire CVD (HW CVD)
- ☞ Microwave CVD

# Hot Wire CVD




Silane molecules catalytically crack above 1500°C, in the presence of heated filaments:

$SiH_4 \rightarrow Si+4H$

$H_2 \rightarrow H+H$ (when $H_2$ dilution is used).

Hydrogen reacts with silane to create radicals :

$H+SiH_4 \rightarrow SiH_3+H_2$

Si is lost in a gas phase reaction:

$Si+SiH_4 \rightarrow Si_2H_4^*$.

$SiH_3$ along with abundant atomic hydrogen facilitates microcrystalline Si growth

# Hot Wire CVD

- W or Ta filament(s), resistively heated
- $T_{sub}$ = 200-500°C
- $T_{wire}$=1600-2000°C
- Deposition rate:
  a-Si:H : **10-150 Å/s**
  μc-Si:H : **5-30 Å/s**
- No ion bombardment; high H flux

Important parameter: substrate to filament distance.

A shorter value allows deposition of microcrystalline Si at a high growth rate

# Hot Wire CVD….advantages

- ☺ *Higher deposition rate, up to 100 x faster as in PECVD (due to high decomposition probability)*
- ☺ *Absence of ion bombardment damage; H radicals serve to control growth (also for low H content in the film)*
- ☺ *Minimal dust formation due to low operating pressures*
- ☺ *Structure controllable from fully amorphous to completely crystalline; deposition of alloys from combinations of source gases*
- ☺ *Low equipment cost*

# Hot Wire CVD….disadvantages

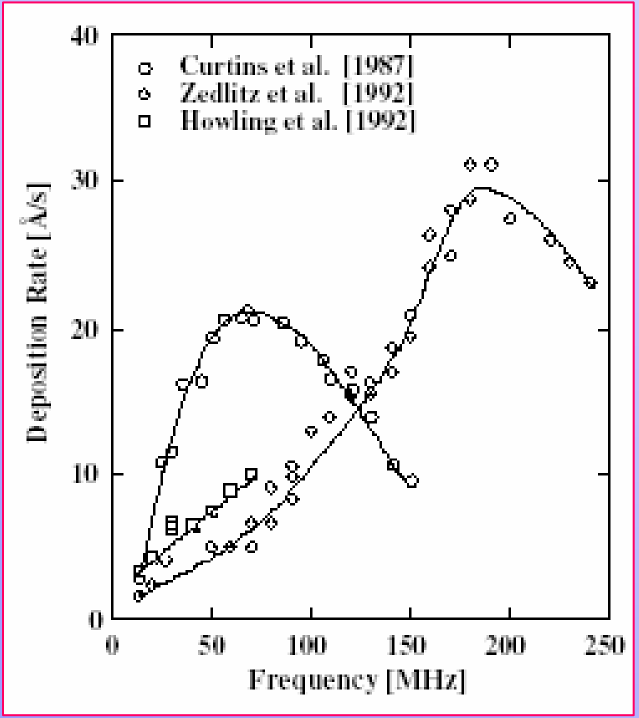
- ☹ *Ageing of the filaments (effect on chemistry)*
- ☹ *Breakage of the filaments*
- ☹ *Contamination of deposited films with metal impurities from the wires*
- ☹ *Non-uniformity of the films and therefore no Large area capability*

# Higher rates for HW a-Si and μc-Si solar cells

| Laboratory | Structure of solar cell | η (%) initial | rate (Å/s) |
|---|---|---|---|
| NREL/UU | SS/Ag/ZnO/ ni(μc-Si)p/ITO/grid | 4.9<br>6.6 | 10<br>6 |
| Utrecht University | plain SS/ni(μc-Si)p/ITO/grid<br>plain SS/ni(μc-Si)p/ITO/grid | 4.8<br>5.7 | 10<br>2.4 |
| TIT, Japan | tex. $SnO_2$:F/ pi(μc-Si)n/ZnO/Ag/Al | 4.8 | 3.4 |
| University Barcelona | flat ZnO:Al/pi(μc-Si)n/M | 2.5 | 8 - 9 |
| Ecole Poly-technique | Asahi $SnO_2$:F/n i(μc-Si)p/Ag | 4.6<br>5.1 | 1.5 ~ 4*<br>2.5 |
| Utrecht University | plain SS/n i(μc-Si)p/n i(a-Si)p/ITO | 8.1 | poly: 5<br>a-Si: 10 |
| NREL | SS/ ni(a-Si)"e"p/ITO/grid | 5.7→3.7<br>6 →4.0<br>5.8→4.8 | 127<br>80<br>50 |

# Very High Frequency CVD

An increase in plasma excitation frequency from the standard frequency of 13.56MHz to values between 70 and 130MHz, permits an increase in deposition rate by a factor of 4–10, both for a-Si:H as well as for μc-Si:H layers.



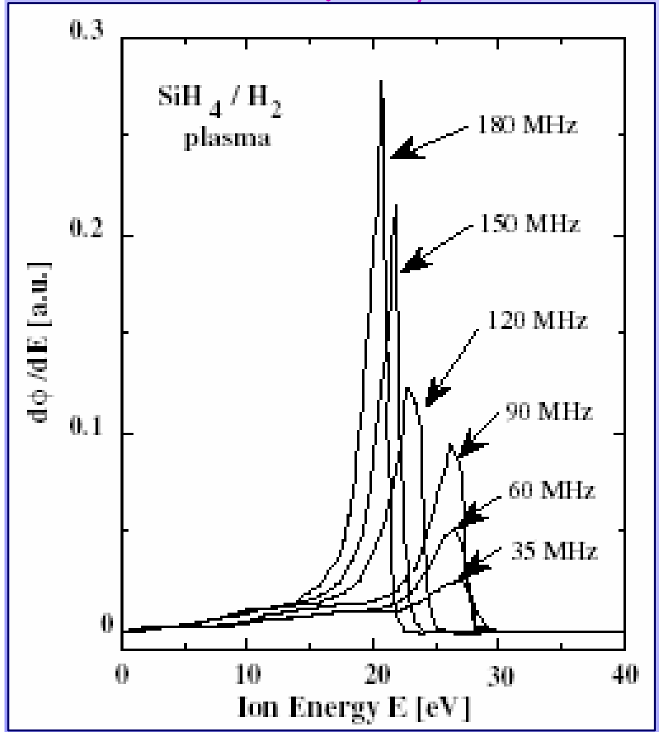

- ✓Curves of deposition rate vs. excitation frequency possess a maximum at a certain "optimal" frequency;
- ✓The decrease of deposition rate at higher frequencies can be due to engineering aspects like reactor design.

# VHF PECVD

☞Radicals are considered to be the main precursors for the growth of both amorphous and microcrystalline silicon.

☞It is agreed from many reports that $SiH_3$ is the main precursor for the device quality films.

☝ It is mainly the ions which determine the final film quality.



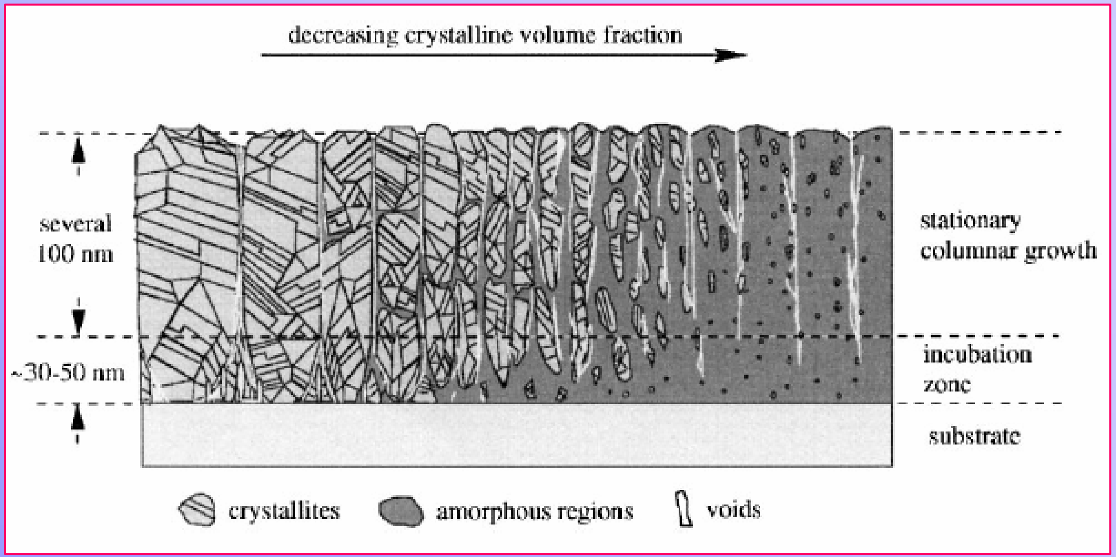

At higher frequencies the peak ion energy is reduced and the ion flux is increased

**The higher ion flux and the lower energy of the ion bombardment lead to a "softer" but "intensified" ion bombardment and might be a reason why VHF-plasmas favour microcrystalline growth.**

*Heintze and Zedlitz, J. Non-Cryst. Sol. 198 (1996) 1038*

# VHF PECVD.....important parameters:

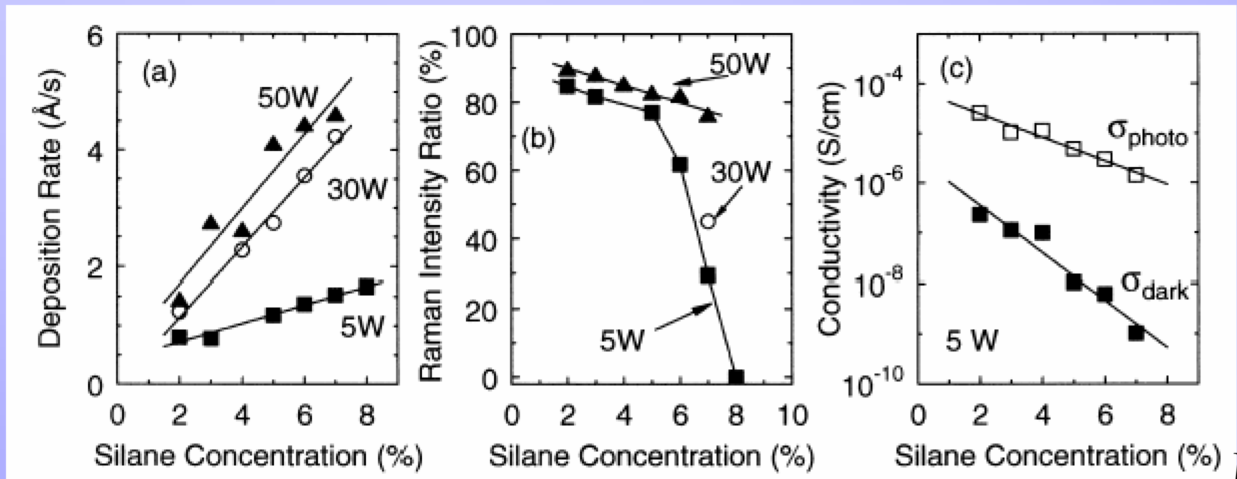
- ✓Hydrogen dilution
- ✓Substrate Temperature
- ✓Chamber pressure
- ✓ Power Discharge
- ✓Flow rate of gas mixture




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

# VHF PECVD....$H_2$ dilution

By increasing the silane concentration from ~2% to 10% the high crystalline volume fraction is maintained initially but drops sharply in a transition region typically around 6-10%.

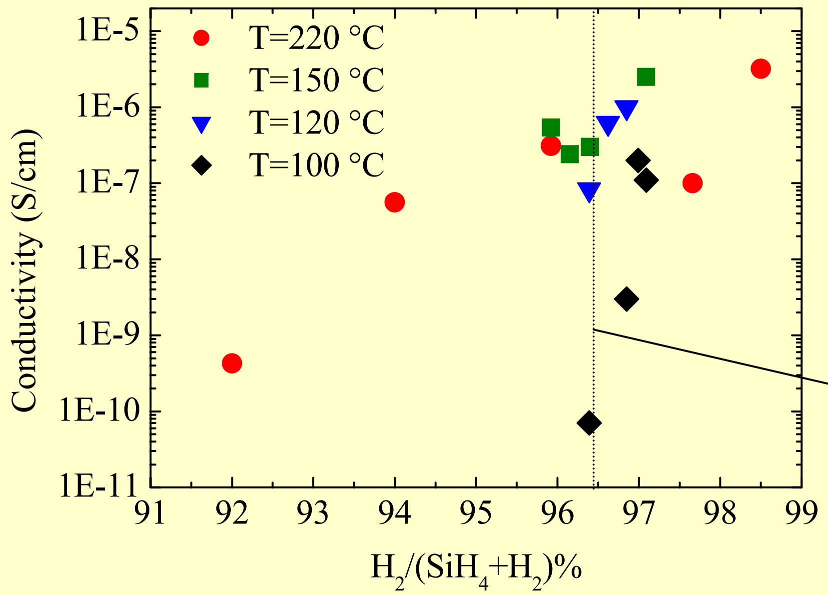



*Vetterl O. et al., Sol. En. Mat. & Sol. Cells, 62 (2000) 97*

☝It is important to study the transition region.

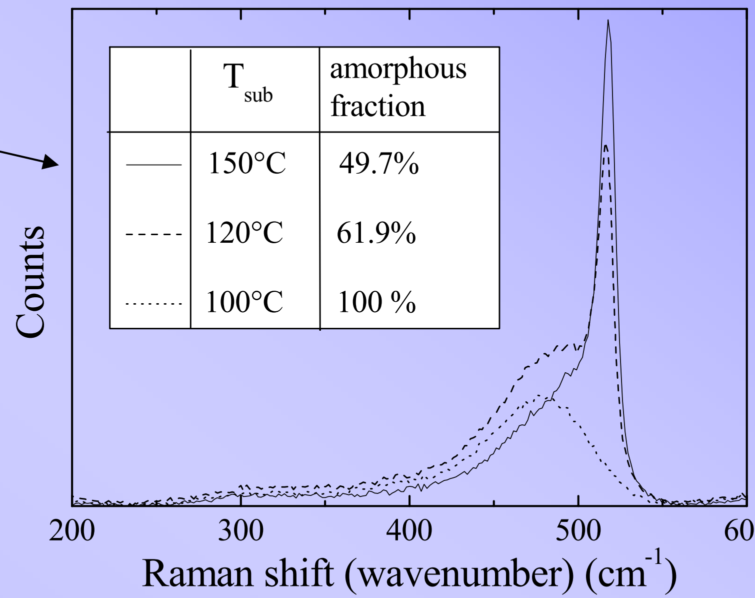
☝In fact, the optimum phase material, which results in the highest solar cells efficiency, was found close to the transition region.

# VHF PECVD.... deposition temperature effects




*P. Delli Veneri et al. Proc. of 19° EPVSEC (2004)1469*

At fixed $H_2$ dilution $\sigma_D$ increases when the growth temperature is raised.




| | $T_{sub}$ | amorphous fraction |
|---|---|---|
| —— | 150°C | 49.7% |
| - - - - | 120°C | 61.9% |
| ········ | 100°C | 100 % |

The a-Si -> μc-Si transition region changes in position.

**Lowering the growth temperature is important:**

- ☞ For the application of μc-Si:H films on flexible substrate
- ☞ To avoid incorporation of impurities from substrate and underlying layers.

## VHF PECVD....further increase of growth rate

### High pressure depletion method

- The high pressure provides sufficient silane molecules and prevents ion damage

- High Discharge power is used to decompose most of the silane:

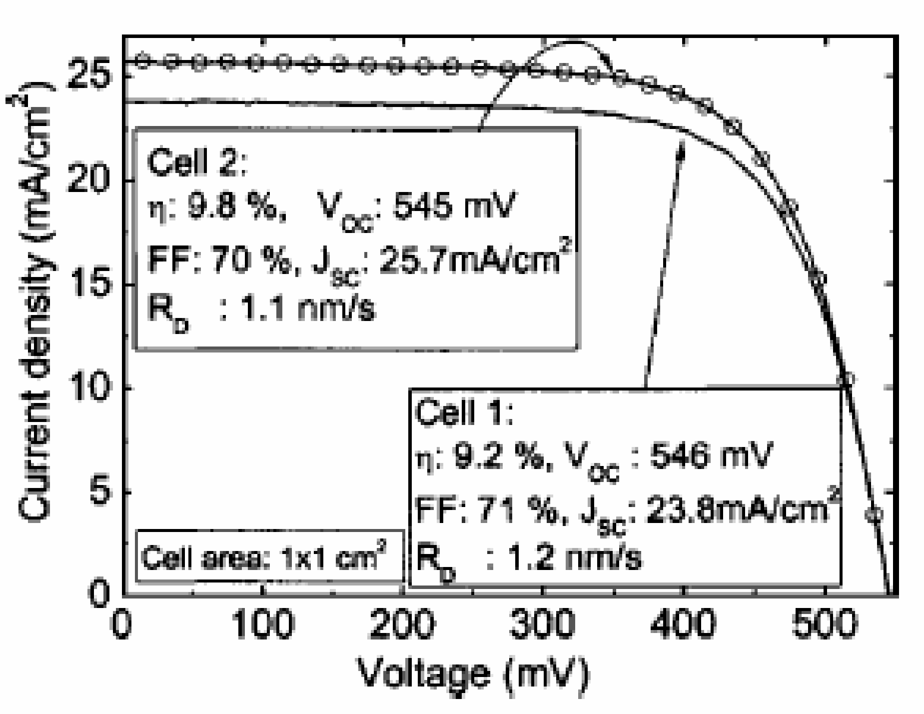
$$SiH_4 \rightarrow SiH_x + (4-x)H.$$

- Under the silane-depletion condition, the reaction

$$SiH_4 + H \rightarrow SiH_3 + H_2$$

where silane molecules annihilate atomic hydrogen, will be suppressed and a high atomic hydrogen density is maintained.

# Recent results obtained with High pressure Deplition method

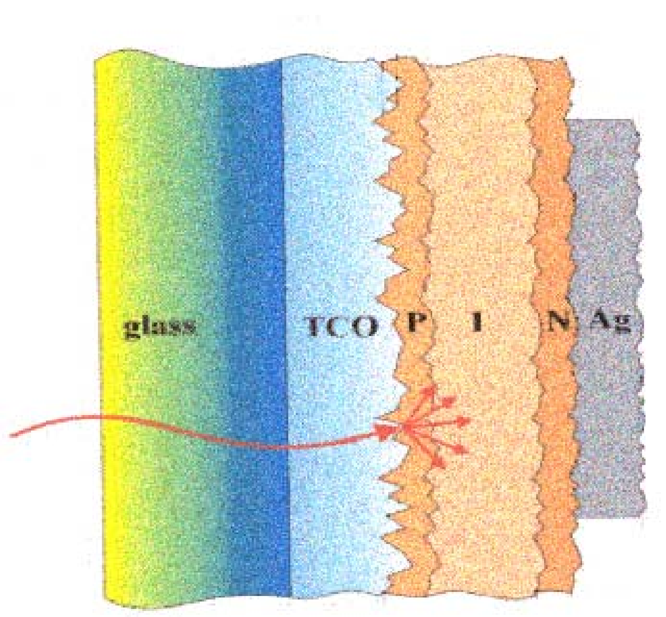


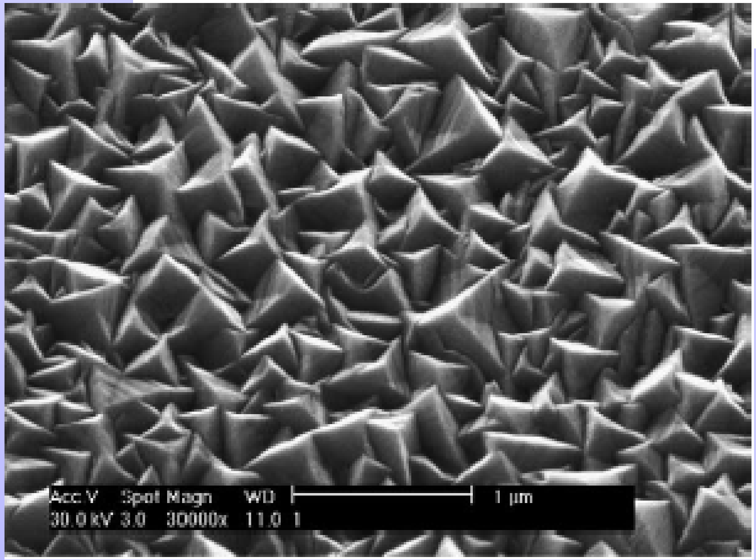

*Mai Y. Et al., JAP 97, (2005) 114913*

- ✓Intrinsic layer deposited at 95MHz
- ✓Deposition pressure: 1.5 Torr
- ✓Discharge power: 60W
- ✓Cell1 tickness: 1.4 µm
- ✓Cell2 tickness: 2.0 µm

## ...other issues related to thin film technology...
## Light trapping

The possibility to use rough transparent conductive oxide (TCO) is fundamental in increasing the efficiency of thin film solar cells




High-quality TCO needs:

- ✓High electrical conductivity
- ✓High transparency
- ✓High light-scattering ability

Microcrystalline solar cells need zinc oxide (ZnO) as transparent conductive oxide for its high stability against hydrogen plasma

## ZnO films can be deposited by:

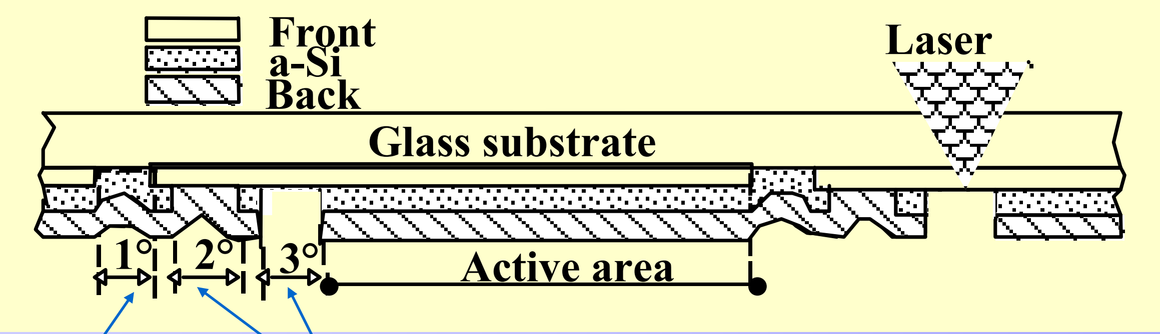
- ✓ LP CVD (the as grown material is high textured)
- ✓ Sputtering (a chemical etching step in diluted acid yields a textured surface)

↓

***The processes involved in ZnO deposition are entirely compatible with low-cost substrates (inexpensive glass, polymers, aluminum, stainless steel etc.)***

# Fabrication of large area modules

**Large area a-Si module interconnection by laser scribing**

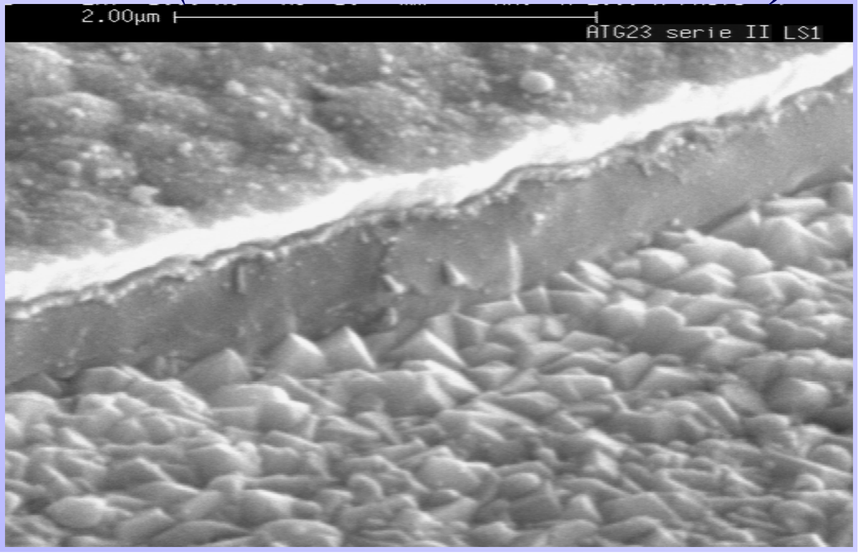



Nd-YLF laser source(λ =523 nm)

Nd-YAG laser source(λ=1064 nm)

In order to reduce the series resistance losses that occur upon scaling up the cell area, the modules are constructed with monolithically interconnected cells. The series connection of the individual cells on the same substrate is achieved by including some laser patterning steps between the layers deposition steps.

*(ENEA Patent RM94A000199)*

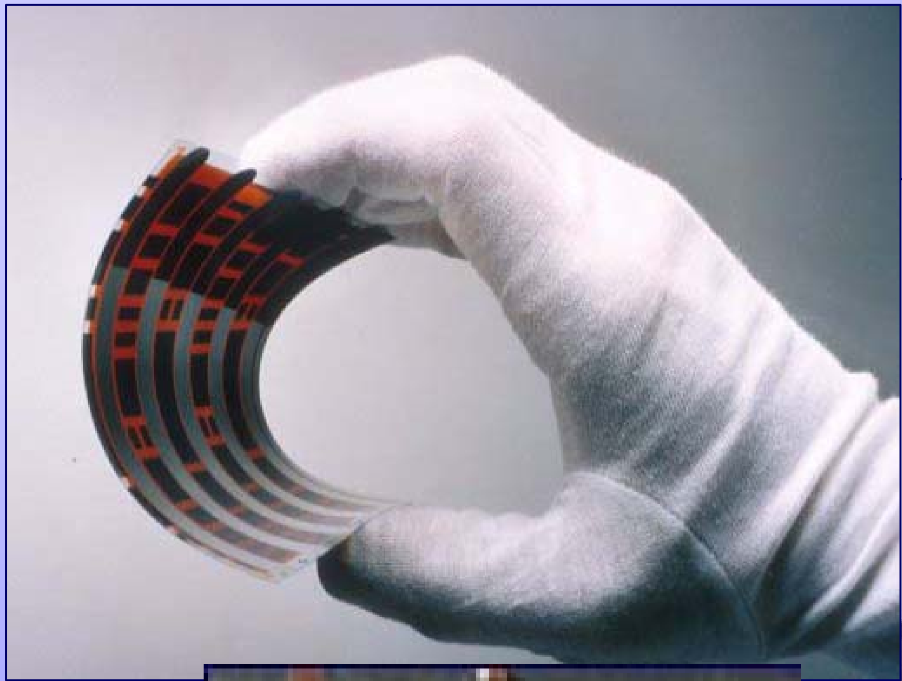


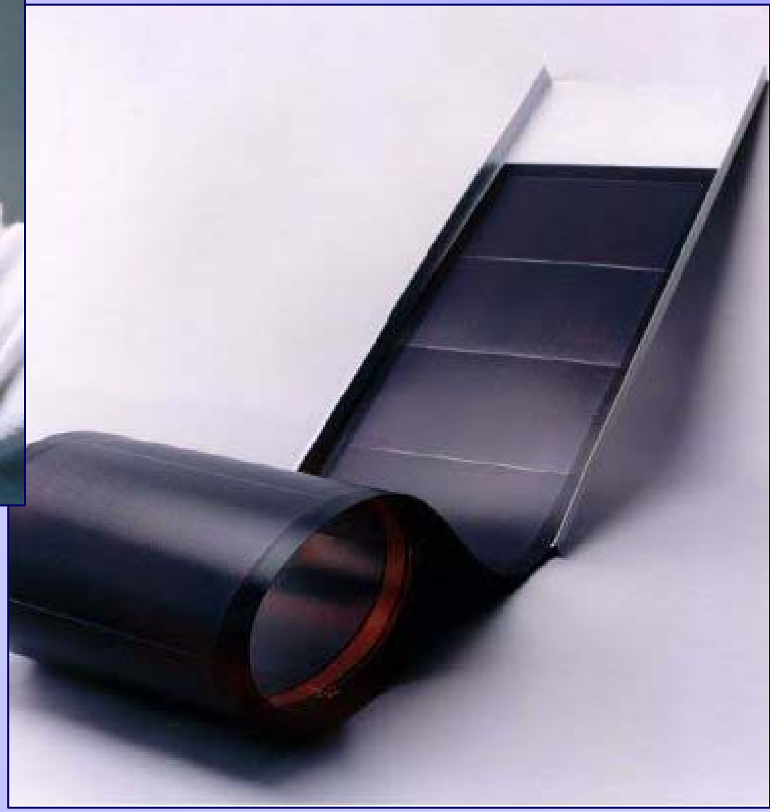
## Amorphous silicon modules with different light trapping

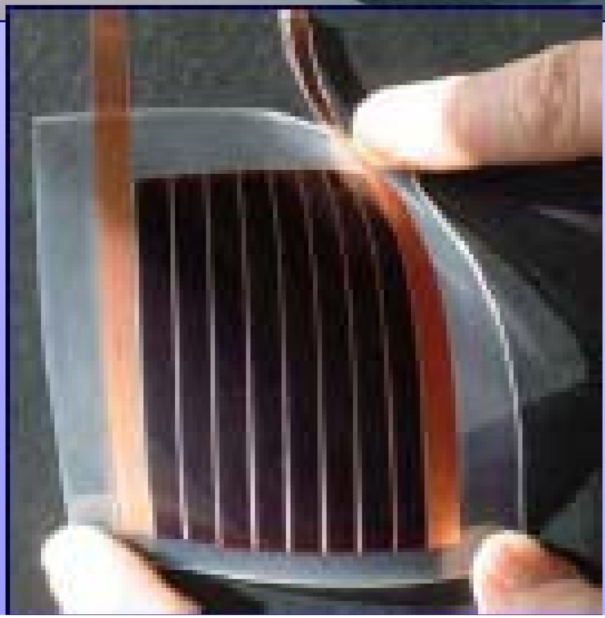
## Semi-transparent modules

**The transmission can be adapted by the absorber thickness, the choice of front TCO and in addition to the amount of scribed area.**

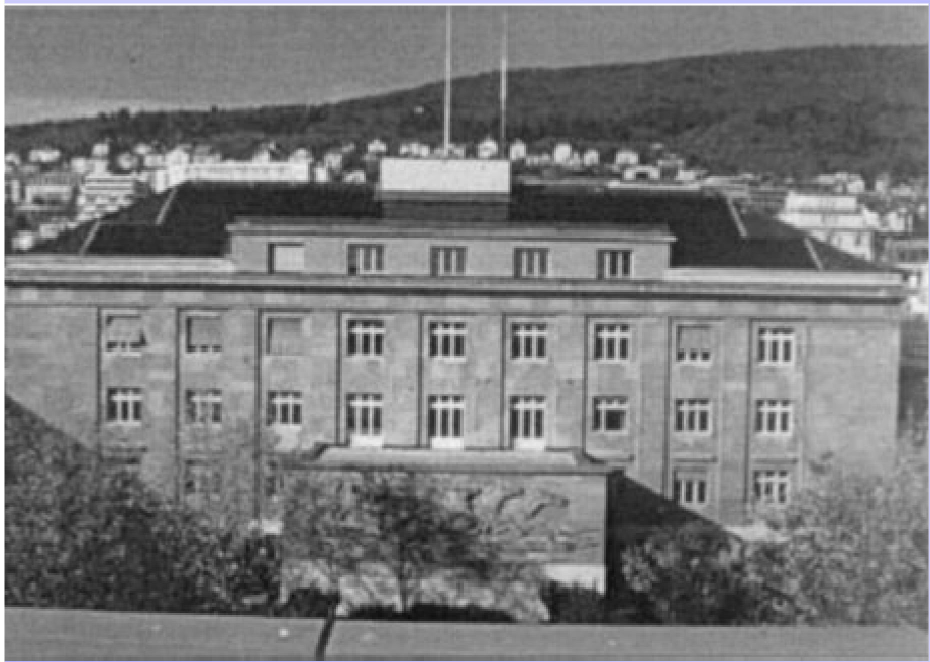
# Flexible substrate



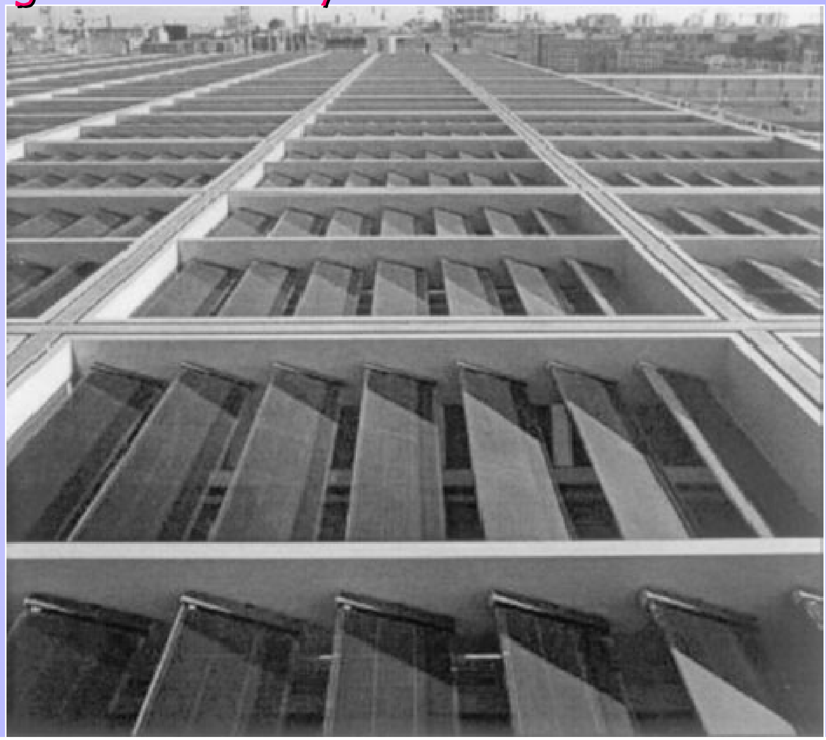




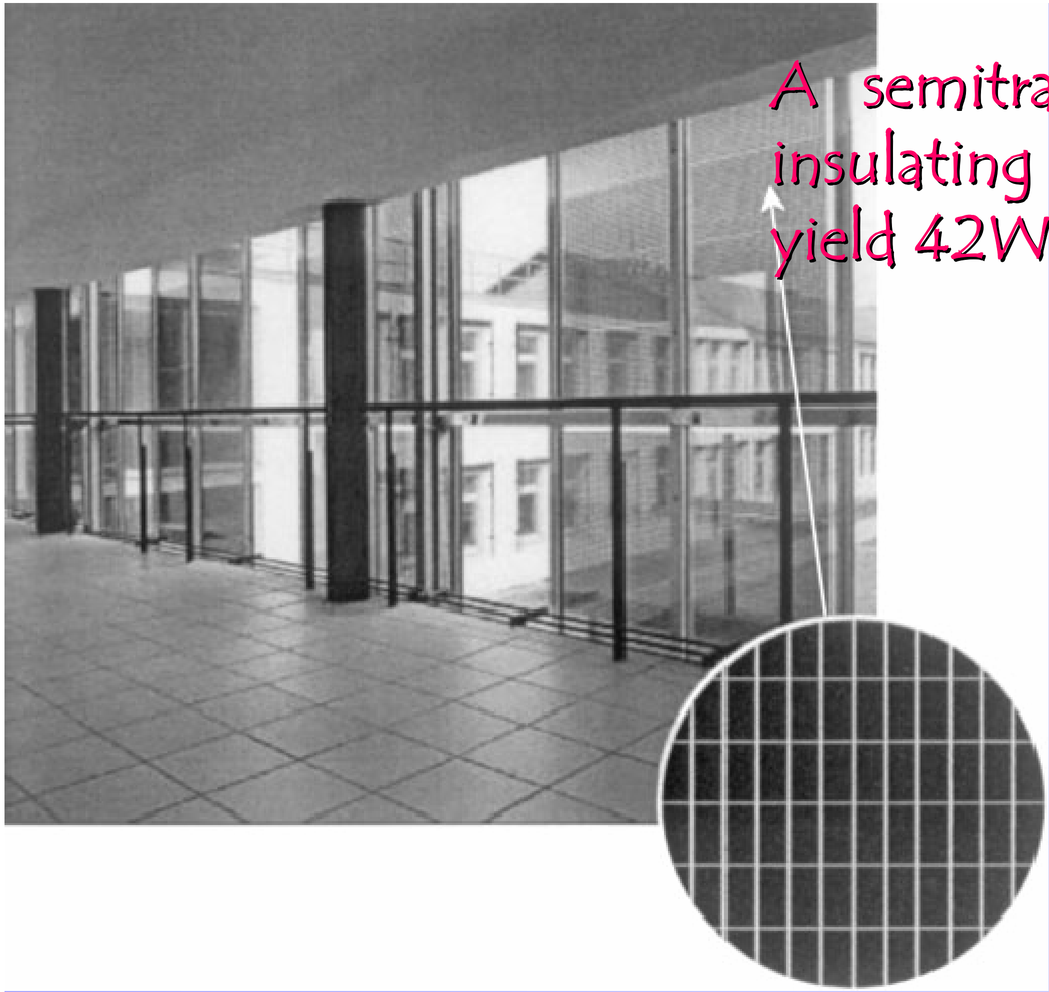
# Architectural integration



A roof-integrated a-Si installation on the building of the Institute of Microtechnology at the University of Neuchatel. It consists of amorphous silicon tandem modules with a nominal power of 6. 4 kW to cover a total area of 122m$^2$; about 16m$^2$ of this area is equipped with semitransparent modules to provide day light to a library area.



A roof construction for an annex building of the German parliament in Berlin that incorporates semitransparent modules (3300m$^2$) arranged as louvers for a nominal power of 123kWp



A semitransparent facade consisting of insulating laminated glass elements that yield 42Wp/m2.

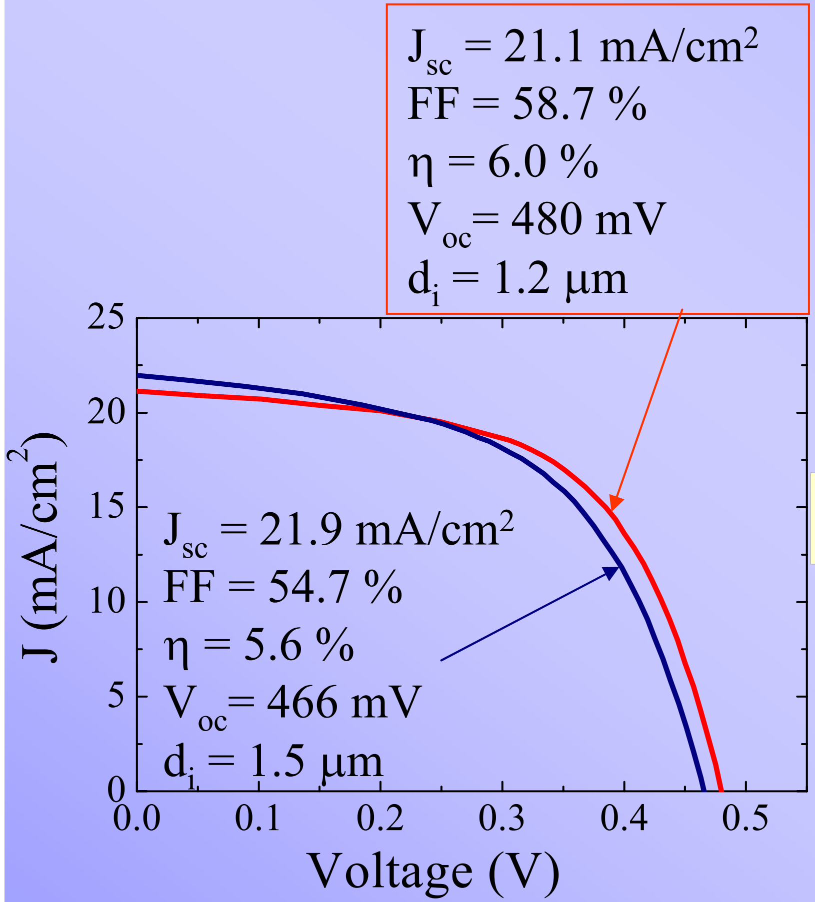
An opaque building facade, installed with a nominal power of 6.5kWp at the Bavarian Ministry for Environmental Protection

## Enea Research Center....Thin film silicon solar cell activity

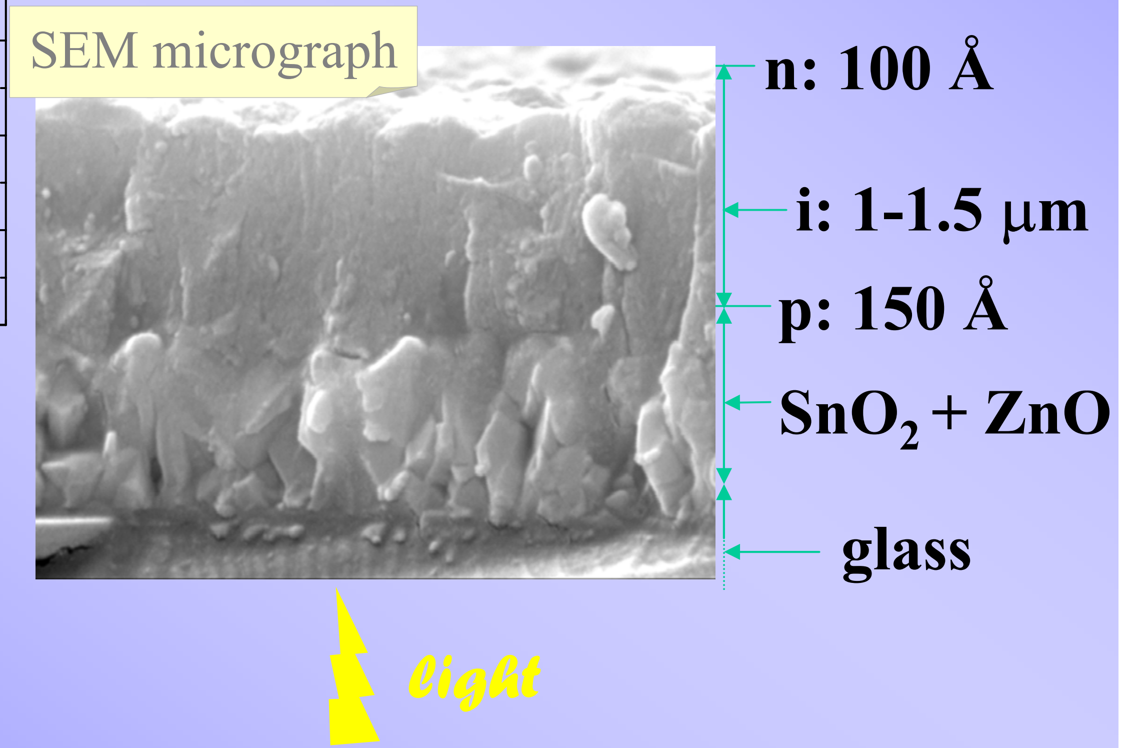
# *Thin film silicon deposition system*

Ultra High Vacuum Cluster Tool System

# *Thin film solar cells:* microcrystalline silicon solar cells




p-i-n type devices
Substrate: glass/SnO2/ZnO
Area: 1 cm x 1 cm



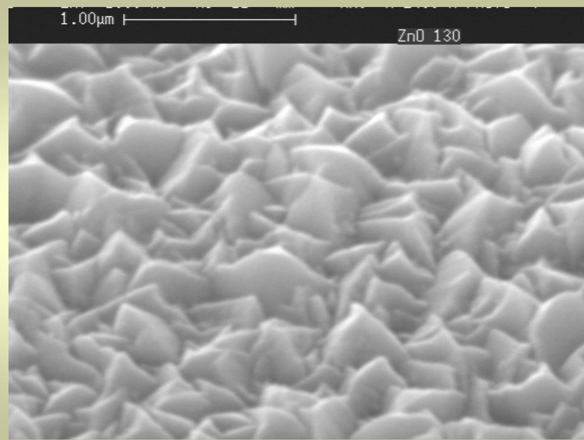
# Thin film silicon solar cells

## TCO development and light trapping strategies

Microcrystalline solar cells need zinc oxide as transparent conductive oxide for its high stability against hydrogen plasma

### 1st approach: ZnO:B deposition by MOCVD

**Since 1994 an activity on ZnO deposited by MOCVD was present in our laboratories and ZnO:B layers were utilised for different solar cells such as: a-Si:H, CIS, heterojunction.**
**The good roughness of this material gave us excellent results in terms of high Jsc values.**



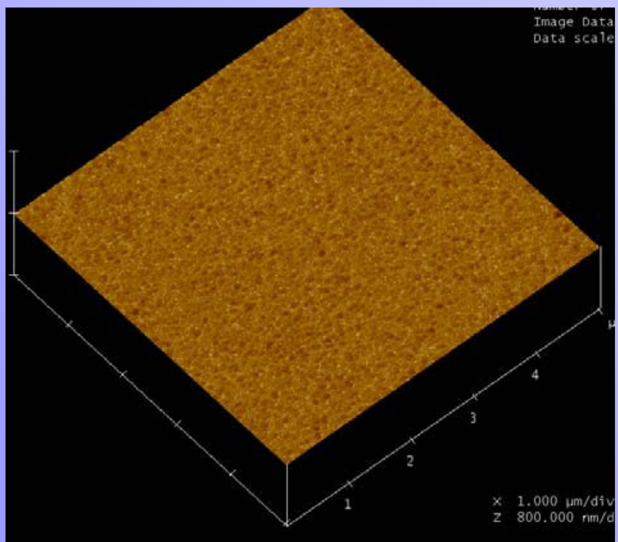

- ✓ The old ENEA apparatus (proprietary design) was able to deposit on 10 x 10 $cm^2$.
- ✓ We have developed and realized a new MOCVD apparatus able to deposit on 30 x 30 $cm^2$.

## 2nd approach: chemical etching of flat ZnO deposited by RF sputtering

- ✓ZnO:Al on glass deposited by RF sputtering. Columnar structure with a grain size of 360 Å
- ✓Etching by diluted solution of HCl (0.5%)

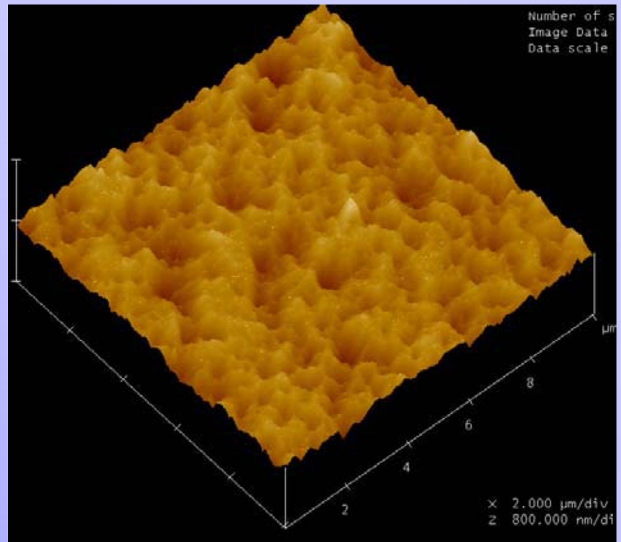
**Before etching**

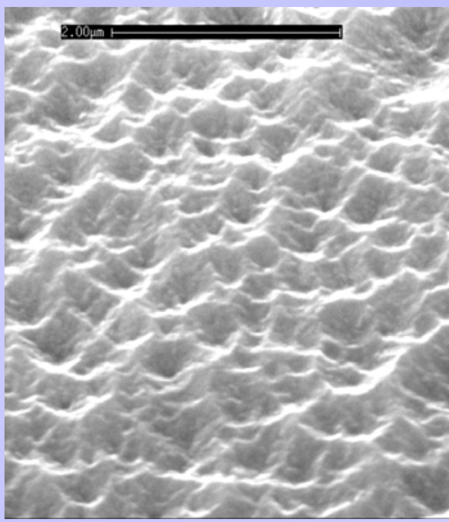
RMS (by AFM): 6nm
Haze: 0.3 %
Rsh: 6 **Ω**/□




**After etching**

RMS = 54 nm
Haze = 24 %
Rsh: 10 **Ω**/□

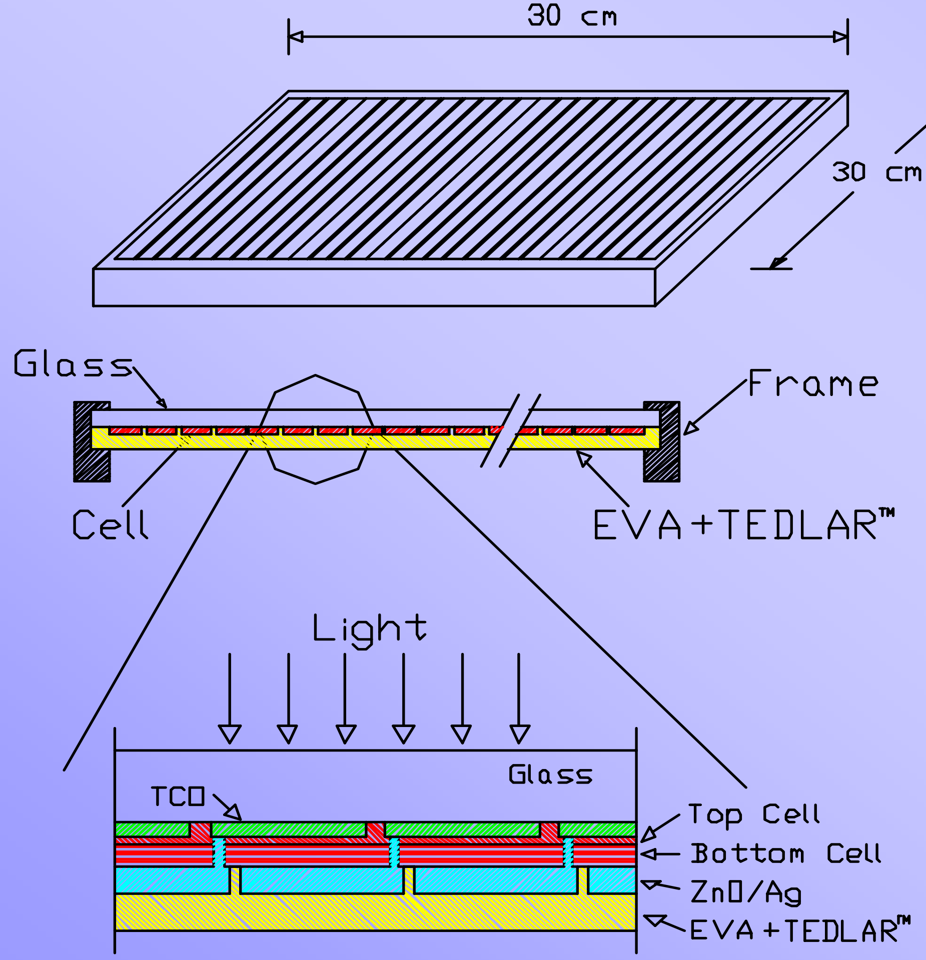


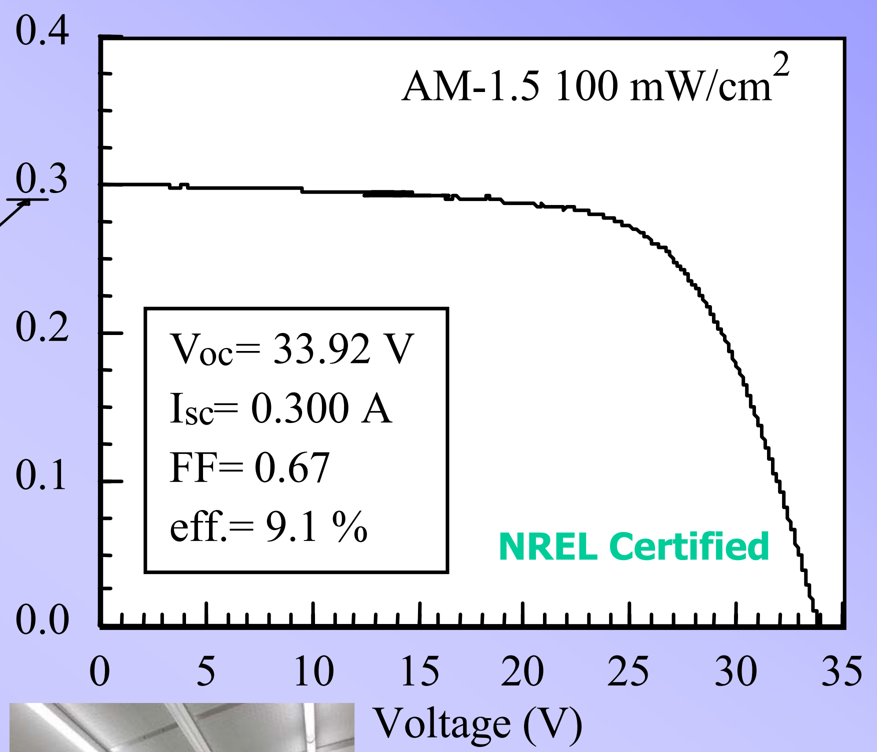



# Thin film silicon solar cells

## Amorphous silicon multijunctions: large area

### a-Si/a-Si module on glass




Single chamber large area deposition system

# Conclusion

**Thin-film silicon constitutes at present one of the most promising material options for low-cost, large-scale terrestrial applications of photovoltaics.**

## Thin films silicon advantages:

- ☺ it is abundant and non-toxic;
- ☺ it allows for low-temperature large area fabrication processes;
- ☺ it involves only a very reasonable quantity of energy for the fabrication of full solar modules;
- ☺ fabrication costs for modules are potentially much lower than those of crystalline silicon modules, even if this so far has not translated into actual corresponding price differences for commercial modules.