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Tip-enhanced Raman Spectroscopy for industrial applications

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Nanotechnology Engineering - academic year 2015/2016

Target

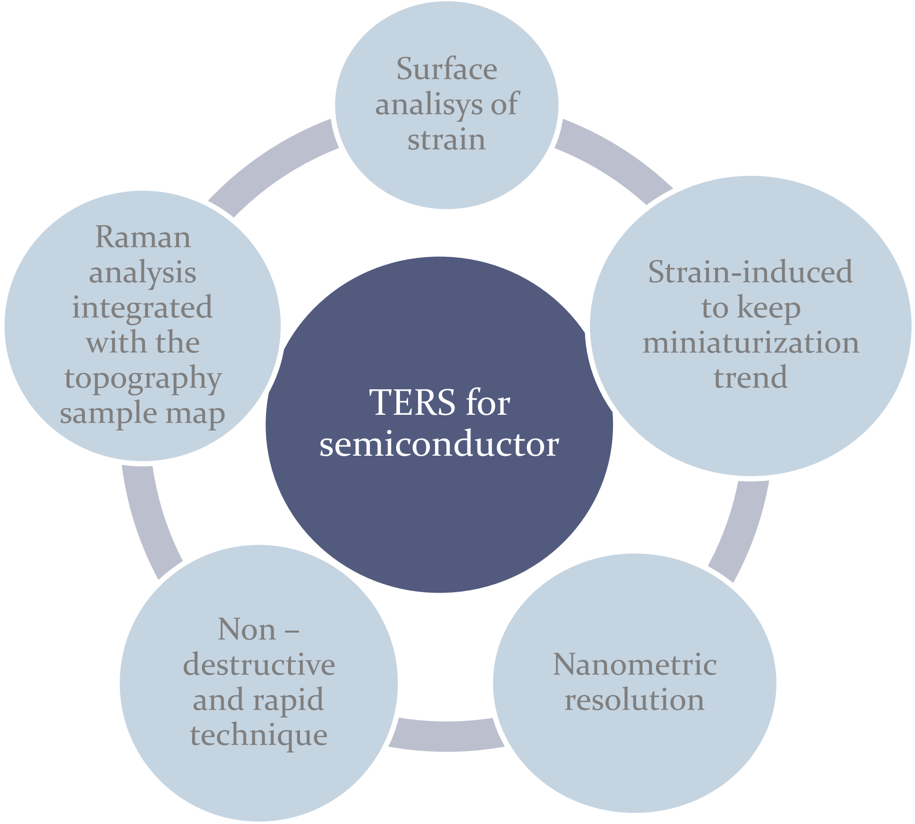
- Grasp a qualitative evaluation of the silicon mechanical stress and strain in electronic nanostructures of production quality devices through the TERS technique

Summary

- Introduction and reference to the theory of Raman effect and Atomic Force Microscope
- The TERS technique
- Analysis configuration and parameters
- Measurement results
- Conclusions and further developments

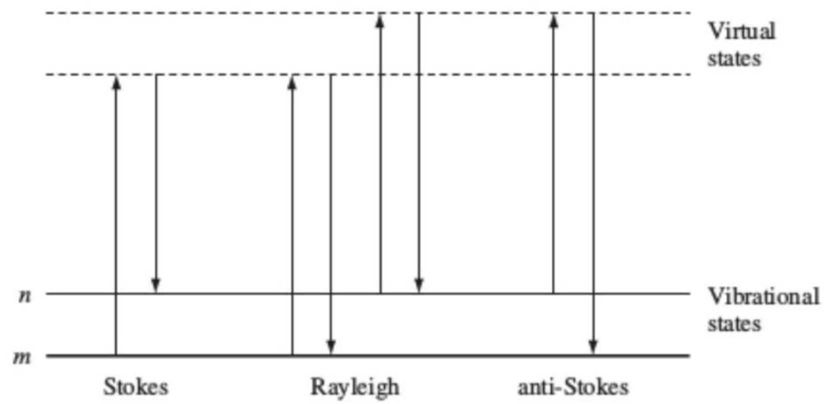
Introduction

- Tip-enhanced Raman spectroscopy (TERS): enhancement of the local field from a point on the surface sample
- It allows to achieve more information than from the conventional techniques with better spatial resolution .



Raman spectroscopy

- The Raman effect describes a kind of interaction between the light and the matter.
- *Elastic* (Rayleigh) and *anelastic* scattering (Raman); the latter occurs only for 1 on 10^6-10^8 photons.
- Through Raman spectroscopy we can estimate the strain of the sample in non-destructive way.
- Raman spectrum: information about strain, crystallinity and quantity of the sample.



E.Smith, G.Dent, *Modern Raman Spectroscopy – A practical approach,* John Wiley & Sons, Ltd (2005)

$$\mathbf{P} = \boldsymbol{\alpha}\mathbf{E} = \boldsymbol{\alpha}E_0\cos(2\pi\upsilon_0 t) = \alpha_0 E_0\cos(2\pi\upsilon_0 t) + \left(\frac{\delta\alpha}{\delta q}\right)_0 q E_0 \cos(2\pi\upsilon_0 t) =$$

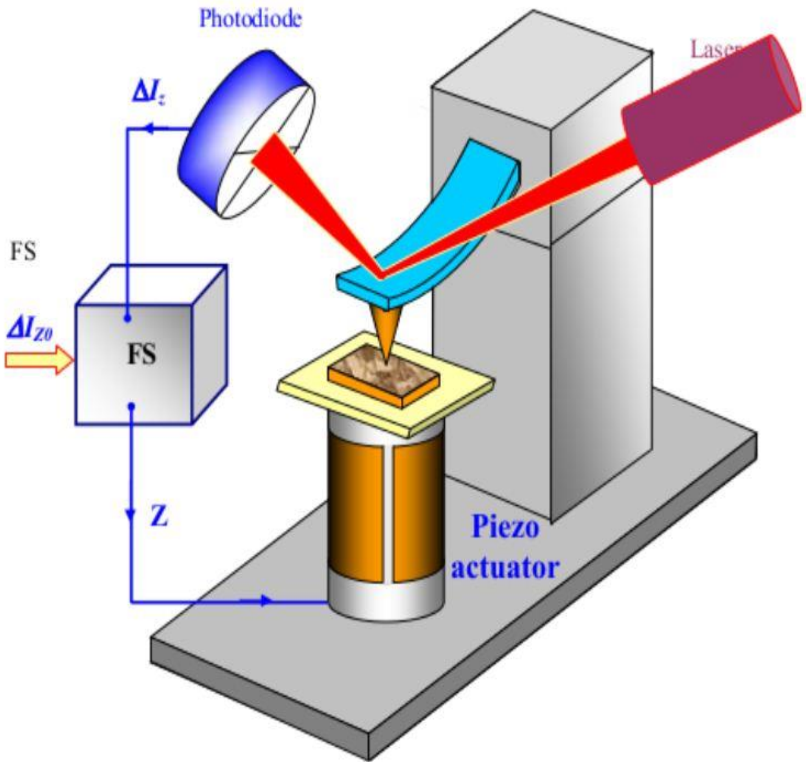
$$= \underbrace{\alpha_0 E_0\cos(2\pi\upsilon_0 t)}_{\text{Rayleigh scattering}} + \underbrace{\frac{1}{2}\left(\frac{\delta\alpha}{\delta q}\right)_0 q_0 E_0 \left[\underbrace{\cos 2\pi(\upsilon_0+\upsilon_m)t}_{\text{Anti-Stokes lines}} + \underbrace{\cos 2\pi(\upsilon_0-\upsilon_m)t}_{\text{Stokes lines}}\right]}_{\text{Raman scattering}}$$

$q = q_0\cos(2\pi\upsilon_m t)$

is the nucleous displacement

Atomic Force Microscopy

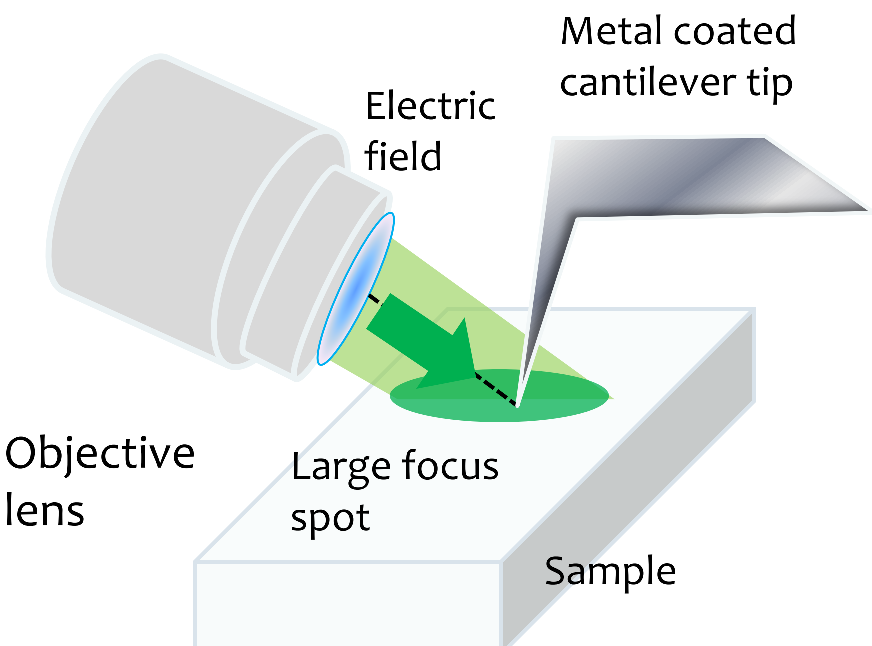
- A kind of scanning probe technique is the Atomic Force Microscope (AFM).
- The tip has a nanometric radius and the sample surface is moved by piezoactuators, with a light-deflection feedback.
- The tip is on a cantilever and it's affected by the interaction with the sample surface.

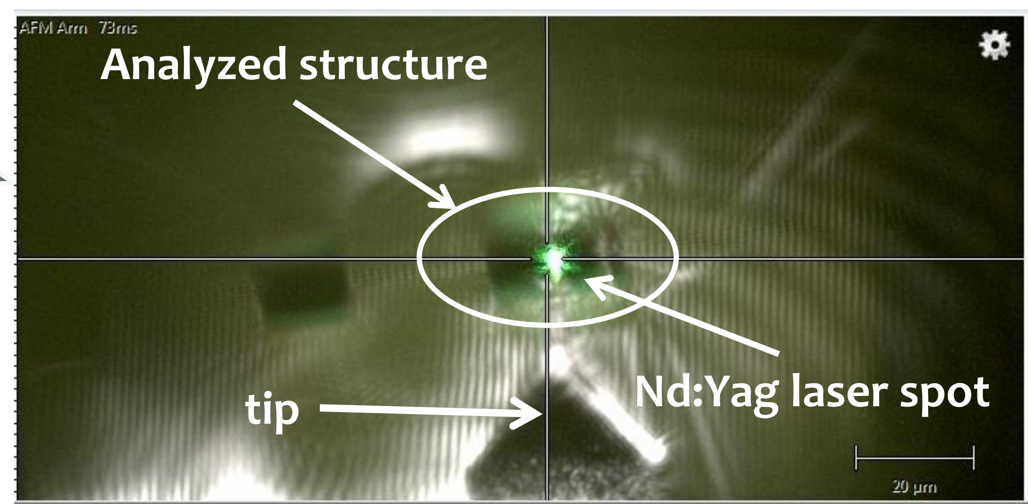


V.L.Mironov, *Fundamentals of scanning probe microscopy*, Nizhniy Novgorod (2004)

What is TERS?

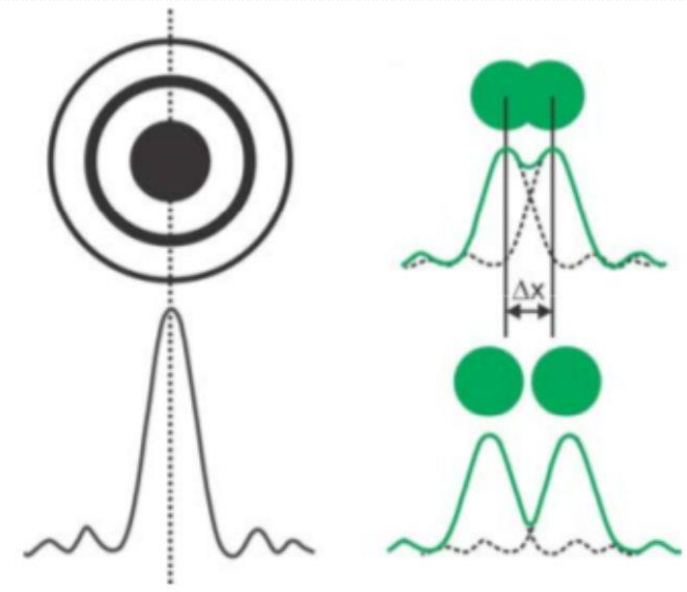
- TERS is an apertureless Scanning Near-field Optic Microscopy technique.
- Two instruments are needed to make TERS: a Raman spectrometer and a Scanning Probe Microscope (SPM).
- A light source excites local surface plasmon resonance on the tip of a scanning probe microscope, to raise the signal from the sample next to the tip apex, called near or local field.





The TERS technique

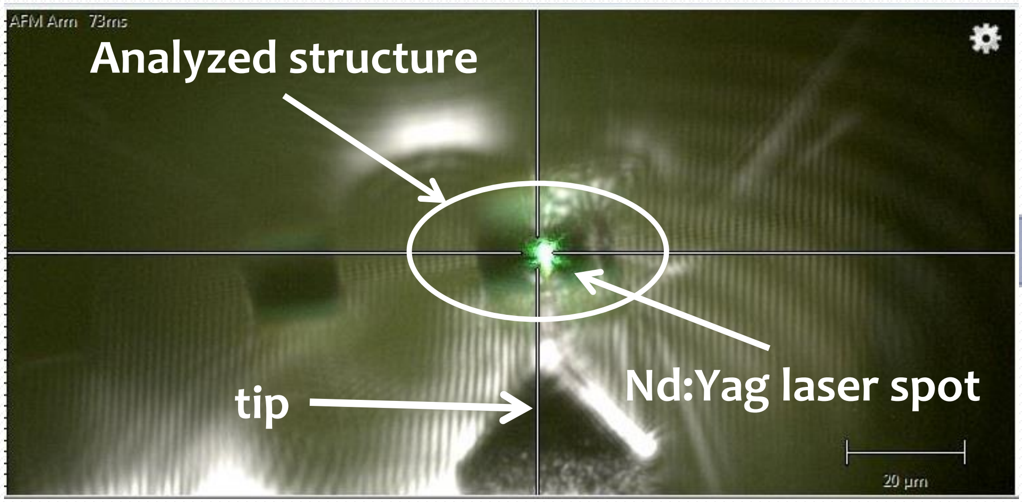
- With this technique it is possible to overcome the light diffraction limit.
- Local Surface Plasmon Resonance (LSPR) are created over the tip apex.
- Resolution under the light spot, similar to the tip radius.
- Proper angle of incidence, tip material and radius.
- Propagation constant of surface plasmon polariton:



$$k_{spp} = k_0 \sqrt{\frac{\varepsilon_{r1}\varepsilon_{rm}(\omega)}{\varepsilon_{r1} + \varepsilon_{rm}(\omega)}}$$

$$\Delta x = \frac{1.22\lambda}{2n\sin\alpha}$$

The TERS technique



Overlapping of the topographic sample map with further chemical and physical information

Tip of the SPM	Antenna for receveing electric field
	Antenna for propagating local field
	Modification of polarizability of the sample

Summary

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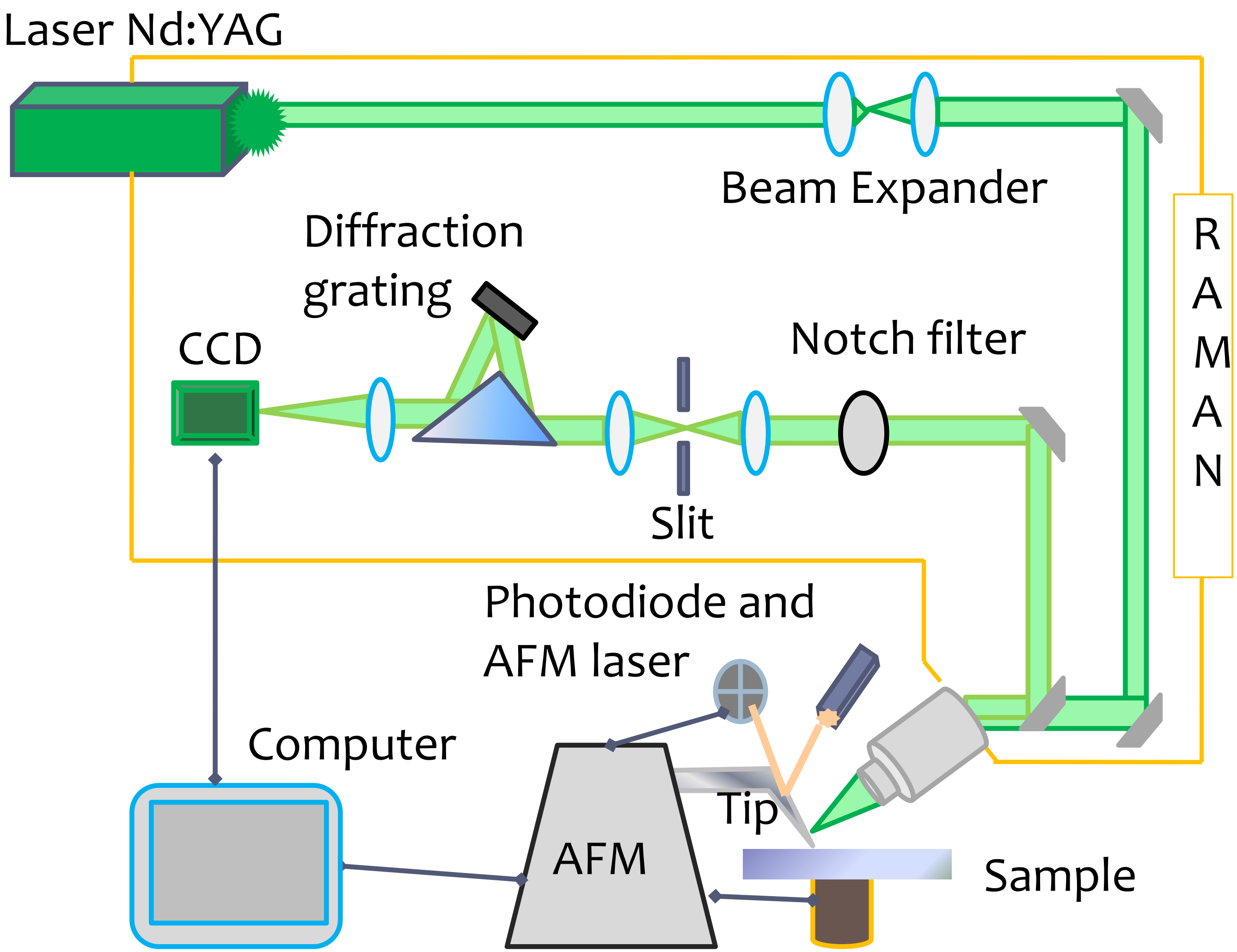
Configuration

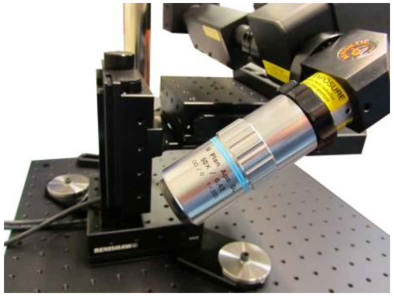


Laser: 532 nm

Angle of incidence: 60° (side-illumination)

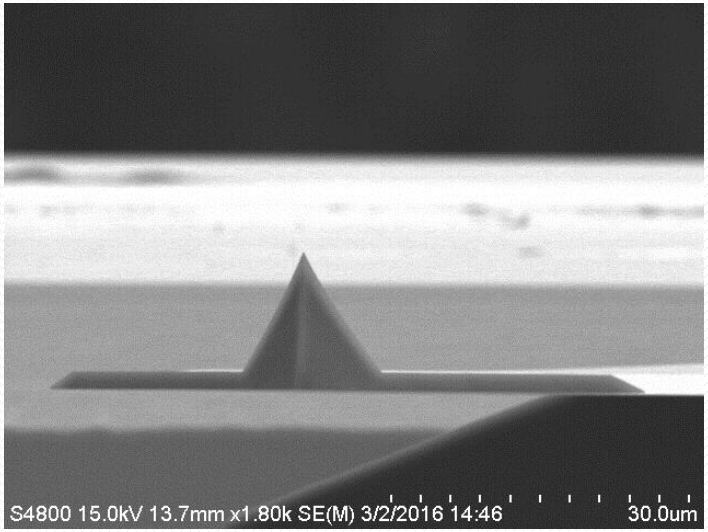
Lens: Mitsutoyo Long Working Distance 50x, N.A. 0,42

Detector: CCD, cooled by Peltier effect

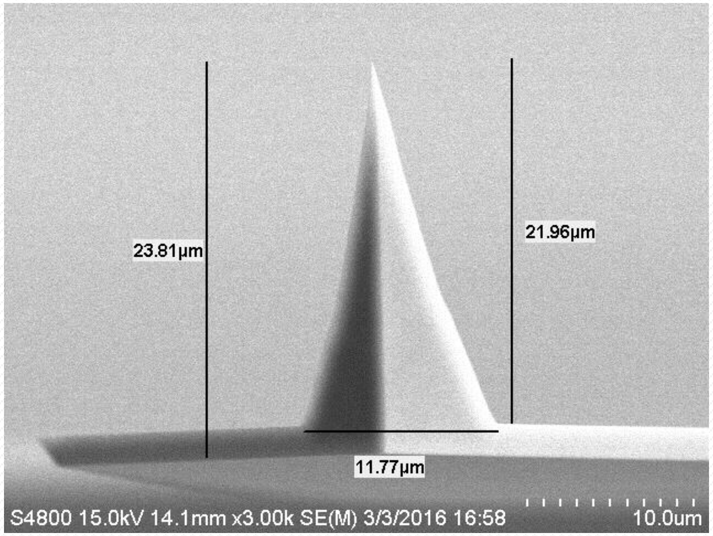


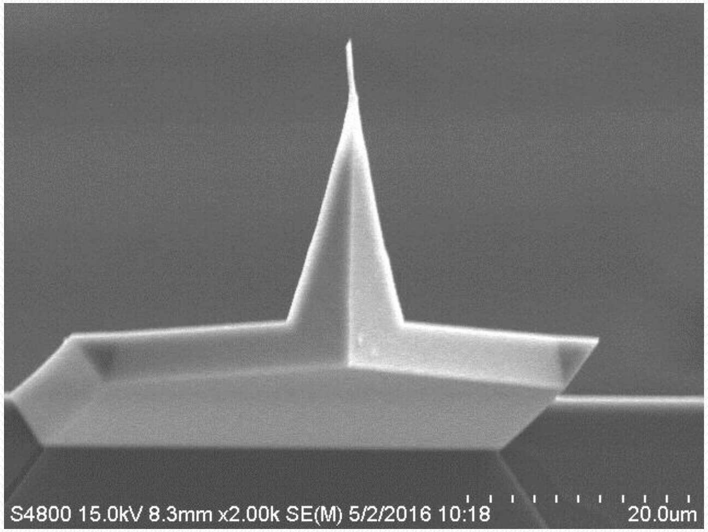
Tip models

"Arrow" type with Ag covering



"ATEC" type with Ag covering



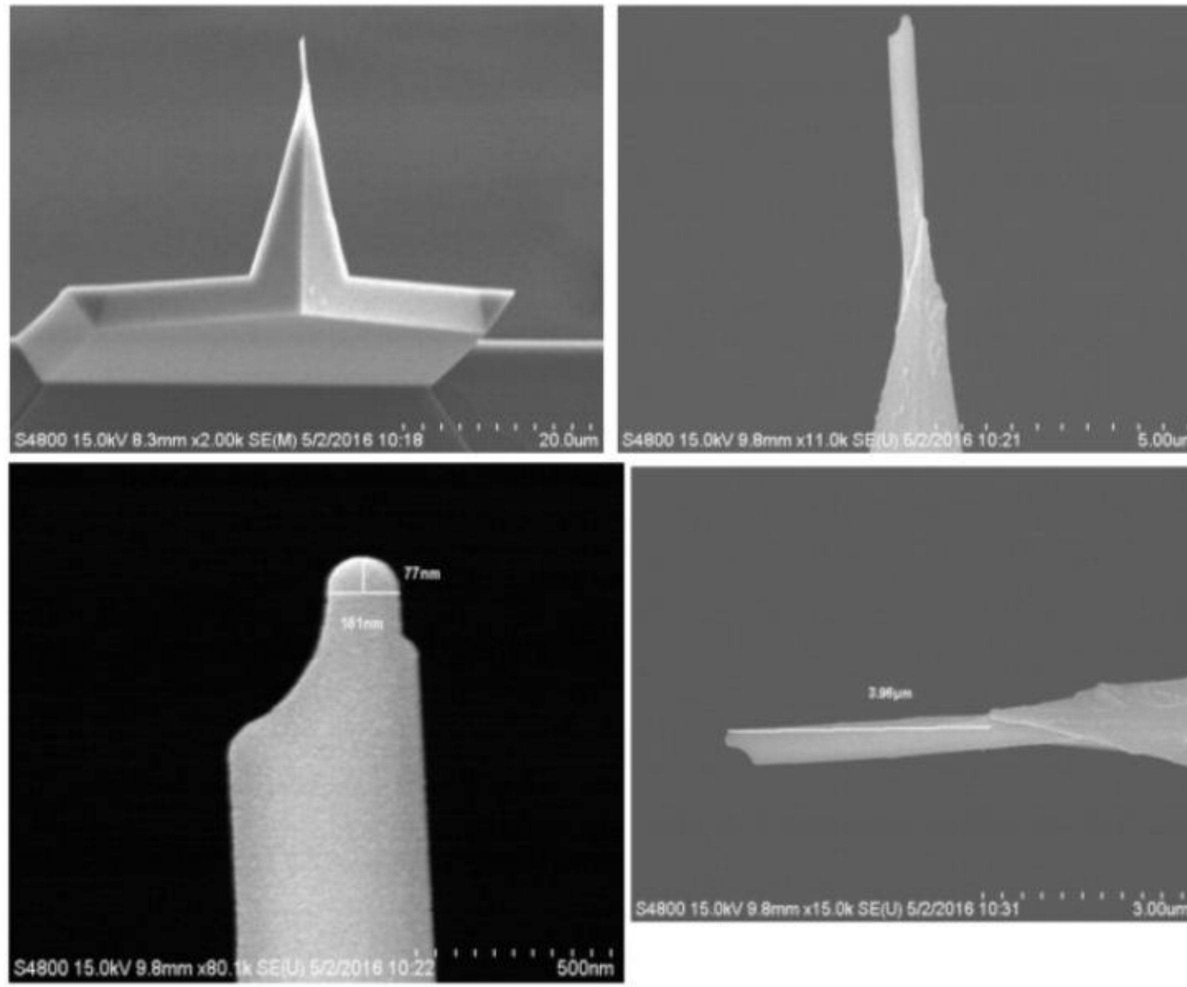


Nauganeedle type with Ag covering and nano-needle

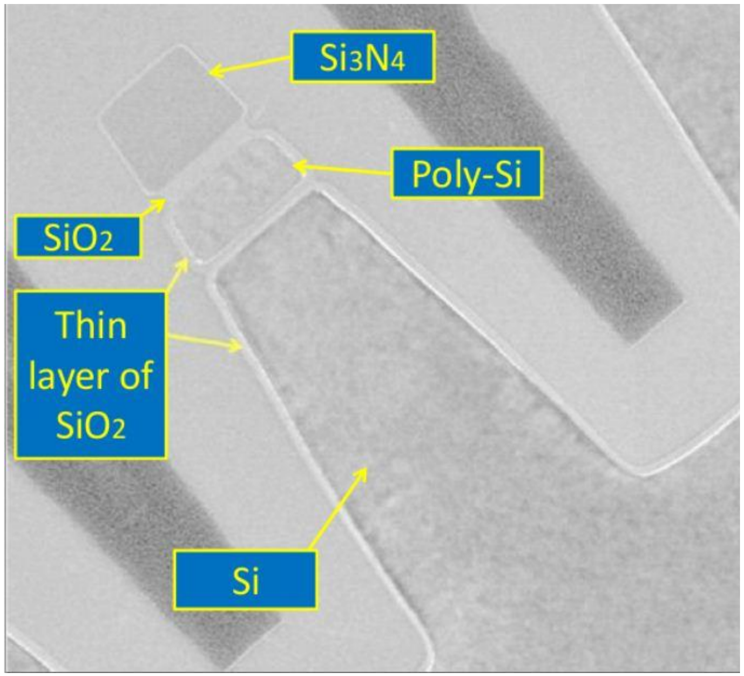
Analysis parameters

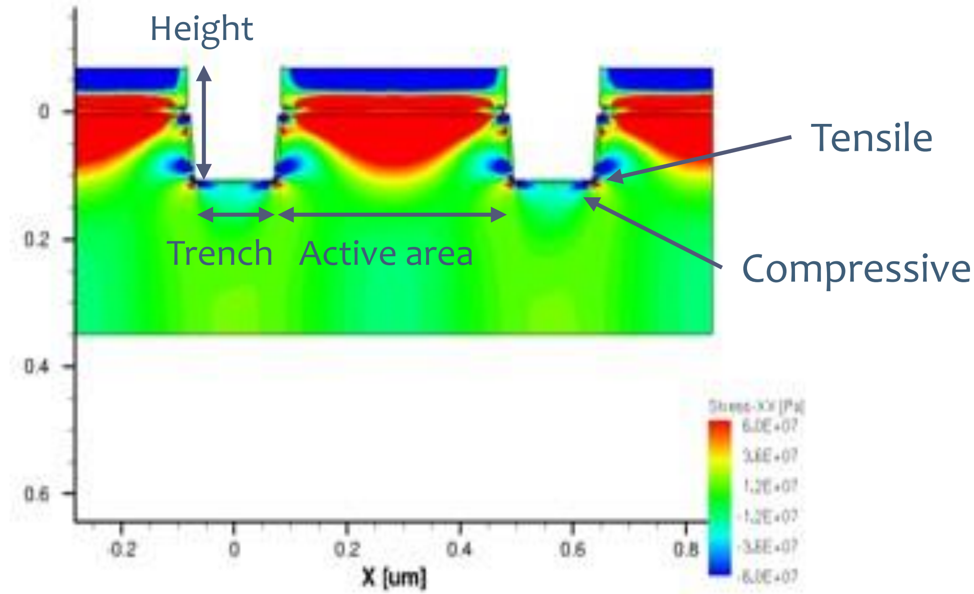
- Kind of tip: Nauganeedle AFM tip with a nano-needle of Ag_2Ga coated in Ag.
- Tip radius: 77 nm
- Nano-needle length:

  3,96 µm
- Laser power on tip: 0,1 mW (1%)
- Exposure time: 1 sec for 5 accumulations



The samples





Poly-silicon layer on silicon wafer → Silicon oxide pad → Silicon nitride pad → Photolitographic process with dry etch → Thin layer of silicon oxide via thermal process

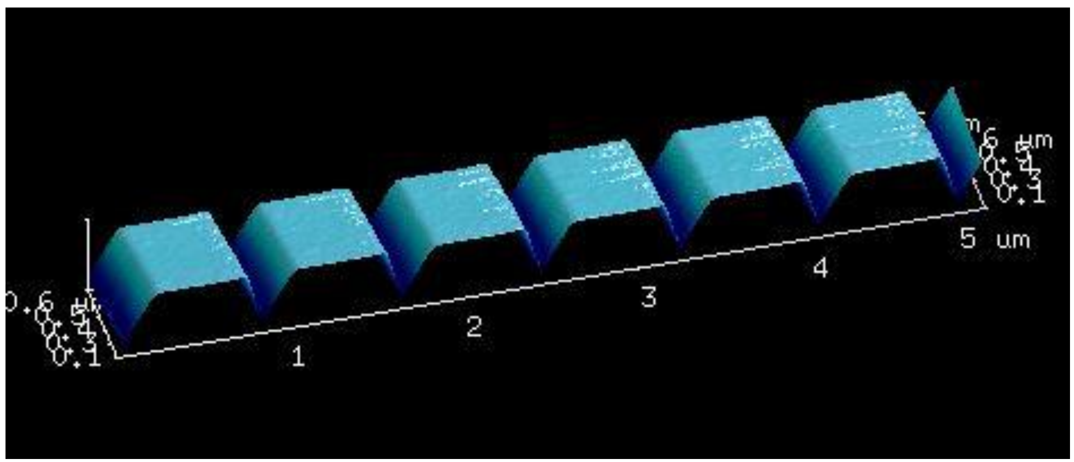
The covering oxide imposes a Si lattice deformation which causes mechanical stress

The samples

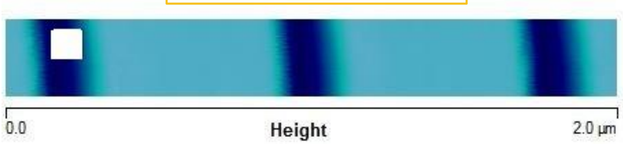
- Two structures on the device were analyzed:

	Structure A	Structure B
Active area (nm)	500	500
Trench (nm)	320	1280
Height (nm)	455	455

Structure A: 2D and 3D image scan

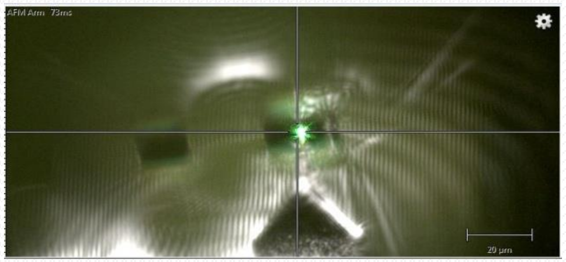


Point Alpha

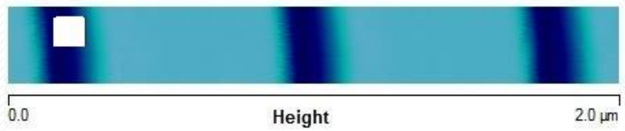


Point Gamma

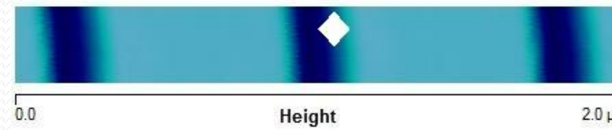
Results



Point Alpha



Point Gamma

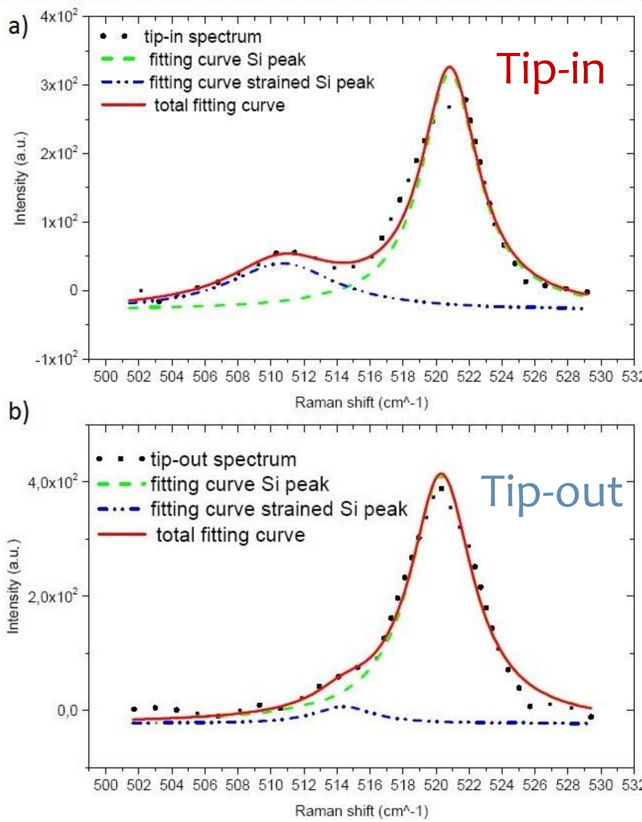


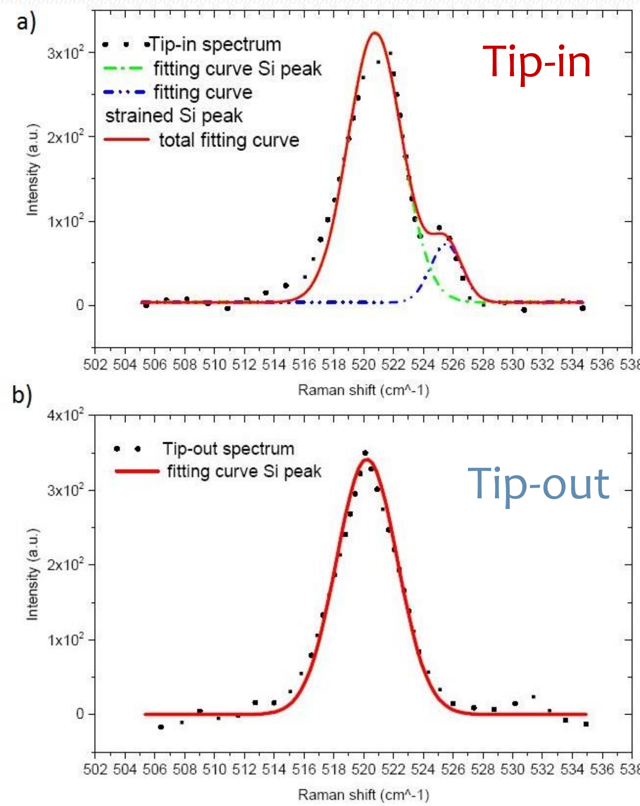
Tip-in spectrum (TERS spectrum)

- Tip in feedback
- Total field=Near field + Far field

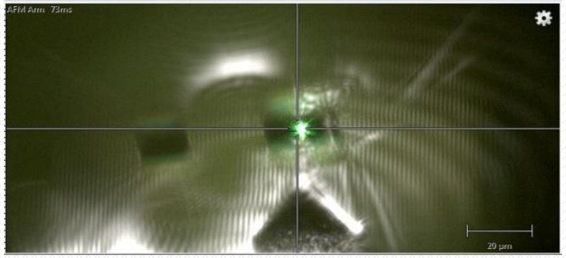
Tip-out spectrum (Raman spectrum)

- Tip is 600 nm above the surface
- Only Far field





Results



Strain of the silicon lattice with TERS:

Secondary peaks

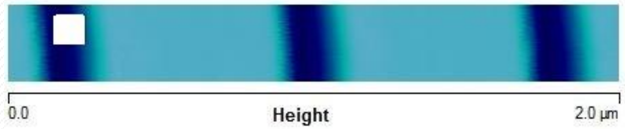
Compressive stress: strained-Si peak on the right of Si peak

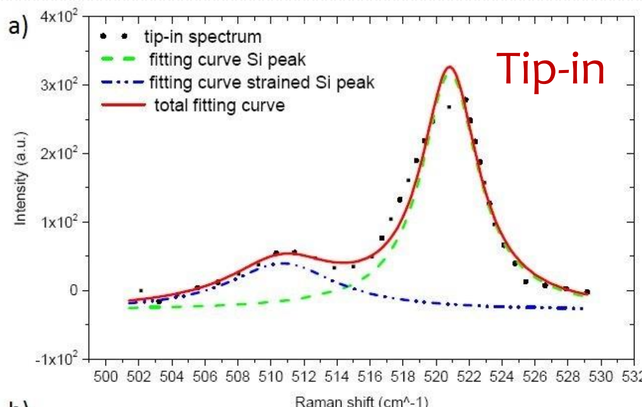
Tensile stress: strained-Si peak on the left of Si peak.

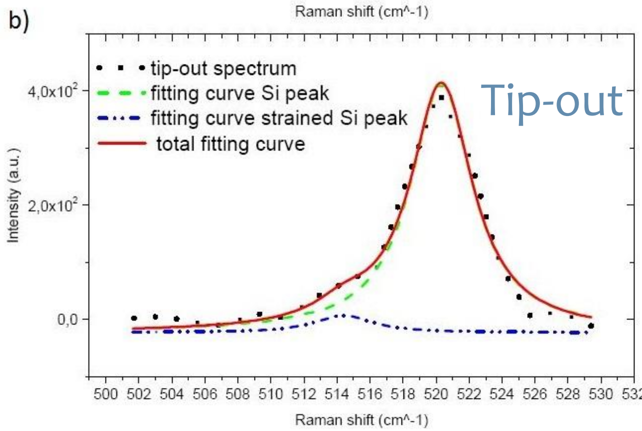
Si peak and strained-Si peaks

S.H.Olsen et al., *Nanoscale characterization for ultimate CMOS and beyond,* Mat. Science in Semicond.Proc., 11 p.271 (2008)

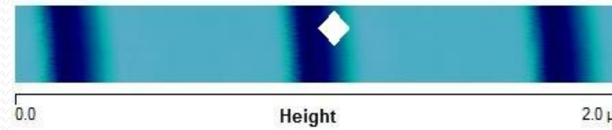
Point Alpha

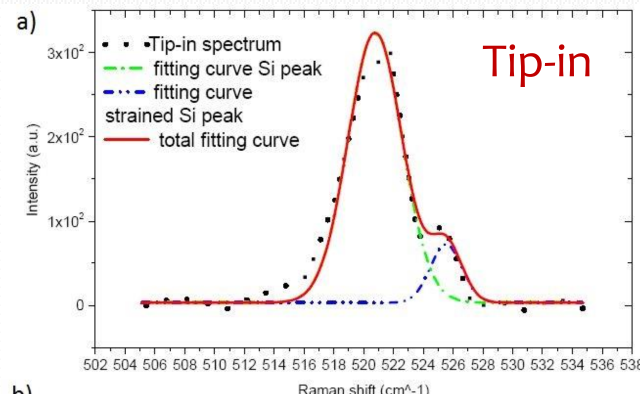


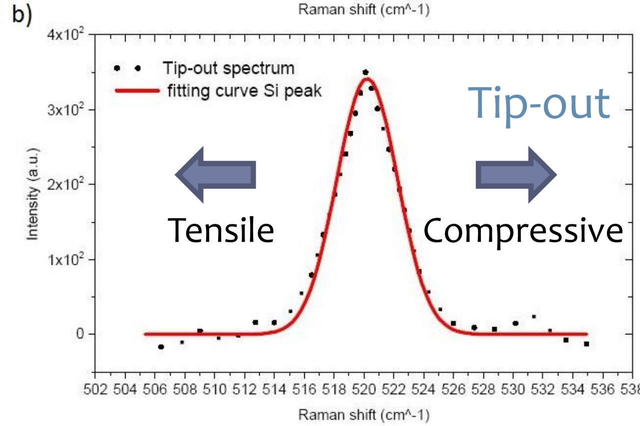




Point Gamma

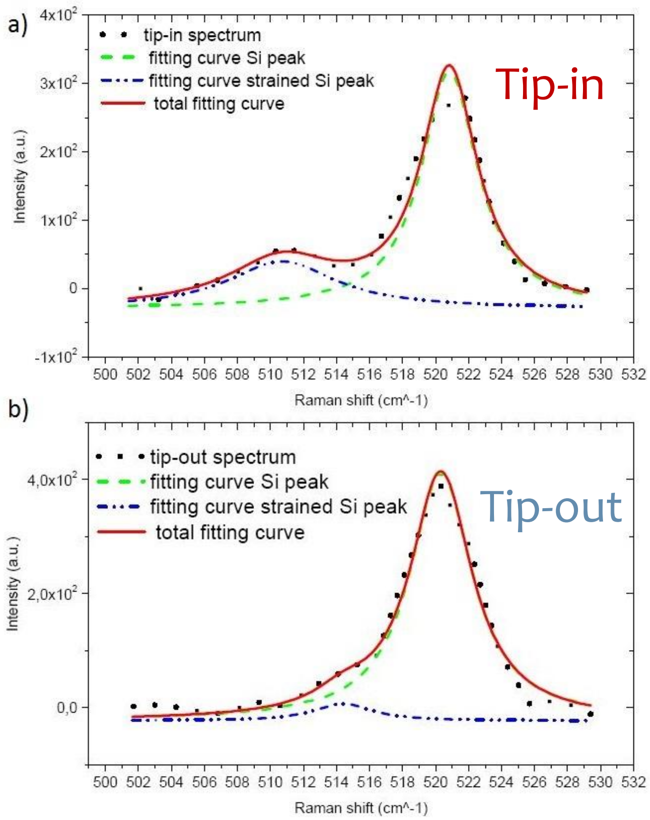






Results

The Contrast and Enhancement Factor are given by:



$$C = \frac{I_{nearfield}}{I_{farfield}} = \left(\frac{I_{totalfield}}{I_{farfield}} - 1 \right) = 1.3$$

$$EF = C \left(\frac{V_{far}}{V_{near}} \right) = 5.7 \times 10^3$$

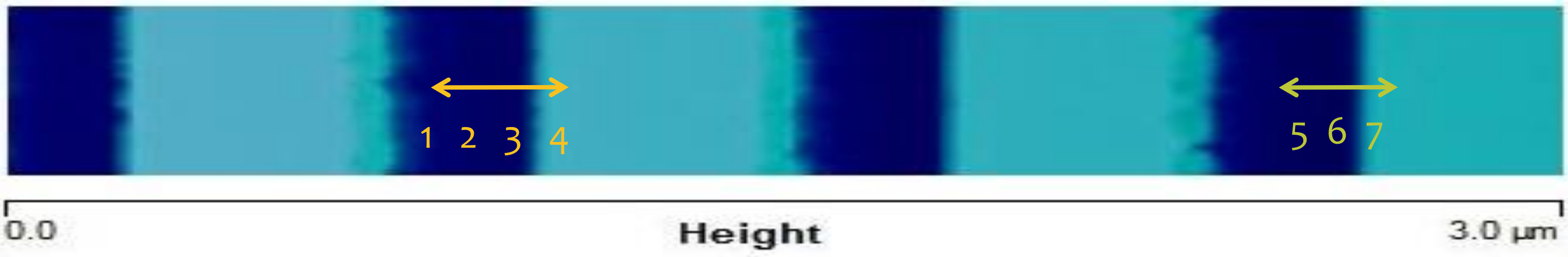
with V_{near} and V_{far} defined as:

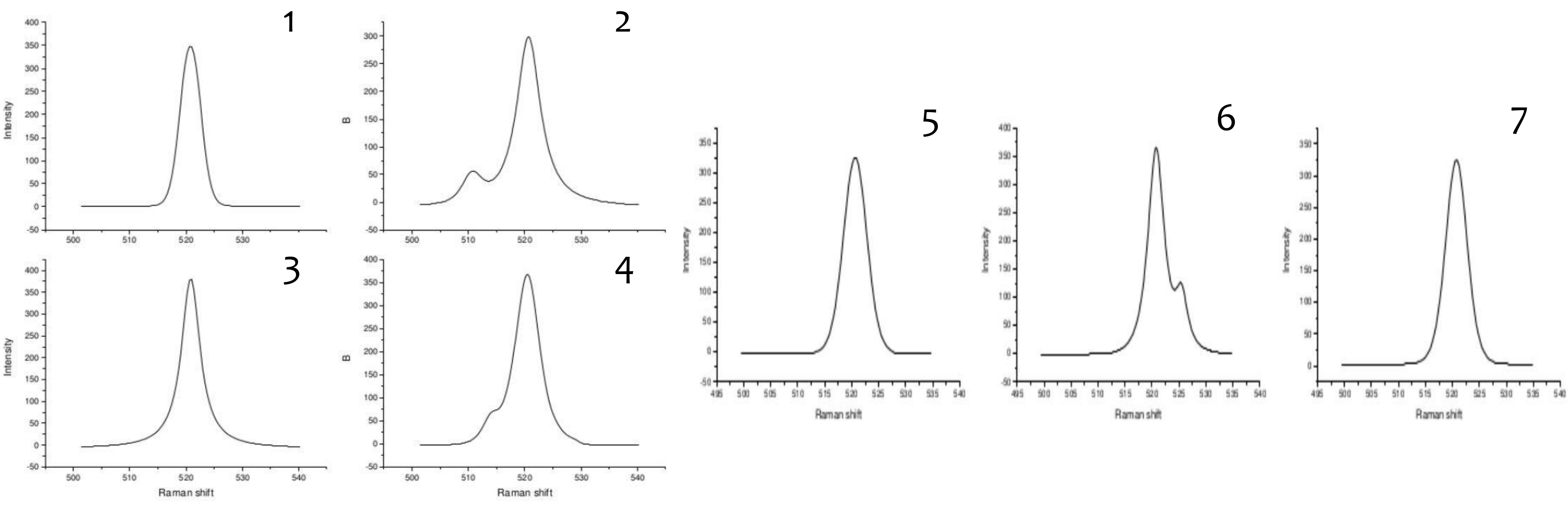
$$V_{far} = \pi \, r_{foc}^2 \, H_{LASERdepth}$$

$$V_{near} = \pi \, r_{tip}^2 \, H_{TERSdepth}$$

A. Tarun et al., *Tip-Enhanced Raman Spectroscopy for nanoscale strain characterization* , Anal.Bioanal. Chem., 394 p.1775 (2009)

Results



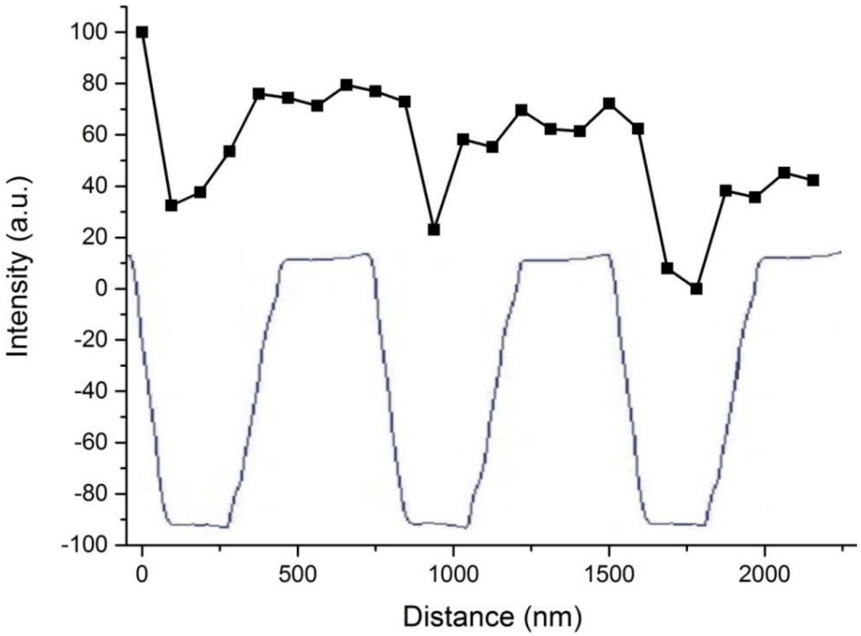


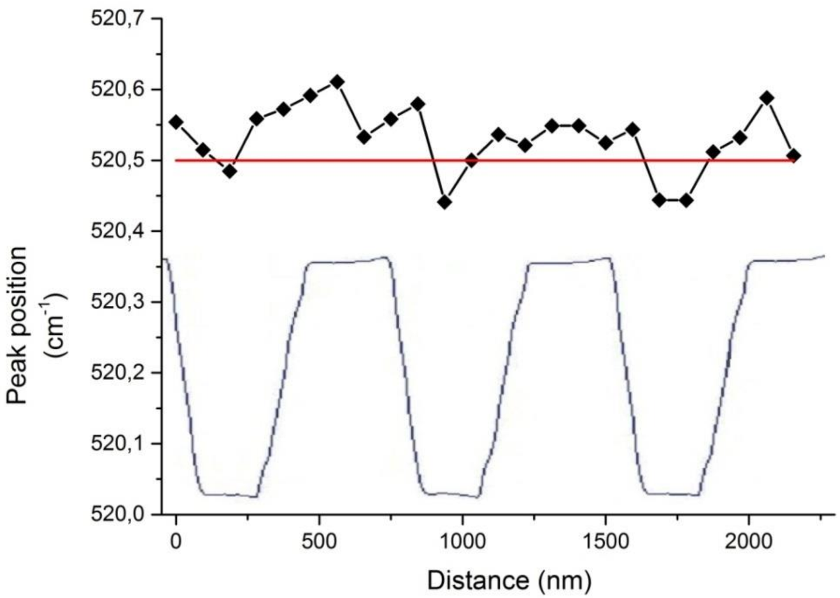
Measurements taken with 94 nm steps.

Results

Spatial resolution

- Measurements repeated on seven different lines on the sample
- 94 nm steps
- Maps of the Si bulk peak





Conclusions

- With TERS technique it is possible to analyze a real silicon device and take qualitative informations over process-inducted stress and strain.
- Preliminary study to develop the technique in an industrial contest for the investigation of stress and strain.
- To improve the results we suggest to study the best configuration for angle, polarization light and tip in order to maximize the Enhancement factor and Contrast.
- As soon as possible we submit the paper to Applied Physics Letters.

Thanks for your Attention!