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Structural, Electrical and Optolectronic Properties of Hydrogenated nc-Si

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NANOcrystalline silicon films for PHOTOvoltaic and optoelectronic applications

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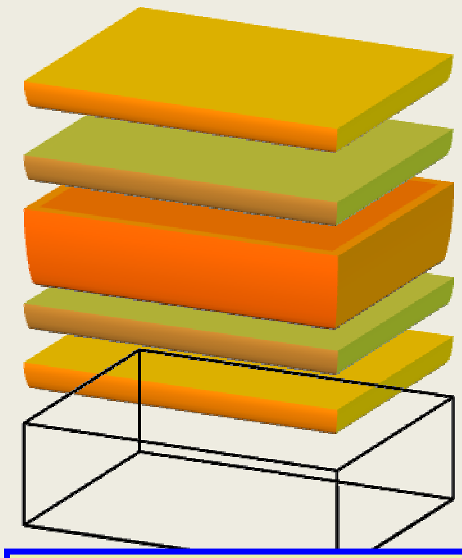
Why nc-Si:H?



Multi-phase: Si ncs in a-Si:H matrix

Disadvantages

low efficiency (<~13%)

Light induced degradation?

Materials properties mostly unknown

Advantages

low deposition temperatures

small material consumption

Higher resistance to light induced degradation phenomena with respect to a-Si:H

natural surface texturing

good match with solar spectrum

AIMS

Correlation between growth parameter and material properties

Optimization of material properties for PV applications

Outline

- Materials
  - UNDOPED nc-Si:H
- Results
  - Structural Characterization
    - Stress measurements and transmission electron microscopy (TEM)
    - Atomic Force Microscopy
    - XRD, Raman spectroscopy, and FTIR
  - Electrical characterization
    - C-AFM
    - Conductivity vs T
  - Optoelectronic characterization
    - SPV (Surface Photovoltage Spectroscopy)
    - Photoluminescence measurements and Quantum confinement studies
- Conclusions
  - Correlation between growth parameters and material properties
- New Results on DOPED nc-Si:H
- Conclusions

Materials

nc-Si:H grown by

Low Energy Plasma Enhanced Chemical Vapour Deposition (LEPECVD)

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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

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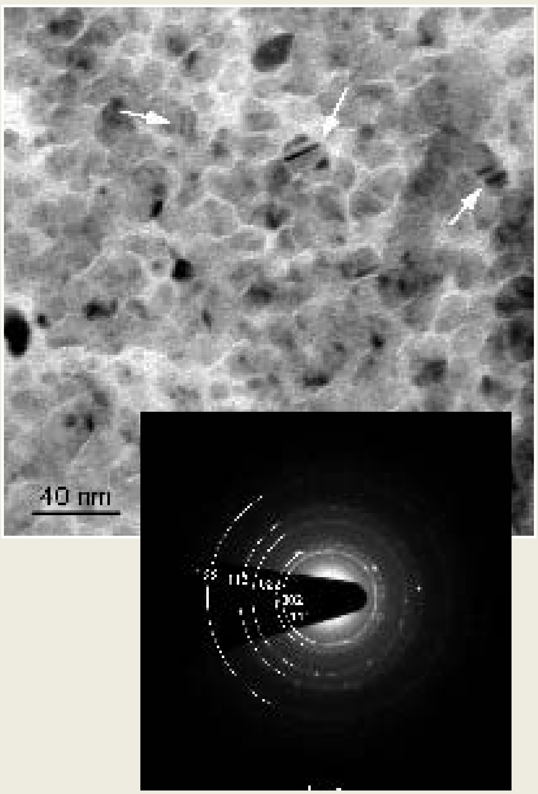
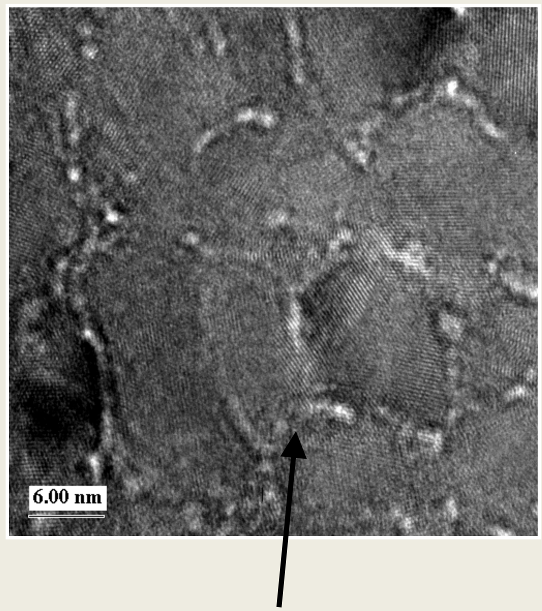
Series I. Plane view observations

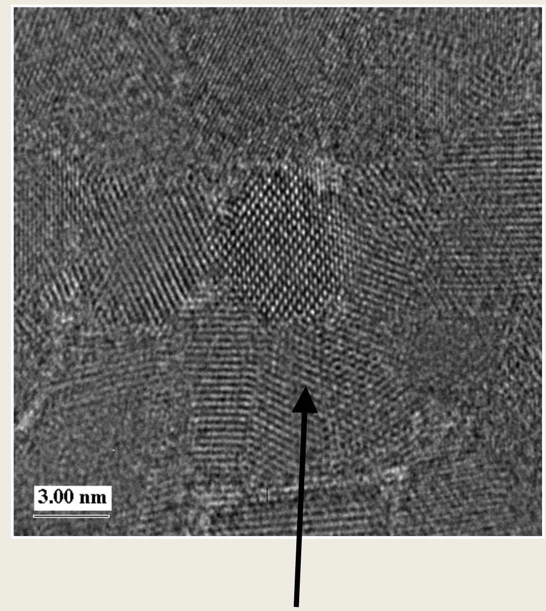
Bright fieldTEM micrograph
& corresponding SAED pattern



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



Nanometric size domains are observed

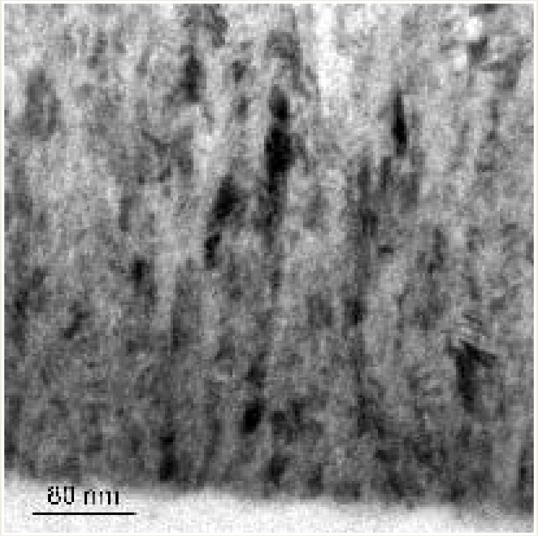


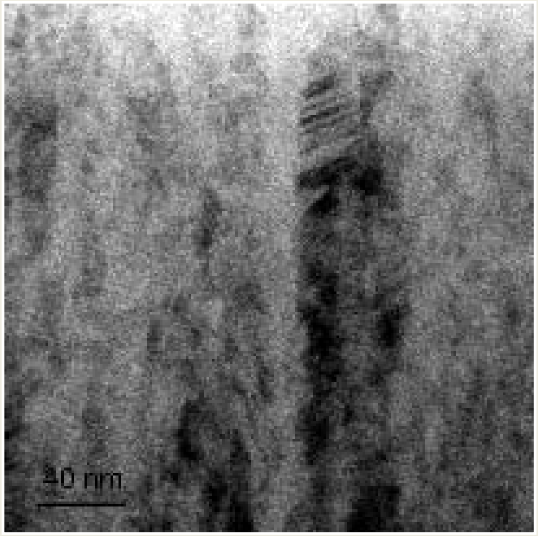
Domains are constituted by misoriented nano-crystals

Various nanocrystal sizes (between 4 to 20 nm)

Series I Cross-section view observations

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





Bright field TEM micrographs (low magnification)

Series II Cross-section view observations

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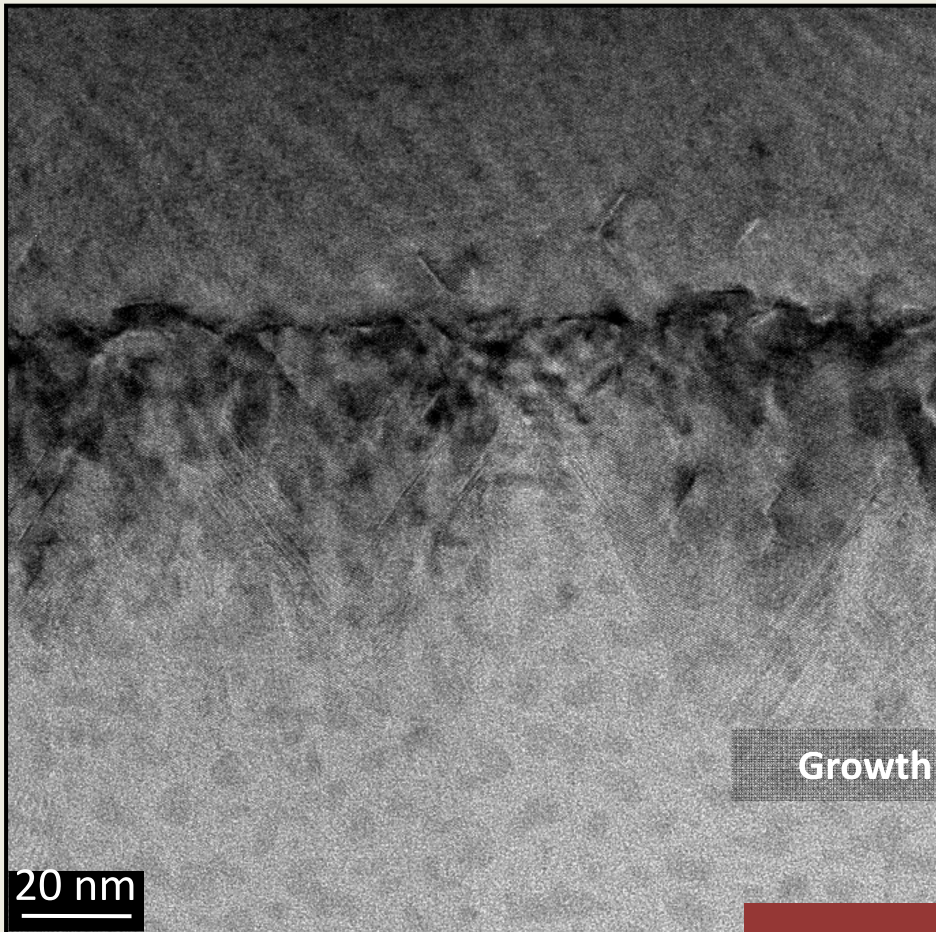
UMR 6242 CNRS, Universités Paul Cézanne, Provence et Sud Toulon-Var



Growth direction

Single crystal — SUBSTRATE

INTERFACE

High crystallinity

Low crystallinity

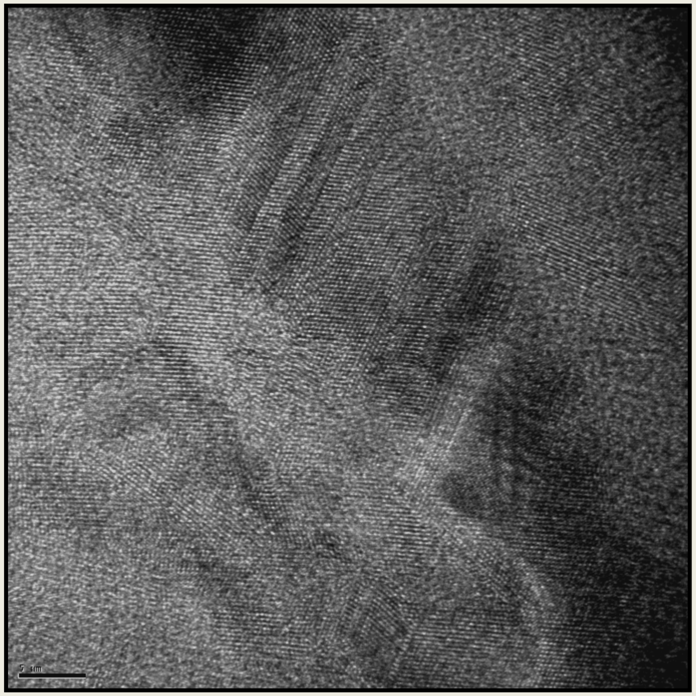
nc-Si layer

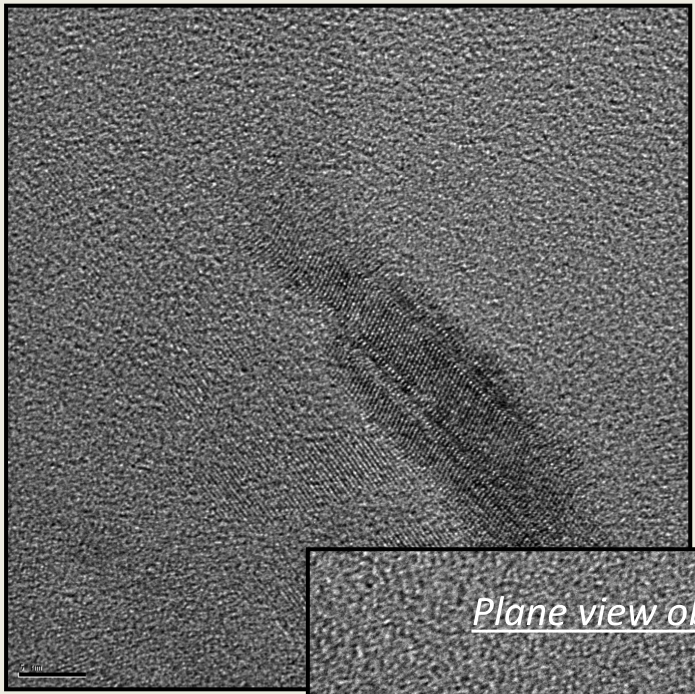
Superficial part of the layer :

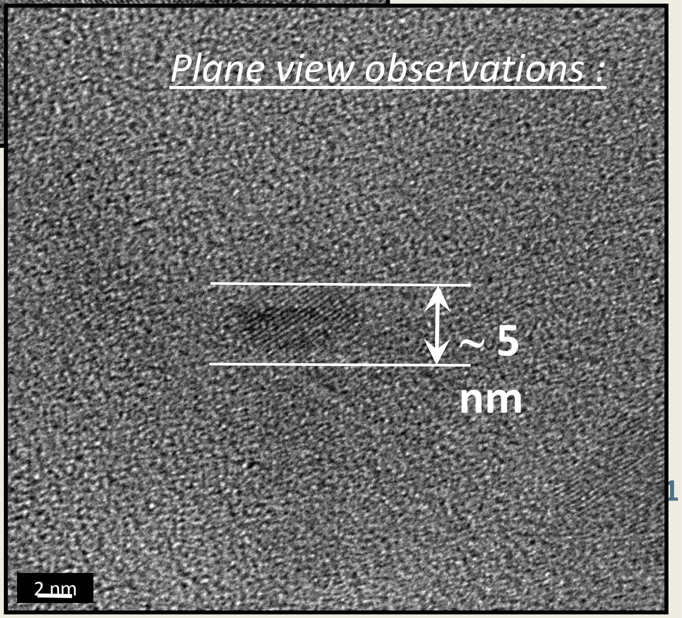
Transition from crystalline to amorphous structure.

The elongated columns become isolated small nanocrystals

Series III Cross-section and plan-view observations :





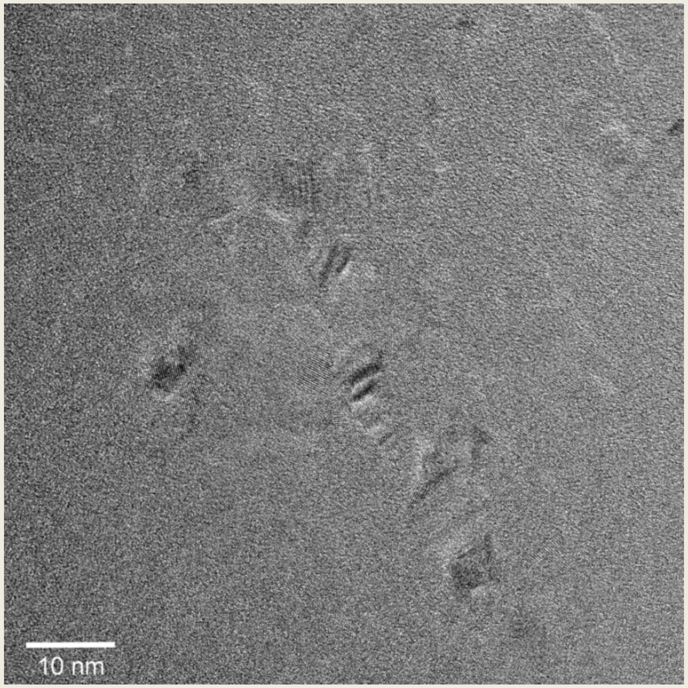


nc-Si layers contain numerous columnar nanocrystals

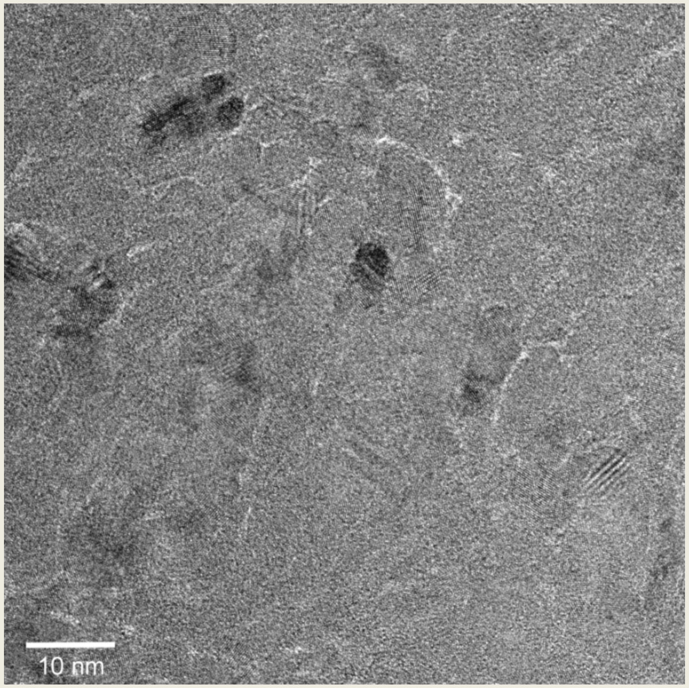
Twins are frequently observed

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 :

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

All the sample series. General Scheme

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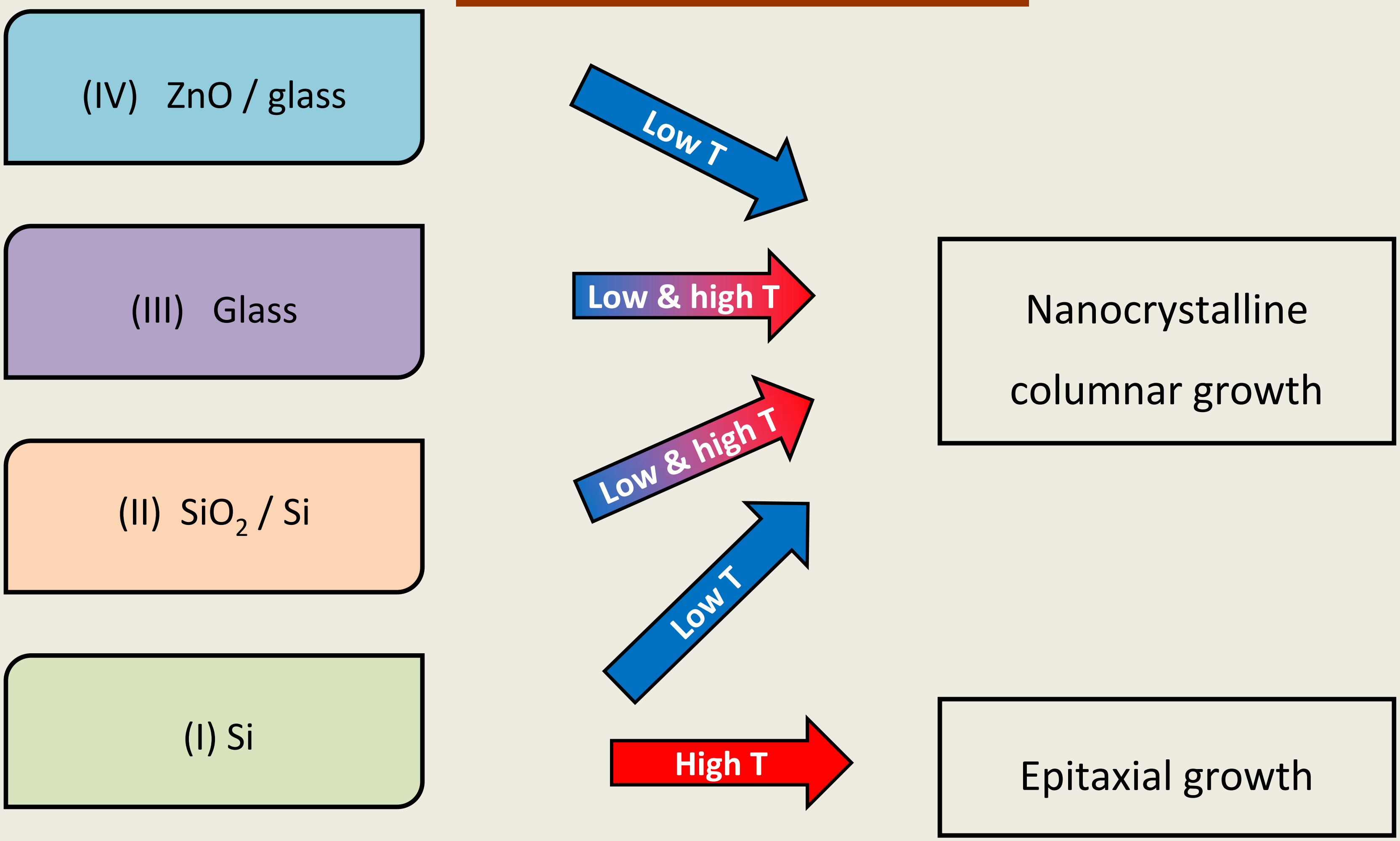
UMR 6242 CNRS, Universités Paul Cézanne, Provence et Sud Toulon-Var

The growth mechanism depends
- on substrate
- on temperature



Morphology by AFM

Roughness *vs* Substrate, thickness, crystallinity
Series I

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

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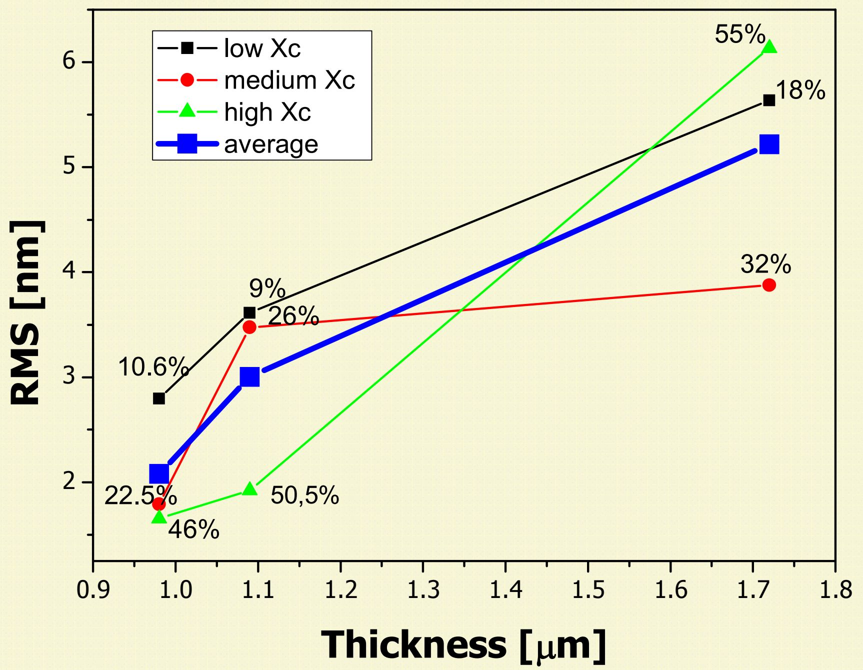

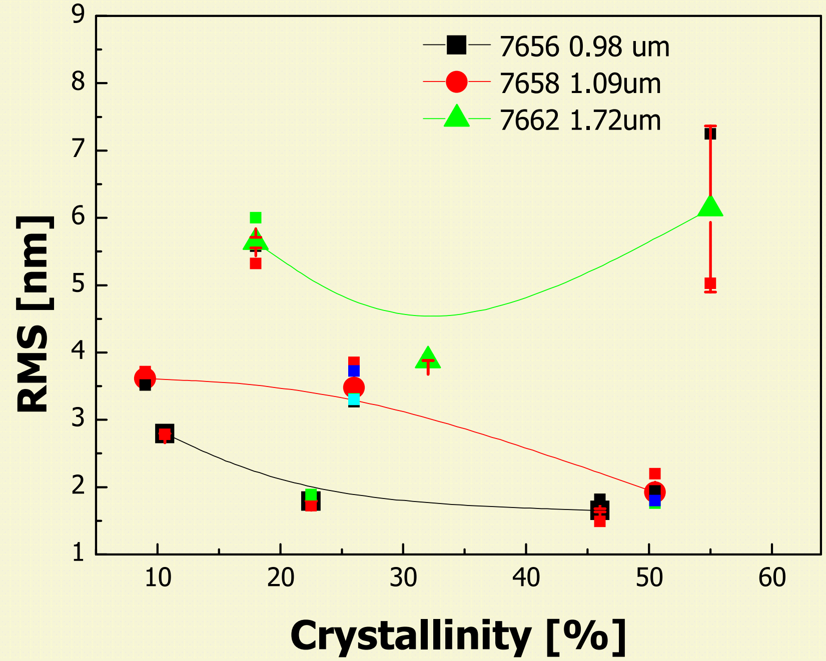

Conclusions:

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

Roughness vs thickness. Summary

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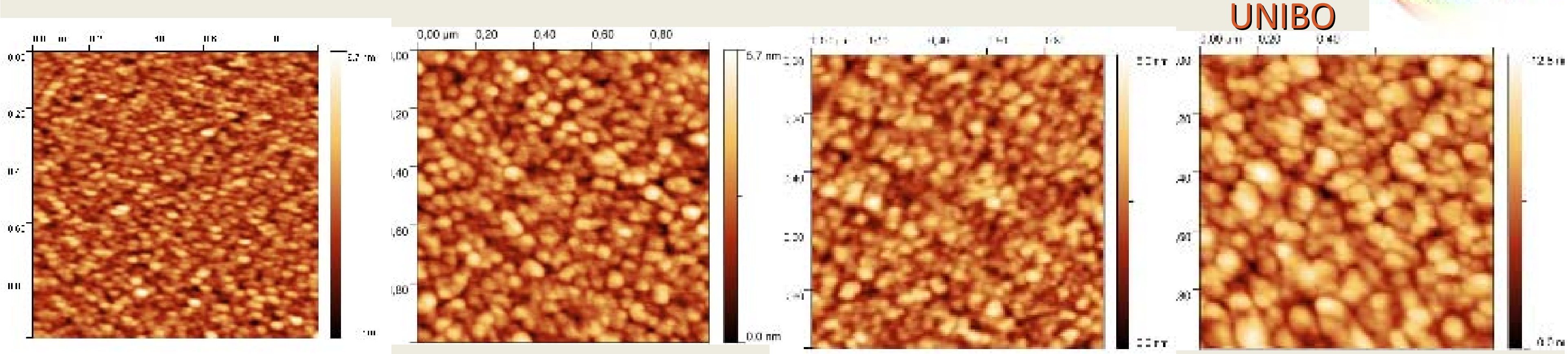
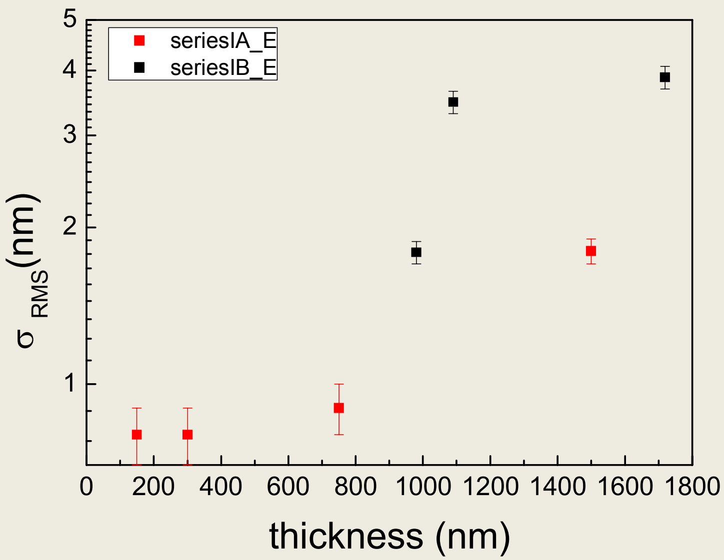


150 300 700 1500

thickness (nm)

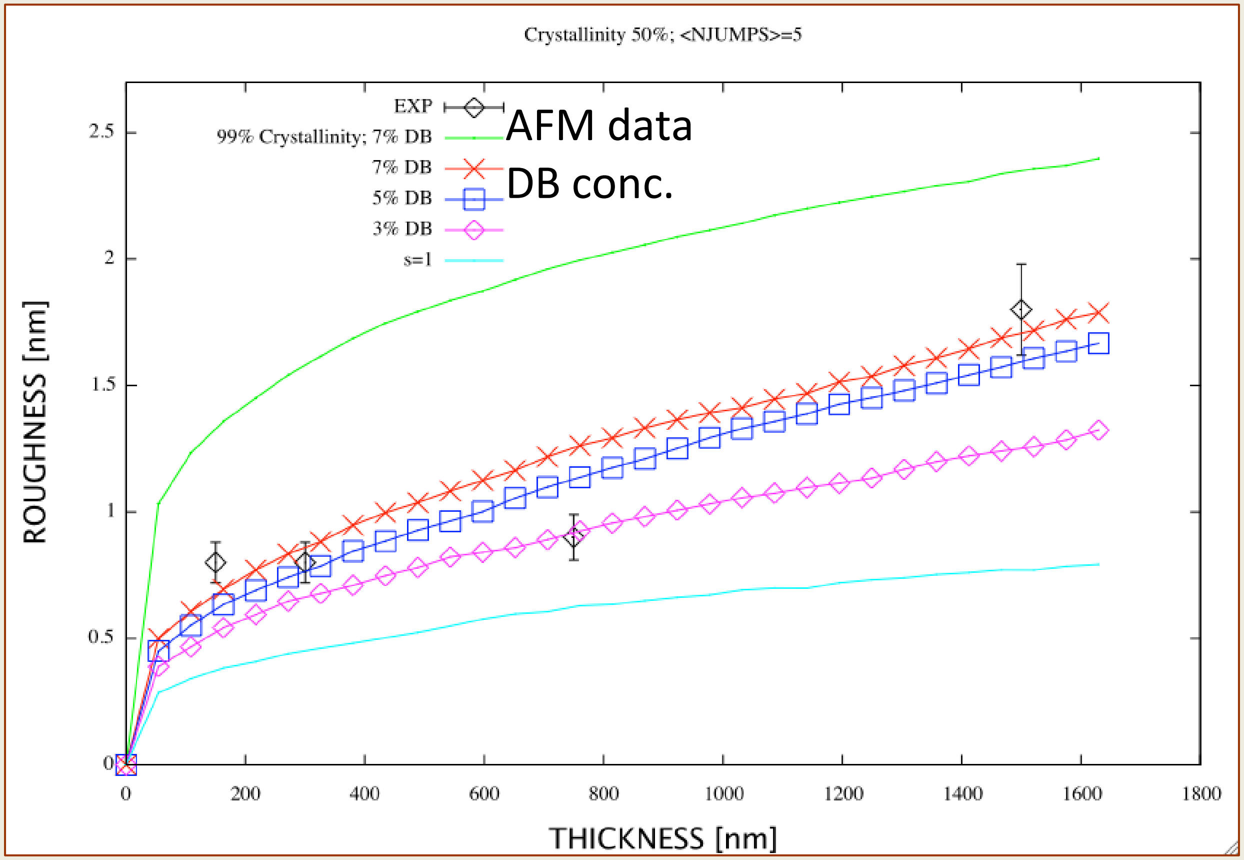


AGS increases for increasing thickness

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

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].

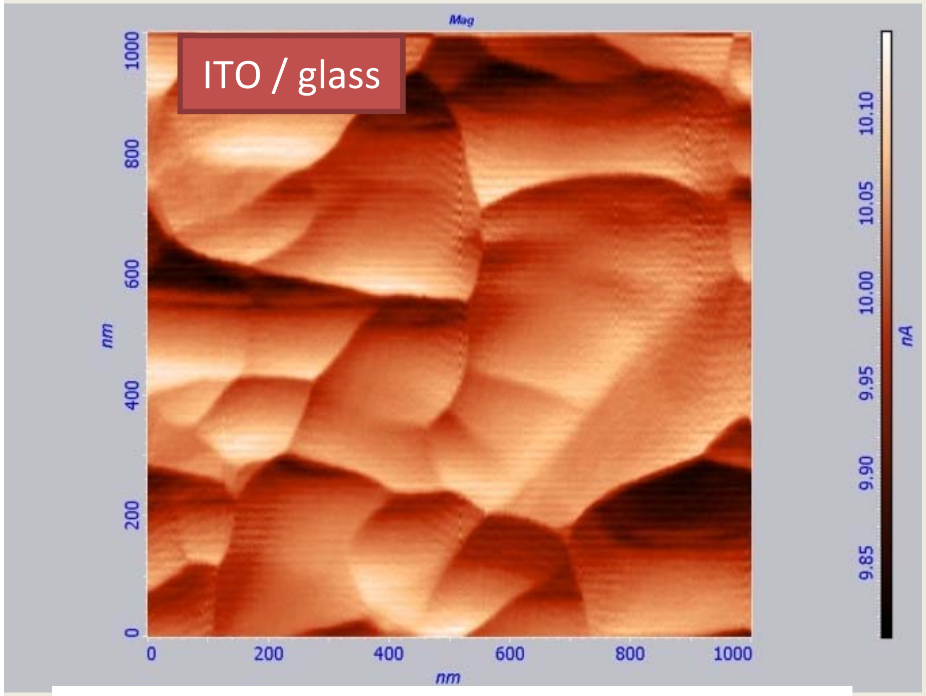


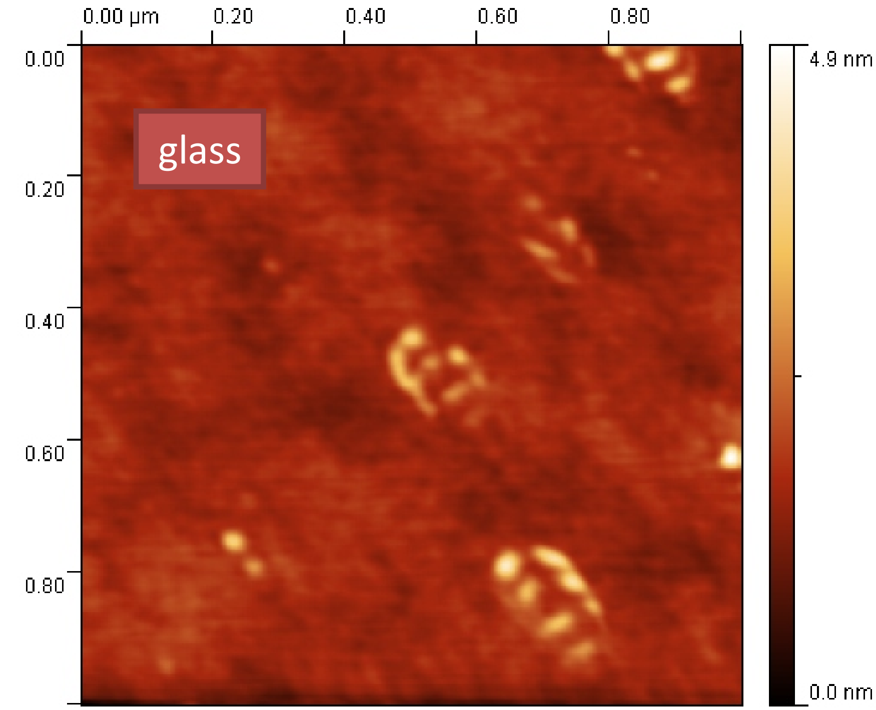
Results

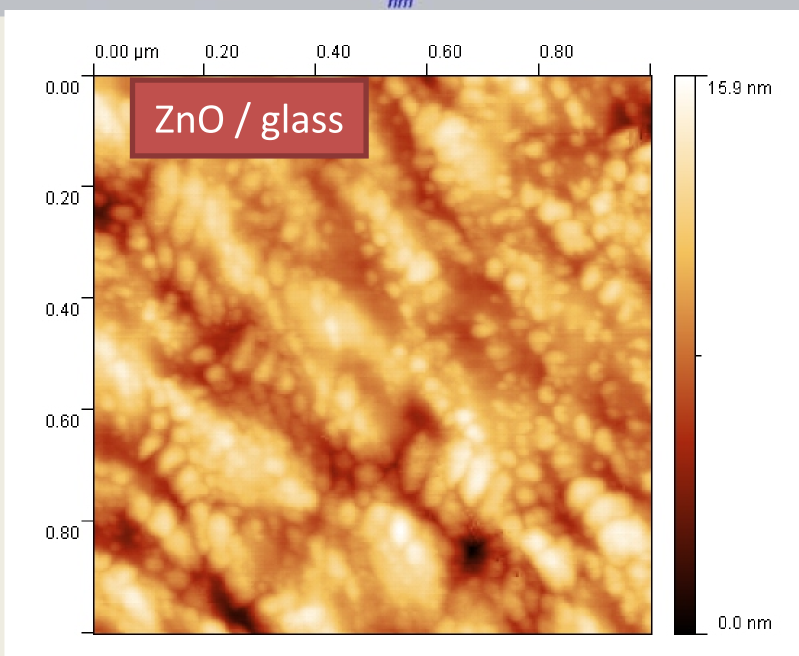
Experimental results are nicely recovered by assuming a crystallinity of 50% and an average hydrogen coverage of 5-7%.

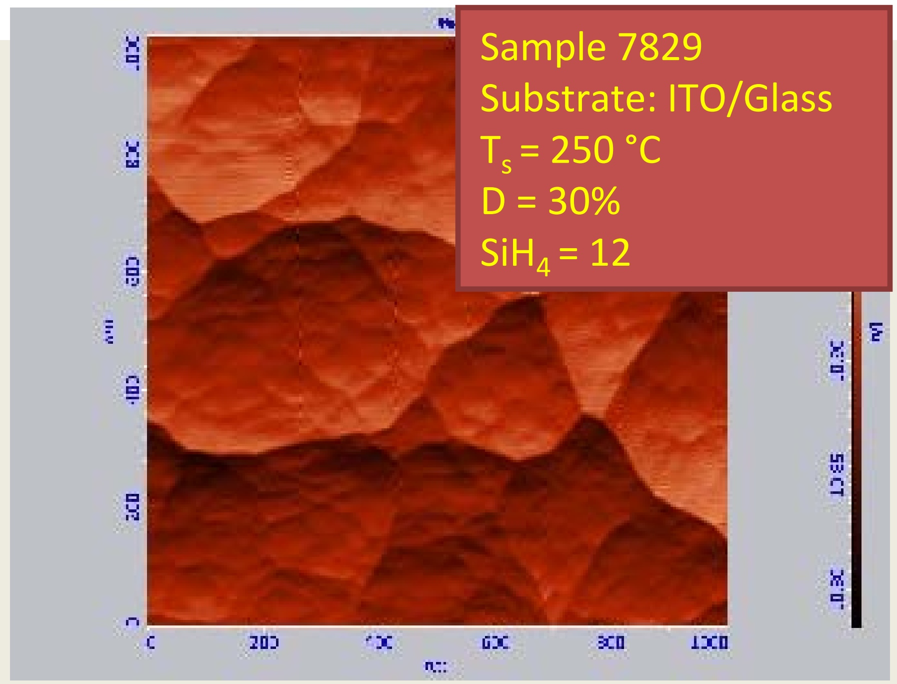
[1] F. Gemma & F. Montalenti, in preparation
[2] S. Cereda et al., Phys. Rev. Lett. 100, 046105 (2008)].

Roughness vs Substrates:









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

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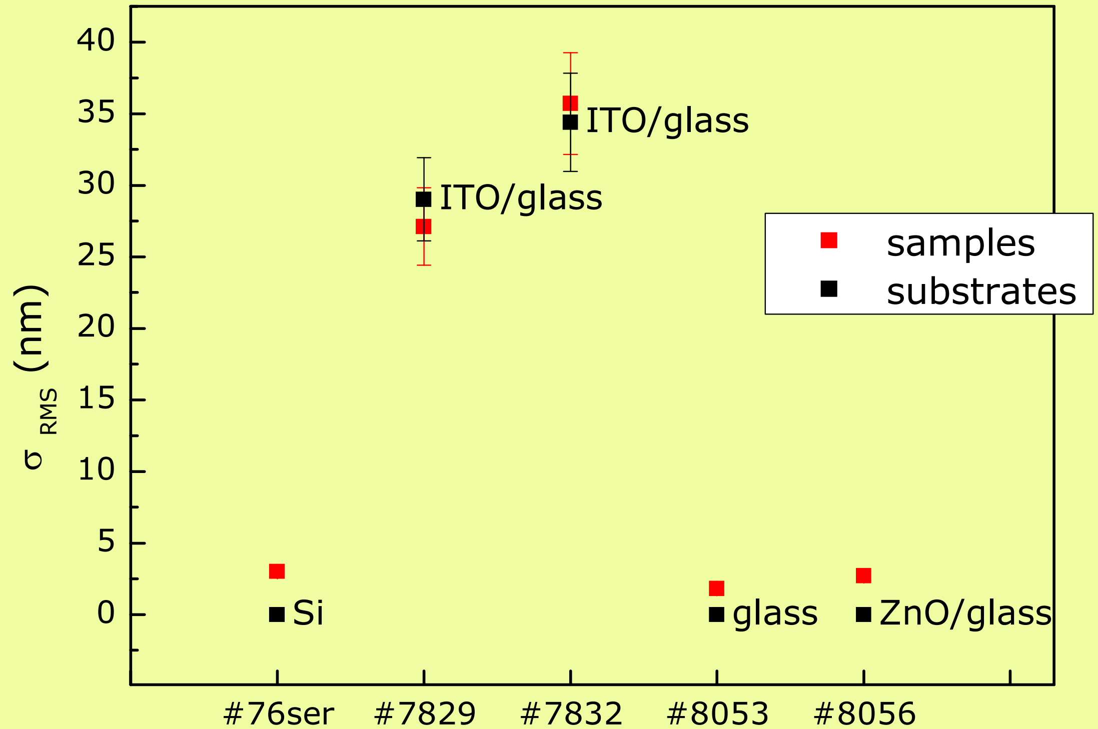
SAMPLE set

Grown on:		σ_{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

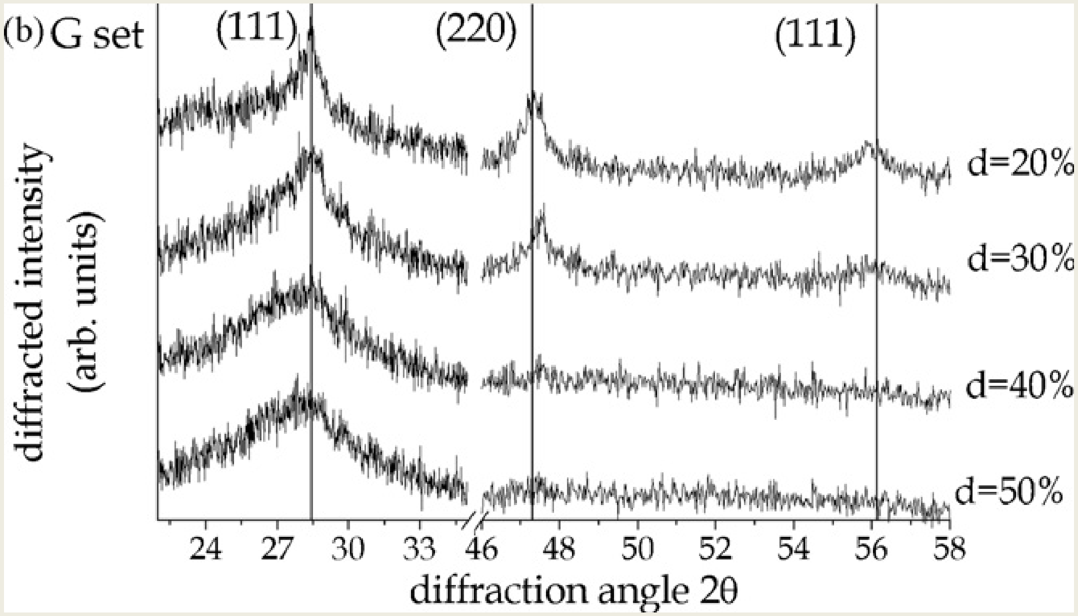
THE RMS ROUGHNESS STRONGLY DEPENDS ON SUBSTRATE

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

Structural characterization: XRD results

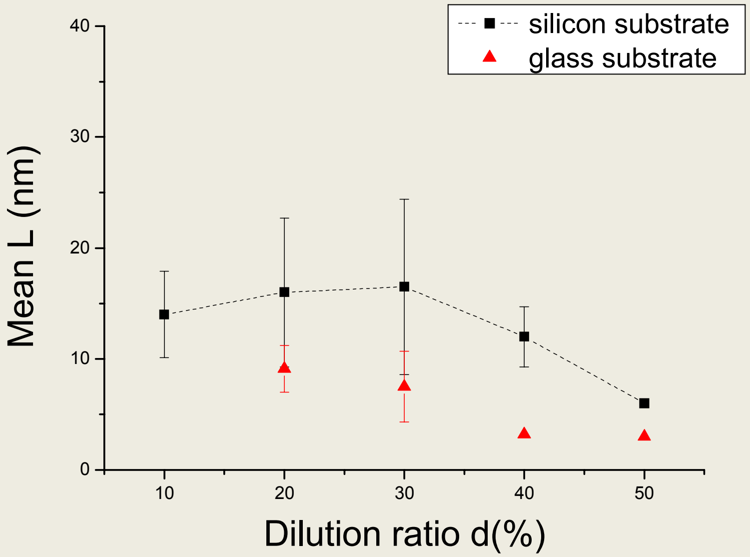
Preferred growth direction

<111> for series I, II and III



Average grain dimension L

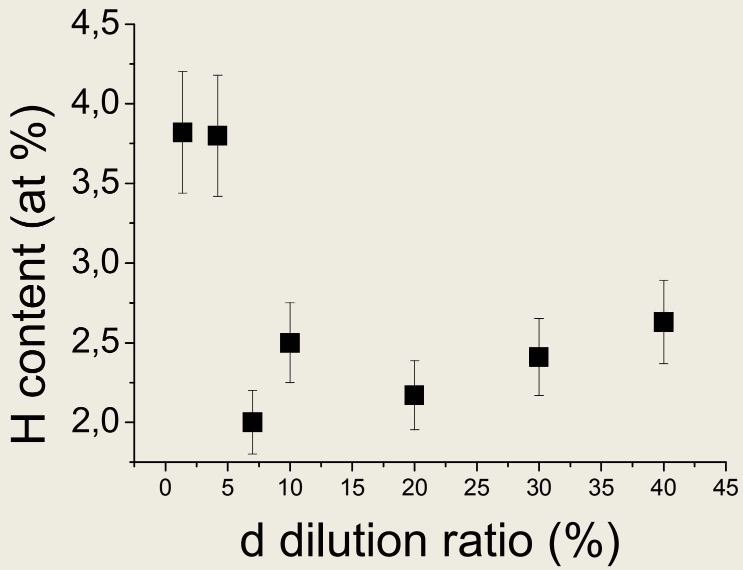
from tens of nm at high silane dilution (d <30%) to few nm (3-5nm) at low silane dilution (d>30 %)

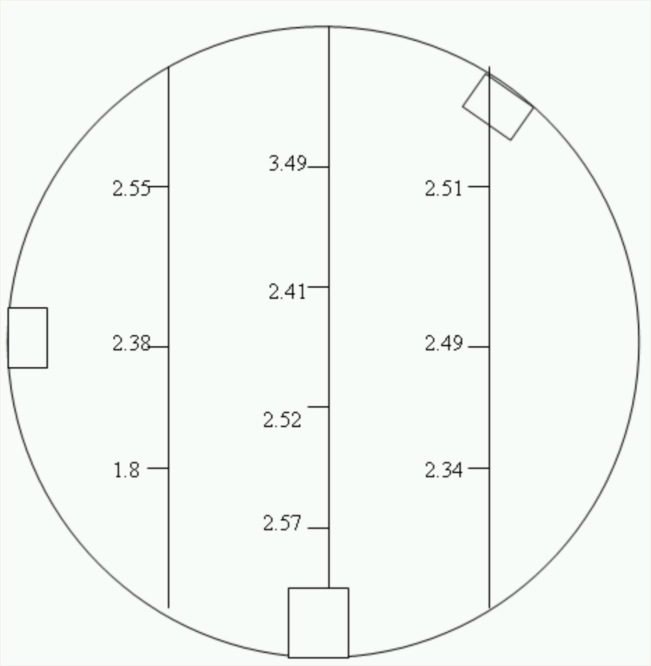


METHODS:

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).

H content determination by FTIR





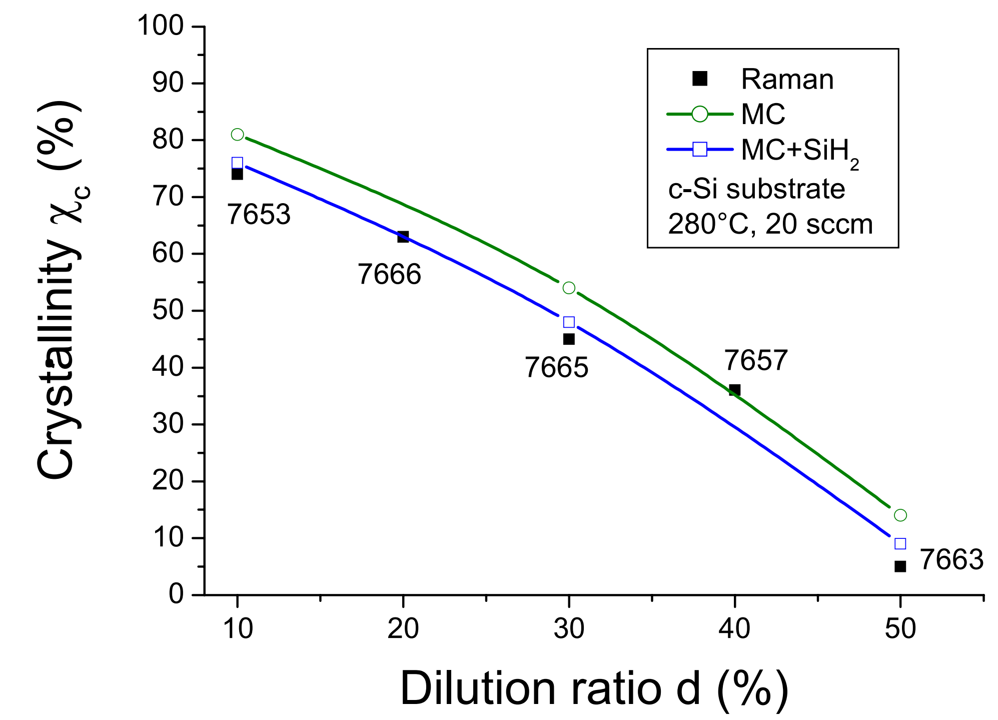
[H] map for the sample #7653 (d=10%)

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]

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.

Outline

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C-AFM The method

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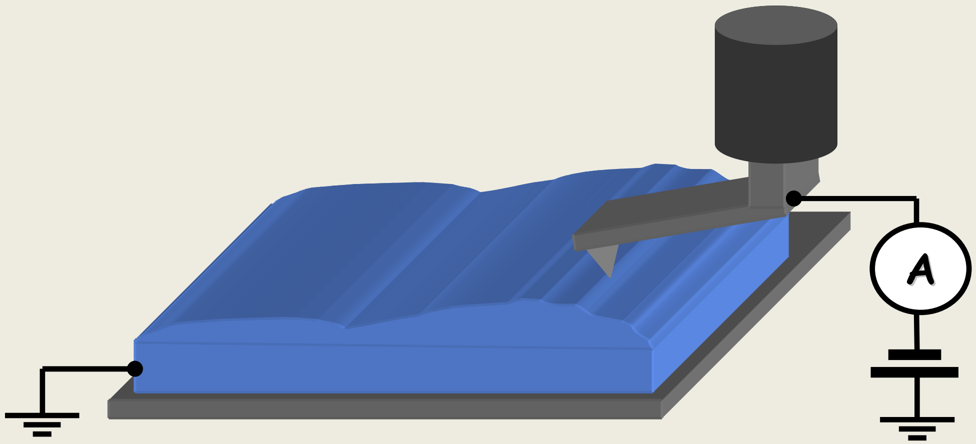
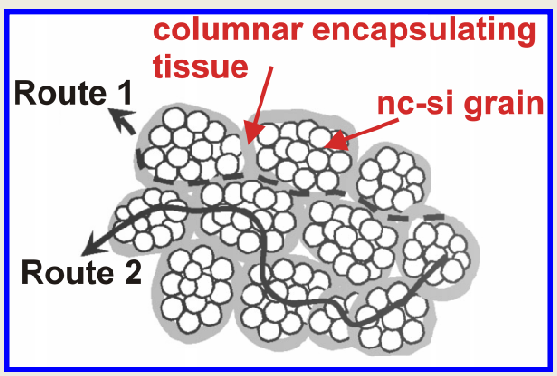


The probe scans the sample surface in contact mode.
A feedback loop keeps the cantilever deflection constant by varying the tip-sample distance. At the same time a bias potential (3V) is applied to the probe and the electrical current is measured. Topography and current maps are obtained simultaneously

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

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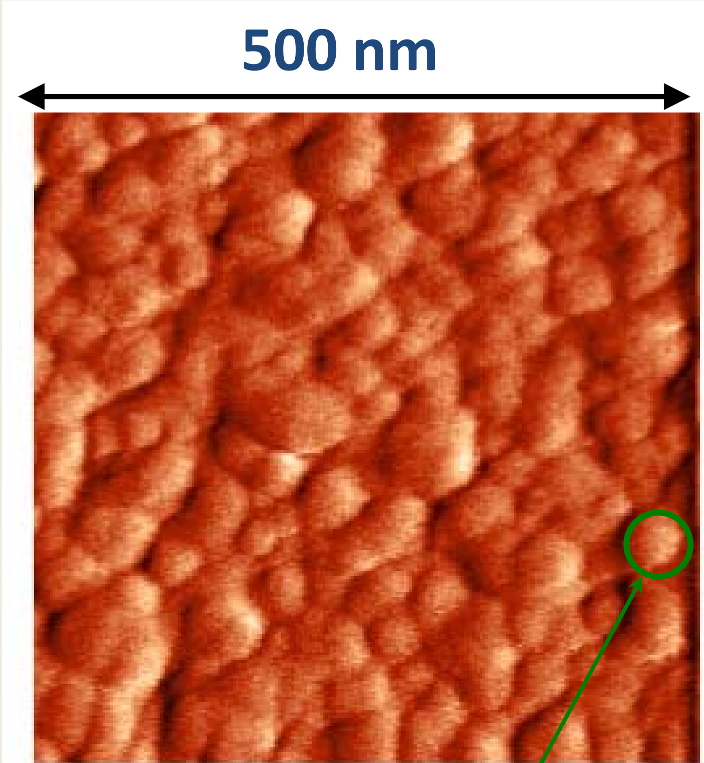

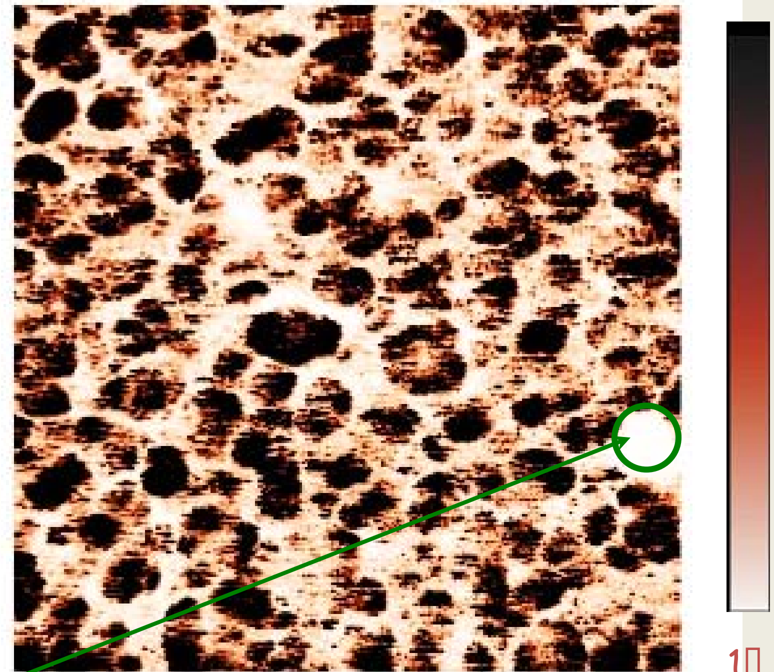

C-AFM maps show conductive grains in a non-conductive amorphous matrix.

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

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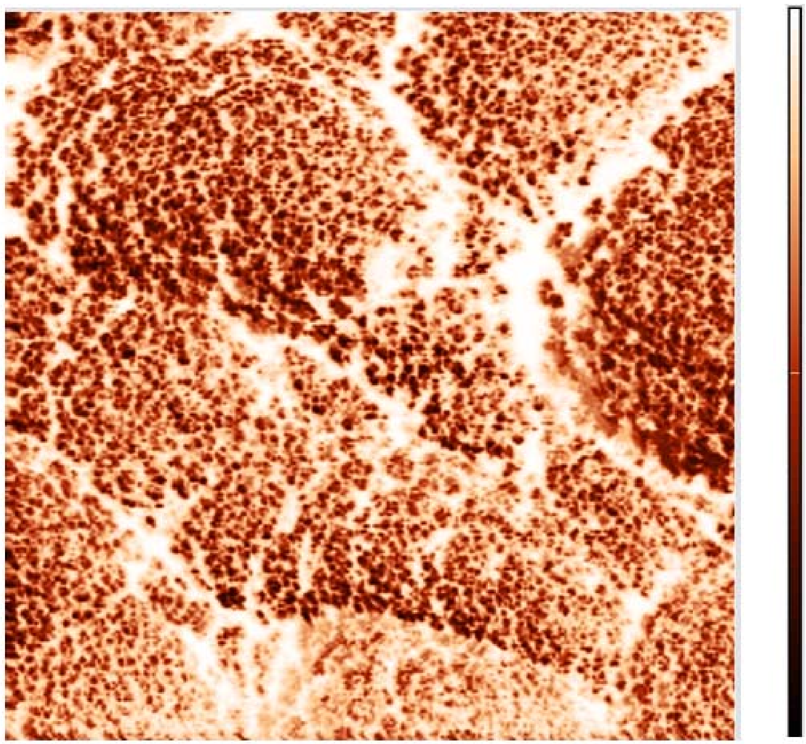
Results: C-AFM (II)

1000 nm

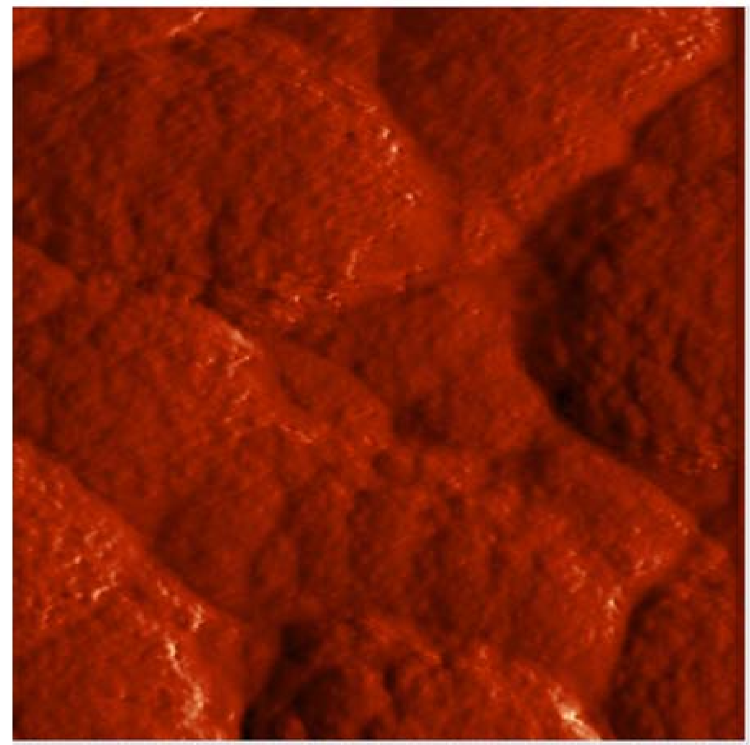
▯ pA



7▯▯ pA

C-AFM

1000 nm



DFL

Samples grown on ITO/glass, Xc▯ 5▯ % dilution 4▯%

Electrical conduction. Conclusions

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- The conduction 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.

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

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

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
- High photosensitivity ≈ 100 for the samples series III (grown on glass), promising for PV applications.

Conductivity measurement setup

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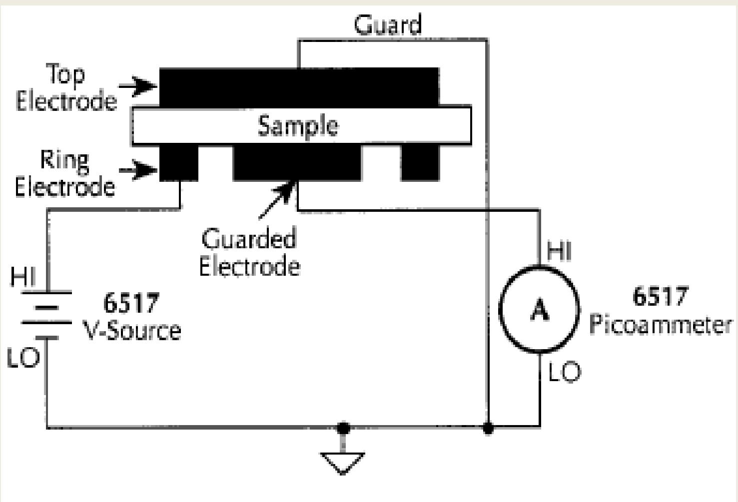
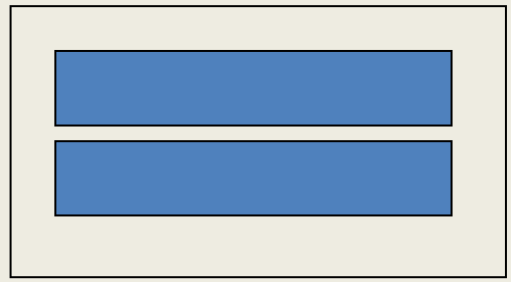
Using a Keithley 617 electrometer in V source mode, we can measure resistance up to 1 TΩ or conductivity down to 1E-9 → 1E-10 S/cm (film thickness)





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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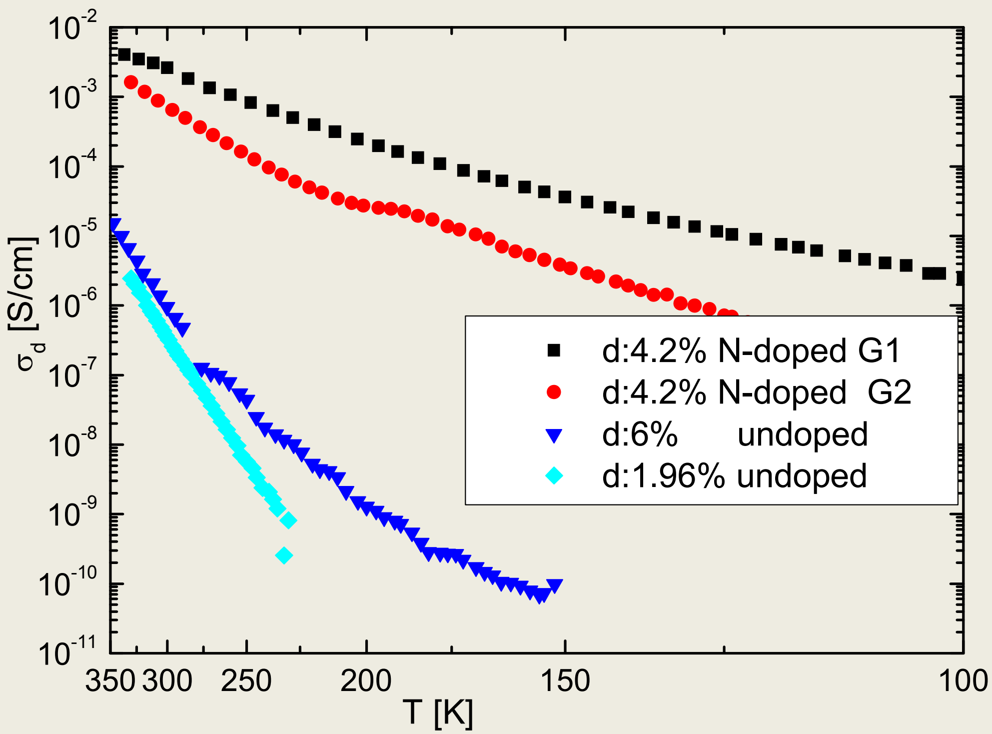

- Activation energies consistent with intrinsic or non intentionally doped μc-Si:H with high crystalline fraction
- both σ and E_a significantly changes with doping

  ➔ **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

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- 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

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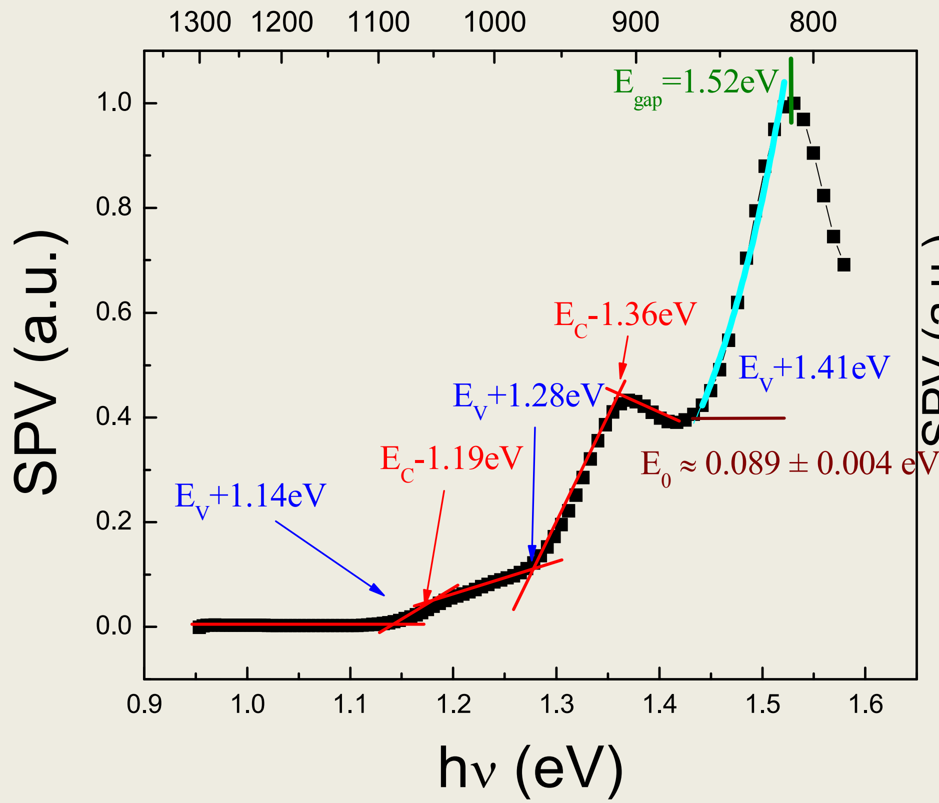
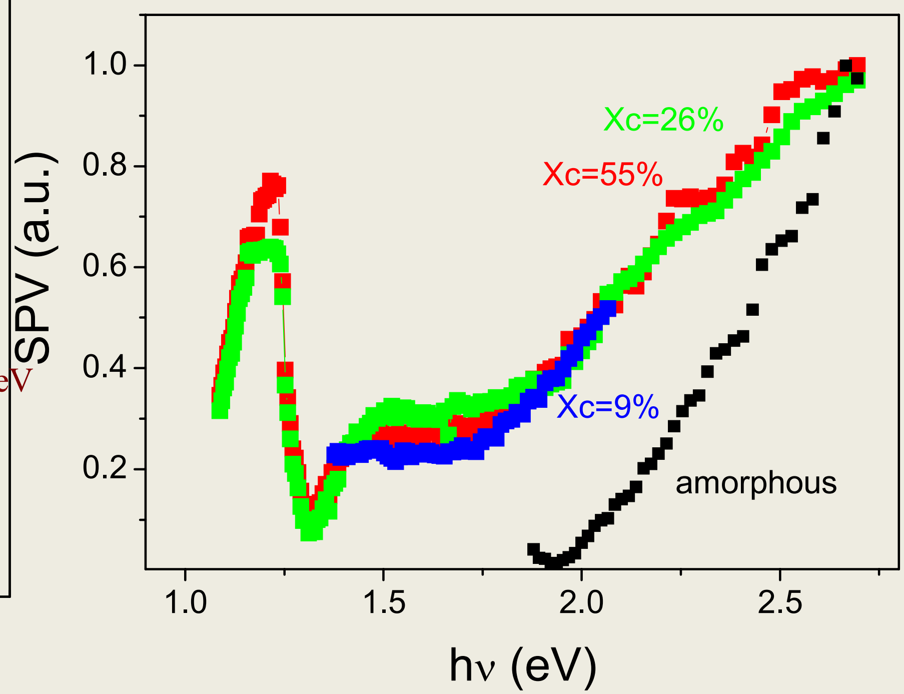
nc-Si:H, grown on Si, Xc > 65 %



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

Energy gap and Urbach tails *vs* crystallinity

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	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)

Defect states: *a*-like vs nc-like

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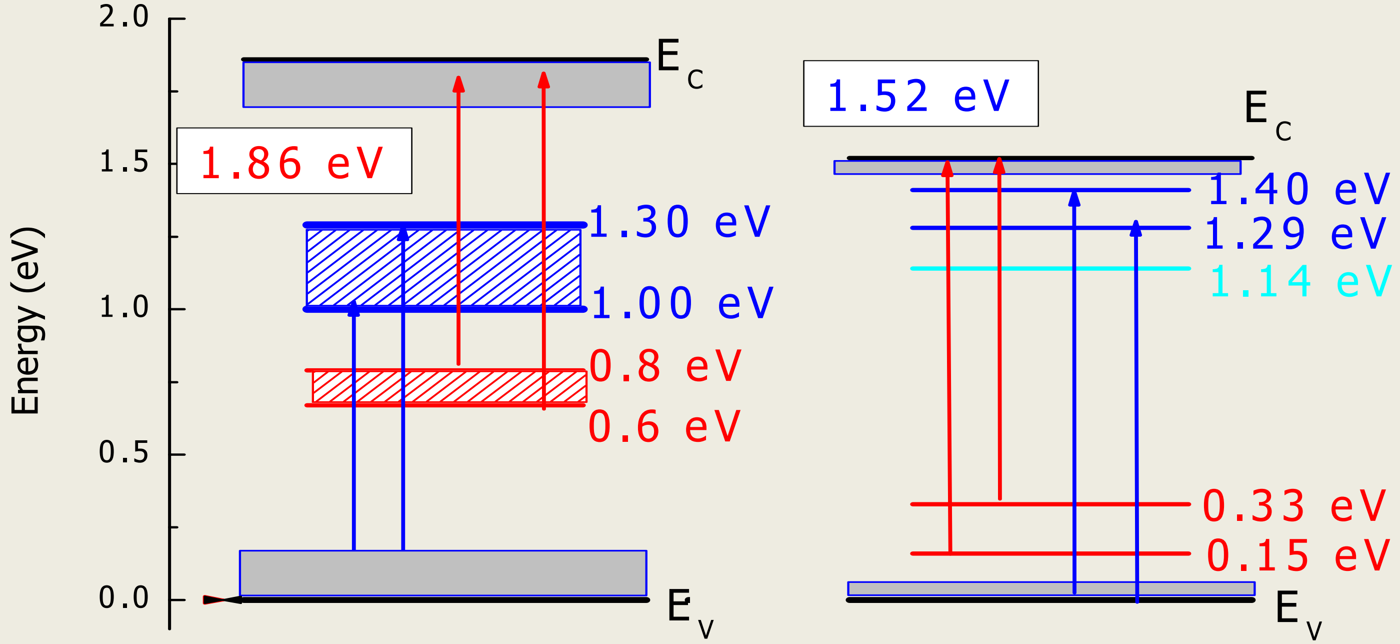
Low X_C
Amorphous-like

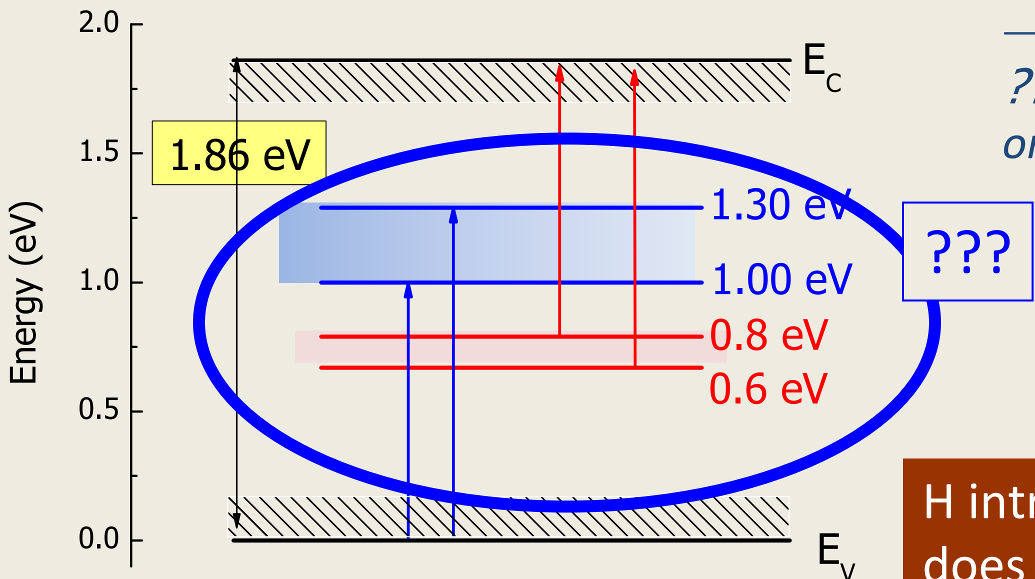
High X_c
nc-Si



Low Xc: high Urbach tails (hundreds of meV), two defect <u>bands</u> localized in the amorphous matrix, high E_G.
High Xc: <u>single-level defect states</u> and detection of the crystalline phase, low Urbach tails (40-80 meV), lower $E_{G.}$

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

UNIBO



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 ation

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

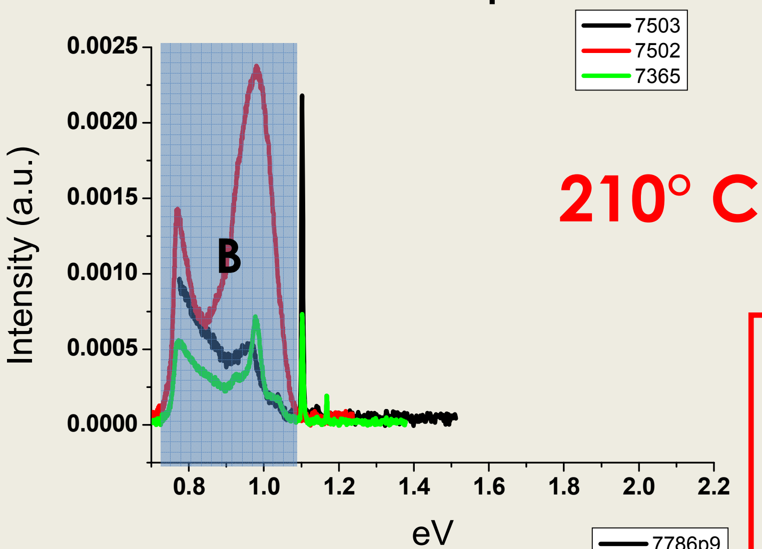
[1] Nadazdy and Zeman, Phys Rev B 2004, Fefer Shapira Balberg APL 1995

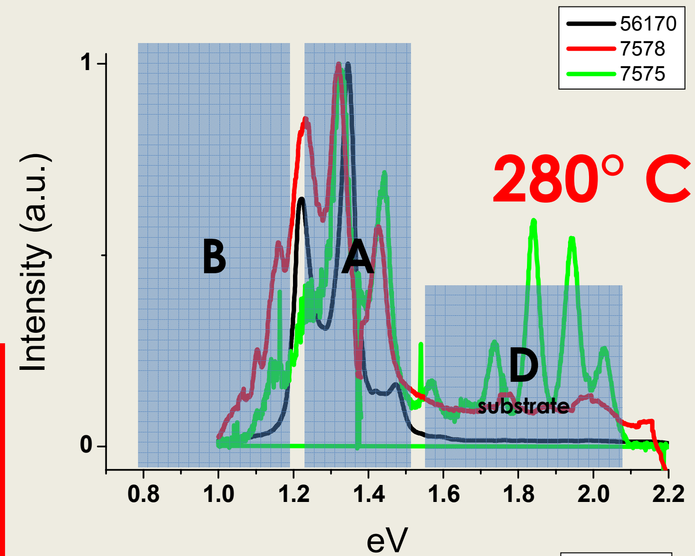
[2 Theory, A. Mattoni, L Colombo, Univ of Cagliari

Emission Spectra by Photoluminescence

Substrate temperature

All substrates
All dilutions





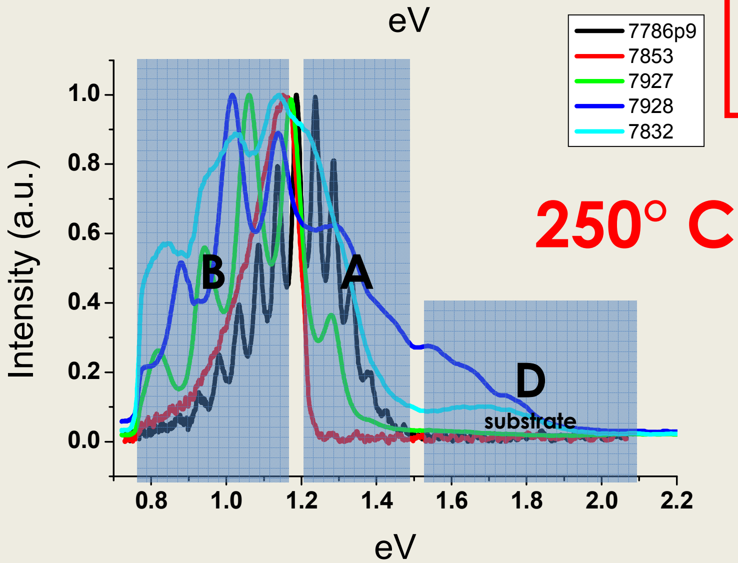
PL Bands

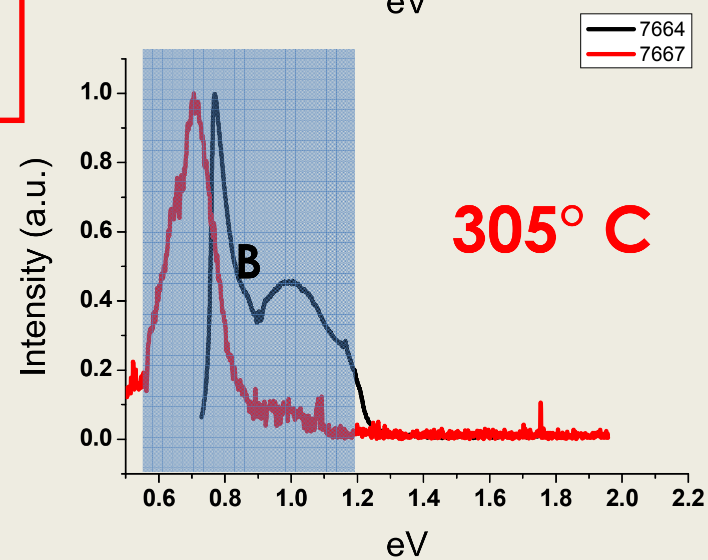
A: States in the a-Si gap

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>**

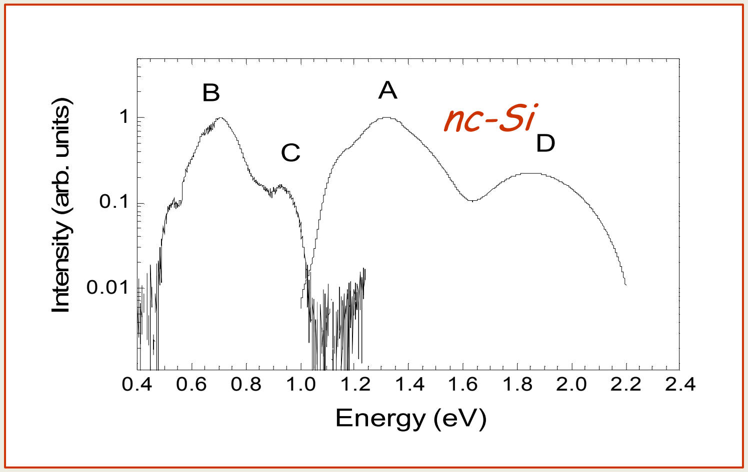
- **Laser Annealing suppreses A band intensity increasing the Mean Grain Size**

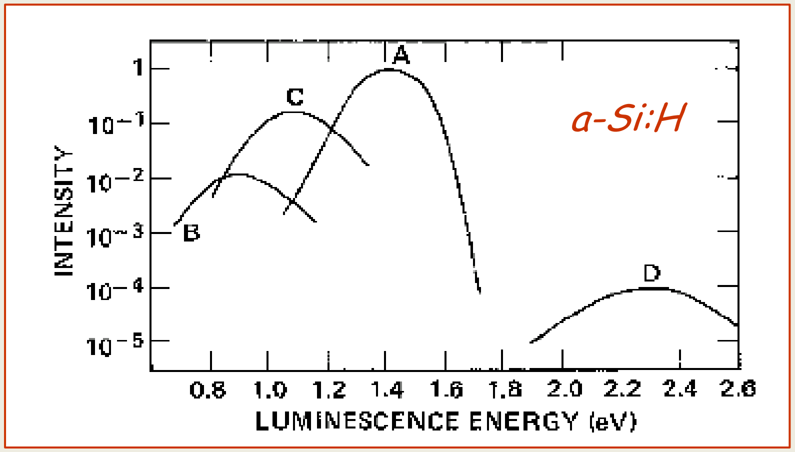
- **nc-Si/a-Si A band and nc-Si/SiO_2 emission band share analogous time distribution G(τ)**

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

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.

Outline

- Materials
  - UNDOPED nc-Si:H
- Results
  - Structural Characterization
    - Stress measurements and transmission electron microscopy (TEM)
    - Atomic Force Microscopy
    - XRD, Raman spectroscopy, and FTIR
  - Electrical characterization
    - C-AFM
    - Conductivity vs T
  - Optoelectronic characterization
    - SPV (Surface Photovoltage Spectroscopy)
    - Photoluminescence measurements and Quantum confinement studies
- Conclusions
  - Correlation between growth parameters and material properties
- Latest results on DOPED nc-Si:H
- Conclusions

Conclusions. Correlation between growth parameters and thin-film properties

Growth parameter	Material property	Detection Method
Dilution factor	crystallinity	Raman
SiH_4 flux	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	SPV
	Photo- emission	PL

Conclusions. 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

DOPED Materials

p type

nc-Si:H grown by

Low Energy Plasma Enhanced Chemical Vapour Deposition (LEPECVD)

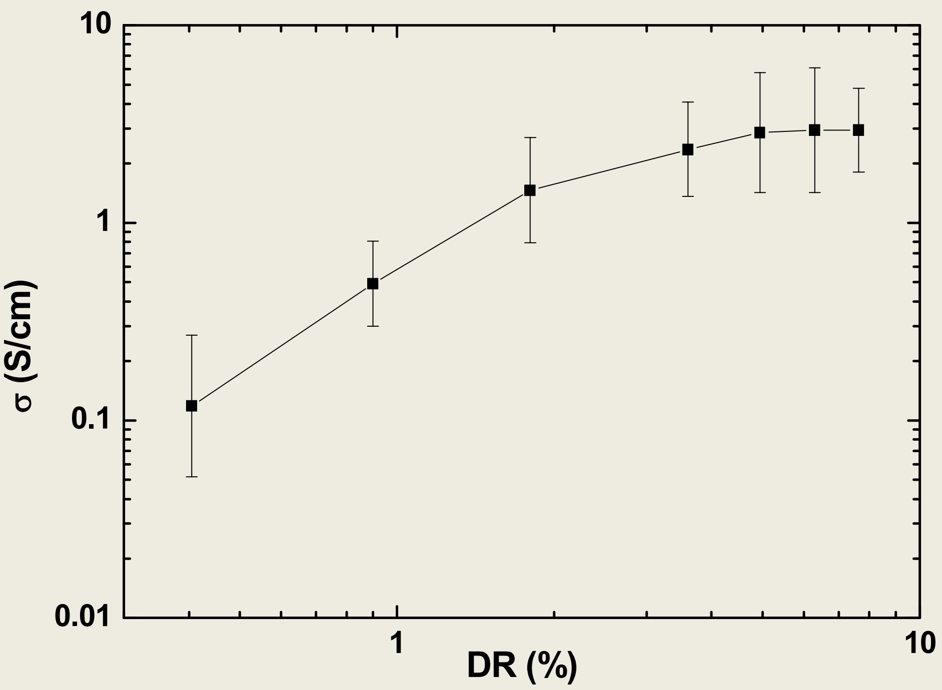
DOPED

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 = $\Phi\ (B_2H_6) / \Phi\ (SiH_4)$

Nanophoto NANOcrystalline silicon films for PHOTOvoltaic and optoelectronic applications

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 **<u>DR 6.3%!!!</u>**

  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

- What do we know about nc-Si:H?
  - Correlation between growth conditions and material properties
  - Microscopic electrical conduction mechanism (conduction occurs through the nanograins)
  - Defect states related to crystal disorder/ strain
- 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.

Nanophoto NANOcrystalline silicon films for PHOTOvoltaic and optoelectronic applications