# Advances in structural, electrical and optoelectronic characterization of thin nanocrystalline silicon films for photovoltaic applications

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# Outline

- Materials
- Methods and Results
  - Structural Characterization
    - Stress measurements and transmission electron microscopy)
    - Atomic Force Microscopy
      XRD, Raman spectroscopy, and FTIR
  - Electrical characterization
    - C-AFM
    - Conductivity
  - Optoelectronic characterization
    - SPV (Surface Photovoltage Spectroscopy)
      Photoluminescence measurements and Quantum confinement studies
- Conclusions

# Materials

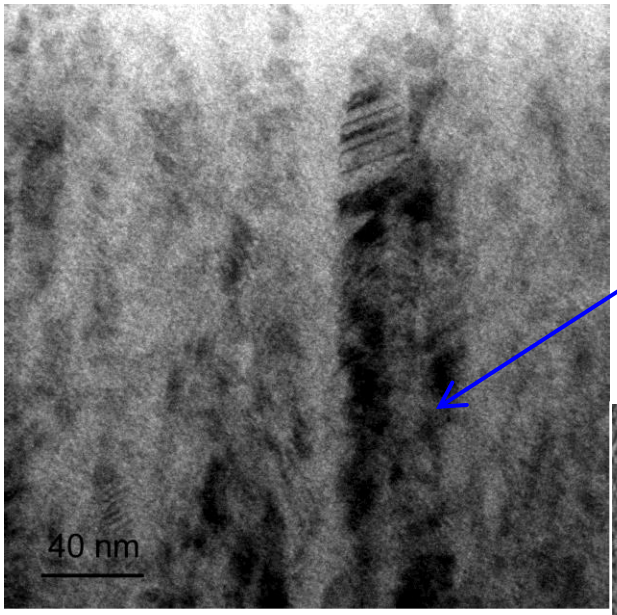
nc-Si:H grown by

Low Energy Plasma Enhanced Chemical Vapour Deposition (LEPECVD)

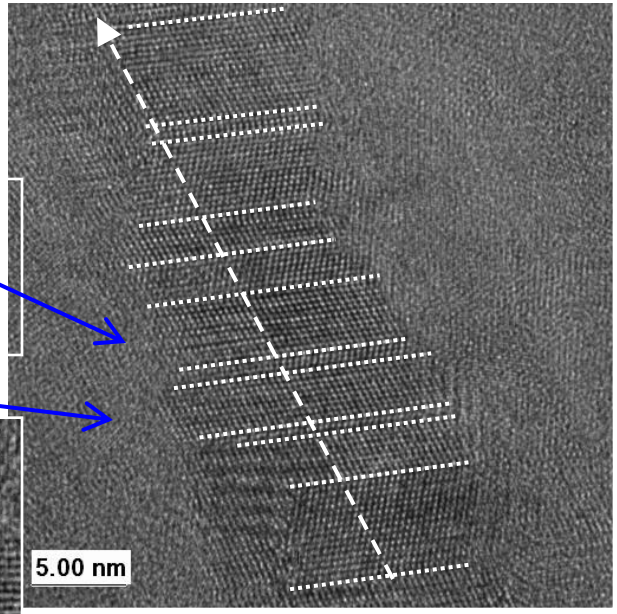
| Substrate | $X_C$ [%] | Ts[°C] | t[mm] | Growth rate [nm/s] |
|---|---|---|---|---|
| $SiO_2$/Si | 65 ÷ 70% | 208 ÷ 280 | 1.5 ÷ 1.7 | 0.17 ÷ 1 |
| Si | 10 ÷ 50% | 280 | 1 ÷ 2 | 2.5 ÷ 3.5 |
| Glass & Glass/ITO | 13 ÷ 80 | 250 | 1 ÷ 4 | 3.1 ÷ 4.3 |

## $SiO_2$/Si substrates

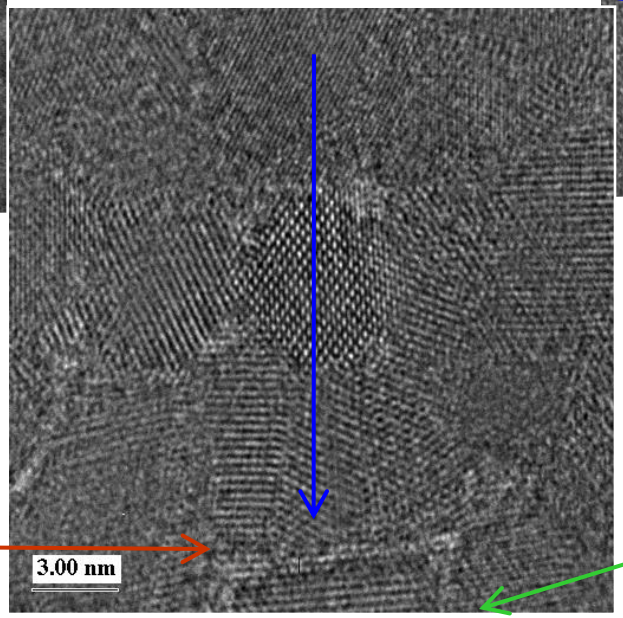
In all the specimens the structure is similar, whatever the growth parameters




Many twins within the nanocrystalline columns embedded in a-Si




40 nm




5 nm

High crystallinity

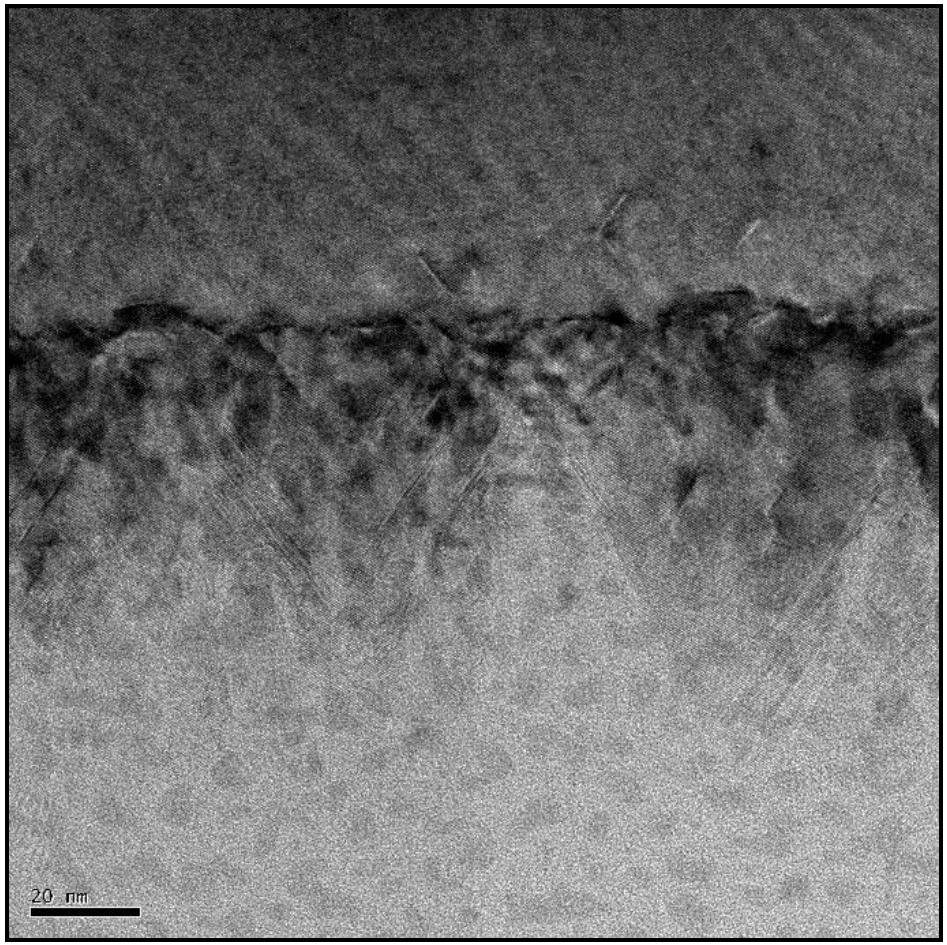
Very thin a-Si intergrain boundaries

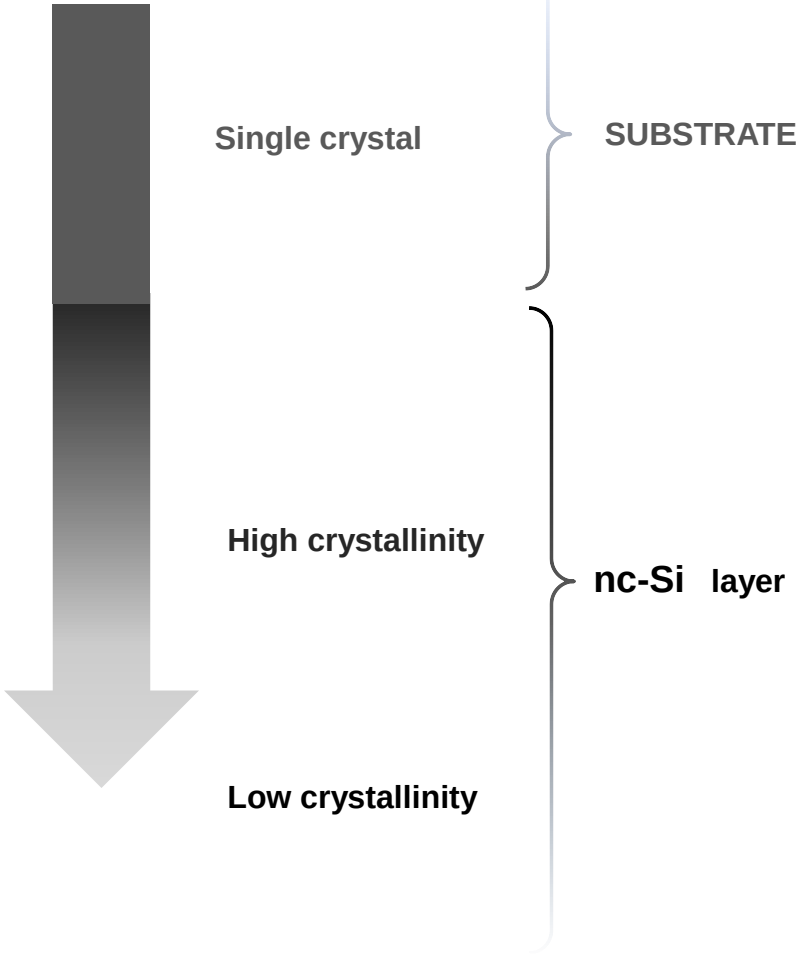
Nanophoto
NANOcrystalline silicon films for
PHOTOvoltaic and optoelectronic applications

# Si substrates

Cross section view: intermediate magnification TEM observations

For all the specimens, the structure is **heterogeneous** along the growth direction

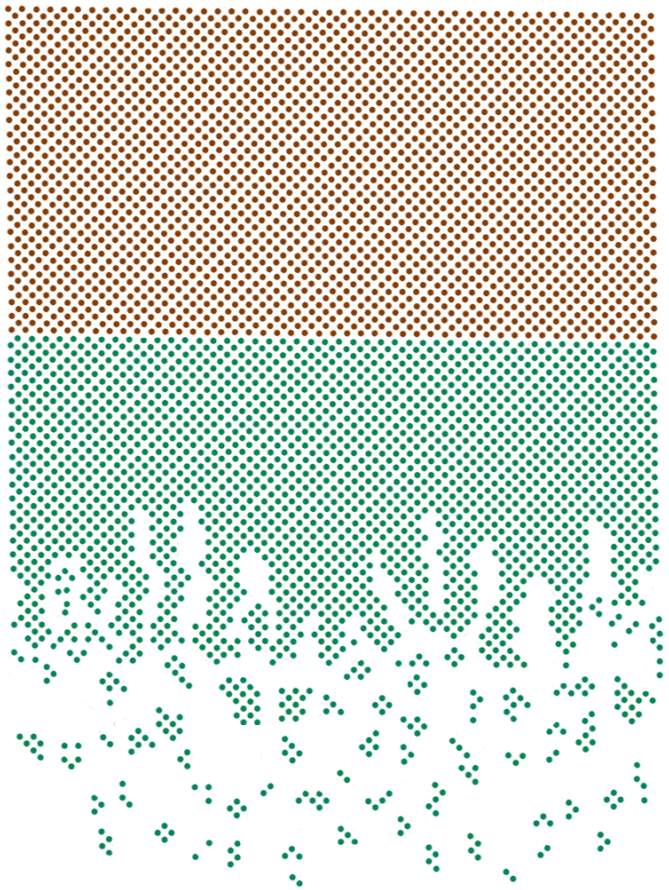


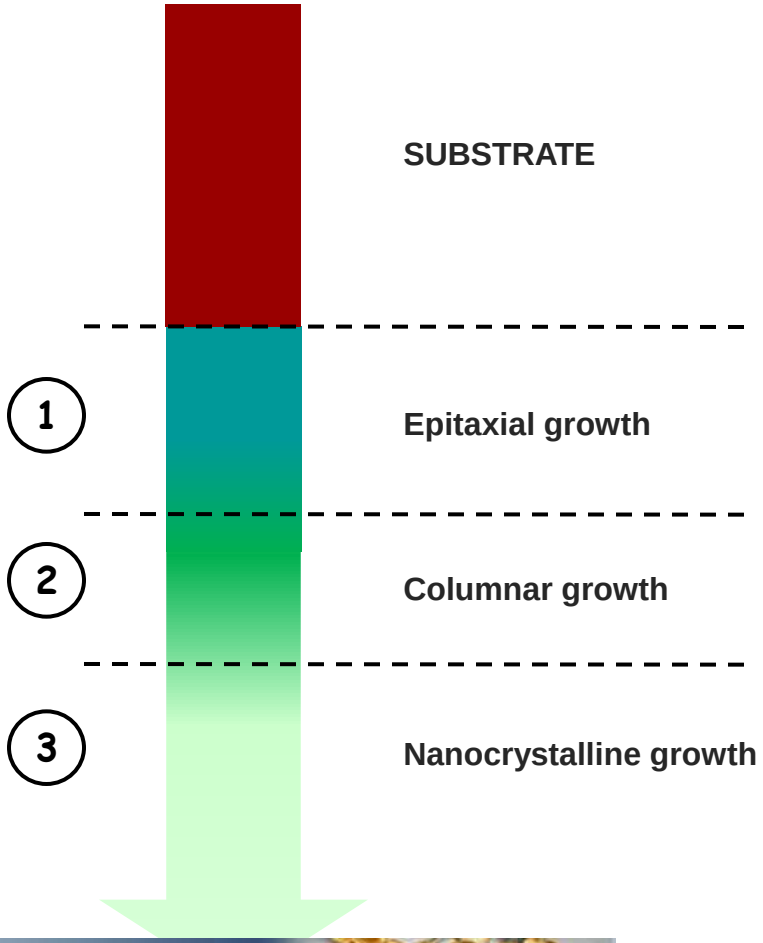




20 nm

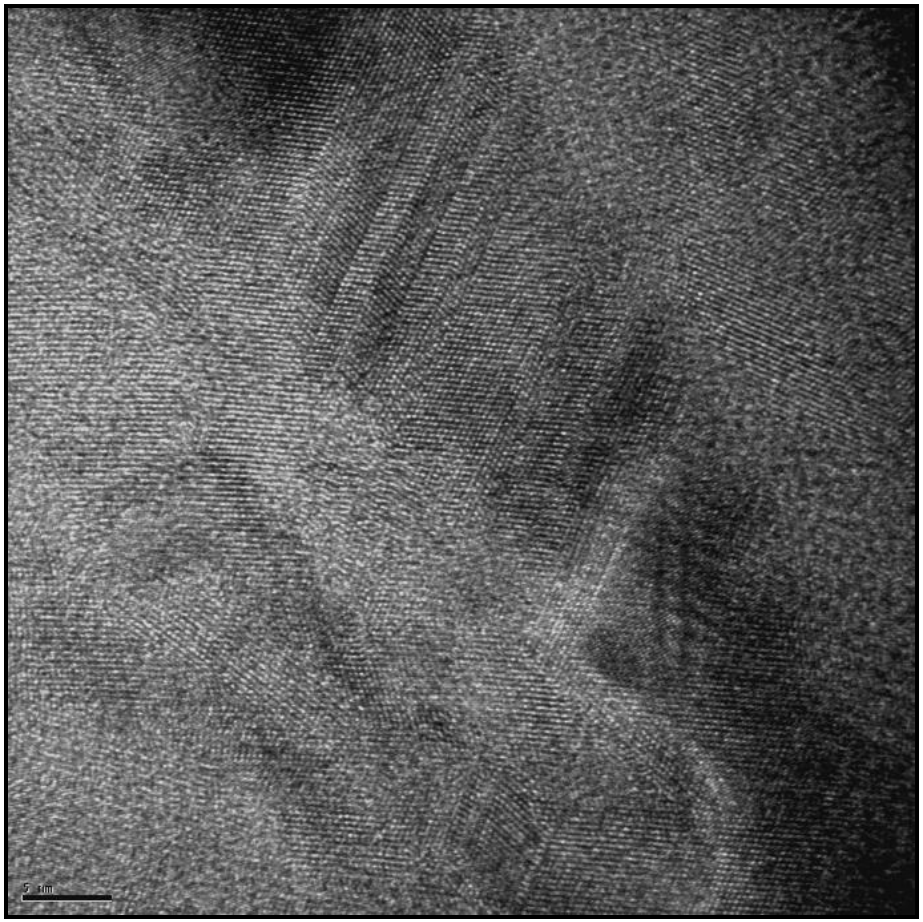
# Si substrate

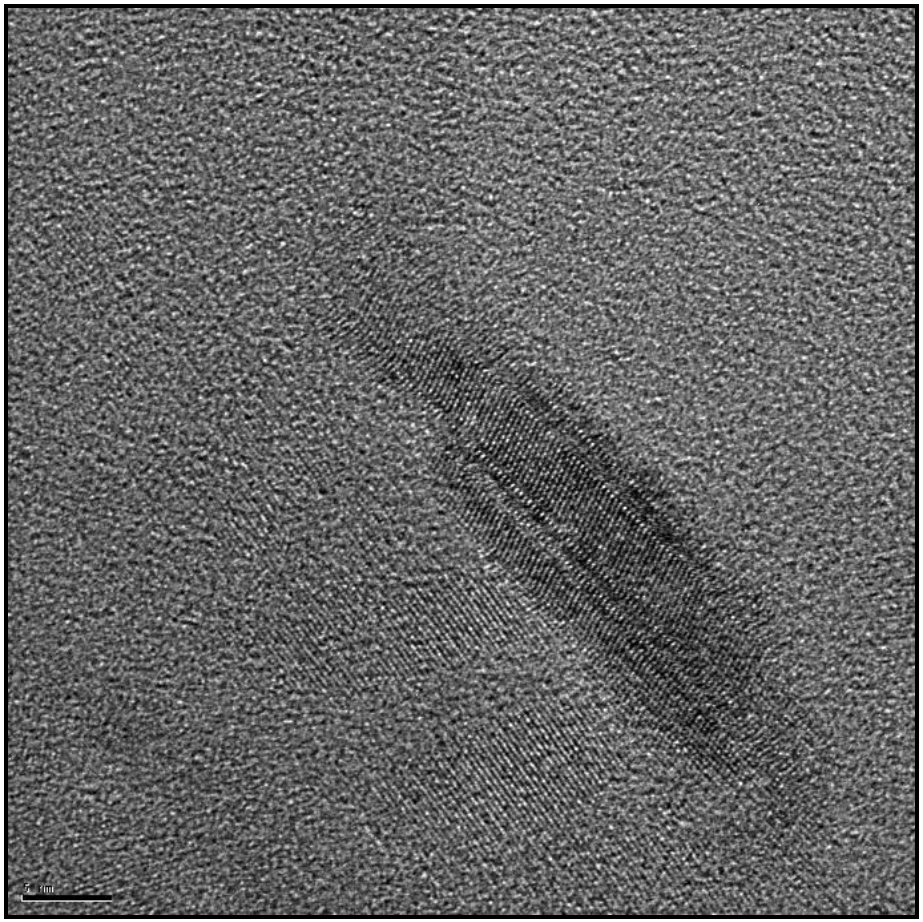
Structural changes along the growth direction : 3 domains…





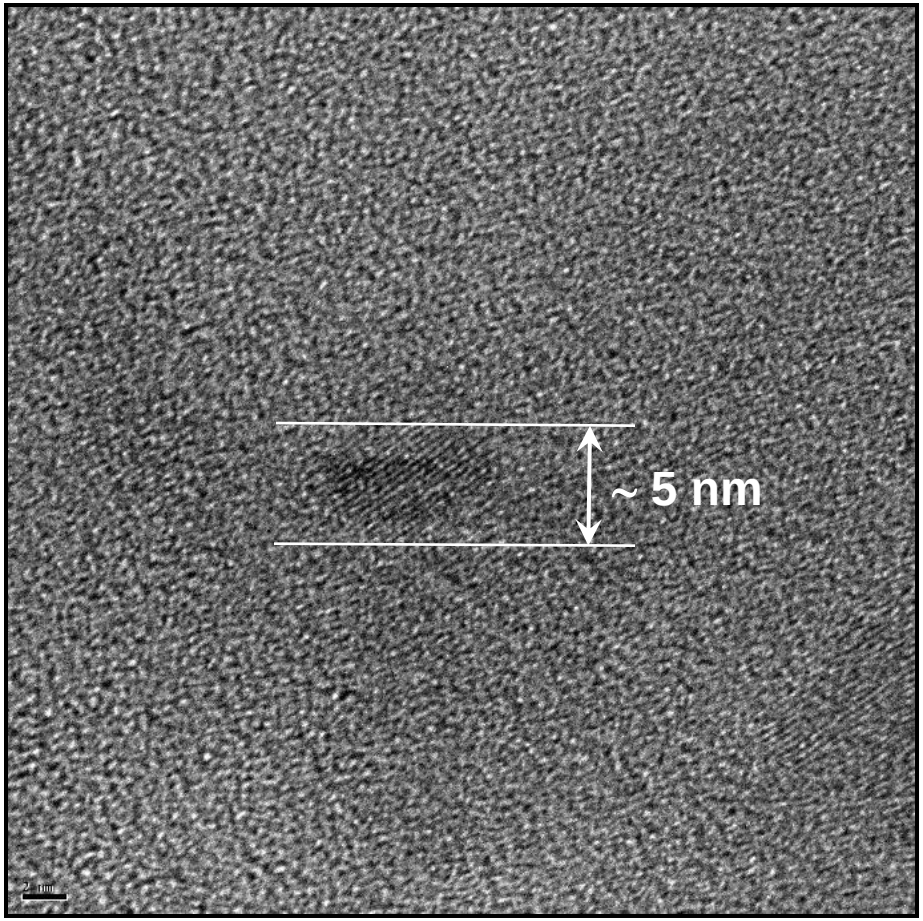
# Substrate Glass
# X-HRTEM observations :
# nc-Si layers contain numerous columnar nanocrystals
# Twins are frequently observed

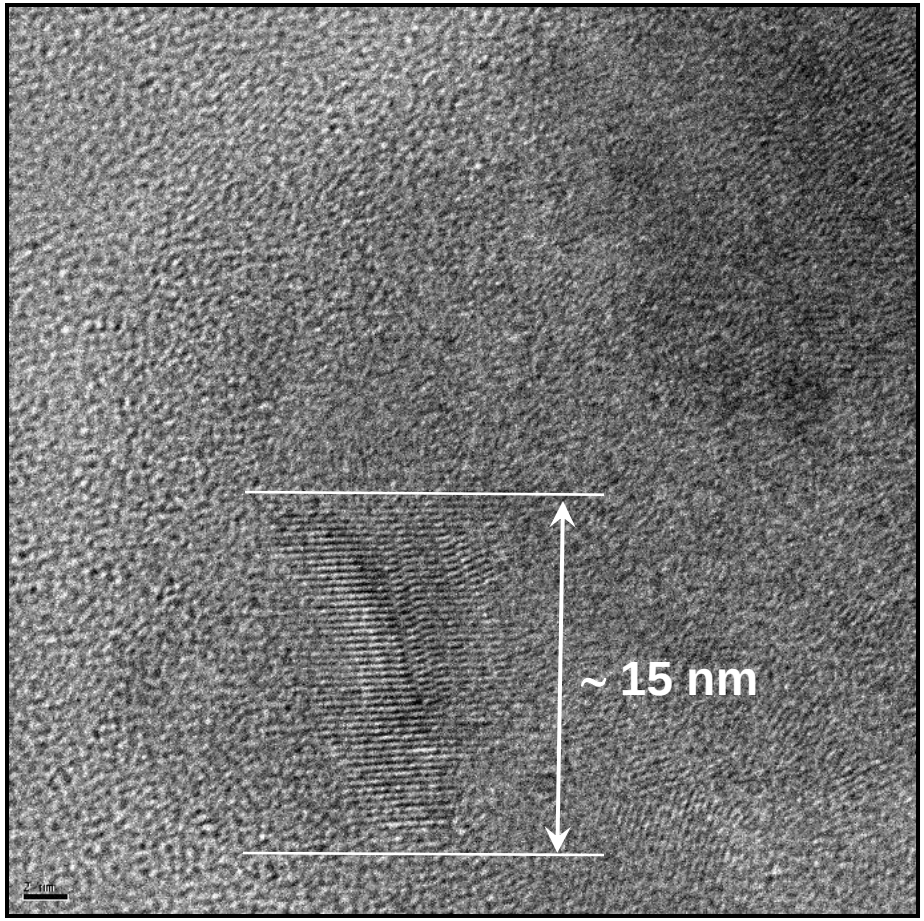


# Substrate Glass

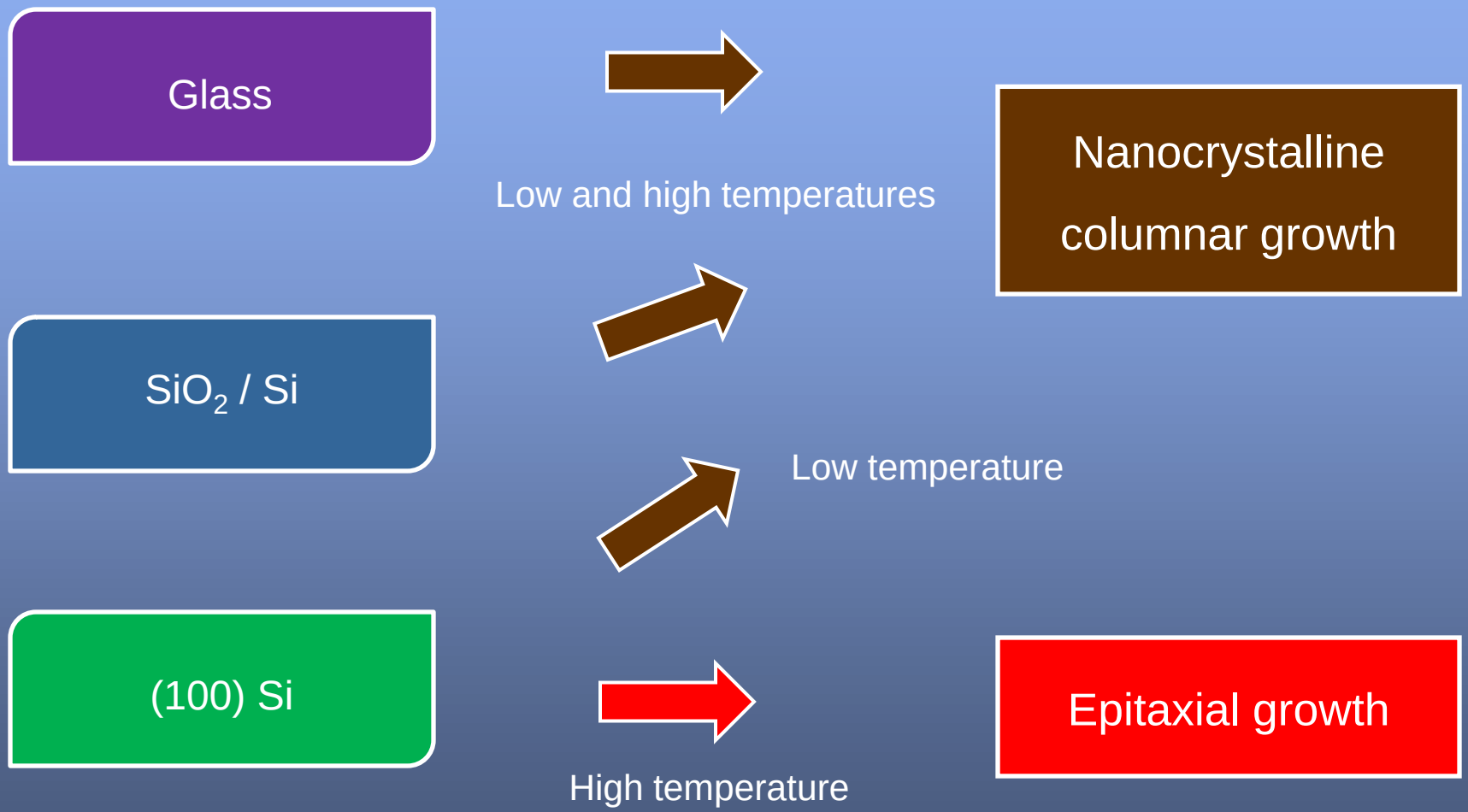
## HRTEM observations in plan-view:
## Diameter and shape of nanocrystalline columns are variable



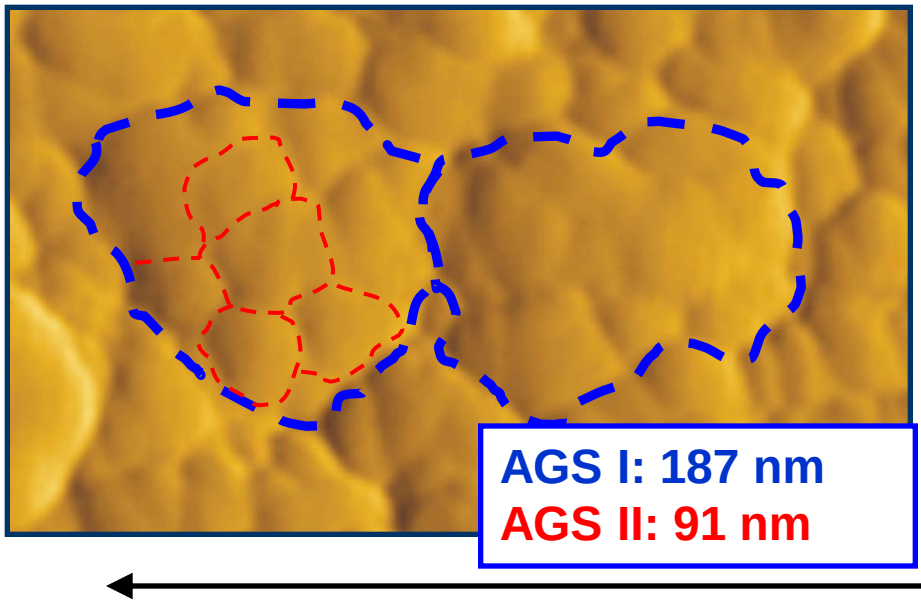

2 nm

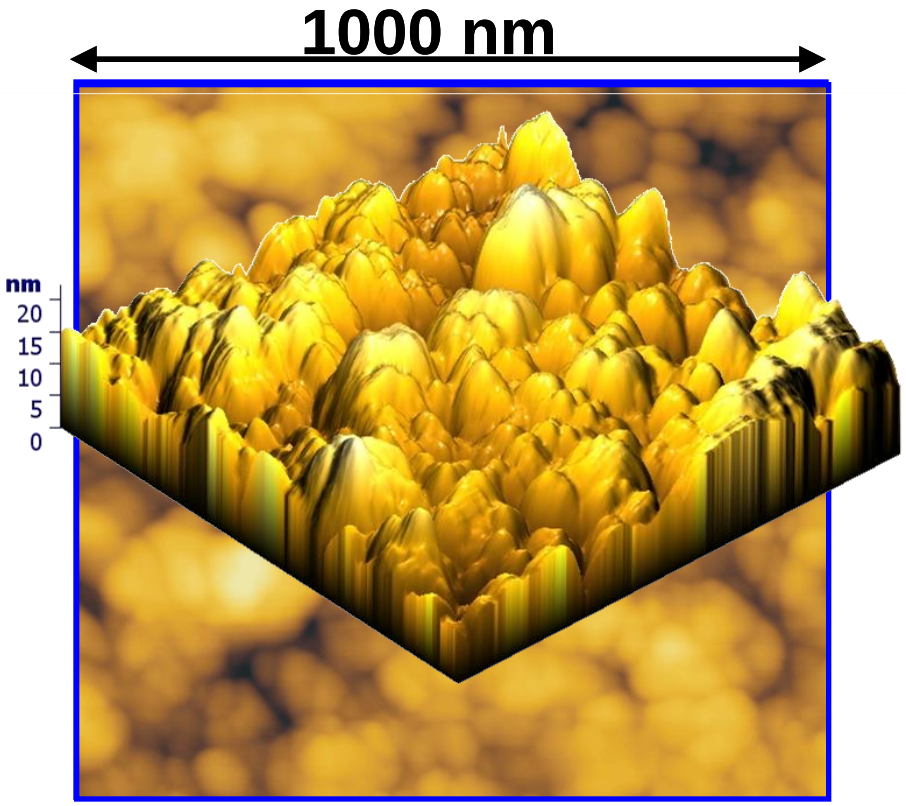
2 nm


Glass
$SiO_2$ / Si
(100) Si
Low and high temperatures
Low temperature
High temperature
Nanocrystalline columnar growth
Epitaxial growth

# Atomic Force Microscopy

**AGS (Average grain size) values:** [100-200] nm




**Average Height:** [10-20] nm

**RMS:** [2-6] nm

# Roughness

| Substrate | Roughness (nm) |
|---|---|
| $SiO_2$/Si and Si | 2÷6 |
| Glass | 4÷5 |
| ITO/Glass | 20 ÷ 40 |

The roughness

- depends on sample thickness
- is almost independent of crystallinity
- depends mainly on substrate

# XRD results

***Orientation:***

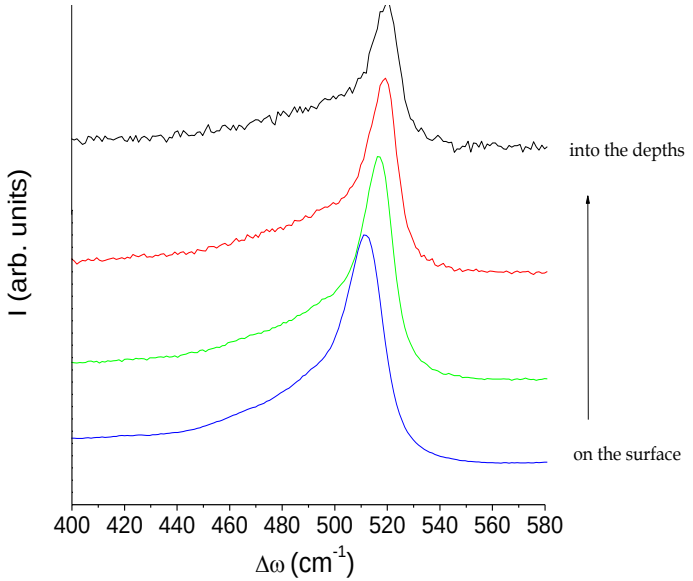
dominant growth direction <111> for all three substrates

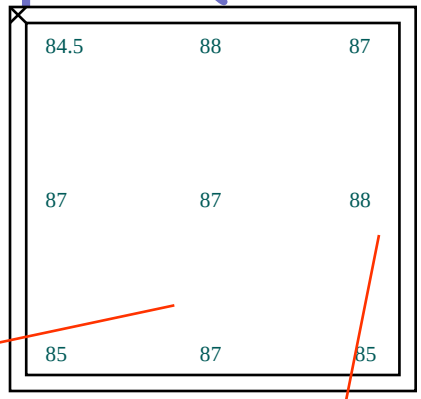
***Average grain dimension:***

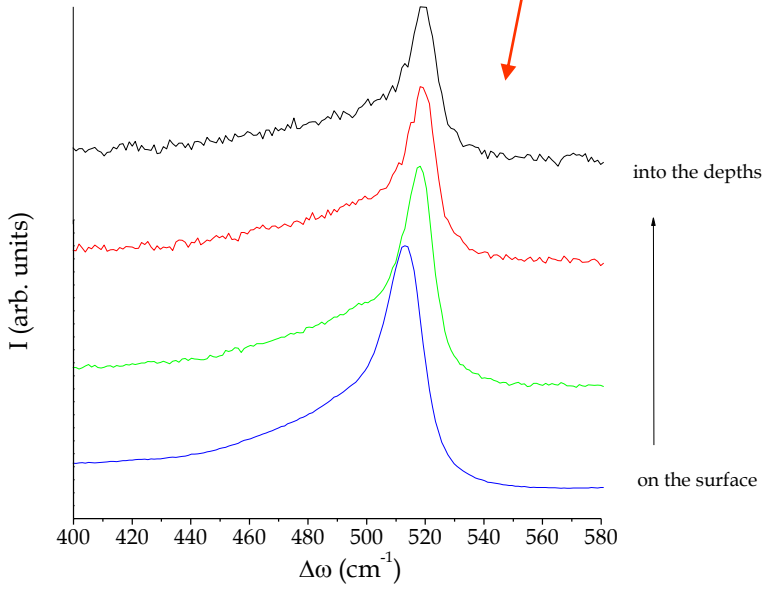
- tens of nm with **$SiO_2$/Si & Si substrates** independently of the silane dilution,
- from tens of nm at high silane dilution (d ≥ 30 %) to few nm at low silane dilution (d < 30 %) with **glass substrate**

# Raman in-depth profile

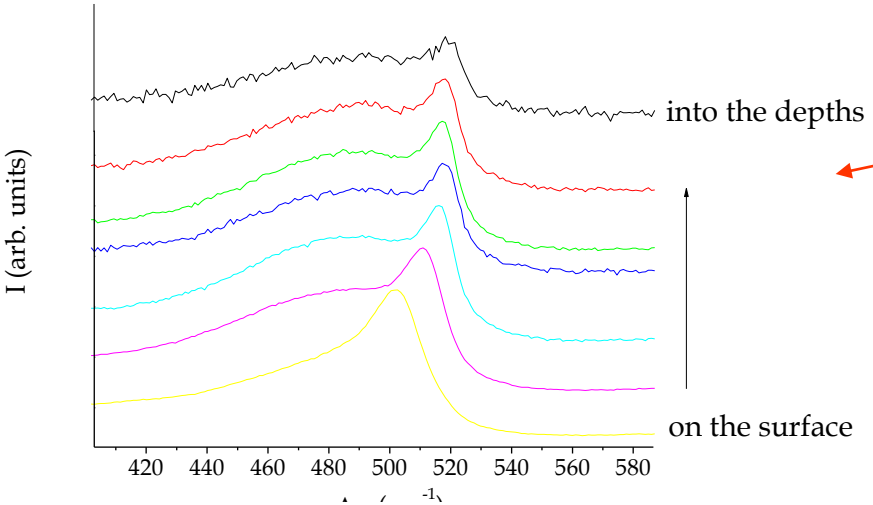
# of high crystallinity samples (low d%)

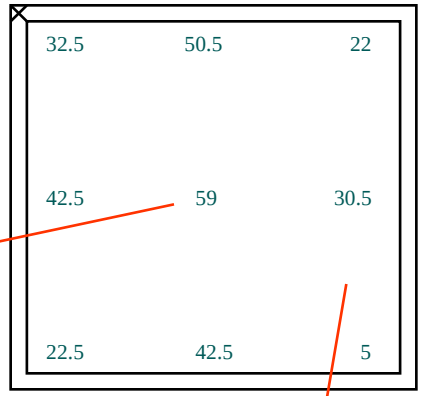


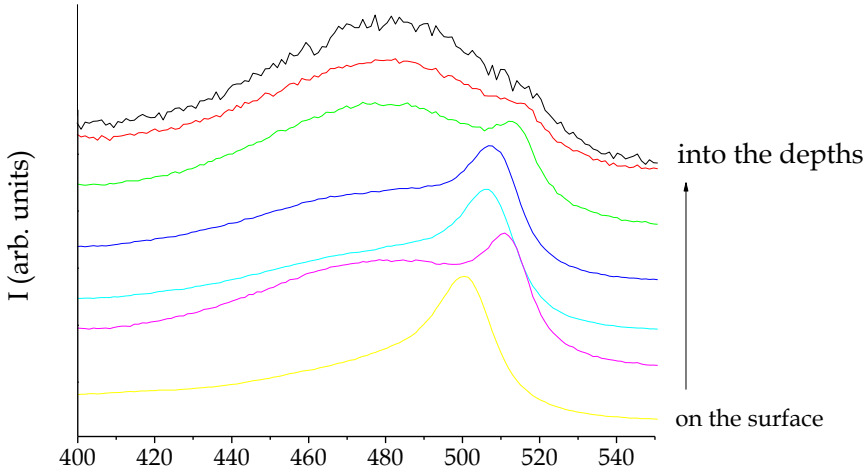



# Raman in-depth profile of a nanocrystalline sample (HIGH d%)

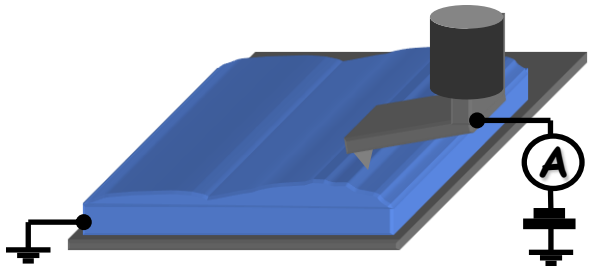


- Transizione c→ a

# Conductivity-AFM



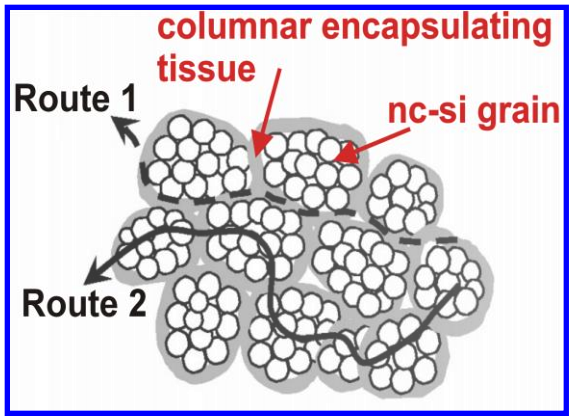

The probe scans the sample in contact mode.

A feedback loop keeps the cantilever deflection constant by varying the tip-sample distance.

At the same time a bias potential (3V) is applied to the probe and **the electrical current is measured**.

Topography and current maps are obtained simultaneously

# C-AFM Transport Mechanisms in nc-Si:H



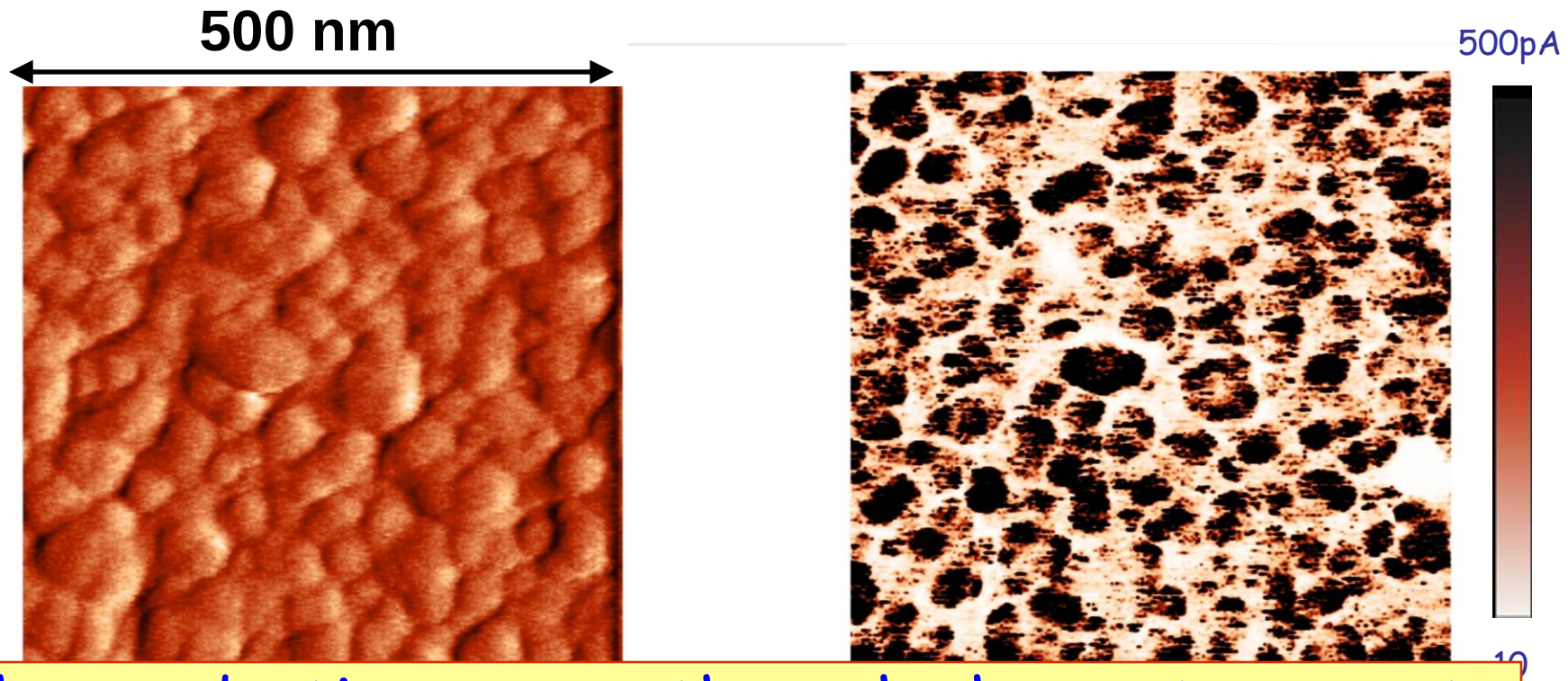

The localization of the charge trasport is still an open problem:

*Route 1* and *Route 2* represent two possibilities supported by experimental data [1,2].

*[**Route 1**, I.Balberg et al., Phys. Rev. B 71 (2005)]*

*[**Route 2**, A.Fejfar et al., J. Non-Cryst. Solids 266-269 (2000)]*

# C-AFM. Results




The conduction occurs through charge transport across the nanograins

This result has been obtained in all the samples.

# Conductivity

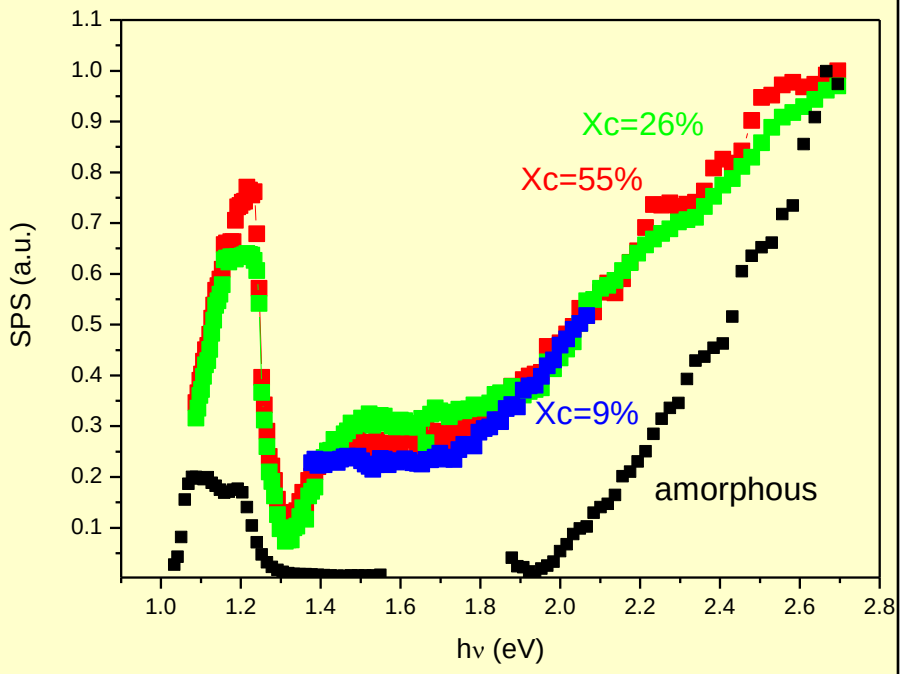
- Low dark conductivity ≈ $10^{-7}$ $Ohm^{-1}cm^{-1}$ for all the samples (good candidate as i- layer for p-i-n cells)

- High photosensitivity ≈ 100 for the samples grown on glass, promising for PV applications

substrates $SiO_2$/Si and Si

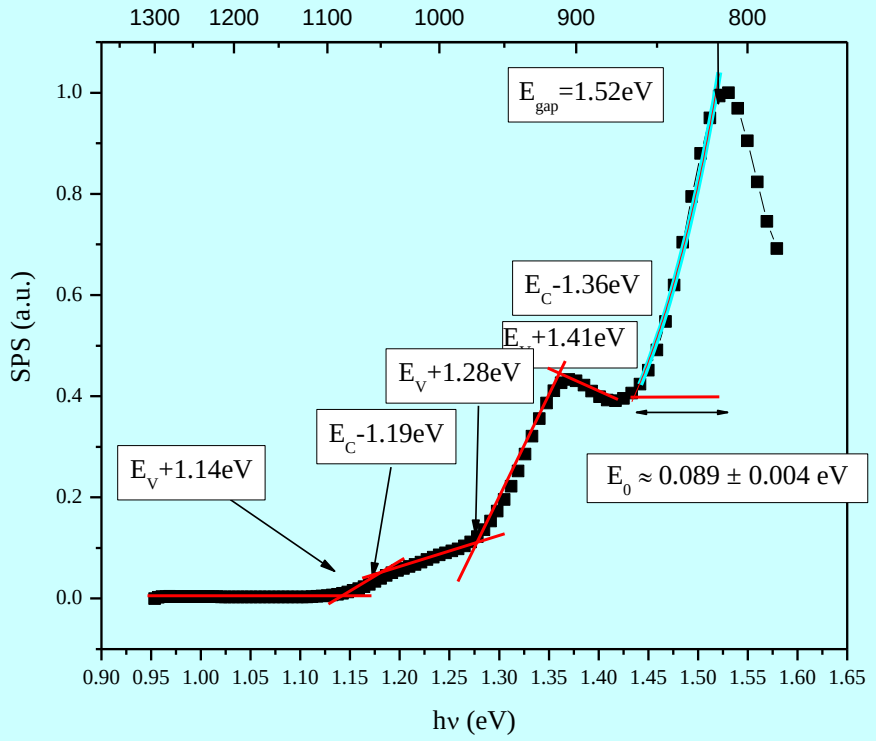
# SPS: Results

## Amorphous-like spectra




All the samples with Xc < 60-70%

## nc-Si:H- spectra



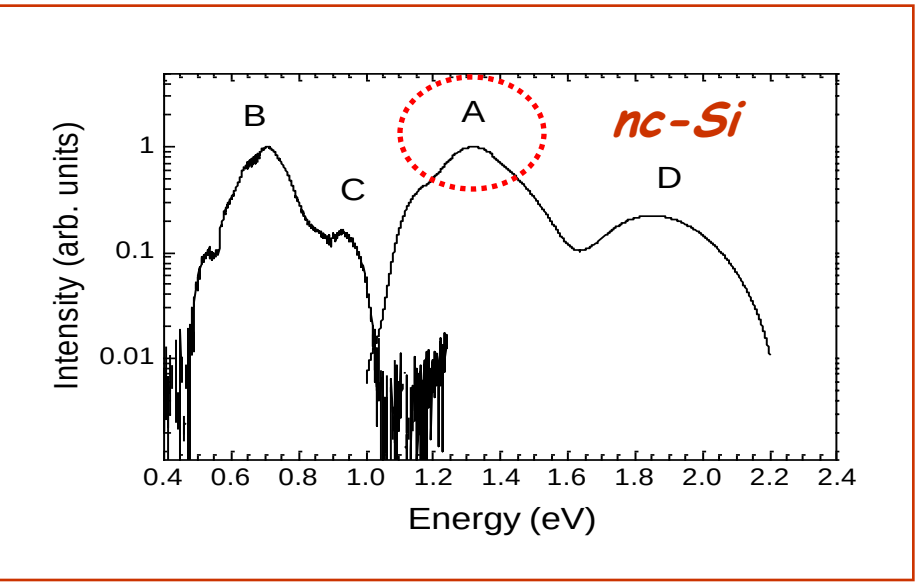

All the samples with Xc > 60-70%

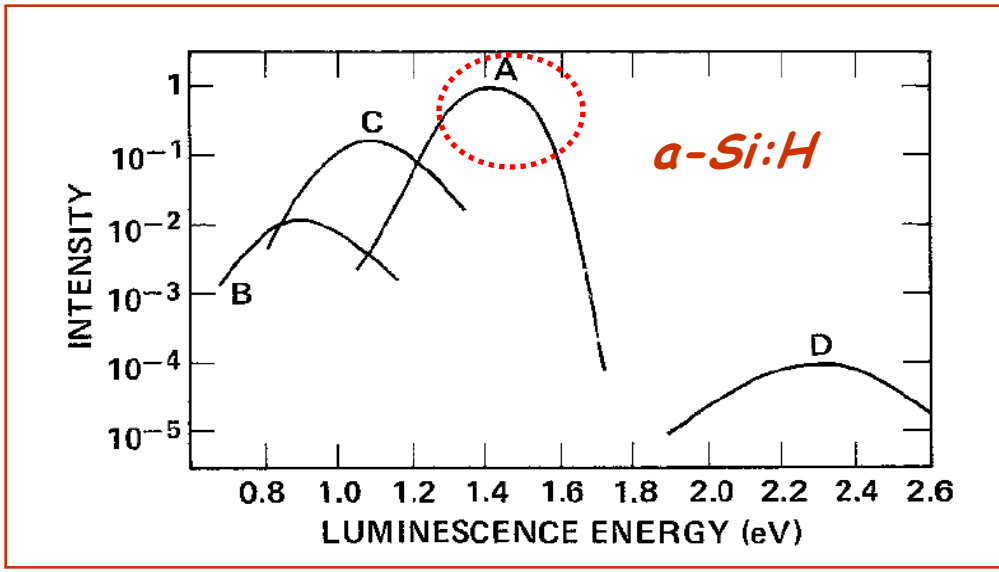
# Quantum confinement

- correlation between crystallinity and intensity of the photoluminescence → **band A**

candidate for emission due to quantum confinement???

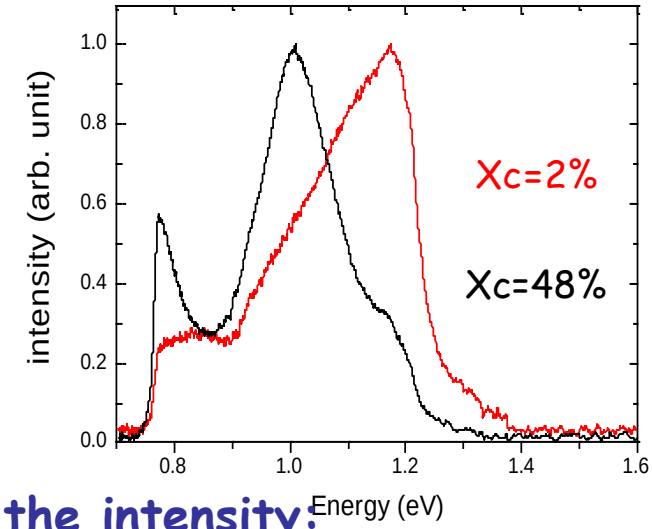
- its energy position between the c-Si and the a-Si gaps.




band A observed also in a-Si:H samples and attributed to localized states in the amorphous matrix.

# Quantum confinement




*PL spectra from regions with different crystallinity Xc*

↓

**origin of the intensity?**

**origin of the shape?**

**about the intensity:**

intensity of band A increases as the crystallinity of the film decreases

possible explanations:

- band A is due to **small** NCs →its intensity decreases when the average NC **size increases** with crystallinity;
- band A is related to the α-phase → its intensity decreases when the relative volume of the amorphous phase decreases in high crystallinity samples

**about the shape:**

the A band lineshape seems to be determined by the size of the NCs

# Conclusions

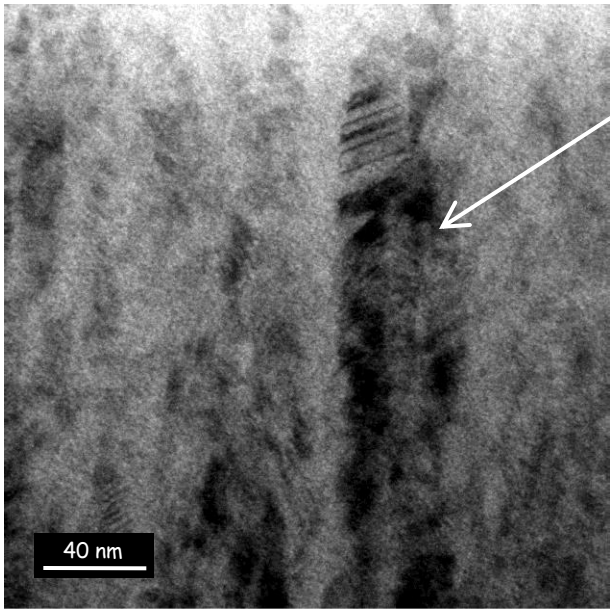
What do we know about nc-Si:H ?

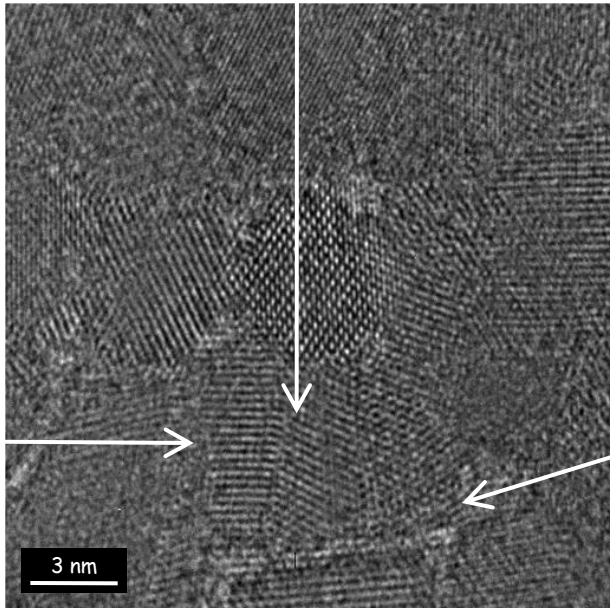
- Substrate and temperature significantly influence the microstructure (TEM) and the surface properties (roughness, AFM)
- The electrical conduction occurs through the nanograins (C-AFM)
- Samples grown on glass show high photogain, very promising for PV applications
- Optical properties are strongly linked to crystallinity (SPS)
- Optical confinement is likely related to the band A, the origin of which is linked to the crystallinity wherever the responsible localized states are

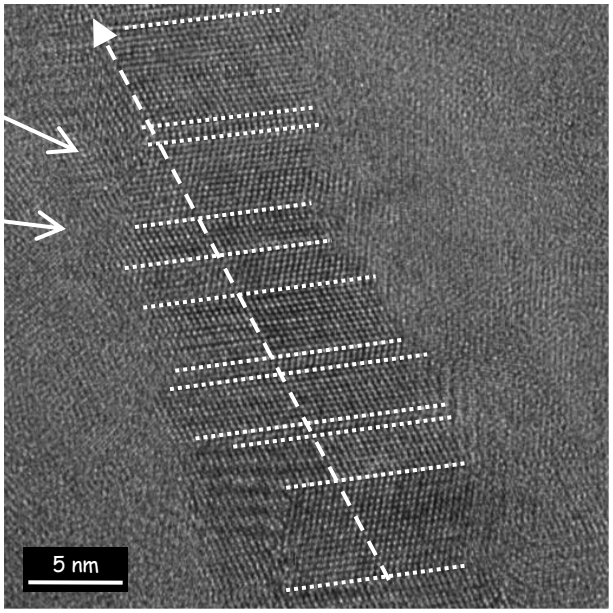
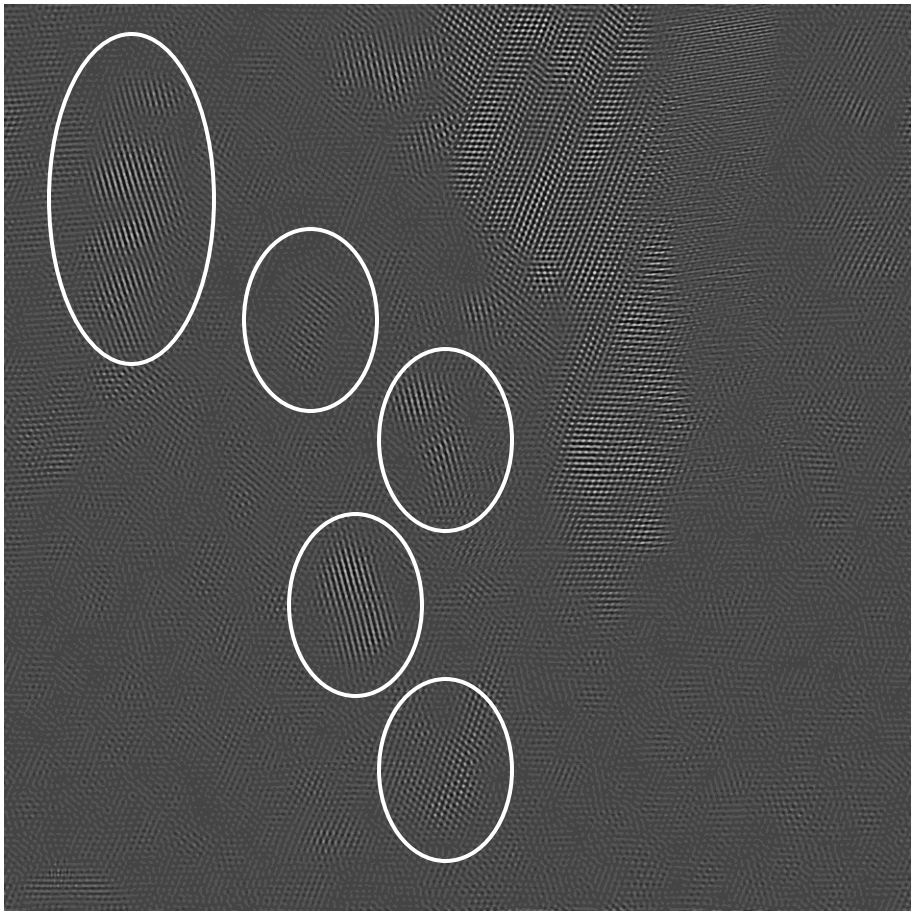
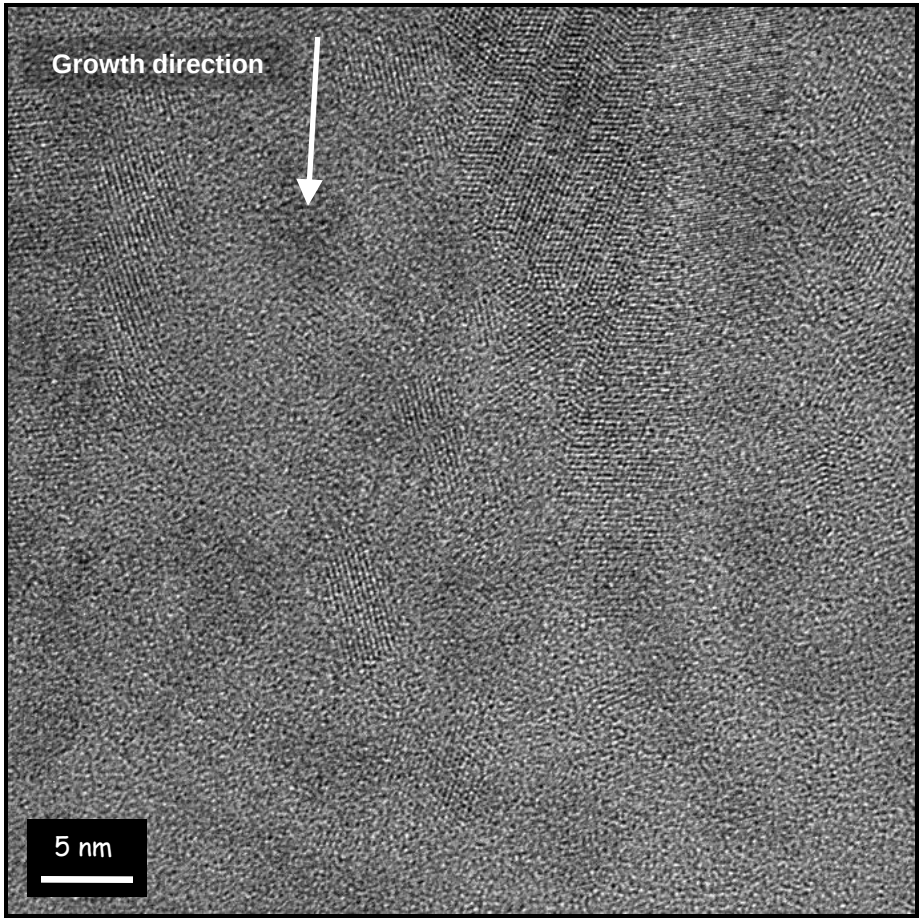
thank you for your attention

## Series I main features : Low mag, HR & X-HR TEM observations

For all the specimens, the structure is similar, whatever the growth parameters






# Series II Microstructure far from the interface : from crystalline to amorphous transition