# Characterization and novel characterization techniques

# (WP3)

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UNIBO

PHoDS Lab

PHysics of defects in Semiconductors

Nanophoto

NANOcrystalline silicon films for PHOTOvoltaic and optoelectronic applications

# Partners involved in the characterization issue (WP3)

UNIBO

- **UNIBO** A Cavallini, D Cavalcoli, M Rossi, A Tomasi, F Detto, L Rigutti, D Natalini
  - *UNIBO- PHOdS LAB Department of Physics, University of Bologna, and CNISM, Bologna, Italy.*
- **TECSEN**, B. Pichaud, M. Texier, A. Genovese
  - *TECSEN, UMR 6122 CNRS, Université Paul Cézanne, Marseille, France*
- **UNIMIB** A. Le Donne, S. Binetti, M. Acciari, S. Pizzini, F Montalenti, P Novikov, L Miglio, S. Sanguinetti, E. Grilli, E. Poliani, M.Guzzi,
  - *Dept. of Material Science University of Milano-Bicocca, Milano, Italy.*
- **UKN** G. Micard, G. Hahn,
  - *University of Konstanz, Faculty of Sciences, Department of Physics, Konstanz, Germany.*
- **L-NESS** D.Chrastina, G Isella,
  - *L-NESS, Physics Dept Politecnico di Milano, Polo Regionale di Como, Como, Italy.*

Nanophoto

NANOcrystalline silicon films for PHOTOvoltaic and optoelectronic applications

# objectives from the nanophoto project

- the <u>experimental study of the correlation between the crystallinity fraction, the grain size, the hydrogen content, the density of the recombination centres</u>, …

- the study of the <u>correlation between microstructure, hydrogen content, optical gap and optical absorption coefficient,</u> in view of an improved minority carrier generation
- ..

- ***WP3*** *collects all the characterization studies and also the quantum confinement studies. To this WP contribute the teams of TECSEN, UKON, UNIMIB and UNIBO, in reason of their different and complementary expertises*.

# Outline

- Material properties
  - UNDOPED nc-Si:H
    - Microstructure
    - Morphology
    - Electrical properties
    - Optical/optoelectronic properties
- Feedback between experiments and theory
- Correlation between material properties and growth parameters
- New experimental methods (or advancement)
  - C-AFM,
  - SPS
  - TEM new sample preparation
- Results on DOPED nc-Si:H
- Conclusions

# Material Properties

# Materials

intrinsic nc-Si:H grown by

**Low Energy Plasma Enhanced Chemical Vapour Deposition (LEPECVD)**

**UNDOPED**

L-NESS

| Sample set | d [%] | $X_C$ [%] | Substrate | Ts[°C] | t[µm] |
|---|---|---|---|---|---|
| Series I | 1 ÷ 20 | 65 ÷ 70 | $SiO_2$/Si | 208 ÷ 280 | 1.5 ÷ 1.7 |
| Series II | 1 ÷ 60 | 10 ÷ 50 | Si | 280 | 1 ÷ 2 |
| Series III | 20 ÷ 70 | 13 ÷ 80 | Glass | 250 | 1 ÷ 4 |
| Series IV | 30 ÷ 50 | 10 ÷ 50 | ZnO/glass | 230 | 1 ÷ 4 |
| Series V | 30 ÷ 50 | 10 ÷ 50 | ITO/glass | 230 | 1 ÷ 4 |

d = dilution factor = $\Phi\ (SiH_4) / [\Phi\ (SiH_4) + \Phi\ (H_2)]$

$X_c$ crystal fraction determined by RAMAN spectroscopy,

t sample thickness

# Material properties

- **What do we know now**, at the end of the nanophoto Project, on nc-Si:H films grown by LEPECVD?
- What the correlation between material properties and growth parameters?

## Characterization

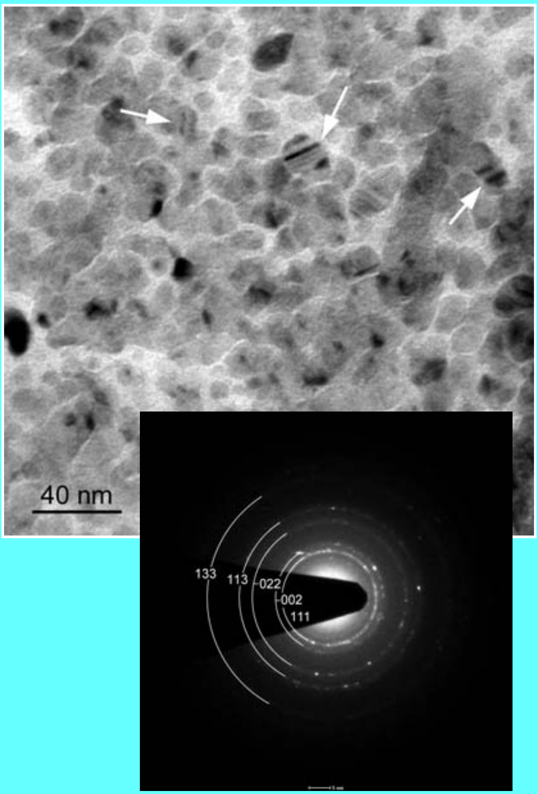
- TEM by TECSEN
- XRD and Raman by UNIMIB
- Raman vs depth by UNIMIB → homogeneity

## Results

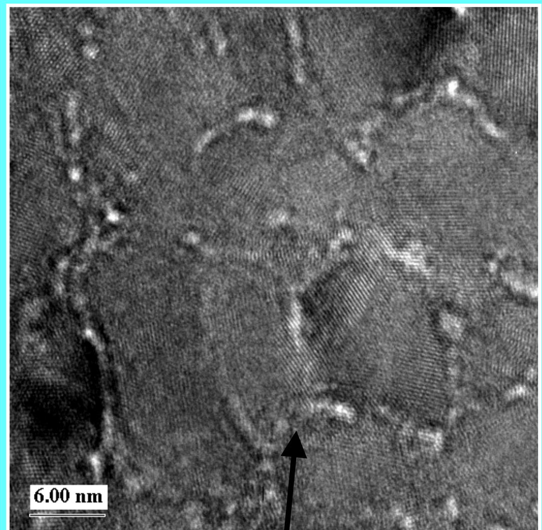
- growth scheme
- homogeneity
  - in depth (growth direction)
  - in plane (along the wafer)

# Series I. Plane view observations

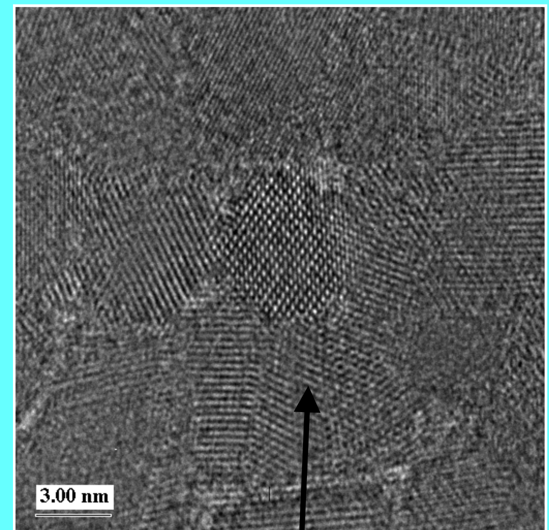
*Bright fieldTEM micrograph*
*& corresponding SAED pattern*




*HR-TEM micrographs*
*Left : under-focalized; Right : No defocus*




**Nanometric size domains are observed**




**Domains are constituted by misoriented nano-crystals**

Various nanocrystal sizes (between 4 to 20 nm)

# Series II Cross-section view observations

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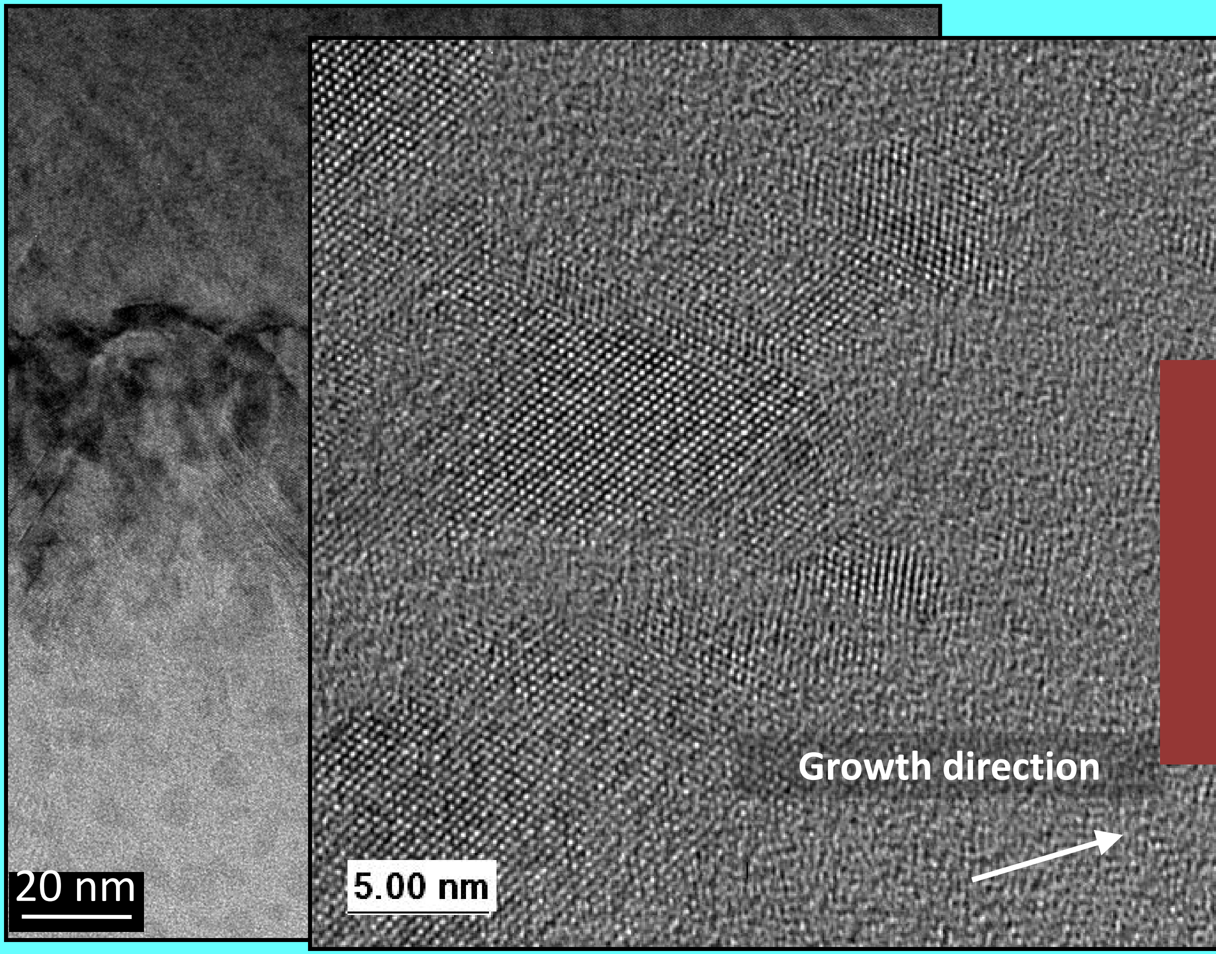
UMR 6242 CNRS, Universités Paul Cézanne, Provence et Sud Toulon-Var
UNIVERSITÉ PAUL CÉZANNE Aix-Marseille III
CNRS CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE




Single crystal

SUBSTRATE

**Superficial part of the layer :**

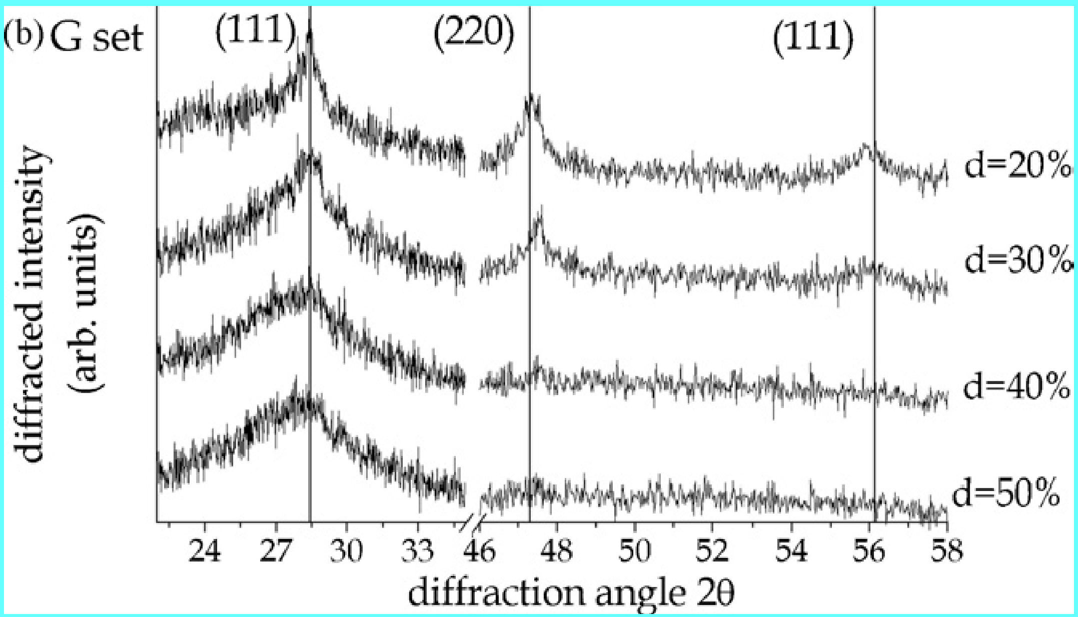
Transition from crystalline to amorphous structure.

The elongated columns become isolated small nanocrystals

# Structural characterization: XRD results

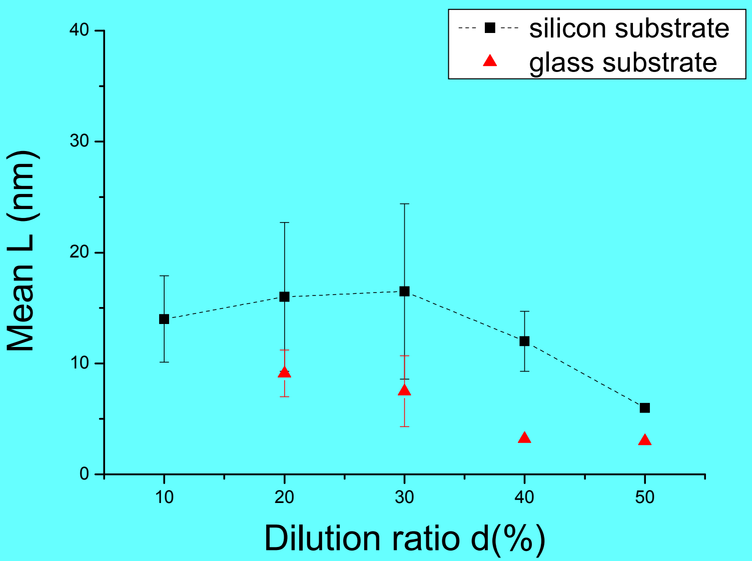
## Preferred growth direction

<111> for series I, II and III




## Average grain dimension L

from tens of nm at high silane dilution (d <30%) to few nm (3-5nm) at low silane dilution (d>30 %)

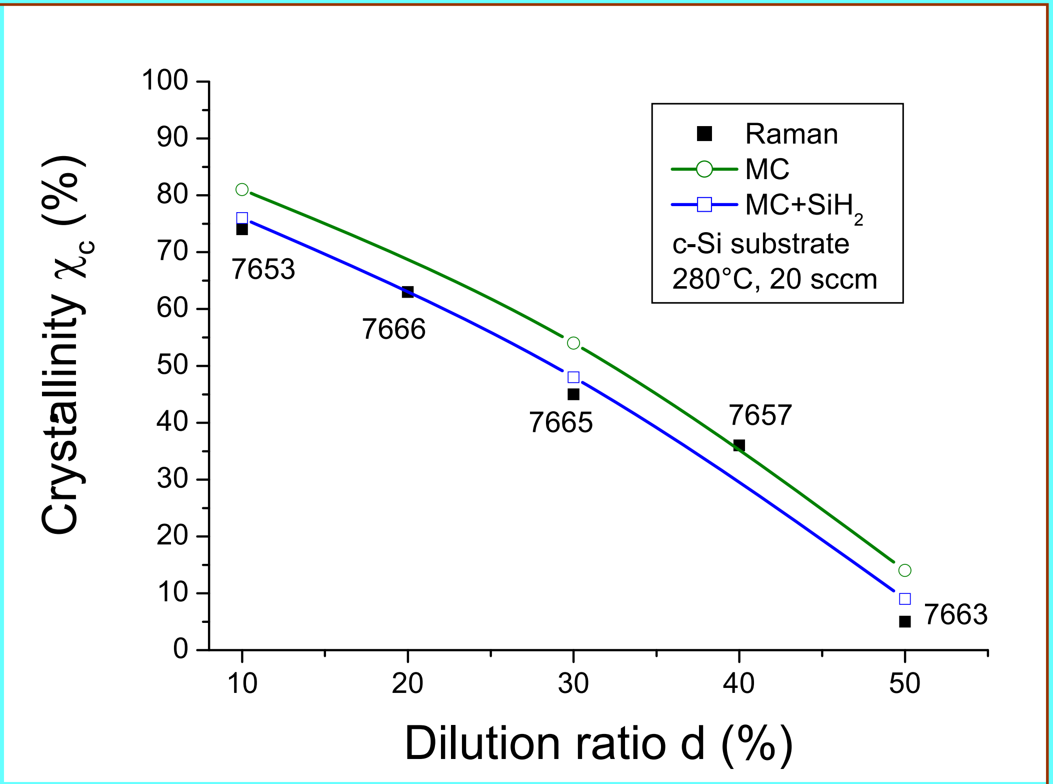



METHODS:

X ray Diffraction (XRD): PANalytical X'PERT-PRO diffractometer (Bragg-Brentano geometry, θ-θ scans); accelerating voltage 40 kV/current 40 mA used to produce a Cu-Ka radiation (1.5406 Å).

# Crystal fraction Xc by Raman Analyses
## (comparison with Kinetic Monte Carlo modeling [1])

- good "crystallinity uniformity" of the samples up to d (dilution factors) = 20 %
- large deviations from uniformity at d>20%:




[1] P. Novikov, F. Montalenti, and L. Miglio, in preparation.

# ...from the collaboration between L-NESS and UNIMIB

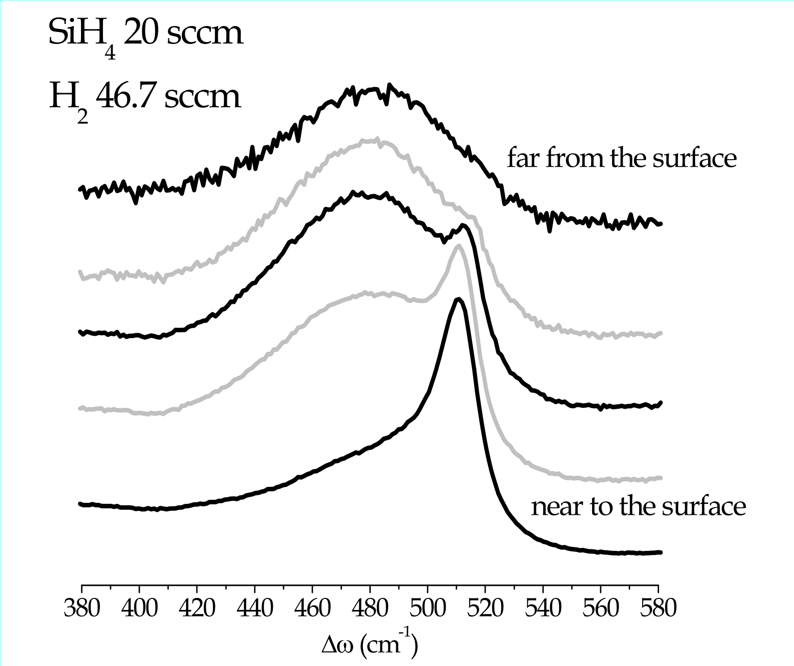
Magnetic field configuration

- ✓ Recent results regarding the crystalline fraction homogeneity in the wafer suggest that the magnetic field configuration is more important than previously considered

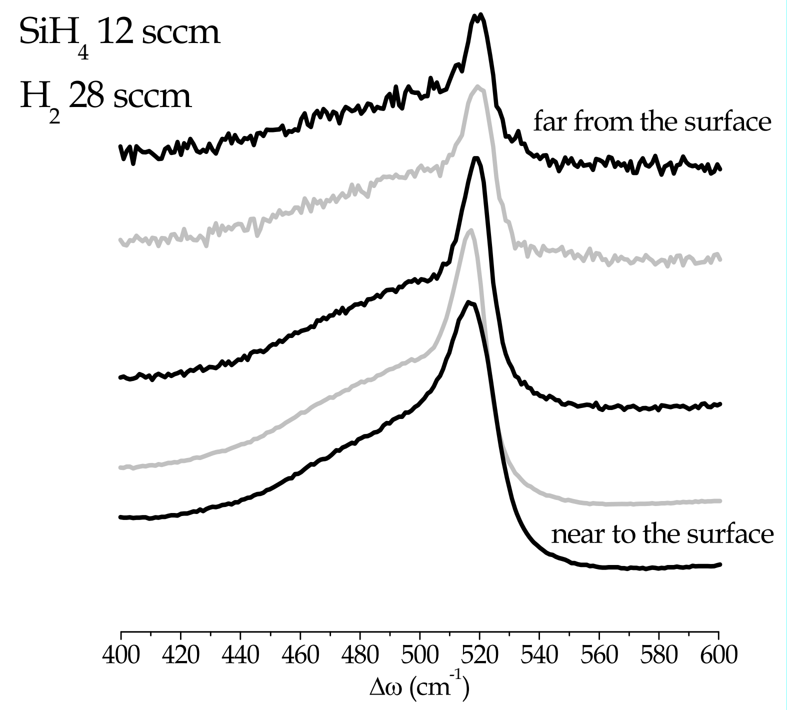
Silane flow influence on the film microstructure:

- ✓ Reducing the silane flow from 20 to 12 sccm increases the crystalline fraction uniformity along the growth direction.

# Homogeneity of the film




This sample presents an **inhomogeneous structure** along the growth direction




This sample shows a **homogeneous structure** along the growth direction!!

⇒ the **same evolution of the morphology** along the growth direction as a function of the SiH4 flux was observed **independently both of the substrate** (ITO-coated glass, ZnO-coated glass and Corning glass) **and of the dilution factor** (d=30%,d=50%).

# All the sample series. Growth General Scheme

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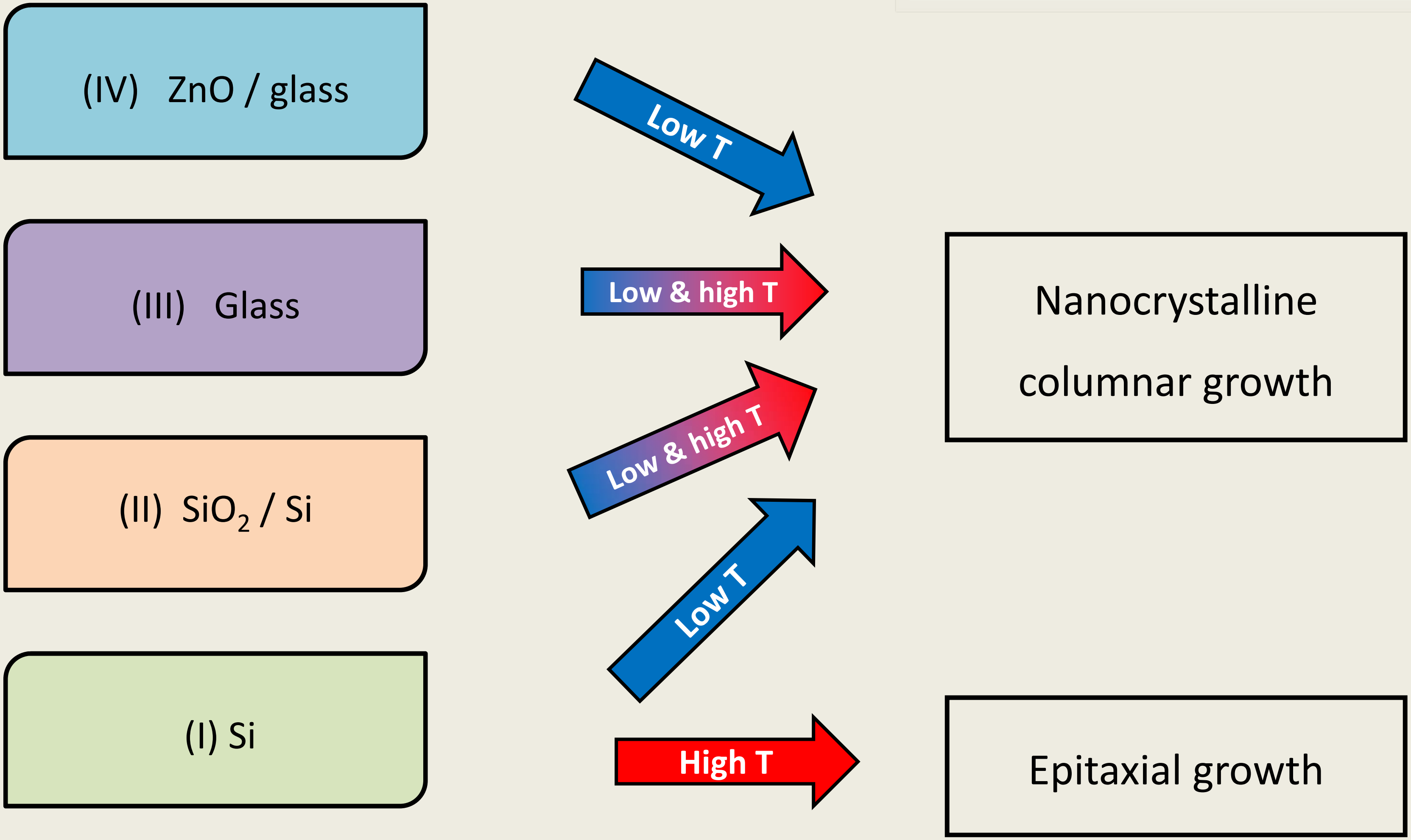
## We know how the nc films grow

The growth mechanism depends
- on substrate
- on temperature



# We know how the uniformity of the film can be obtained

## Homogeneity of the film

- the crystalline fraction <u>uniformity</u> increases along the growth direction if the silane flow increases from 20 to 12 sccm.
- the crystalline fraction <u>homogeneity</u> in the wafer increases by correct adjustment of magnetic field configuration.
- the crystalline fraction <u>homogeneity</u> in the wafer increases by dilution factor up to 20%.
- The crystal fraction decreases as dilution increases further.

# morphology

## Characterization

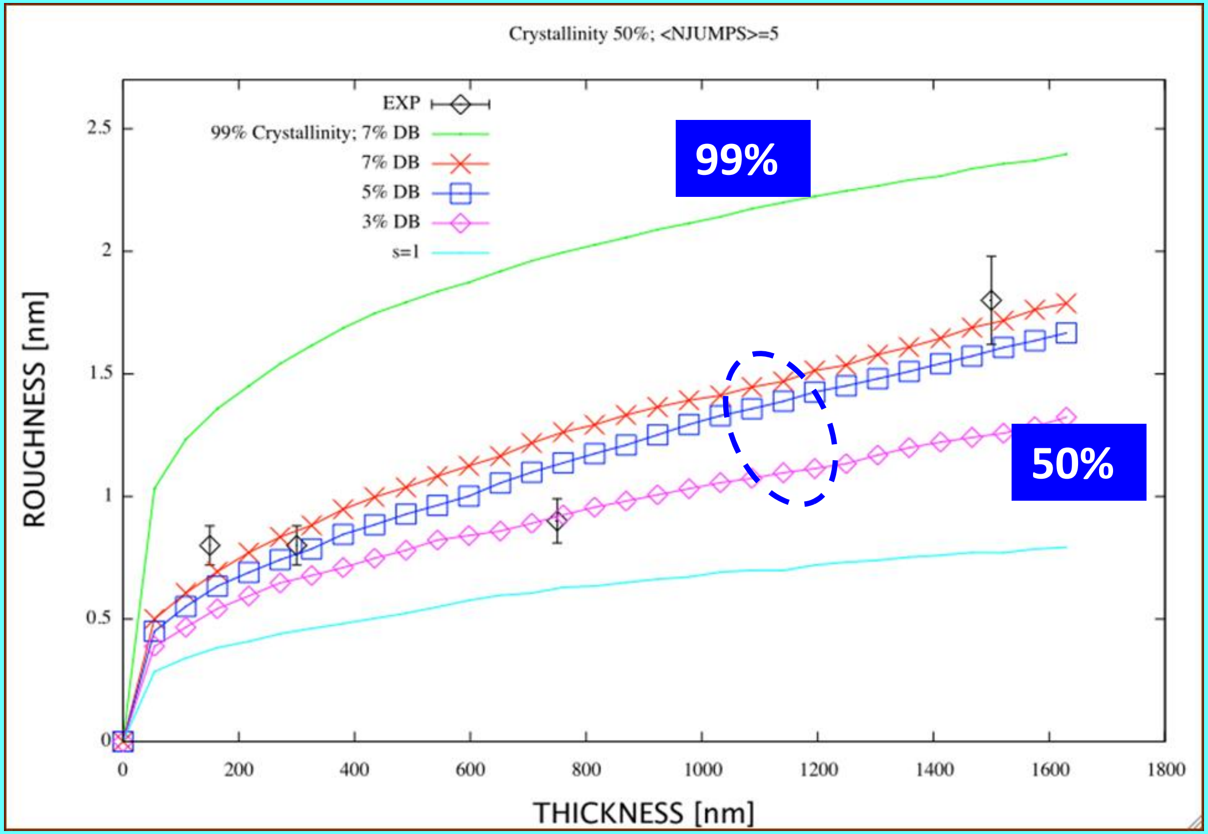
- AFM by UNIBO

## Results

- Surface morphology and roughness as a function of substrate
- Comparison with theory

# Roughness- simulation

**The evolution of the roughness vs thickness simulated by a simple atomistic Kinetic Monte Carlo model [1] including hydrogen-coverage and crystallinity dependent impact-following events. Activated diffusion, instead, is assumed to be frozen [2].**



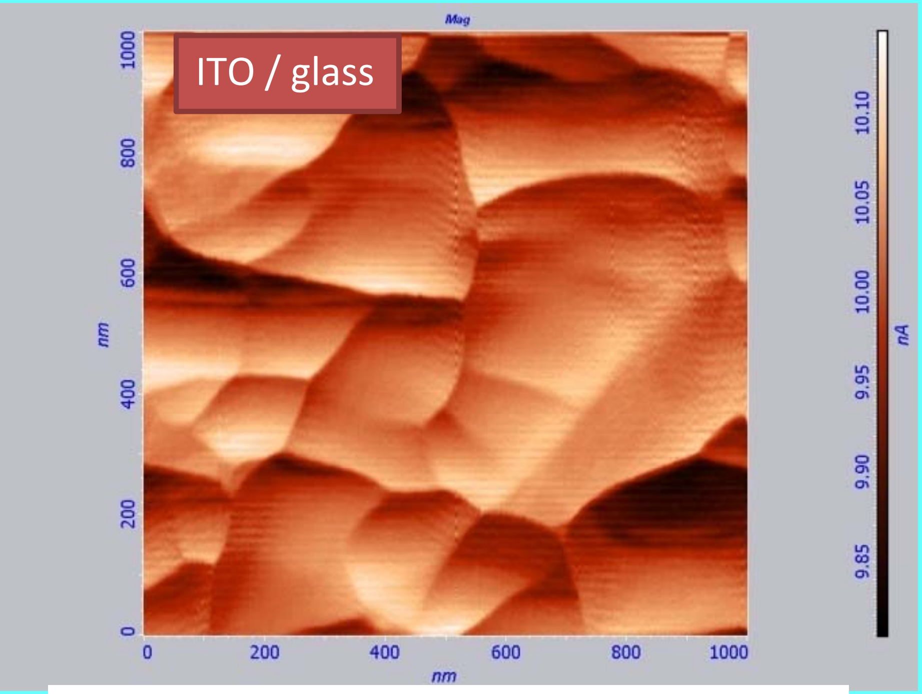

## Results

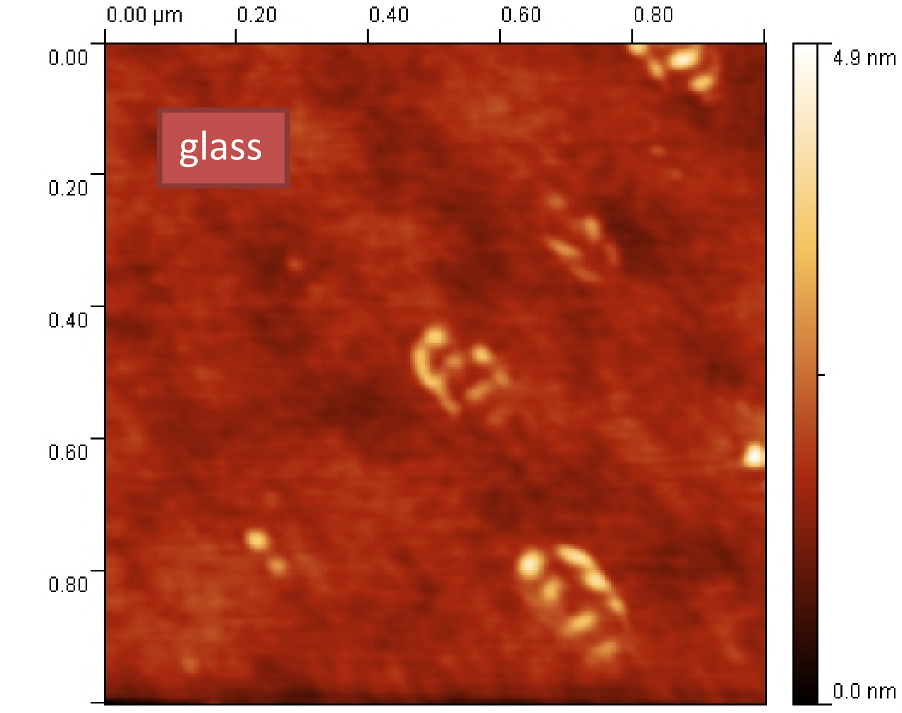
**Experimental results are nicely recovered by assuming a crystallinity of 50% and an average hydrogen coverage of 5-7%.**

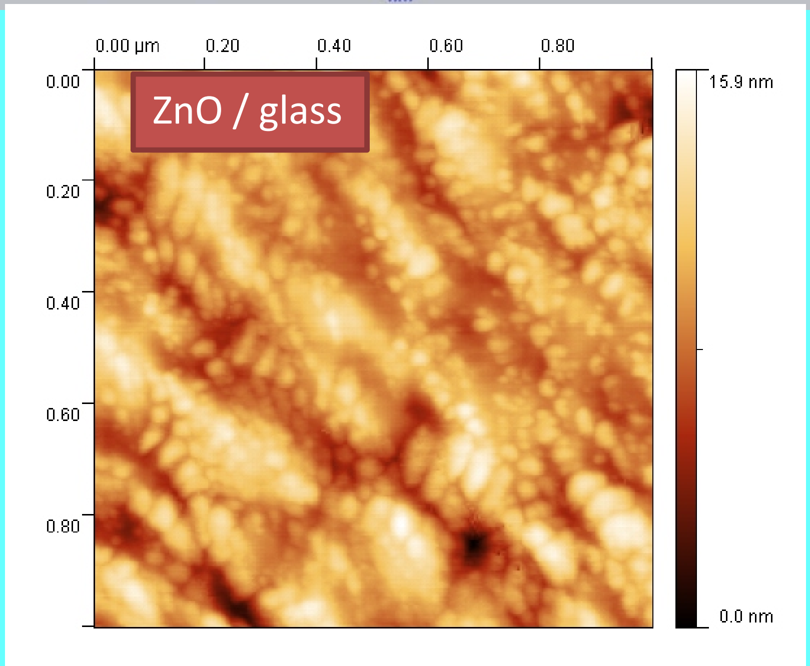

*[1] F. Gemma & F. Montalenti, in preparation*

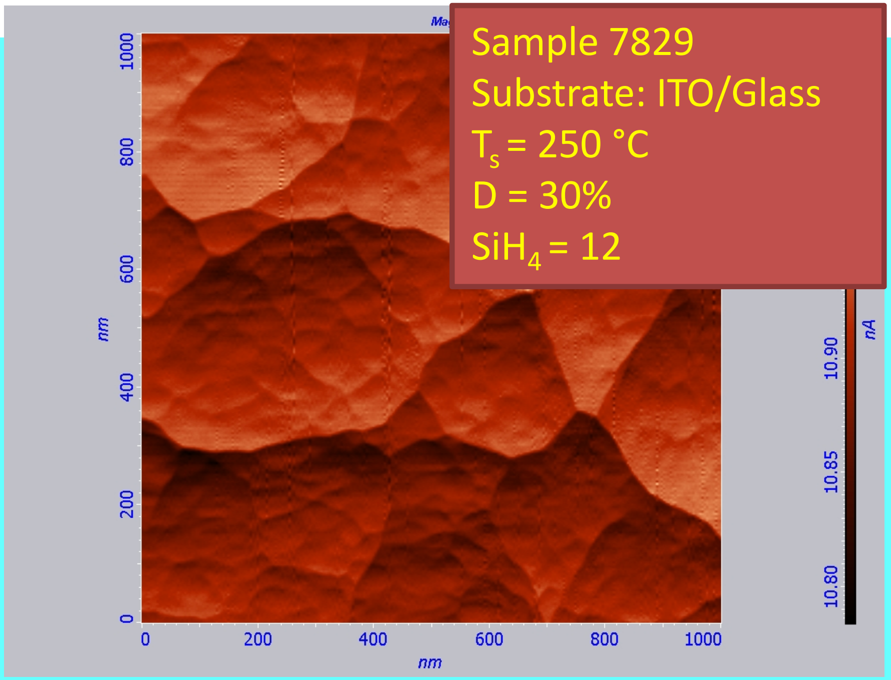
*[2] S. Cereda et al., Phys. Rev. Lett. 100, 046105 (2008)].*

# Roughness vs Substrates:



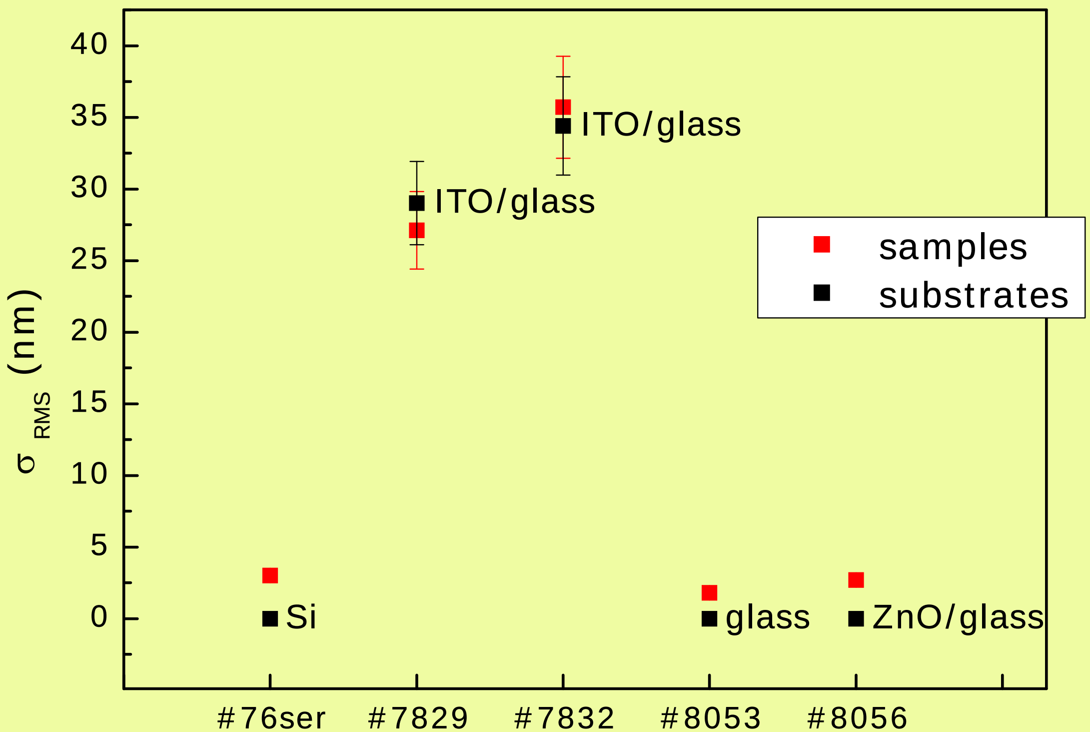




Sample 7829
Substrate: ITO/Glass
$T_s$ = 250 °C
D = 30%
$SiH_4$ = 12

# TOPOGRAPHY: Roughness *vs* substrate (summary of all the samples and substrates)

UNIBO

| SAMPLE set Grown on: | | $\sigma_{RMS}$ (nm) |
|---|---|---|
| I /II | Si or SiO/Si | 2÷6 |
| III | glass | 4÷5 |
| IV | ZnO/glass | 5÷ 6 |
| V | ITO/ glass | 20 ÷ 40 |




Conclusion

THE RMS ROUGHNESS STRONGLY DEPENDS ON SUBSTRATE

Morphology (Average Grain Size, AGS and roughness) depends
- on substrate
- on thickness

## We know how to obtain a rough (textured) surface

- Surface roughness depends on substrate
- Surface roughness increases with thickness

# Electrical properties

## Characterization

- C-AFM, UNIBO
- Electrical conductivity UNIMIB, UKON

## Results

- Conduction at a microscopic level
- Best material with optimum electrical conductivity

We know how to optimize photosensitivity and conductivity

# Conductivity. Results

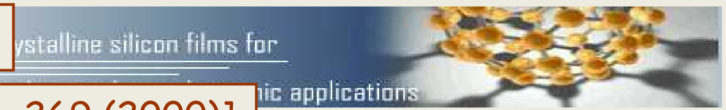
## Dark conductivity measurements in planar configuration

- Low dark conductivity values obtained for all the sample series ≈ $10^{-7}$ $Ohm^{-1}cm^{-1}$ (good candidate as i- layer in for p-i-n cells)
- Low photosensitivity ≈ 2 for sample series I and II (growth on Si and $SiO_2$/Si)
- High photosensitivity ≈ 100 for the samples series III (grown on glass), promising for PV applications.

We know where (in which phase) does the current flow

# Electrical conduction at microscopic level

- Controversial results in literature on conduction mechanisms in nc-Si:H [1,2].
- The conduction in the present films is localized within the nanocrystallites, the proposed mechanism is transport via the crystallites [2].
- The amorphous tissue surrounding the nanocrystals is non conductive $E_G$(a-Si:H) > $E_G$(c-Si).
- Intrinsic nc-Si:H
  - the conductive nanocrystals are mainly located in the "hills" of the structure.
- Doped nc-Si:H
  - the conductive nanocrystals are mainly, but not only, located in the "valley" of the structure.




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

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

# Optical/Optoelectronic properties

## Characterization

- SPS, UNIBO
- Optical Transmission UNIMIB, UKON, UNIBO
- PL, UNIMIB

## Results

- Energy Gap, Urbach tails
- Defect states
- Film thickness
- PL emission bands

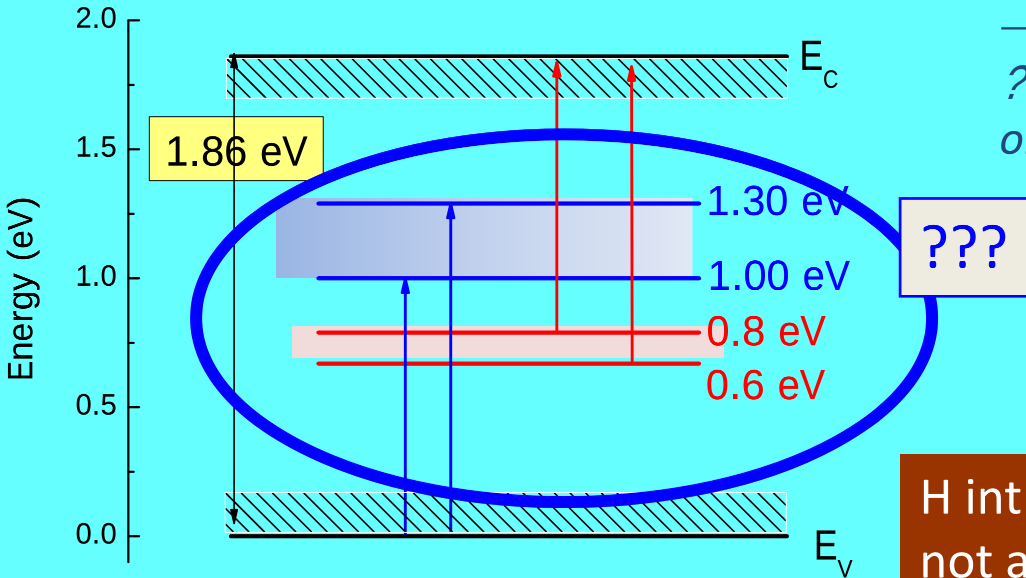
UNIBO

# Energy gap and Urbach tails *vs* crystallinity

| | GAP (eV) | Urbach tails |
|---|---|---|
| Amorphous | 1.87 (Tauc) | few hundreds of meV |
| Low Xc (<65%) amorphous-like | from 1.3 to 1.87 (Tauc) | few hundreds of meV |
| High Xc (>65%) nc-like | From 1.40 to 1.53 eV | few meV (<10meV) |

UNIBO

# Amorphous or Amorphous-like Si intra-gap states. Origin of defective states? test by Hydrogenation




excitation from VB to state
→occupied by *h*
*?? $D^0$ or $D^+$ [1]*
*or strain-related defects [2]*

excitation from state to CB
→occupied by *e*
*?? D0 or D -[1]*
*or strain-related defects [2]*

H introduction (by etching at roomT) does not affect substantially the SPV peak, which is related to the defect

These states should be not related to DBs, but to strain-related defects [2]

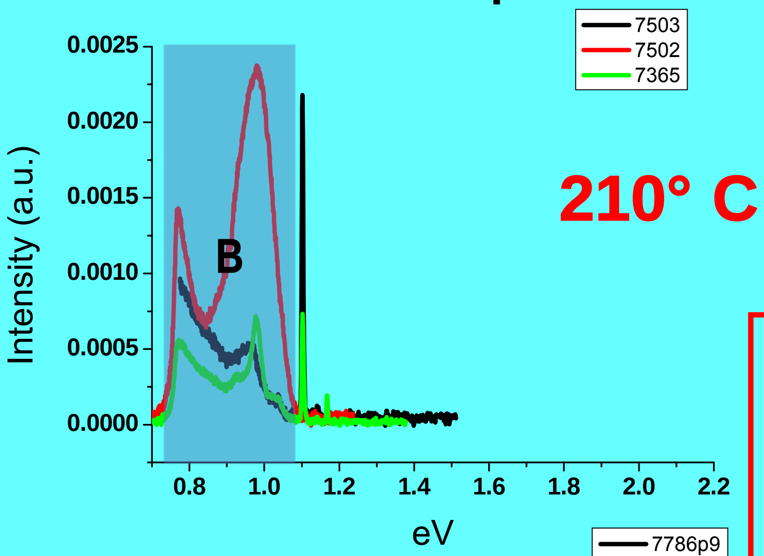
*[1] Nadazdy and Zeman, Phys Rev B 2004, Fefer Shapira Balberg APL 1995*

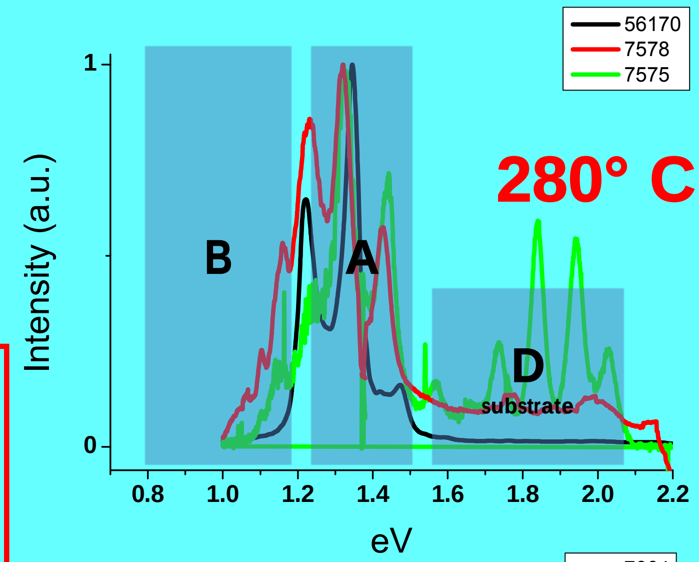
*[2 Theory, A. Mattoni, L Colombo, Univ of Cagliari*

# Emission Spectra by Photoluminescence

## Substrate temperature

All substrates
All dilutions



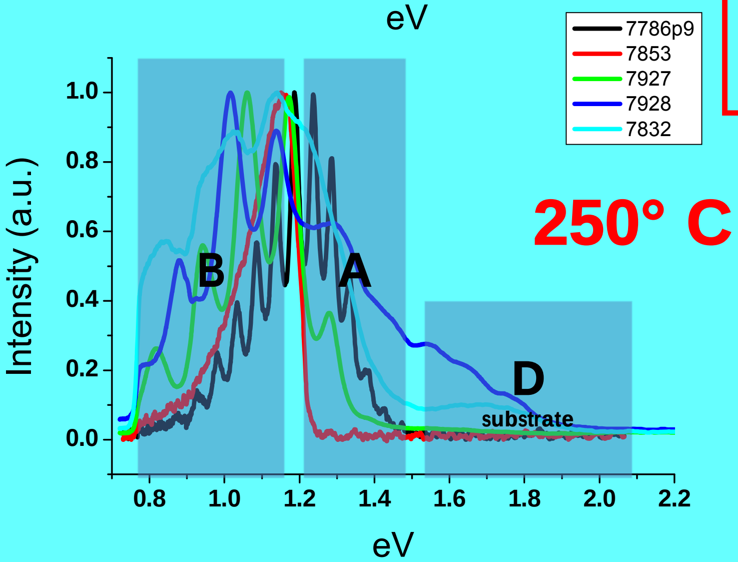

PL Bands

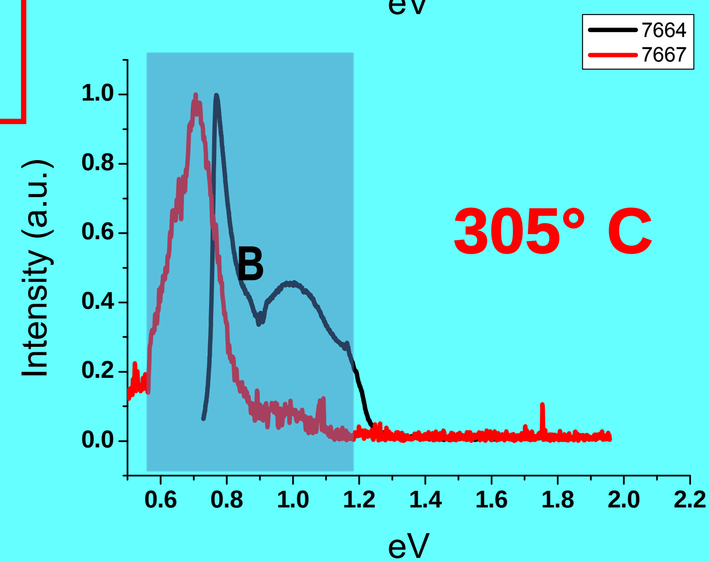
A: States in the a-Si gap

B: Deep defects in nc-Si

D: Substrate effects

(Street, *Advances In Physics*, **1981**, 593-676 )



# PL Summary.

- **Grain Size is strictly related with <u>A band</u> emission. Crystallinity with <u>B band</u>**
- **Laser Annealing suppresses A band intensity increasing the Mean Grain Size**
- **nc-Si/a-Si A band and nc-Si/$SiO_2$ emission band share analogous time distribution G($\tau$)**

***A band* is the recombination of *confined exciton* in silicon nanocrystal inclusions in a-Si**

Optical/Optoelectronic

**We know the energy gap (solar spectrum matching?) the origin of defect states, the origin of the main PL bands.**

- Energy gap ranging from 1.3 to 1.87 eV
- Urbach tails few meV for highly crystalline films, hundreds of meV for nearly amorphous films
- Defect states not related to DBs (as usually reported in literature), likely related with crystal disorder.
- PL A band related to recombination of confined exciton in silicon nanocrystal inclusions in a-Si.

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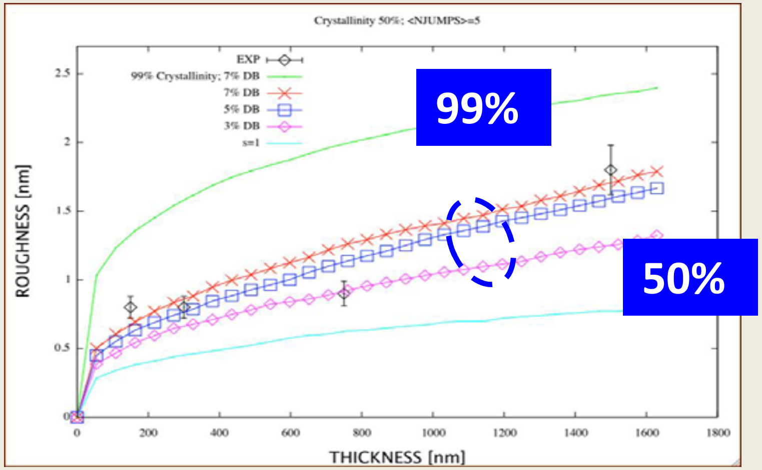
NANOcrystalline silicon films for PHOTOvoltaic and optoelectronic applications

# Feedback between experiments and theory

- modeling on roughness




- modeling of optical properties (absorption)

# Correlation between material properties and growth parameters

# Correlation between growth parameters and thin-film properties

| Growth parameter | Material property | Detection Method |
|---|---|---|
| Dilution factor | crystallinity | Raman |
| $SiH_4$ flux/ B config | Crystal fraction homogeneity | Raman |
| substrate | Microstructure | TEM |
| | Morphology (roughness, AGS) | AFM |
| temperature | Microstructure | TEM |
| thickness | Morphology (roughness, AGS) | AFM |
| Dilution factor/ crystallinity | Conductivity | I-V |
| | Defects, energy gap, crystal disorder | SPS |
| | Photo- emission | PL |

# Material properties independent on growth parameters

| Material property | Detection Method |
| --- | --- |
| Electrical transport at nanoscale | C-AFM |
| H content | FTIR |
| Preferential orientation | XRD |
| Average nanocrystal dimension | TEM |

# New characterization methods

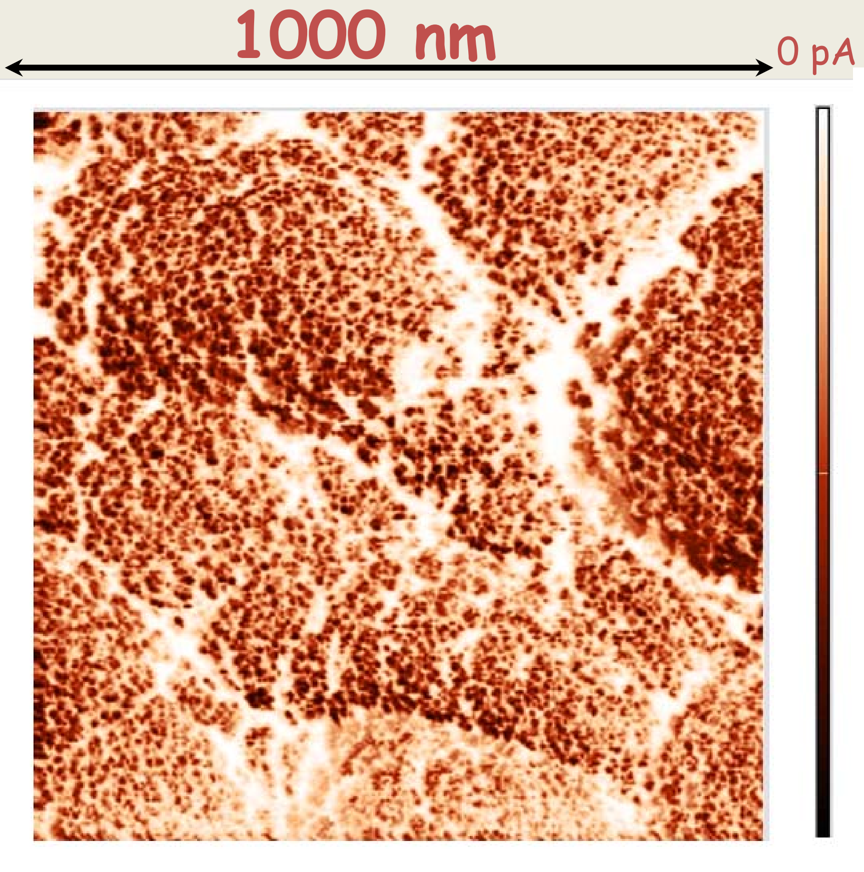
# Characterization methods

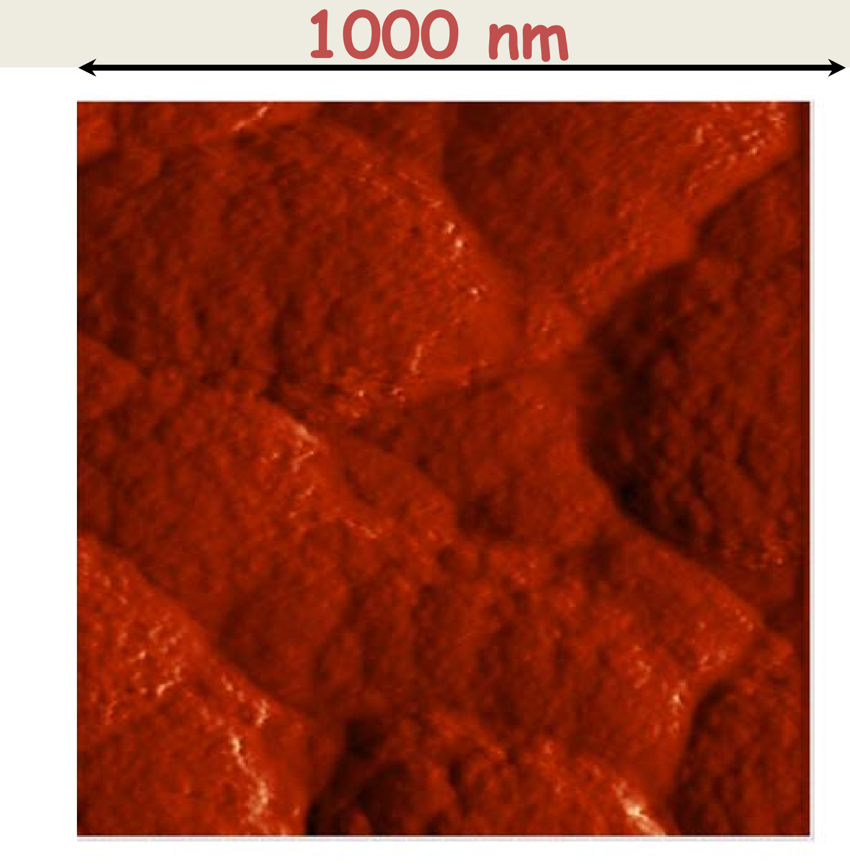
- What the new experimental methods developed within the Project?
- What the advancement in the estabilished ones?

# C-AFM Conductive AFM

UNIBO

Only very recently applied to nc-Si:H [1,2] but with controversial results
Allows for the **the localization of the trasport properties in nc-Si:H**





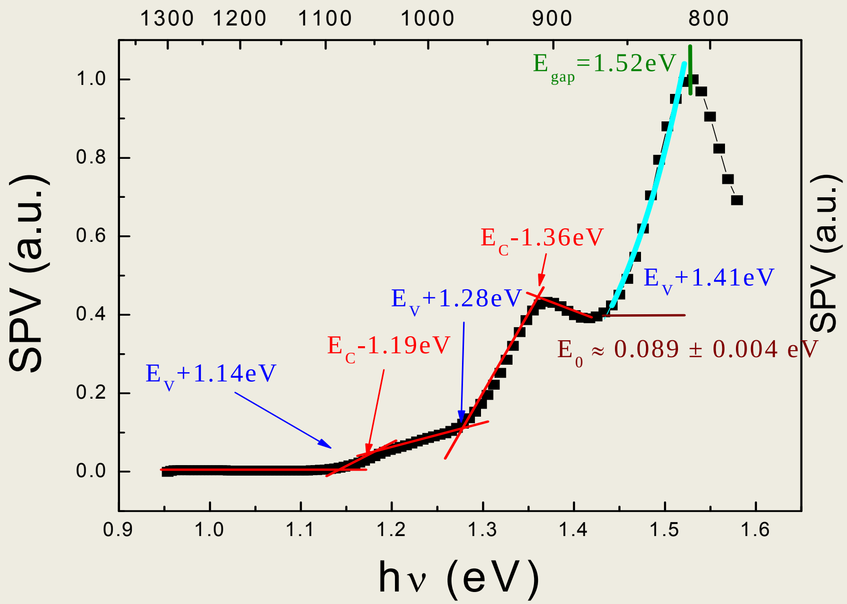
*[1], I.Balberg et al., Phys. Rev. B 71 (2005)]*

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

# SPS
# Surface photovoltage Spectroscopy

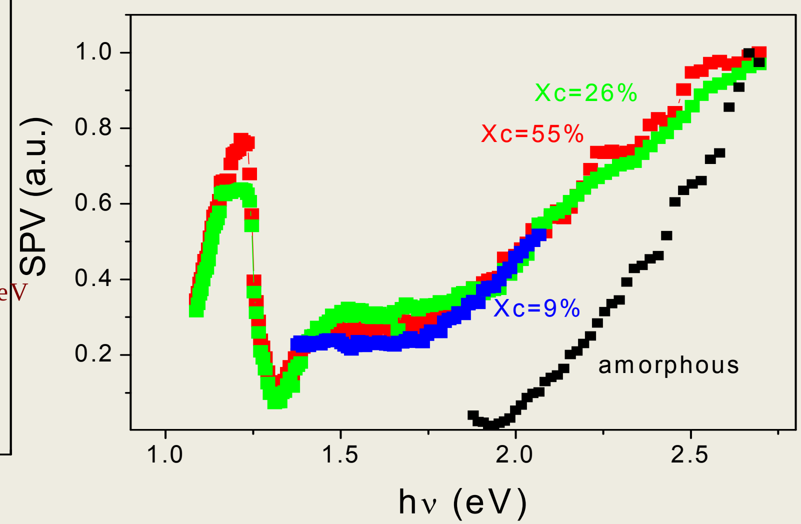
- Non contact method
- Allows for the determination of defect states and optical properties
- Allows for the identification of transition region nearly amorphous-nearly crystalline.
- *Never applied to nc-Si:H*

**nc-Si:H, grown on Si, Xc > 65 %**




Optical behavior typical of nc-Si:H; optical transitions at discrete energy levels, tail states lower than 0.1 eV

**nc-Si:H, grown on Si, Xc < 65 %**



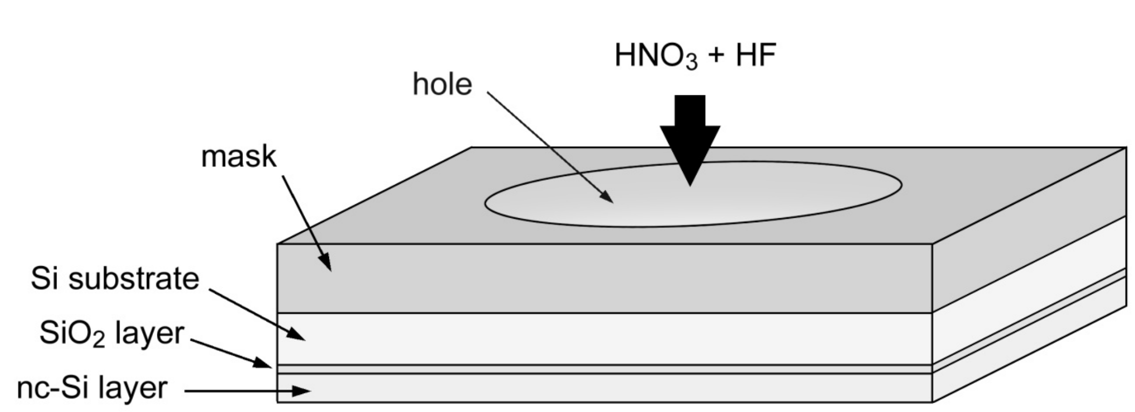

Optical behavior typical of a-Si:H; optical transitions at band states, tail states larger than 0.1 eV

# TEM in plan view, new **thinning procedure for HR-TEM study**

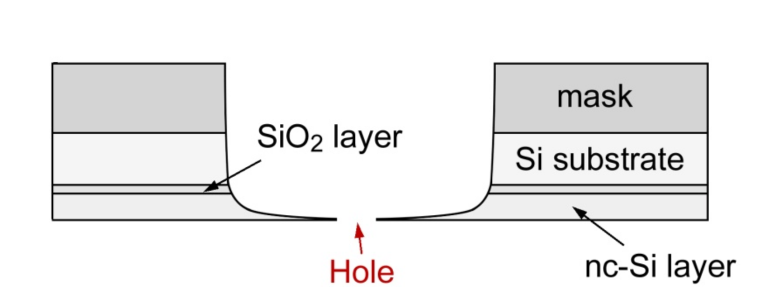
<u>The double-wedge polishing method</u>

This method allows us to carry out TEM observations in **plane view** of a same sample, at various depths.

# Thinning procedure for HR-TEM study: chemical etching




**After etching :**

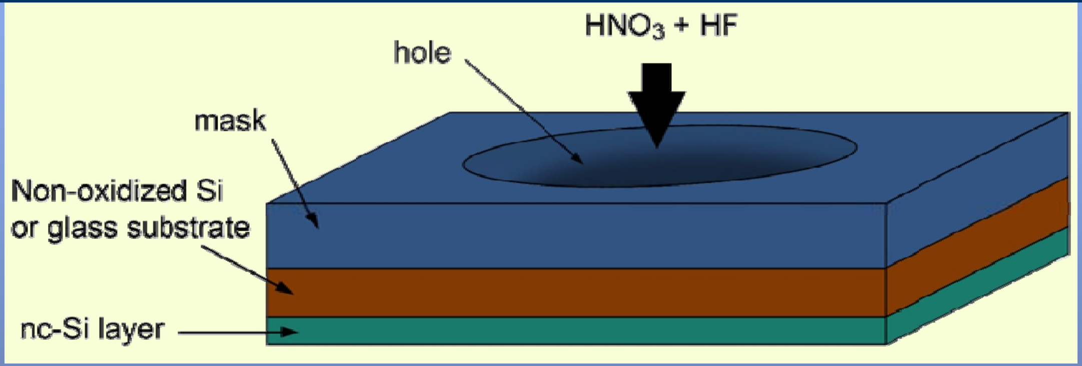



- Very thin areas suited to HR-TEM study
- No amorphisation
- No contamination

# Experimental details :
## TEM thin foil preparation for plan-view observations (HRTEM)

Experimental procedure :

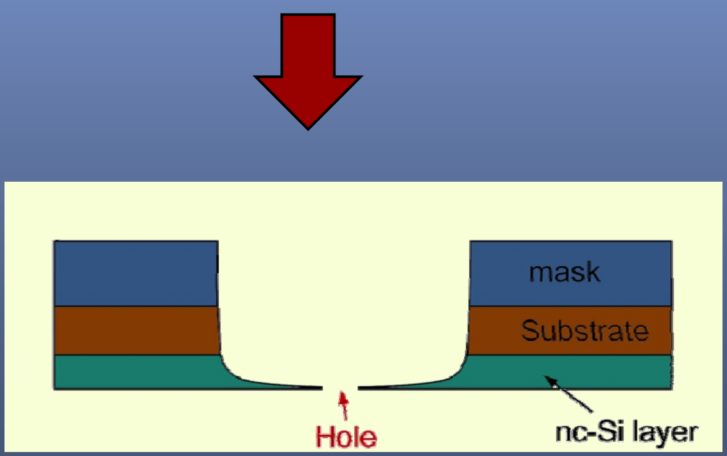
1) Mechanical thinning (Tripod)
2) Protective layer deposition (mask)
3) Chemical etching




Chemical etching :

**$HNO_{3\ (0.9)}$ + HF $_{(0.1)}$ solution**

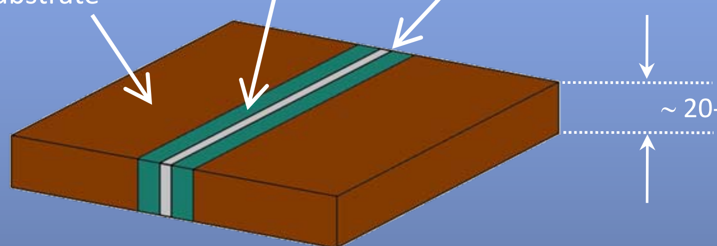
Etching rate : ~100 nm / s



# Experimental details :

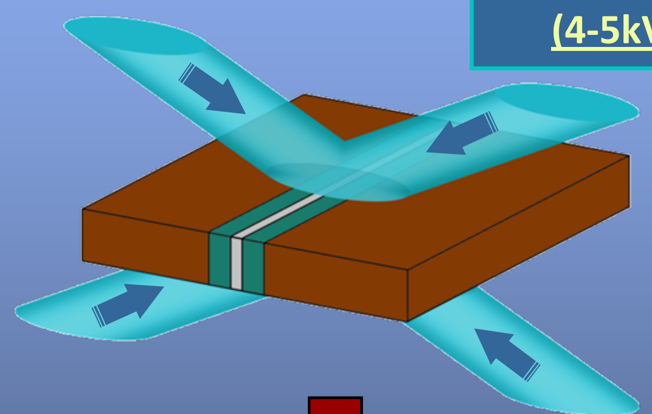
## TEM thin foil preparation for cross-section observations (X-HRTEM)

### 1 Mechanical thinning (Tripod )

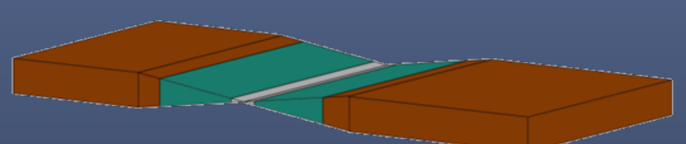



### 2 Ion Milling (Gatan PIPS )

**$Ar^+$ beams (4-5kV)**

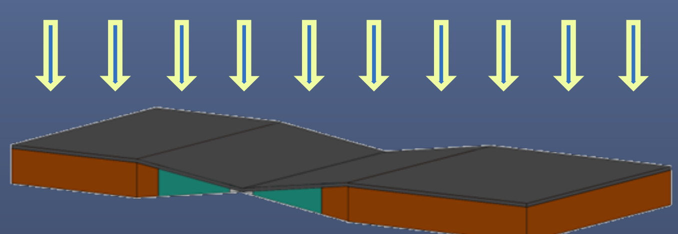


Thin foils for X-HRTEM (edge shaped)

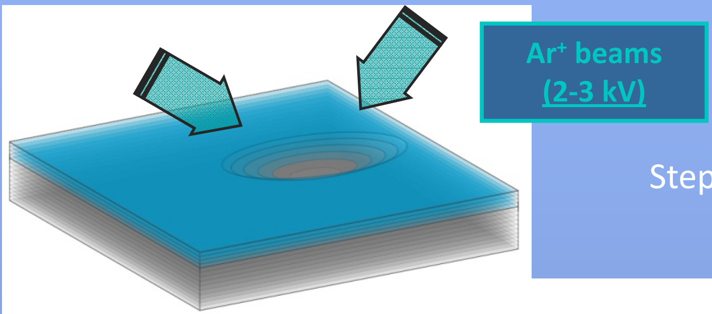


### 3 Samples deposited on glass only

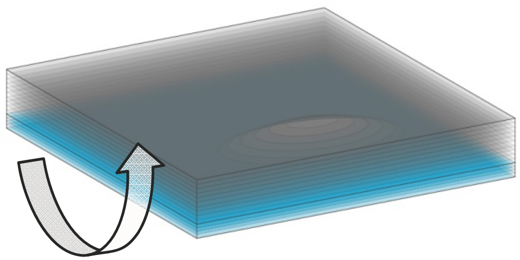
Carbon coating deposition



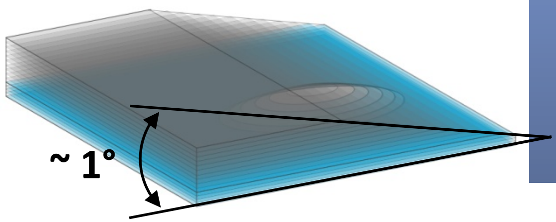
# The double-wedge polishing method : experimental procedure (1)



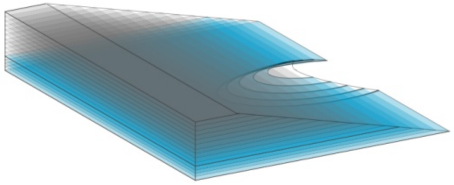

Step 1 : Formation of a dimple in the deposited film.
(using dimple-grinder or ion milling)



Step 2 : The sample is turned upside down and glued on the Tripod pyrex™.
(the deposited film facing the pyrex)

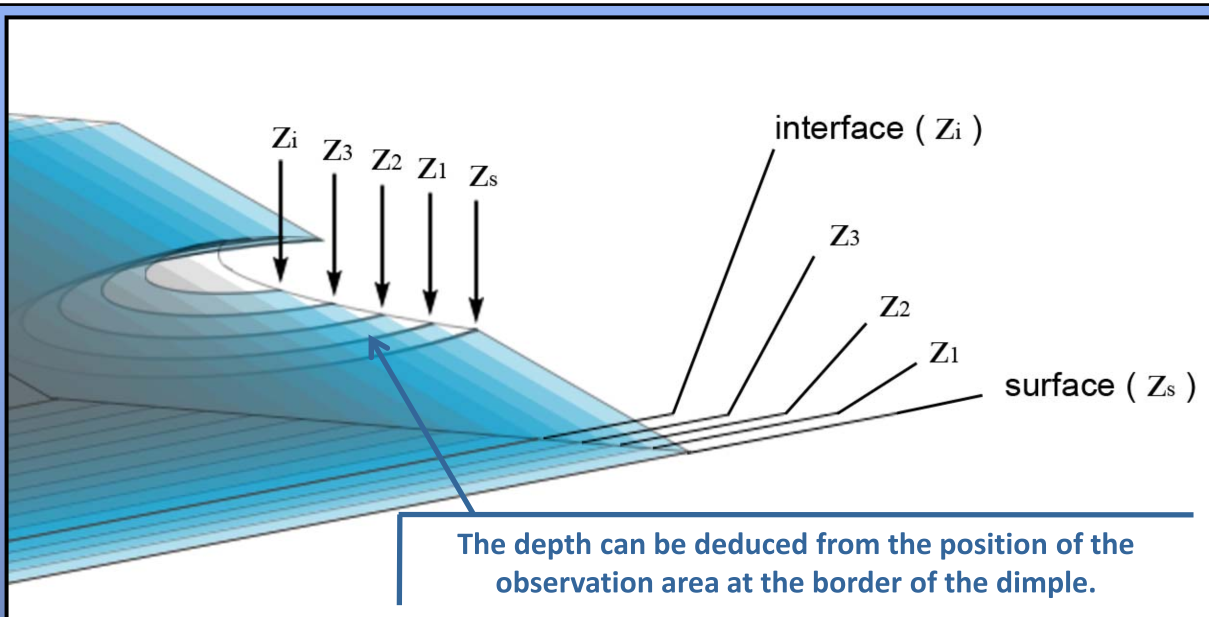



Step 3 : The substrate side of the sample is mechanically grinded with a slope of about 1°.



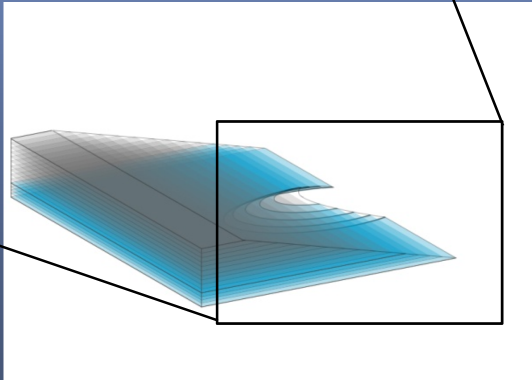
Step 4 : The polishing is stopped when the edge intersects the dimple

# The double-wedge polishing method : experimental procedure (2)




This method allows us to carry out TEM observations in **plane view** of a same sample, at various depths.

Step 4 : The polishing is stopped when the edge intersects the dimple

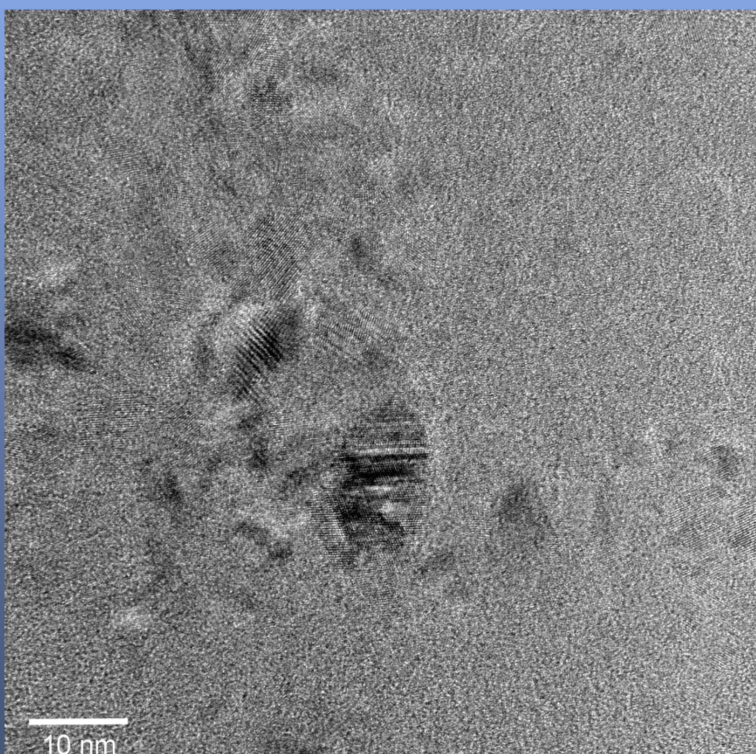


# The double-wedge polishing method : results(1)

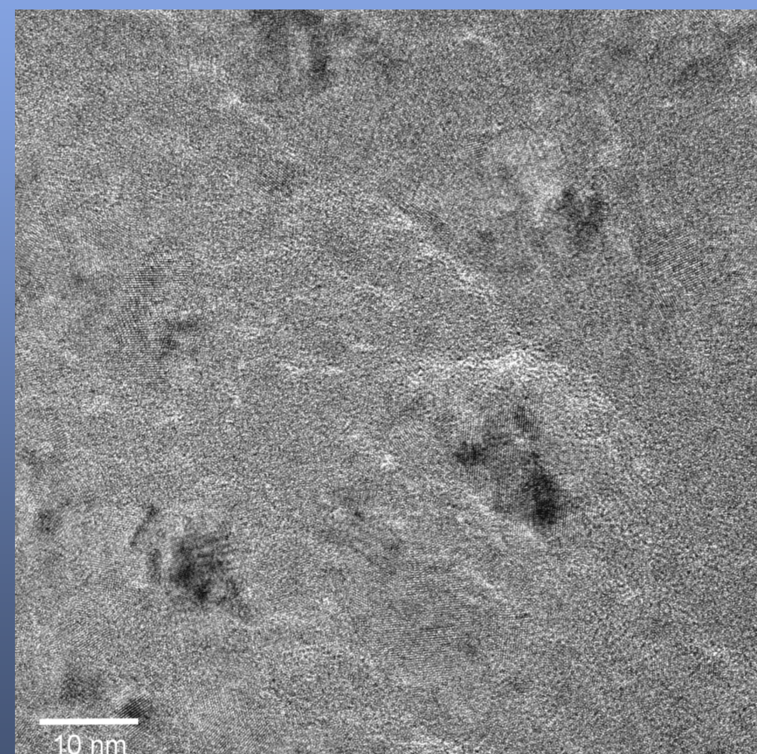
**TEM observations in "quasi" plane view (10° off):**

Central zone : 0.4 µm → 0.8 µm

**Depth: 0,5 µm**



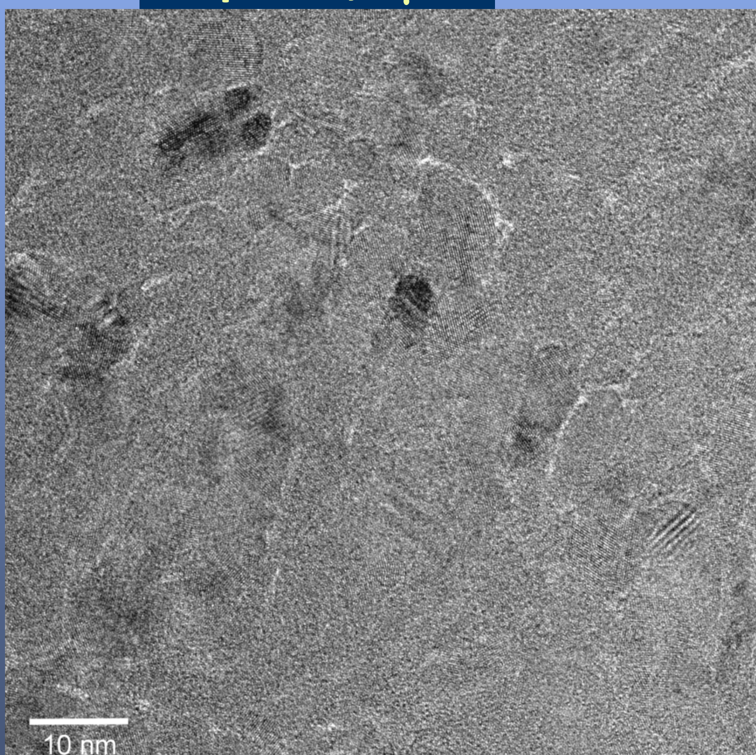

**Depth: 0,6 µm**



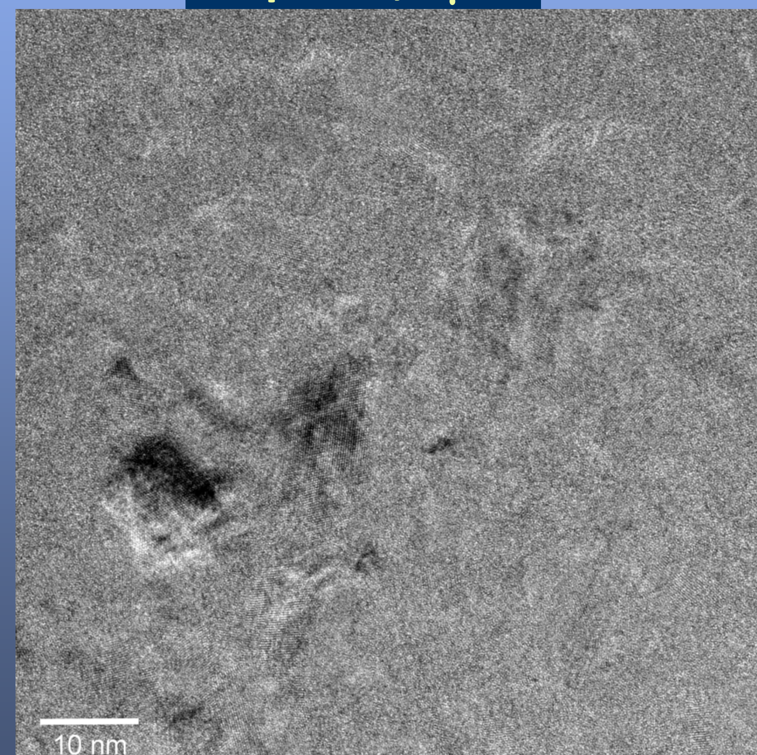
# The double-wedge polishing method : results (2)

**TEM observations in “quasi” plane view (10° off):**
**Central zone : 0.4 µm → 0.8 µm**

**Depth: 0,7 µm**



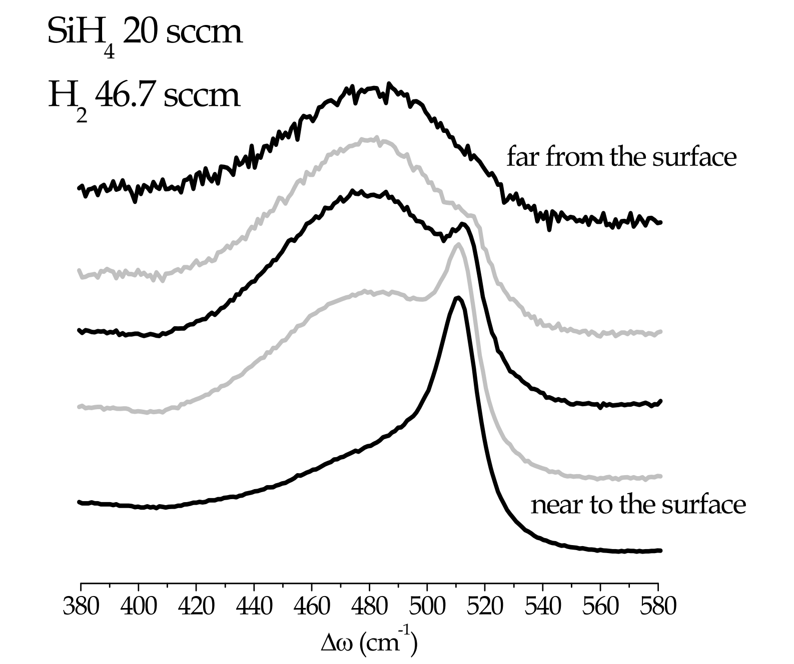

**Depth: 0,8 µm**

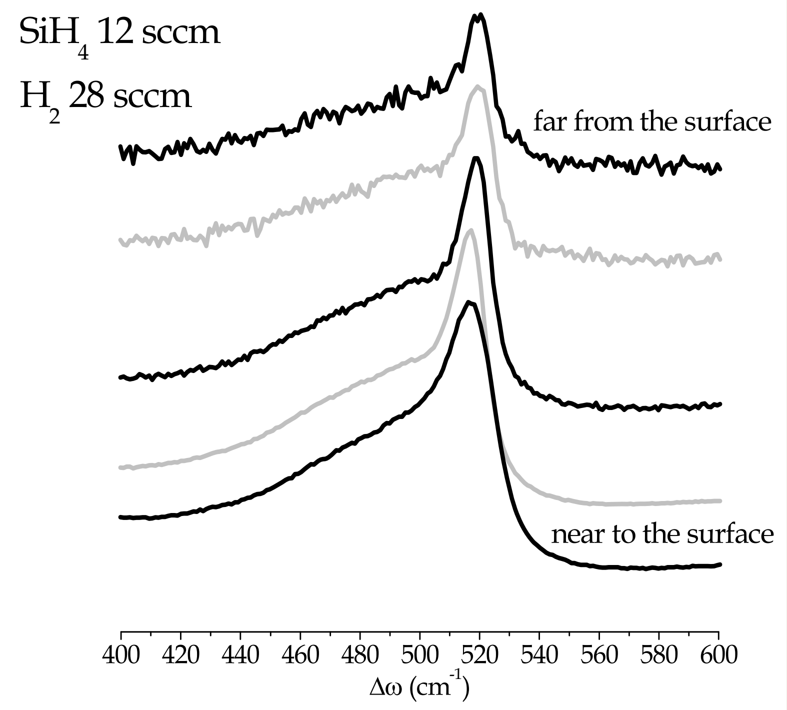


# Raman vs depth...

- Raman at different penetration depth..

# Raman vs depth... Homogeneity of the film



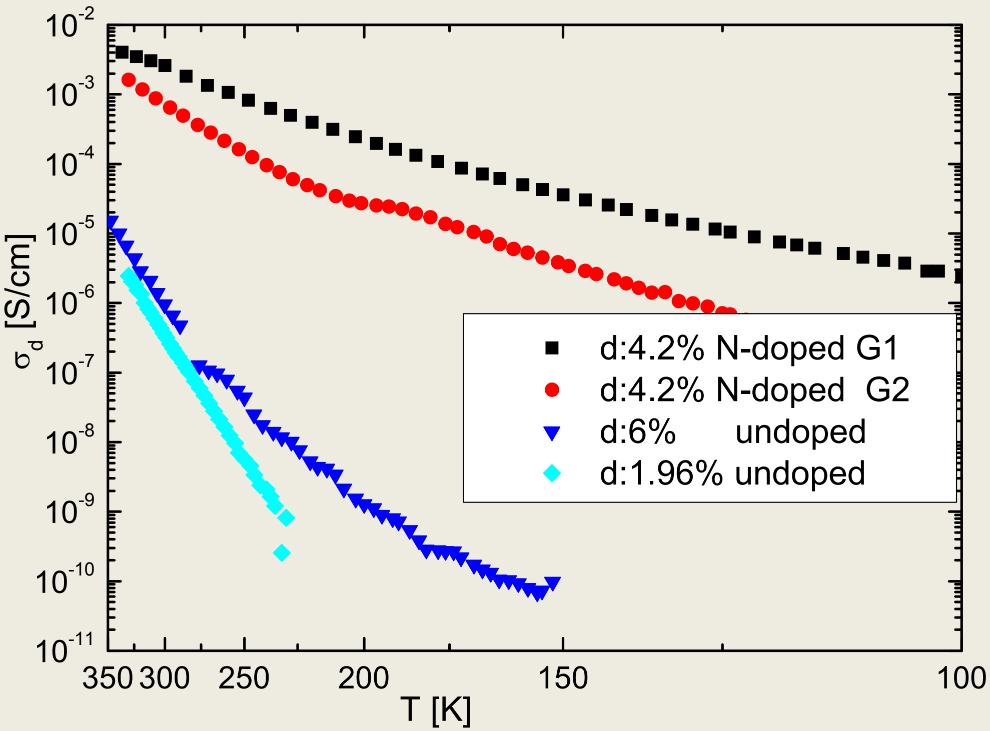

This sample presents an **inhomogeneous structure** along the growth direction

This sample shows a **homogeneous structure** along the growth direction!!

⇒ the **same evolution of the morphology** along the growth direction as a function of the SiH4 flux was observed **independently both of the substrate** (ITO-coated glass, ZnO-coated glass and Corning glass) **and of the dilution factor** (d=30%,d=50%).

# Conductivity. Low dilution samples



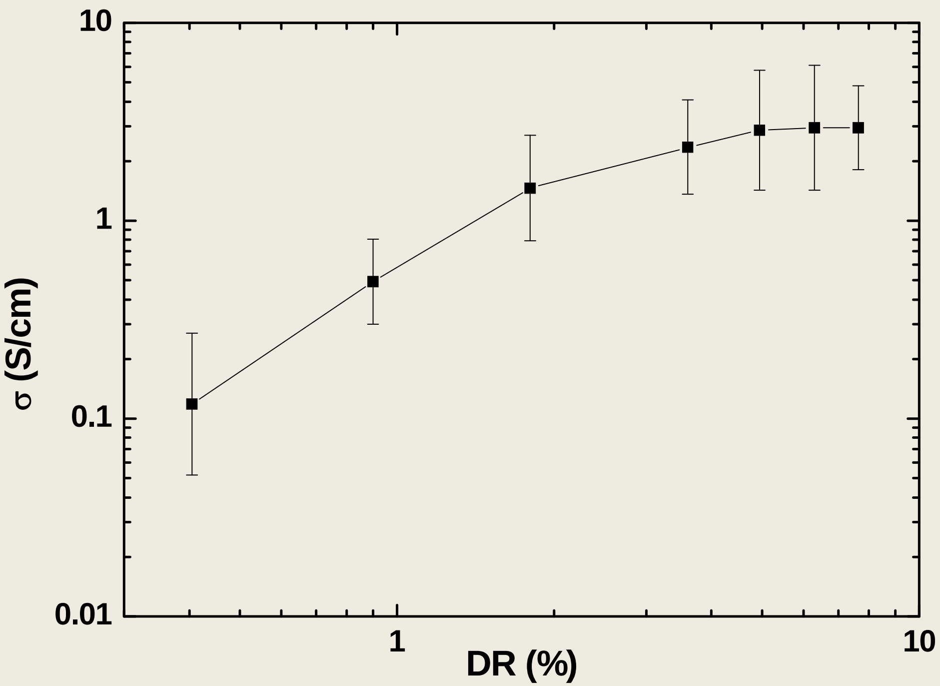



- Activation energies consistent with intrinsic or non intentionally doped μc-Si:H with high crystalline fraction
- both σ and $E_a$ significantly changes with doping

➔ **no Fermi level pinning as reported for a-Si**

| High T | 6733 I d:1.96% | 7578 I d:6% | 7446 N doped | 7445N doped |
|---|---|---|---|---|
| $E_a$ (eV) | 0.52 ± 0.02 | 0.50 ± 0.02 | 0.20 ± 0.02 | 0.12 ± 0.02 |
| $\sigma_{RT}(\Omega^{-1}.cm^{-1})$ | 3.2 E-7 | 1.4 E-6 | 6.0 E-4 | 2.6 E-3 |

# Conductivity of the p-doped nc-Si:H films




- As expected the conductivity increases with doping ratio to reach a maximum of 5-6 S/cm at **DR 6.3%!!!**

  *In the literature the optimum DR is between 0.4 and 0.8% for VHF-PECVD or HWCVD*

- The conductivity on one wafer varies for a factor 3 to 6

# Conclusions (1)

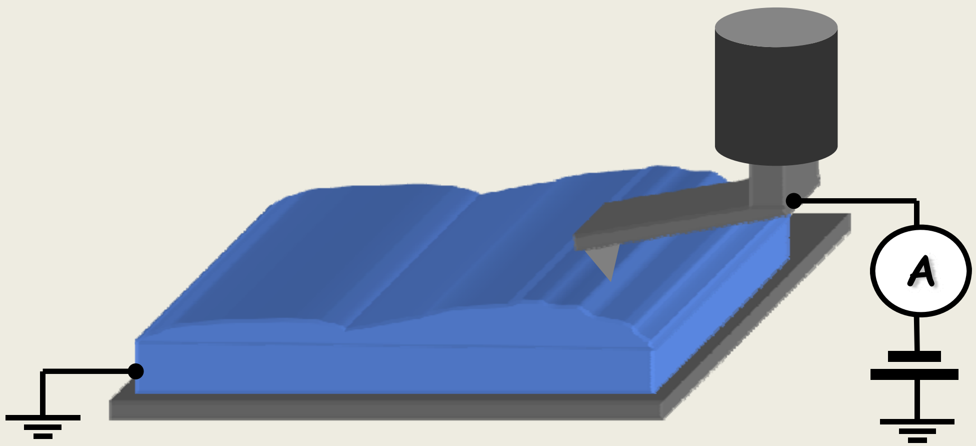
- What do we know now on nc-Si:H?
  - The growth mechanism
  - The electrical conduction mechanism
  - The origin of defect states and of the PL emission band
  - We know
    - how to obtain a uniform material
    - How to obtain high photogain
  - We know the correlation between growth parameters and material properties
- During the project we developed /applied innovative characterization methods
  - C-AFM, SPS, double wedge polishing method for plain view TEM maps at different depths in the same sample, Raman vs depth ..
- Feedback between experiments and growth
- Exp Results as input for modeling

# Conclusions(2)

- Is nc-Si:H a good material for PV applications?
  - high photogain obtained in some samples, very promising for PV applications, further improvements are possible
  - The knowledge of the correlation between material properties and growth conditions allows for solar cell optimization.

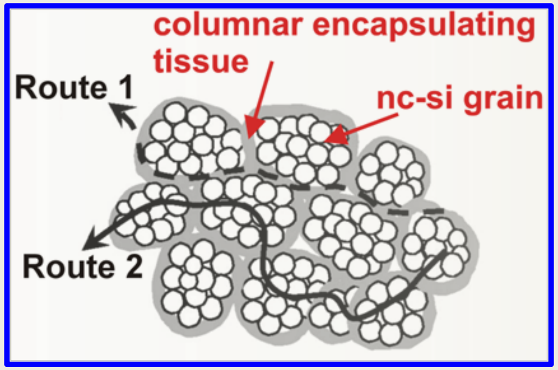
# C-AFM The method

UNIBO




The probe scans the sample surface 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



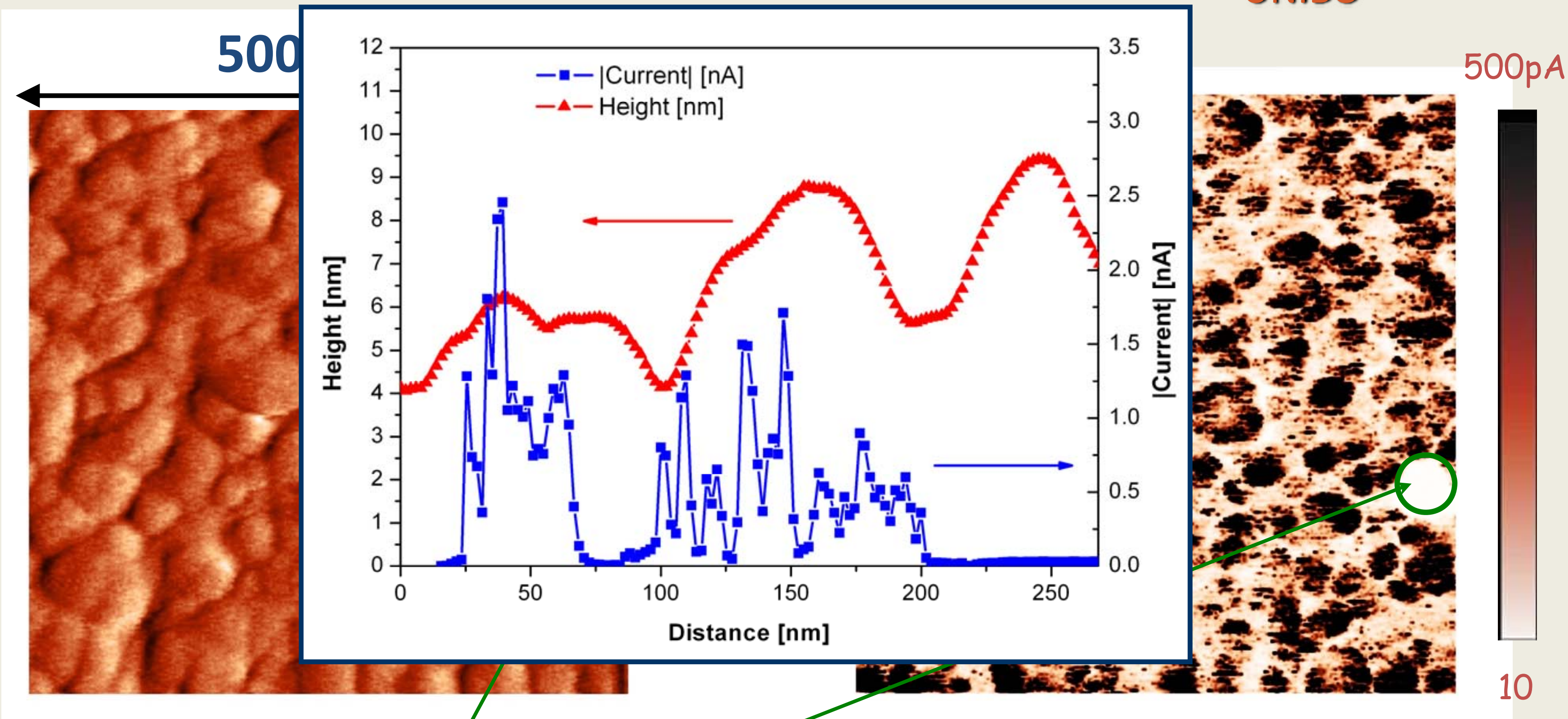

**The localization of the trasport properties in the material is still an open problem. *Route 1* and *Route 2* represent two possibilities supported by experimental data [1,2].**


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

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

# Results: Electrical Conduction
# Intrinsic nc-Si:H

UNIBO




**C-AFM maps show conductive grains in a non-conductive amorphous matrix.**

Not all the grains show the same conductivity, some grains are non-conductive

All the intrinsic samples (grown on Si, Glass,…) show the same behavior

# Outline

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  - Electrical characterization
    - C-AFM
    - Conductivity vs T
  - Optoelectronic characterization
    - SPV (Surface Photovoltage Spectroscopy)
    - Photoluminescence measurements and Quantum confinement studies
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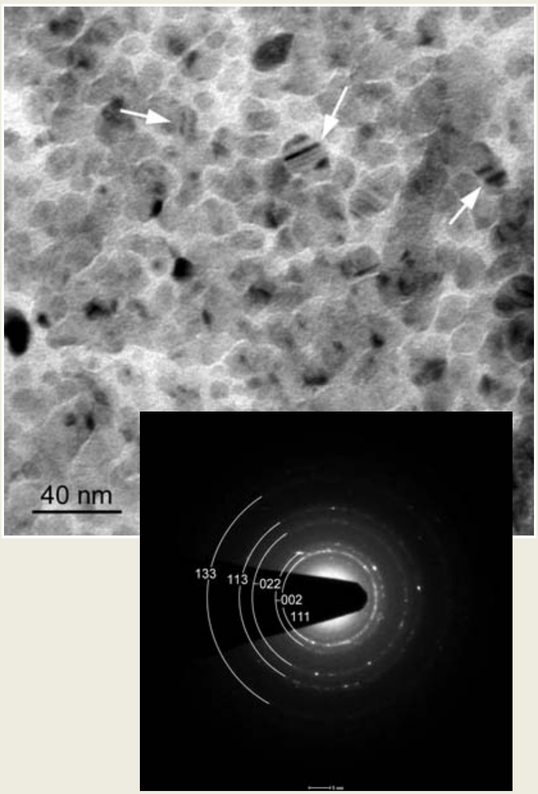
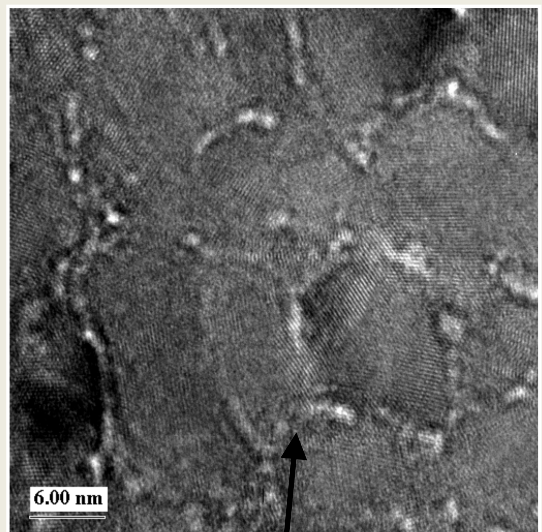
  - Correlation between growth parameters and material properties
- New Results on DOPED nc-Si:H
- Conclusions

# Series I. Plane view observations

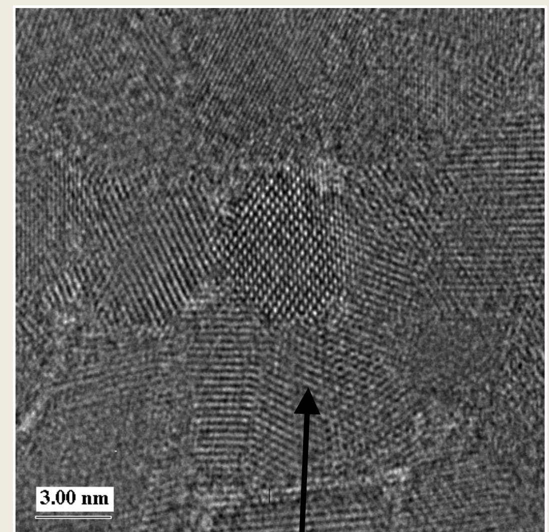
*Bright fieldTEM micrograph*
*& corresponding SAED pattern*




*HR-TEM micrographs*
*Left : under-focalized; Right : No defocus*




**Nanometric size domains are observed**



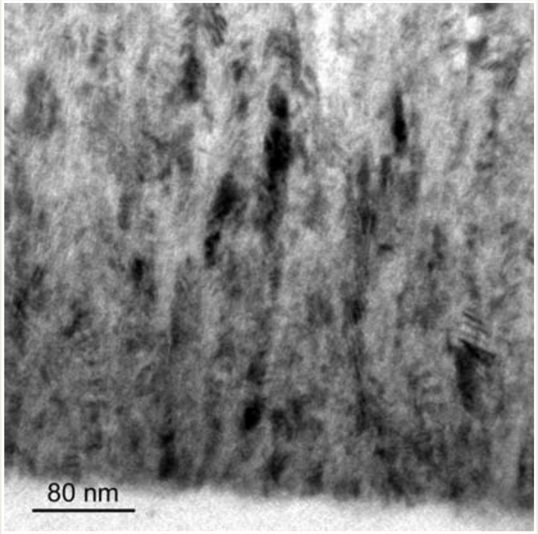

**Domains are constituted by misoriented nano-crystals**

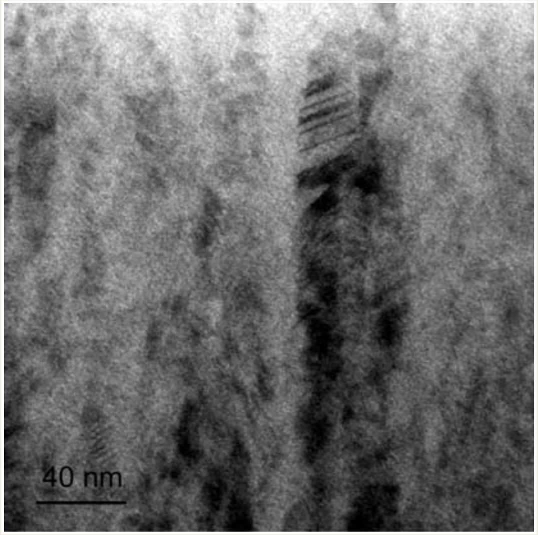
Various nanocrystal sizes (between 4 to 20 nm)

# Series I Cross-section view observations

Im2np Institut Matériaux Microélectronique Nanosciences de Provence
UMR 6242 CNRS, Universités Paul Cézanne, Provence et Sud Toulon-Var
UNIVERSITÉ PAUL CÉZANNE Aix-Marseille III
CNRS CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

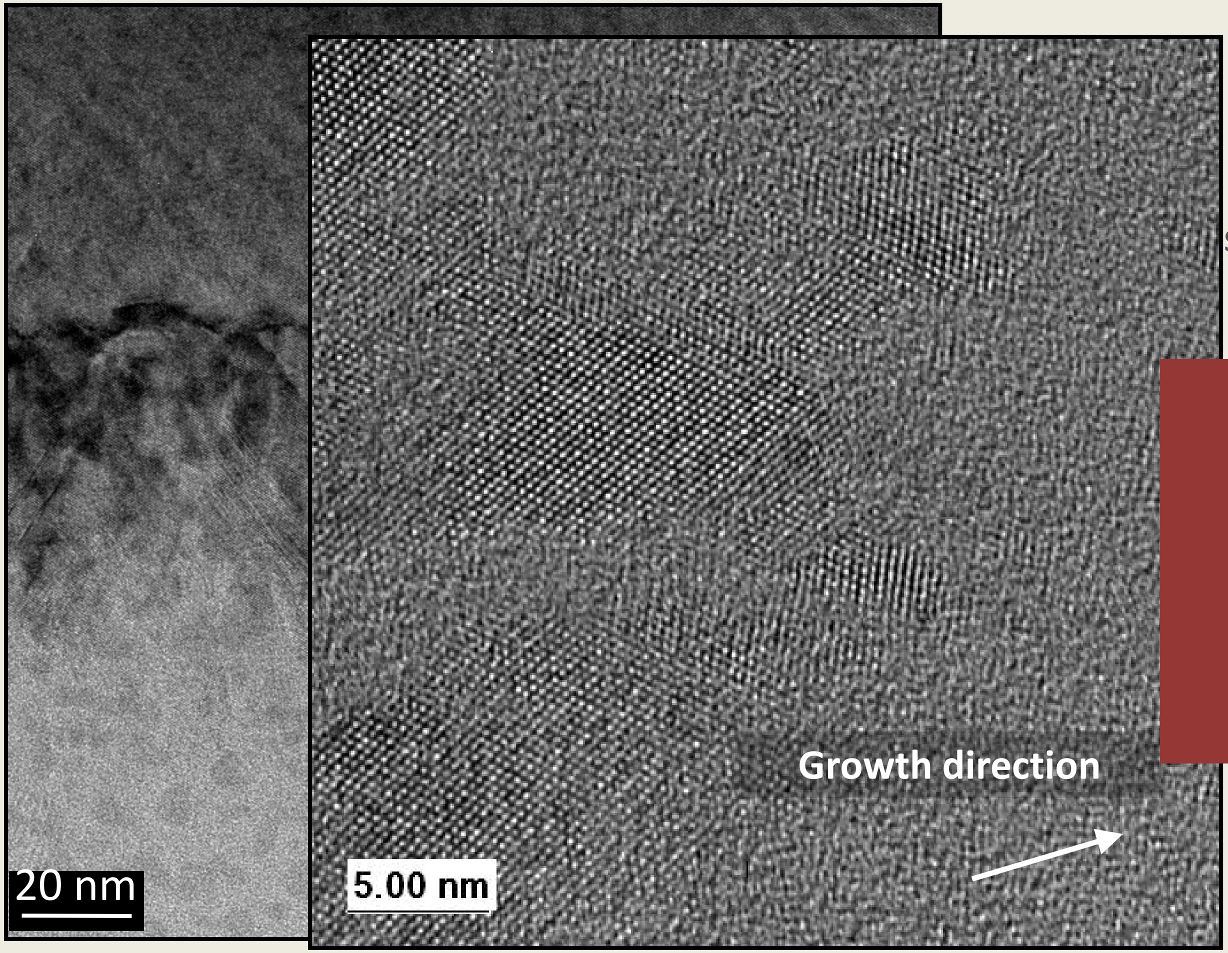
- **Columnar growth**
- **Fringe contrasts : twinning within the columns**




*Bright field TEM micrographs (low magnification)*

# Series II Cross-section view observations




Single crystal

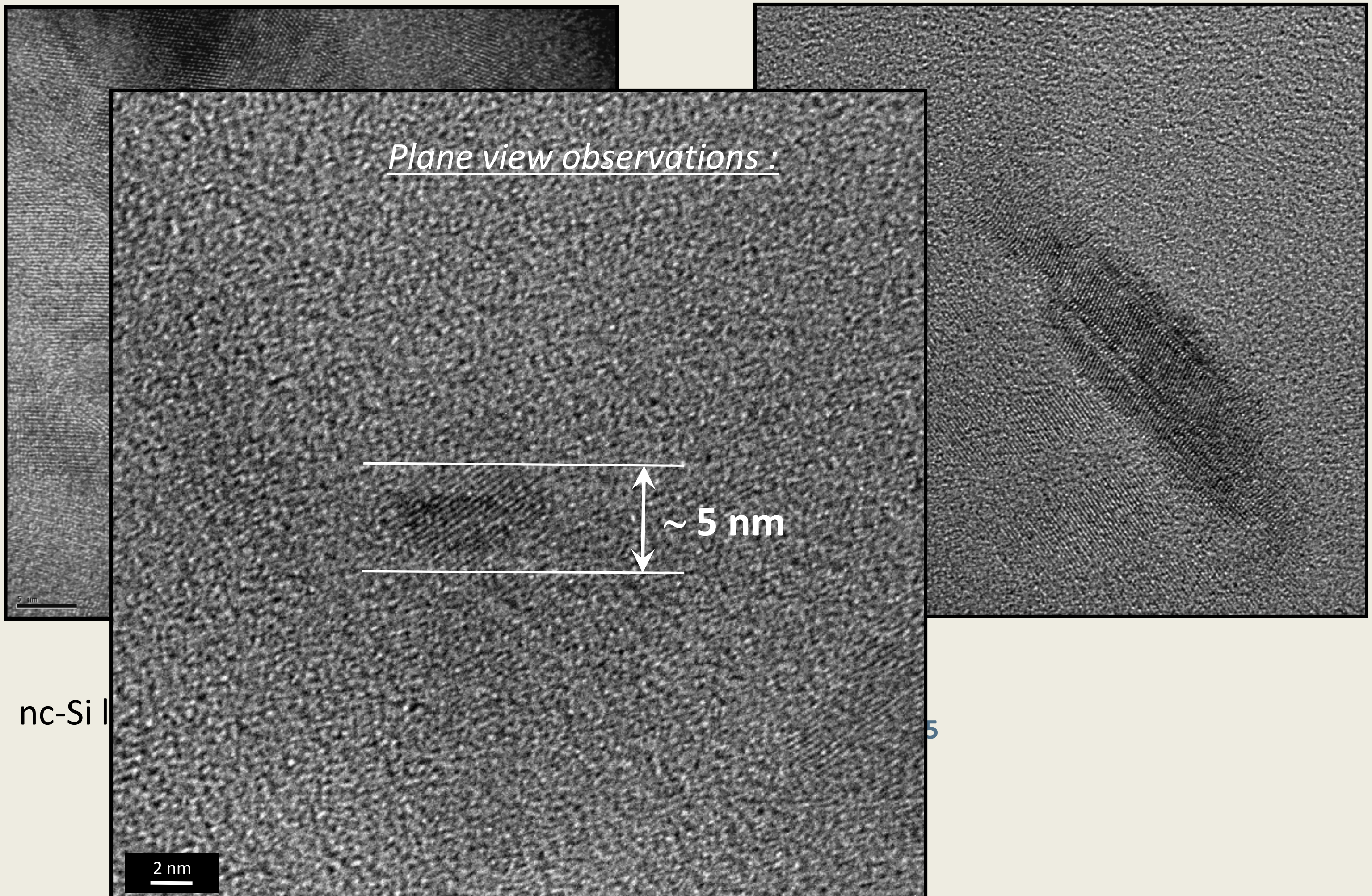
SUBSTRATE

**Superficial part of the layer :**

Transition from crystalline to amorphous structure.

The elongated columns become isolated small nanocrystals

# Series III Cross-section and plan-view observations :

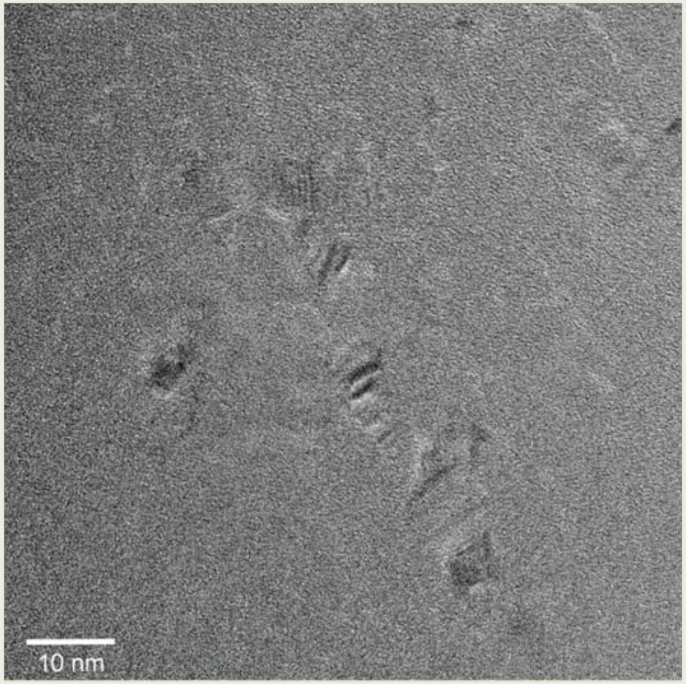



nc-Si l

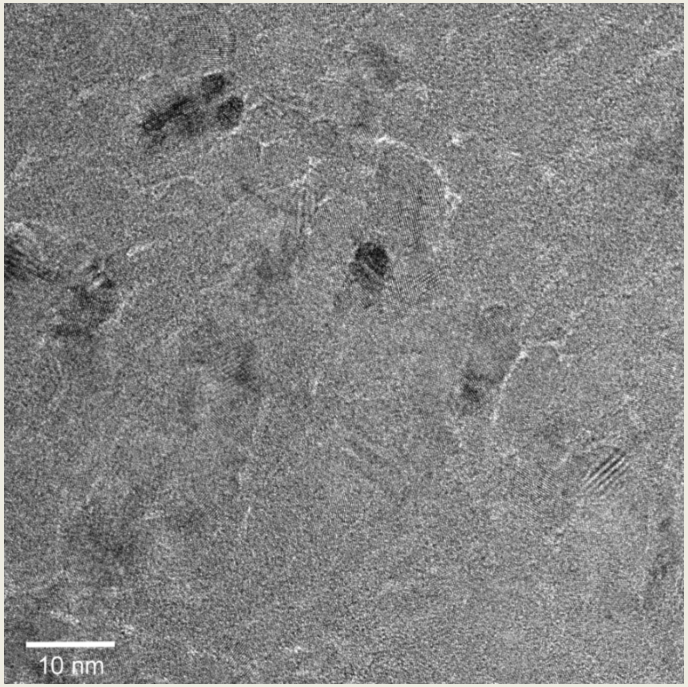
5

# Series IV Plane view observations

Area close to the ZnO film




Central part of the nc-Si layer




**Crystallinty seems to vary depending on the investigated area :**

$\chi_c$ **low** close to the ZnO film *vs* $\chi_c$ **higher** after only a few tens of nanometres

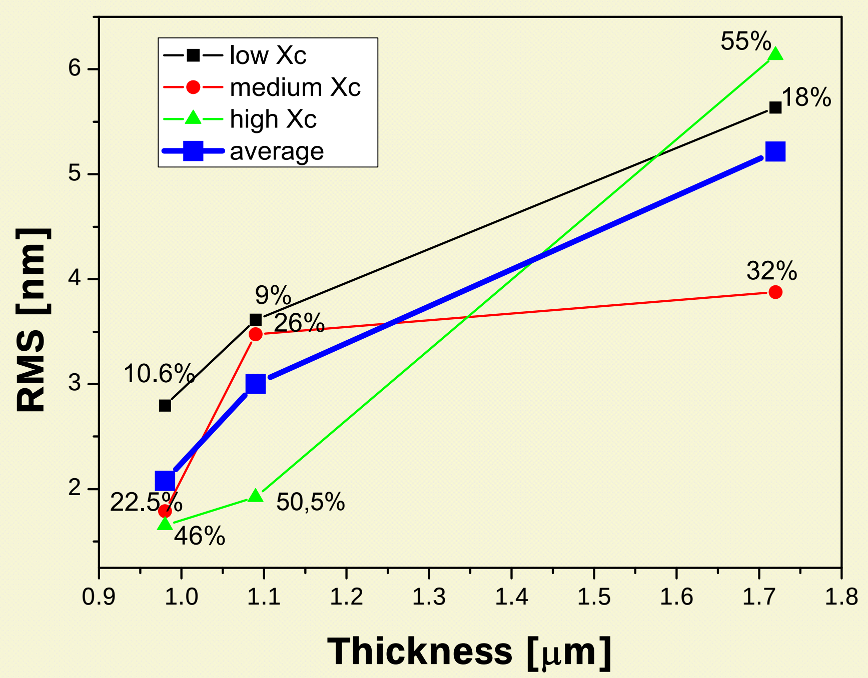
# Morphology by AFM

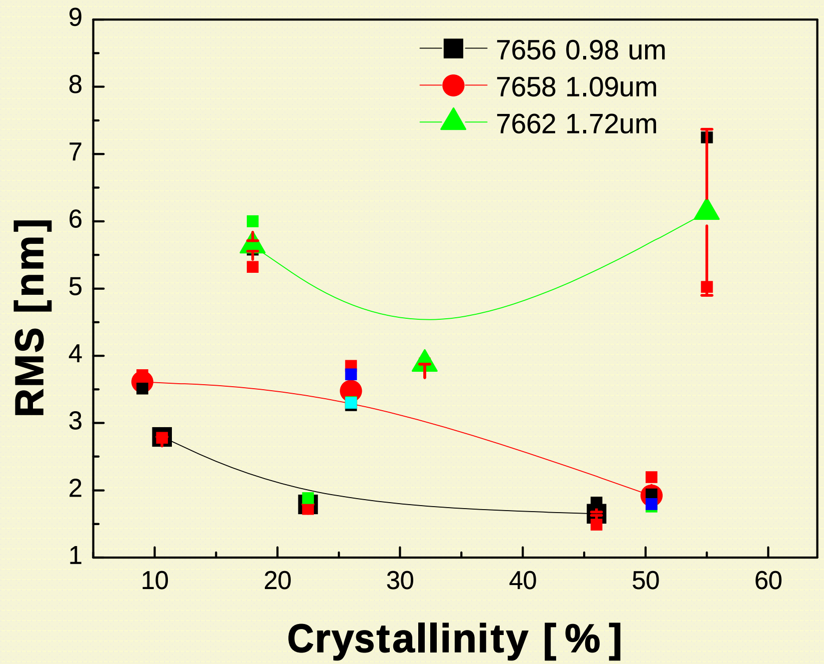
$$\sigma_{RMS} = \sqrt{\frac{\sum_{i=1}^{N}(Z_i - \overline{Z})^2}{N}}$$

UNIBO

PHoS Lab – PHysics of defects in Semiconductors

Roughness *vs* Substrate, thickness, crystallinity
Series I




Conclusions:

- RMS increases vs film thickness
- RMS is independent on crystallinity

# Roughness vs thickness. Summary

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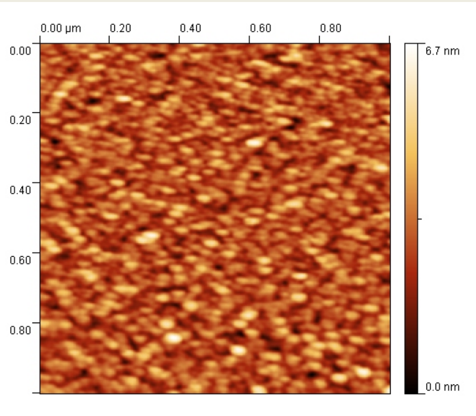
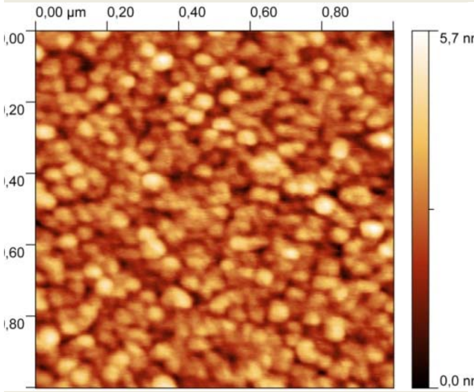
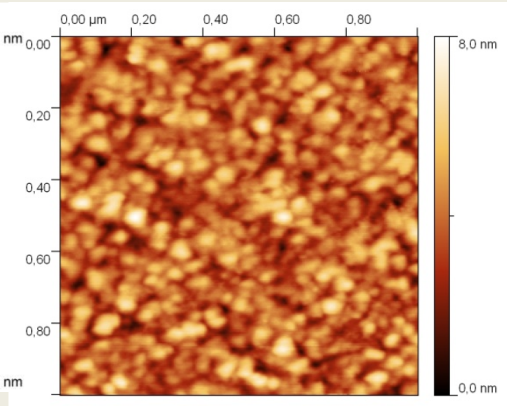


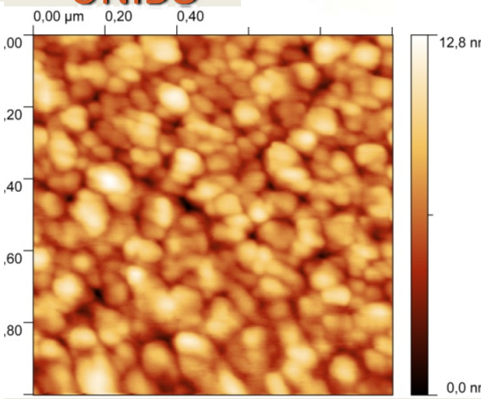

8129




8130

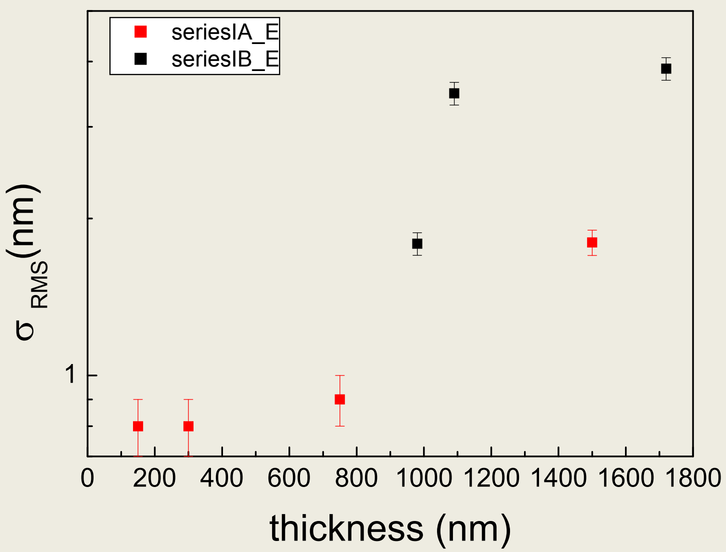



8127




8126

AGS increases for increasing thickness

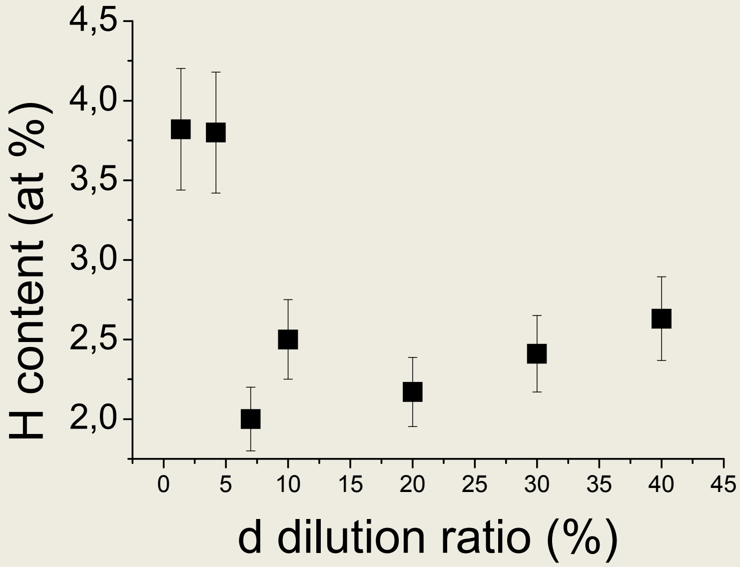


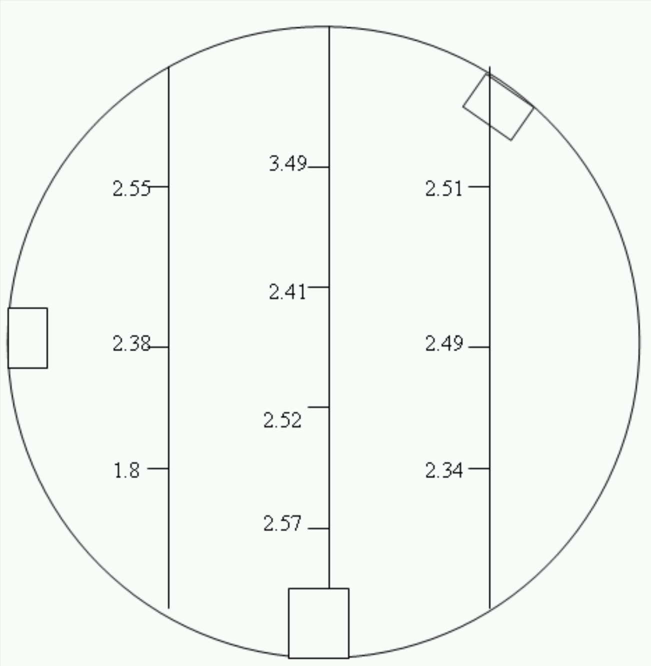

AFM analyses: 12 maps in different areas of the samples 1X1 μm

FFT of the maps to remove noise and artifacts (tilting, piezo drift, acustic noise)

The error bars are the standard deviation of the RMS roughness values on the different maps

# H content determination by FTIR




**[H] map for the sample #7653 (d=10%)**

relatively low (around 2.5%) H concentration in all samples

Obtained from the values of integrated absorption of the Si-H wagging-rocking mode at 640 $cm^{-1}$ [Y. He, C. Yin, L. Wang, X. Liu, G.H. Hu, J.App.Phys. 75 (1994) 797]

# Results: C-AFM (II)

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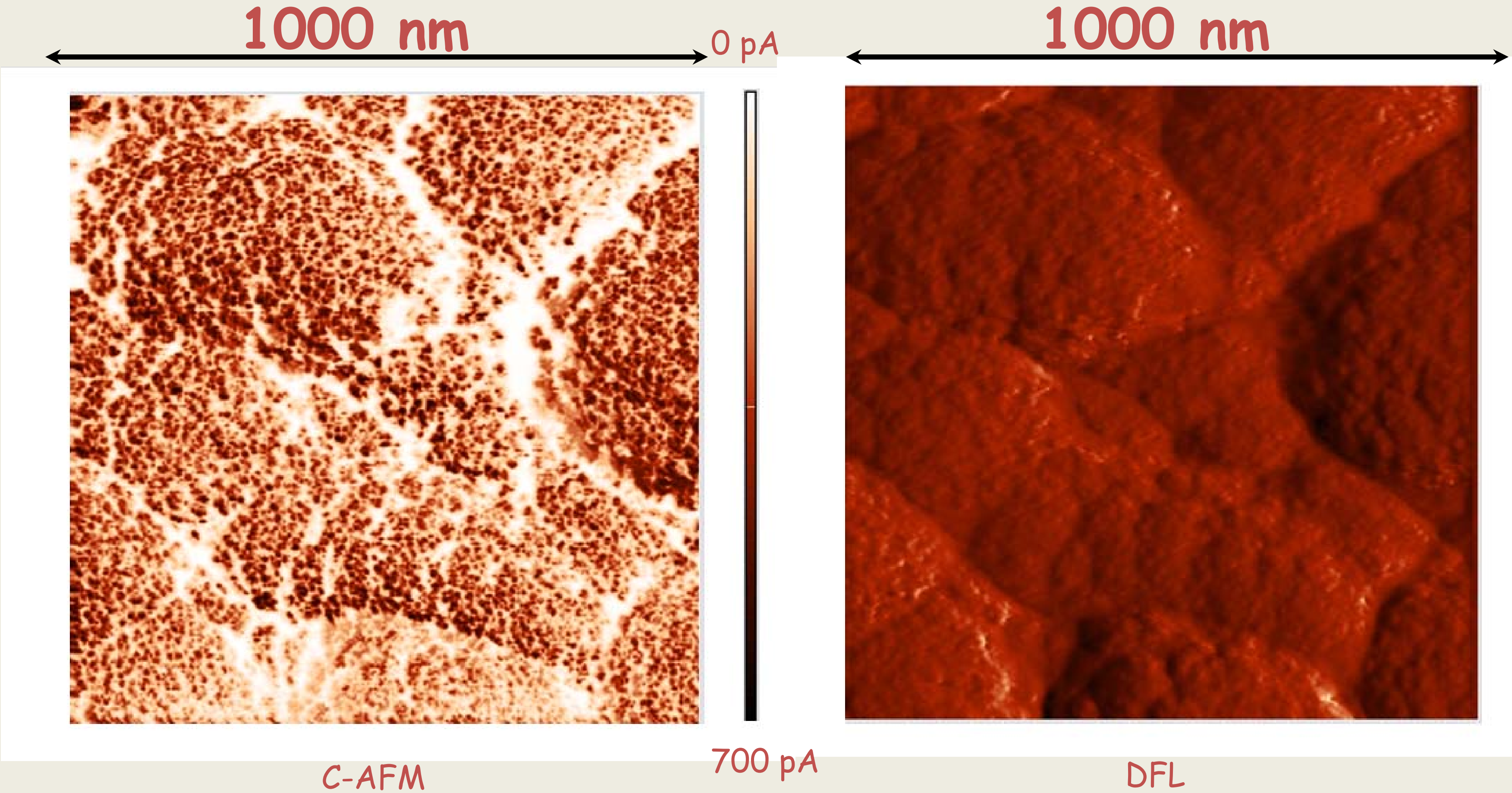
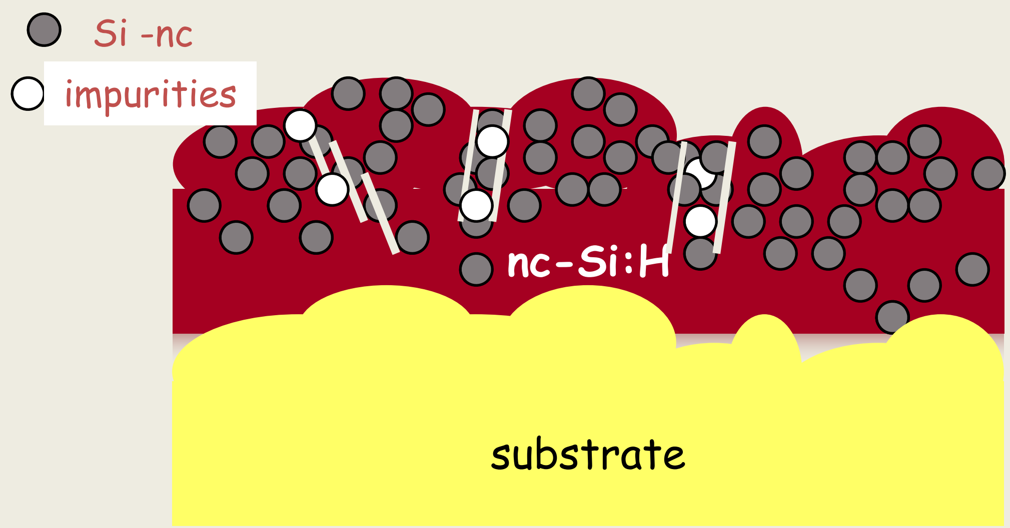



Samples grown on ITO/glass, Xc= 50 % dilution 40%

# Electrical conduction: a tentative explanation

The borders between grains are highly disordered
strained regions

They behave as preferential site for impurity incorporation




In doped nc-Si

impurities: B O, H,.....

These impurities cause an increase in the conductivity

In intrinsic nc-Si

impurities: O, H, C, O-H complexes

These impurities capture free carriers

These borders are potential barriers for free carriers.

# Conductivity measurement setup

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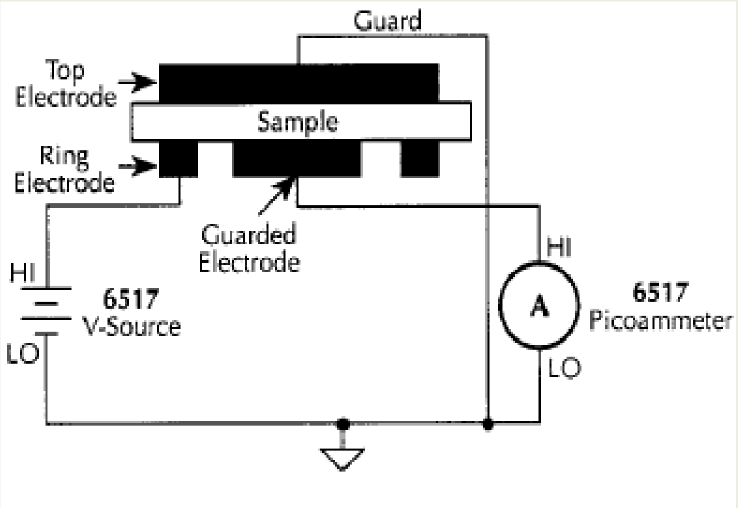
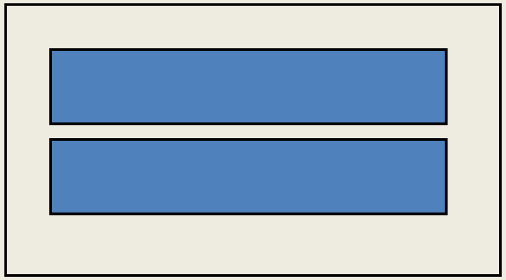
Using a Keithley 617 electrometer in V source mode, we can measure resistance up to 1 TΩ or conductivity down to 1E-9 → 1E-10 S/cm (film thickness)



Rectangular contact: 10 *3 mm

Electrode distance : 0.5 mm

Structure Ti(50nm)/Pd(50nm)/Ag(1µm)

Annealed for 90 min at 180°C in Ar, Ar/H

Temperature can be swept between 80 and 340 K

Voltage can be swept between -105 and +105 V

# Conductivity. Low dilution samples

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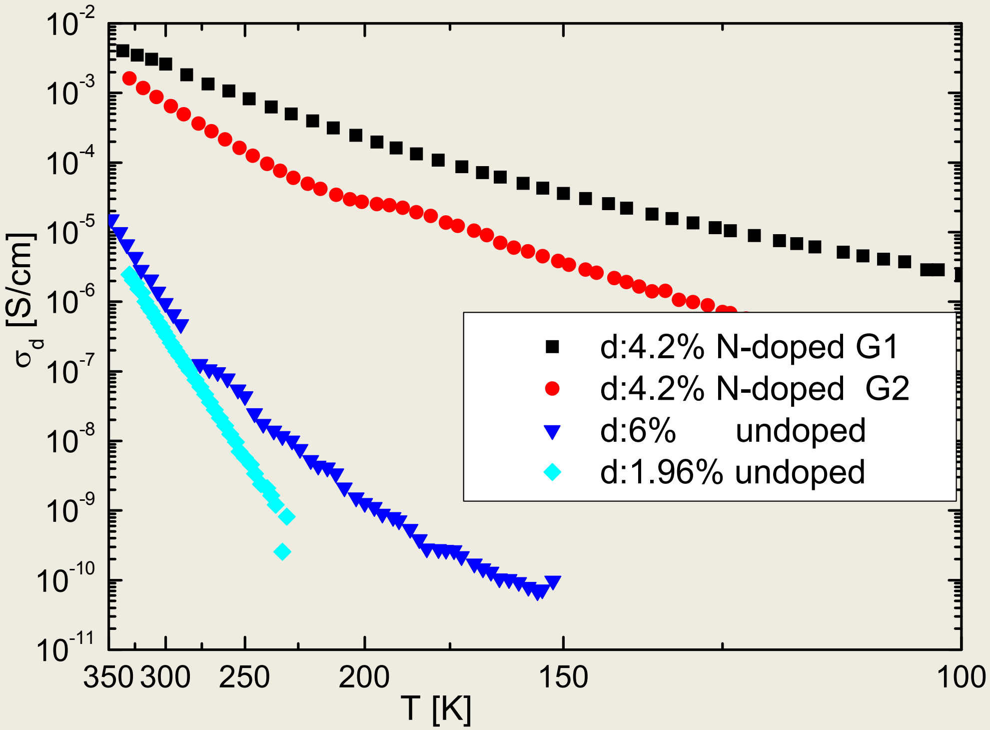


- Activation energies consistent with intrinsic or non intentionally doped µc-Si:H with high crystalline fraction
- both σ and $E_a$ significantly changes with doping

➔ no Fermi level pinning as reported for a-Si

| High T | 6733 I d:1.96% | 7578 I d:6% | 7446 N doped | 7445N doped |
|---|---|---|---|---|
| $E_a$ (eV) | 0.52 ± 0.02 | 0.50 ± 0.02 | 0.20 ± 0.02 | 0.12 ± 0.02 |
| $\sigma_{RT}(\Omega^{-1}.cm^{-1})$ | 3.2 E-7 | 1.4 E-6 | 6.0 E-4 | 2.6 E-3 |

# Ideal conductivity characteristics for solar cells

Universität Konstanz

- Bibliographic study establish that the best compromise between
  - Amorphous
    - Poor dark conductivity $10^{-11}$-$10^{-9}$ S/cm (high recombination)
    - High photogain :1000-10000 : very good light absorption
  - And Crystalline silicon
    - High dark conductivity $10^{-4}$-$10^{-5}$ S/cm (low recombination)
    - Low photogain :1-5 : low light absorption
  - Should be nc-Si with:
    - Medium dark conductivity $10^{-7}$ S/cm
    - Medium photogain : 100

so the best samples for PV aplications should be close to the a-nc transition

- The best samples already grown show a dark conductivity of $10^{-8}$ S/cm for a photogain around 100

➔ These samples will have lower electrical performance than the recommended ones from literature ??? perchè???

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    - C-AFM
    - Conductivity vs T
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# Surface Photovoltage Spectroscopy for :

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- Identification of the nc-Si→ *a*-Si transition
- Determination of the energy gap $E_G$ of the multiphase material
- Determination the crystal disorder via the amplitude of the Urbach tails
- Characterization of defective states (levels and bands)

# Amorphous-crystalline transition (i)
# Energy gap and defective states

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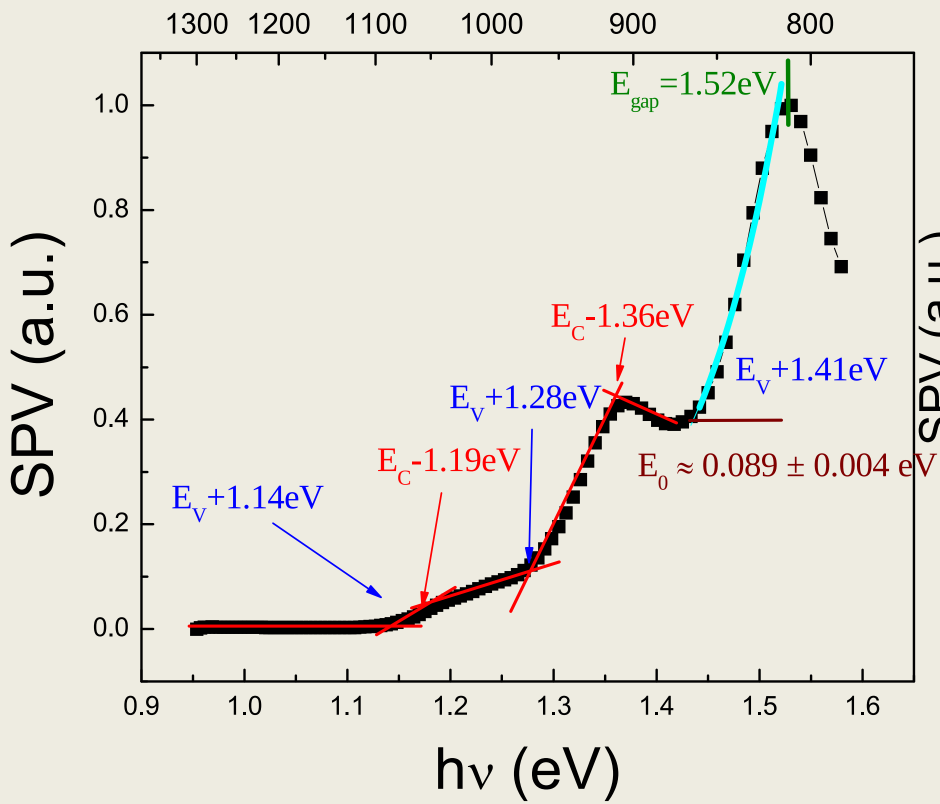
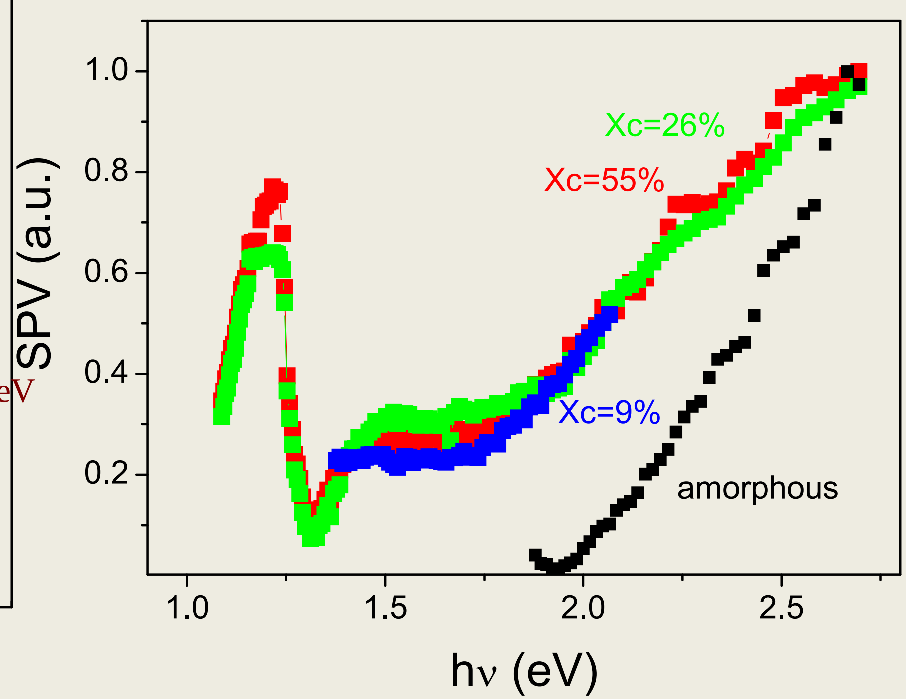
## nc-Si:H, grown on Si, Xc > 65 %




Optical behavior typical of nc-Si:H; optical transitions at discrete energy levels, tail states lower than 0.1 eV

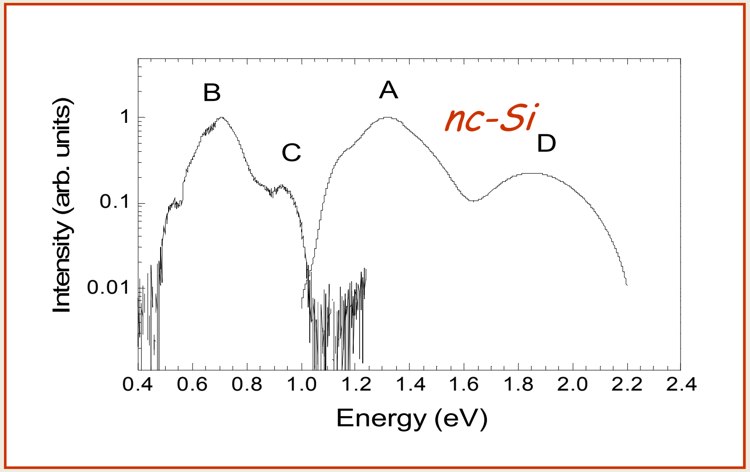
## nc-Si:H, grown on Si, Xc < 65 %

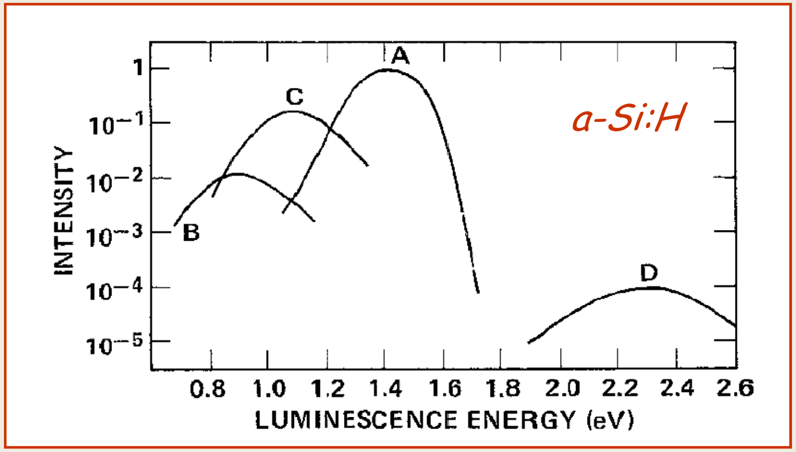



Optical behavior typical of a-Si:H; optical transitions at band states, tail states larger than 0.1 eV

# Quantum confinement studies

- A correlation between the crystallinity and the intensity of the photoluminescence band **A** was found.
- This band could be generated from the emission of quantum confined states due to its energy position between the c-Si and the a-Si gaps.




The same band (*A*) could be observed also in a-Si:H samples and, in the literature, it has attributed to localized states in the amorphous matrix.

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- Latest results on DOPED nc-Si:H
- Conclusions

# DOPED Materials

# p type

nc-Si:H grown by

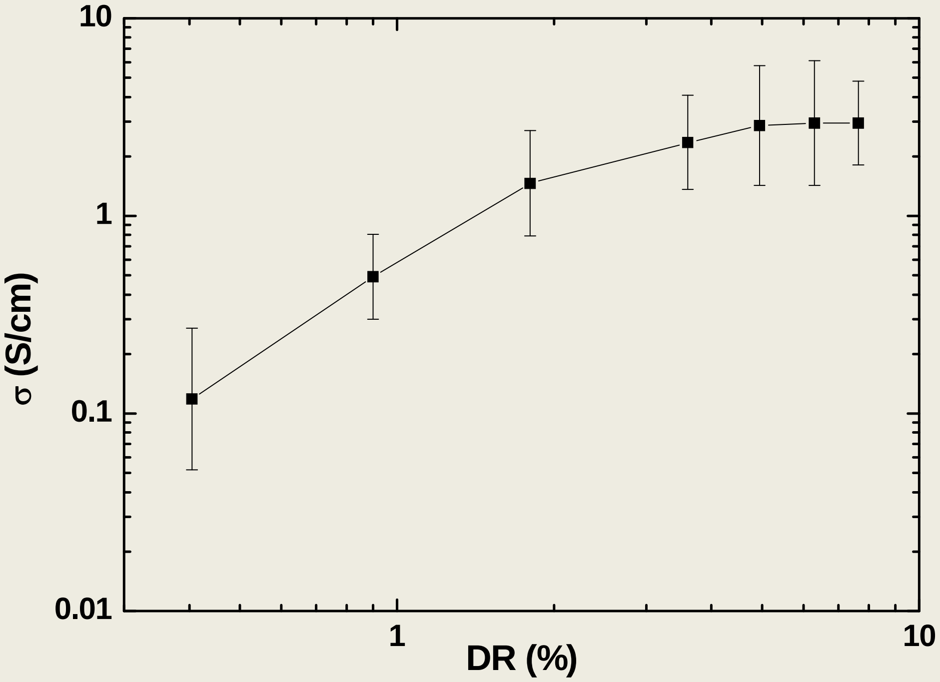
**Low Energy Plasma Enhanced Chemical Vapour Deposition (LEPECVD)**

**DOPED**

| Sample set | DOPANT | d [%] | dr [%] | Substrate | Ts[°C] | t[nm] |
|---|---|---|---|---|---|---|
| DOPED I p-type | B ($B_2H_6$ ) | 1 ÷ 10 | 1 ÷ 10 | Glass ZnO/glass | 250 | 80 |
| DOPED II n-type | P ?? controllare e | 1 ÷ 10 | 1 ÷ 10 | ZnO/glass | 250 | 80 |

d = dilution factor = $\Phi (SiH_4)/ [\Phi (SiH_4) + \Phi (H_2)]$
$X_c$ crystal fraction determined by RAMAN spectroscopy,
t sample thickness
dr = dopant dilution ratio = $\Phi (B_2H_6)/ \Phi (SiH_4)$

# Conductivity of the p-doped nc-Si:H films

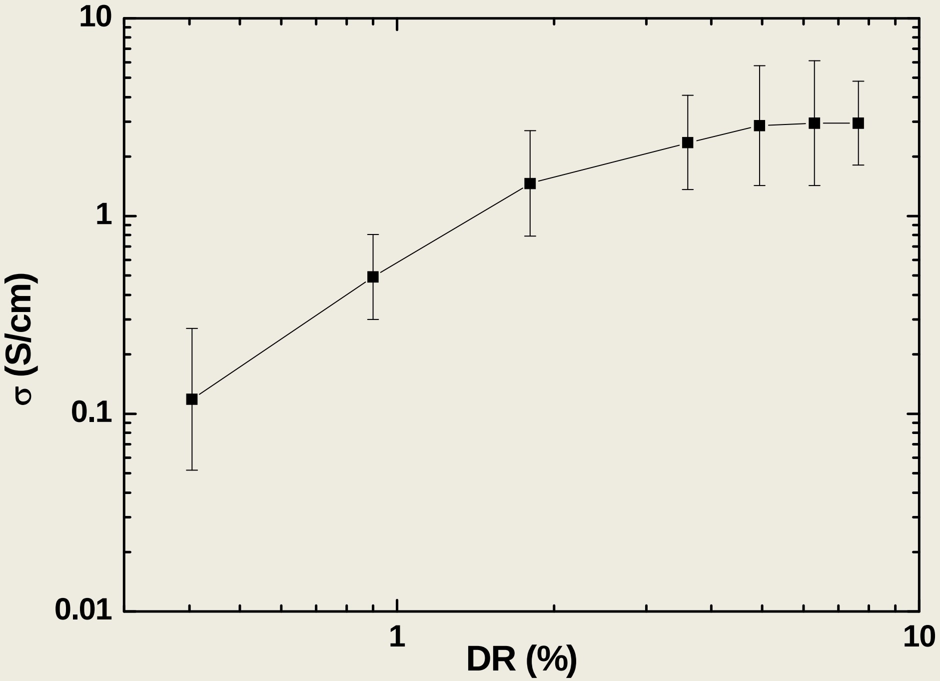



- As expected the conductivity increases with doping ratio to reach a maximum of 5-6 S/cm at **DR 6.3%!!!**

  *In the literature the optimum DR is between 0.4 and 0.8% for VHF-PECVD or HWCVD*

- The conductivity on one wafer varies for a factor 3 to 6

# Conductivity of the p-doped nc-Si:H films




- As expected the conductivity increases with doping ratio to reach a maximum of 5-6 S/cm at **DR 6.3%!!!**

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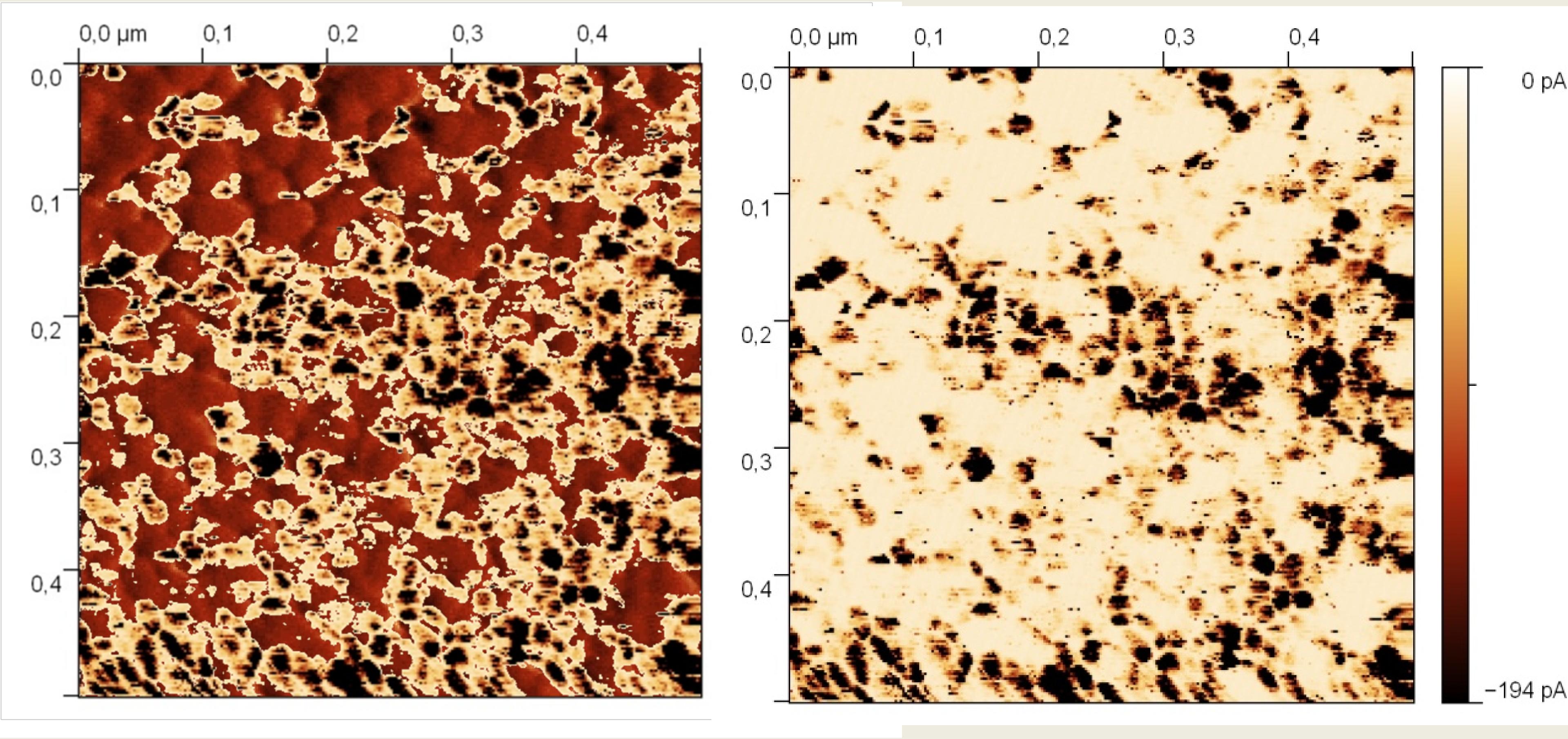
# Latest results: Electrical Conduction p-doped nc-Si:H

UNIBO




**C-AFM $V_{bias}$=1 V**