ROMA TRE
Università degli Studi

INTEGRATED APPROACH FOR HIGH RESOLUTION SURFACE CHARACTERIZATION: COUPLING FOCUSED ION BEAM WITH MICRO AND NANO MECHANICAL TESTS

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ROMA TRE, SOME NUMBERS...

www.uniroma3.it

- Founded in 1992
- One of the 4 State University in Rome (9 in total)
- 175.000 m^2
- More than 40.000 students (4.100 enrolled in Engineering)
- More than 700 Researchers and Professors
- Faculty of Engineering:
  - Civil
  - Computer Science
  - Electronic
  - **Mechanical**
    - ***Materials Science and Technology research group (STM Group)***

EVERGREEN NEEDS

Functional and structural behavior are strongly influenced by micro-structural effects (grain size, defects, precipitates, interfaces, porosity,…)

- Ok, not really a news; however…
- **Engineered surfaces** are spreading quickly also in non high-tech products (also in mass products);
- Industrial application of surface modification and coating techniques requires **mechanical and functional characterization** of:
  - Nano-structured materials and coatings
  - Nano-systems
  - Nano-structures
- **Multi-scale** characterization (quick and cheap) procedures are therefore strongly needed for a pletora of needs in:
  - Development
  - Production
  - Maintenance and survey

INCIPIT

- Conventional characterisation techniques are <u>not completely exhaustive</u> for describing all micro-structural aspects which necessarily determine the actual behaviour of nano-structured materials and coatings

- New developed procedures should also be compatible for in-line quality control processes, or at least cost-saving with respect to traditional high resolution characterisation techniques.

- Needs of standards and standardization procedures

Evolution of characterization techniques and new potential of their synergic uses

beyond a simple observation

Evolution of characterization techniques and new potential of their synergic uses

"choose, touch, feel and see"

OUTLINE

Evolution of two "traditional" techniques

- Visualization and machining at the nanoscale
  - Resolution
  - Other probes than e$^-$
  - Not only Imaging, but also Milling and Deposition
- Mechanical tests (nanoindentation)
  - Applied forces and displacement measurement
  - CSM method

Examples

- I Nb coatings for superconducting cavities
- II Residual stress measurement at the micro-scale

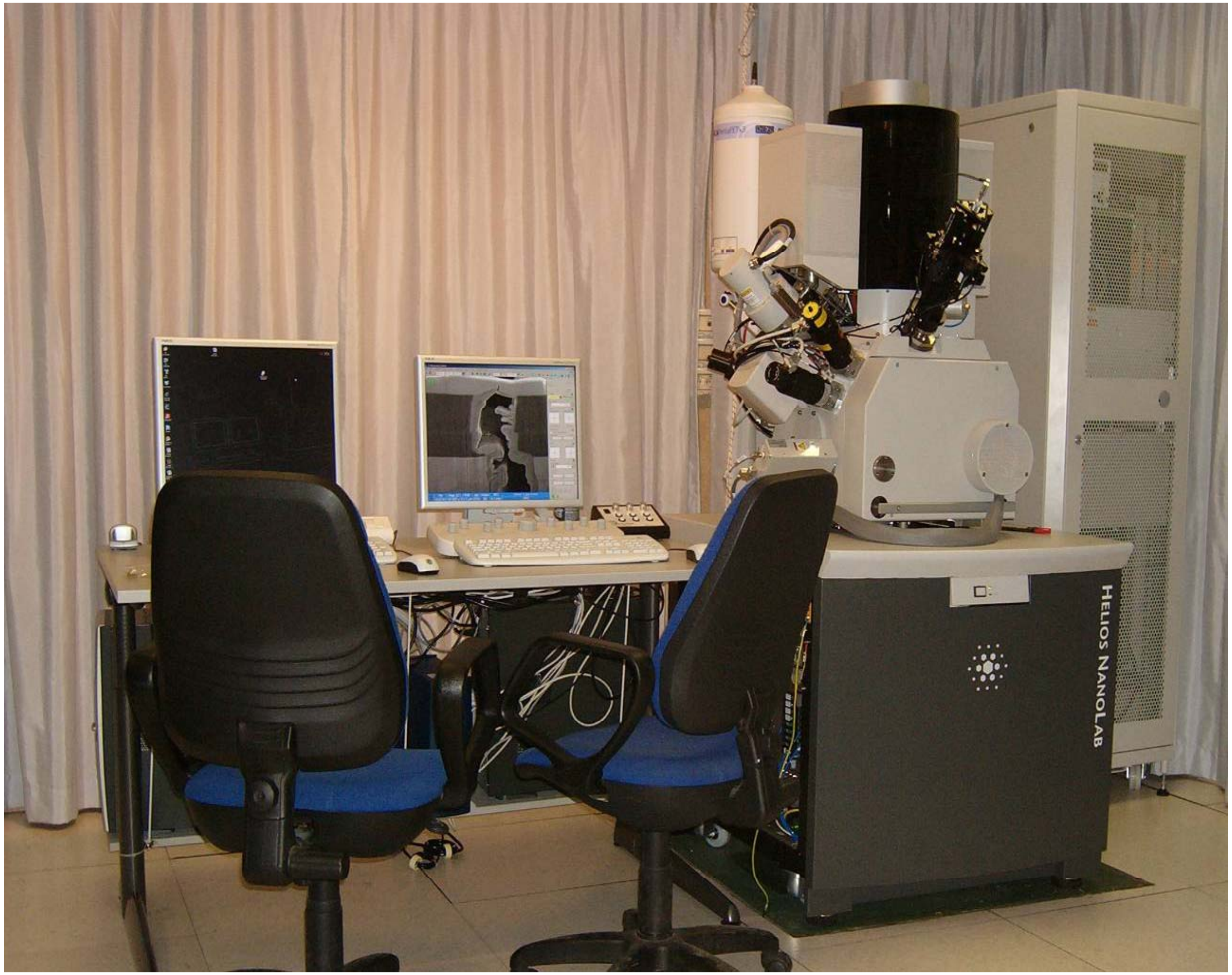
ROMA TRE DUAL BEAM

FEI
Helios 600
Nanolab

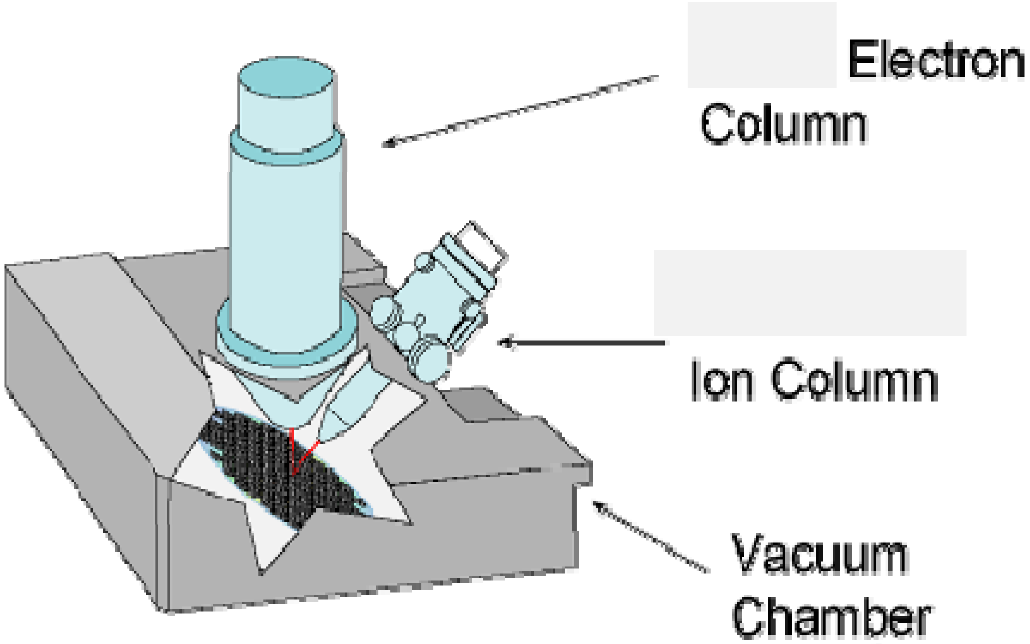
Detectors:
SE, SI, TLD (SE+BSE), STEM.

TEM lamellae preparation system (Omniprobe)

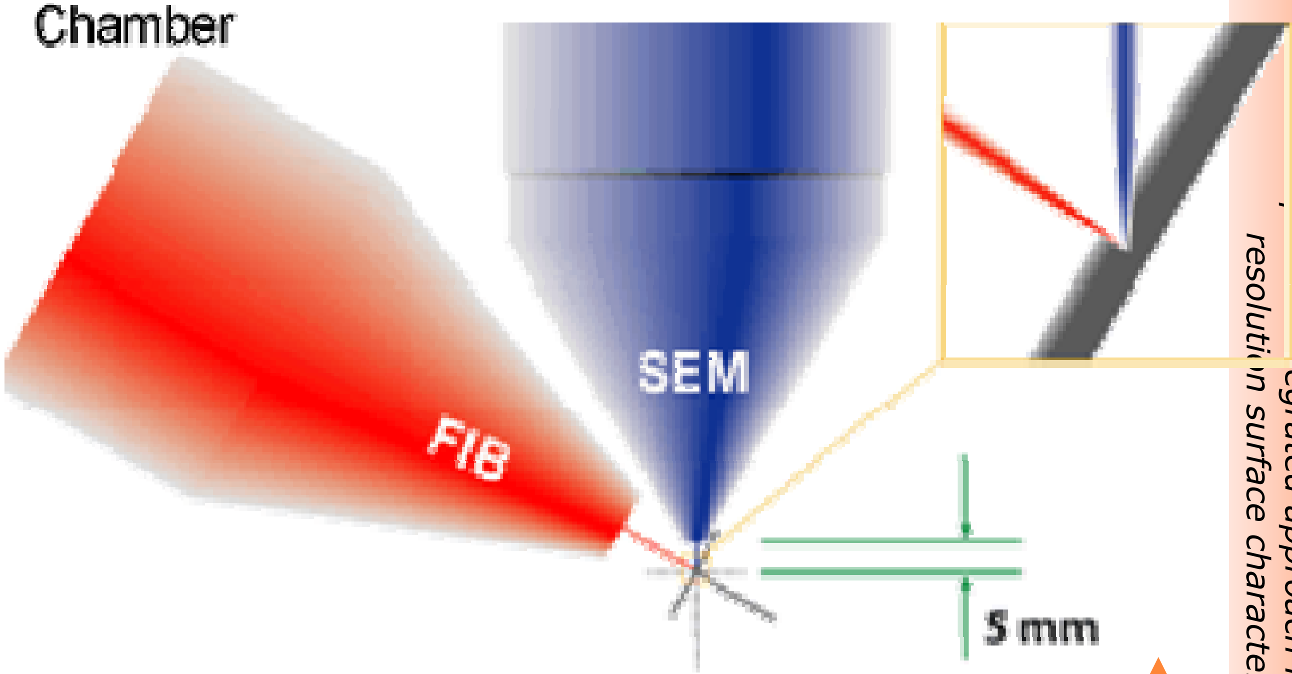
EDS system



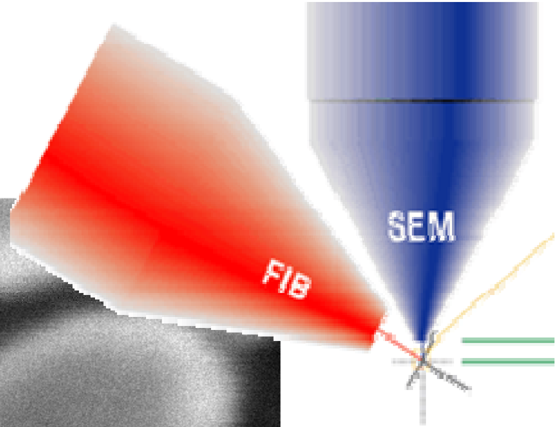
Dual Beam Microscopy (FIB-SEM)

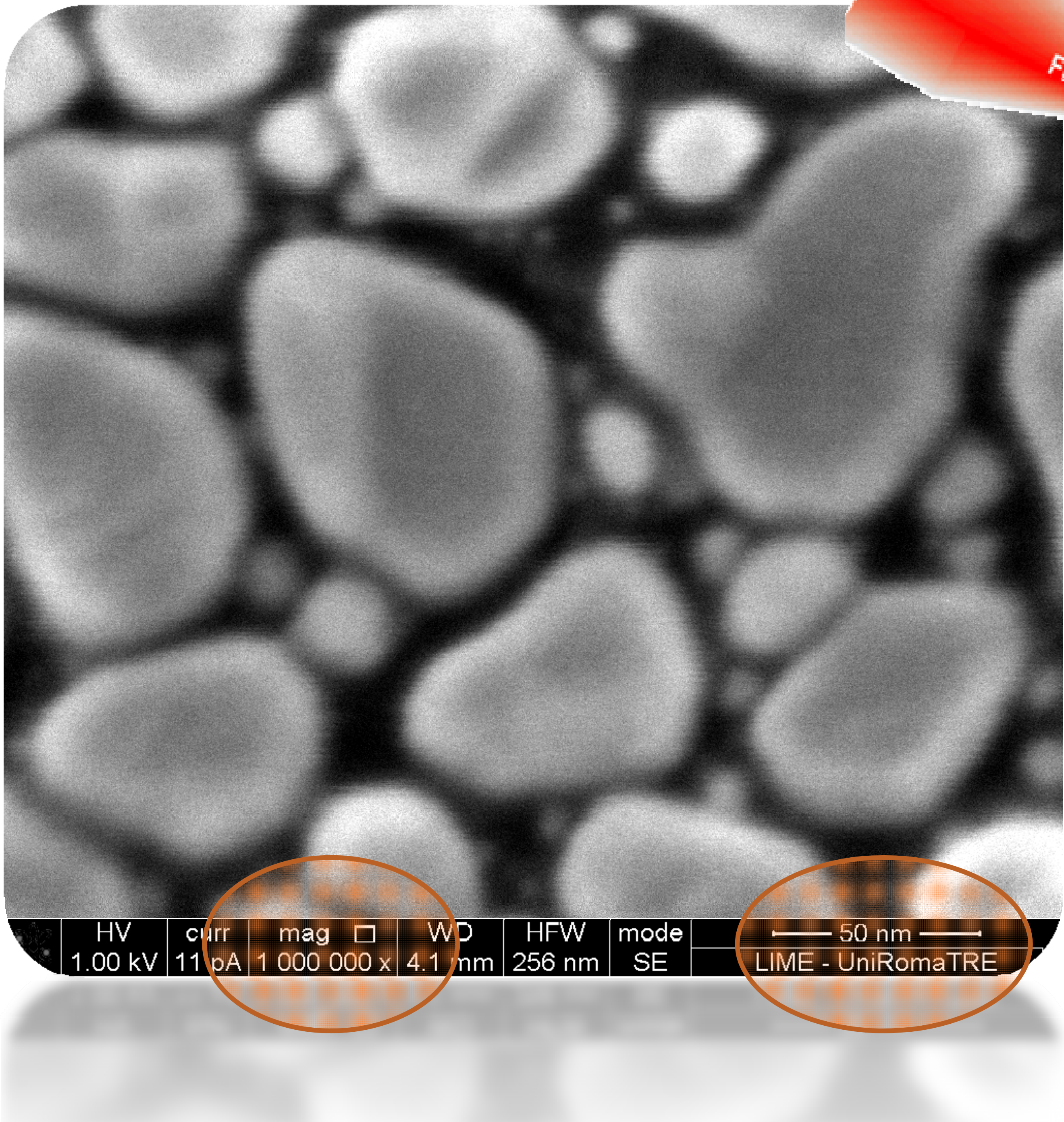


SEM Column: **0,76 nm** @ 15 kV
FIB Column: 5 nm @ 30 kV
(spatial resolution)

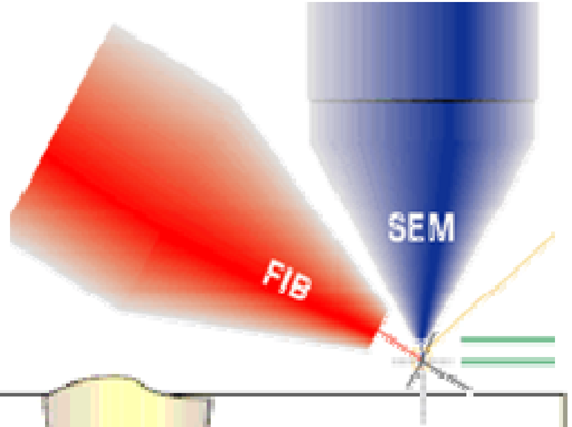


HIGH RESOLUTION SEM:

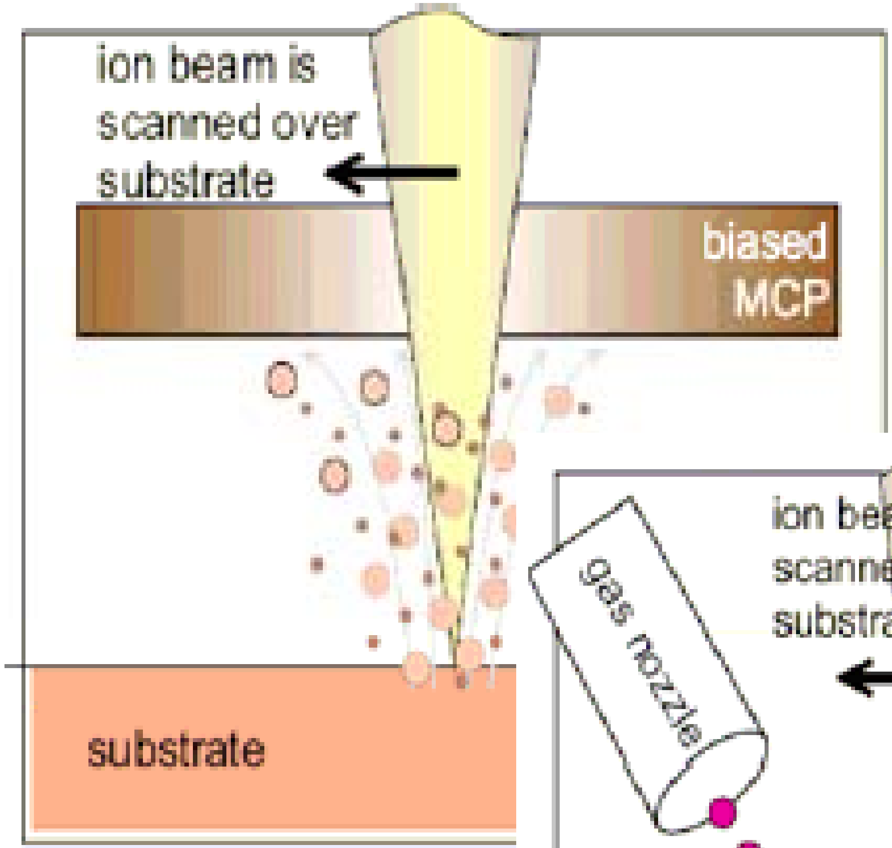


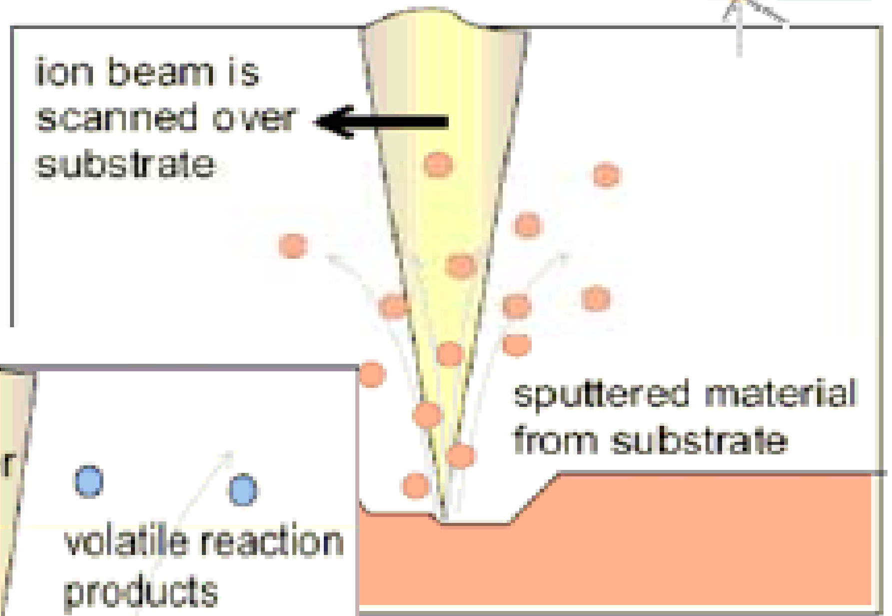


PRINCIPAL FIB MODES

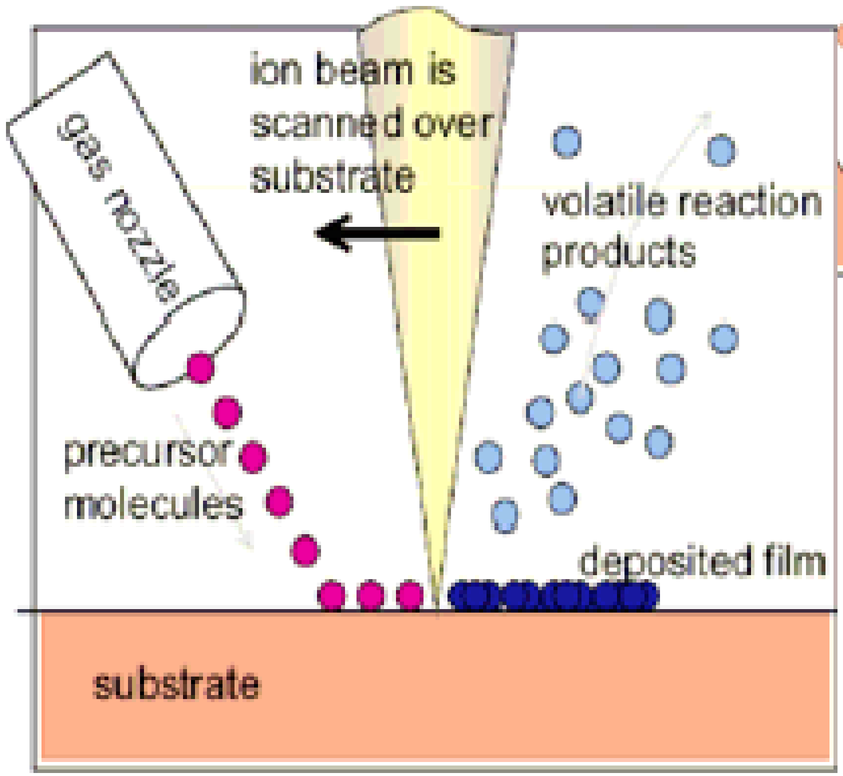


Imaging:





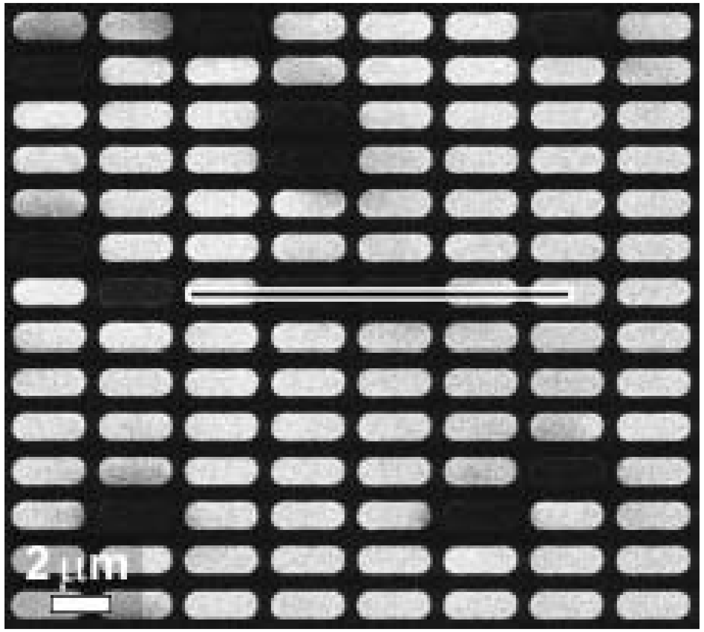
Milling:



Deposition:

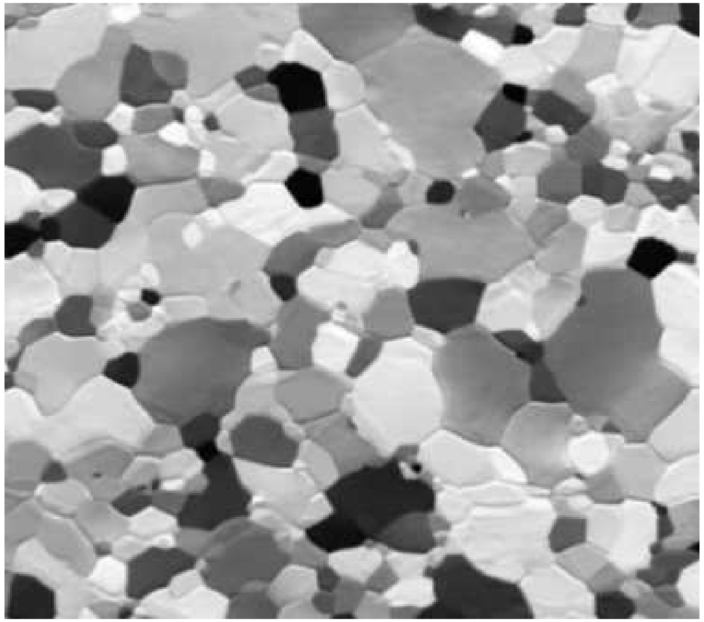
FIB MODES: ION IMAGING

- *Voltage contrast*: insulators appear dark while grounded conductors are bright.

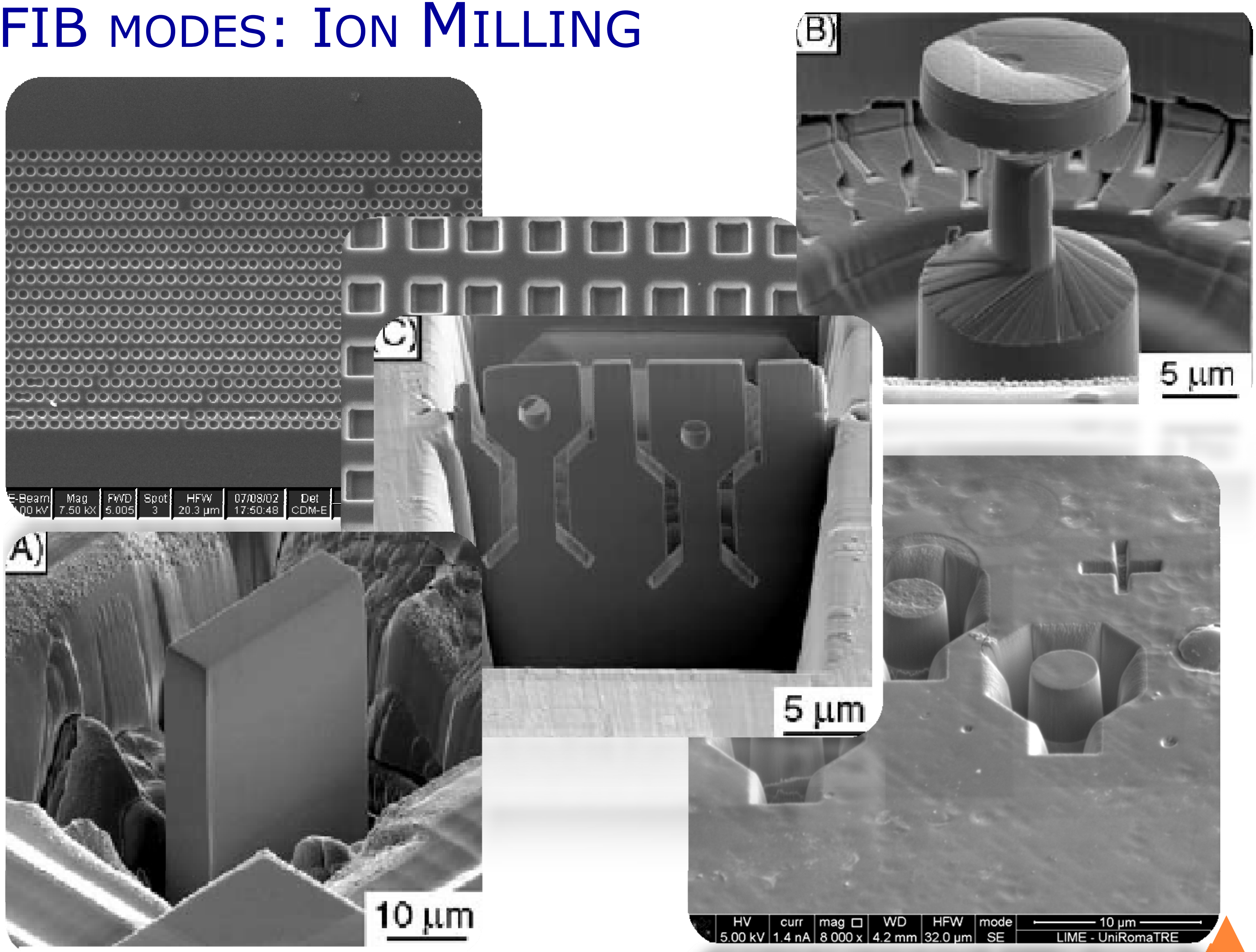


- *Materials contrast*: differences in yield of secondary particles due to the way energy is lost in the material.

- ***Crystallographic orientation contrast*** (channeling contrast): incident ions are channeled down between lattice planes of the specimen.

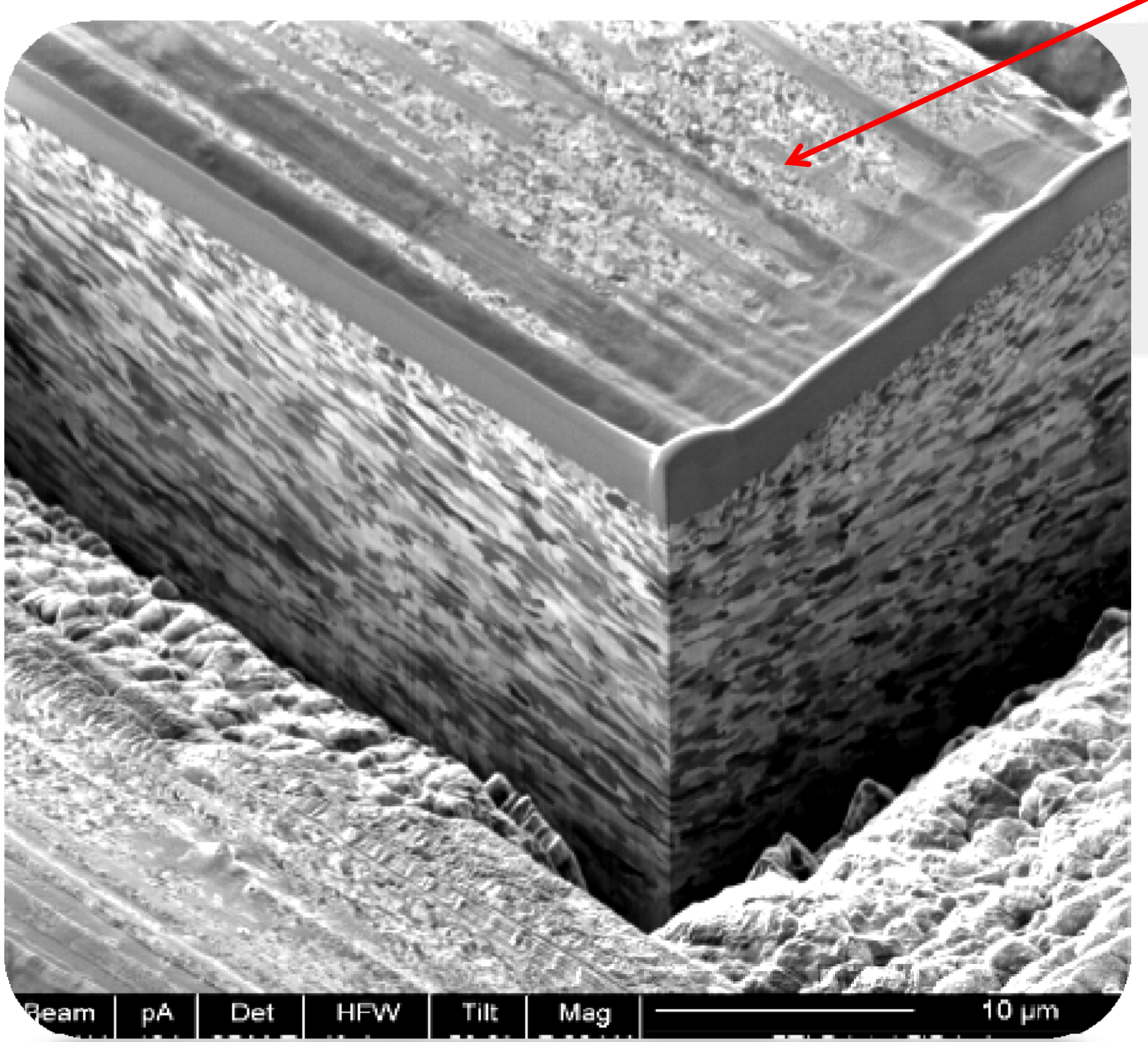


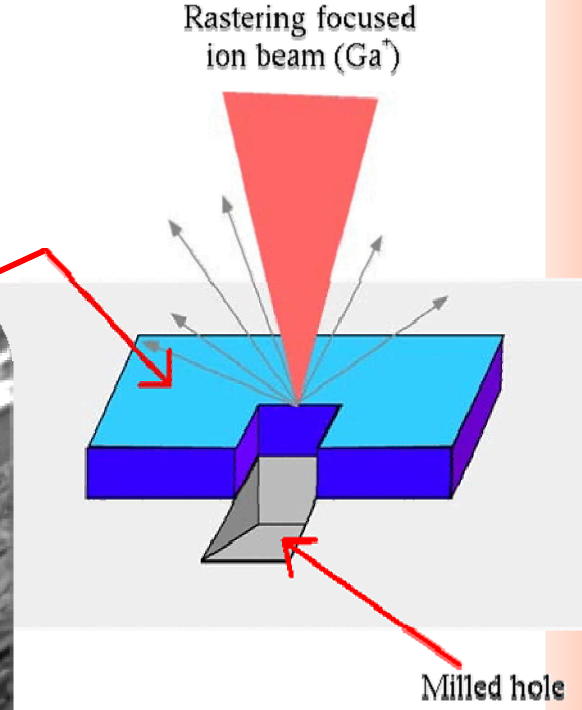
FIB modes: Ion Milling



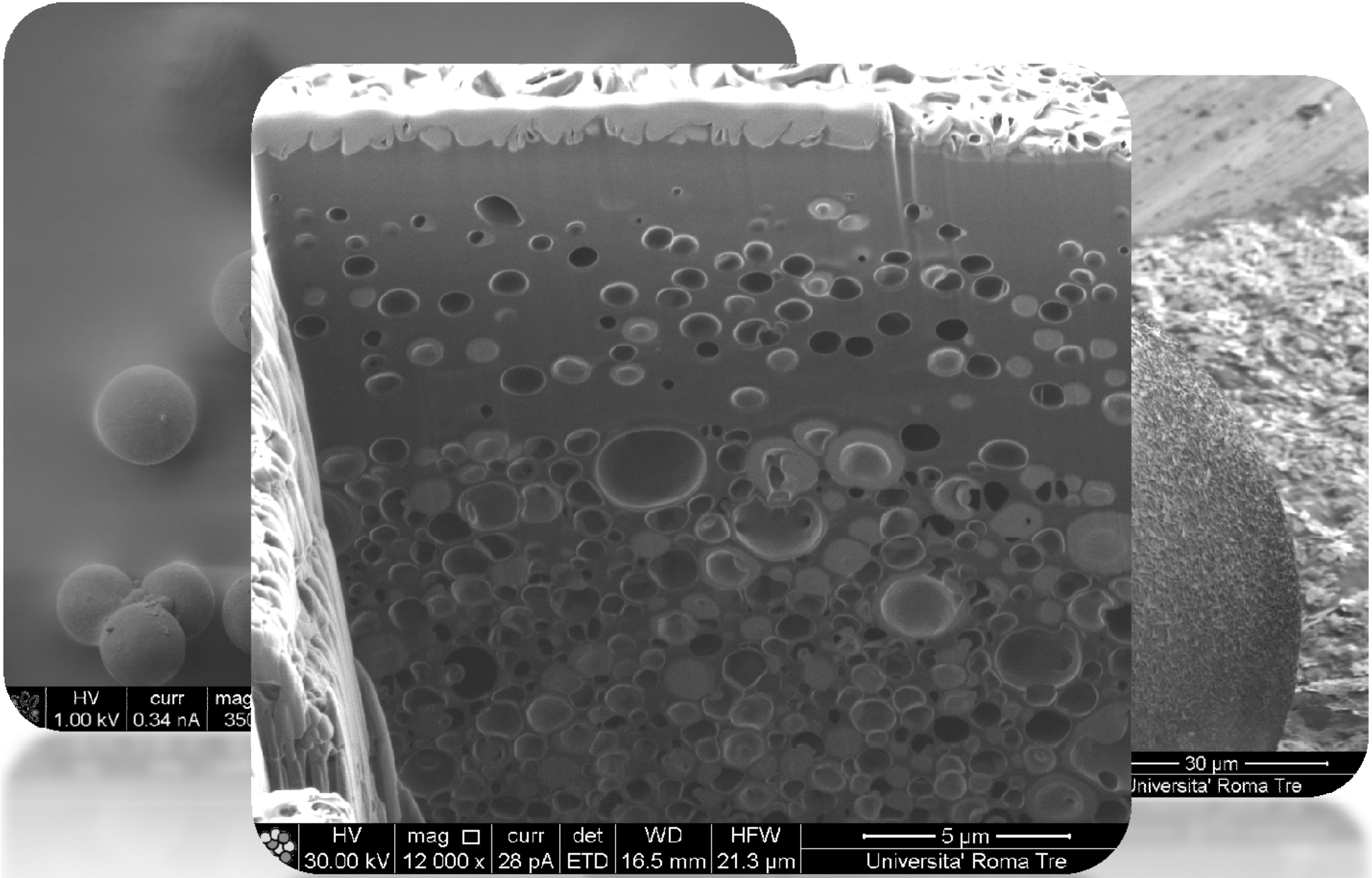
FIB MODES: DEPOSITION (PT)

CROSS SECTIONS





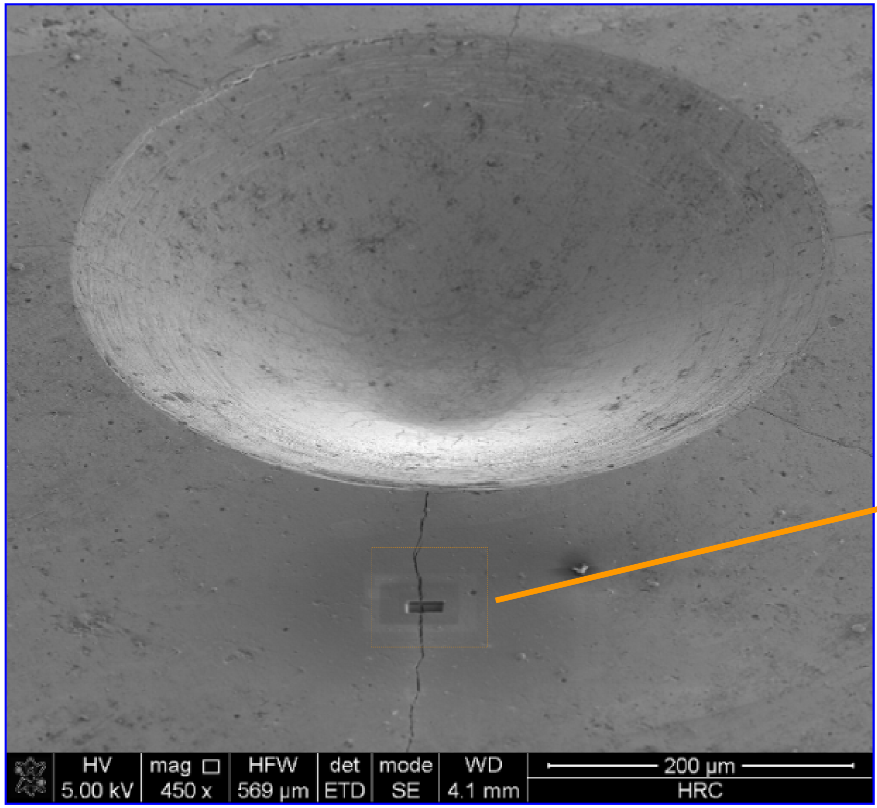
CHARACTERIZATION WITH DUAL BEAM MICROSCOPY

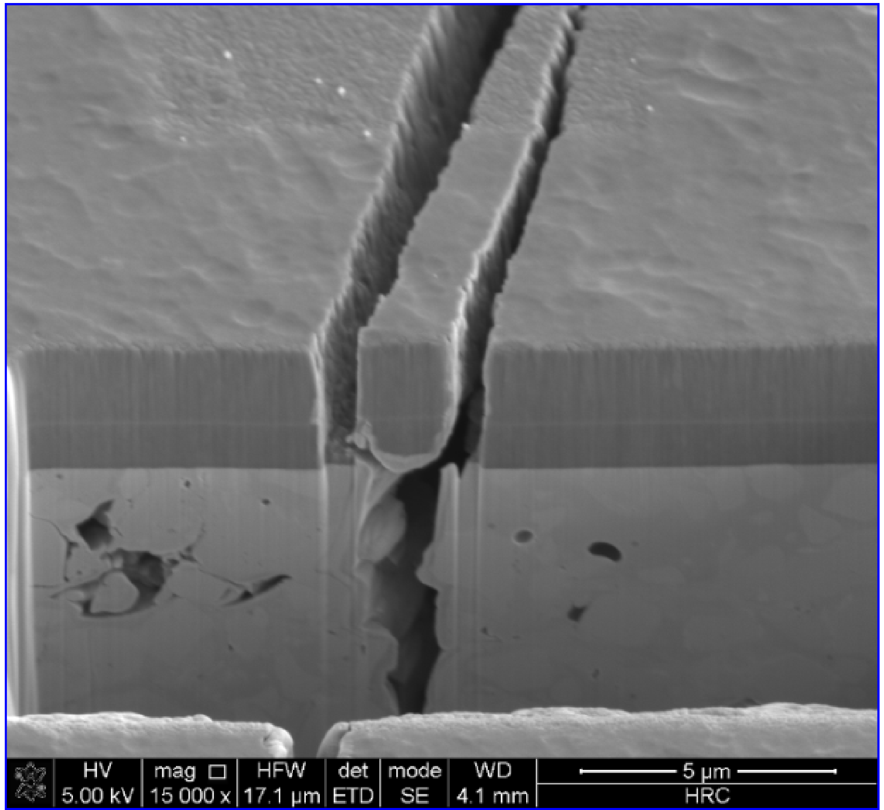


CHARACTERIZATION WITH DUAL BEAM MICROSCOPY

Multiscale and multitechnique approach to mechanical characterization of tribological coatings

Rockwell C adhesion test

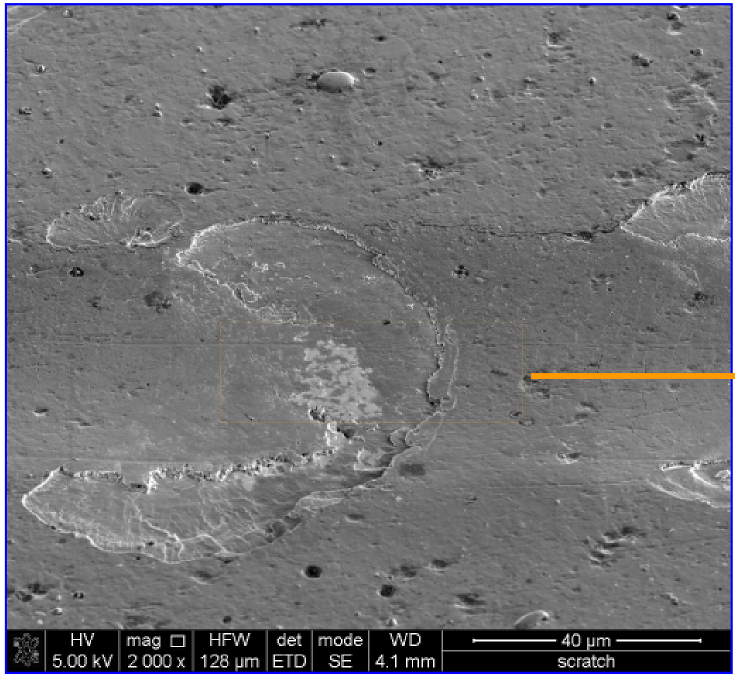


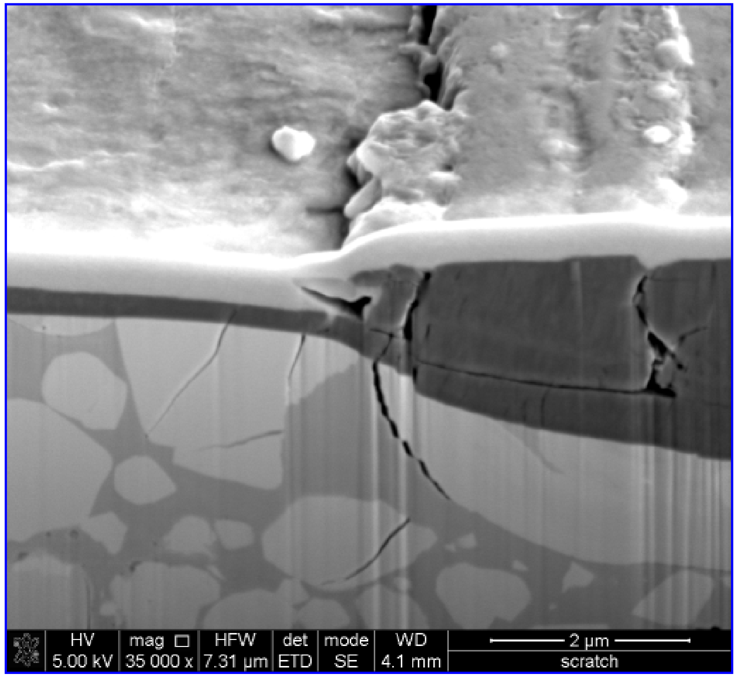


Characterization with Dual Beam Microscopy

Multiscale and multitechnique approach to mechanical characterization of tribological coatings

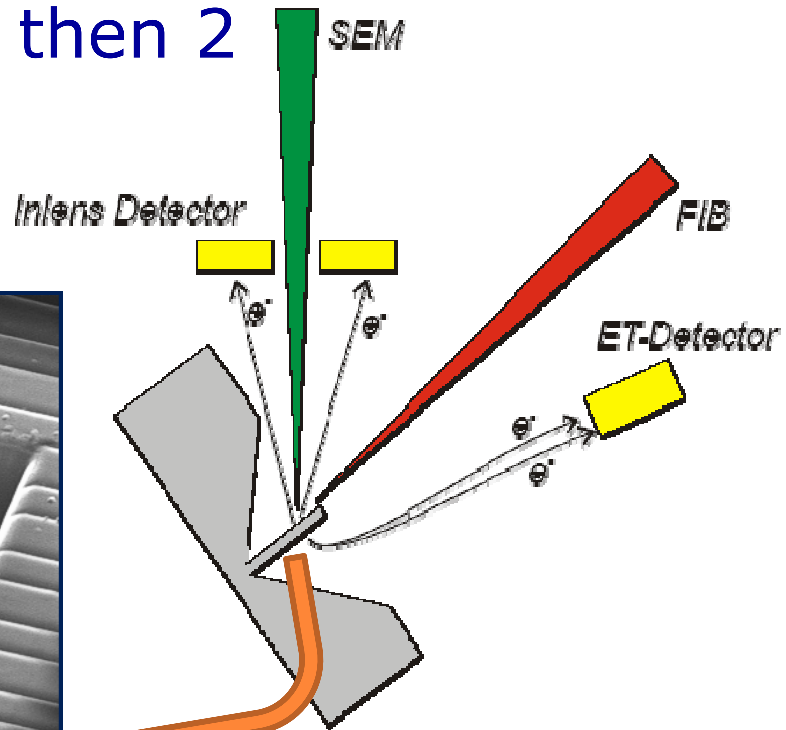
Scratch test
L_{c3} failure

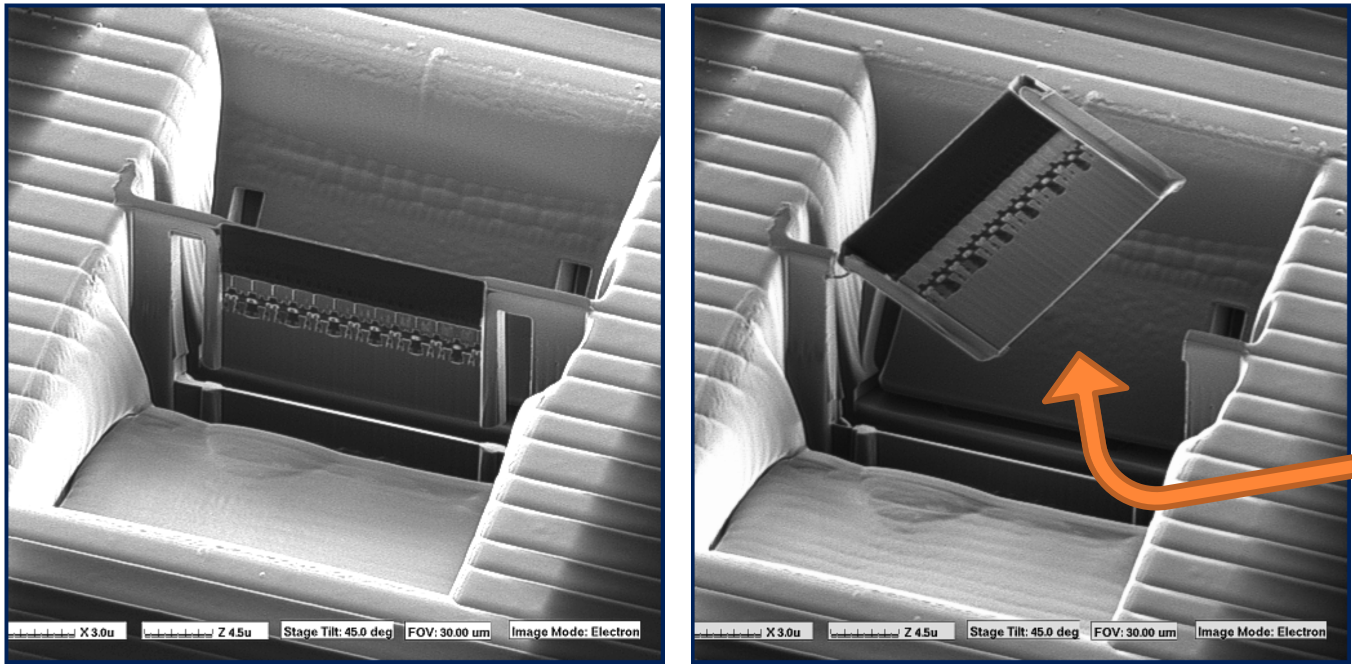




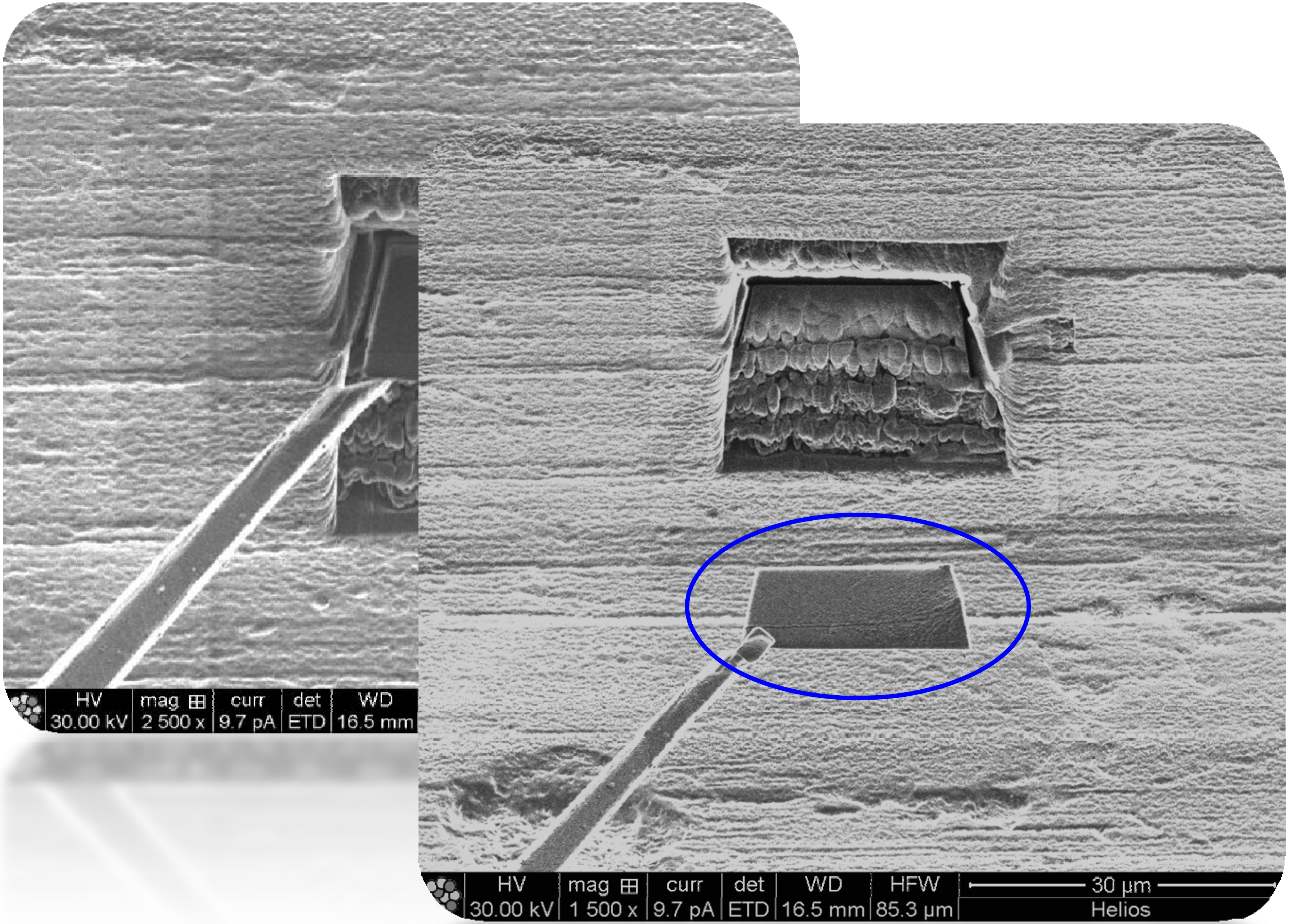
TEM SAMPLE PREPARATION WITH FIB

- The sample surface is investigated before cutting to determine the area of interest.
- Then the sample is milled and polished with predefined milling patterns
- <u>Time for a lamella preparation</u>: less then 2 hours with expert operator

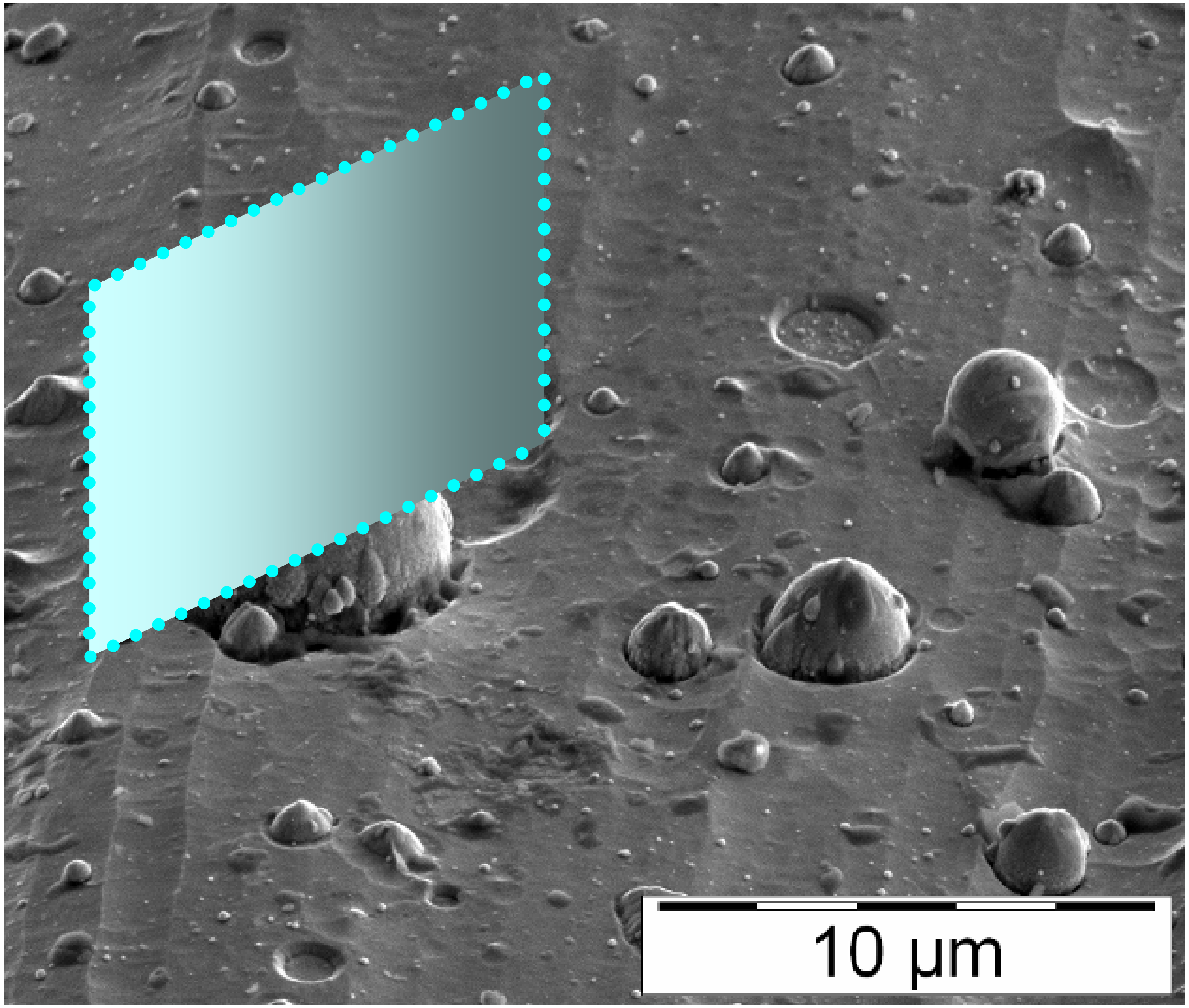




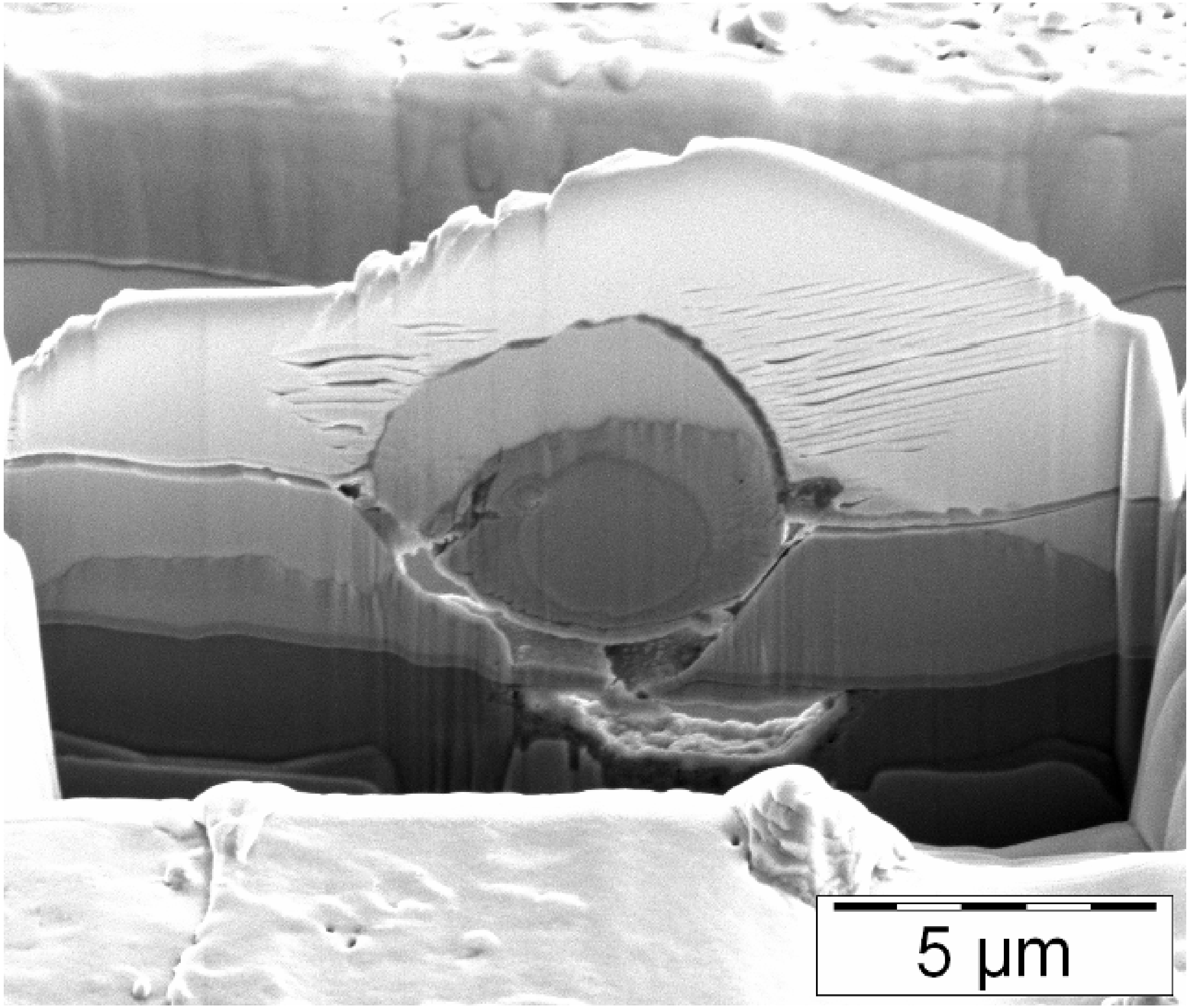
TEM LAMELLAE ESTRACTION



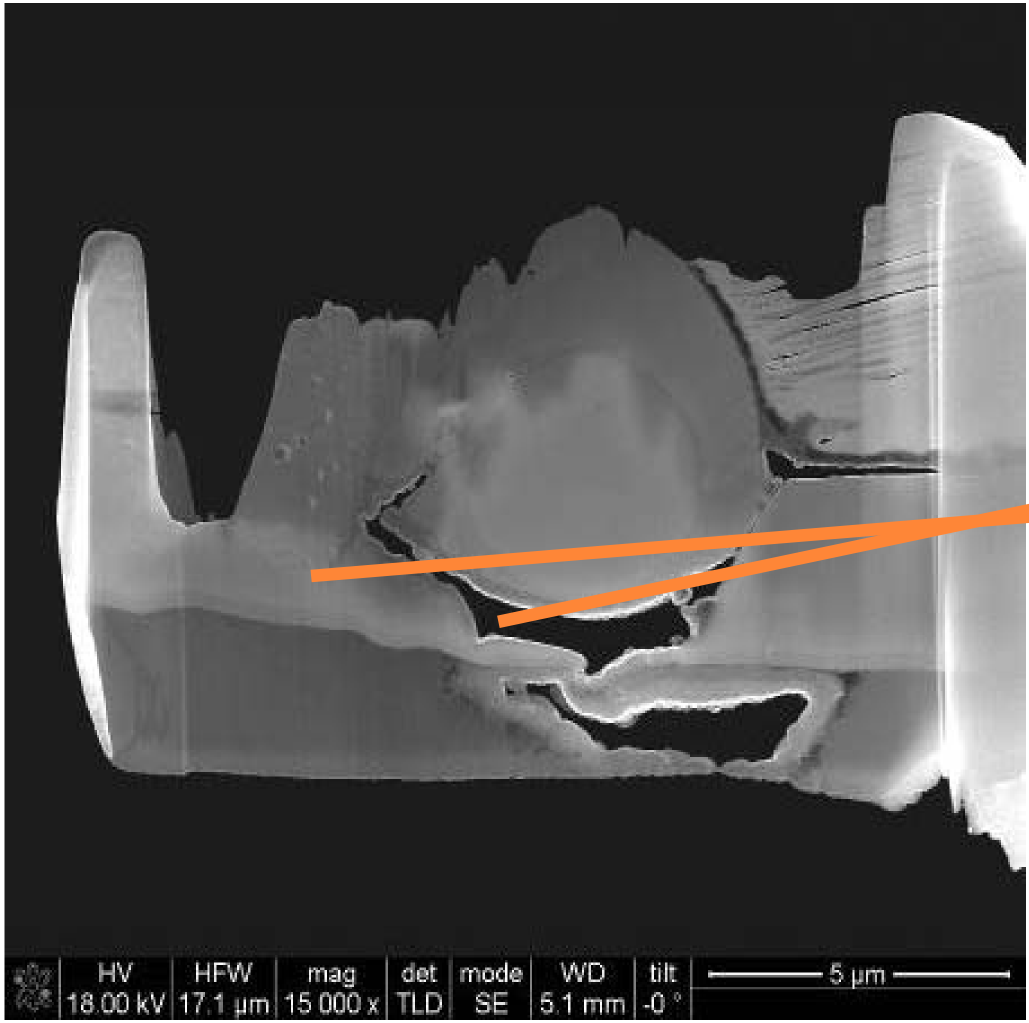
SITE SPECIFIC TEM X-VIEW

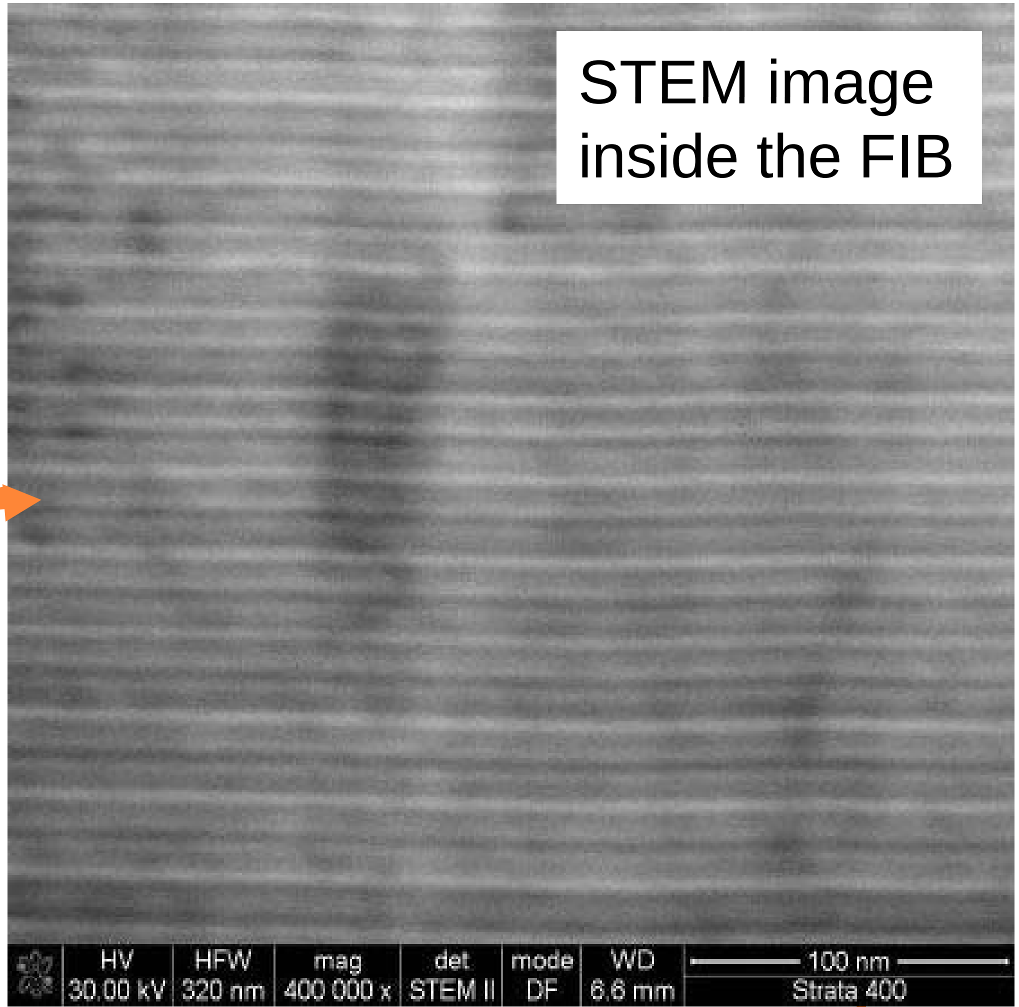


Site specific TEM X-View

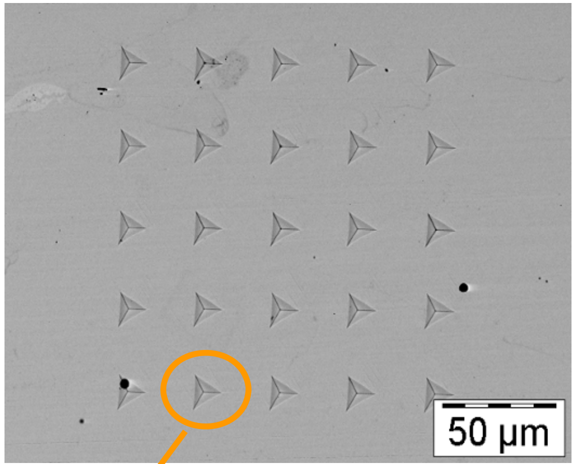


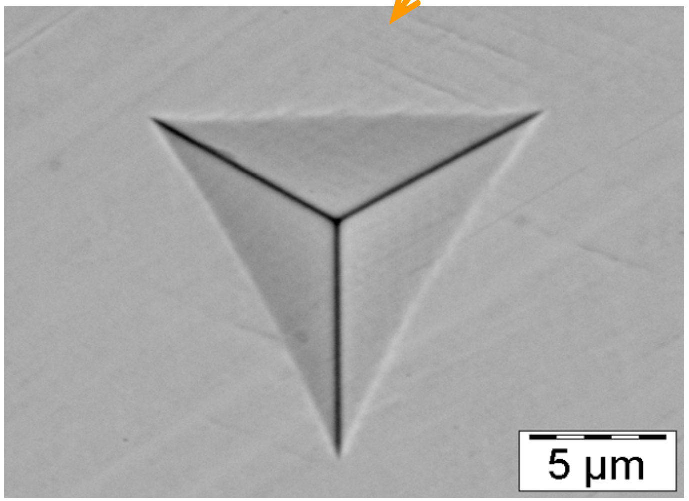
SITE SPECIFIC TEM X-VIEW





UNIVERSITY ROMA TRE NANOHARDNESS TESTER



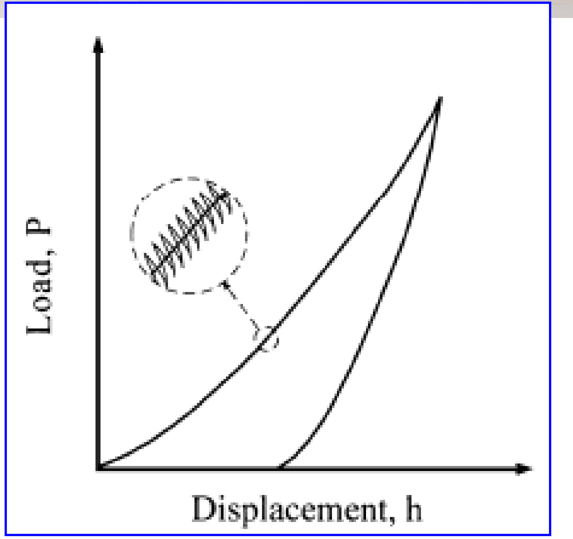


Berkovich tip

NANO INDENTER

SYSTEM SPECIFICATIONS

Standard Indentation Head Assembly	
Displacement resolution	<0.01 nm
Total indenter travel	1.5 mm
Maximum indentation depth	>500 μm
Load application	Coil / magnet assembly
Displacement measurement	Capacitance gauge
Loading capability	
Maximum load (standard)	500 mN
Maximum load with DCM option	10 mN
Maximum load with high-load option	10 N
Load resolution	50 nN
Contact force	<1.0 μN
Load frame stiffness	≈5 x 10^6 N/m
Indentation placement	
Useable sample area	100 x 100 mm
Position control	automated remote with mouse
Positional accuracy	1 μm



CSM Method

INTEGRATED CHARACTERIZATION APPROACH

Models

Microhardness

Nanoindentation

Indentation Size Effect (ISE) curves: analysis of hardening behaviour

Fracture toughness of bulk ceramics

Elastic modulus and mechanical anisotropy

Intrinsic hardness of thin films

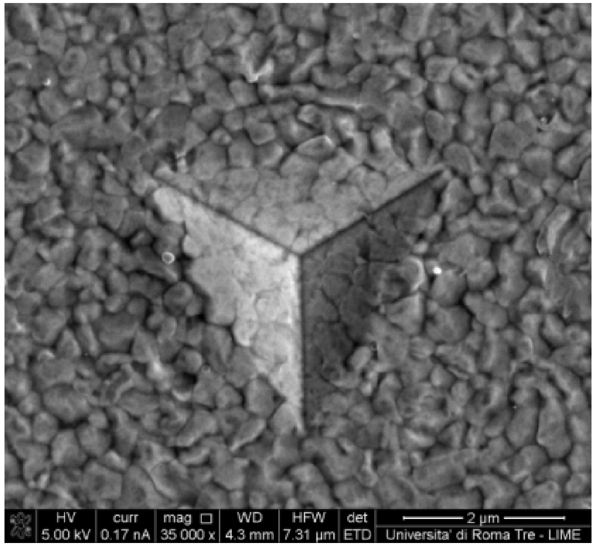
Adhesion of thick coatings

Advanced Microscopy Techniques
HR-SEM
FIB
AFM
TEM

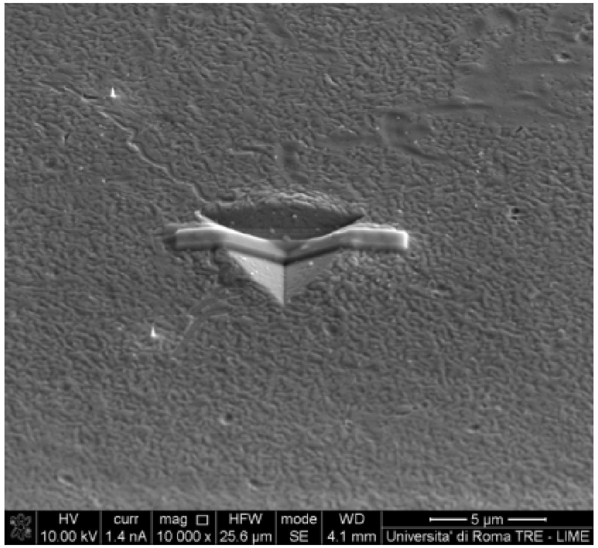
Correlation to microstructure
Correlation to in-service behavior and/or functional properties

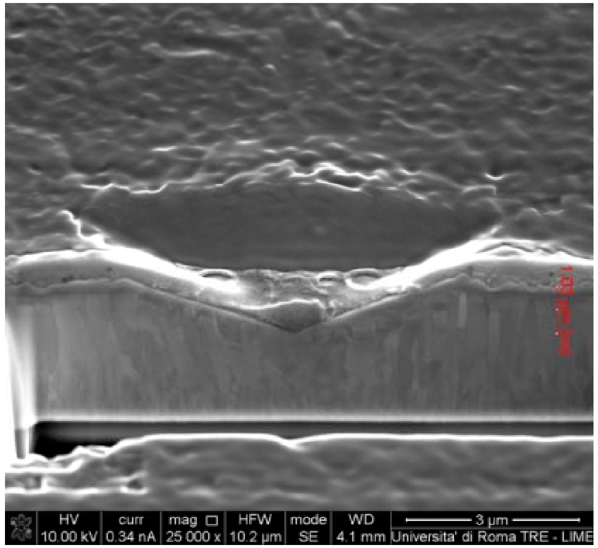
Nanoindentation on Nb thin films

- Pt deposition and FIB sectioning

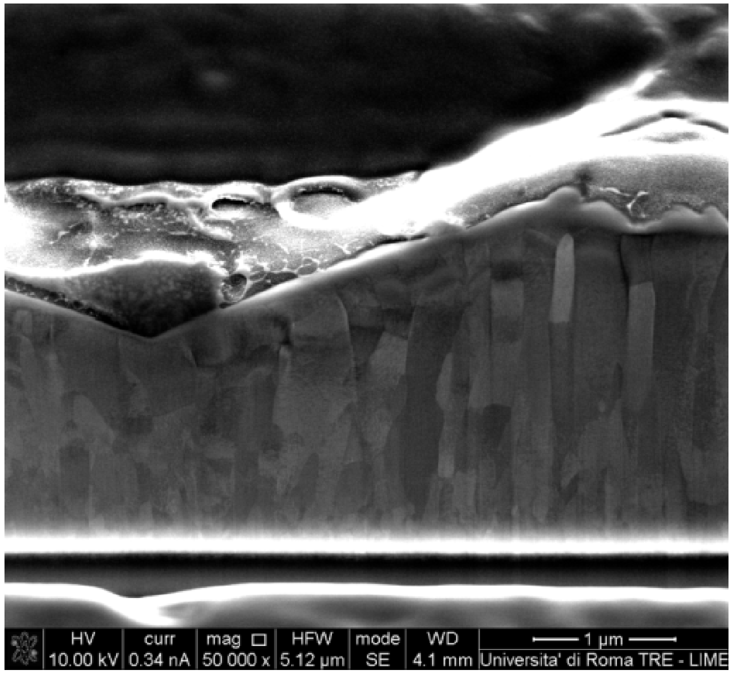


500 nm





Partial re-crystallization during plastic deformation;
Relative sliding of columnar grain

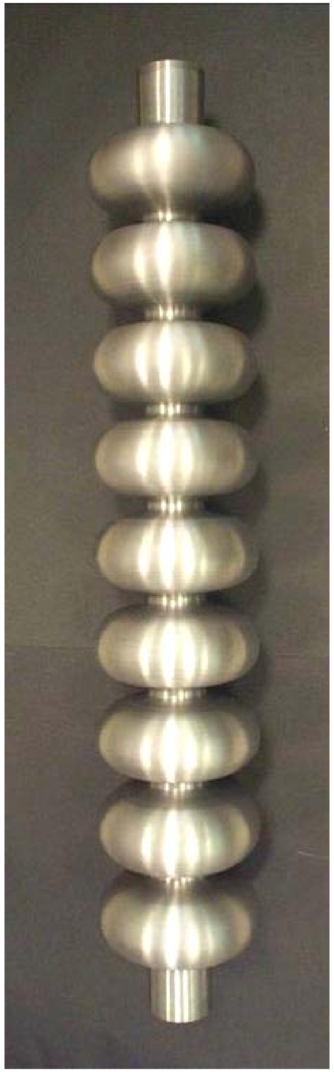


Direct measurement of piling-up
Evaluation of the effects of roughness on contact area
Analysis of deformation mechanisms

CASE STUDY I

- **Characterization of Nb superconductive coating through nano-mechanical testing and AFM-FIB / SEM-TEM analyses**

Resonant Cavities for particle accelerators



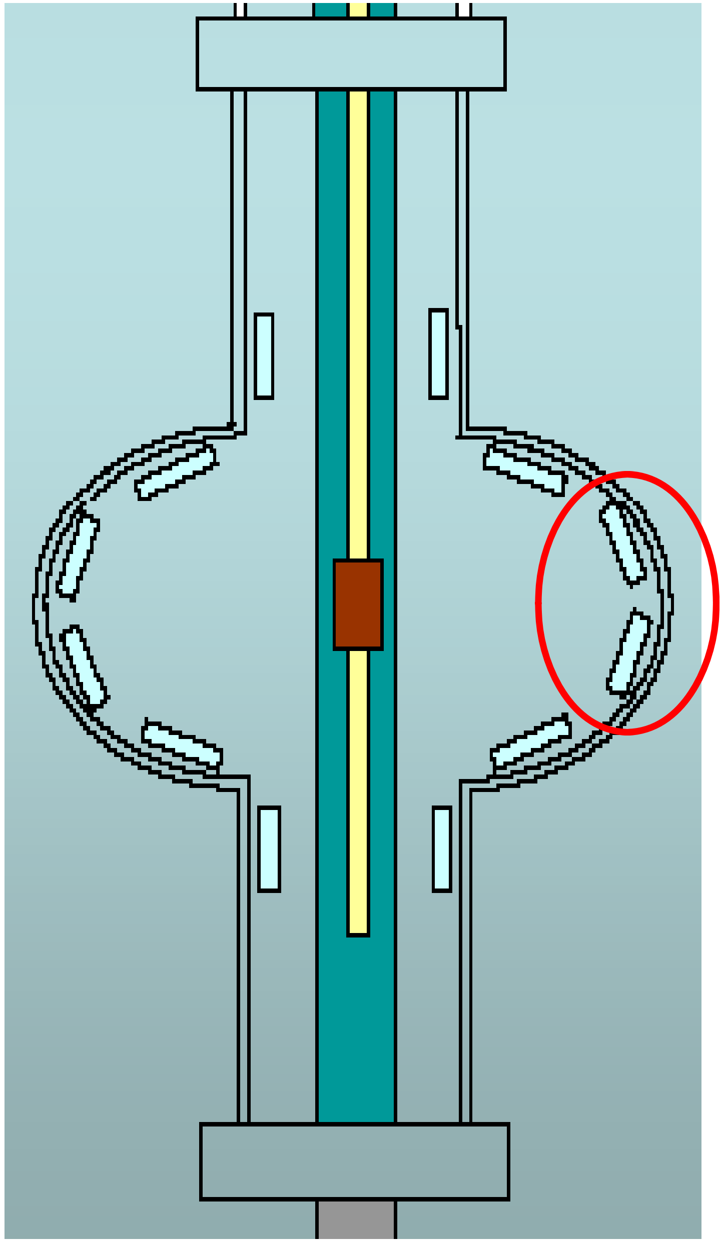
Bulk Niobium

Very low
Surface
electrical
resistance
(~nΩ a 1,8 K)

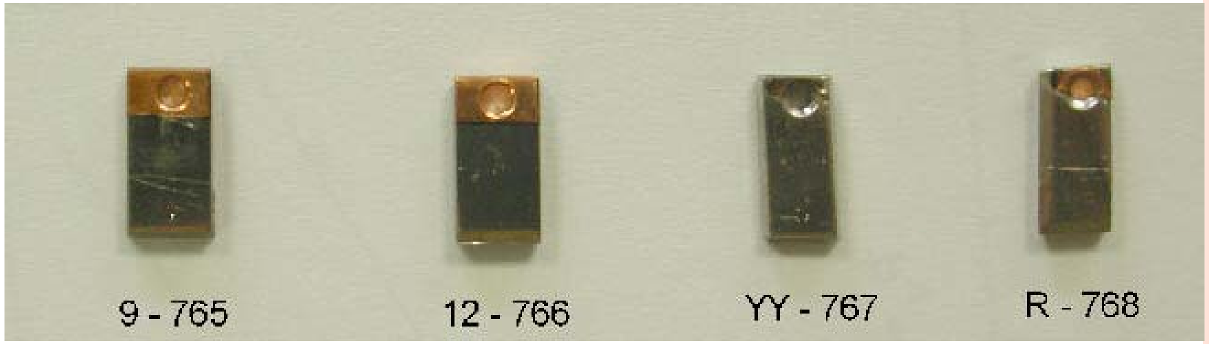
Niobium Coated (PVD)
Copper cavity

Lower costs
Higher thermal stability
But…
Significantly lower
superconducting
properties; WHY?

MATERIALS: COMPARISON OF TWO DEPOSITION PROCEDURES



9	765	**CERN** type sputtering
12	766	**CERN** type sputtering
YY	767	**BIAS** type sputtering (100V)
R	768	**BIAS** type sputtering (100V)

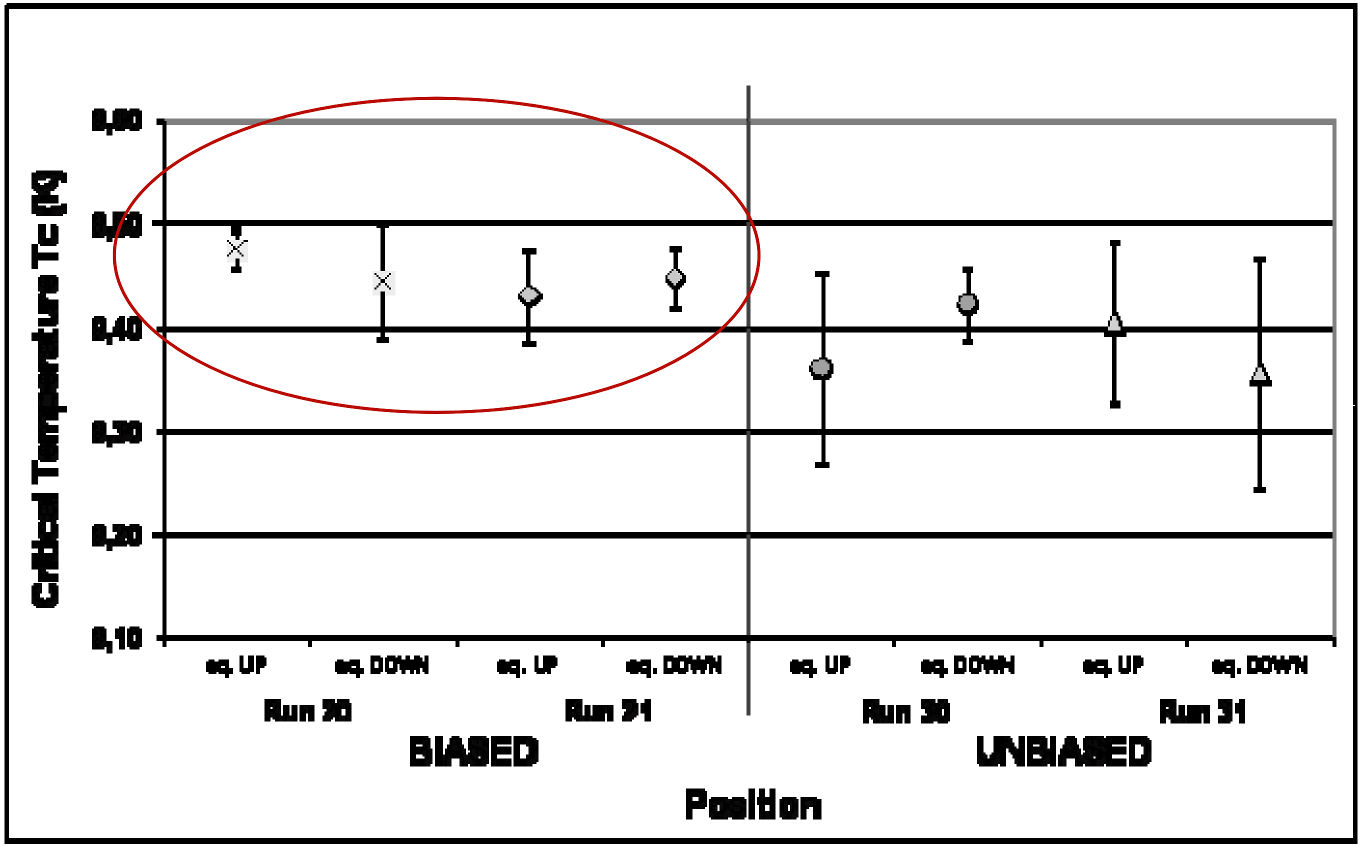


- Same coatings both on Copper and Quartz substrate.

RESONANT CAVITIES FOR PARTICLE ACCELERATORS

- Quality control measurement (RRR and T_c) are usually performed on Nb film deposited on Quartz substrate
  - Even if useful as threshold parameters, RRR and Tc measured on Quartz, can lead to erroneous extrapolation for coatings deposited on copper substrate

MICROSTRUCTURE TO FUNCTIONAL PROPERTIES: CRITICAL TEMPERATURE

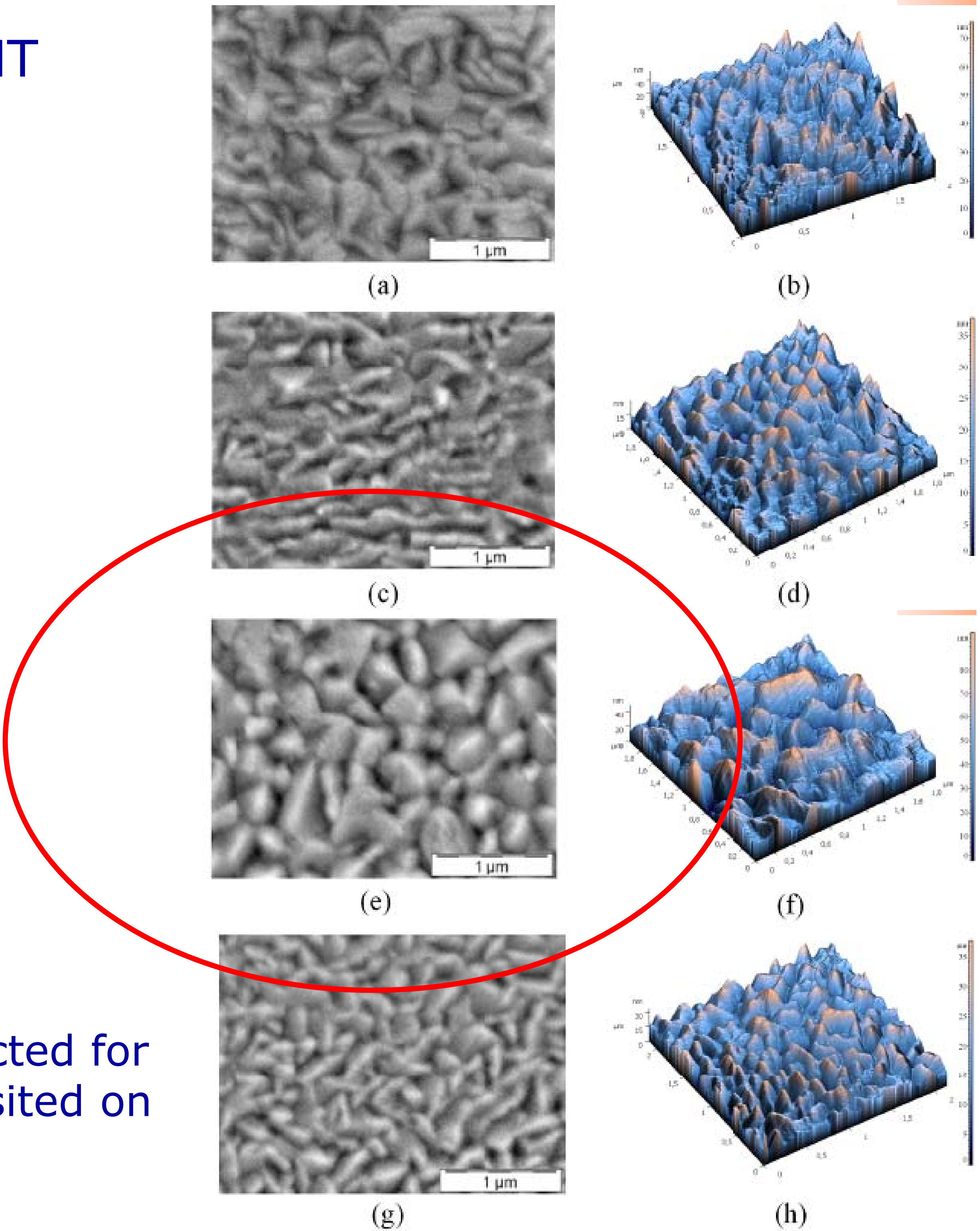


A critical temperature of 9,5 K is very unusual

- This suggest that strong microstructural differences do exist for BIASED coatings (density, grain size, lattice distortion, residual stress, resputtering)

Coatings on different substrate

- **Nb on COPPER substrate**
  - BIASED (a-b)
  - UNBIASED (c-d)
- **Nb on QUARTZ substrate**
  - BIASED (e-f)
  - UNBIASED (g-h)



A different behaviour is expected for the BIASED **Nb** coating deposited on **Quartz** substrate

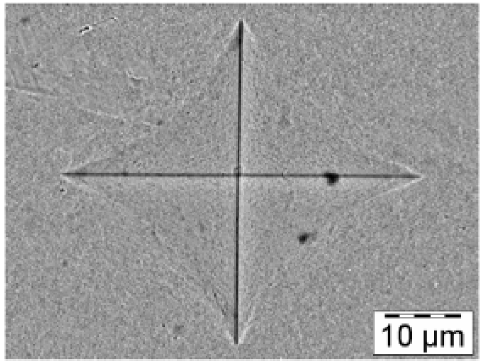
CORRELATION OF MECHANICAL WITH FUNCTIONAL PROPERTIES

- Superconducting properties of MS-PVD Nb films are significantly affected by
  - Grain size
  - surface roughness
  - coating density
  - interfaces integrity

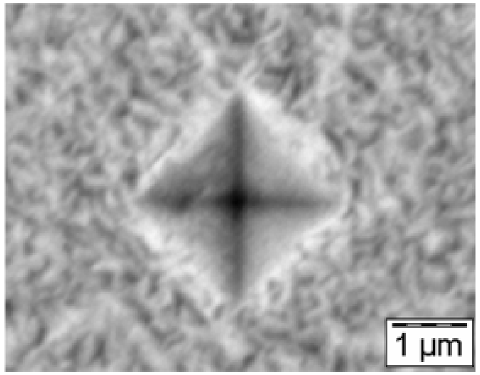
- So are Mechanical properties:

HARDNESS MEASUREMENTS ON FUNCTIONAL COATINGS

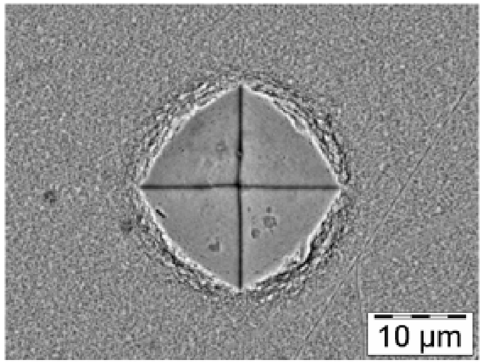
- Can hardness testing (coupled with FIB-SEM validation) be useful for the prediction of functional performances of Nb thin films?



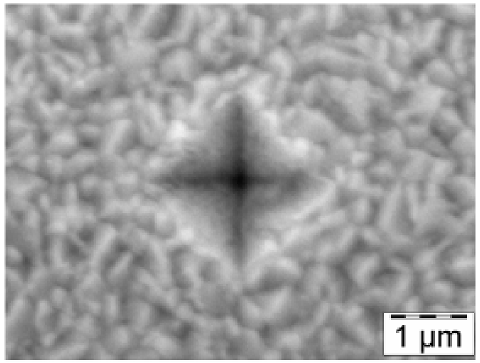
(c)



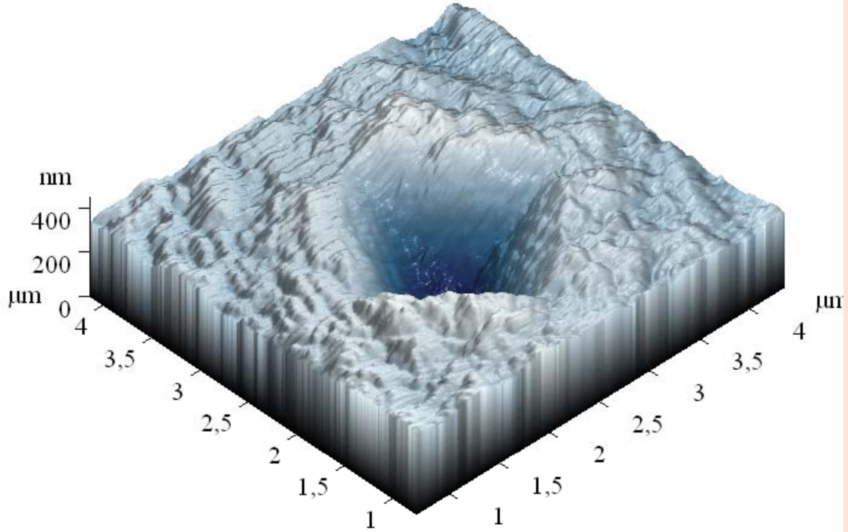
(d)



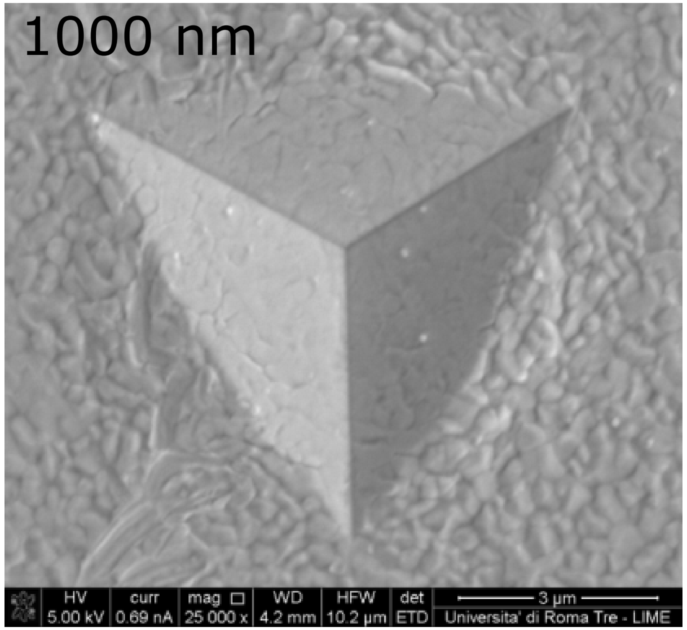
(e)

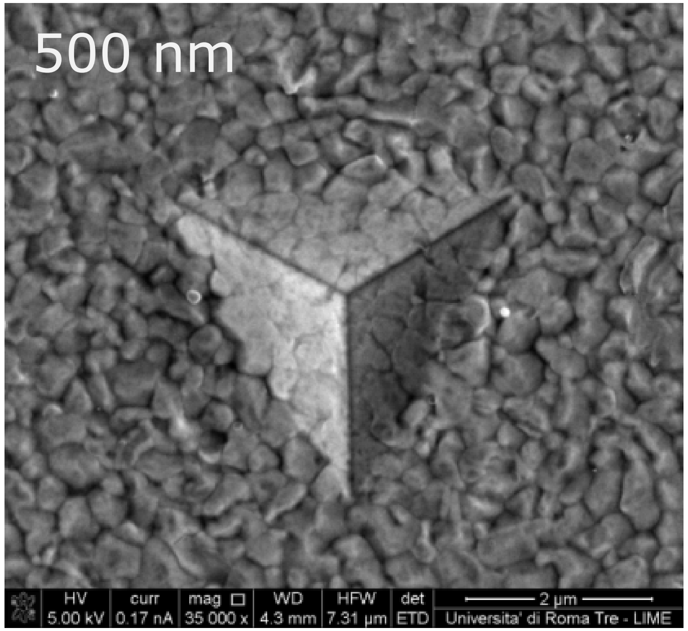


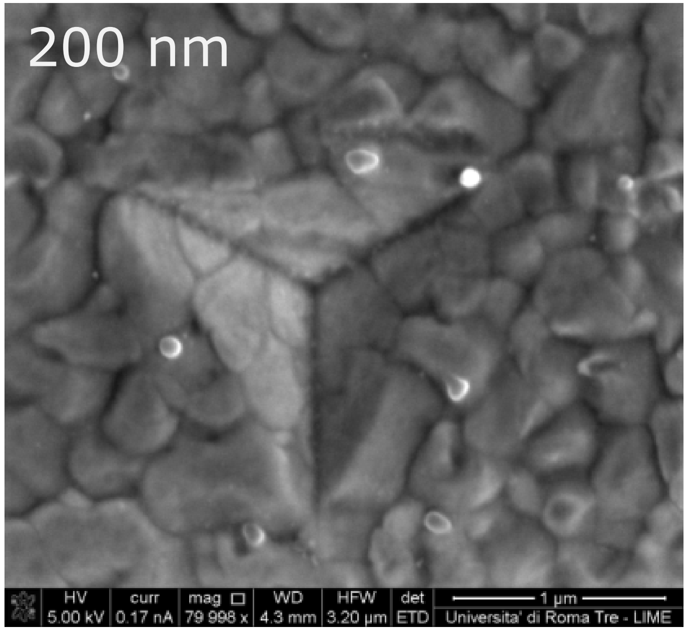
(f)

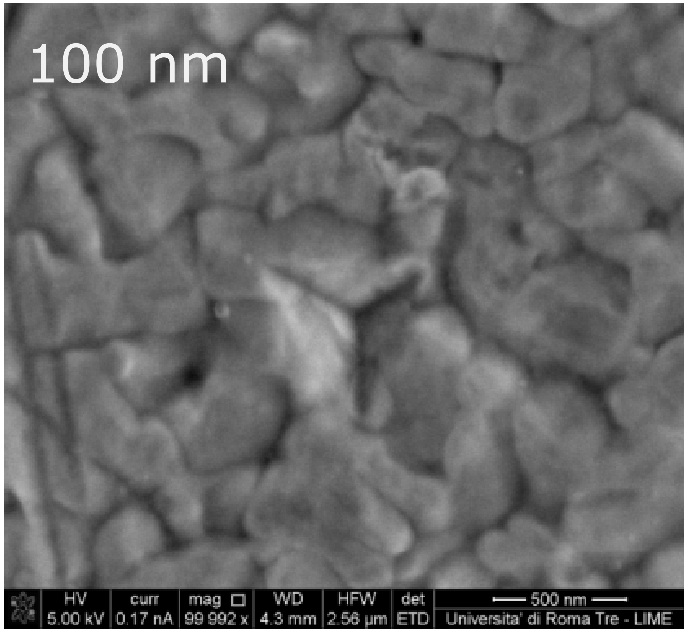


NANOINDENTATION ON NB THIN FILMS









HARDNESS MEASUREMENTS ON FUNCTIONAL COATINGS

Sample code	Description	Nanoindentation		Standard micro-indentation
		H (GPa)	**E (GPa)**	**H (GPa) Korsunsky model**
796	**Nb on Cu BIAS type**	3,10 ± 0,58	101,5 ± 23,61	2,51 ± 0,15
797	**Nb on Quartz BIAS type**	1,63 ± 0,30	76,22 ± 48,99	1,75 ± 0,12
803	**Nb on Cu CERN type**	2,59 ± 0,35	108,68 ± 11,65	2,38 ± 0,15
804	**Nb on Quartz CERN type**	2,19 ± 0,31	95,95 ± 26,31	2,01 ± 0.10

OXIDE LAYER CHECK

Halbritter, Journal Of Applied Physics **97**, 083904 (April, 2005)

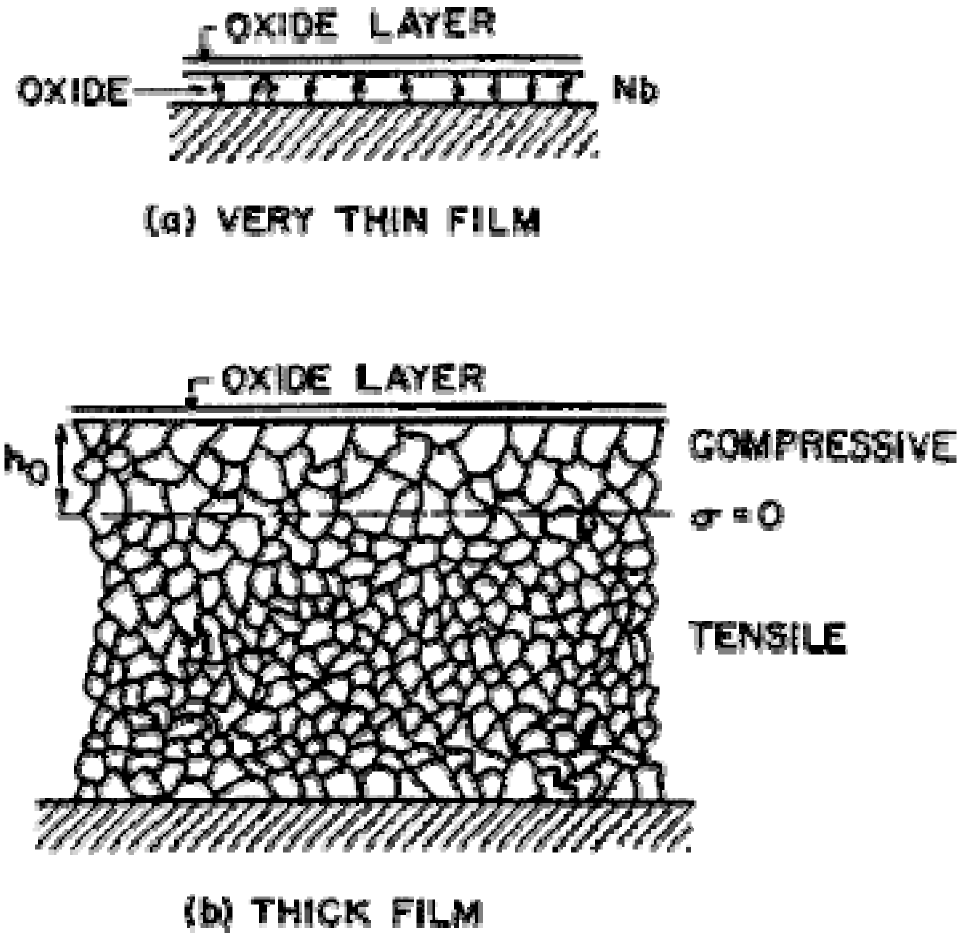
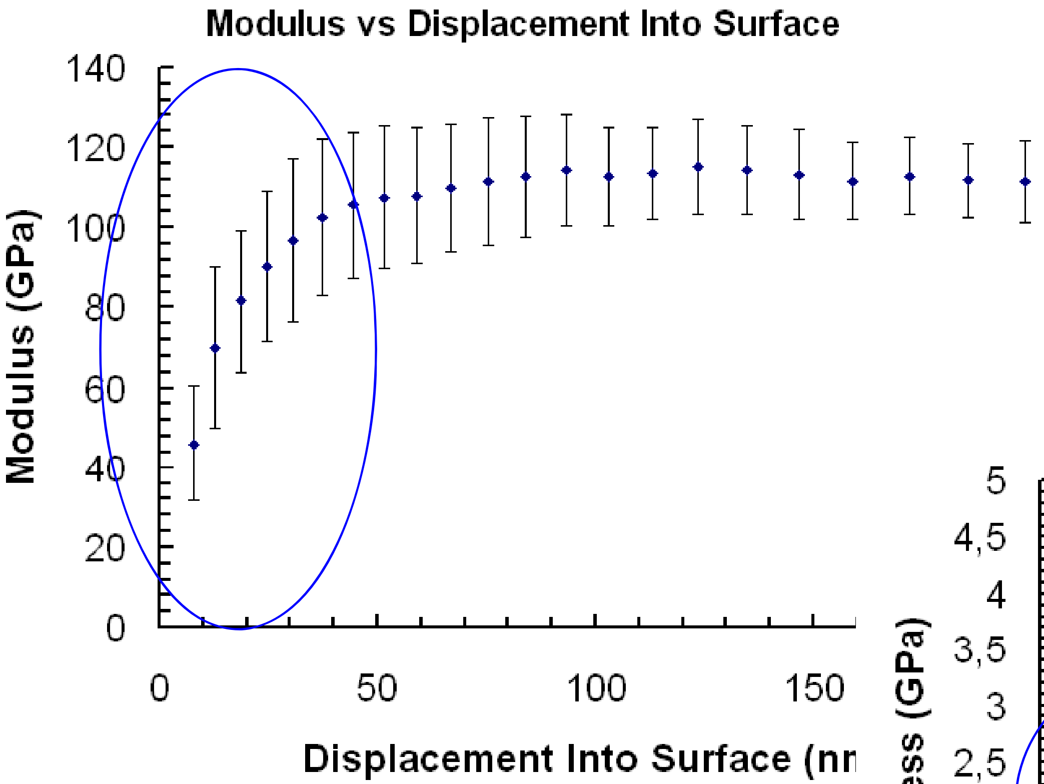
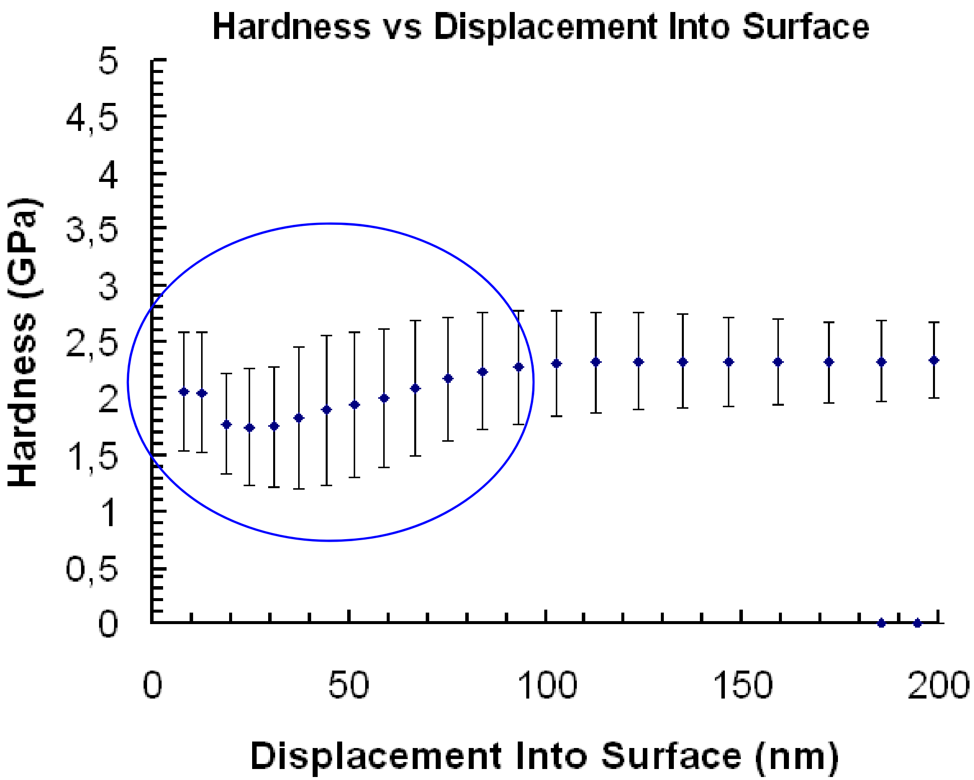


FIG. 1. Schematic cross section[13] of Nb/substrate composite: (a) Nb film oxidized along columns/grain boundaries. (b) Thick Nb film with compressed Nb layer by oxidation along the columns up to a depth of about $W \approx 0.01-3$ μm removing H_2 out of the interface layers. Below the surface layer column/grains are under tensile stress depending on sputter condition and on implanted sputter gas.

NANOINDENTATION (CSM) ON NB THIN FILMS



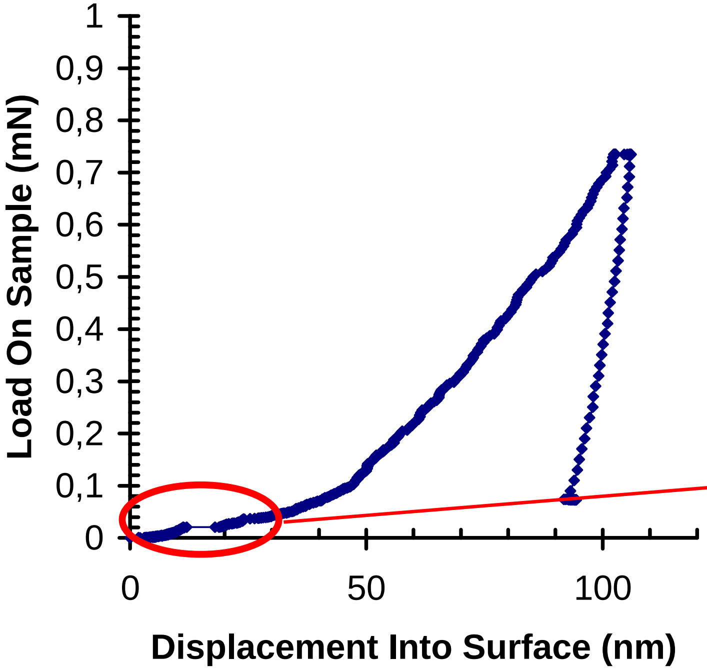
200 nm



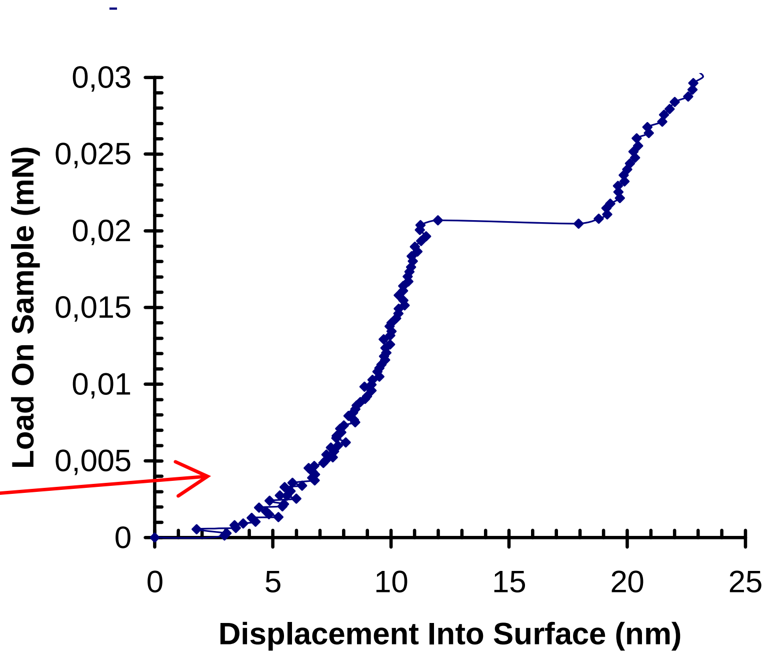
Elastic modulus at **25** nm:
94,1 ± **22,27** GPa

Elastic modulus at **100** nm:
112,9 ± **12,22** GPa

OXIDE LAYER CHECK VIA NANOINDENTATION



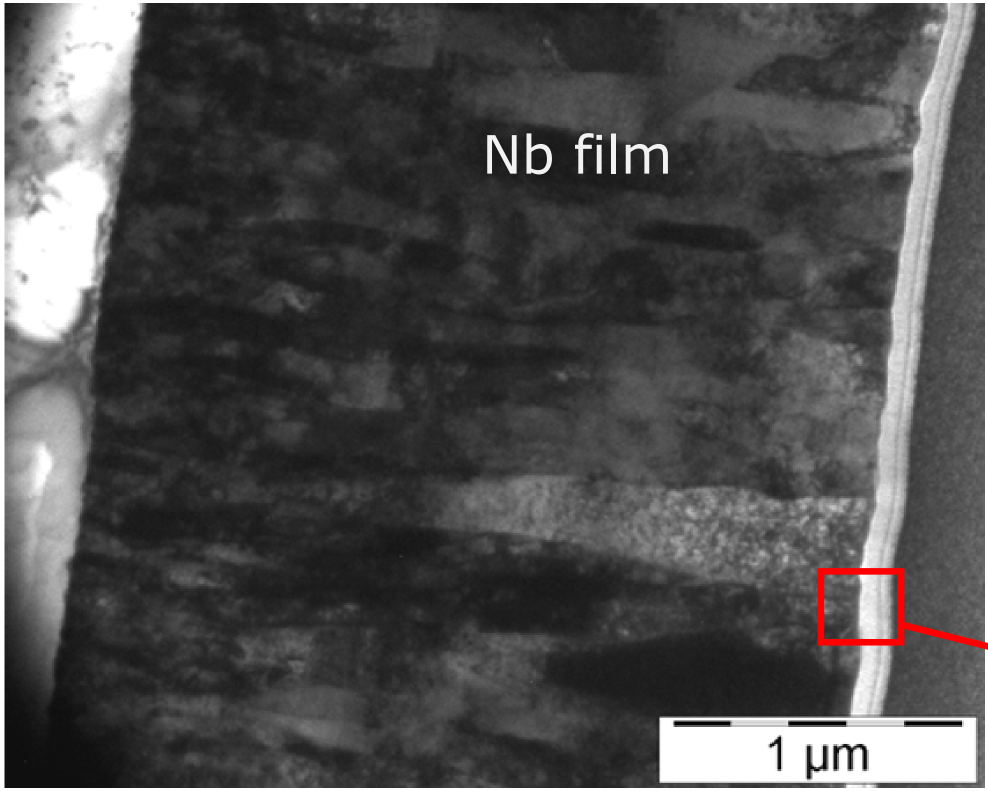
Niobium film load-depth curve



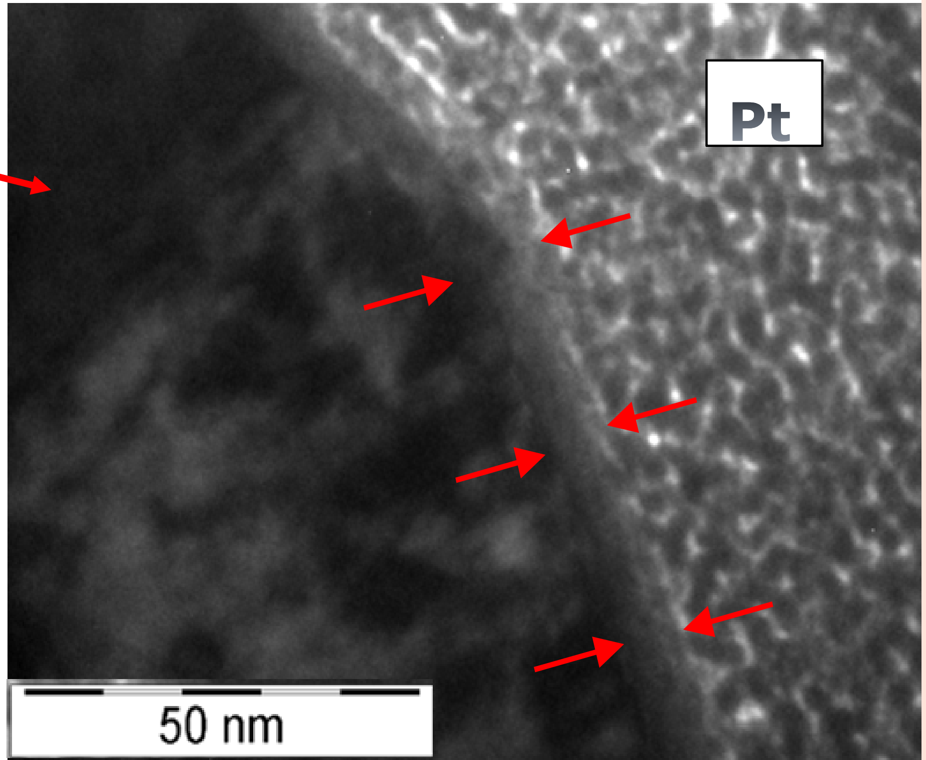
Niobium film: Detail of a load-depth curve

Indenter pop-in systematically at ~ 10 nm depth

TEM ANALYSIS OF THE OXIDE LAYER



TEM sample preparation by FIB lamella thinning



CASE STUDY I: CONCLUSIONS

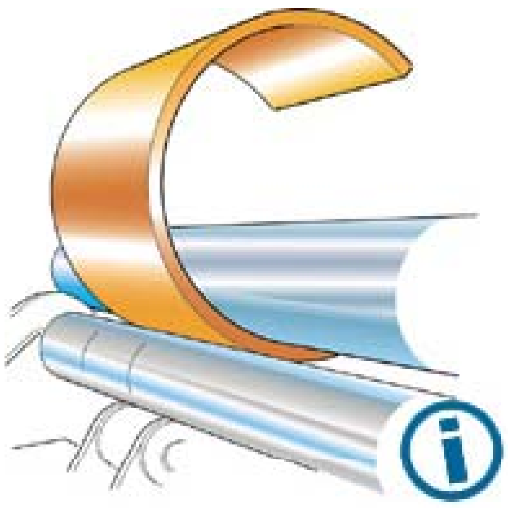
- In case of a soft-on-hard system, substrate can significantly affect the mechanical behavior of the coating;
- Different micro-structural effects and deformation mechanisms were observed at different applied loads
- Surface micro-roughness, coating density, and thickness of the surface oxide layers are strictly related to superconducting properties;
- The coupled use of microscopy techniques and hardness testing has been the key point of all research activities

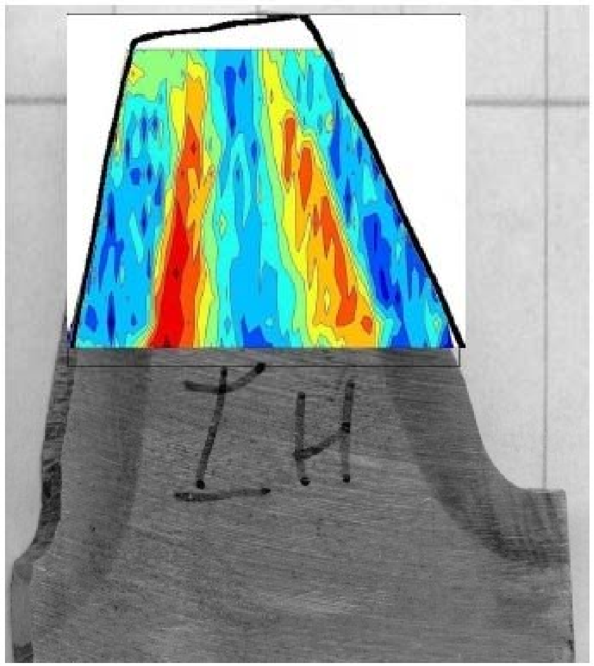
CASE STUDY II

- **Residual Stress Evaluation at the Micrometre Scale: FIB Ring Drilling, Digital Image Correlation and Nanoindentation**

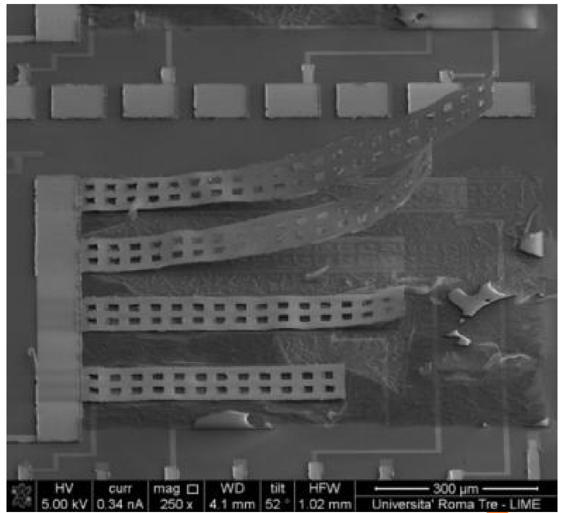
INTRODUCTION

- **Residual stresses** (RS) play a crucial role in determining the deformation behaviour and performance of engineered components and materials <u>at any scale</u>;
- They come from unreleased (inelastic) deformation that remain after external forces has been removed.



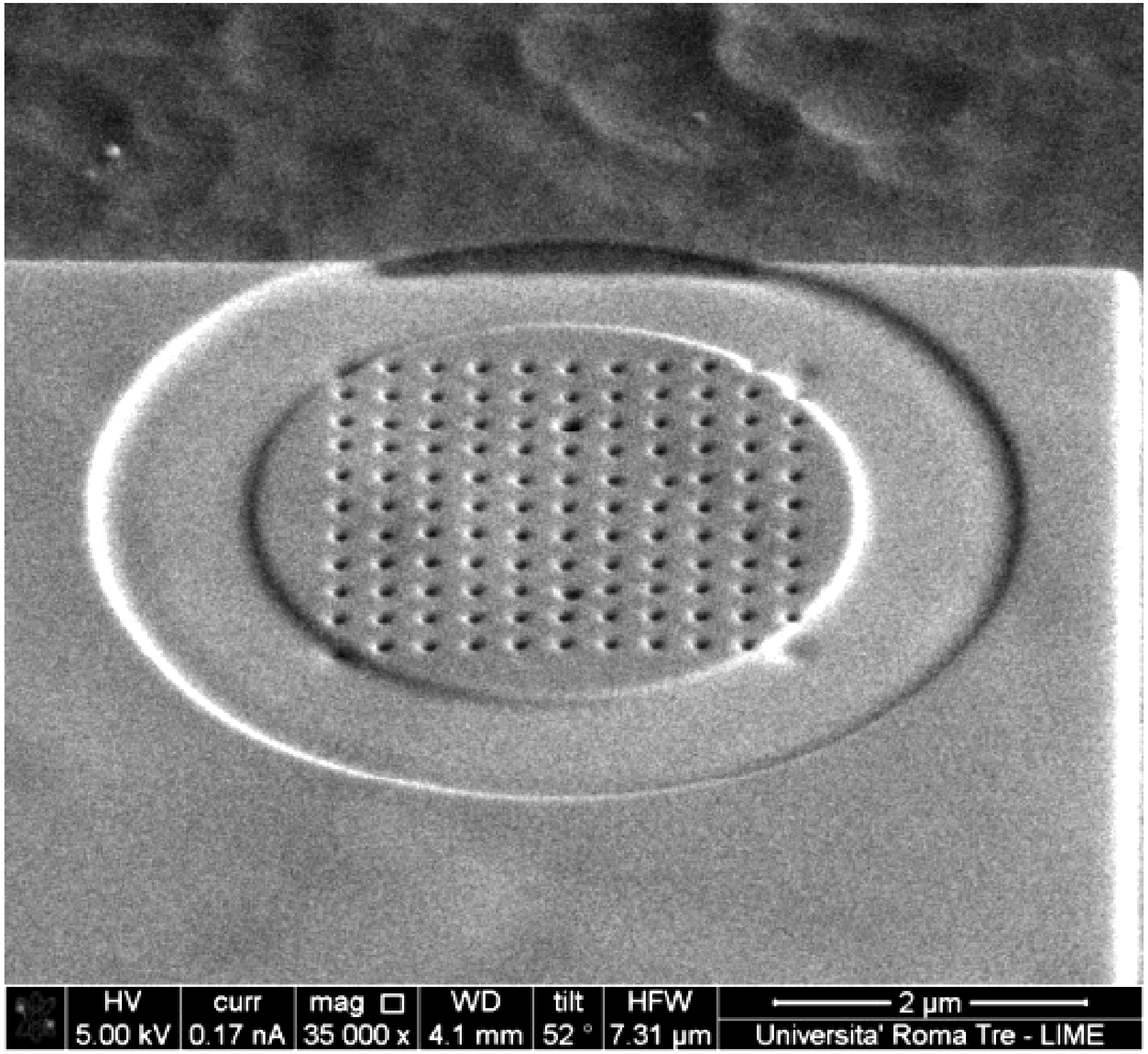


Gear tooth



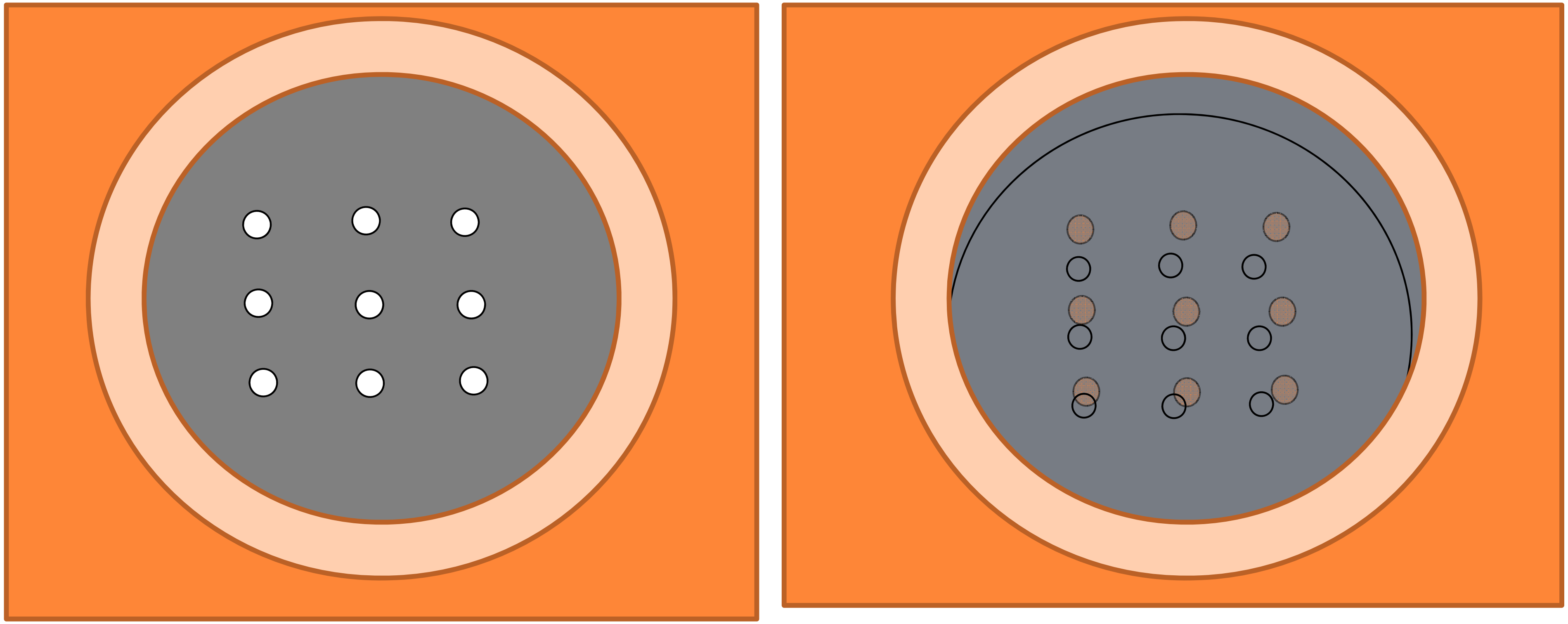
FIRST METHOD, USING IMAGING CORRELATION:

1. Deposition of a Pt slice and milling of a reference dot pattern.



First method, using imaging correlation:

2. Measuring the holes displacement (in X, Y and 45°) used to calibrate the FEM model.



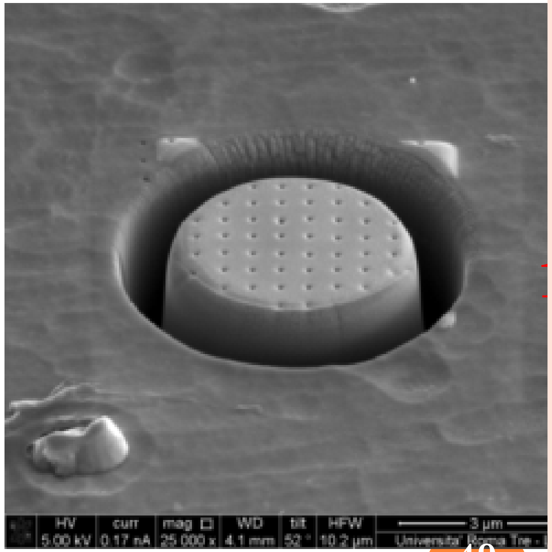
Before ring cutting — After ring cutting

In this way is possible to measure all in-plane relaxation strain components.

RESULTS – ONE STEP MILLING

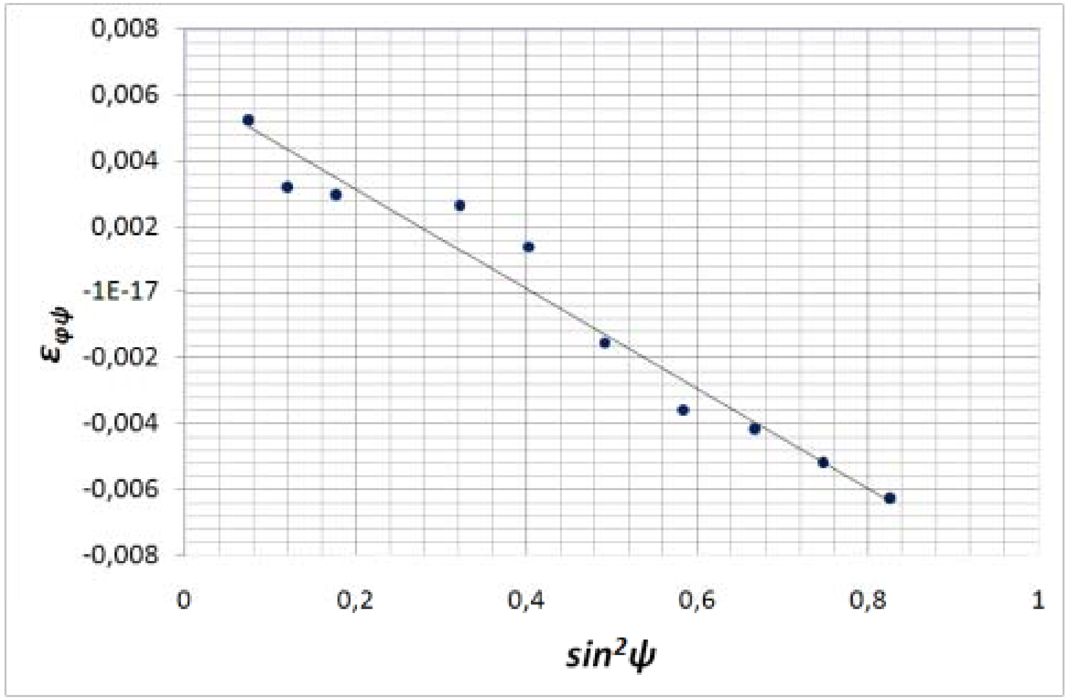
	Strain at maximum depth [um]	Calculated stress (FEM) [Pa]	Calculated stress (FEM) **Corrected with slope [Pa]**
Test-1	0.009	-6.00E+09	-5.96E+09
Test-2	0.0082	-5.47E+09	-5.35E+09
Test-3	0.009	-6.00E+09	-5.87E+09
Test-4	0.0097	-6.47E+09	-6.33E+09
Test-5	0.0103	-6.87E+09	-6.72E+09

- Analysis of the actual geometry of the pillar;
- The actual slope of the pillar is reproduced in the FEM model for stress-strain calibration



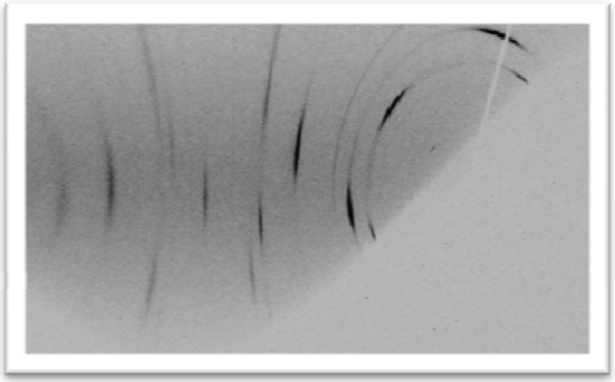
Calculated average stress: **-6.04 ± 0,51 GPa**

METHOD VALIDATION VS XRD-SIN$^2\psi$



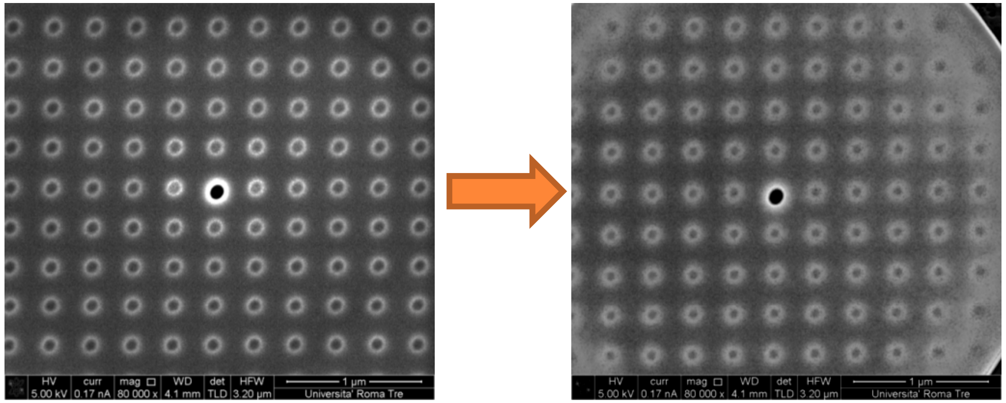
$$\varepsilon_{\phi\psi} = \frac{1+\nu}{E}\sigma_{\phi}\sin^2\psi - \frac{\nu}{E}(\sigma_{11}+\sigma_{22})$$

σ_{φ} = - 5.840 GPa

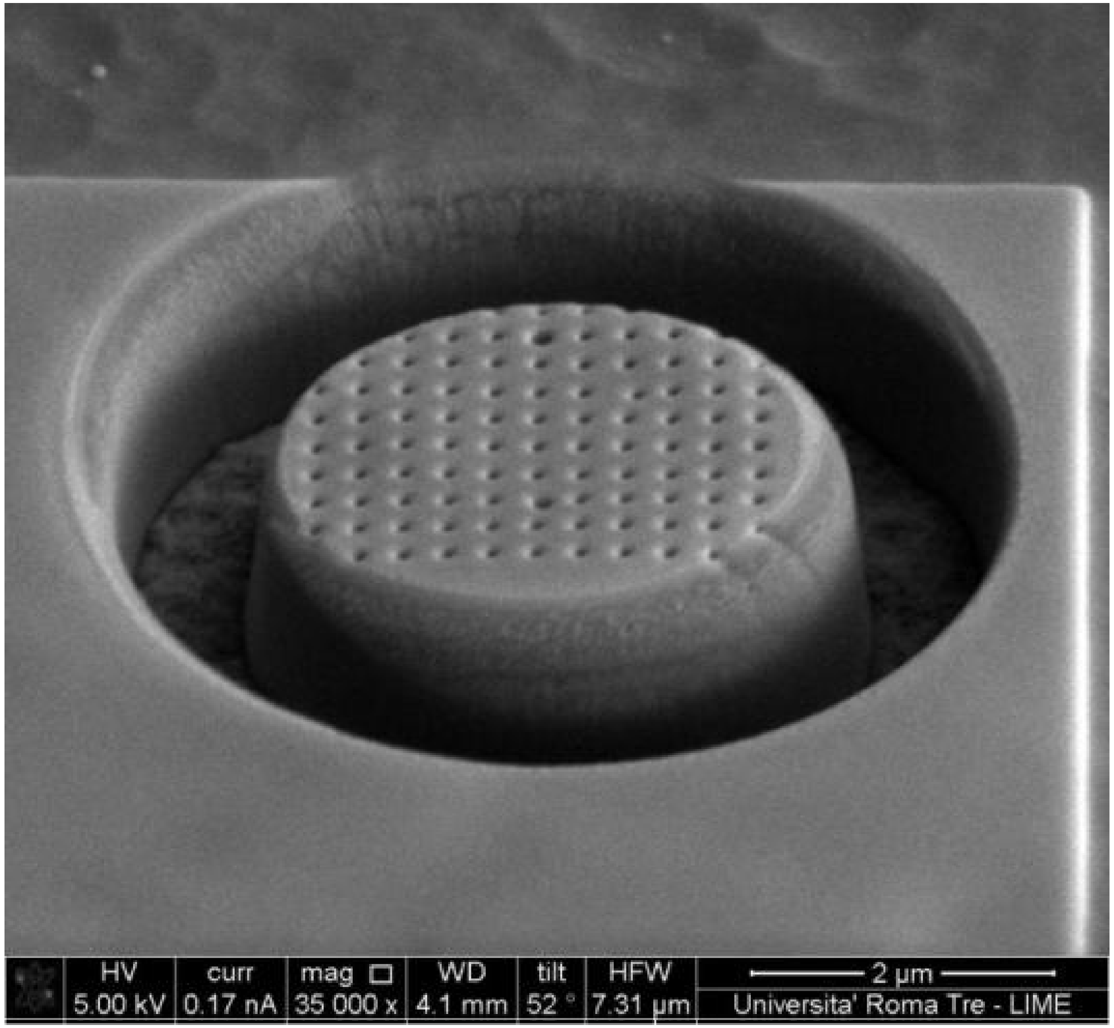


- Data from XrD measurement not easily readable due to a strong texturing of the TiN coating;
- Nevertheless, <u>obtained values are comparable with FIB obtained values</u>

PROCEDURE DETAILS

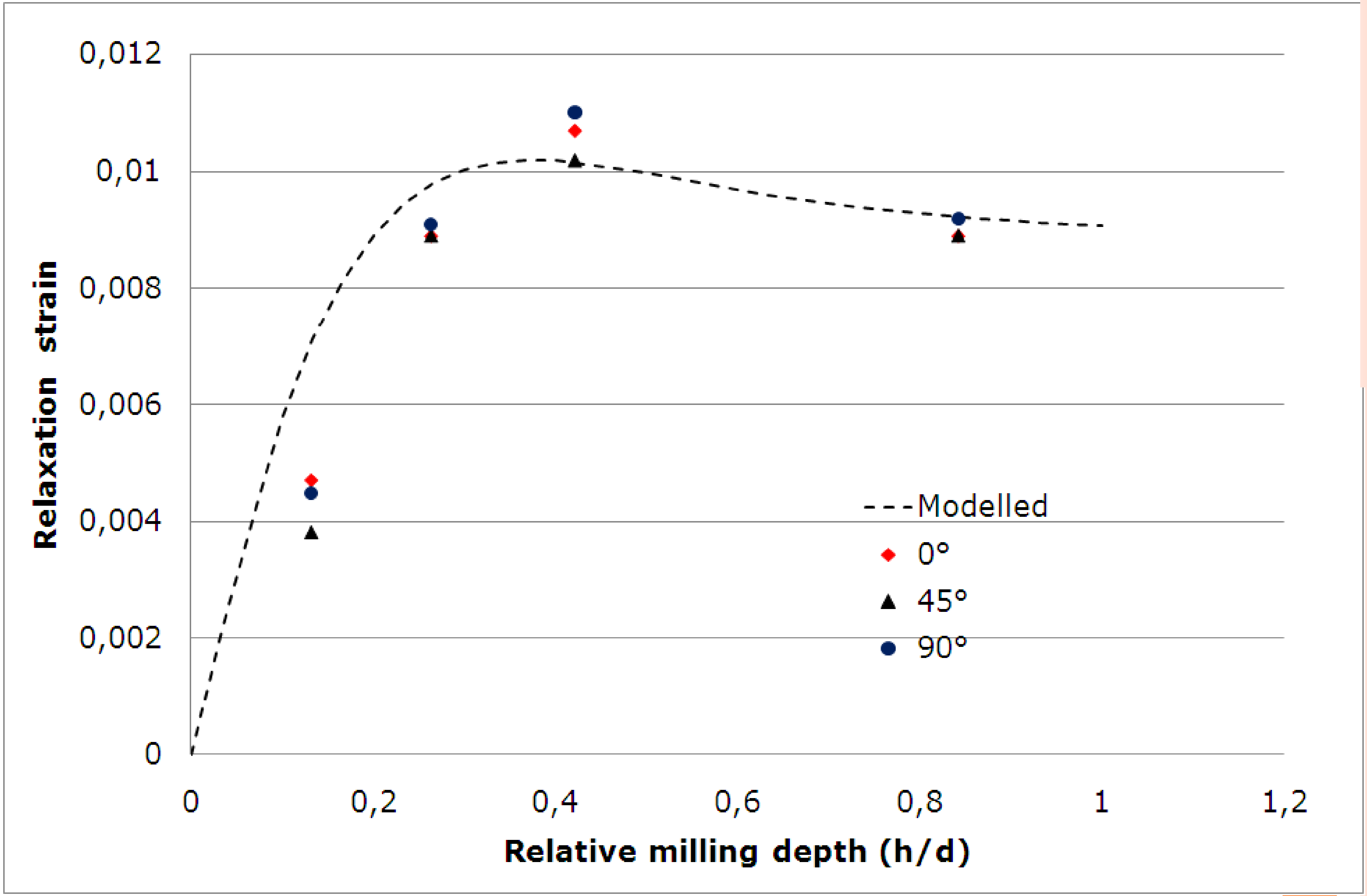


Z=0 vs each step



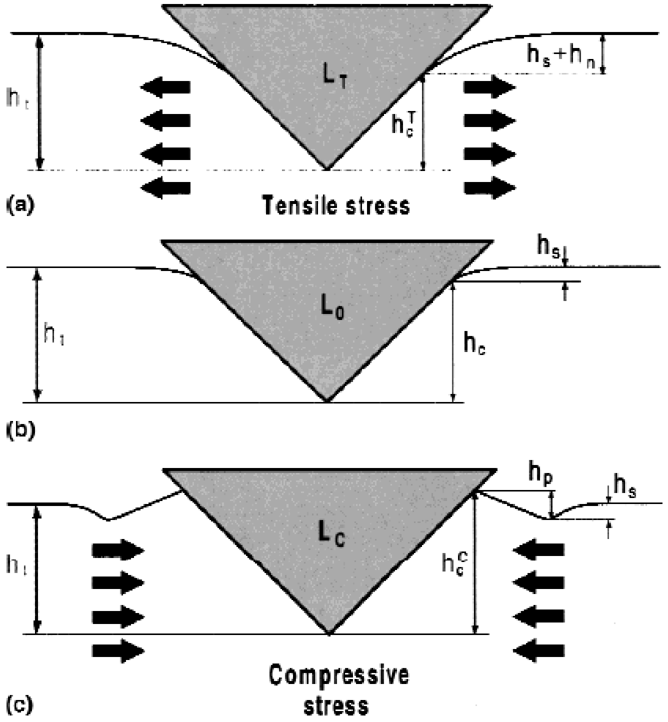
- Incremental Milling;
- Steps of 200 nm
- The pillar size ***d*** is equal to the coating thickness
- The maximum milling depth is equal to the coating thickness (3.8 µm)

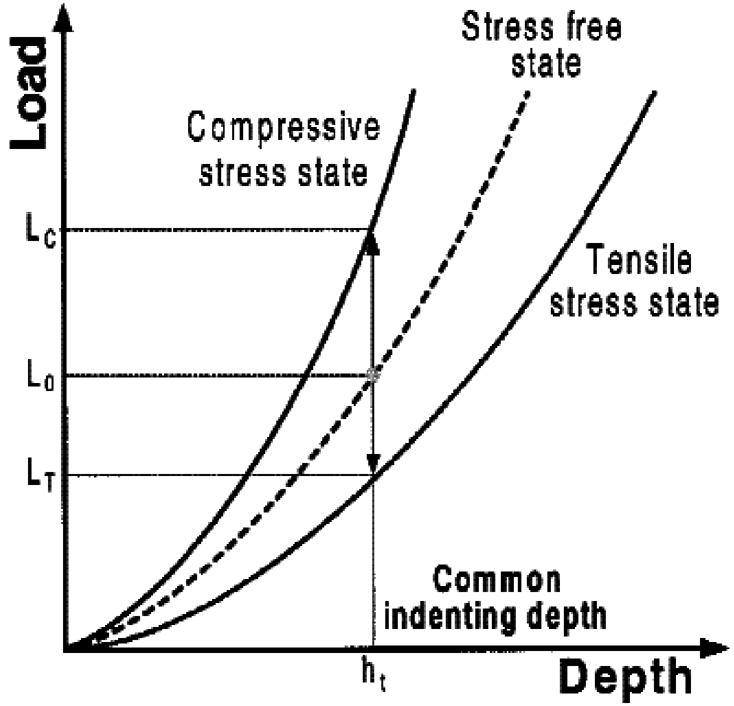
EXPERIMENTAL DATA



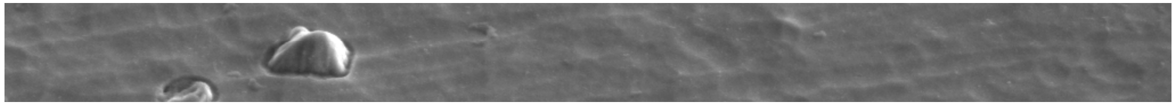
SECOND METHOD, USING NANOINDENTATION:

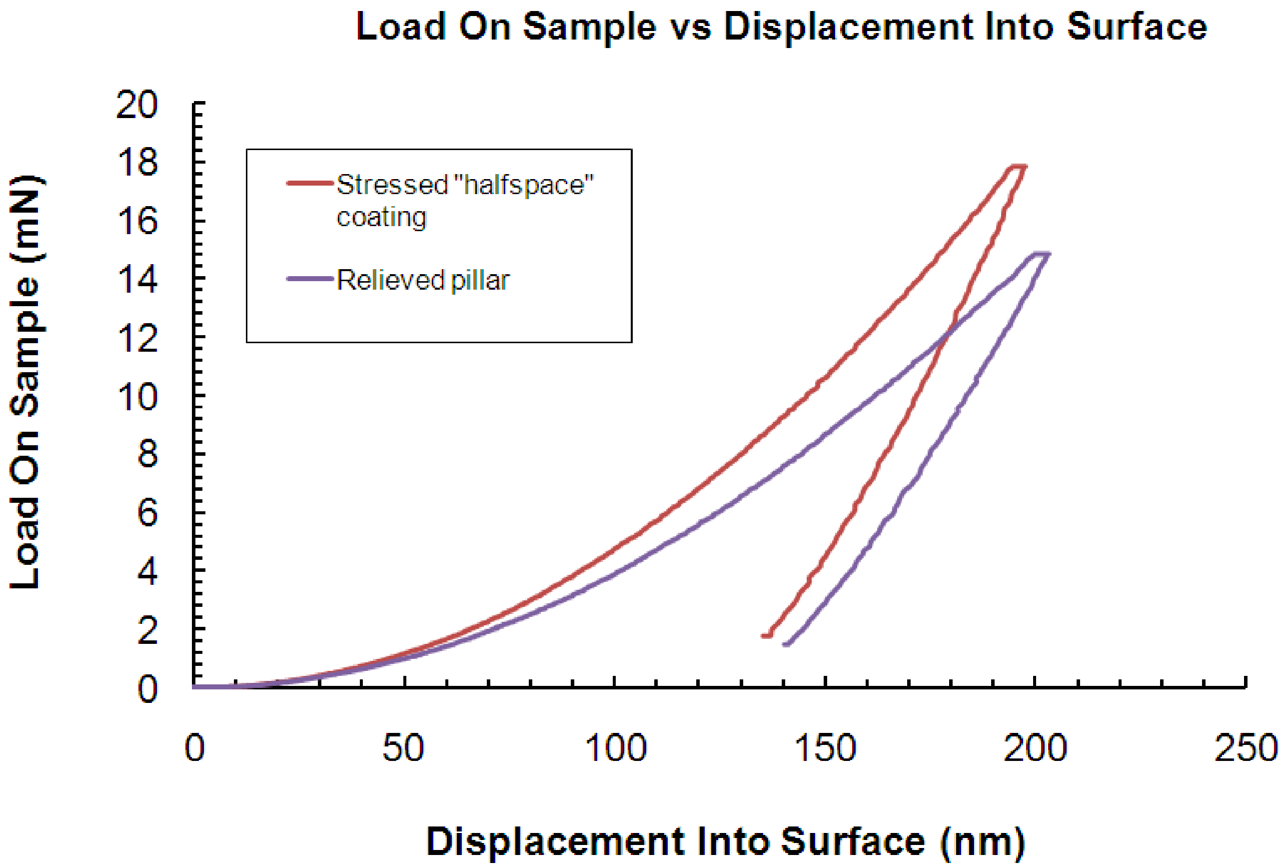
- A difference in the shape of the load-depth curve is therefore directly correlated to the presence of a biaxial residual stress state, due to changes in the actual contact area during indentation.



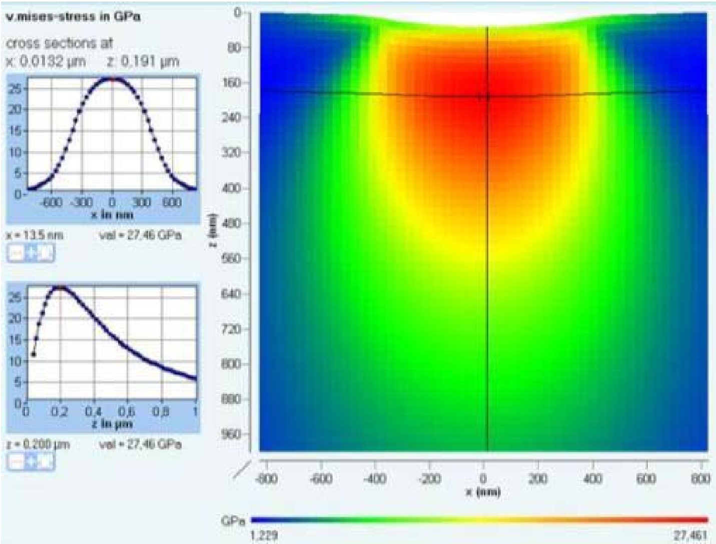


SECOND METHOD, USING NANOINDENTATION:

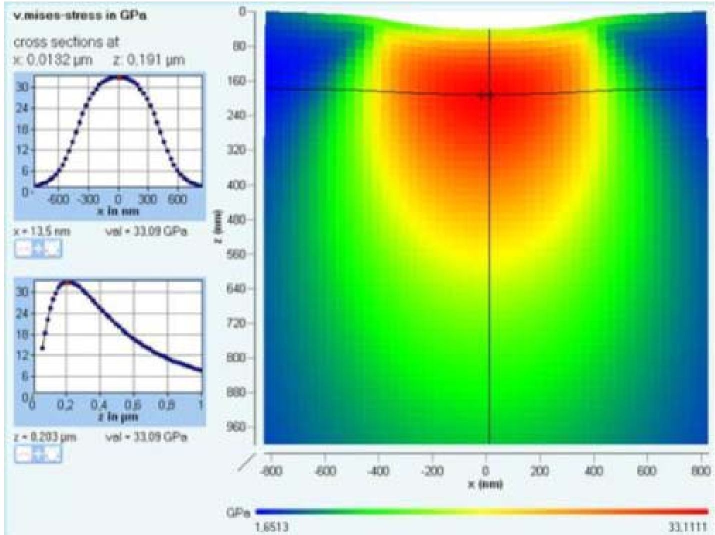




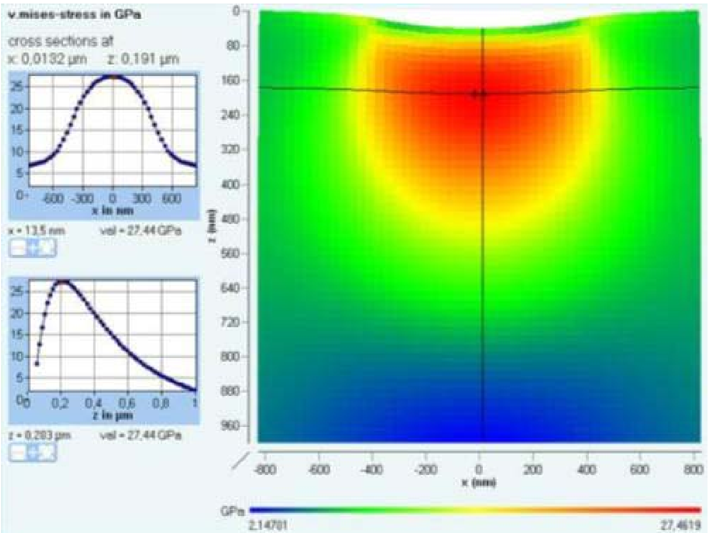
RESULTS – STRESS CALCULATIONS



a) Pillar – stress free – as measured



b) Halfspace stressed coating – as measured



c) Modelled: Halfspace coating + RS

- **Evaluation the contact stress field in the moment of unloading for both stressed surface and stress relieved pillar.**
- **In this way, a residual stress stat of – 5,653 Gpa was evaluated by comparison of the two set of load-depth data.**

CONCLUSIONS

- Research activities at LIME are focused on the development and application of high resolution, multi-technique, multi-scale procedures for the mechanical/micro-structural characterisation of surfaces.
- In case of non homogeneous materials and coatings, the use of nano-indentation techniques, even at very low indentation depths, can be useful for a quick detection of important micro-structural aspects
- By the **combination** of micro- and nano-hardness testing and SEM-TEM-FIB-AFM microscopy techniques, a comprehensive characterisation of nanostructured coatings and complex structures can be achieved.

Possible contribution to Condensed Matter Nuclear Science, some ideas:

- Residual stress Measurements on Pd foils or tubes:
  - Young's Modulus (E): 118-124 Gpa
  - Poisson ratio (nu): 0.385-0.395
  - Yield Stress (YS): 50-200 MPa (Pd bulk)

100 MPa residual stresses (0,5 YS), would led to <u>0,05% relative relaxation</u> (epsi = sigma*(1-nu)/E)

Possible contribution to Condensed Matter Nuclear Science, some ideas:

- Surface and local mechanical properties (even inter-grain):
  - density gradients
  - real and apparent elastic modulus
  - Embrittlement phenomena

Possible contribution to Condensed Matter Nuclear Science, some ideas:

- Site specific investigation on surface and subsurface:
  - micro/nano-structural changes (micro-cavities formation concerns)
  - Elemental analyses via FIB TEM of the very surface and interfaces at grain boundaries (gradients)
  - Electrodes decoration or patterning for a systematic study of roughness influence to micro-structural changes during the experiment
  - High aspect ratio patterning (i.e. pillar forest) to investigate surface vs. volume and fluido-dynamic effects during the experiment
  - More to your imagination…!

THANK YOU FOR YOUR KIND ATTENTION

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