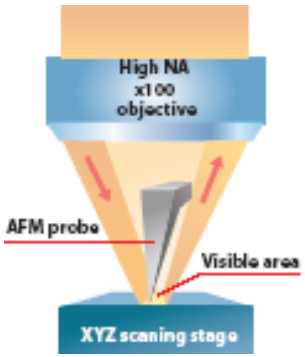
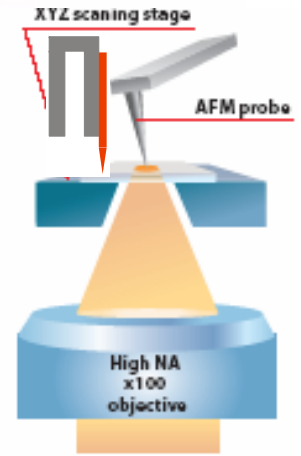
Combination of Scanning Probe Microscopy, SNOM and Confocal Raman microscopy





www.ntmdt.com

NT-MDT
Molecular Devices and Tools for NanoTechnology
Contact: Dr. Pavel Dorozhkin, dorozhkin@ntmdt.com

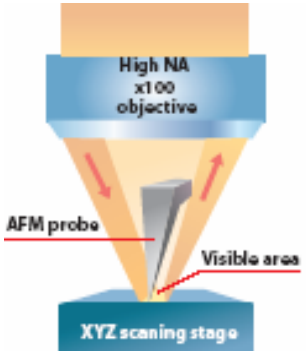
Combined Scanning Probe Microscopy and Micro/Nano Raman Studies of Modern Nanostructures

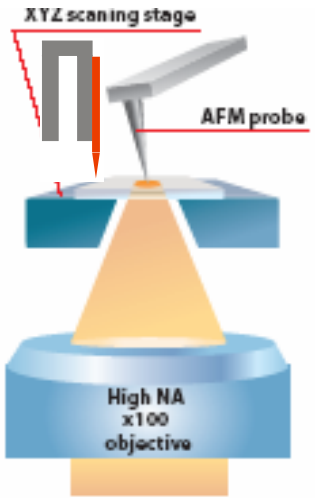
1. AFM – Raman – SNOM instrumentation

2. “Classical” AFM-Raman applications (nanowires, graphene, polymers etc.)

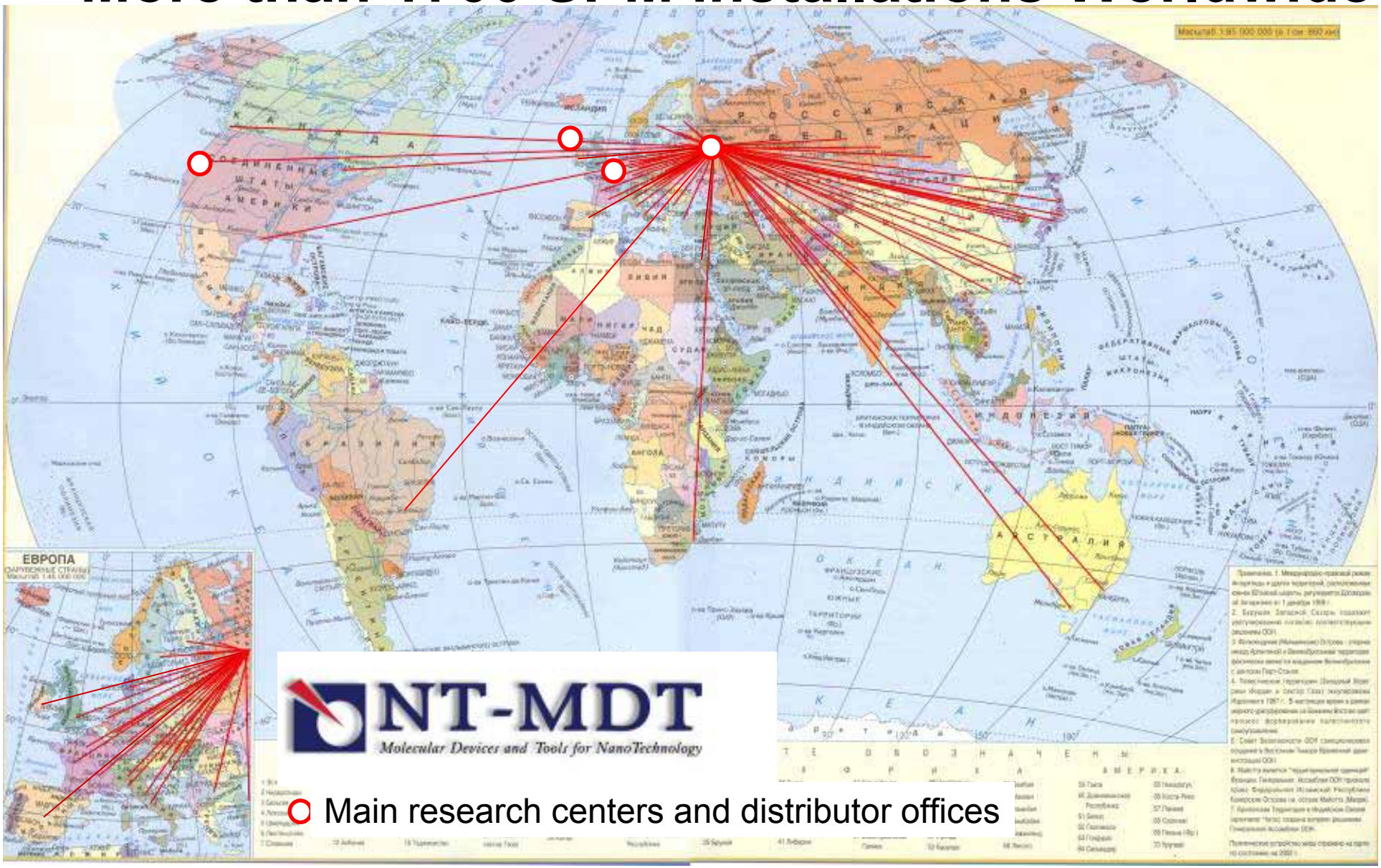
3. Tip Enhanced Raman Scattering

4. SNOM applications (plasmonics, lithography, bio)



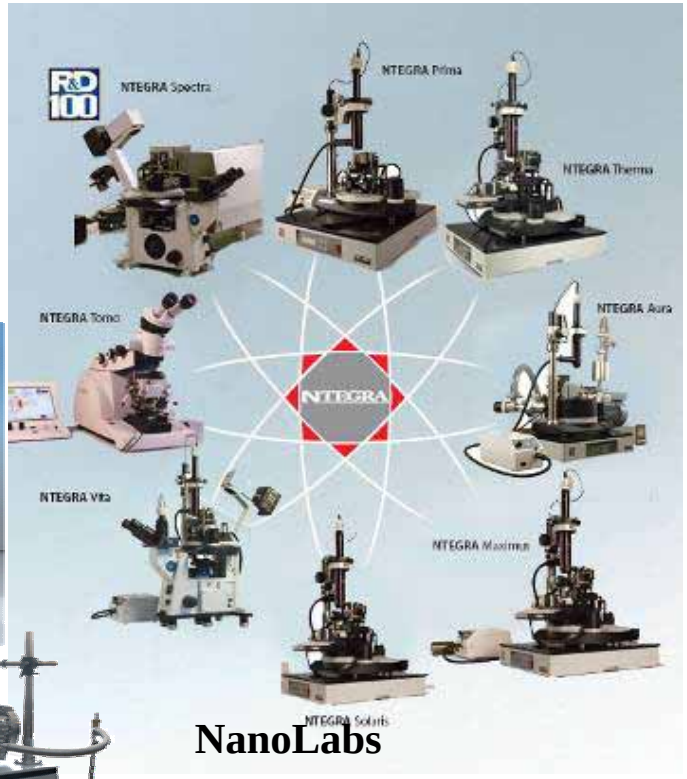


- **More than 18 years on the SPM market**
- **More than 1700 SPM installations Worldwide**



NT-MDT Product line

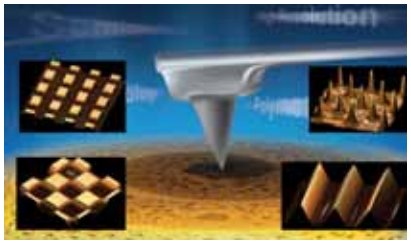

NANOFABs



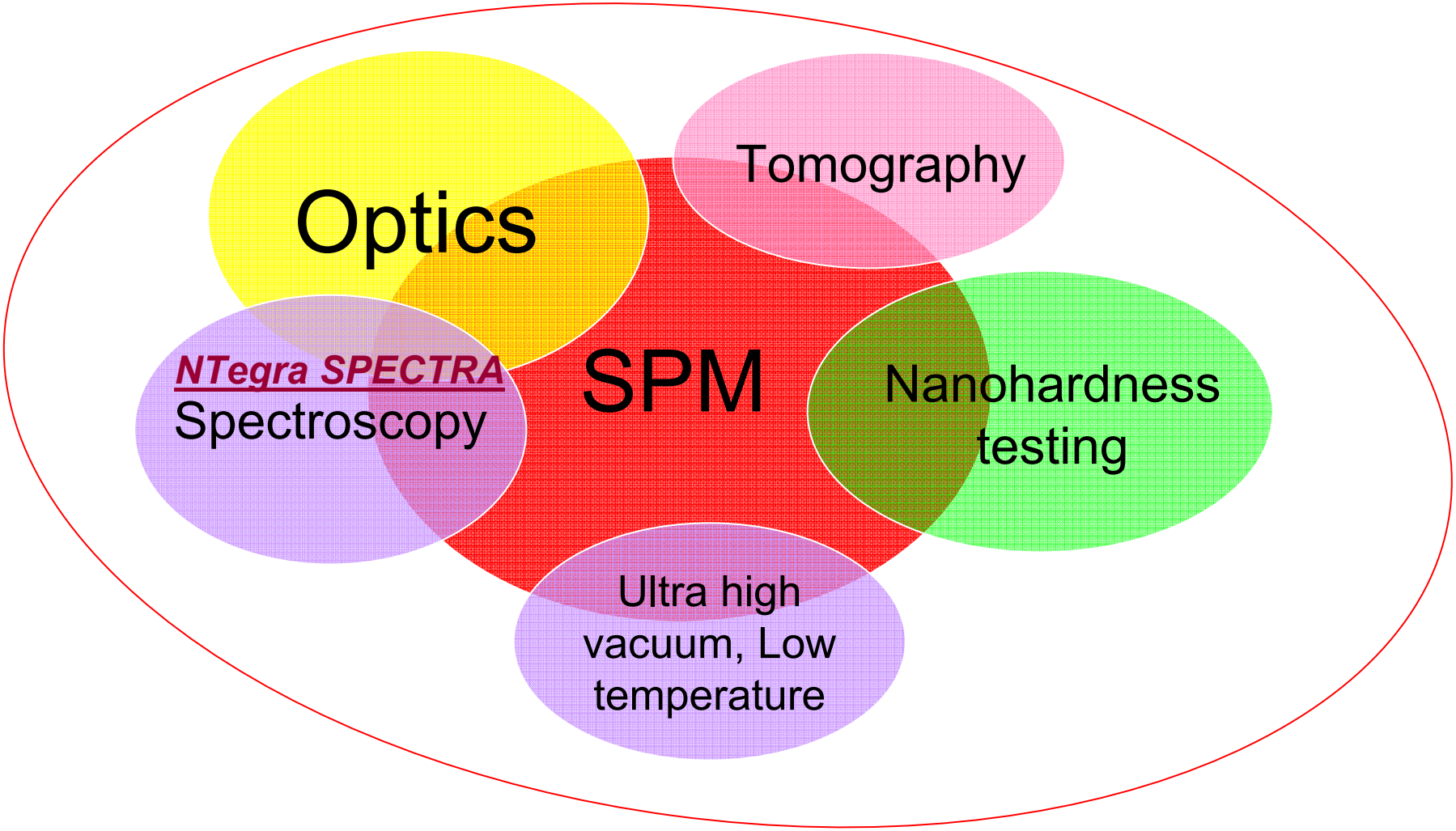
NanoLabs


Educations

Accesories



iNTEGRAting AFM “cutting edge” technology



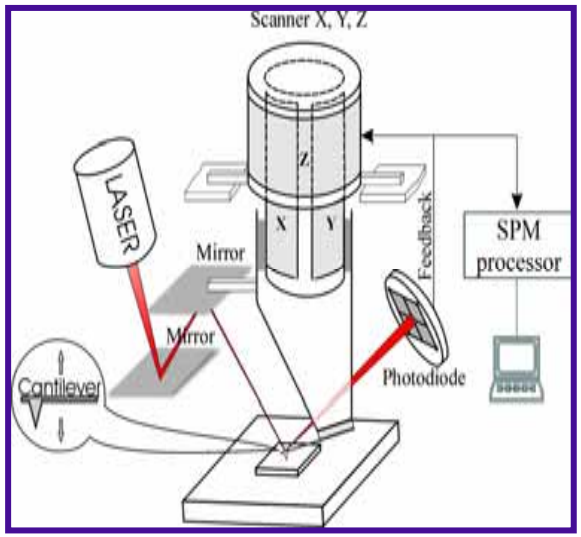
NT-MDT
Molecular Devices and Tools for NanoTechnology

SPM measuring modes supported by NT-MDT

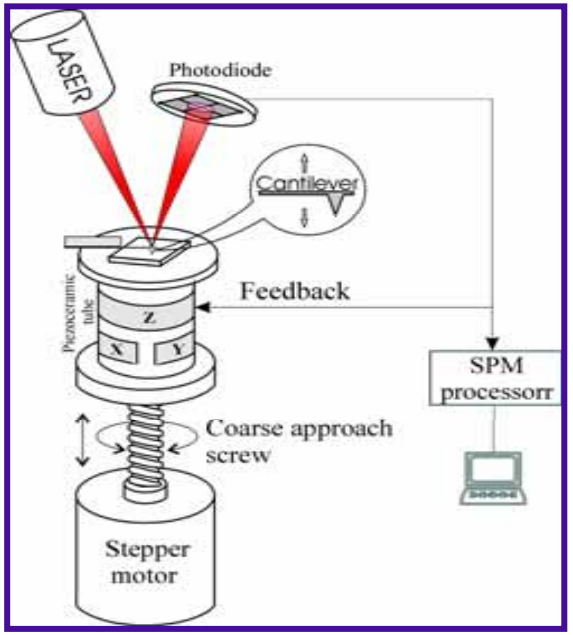
More than 40 possible different modes!!!

- **STM**
- **Contact AFM**
- **Lateral Force Microscopy**
- **ResonantMode -Semicontact**
- **Noncontact AFM mode**
- **Phase Imaging**
- **Force Modulation (viscoelastisity)**
- **Magnetic force Microcopy**
- **Electrostatic Force Microscopy**
- **Adhesion Force Imaging**
- **AFM Lithography-Force**
- **Spreading Resistance Imaging (SRI) in Currents 30fA-50nA**
- **AFM Nanolitogrphy (voltage and scratching)**
- **Scanning Capacitance Imaging (SCI) (dCdZ, dCdV)**
- **Scanning Kelvin probe microscopy (SKM)**
- **Force distance curves**
- **Force Volume**
- **Nanomanipulation**
- **Piezoresponce Mode**
- **Sample heating for in-siu melting**
- **I/V spectroscopy, I(Z) spectroscopy etc.**
- **AFAM**
- **Electrochemistry**
- **SNOM**

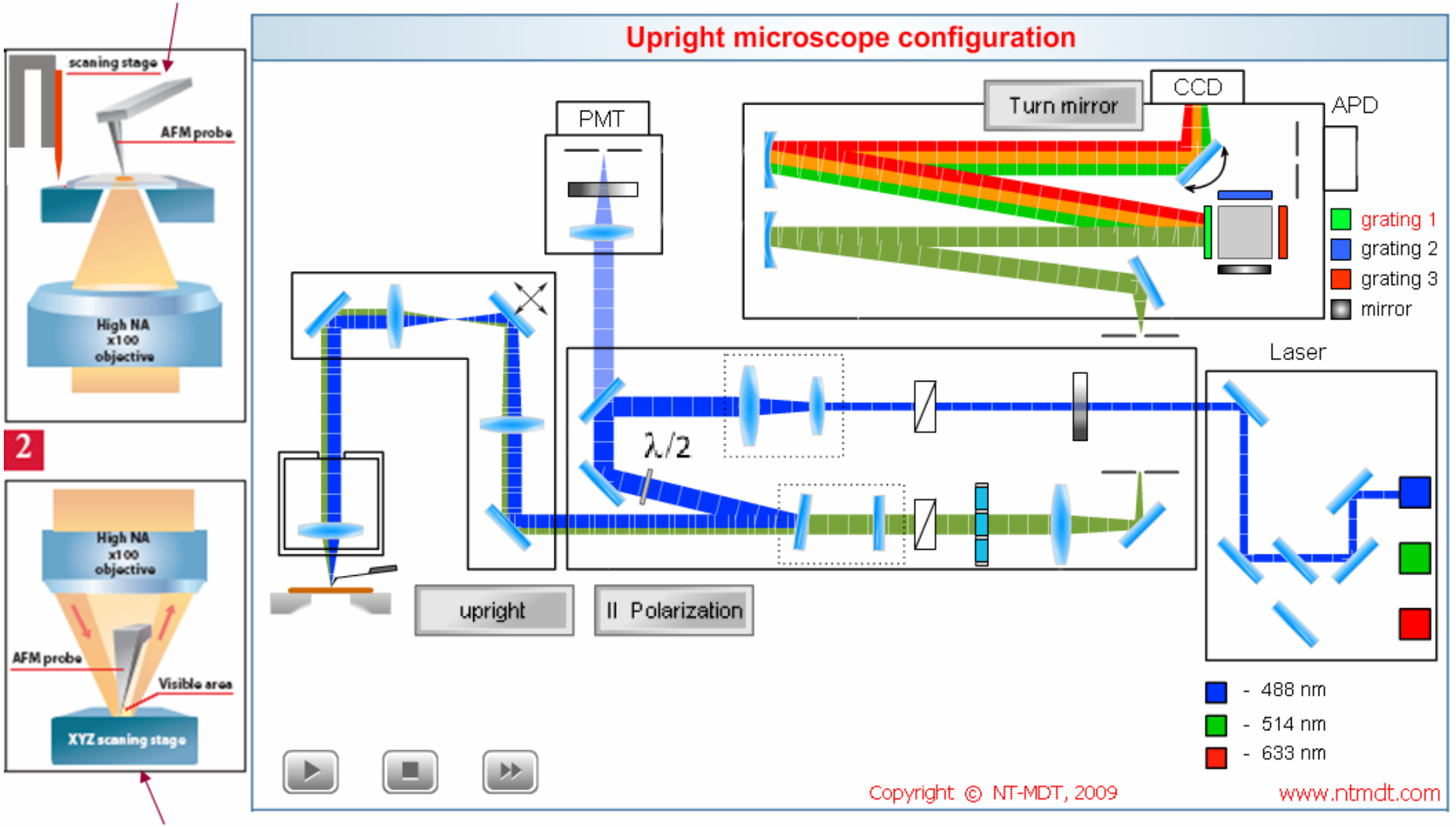
Scan by tip ->



Scan by sample ->

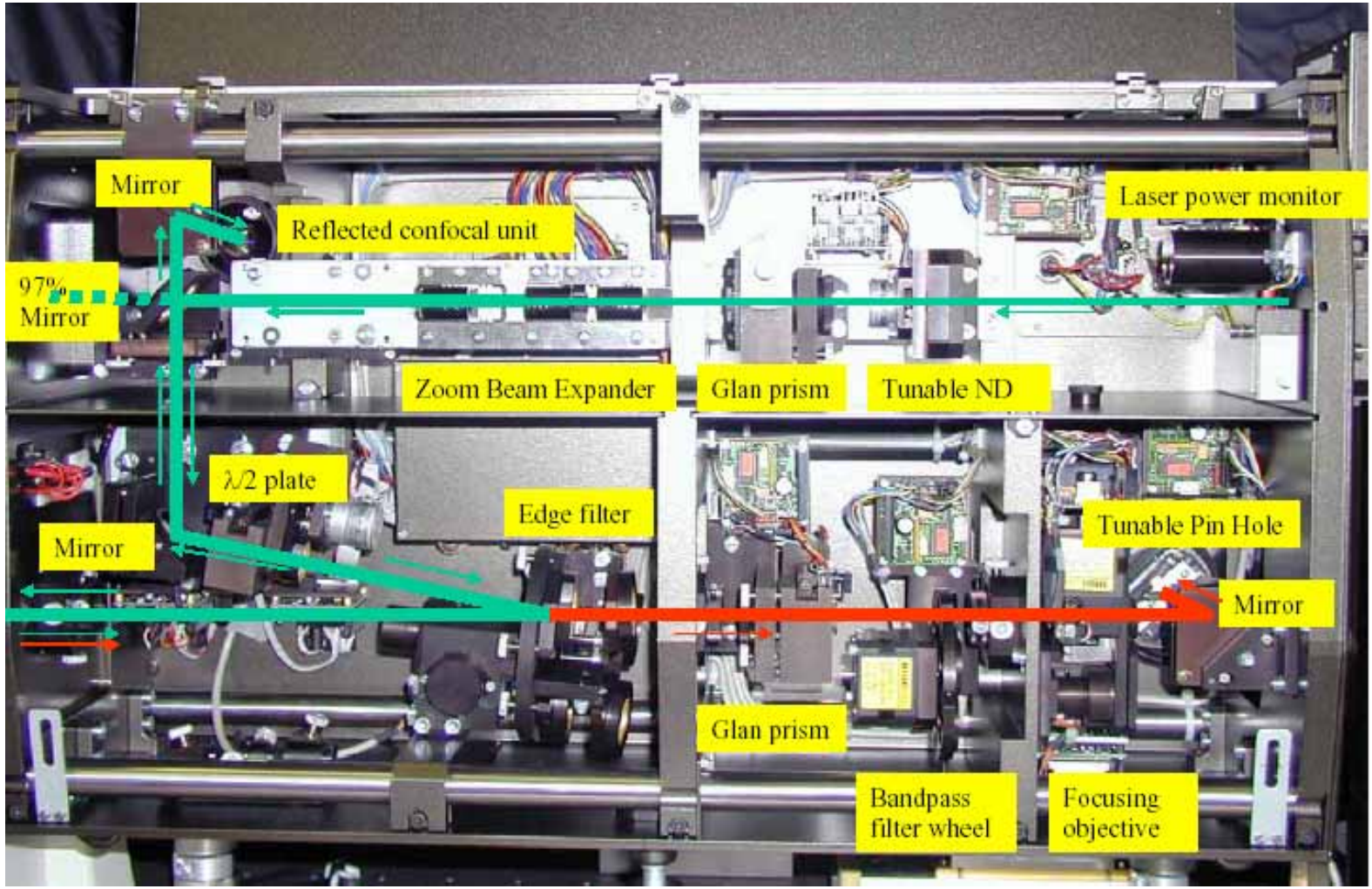


Cantilever XYZ- scanning +
independent sample XYZ-scanning
(6 Independent Closed-Loop coordinates)



Laser spot XYZ - scanning +
independent sample XYZ-scanning
(6 Independent Closed-Loop coordinates)

Optical system configuration



Optical module by SOLAR –TII – NT-MDT

All in one box. All is automated. Run by one program

Main features of Solar confocal Raman module

- Easy change between 3 lasers (two mouse clicks, NO need to change anything manually). Beam expander automatically adjusts to a chosen laser and objective.

- Flexible polarization optics (all motorized, controlled by software). Polarizers are installed both in excitation and detection channels. Cross-polarization measurements available.

- Very high optical throughput. Special mirrors are used in spectrometer: ~98% reflection each mirror. Ultra fast imaging (30 msec per point and less)

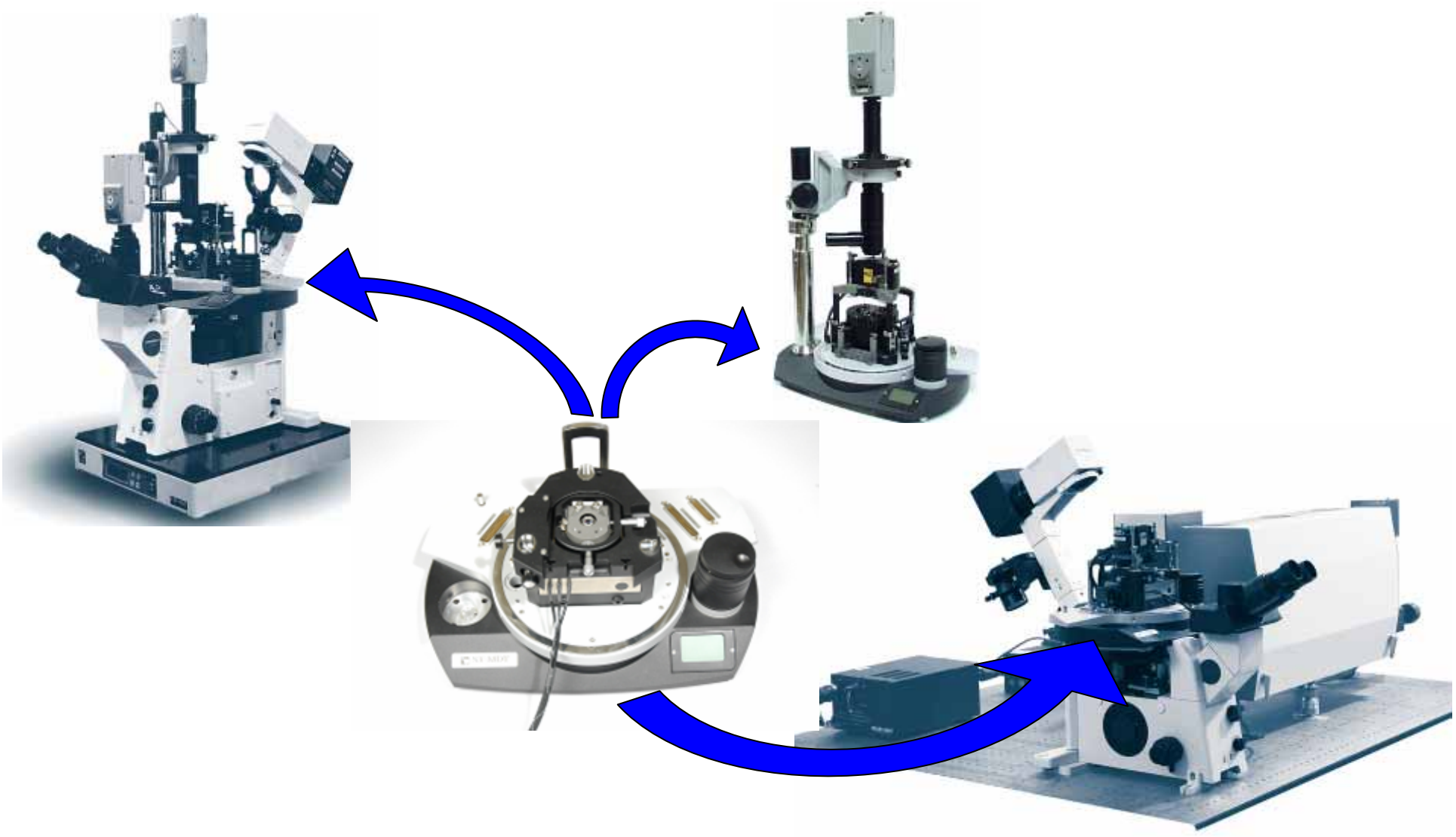
- Confocal pinhole is motorized. Pinhole diameter is adjustable (to switch between high throughput and confocal modes)

- Free slots (motorized) are available for additional filters/polarizers

- 4 different motorized gratings. 3 detection ports with various detectors

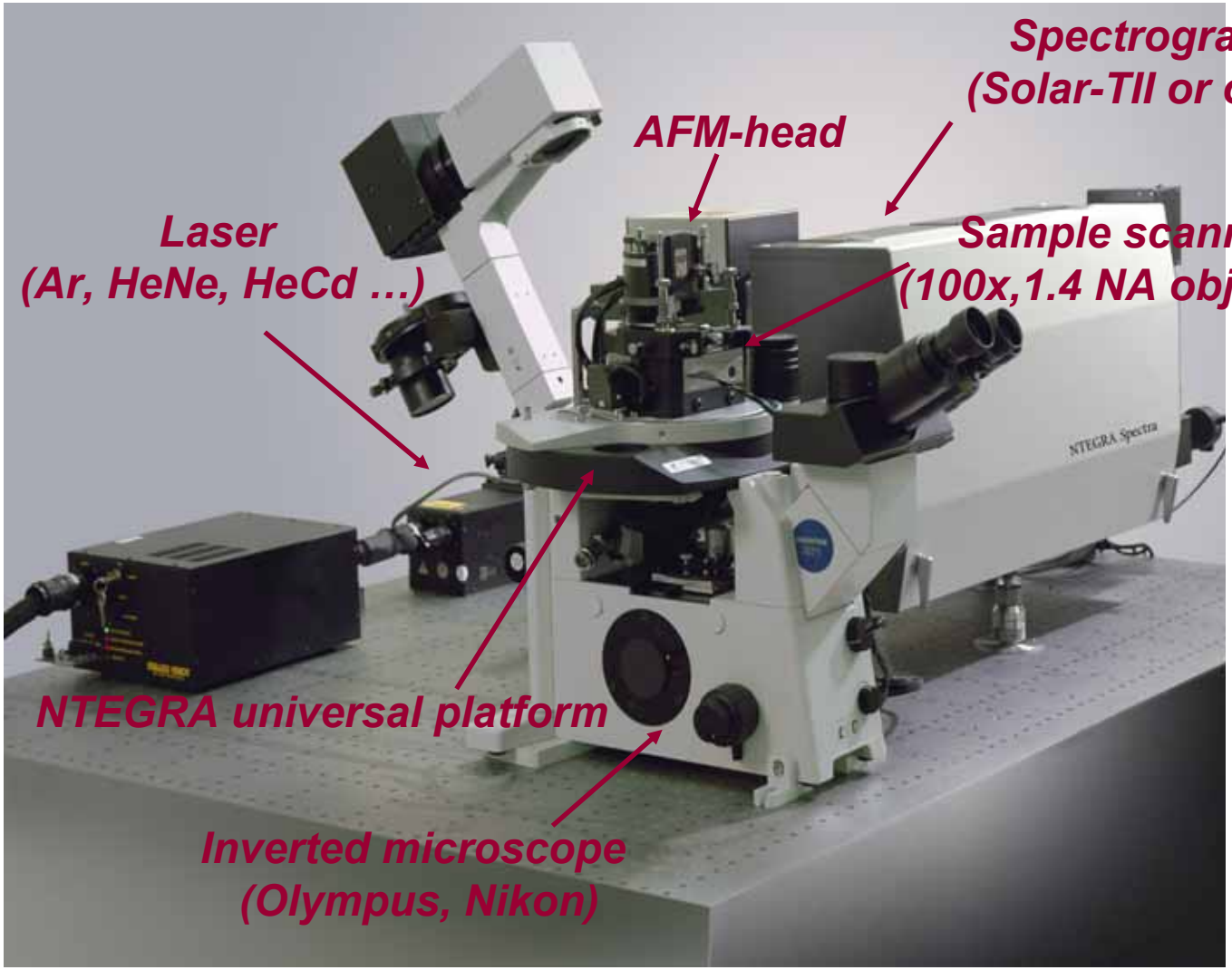
-Ultra high dispersion Echelle grating for high spectral resolution (down to 0.14 1/cm - pixel to pixel distance

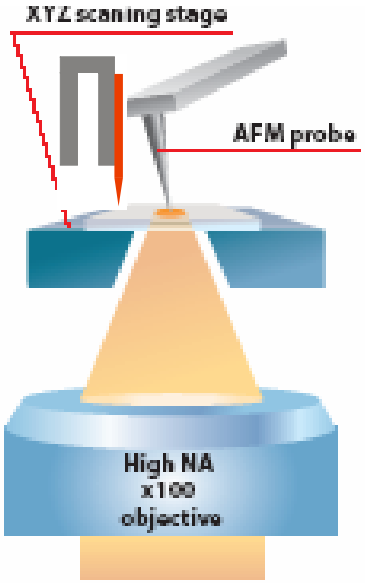
Universal basement



NTEGRA Spectra
Inverted microscope setup (for transparent samples)

“AFM + SNOM + 3D confocal Raman microscope” system

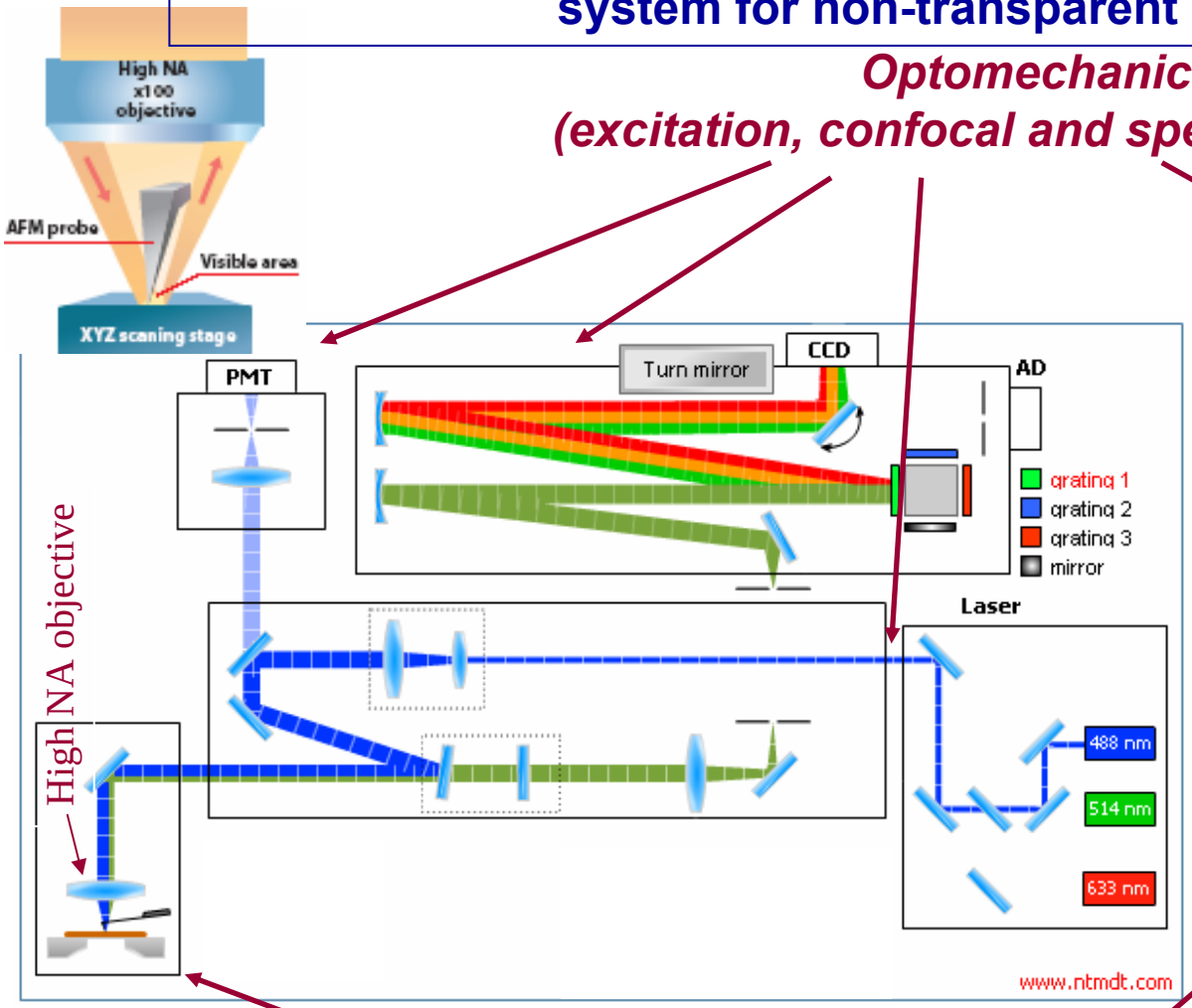




NTEGRA Spectra in upright setup

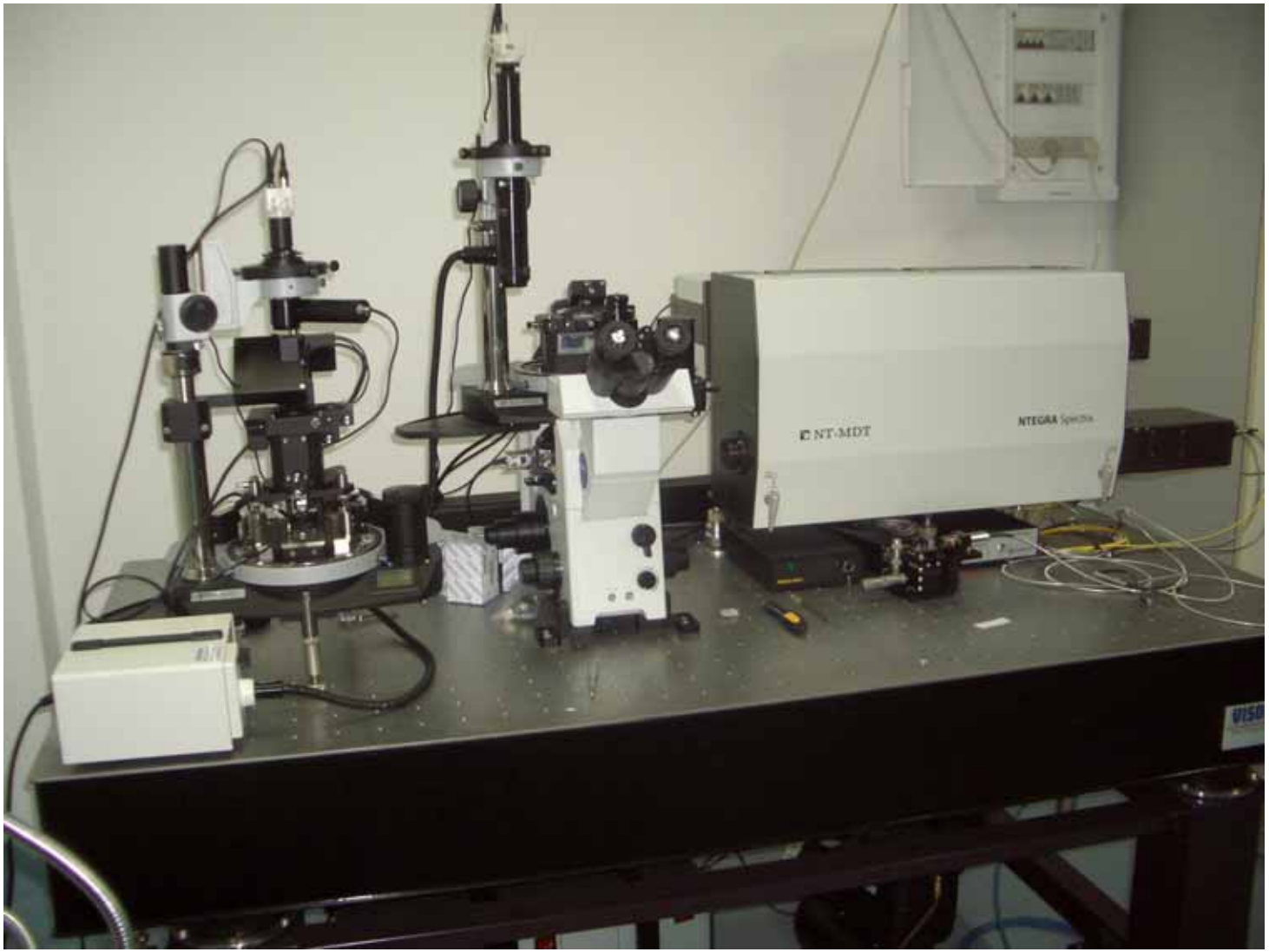
"AFM + SNOM + 3D confocal Raman microscope"
system for non-transparent samples

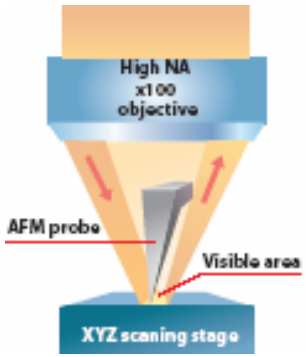
Optomechanical unit
(excitation, confocal and spectrometer modules)



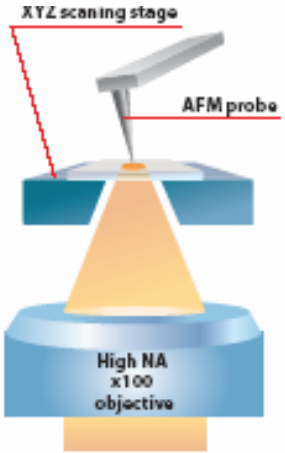
High Aperture AFM

NTEGRA Spectra, Upright + Inverted (with one confocal Raman module)





+



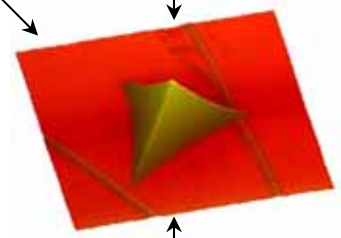
Combination of AFM with Raman

One object – many techniques

Atomic-force microscopy: mechanical, electrical, magnetic properties and nanomanipulations

Confocal Raman: imaging and spectroscopy

Near-field optical microscopy

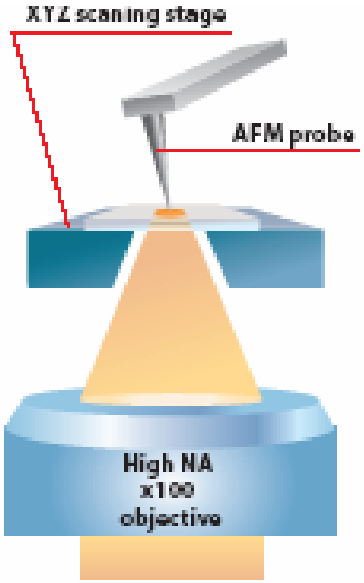


Confocal fluorescence: imaging and spectroscopy

Conventional white light microscopy and reflected laser confocal imaging

Tip Enhanced Raman and Fluorescence microscopy

Measurements in air, in liquid or in controlled enviroment



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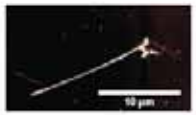
- Raman microscopy for unambiguous chemical identification: fully-flexible Renishaw inVia Raman microscope
- Fully TERS capable (tip-enhanced Raman scattering)
- Highly efficient direct optical coupling (no optical fibres) minimises Raman measurement times
- inVia supports a wide range of Raman excitation wavelengths, enabling the analysis of the most challenging materials
- Available with upright and inverted geometry microscopes
- Integrated software control from a single computer



AFM topography image of nanowire

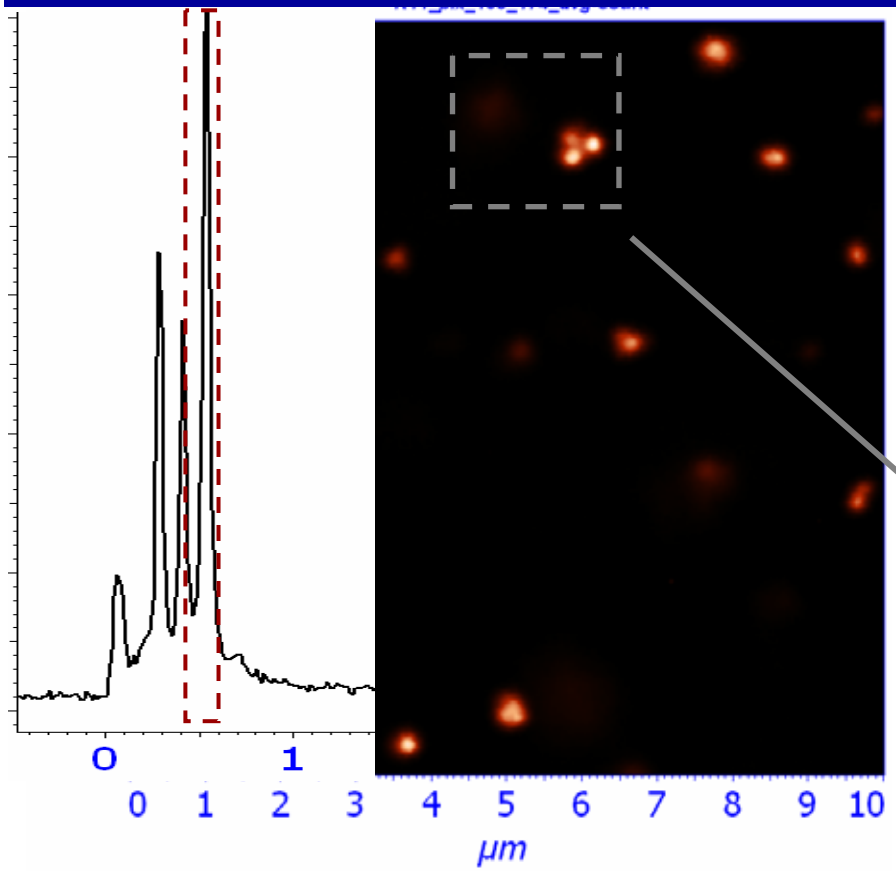
Corresponding Raman image of nanowire

Come and see an inVia/NTEGRA system at Renishaw's ICORS 2008 exhibition booth 4/5

NTEGRA Spectra

Confocal Raman/Fluorescence - critical resolution

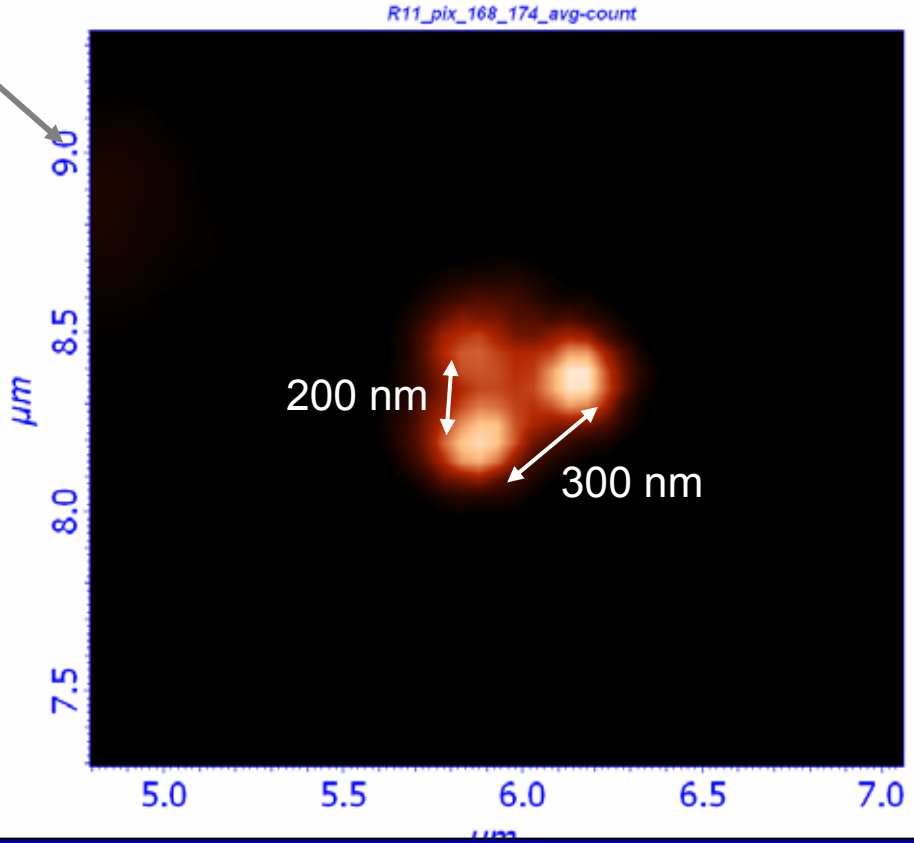
Resolution test: features 200 nm apart are clearly resolved



Sample: Mineralic toothpaste

Resolution: < 200 nm

Line #1, Integral intensity



Raman map measurement parameters:

Objective: 100x, oil immersion

Laser: 473 nm, Grating: 150 lines/mm

Exposure time 0.3 sec

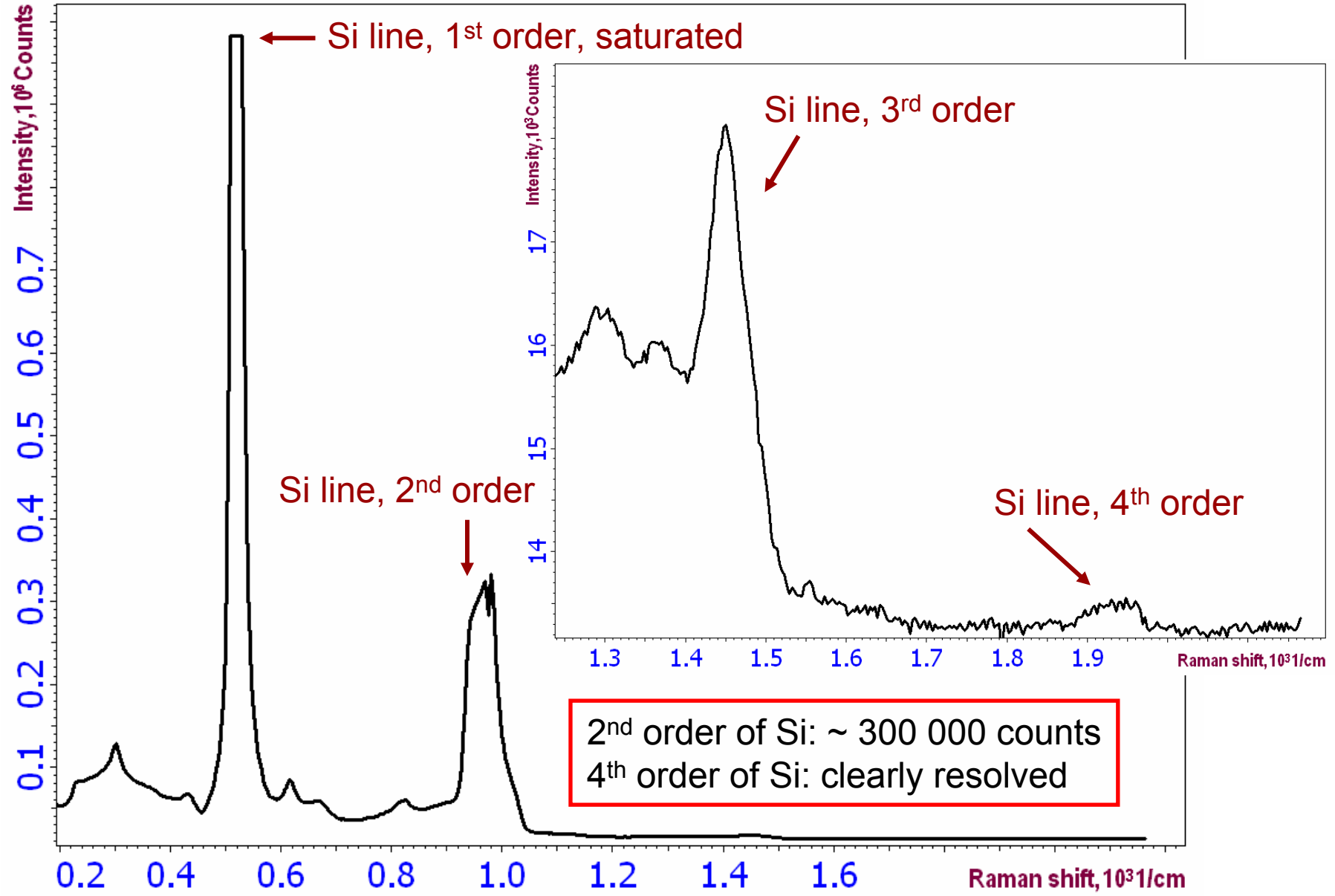
Spectra per sec: >3

Point number: 200x200 pix

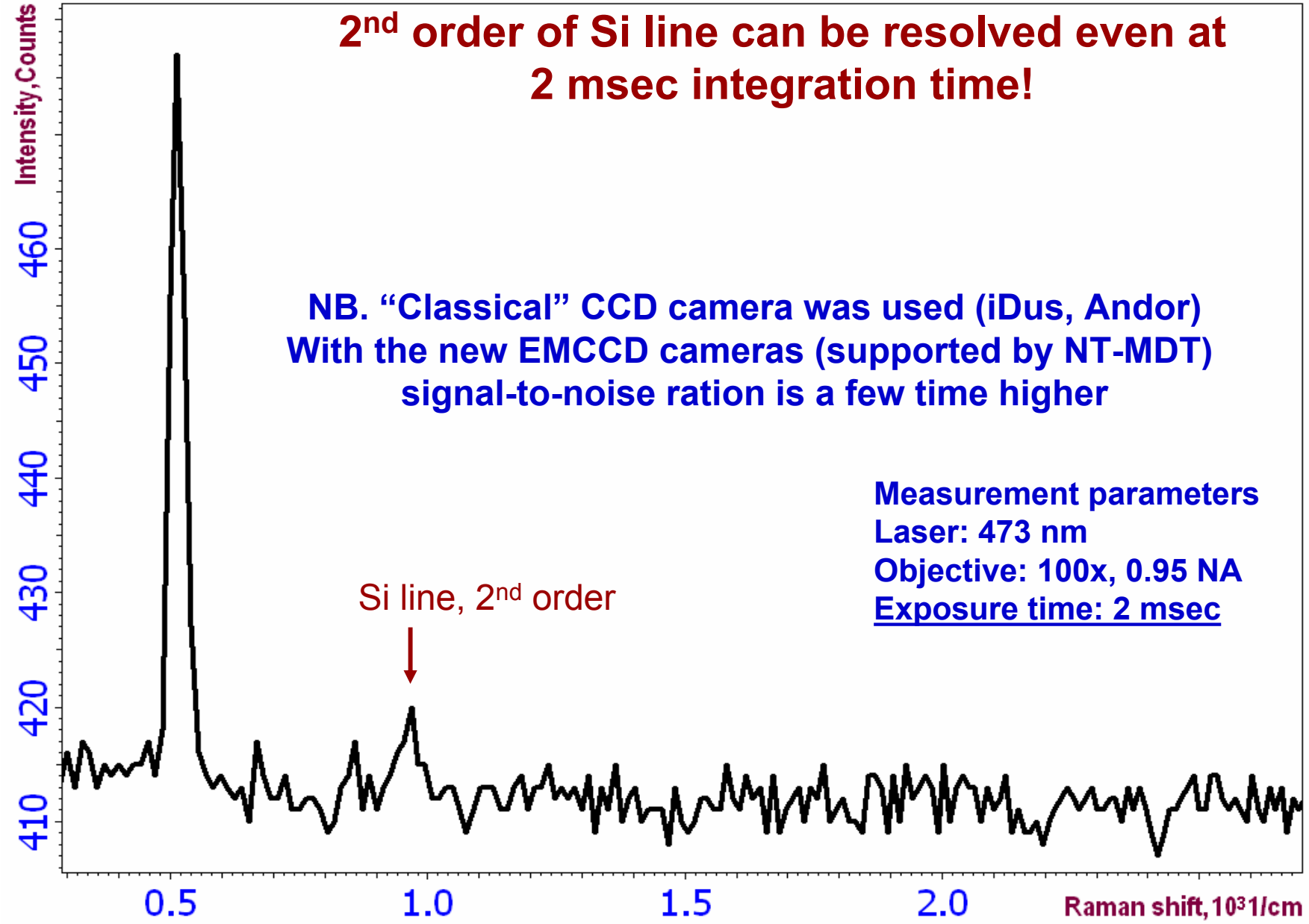
NT-MDT

Such resolution can be demonstrated for EVERY system installed

Sensitivity: 4th order of Silicon Raman band is clearly resolved



Sensitivity test, Si (100)



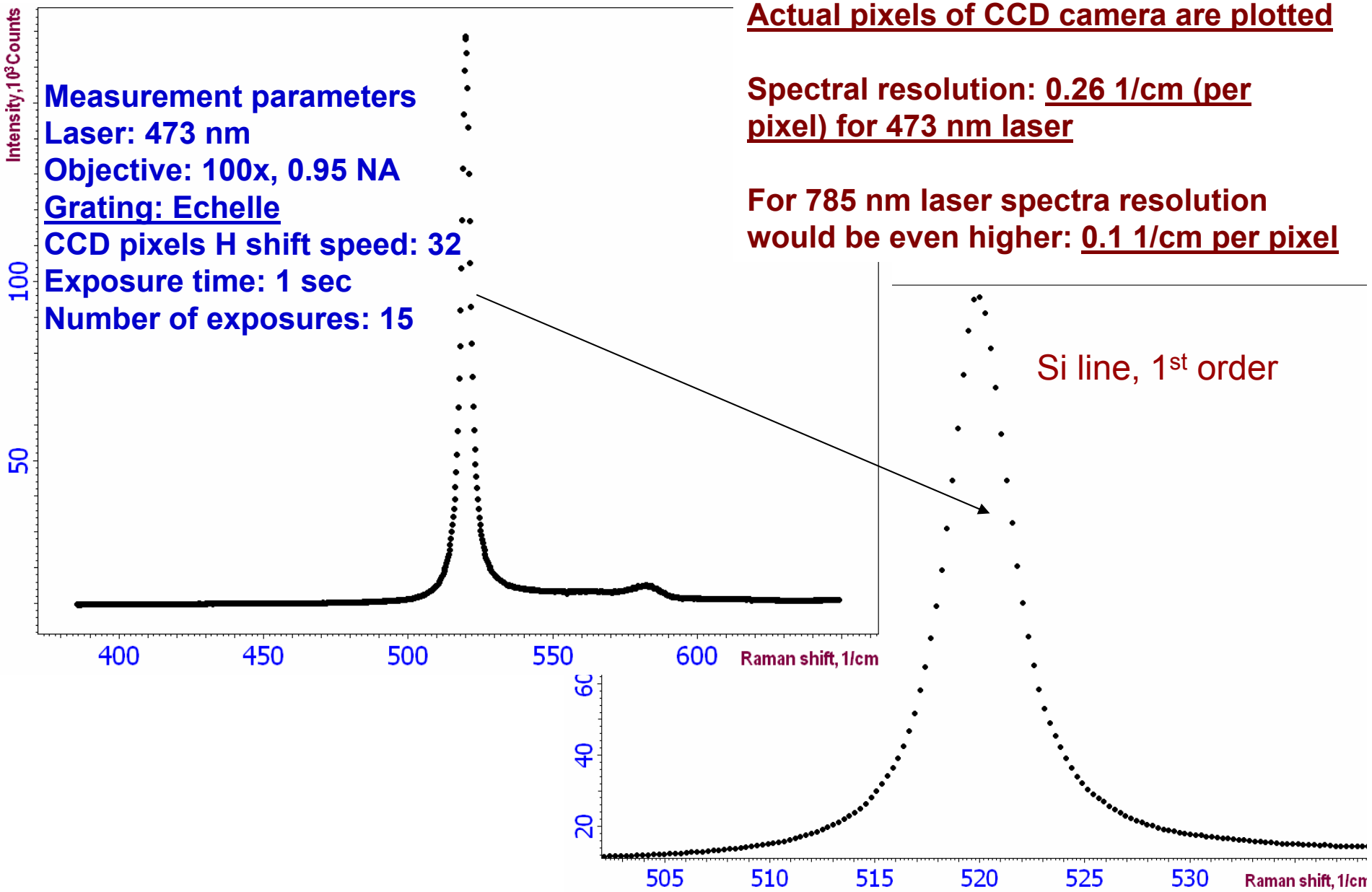
Extremely high spectral resolution by Echelle grating

Measurement parameters
Laser: 473 nm
Objective: 100x, 0.95 NA
Grating: Echelle
CCD pixels H shift speed: 32
Exposure time: 1 sec
Number of exposures: 15

Actual pixels of CCD camera are plotted

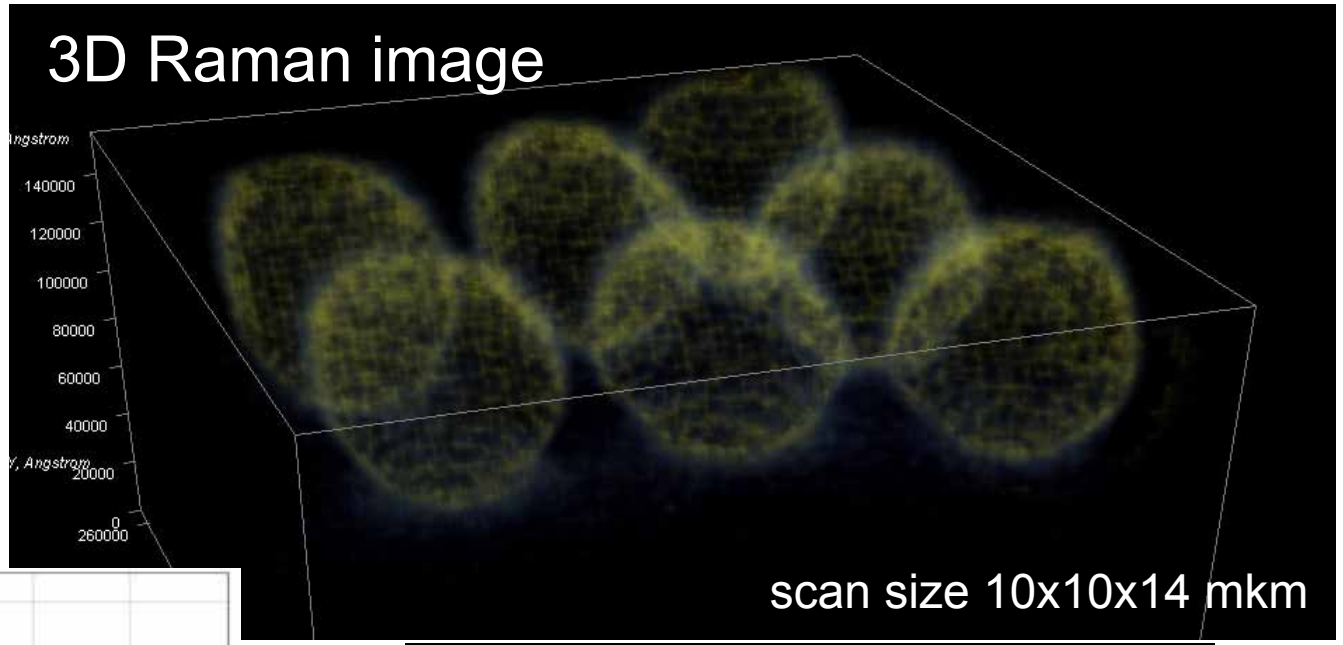
Spectral resolution: 0.26 1/cm (per pixel) for 473 nm laser

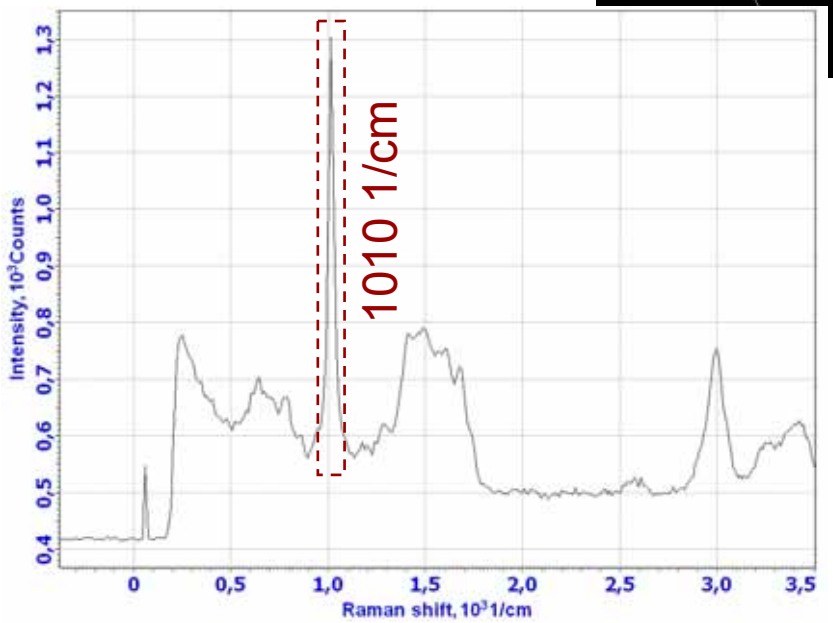
For 785 nm laser spectra resolution would be even higher: 0.1 1/cm per pixel

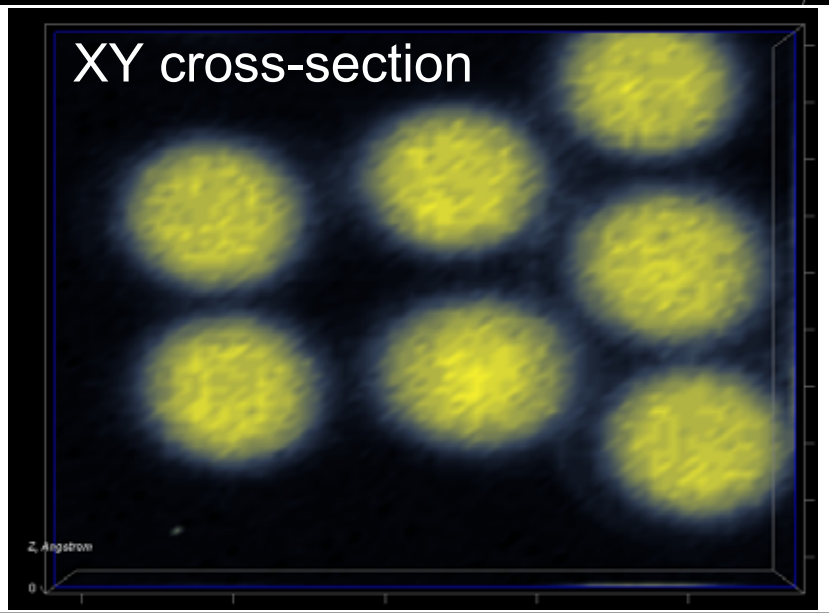


3D Raman mapping, Polystyrene microspheres

X,Y - resolution: 200 nm
Z – resolution: 500 nm



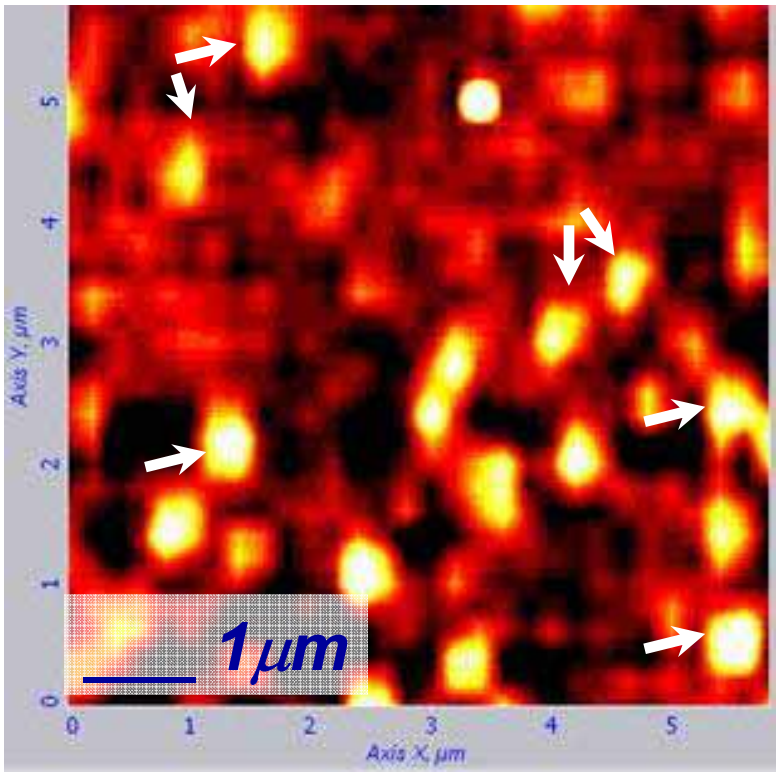




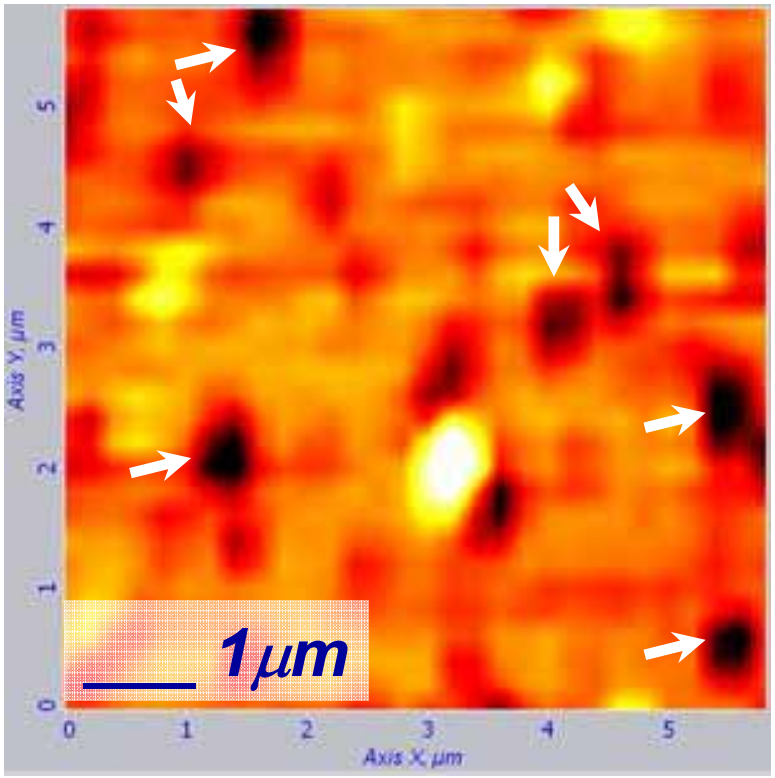
NTEGRA Spectra
AFM - Raman “classical applications”

Quantum dots
Silicon nanowires
Stress in Silicon
Carbon nanotubes
Graphene
Bio objects

Confocal Raman, Ge dots on Si



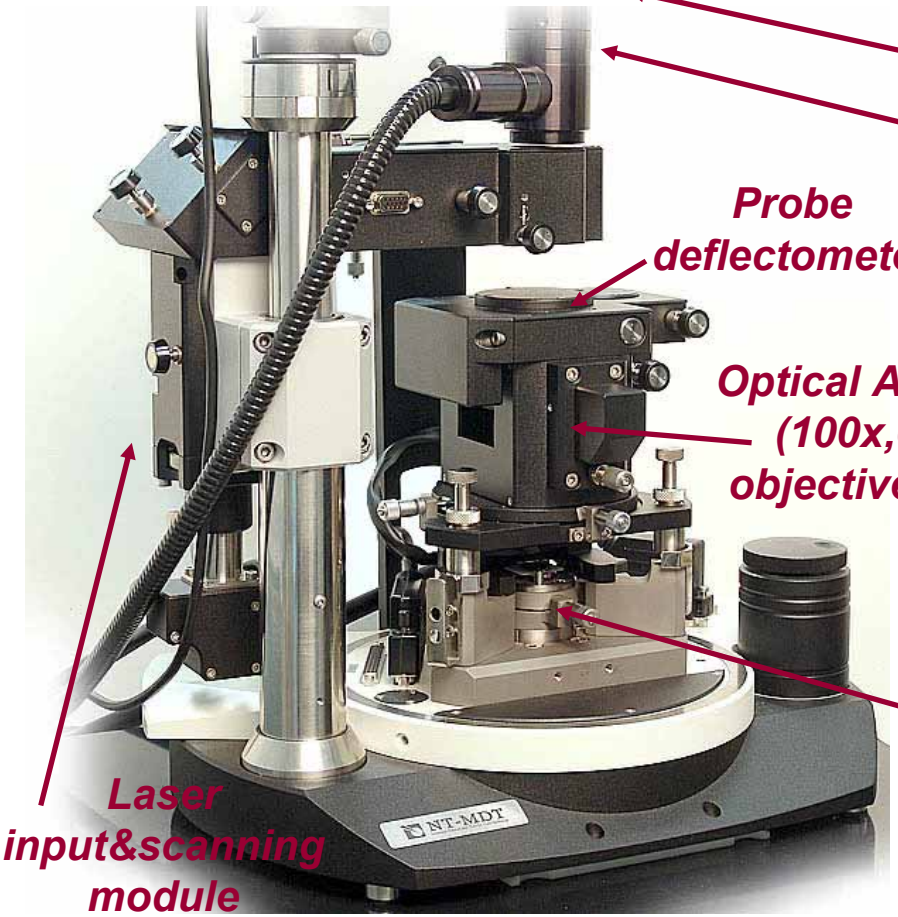
Ge line (412 cm^{-1})



Si line (520 cm^{-1})

Sample courtesy: Dr. Torzo
Data measured: I. Dushkin, NT-MDT

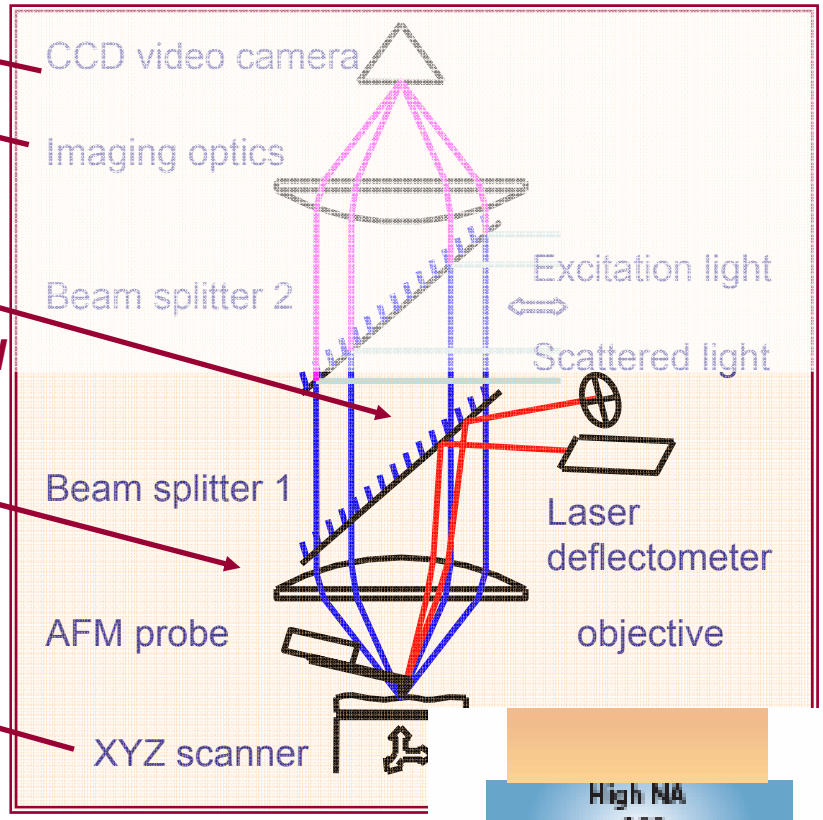
AFM with 100x 0.7 NA objective in upright configuration – for non-transparent samples



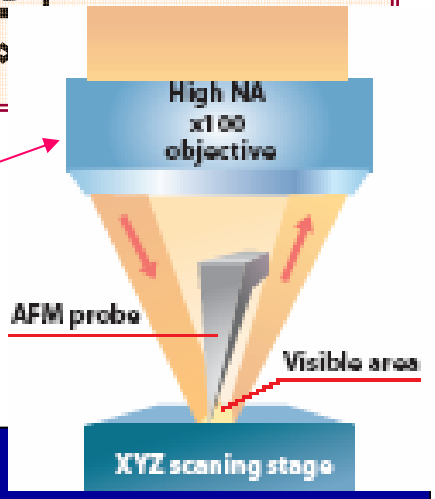
Probe deflectometer

Optical AFM head (100x,0.7 NA objective inside)

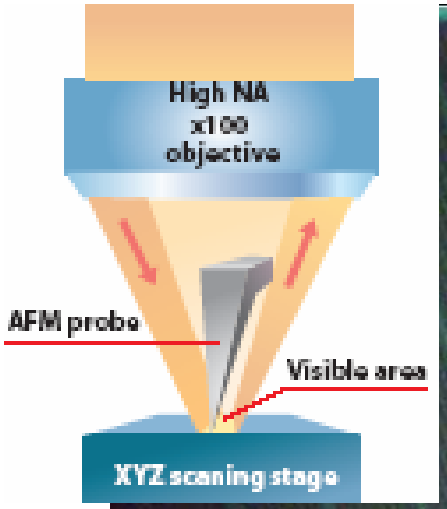
Laser input&scanning module



NA=0.7
400 nm resolution



AFM cantilever under 100x objective (in upright geometry)



1 μm height letters are readable – thanks to 100x objective (see next slide for AFM)

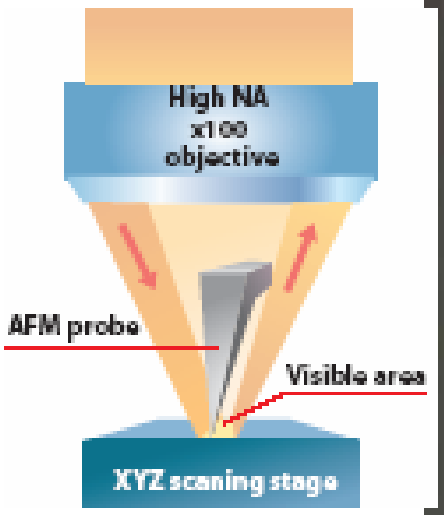
Black spot at the apex of cantilever is the exact point there the tip touches substrate !!!

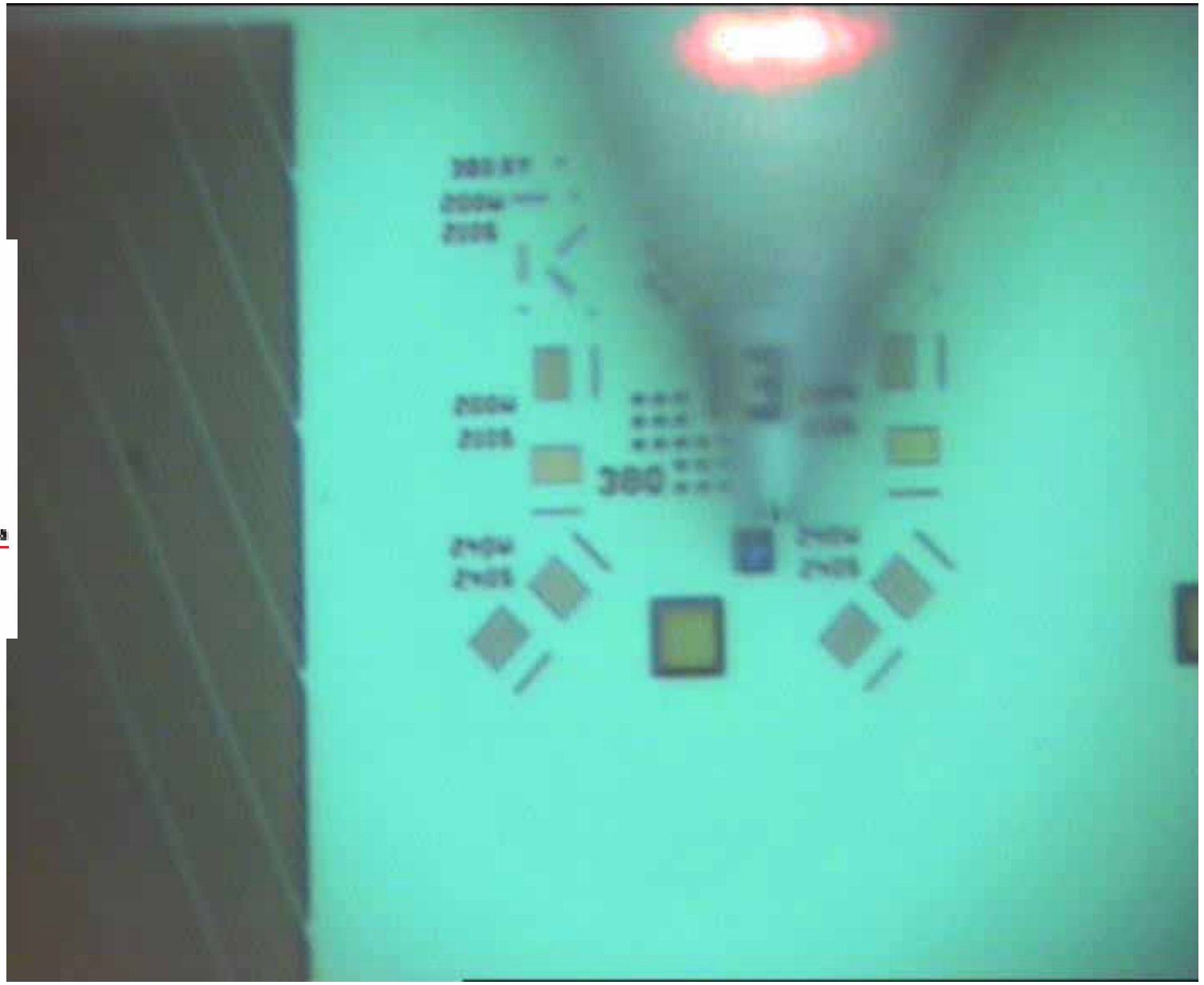
AFM probe over a structured Si substrate. View through 0.7NA 100x objective

Apex of opaque Si tip looks transparent on the image!

This unique observation is due to high aperture (0.7 NA) of the imaging objective

AFM cantilever under 100x objective – you see precisely what and where you are scanning`!

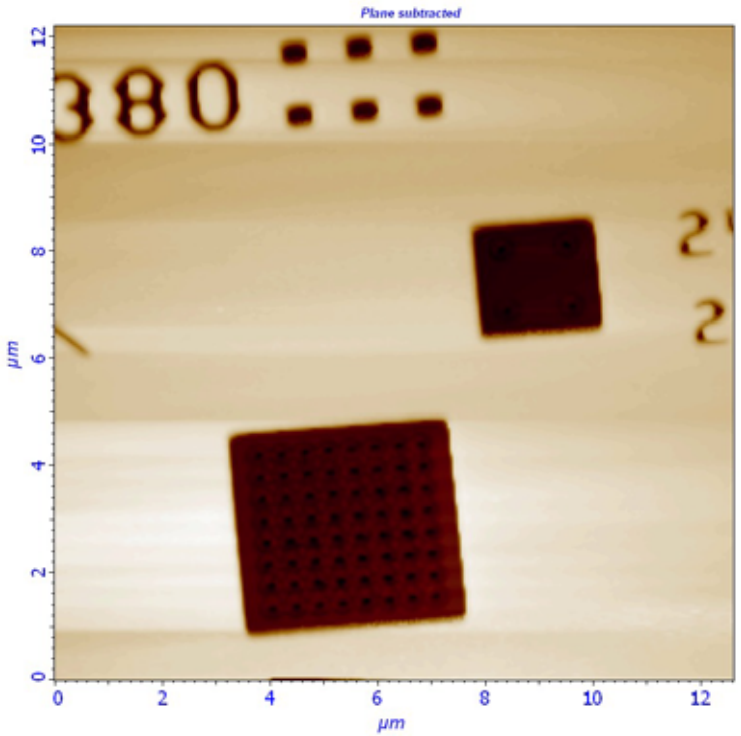




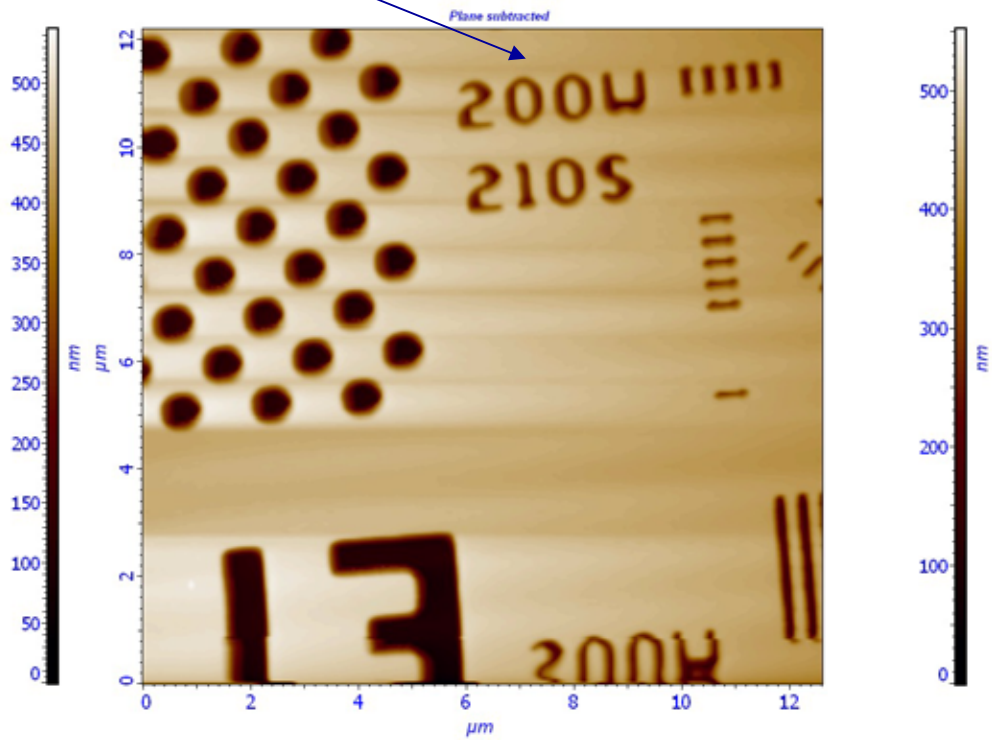
NTEGRA Spectra

Simultaneous imaging and AFM scanning

1 µm height letters (see previous slide) can now be resolved with ultimate nanometer-scale resolution of AFM



Topography 12.6x12.6 µm^2



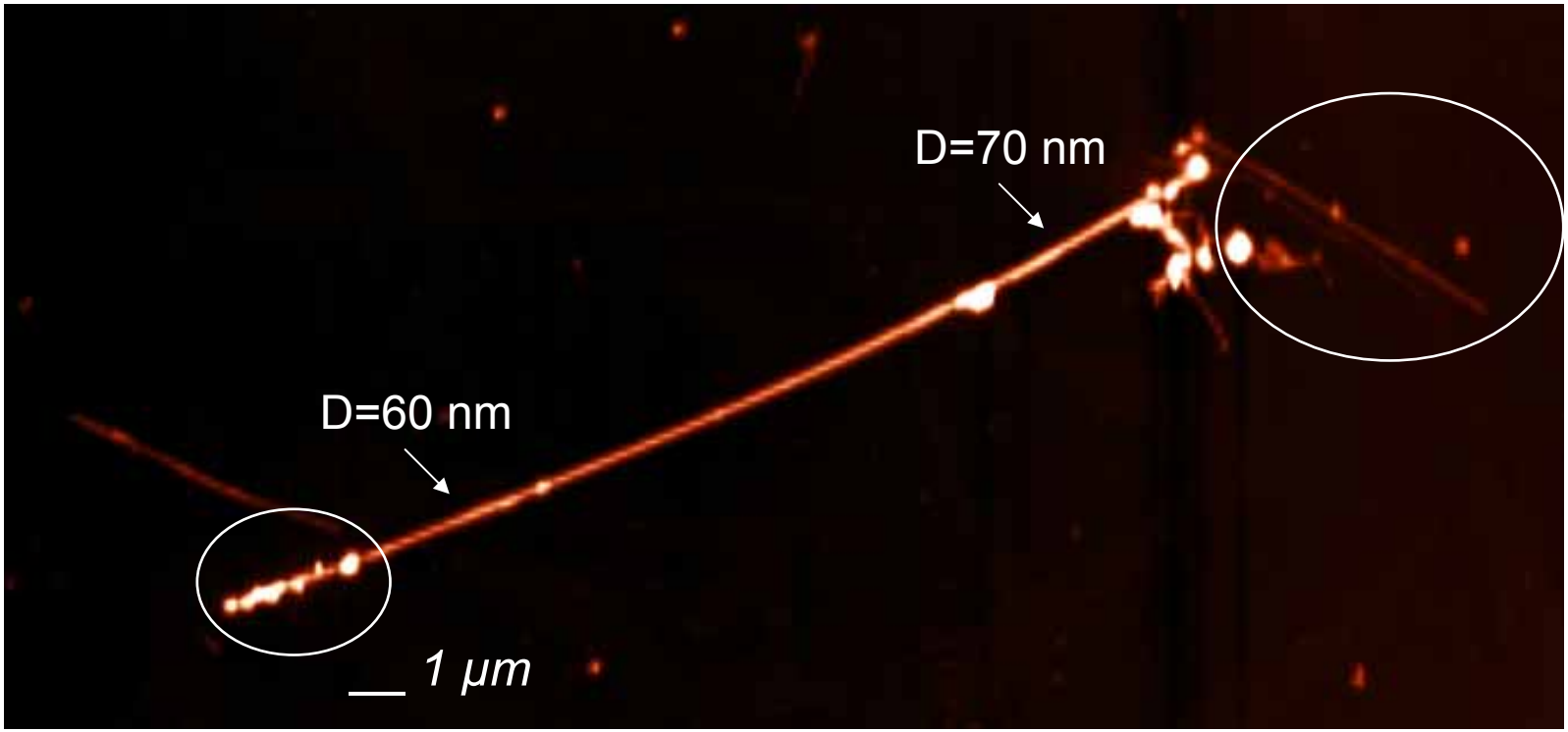
Topography 12.6x12.6 µm^2

AFM-image from the same sample area as on previous slide

NTEGRA Spectra AFM – Raman system

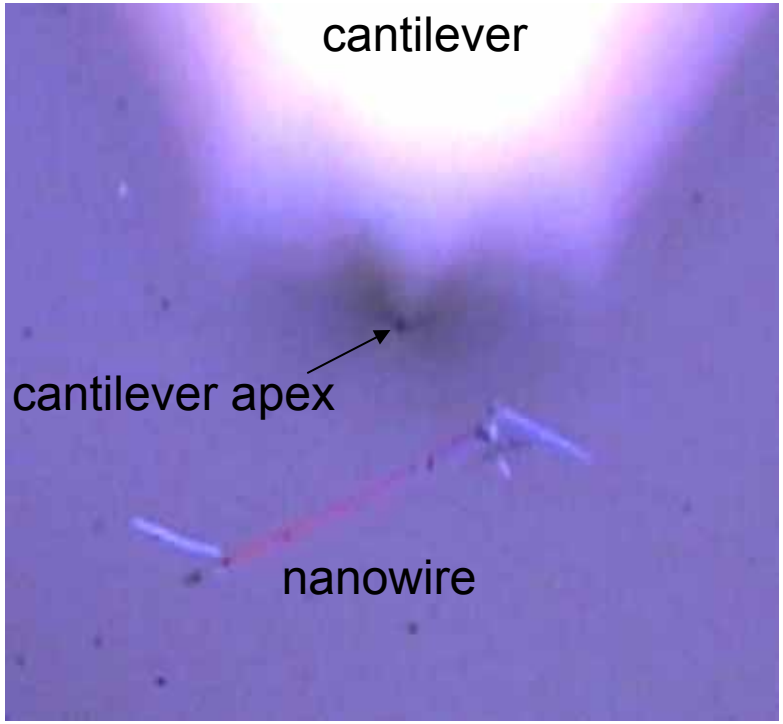
Silicon nanowires

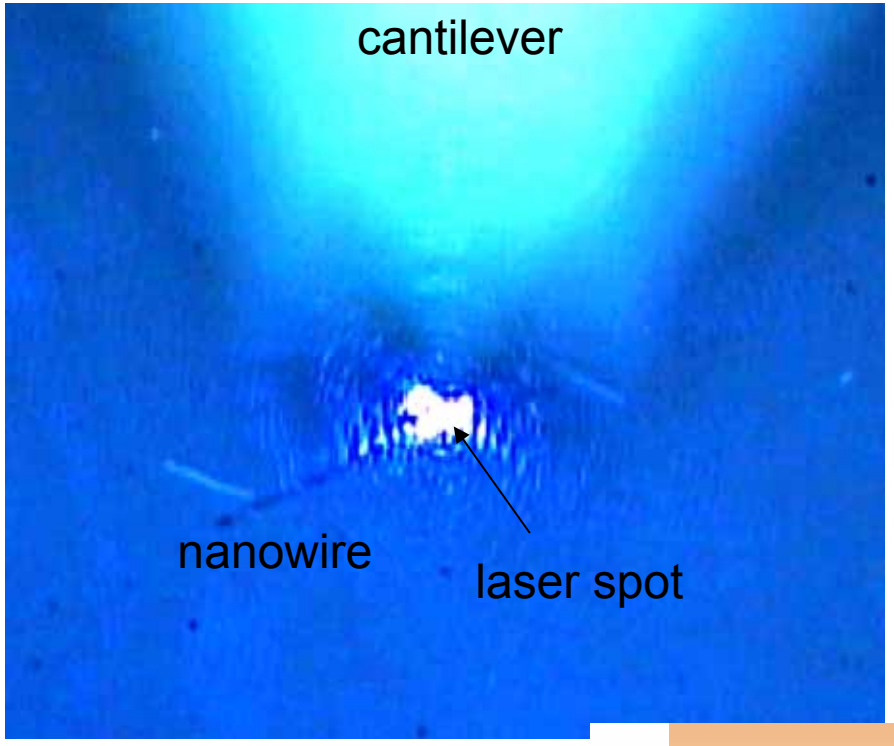
Si nanowire, AFM topography

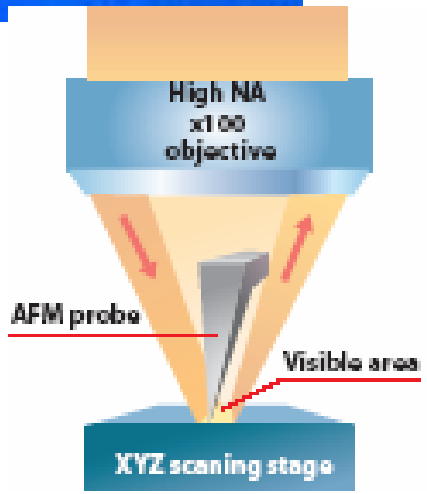


NT-MDT NTEGRA Spectra + Renishaw Raman microscope

Si nanowire

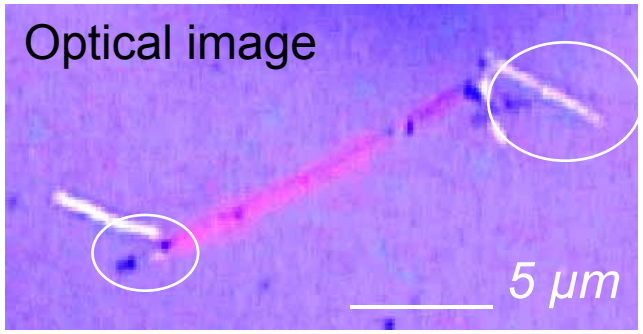


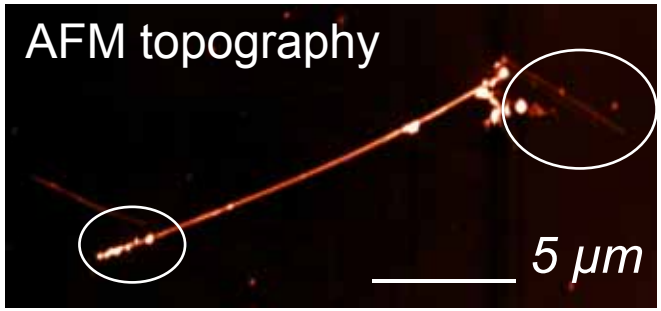


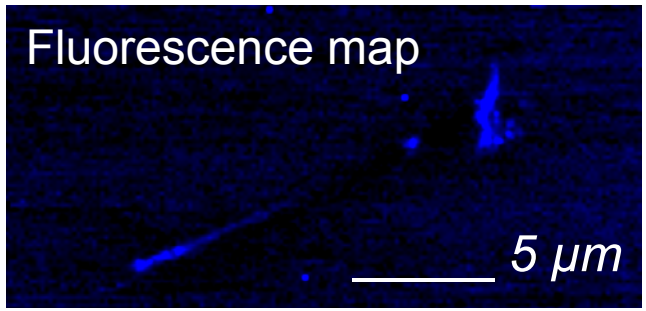


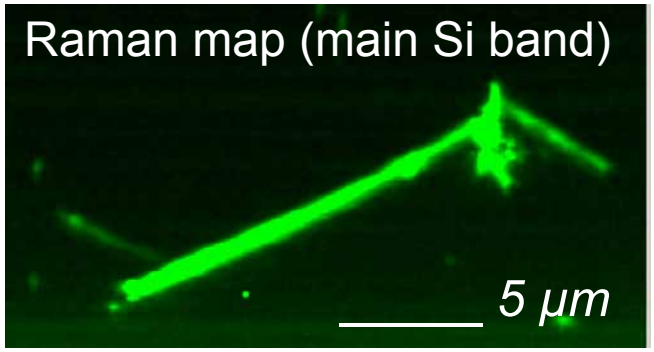
+ VIDEO

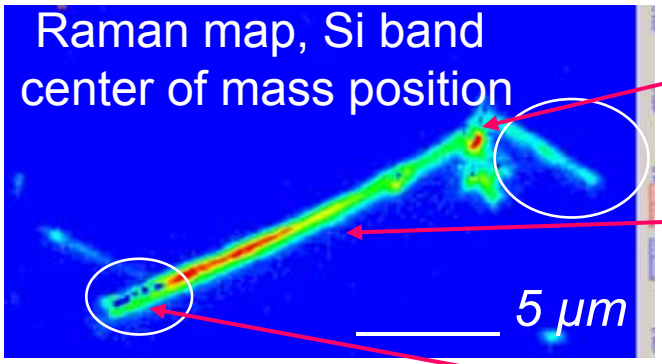
Si nanowire

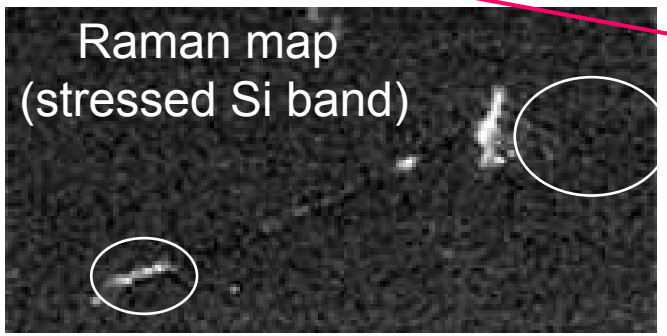


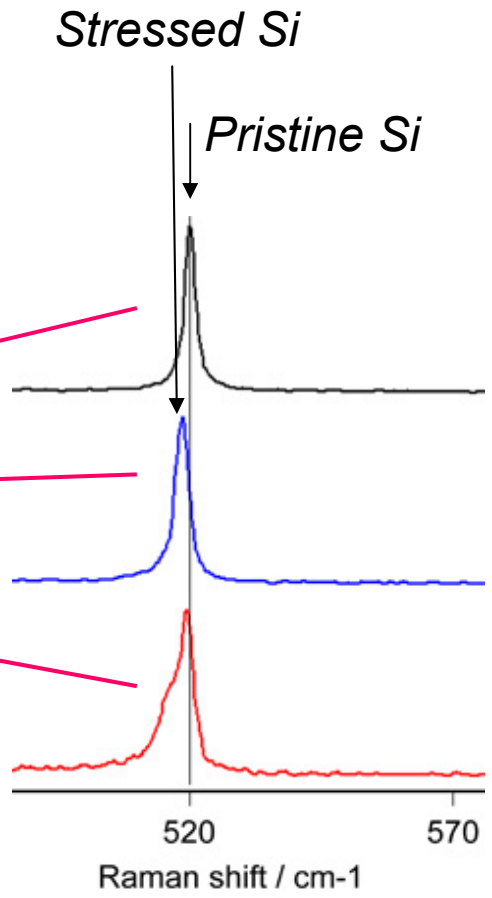








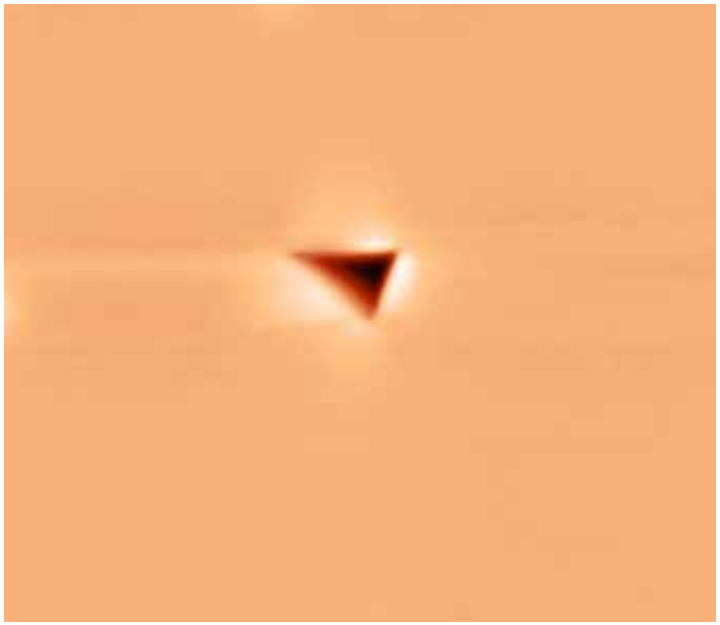




NT-MDT NTEGRA Spectra + Renishaw Raman microscope

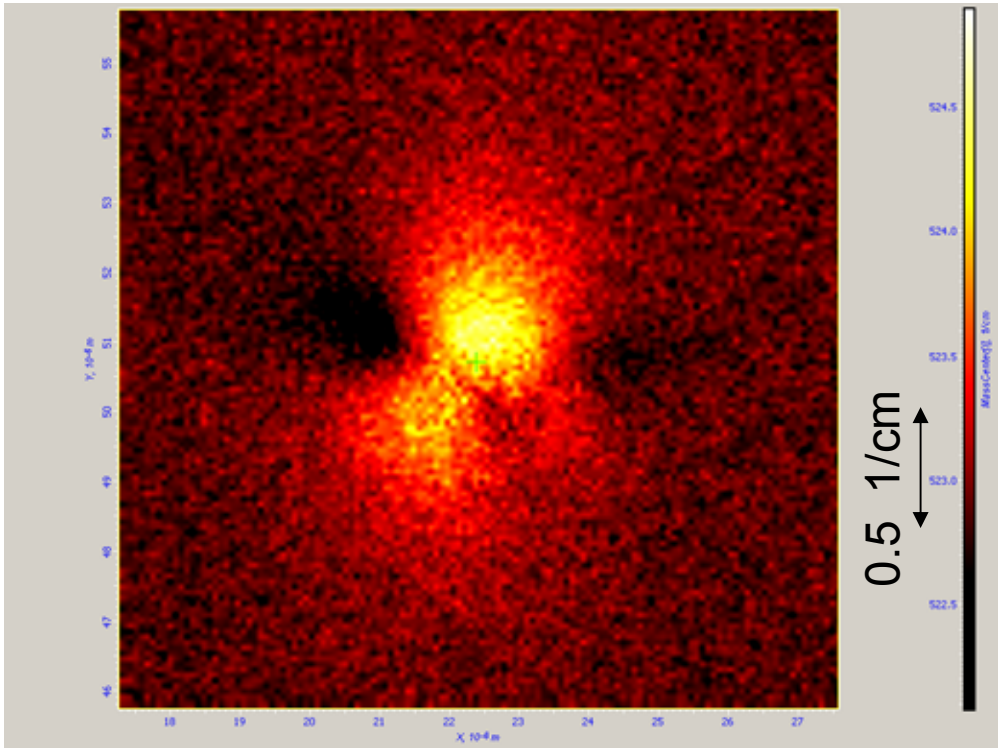
Mapping stress in Si by spectral shift of 520 cm^{-1} line

Stress distribution around nanoindentation in Silicon substrate



AFM topography of indentation in silicon substrate

Scan size: 12x12 micron



Center of mass position shift of 520 *1/cm* silicon line – proportional to stress distribution around the indentation.
Spectral resolution: better then 0.1 1/cm

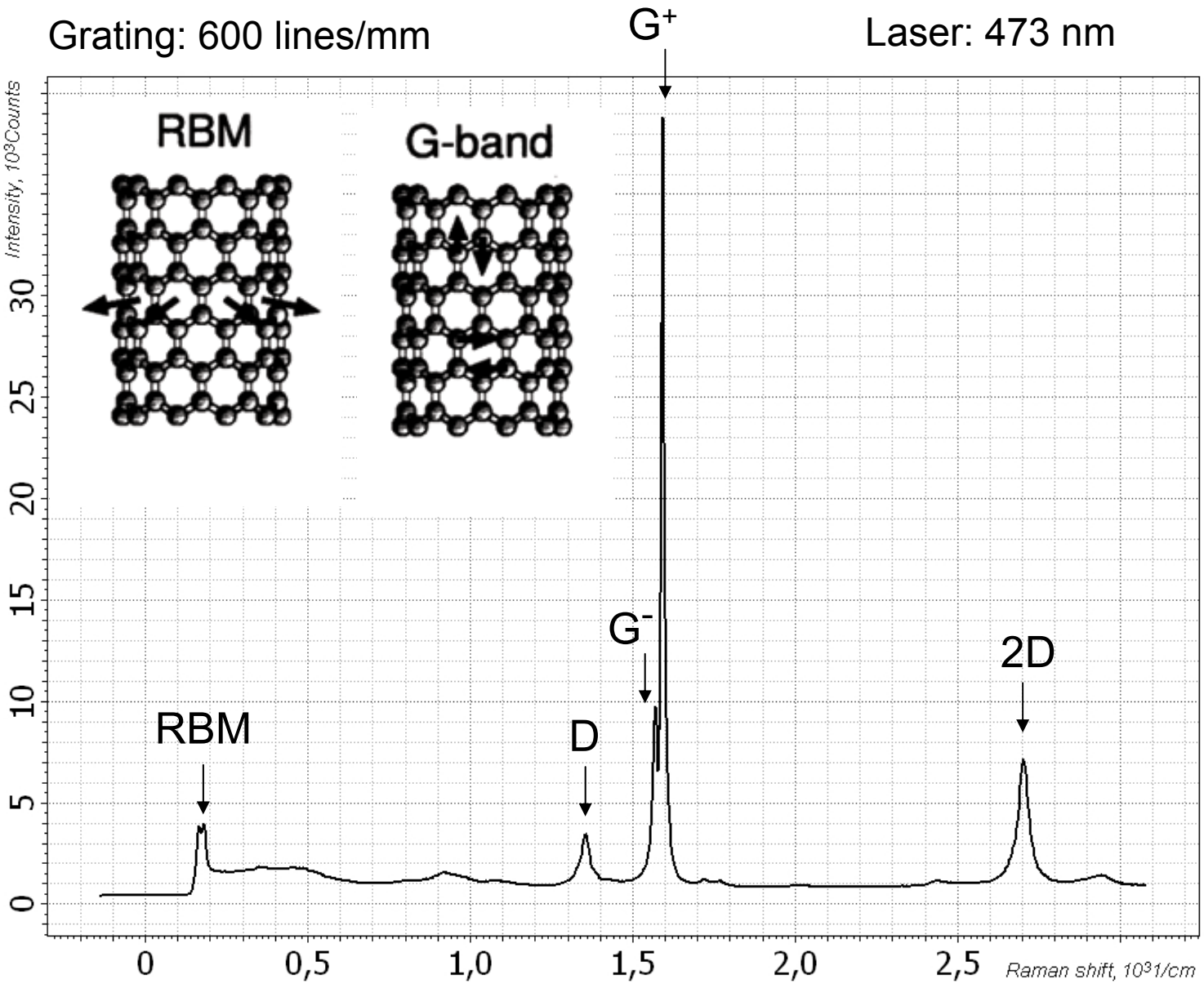
$$\sigma(MPa) = -435\ \Delta\omega\ (1/cm)$$

Data measured: S. Timofeev, A. Shelaev, S. Leesment, and P. Dorozhkin, NT-MDT

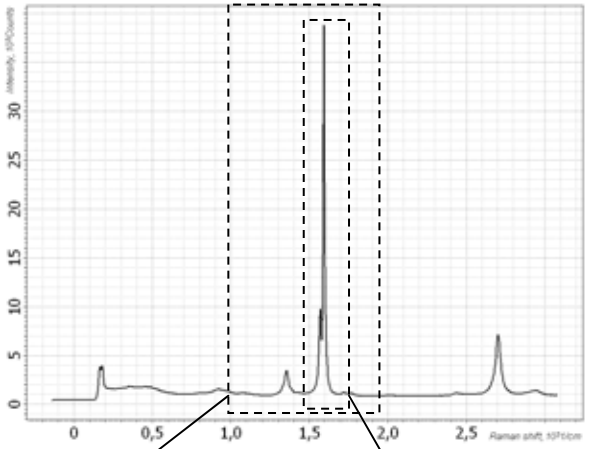
NTEGRA Spectra AFM Raman system

Application to carbon nanotubes

Sample: SWCNs, Overall Raman spectrum of individual NT agregate

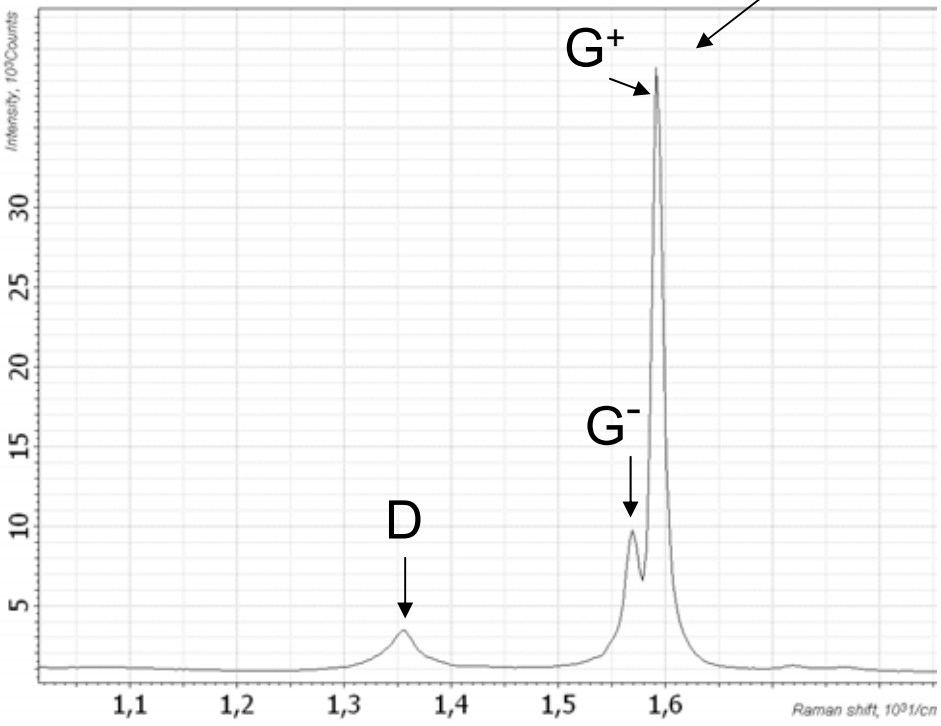


Details of Raman spectrum (by high resolution gratings)

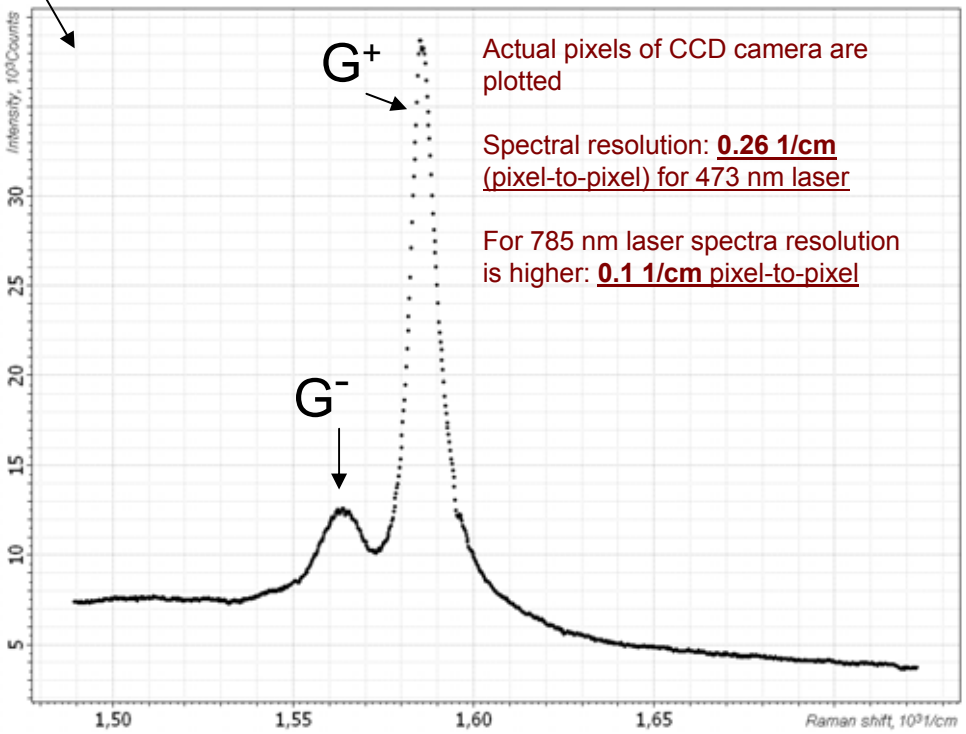


Grating: 600 lines/mm

Note extremely high spectral resolution of Echelle grating



Grating: 1800 lines/mm



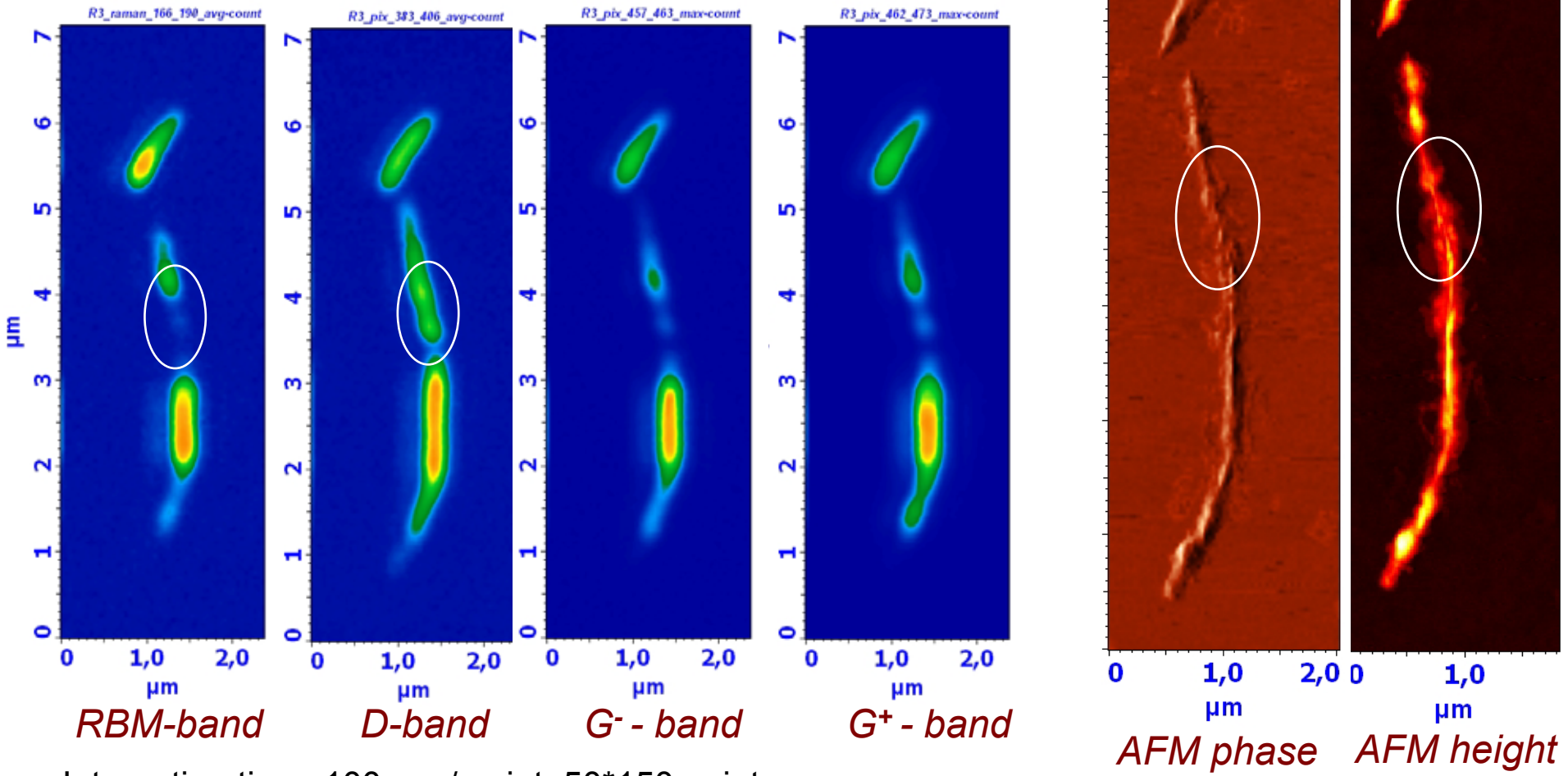
Actual pixels of CCD camera are plotted

Spectral resolution: **0.26 1/cm** (pixel-to-pixel) for 473 nm laser

For 785 nm laser spectra resolution is higher: **0.1 1/cm** pixel-to-pixel

Grating: Echelle (for ultra high spectral resolution)

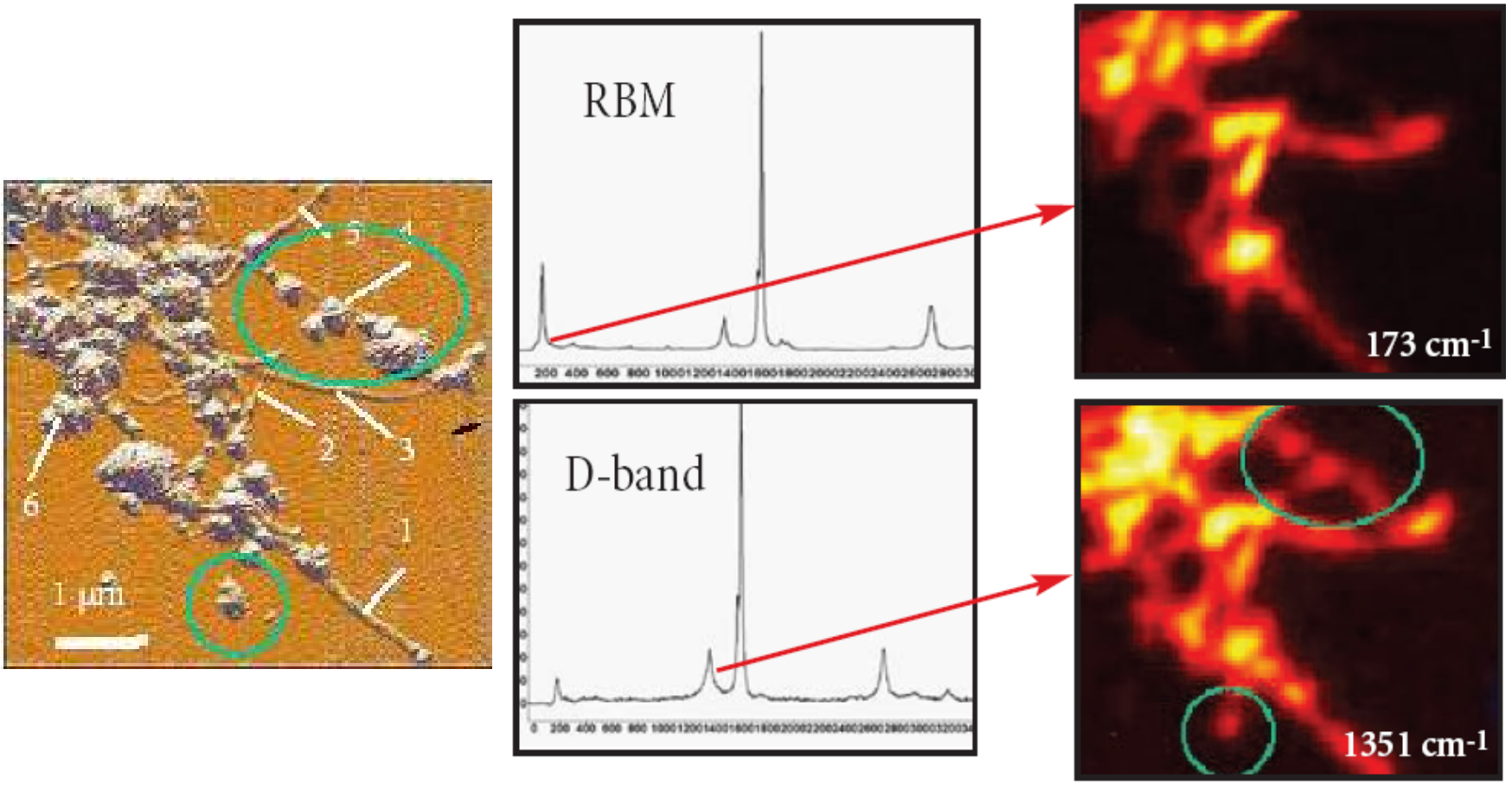
Intensity distribution of different Raman bands & AFM topography image of individual NT agregate



RBM-band *D-band* *G^- - band* *G^+ - band* *AFM phase* *AFM height*

Integration time: 100 ms / point. 50*150 points.
Total spectrum was acquired at each point of the scan. After measurement, different Raman bands are chosen and their intensity distribution is analyzed. All the images (AFM + all Raman maps) can obtained simultaneously, in a single experiment, without any moving of the sample or objective

AFM – Raman mapping of raw carbon nanotube material

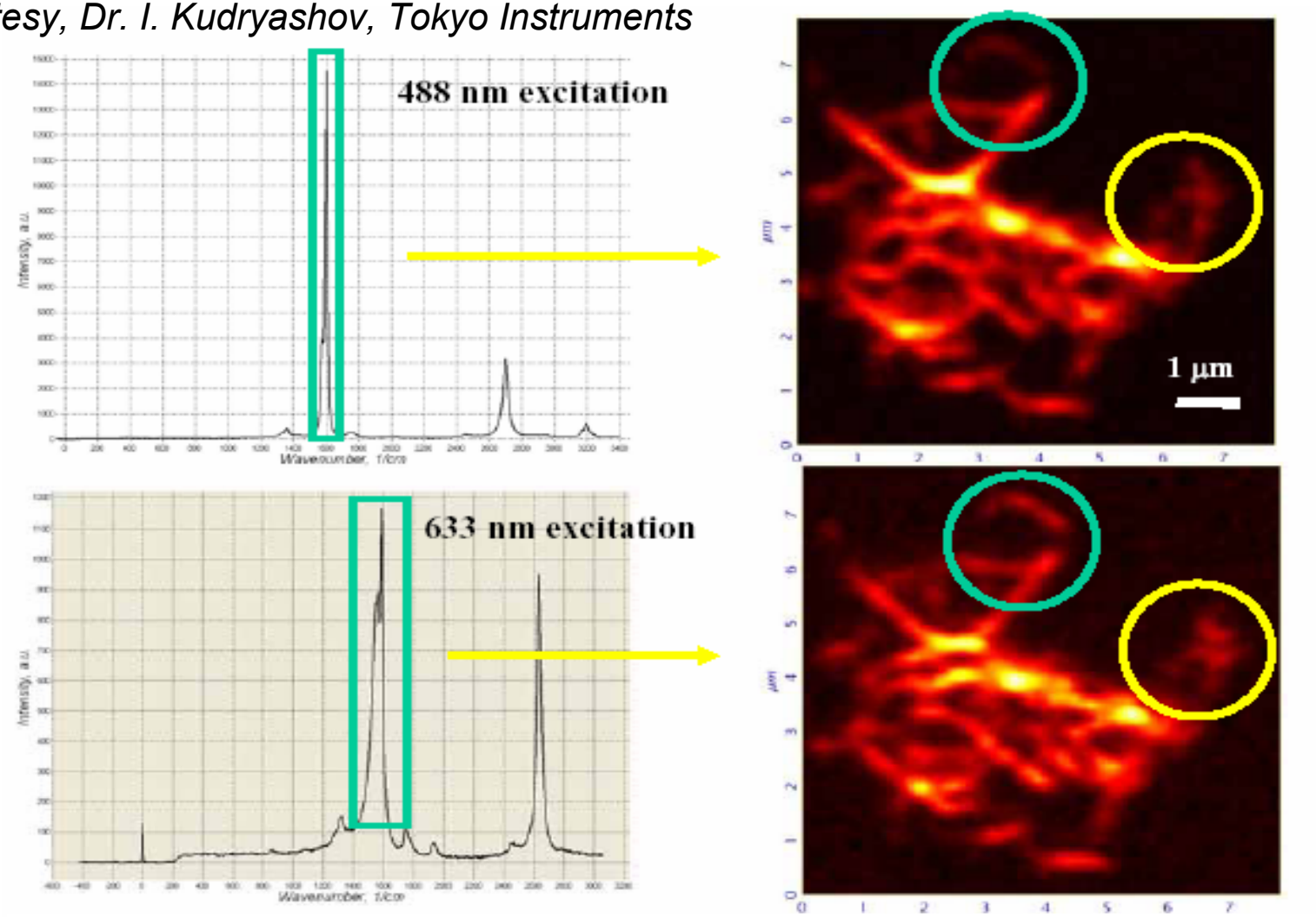


AFM image, Raman spectra and Raman images of single-walled carbon nanotubes. Amorphous carbon is visualized in D-band (1351 cm^{-1}) while well structured nanotubes are present in RBM- band (173 cm^{-1}). Raman images size 5x5 µm.

Images courtesy of Dr.Kudryashov, TII, Tokyo, Japan.

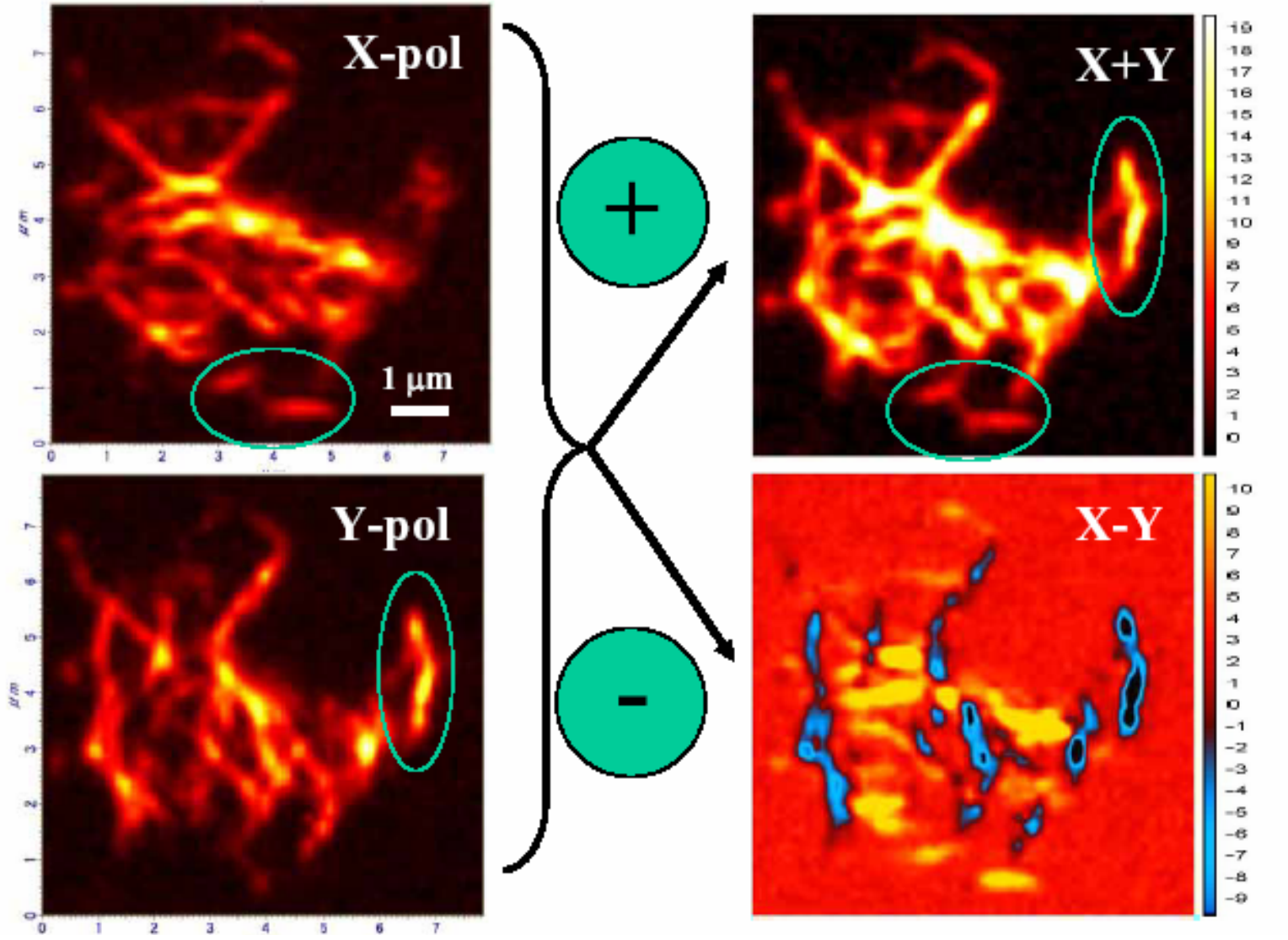
Different excitation lasers

Image courtesy, Dr. I. Kudryashov, Tokyo Instruments



Raman image of carbon nanotube raw material
1593 cm^{-1} (G-band)

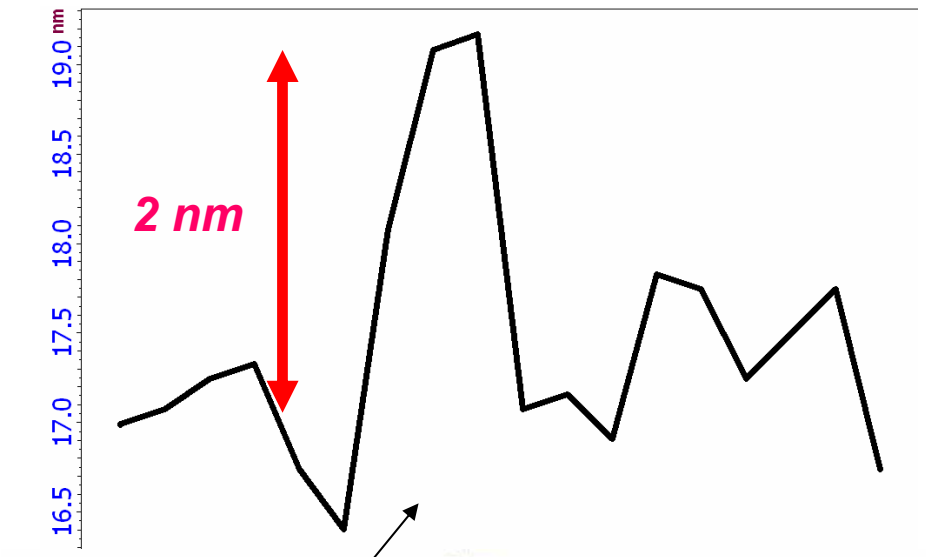
Confocal Raman in polarized mode

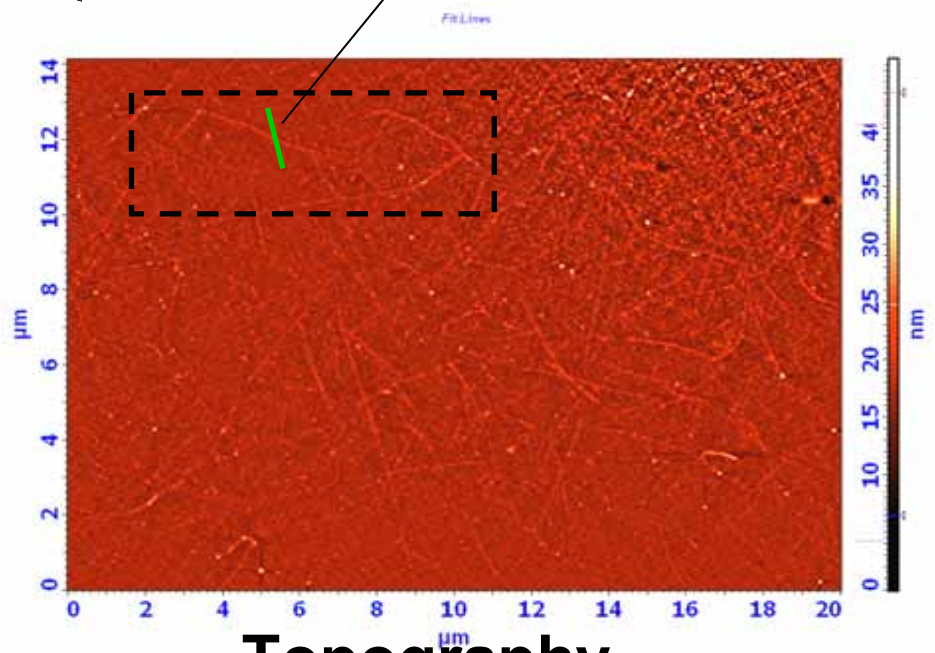


Confocal Raman image at 1593 cm^{-1} (G-band), 633 nm excitation

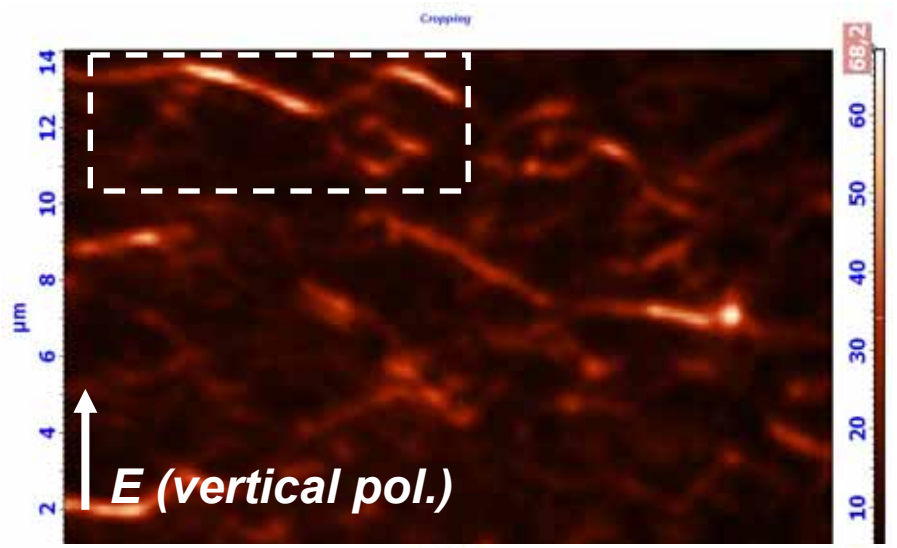
Image courtesy, Dr. I. Kudryashov, Tokyo Instruments

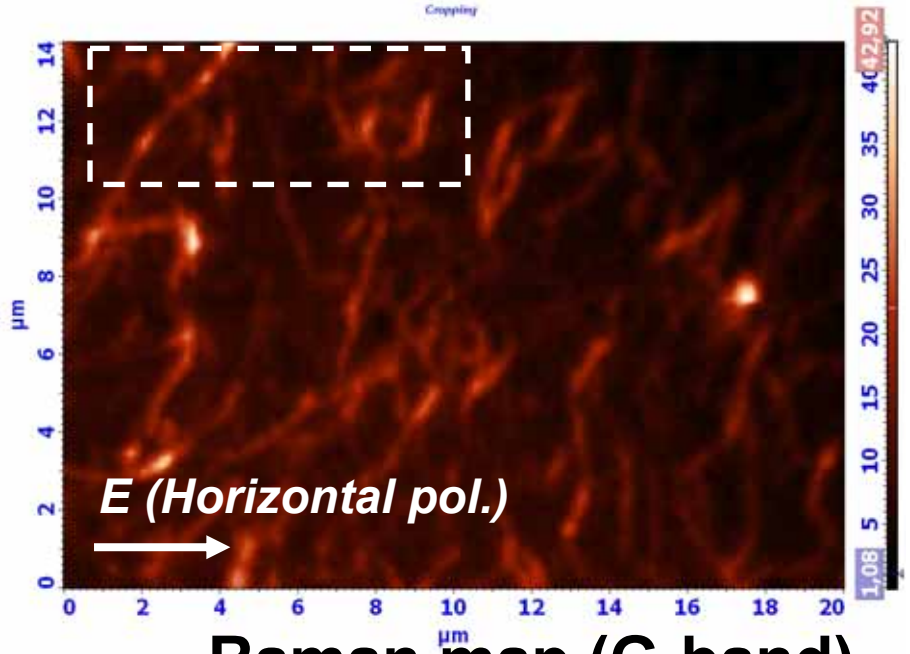
Sensing individual SWNTs on Si substrate





Topography



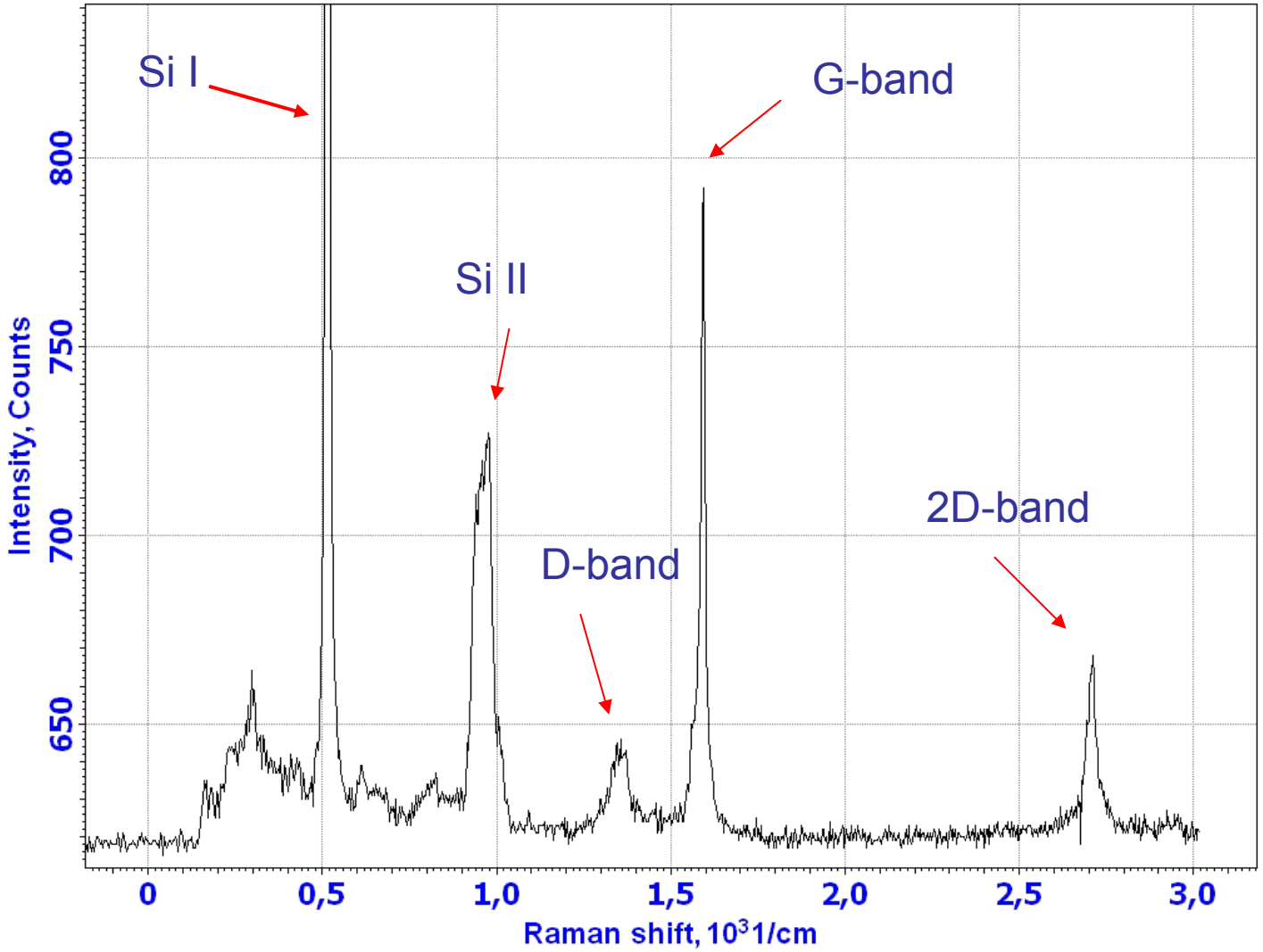


Raman map (G-band)

NT-MDT

Spectral integration time at 1 point : 100 msec

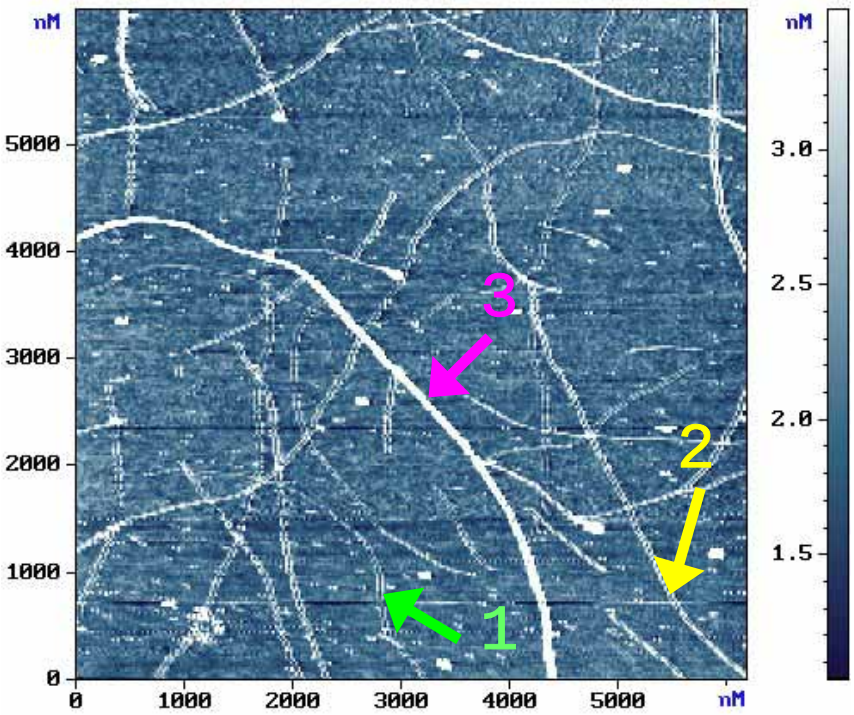
Sensing individual SWNTs on Si substrate



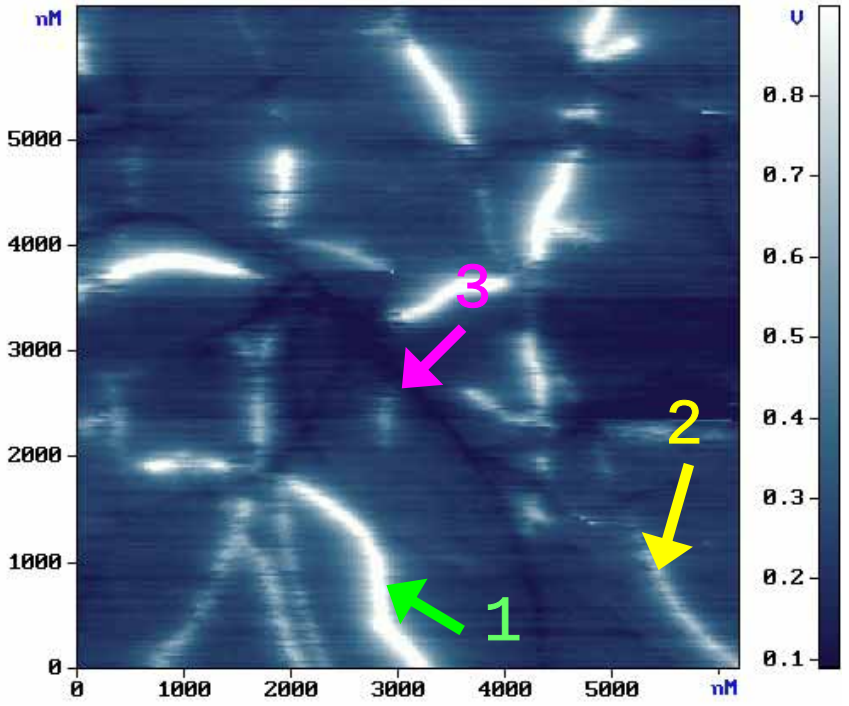
NT-MDT

Spectral integration time: 100 msec , laser wavelength : 473 nm

Carbon nanotubes: Work function mapping by Kelvin microscopy



Topography



SKM image

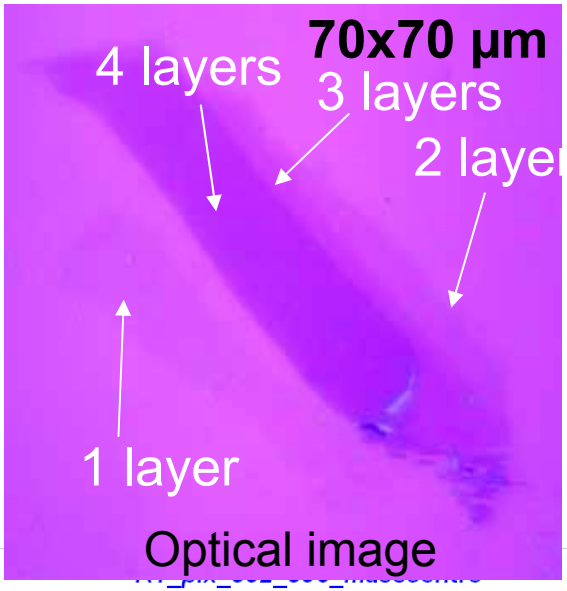
It should be noticed that SKM image reveals three kinds of nanotubes :

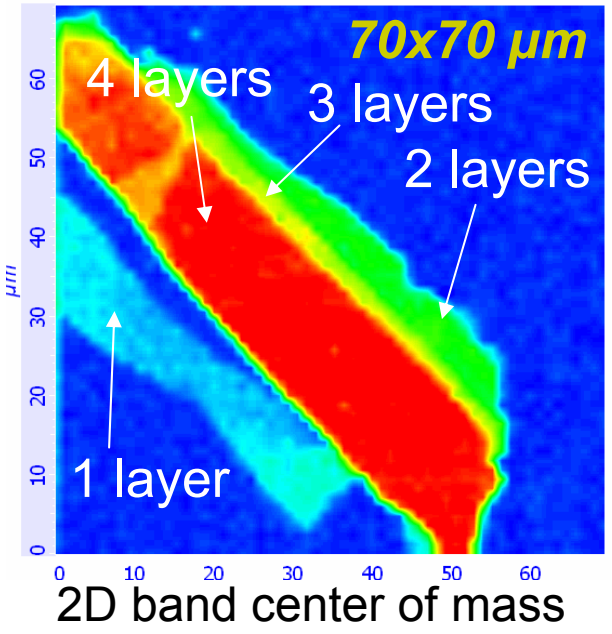
1) Nanotubes with electric potential about 1 V, these nanotubes have smallest diameter (about 1.5 nm)
2) Nanotubes with electric potential about 0.5 V which have diametr about 2-3 nm
3) Thickest nanotubes which give smallest contrast in SKM and have biggest diametr (4 nm)

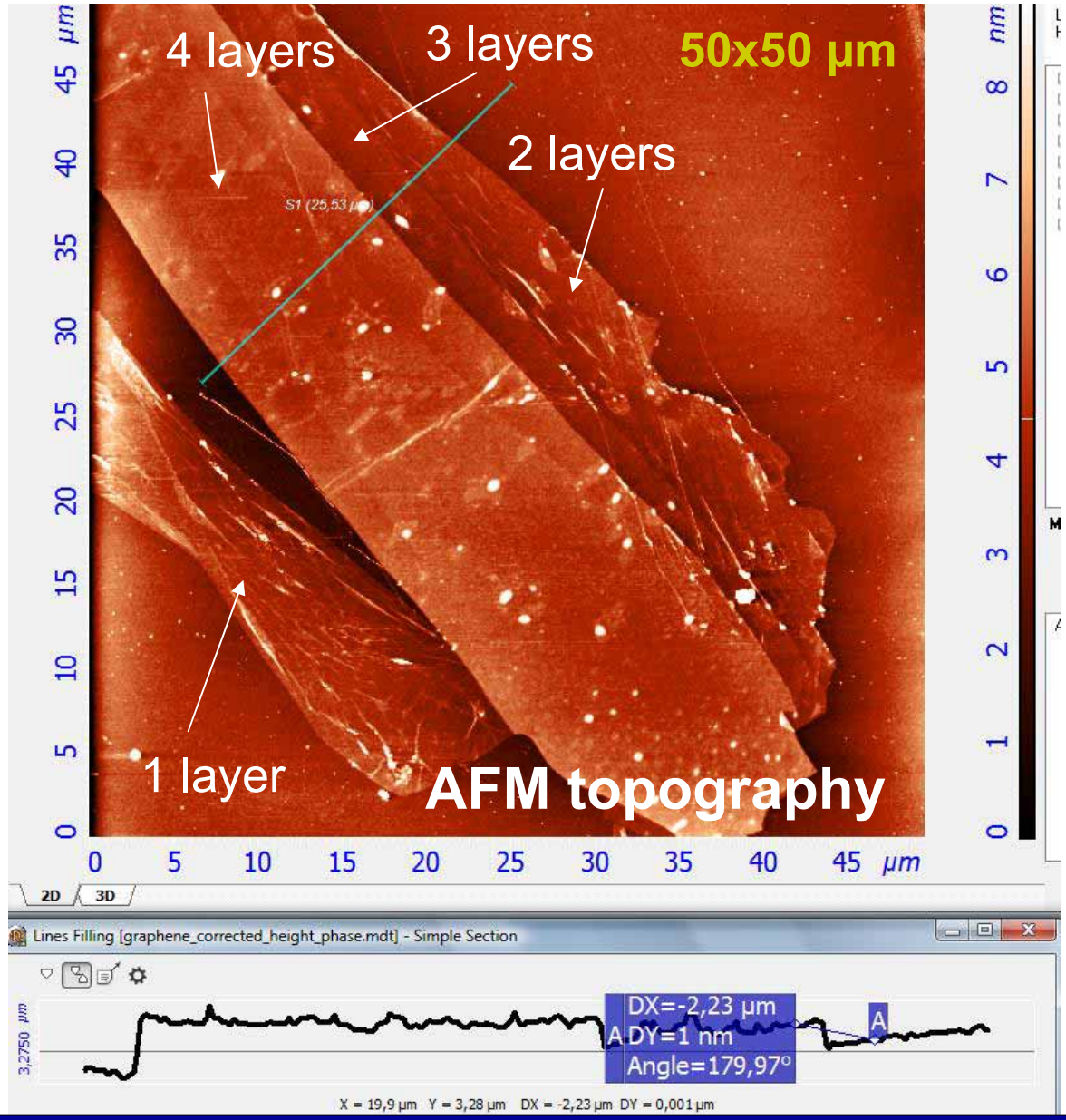
NTEGRA Spectra

AFM - Raman of Graphene

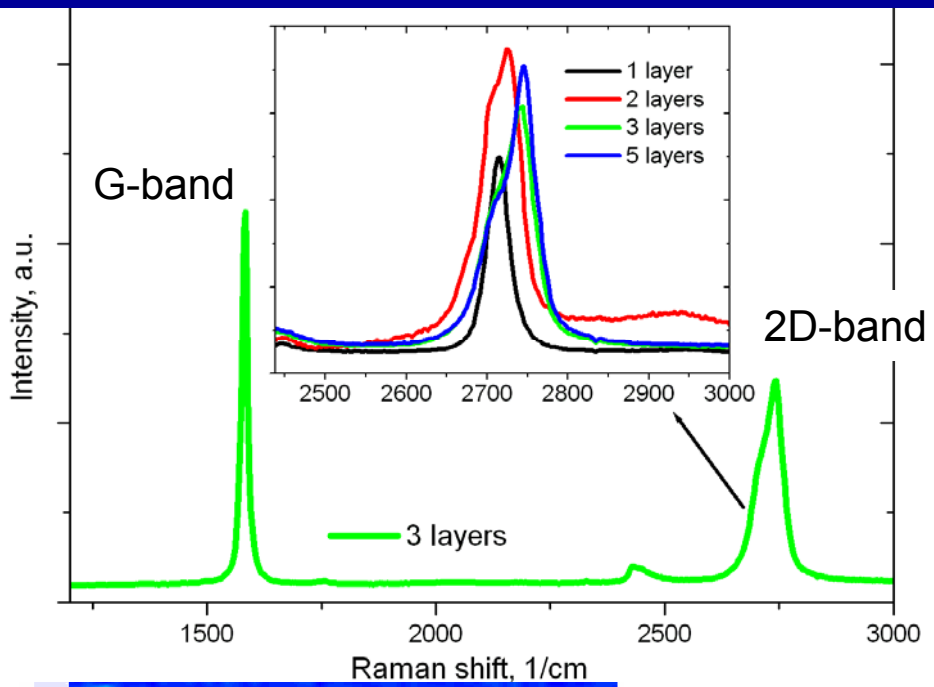
Graphene flakes: AFM & Raman microscopy

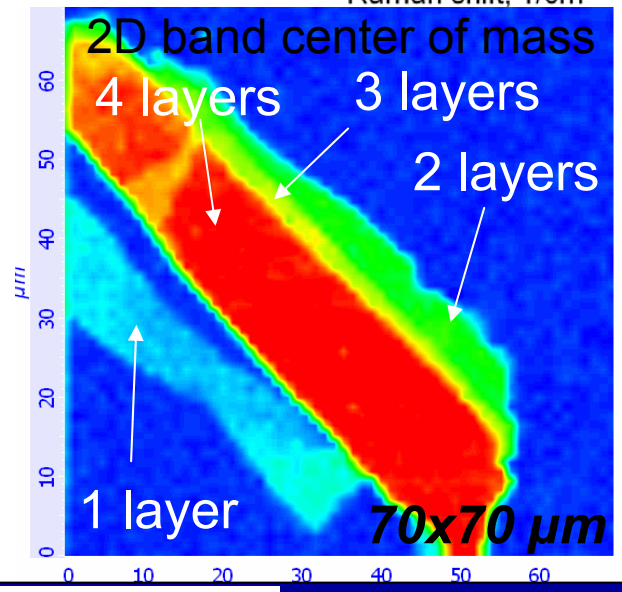




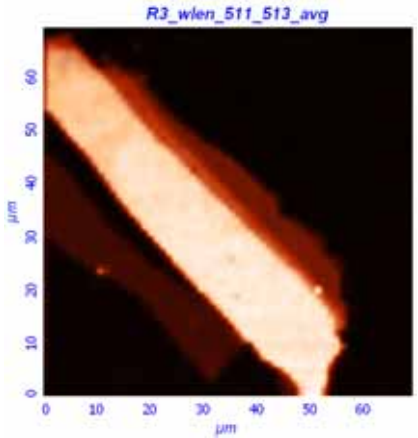


Raman spectroscopy of graphene flakes

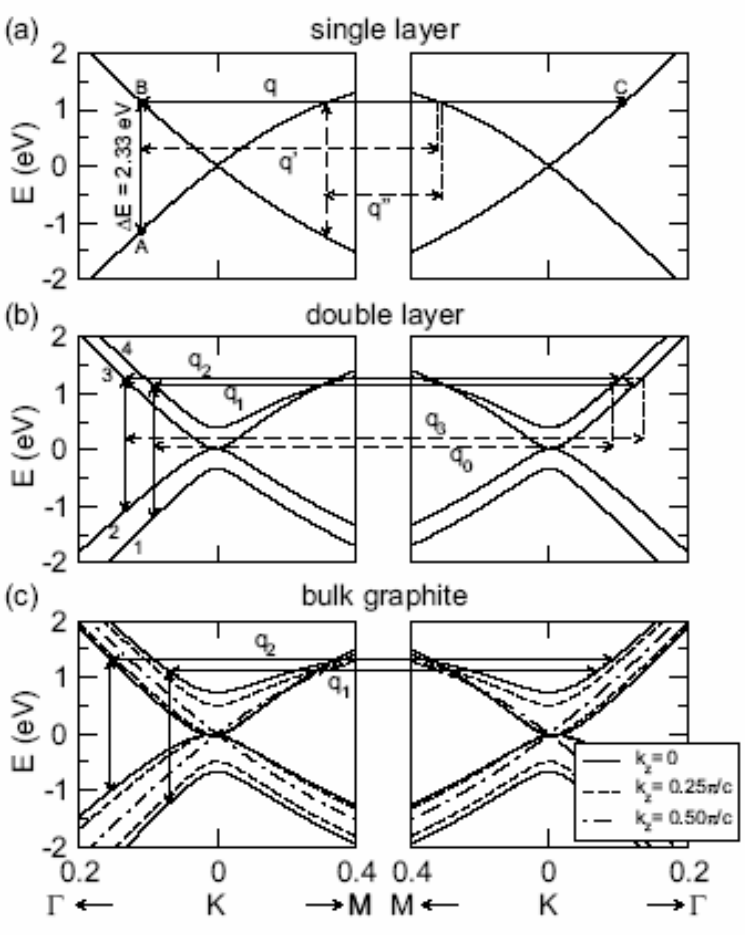




G-band intensity



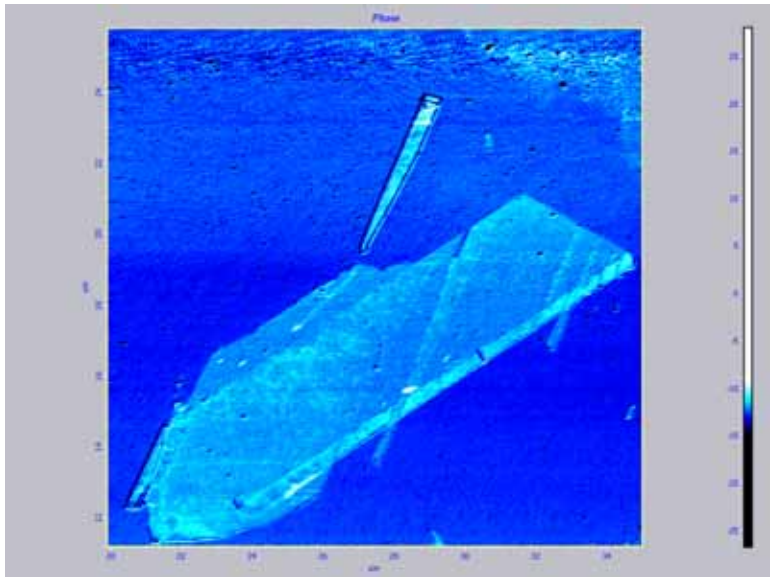
From: Davy Graph et al., 2006



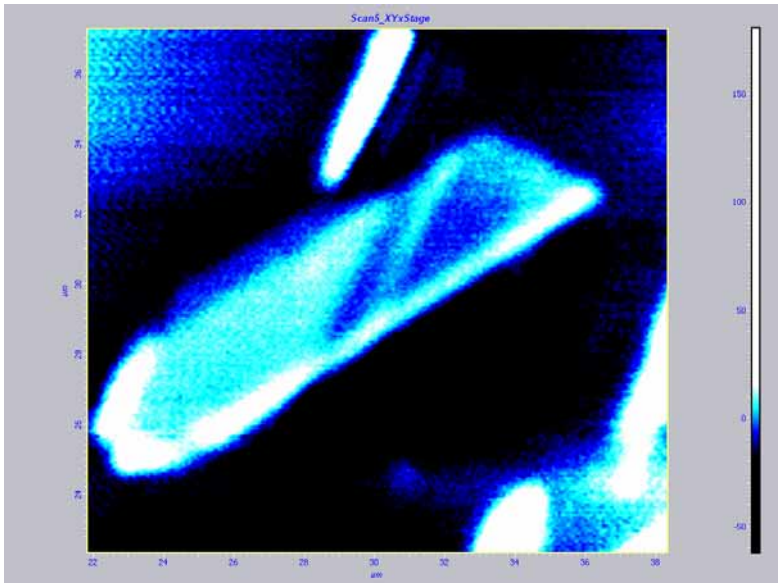
Double resonant Raman scattering – origin of 2D peak

Graphene flake #1 - confocal mapping

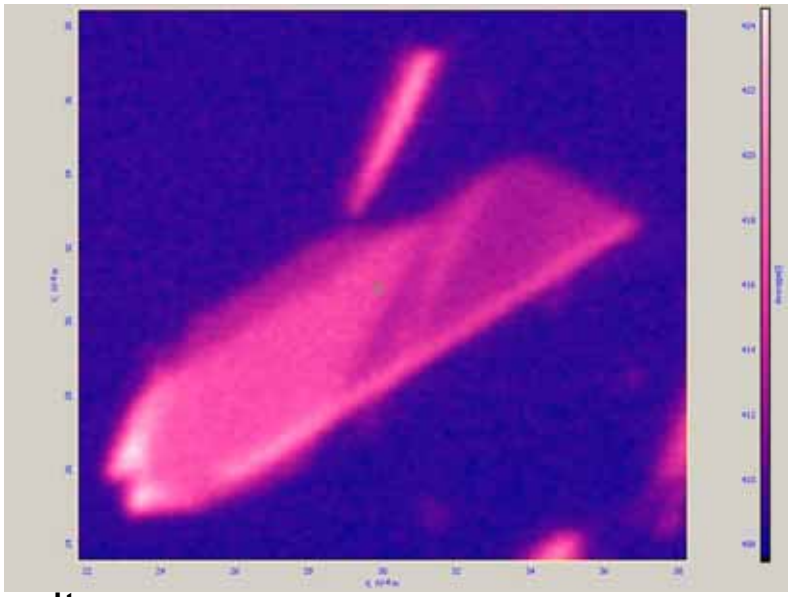
Scan size: 16x14 µm



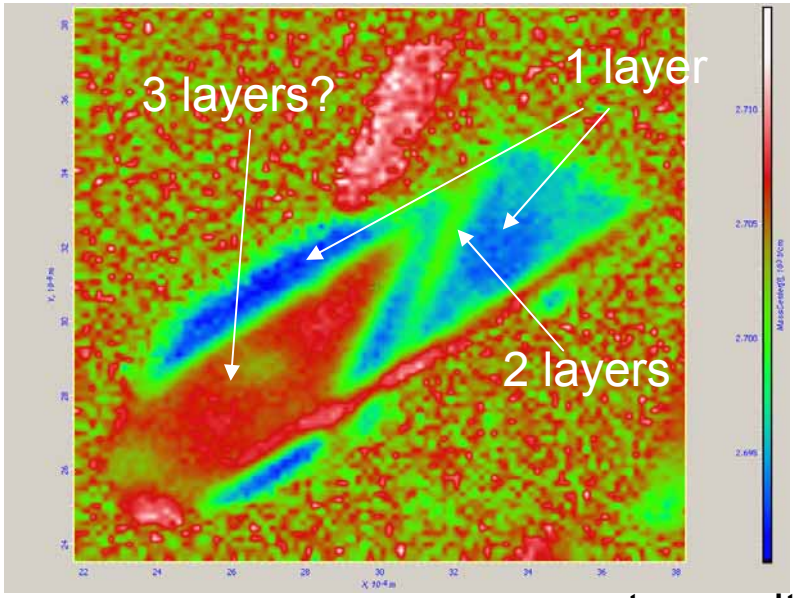
AFM Phase image



Confocal laser image, 633 laser



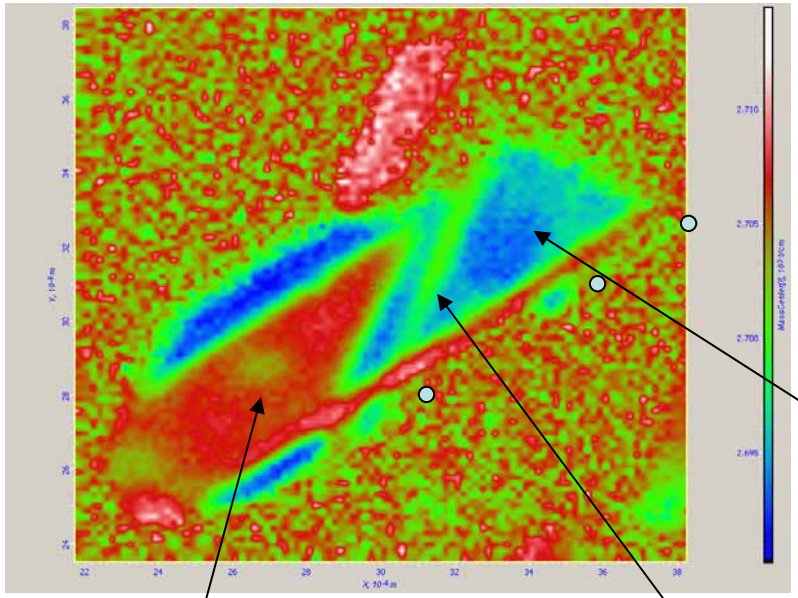
intensity

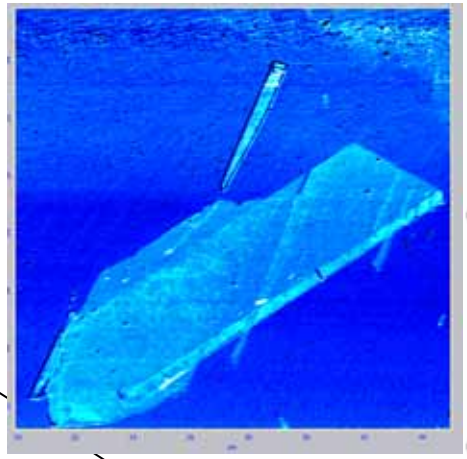


mass center position

Confocal Raman map, D*-line

Graphene flake #1 - point spectroscopy
633 nm laser, 2D band

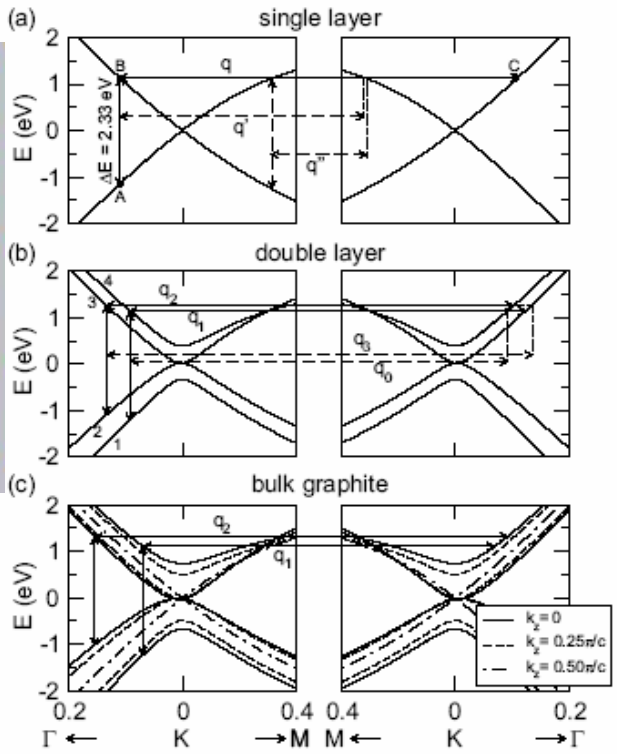


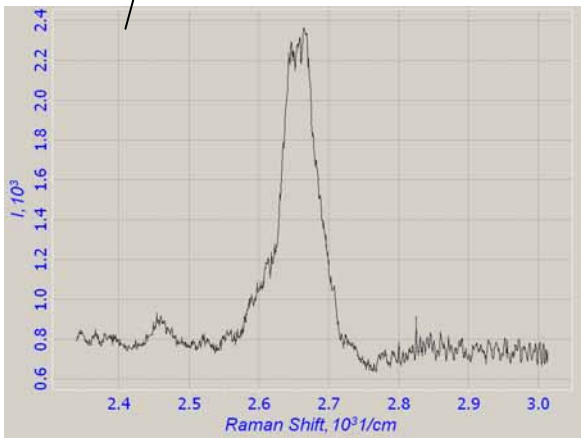


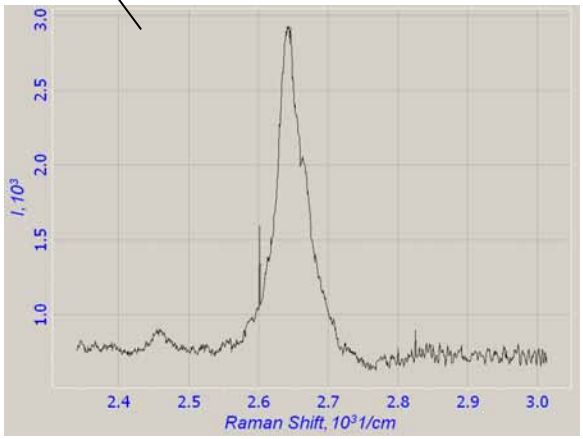
AFM

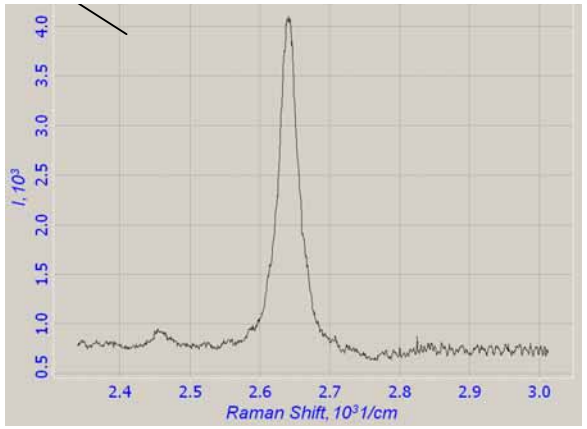
Raman map (center of mass of 2D band)

From: Davy Graph et al., 2006

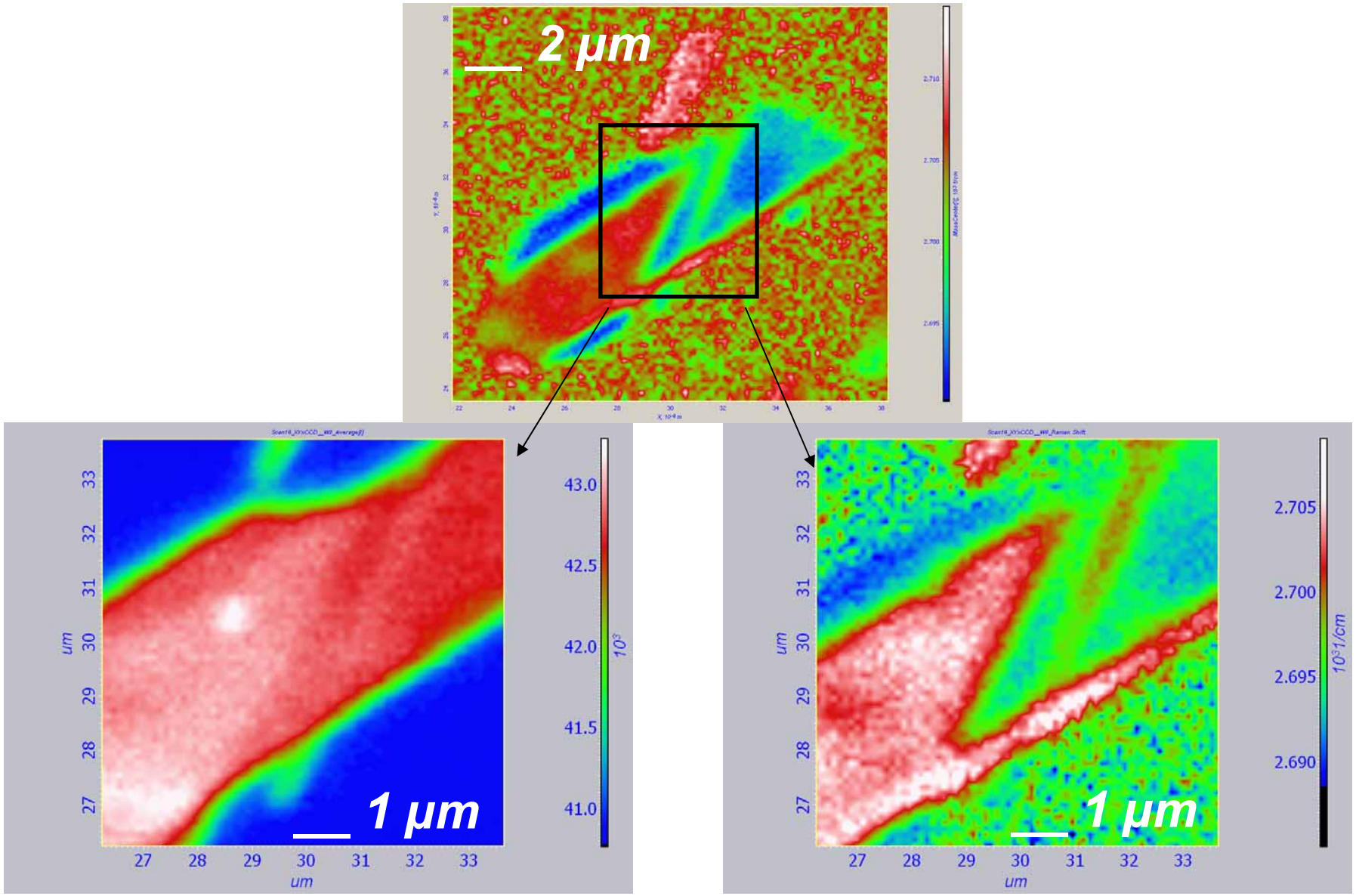








Graphene flake #1 - confocal Raman mapping



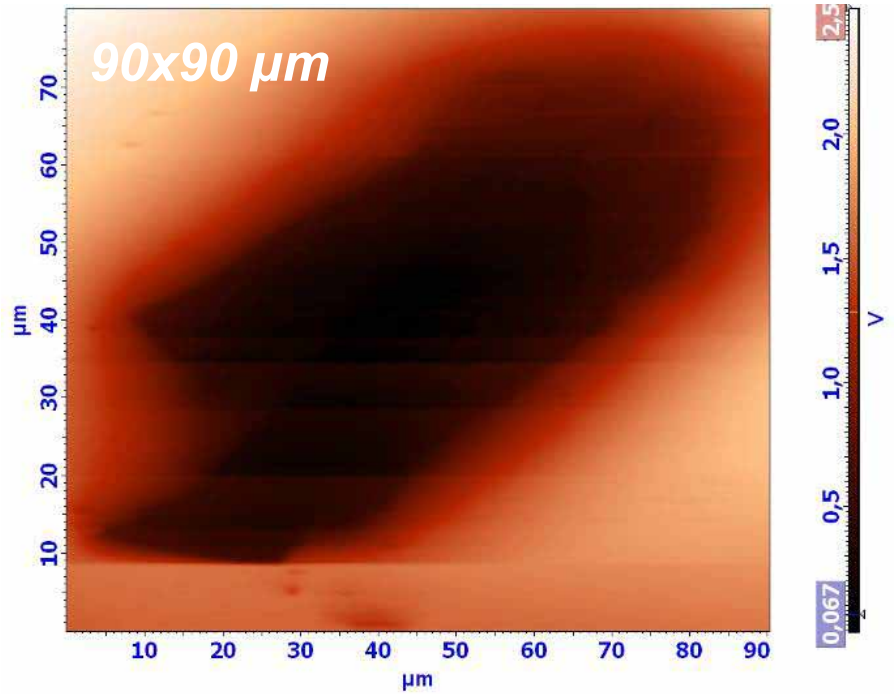
intensity

Confocal Raman map, D*-line

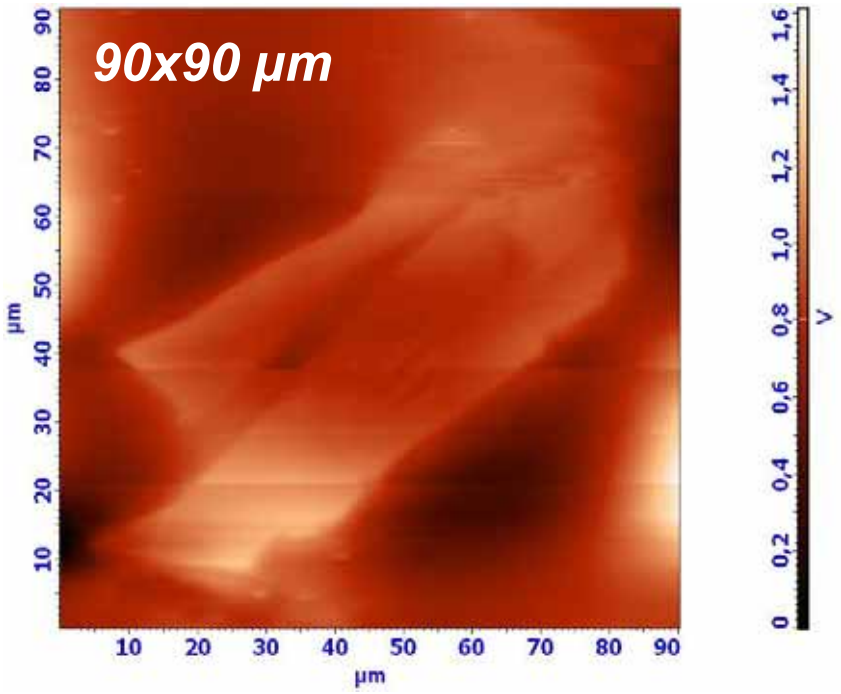
mass center position

Graphene, Scanning Kelvin Microscopy

SKM, graphen was negatively charged prior to scanning (-3V)

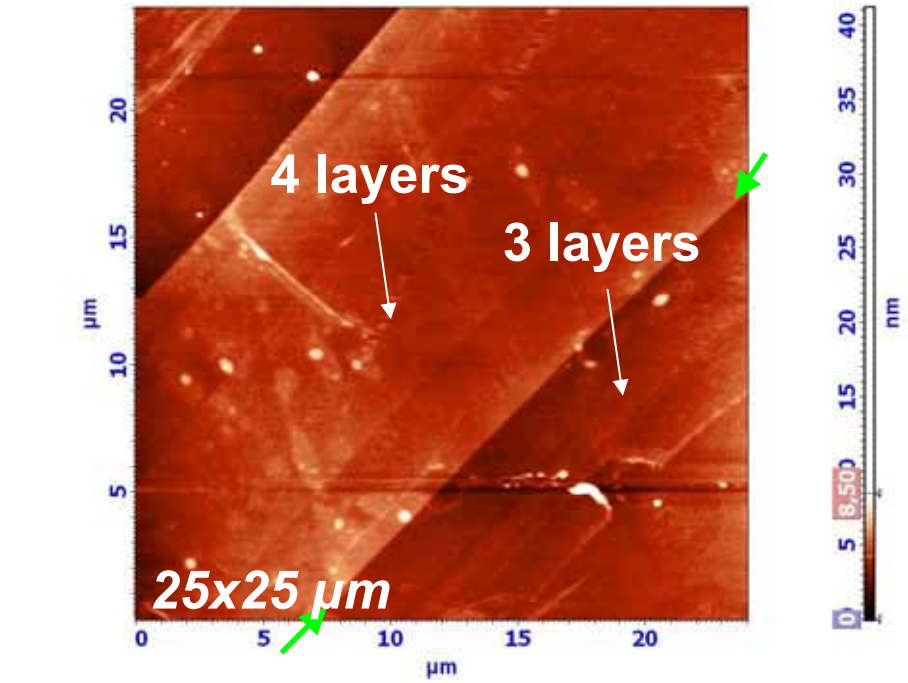


SKM, graphen was positively charged prior to scanning (+3V)

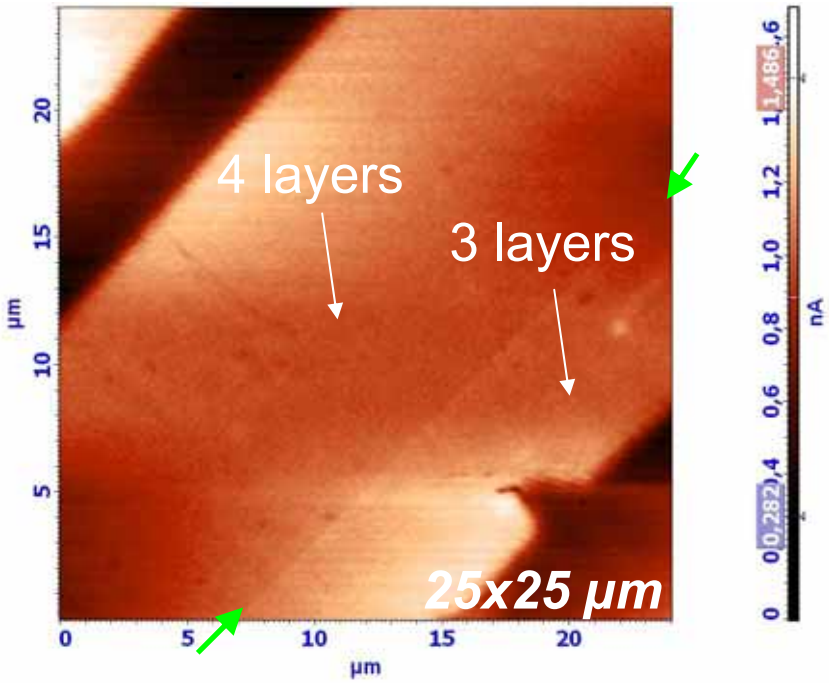


The flakes were charged by applying +/- 3V voltage with conductive cantilever to several points of the flake
Resulting charge is uniformly distributed across the flake

Graphene, Scanning Capacitance Microscopy



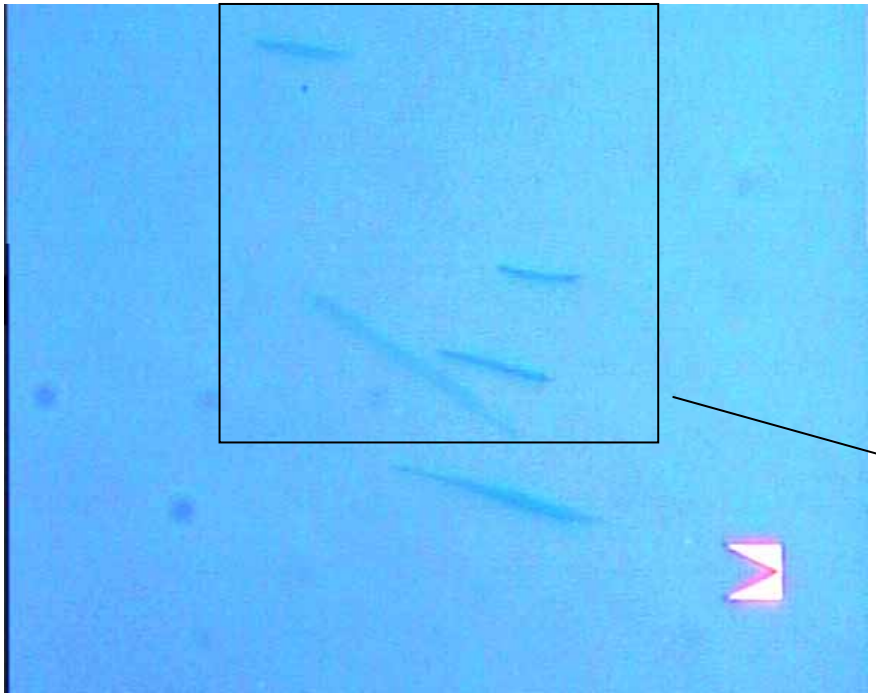
Height



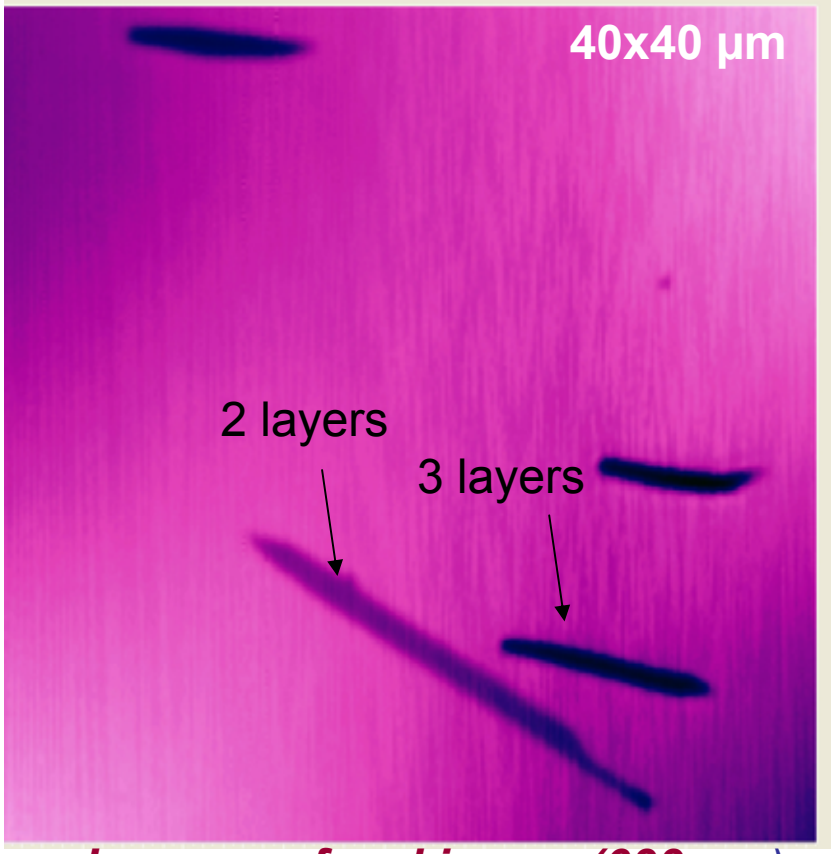
SCM

Boundary between different layers

Data courtesy, J. Smet, Max Plank Institute & Pavel Dorozhkin, NT-MDT



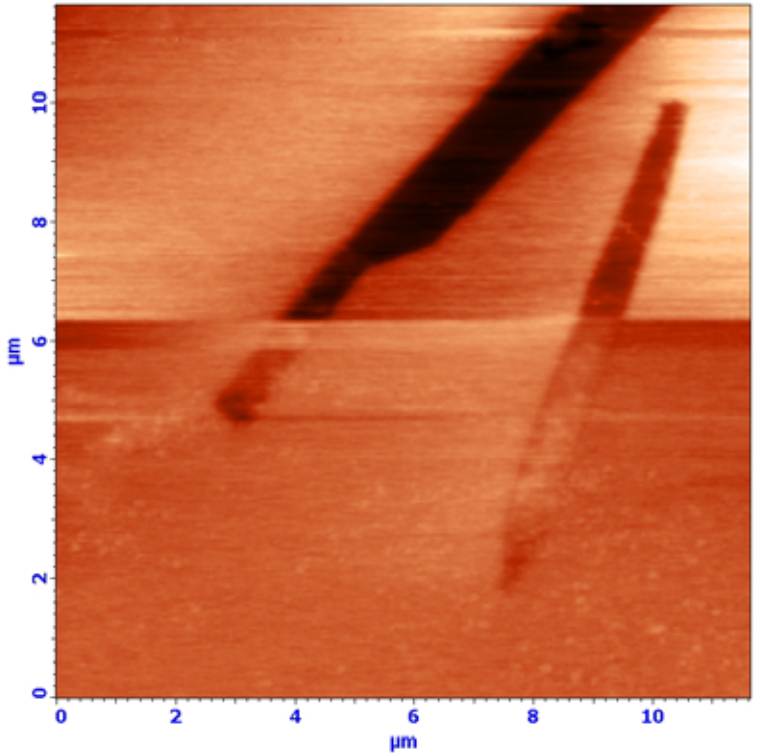
Optical image, made through 100x objective. Both 2-layer and 3-layer flakes are seen



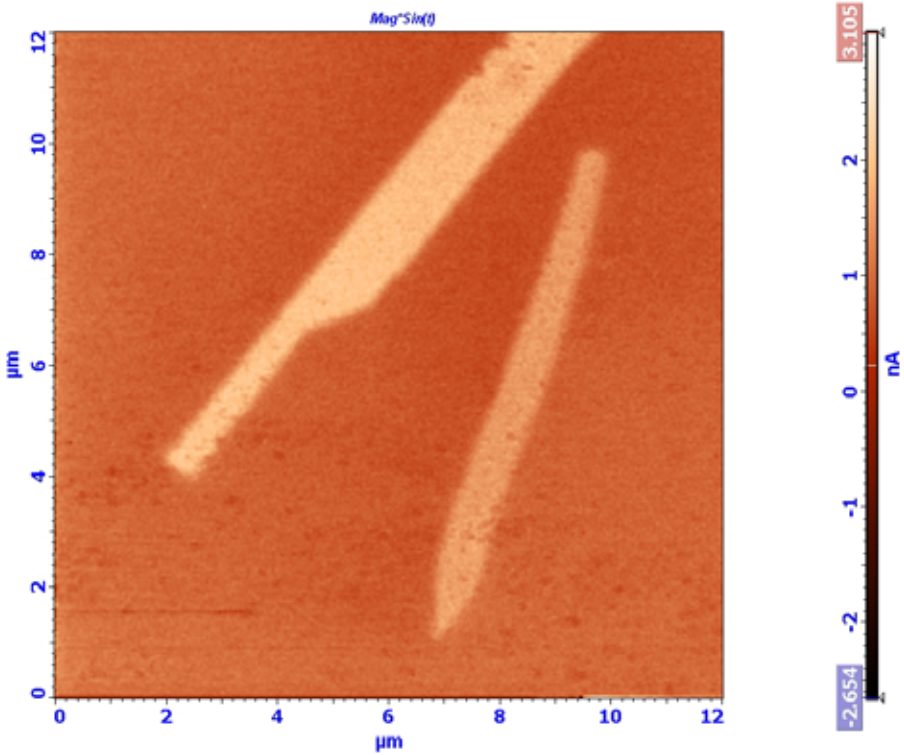
Laser confocal image (633 nm)
High contrast of double and triple layer graphene is observed. Good contrast for single layer graphene is expected

Confocal laser imaging with 633 nm laser proved to be the fastest and most efficient way to find single layer graphene flakes on Si/SiO2 substrate

Kelvin Probe Microscopy & Electrostatic Force Microscopy



SKM image
Flake potential is not constant - sudden recharging can occur



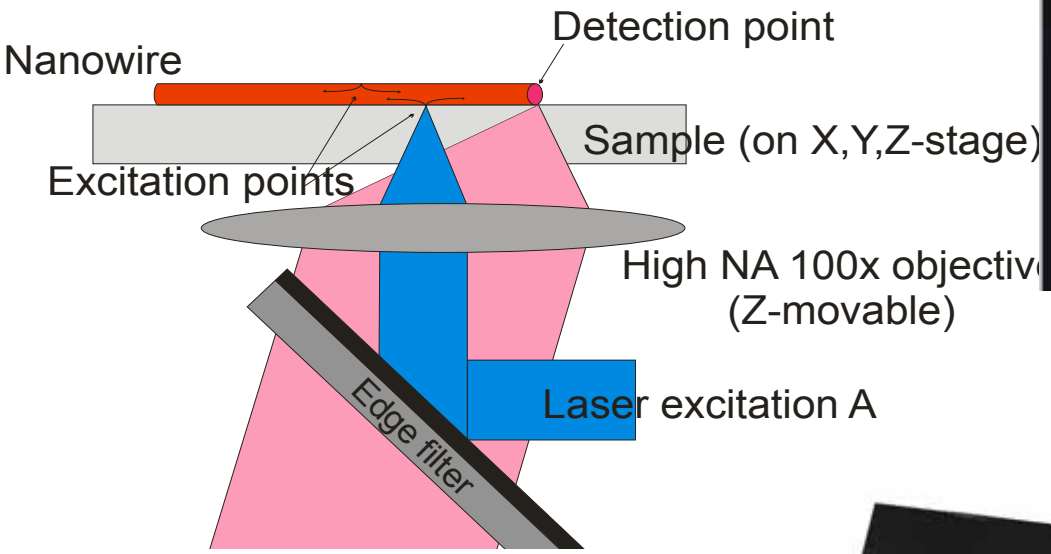
EFM image

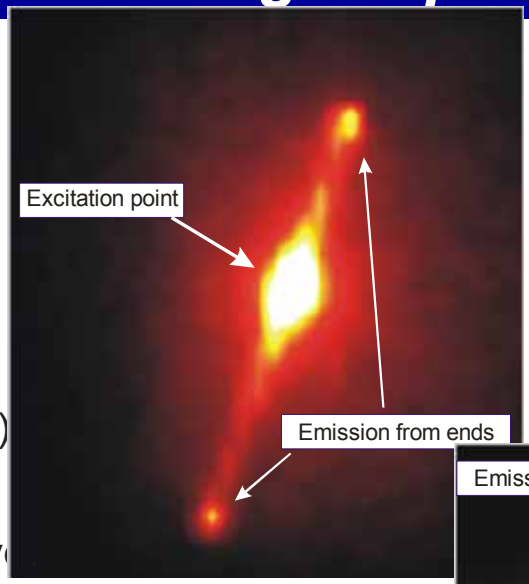
Data courtesy, J. Smet, Max Plank Institute & E. Kuznetsov, NT-MDT

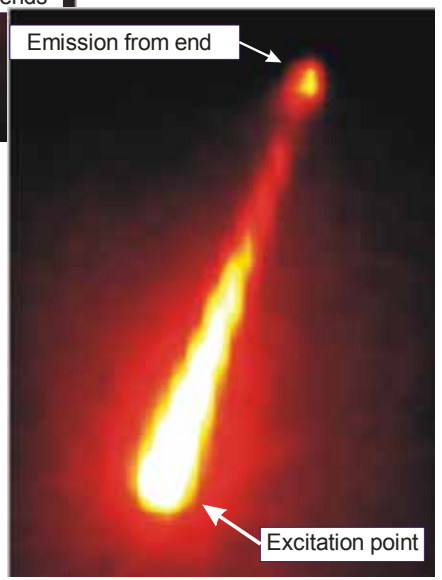
NTEGRA Spectra

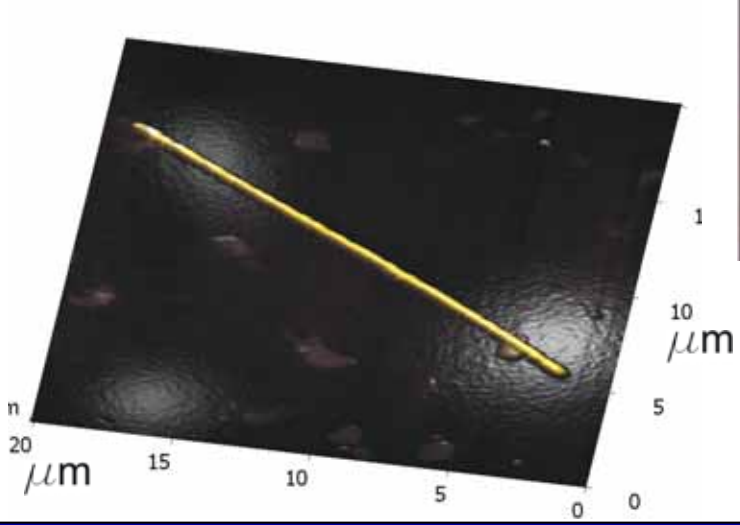
Light transport in nanostructures

Light Transport studies with NTegra Spectra

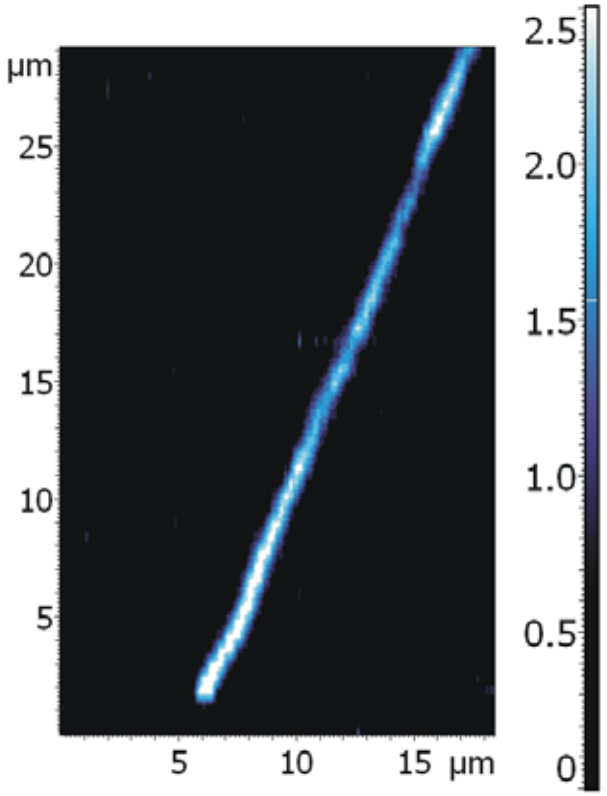


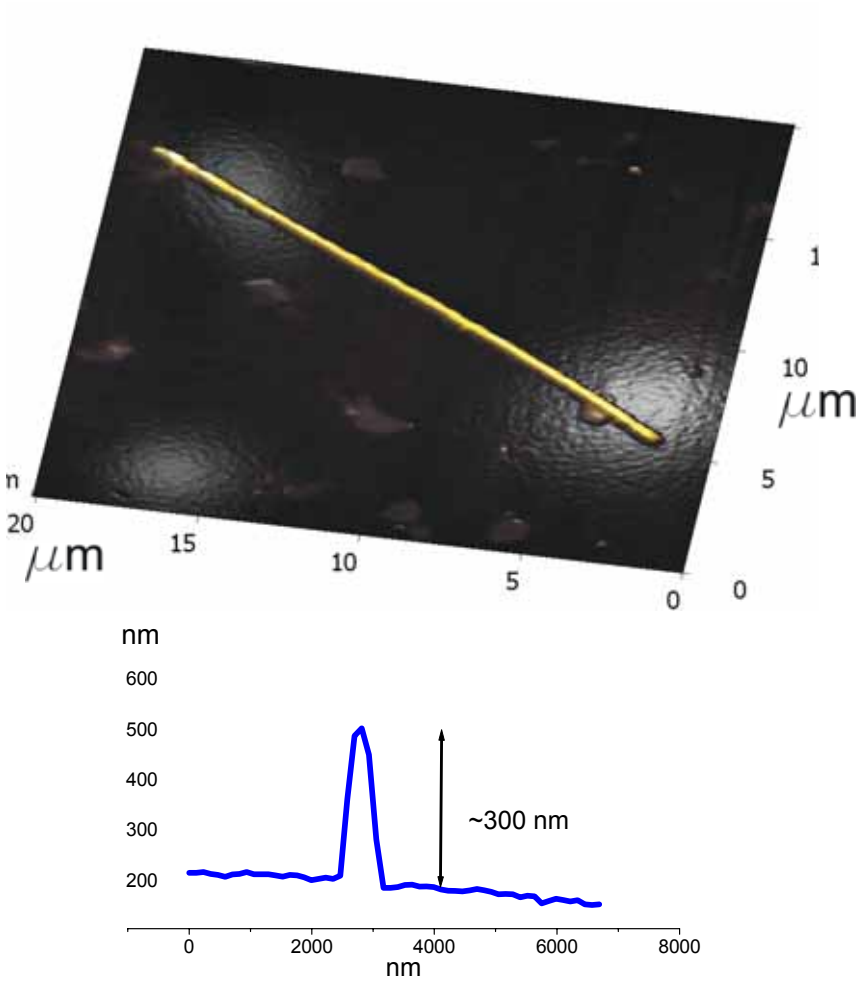






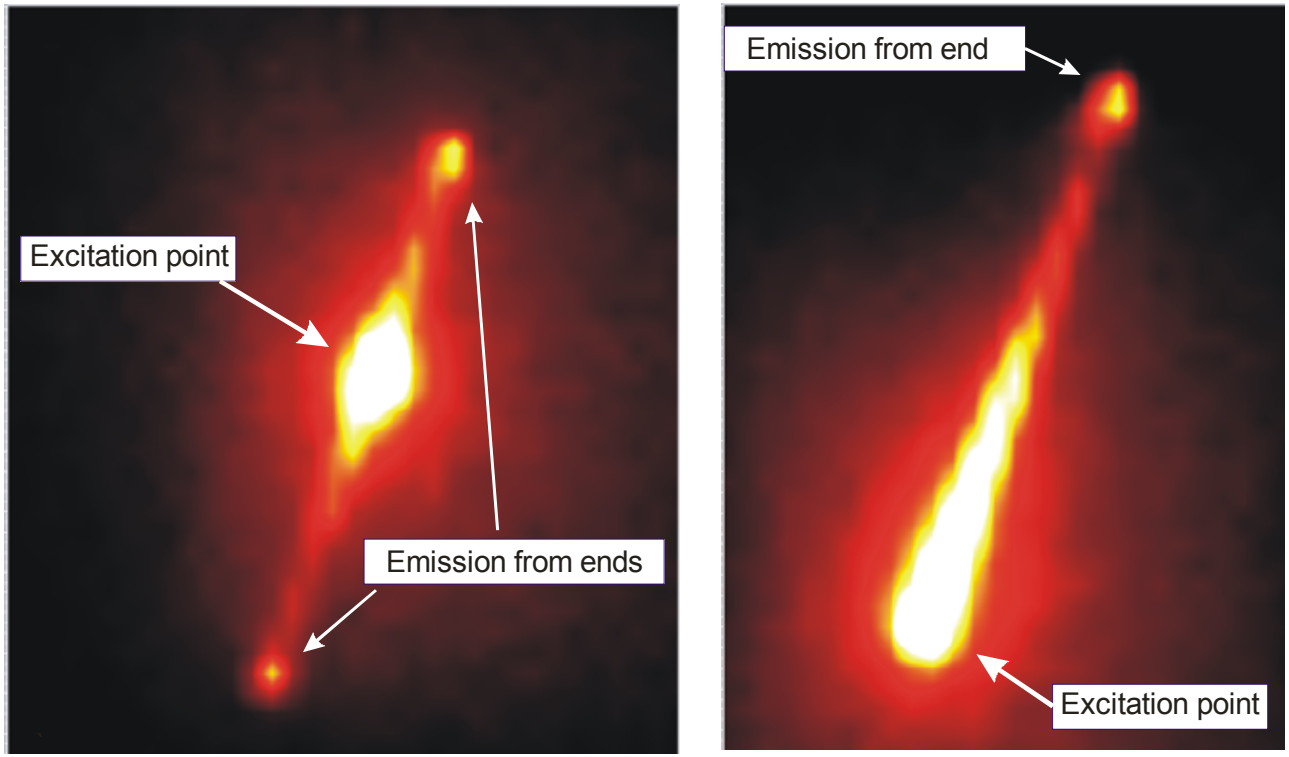
Light Transport studies with NTegra Spectra





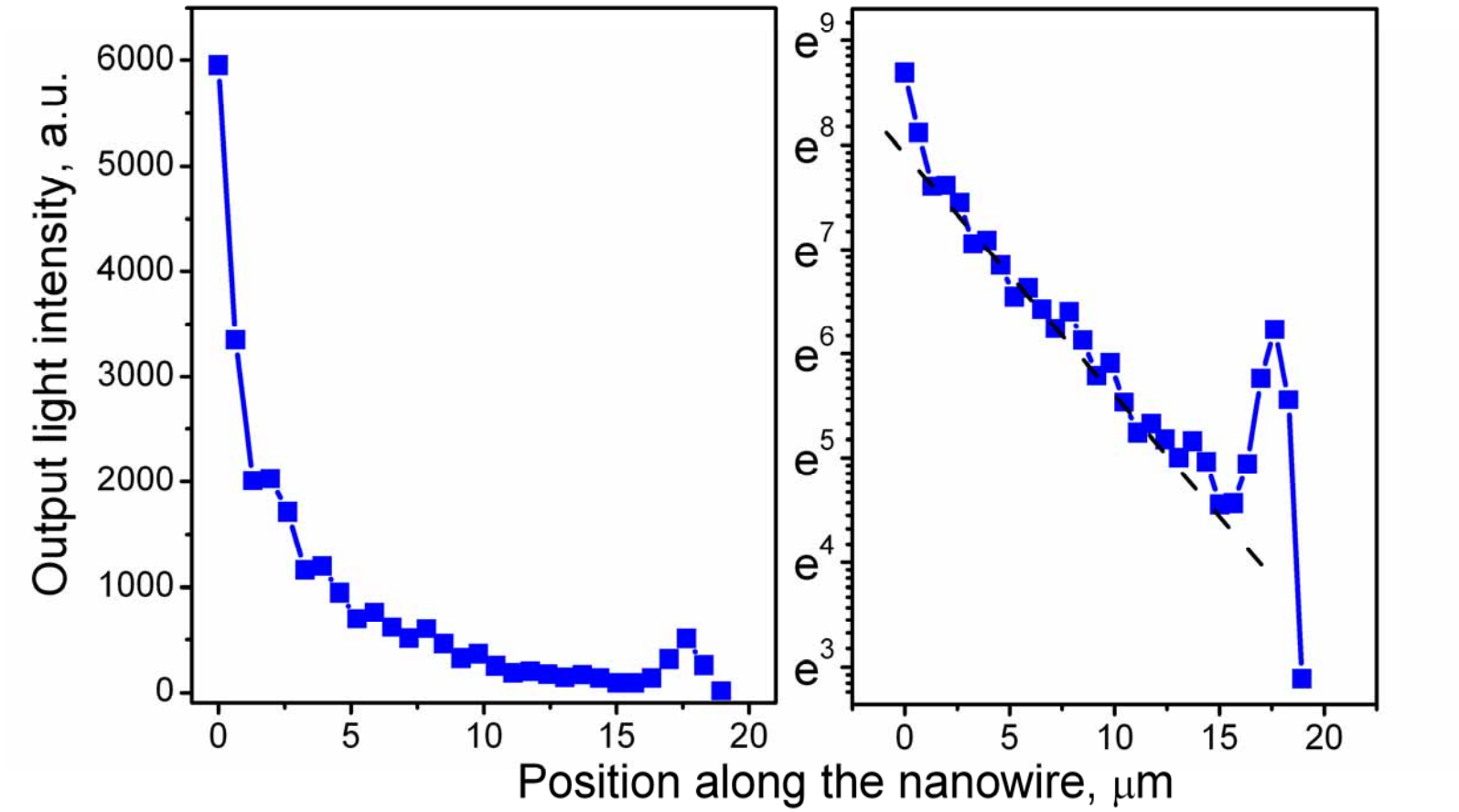
Confocal fluorescence image (660-800 nm) and AFM image of the nanowire

Light Transport studies with NTegra Spectra



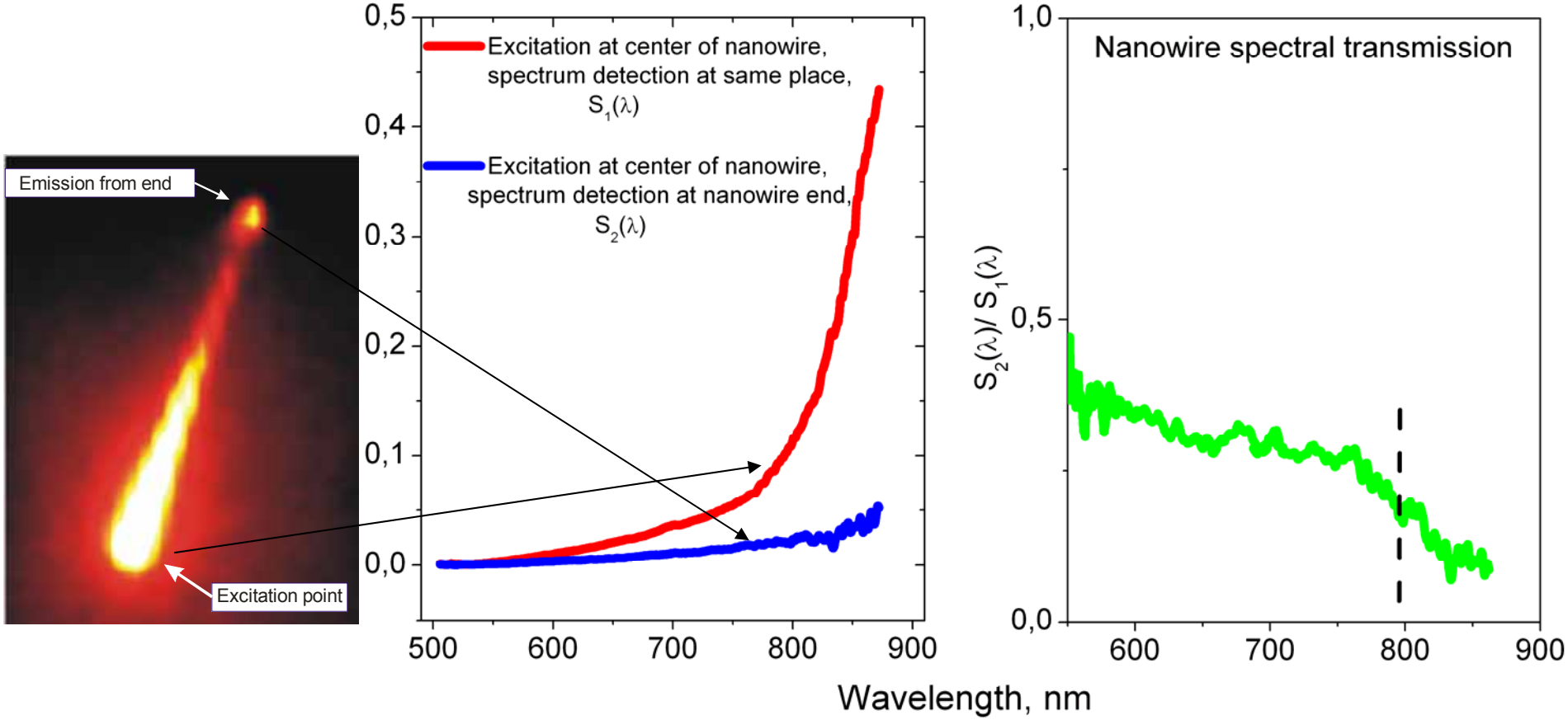
Nanowire is excited by 488 nm light at the body (left image) and at the left end (right image). Excitation green light is completely cut off from the image by two edge filters (with 10-6 transmission).
Part of the nanowire radiation (>10%) is transmitted through the nanowire and is emitted from nanowire ends.

Light Transport studies with NTegra Spectra



Emission intensity distribution along the nanowire, excited at the left end

Light Transport studies with NTegra Spectra

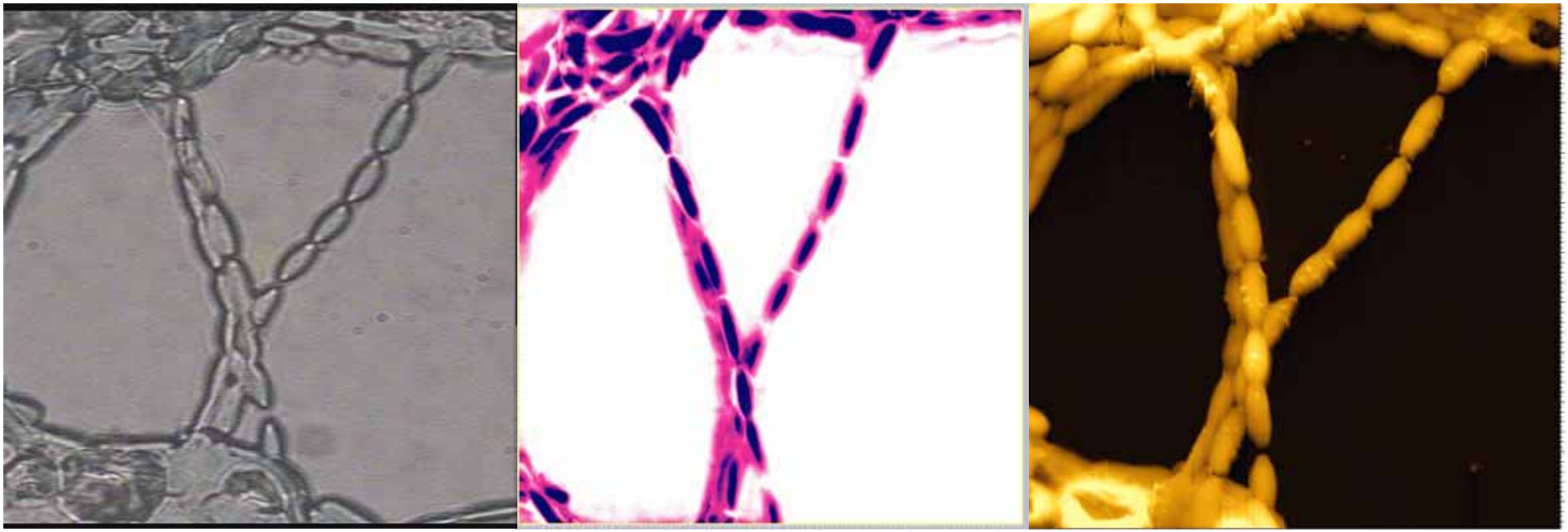


Nanowire is locally excited at the center. Red curve shows spectrum taken at the excitation point [in the middle of the nanowire]. Blue curve is the transmitted light spectrum taken at the right nanowire end. Green curve shows spectral transmission function of the nanowire

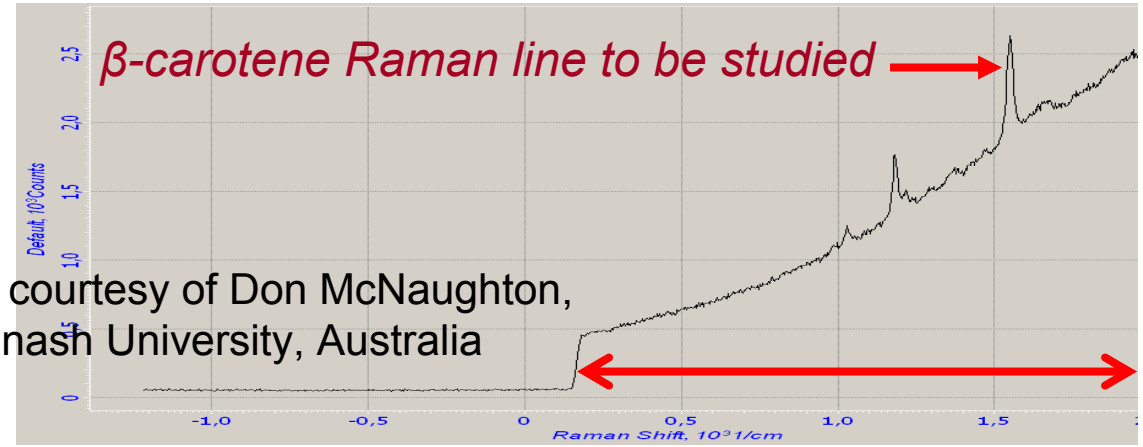
NTEGRA Spectra

Beta-carotine distribution in algal cells

Beta-carotine distribution in algal cells



Optical image | Confocal Laser | AFM topography



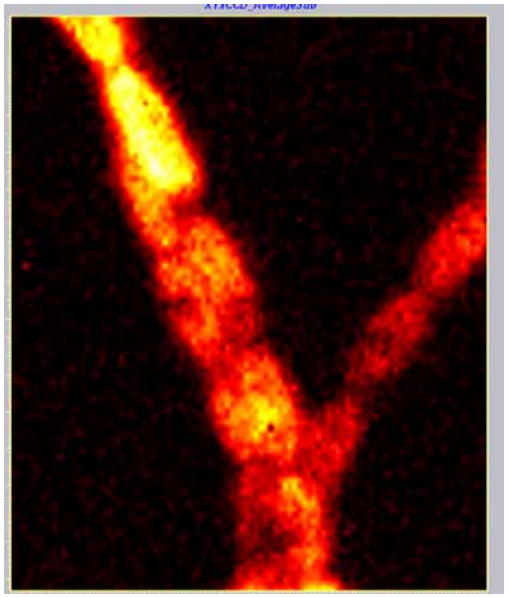
Sample courtesy of Don McNaughton,
Monash University, Australia

Tail of luminescence (centered at ~630 nm)

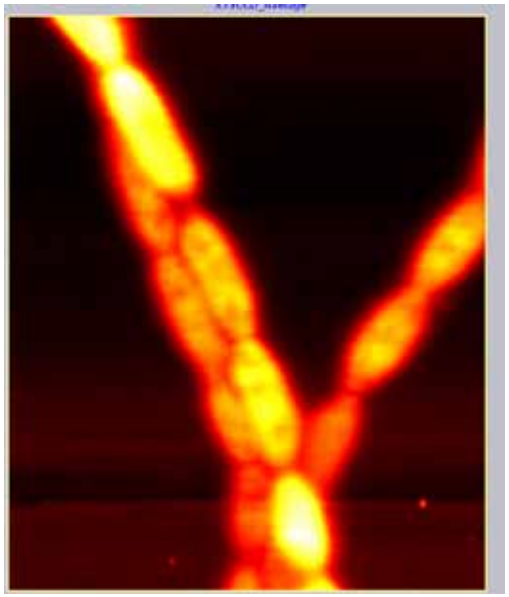
Beta-carotine distribution in algal cells

Laser power: 0.02 mWt

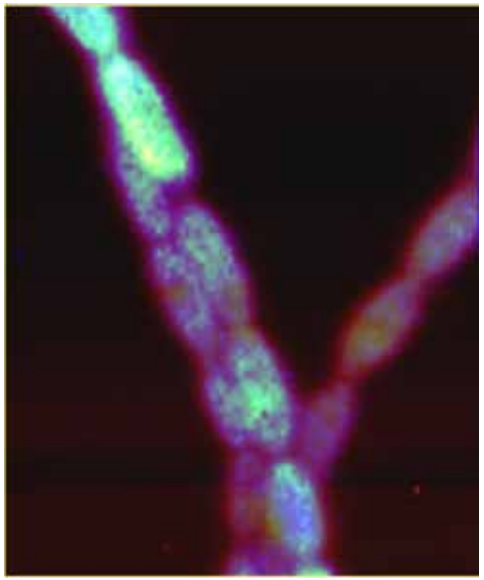
Scan size: 25x25 μm



Raman line (1548 cm^{-1}) map



Luminescence map

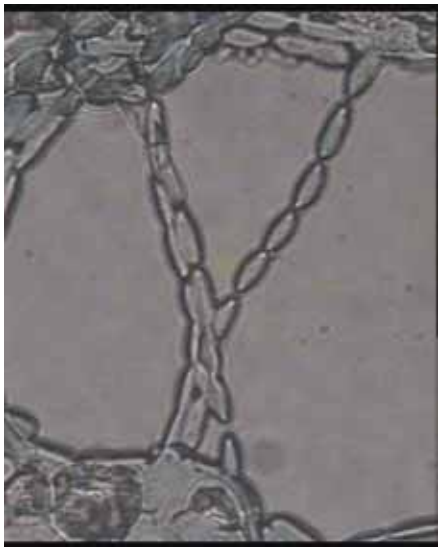


Luminescence (yellow) & Raman (blue)

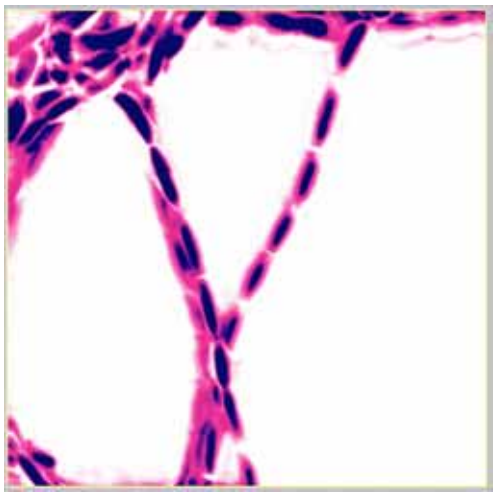
At low laser power, Raman and luminescence maps show nearly identical intensity distribution

N.B. All three Raman lines of β-carotene show the same distribution along the sample - only their intensity is different

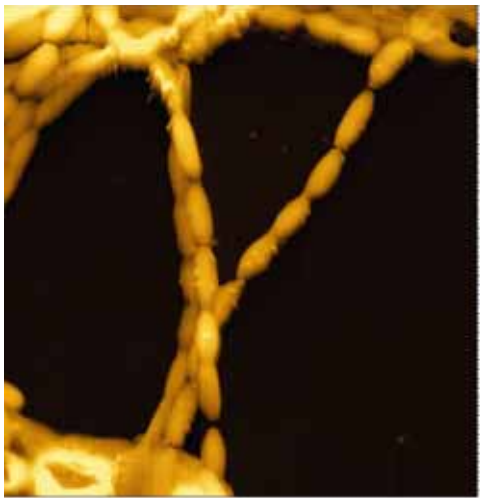
Confocal laser & Raman, AFM and direct images of the same algal cells structure



Optical microscope image (with 100x objective)

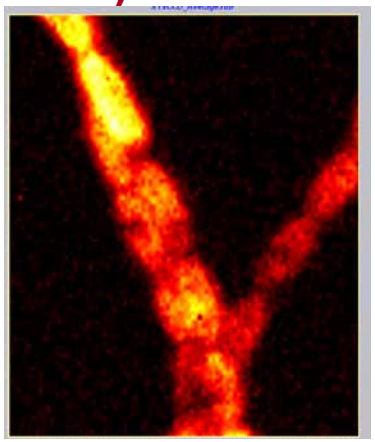


Confocal laser image

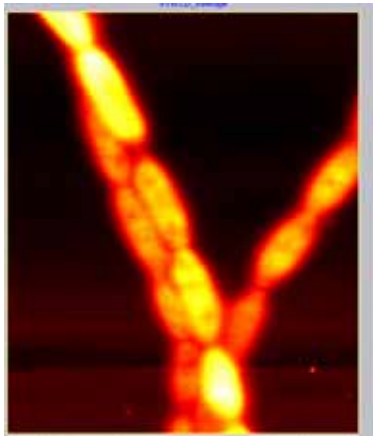


AFM-image

Image size:
25x25 µm



Raman map



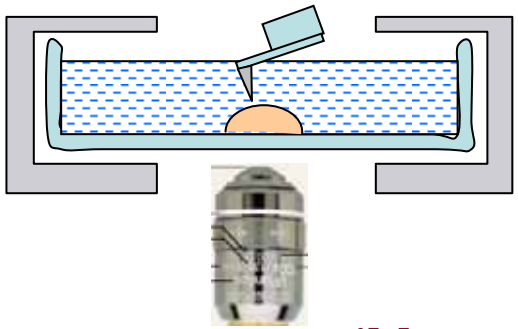
Luminescence map

Magnetic-,
Kelvin-,
Electrostatic-
Acoustic Force-
Capacitance –
Spreading resistance …
Sacnning Probe images

NTEGRA Spectra

Measurements in liquid

AFM + Raman + SNOM in liquid

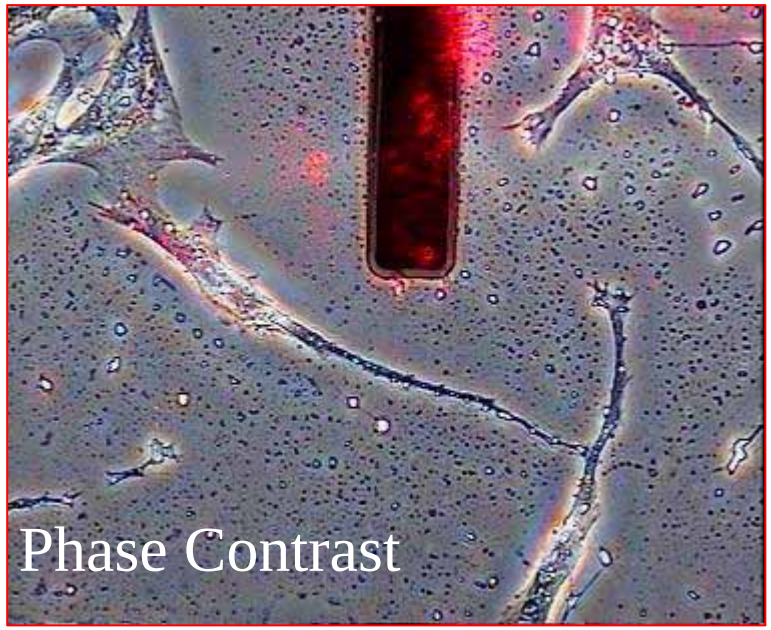


NT-MDT Closed-liquid cell with heating

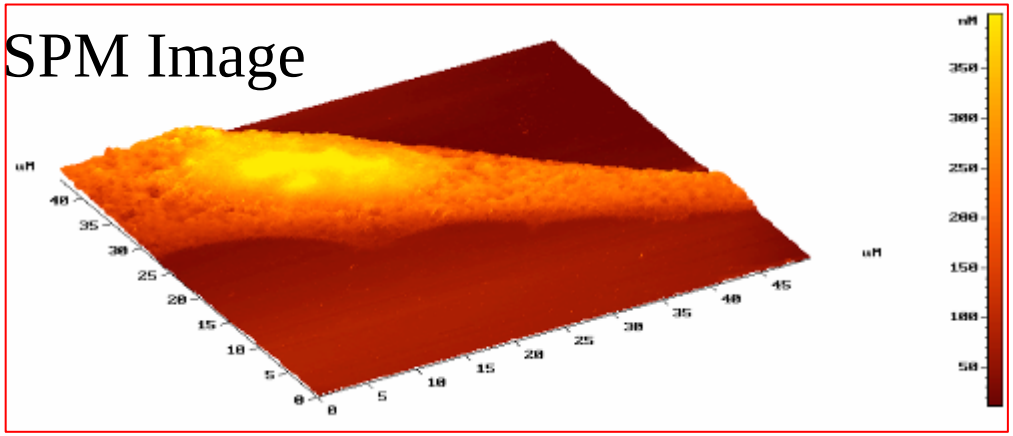
Possible to use with AFM + SNOM + Confocal Raman (Confocal fluorescence), work with living cells. Flow-trough possibility.

WORKS WITH AFM/SNOM/ RAMAN (INVERTED)

Transparent samples observations

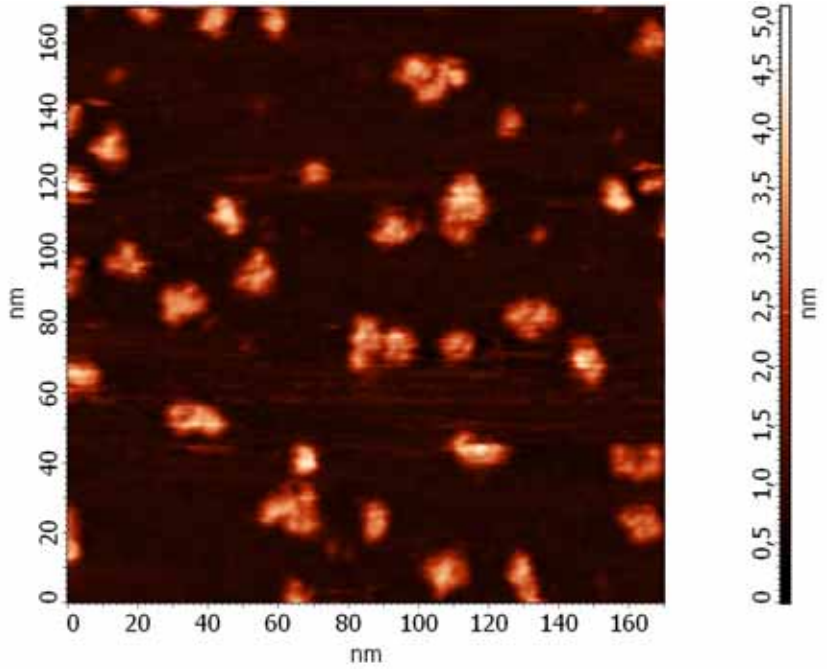


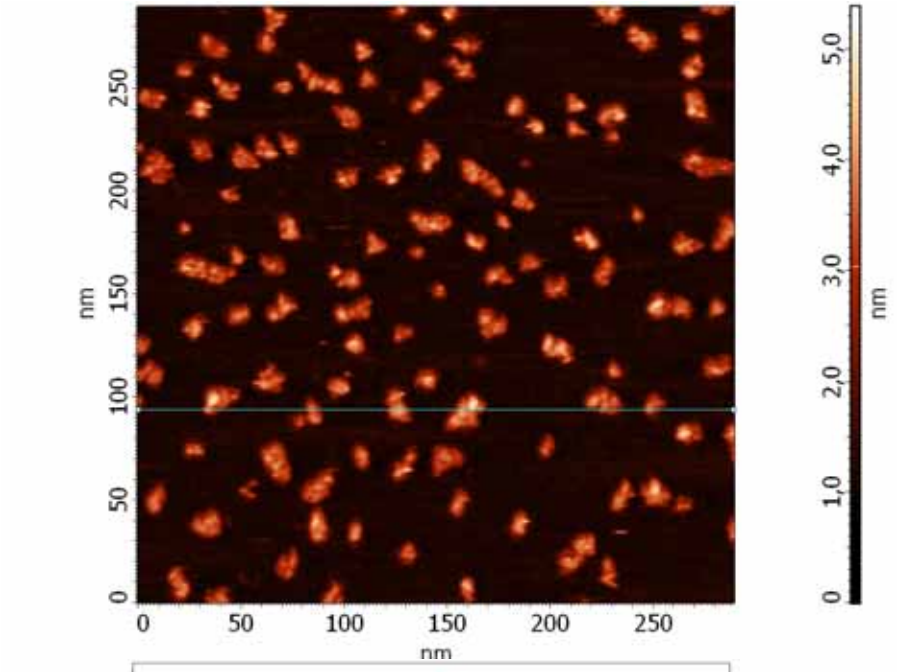
Optical images of **human embryo fibroblast** cells obtained during AFM scanning process

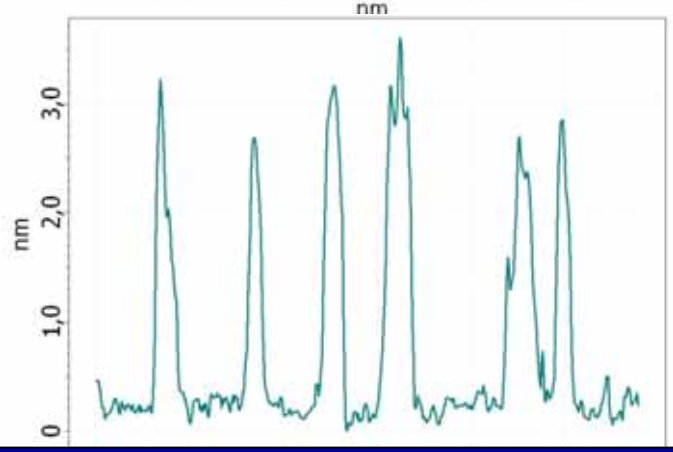


AFM in liquid

Proteins in buffer solution

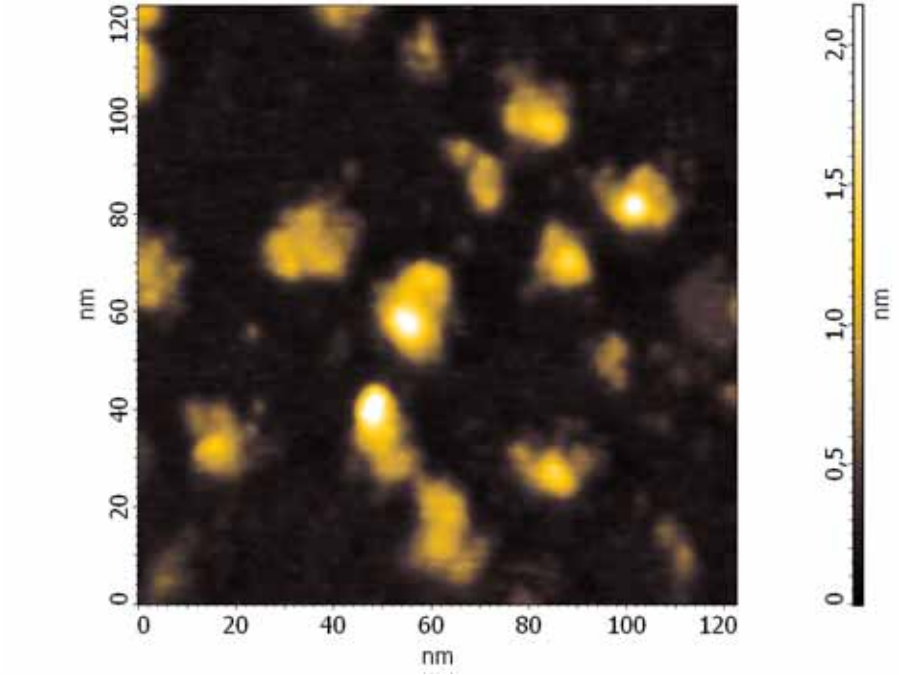


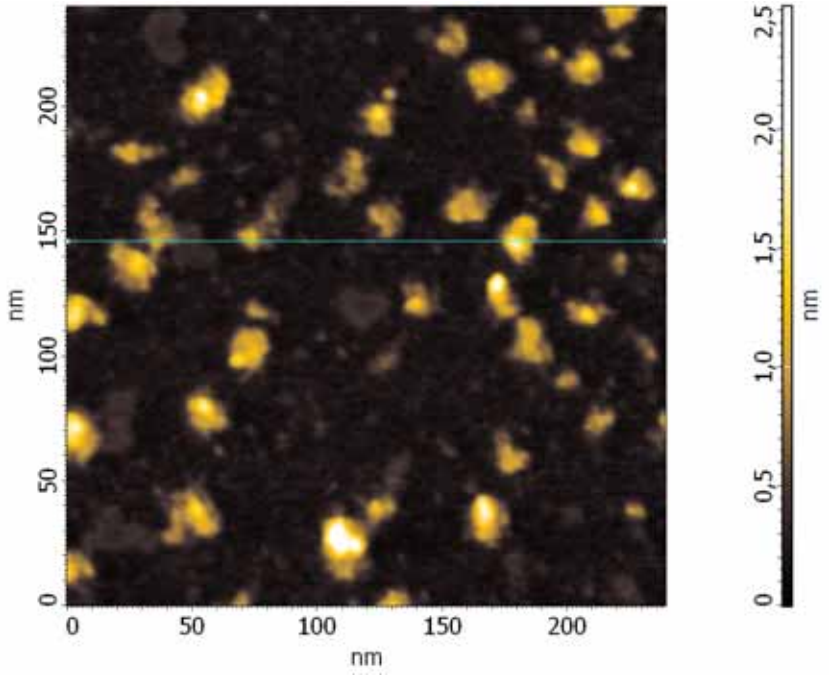


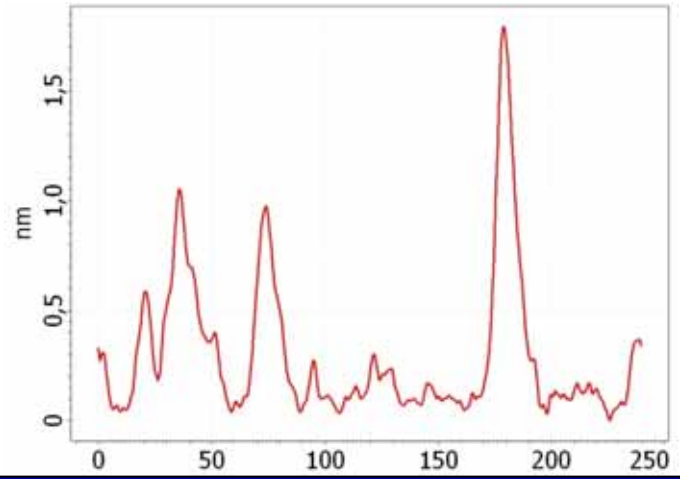


Data measured: M. Savvateev, NT-MDT

AFM performance: proteins on a dried substrate

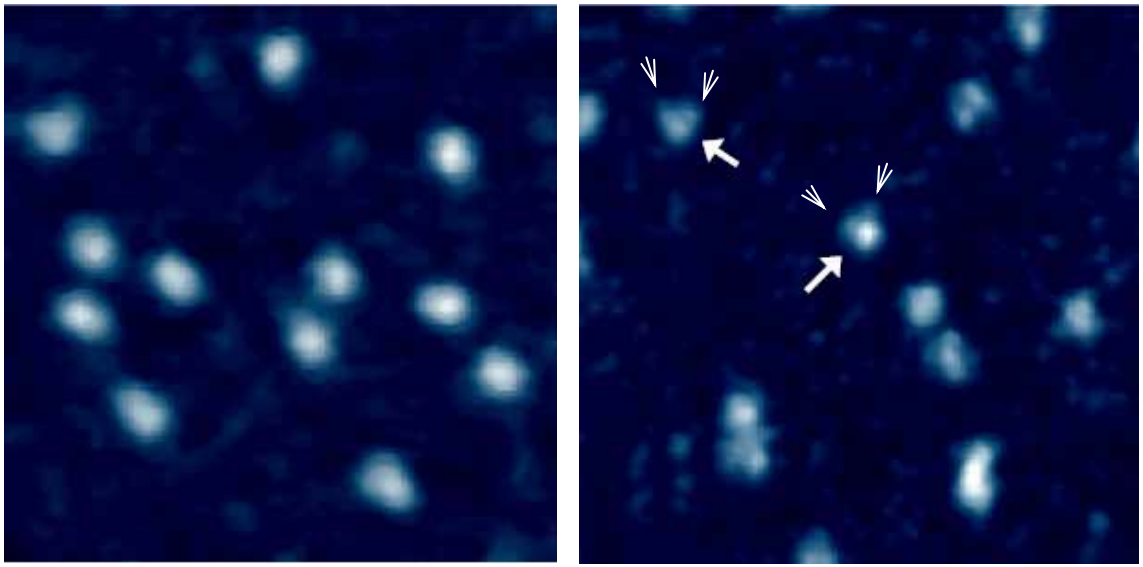




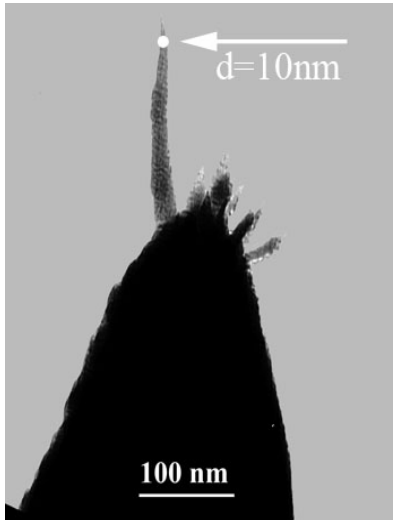


Data measured: M. Savvateev, NT-MDT

Probe sharpness is important



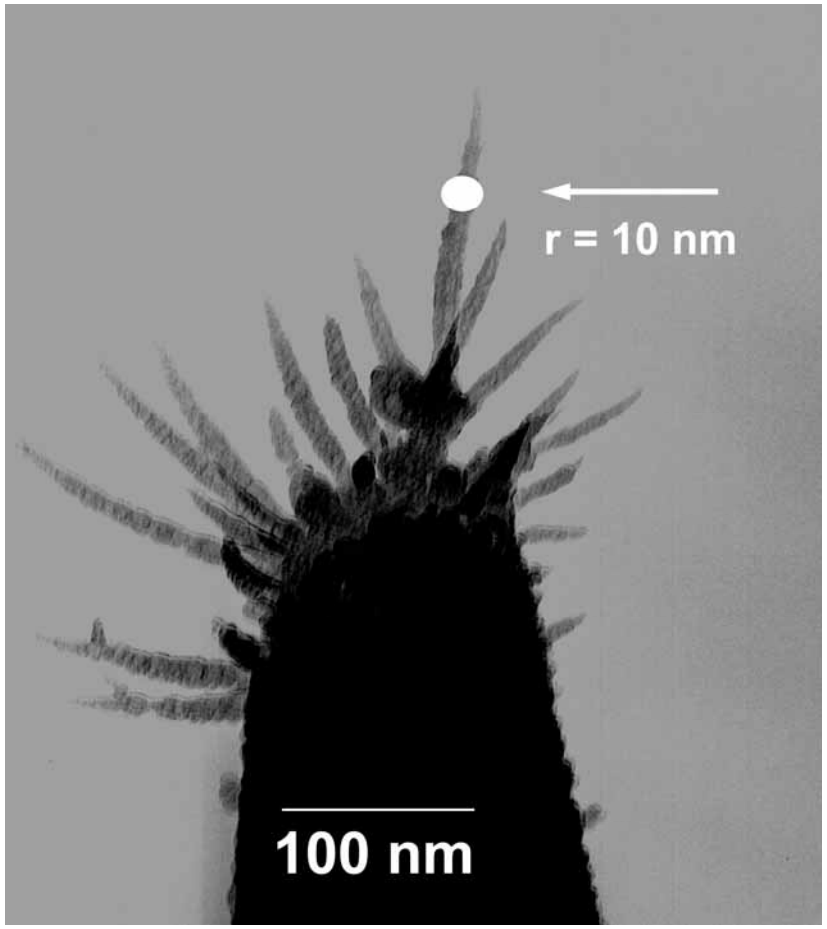
AFM images of **ricin molecules** on mica.
Scans size 170x170 nm, Z scale 1nm.



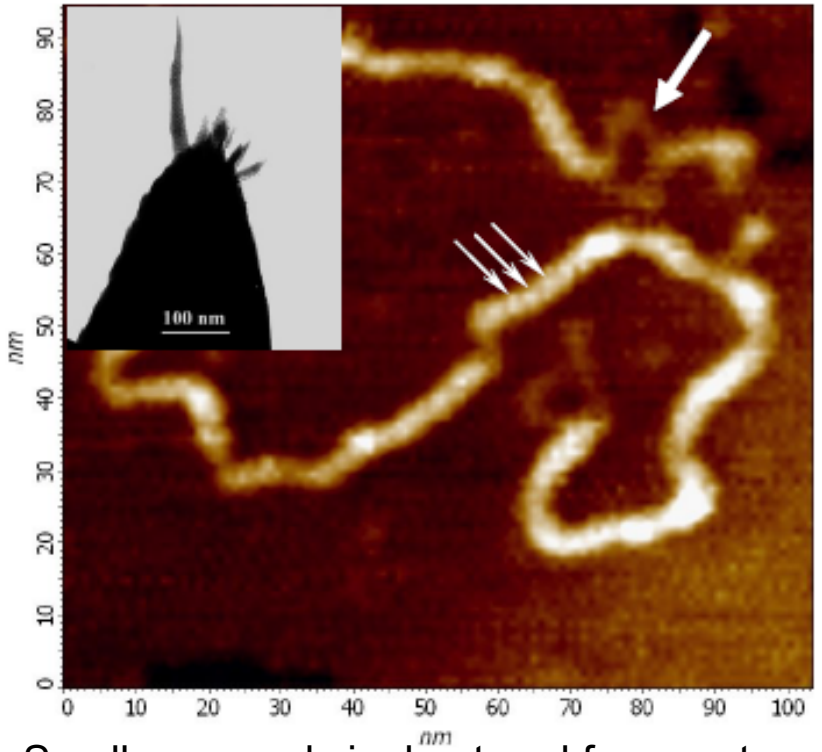
TEM images of ultra-sharp AFM probe tips

Left image was obtained by silicon probe with a tip of common form. Molecules look like globules, their domain structure is failed to be visualized.

Super Resolution with DLC NanoTips.



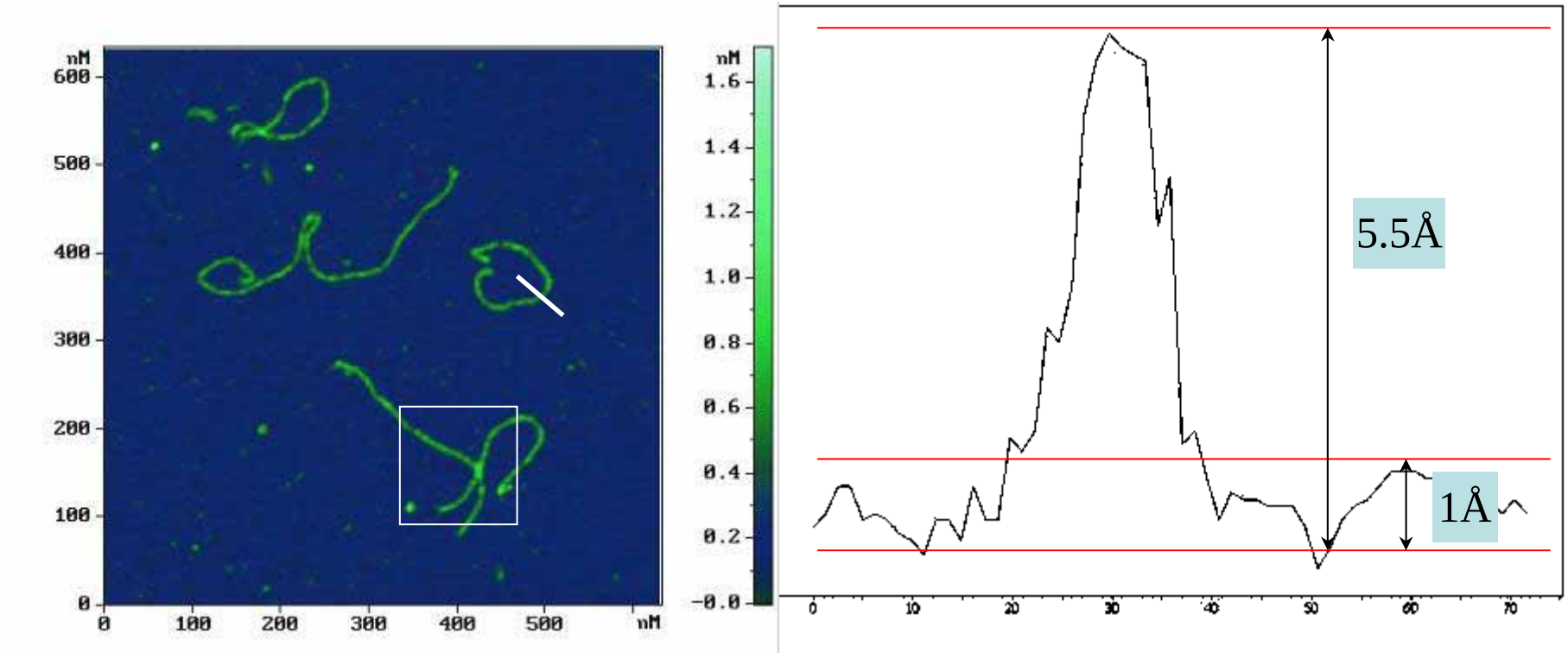
TEM Probe image



Small unwound single-strand fragments can be seen (bold arrow on the scan) and even helical pitch of the DNA molecule can be resolved (thin arrows) al. *Nanotechnology* (2007), V18, N22, p.225102.

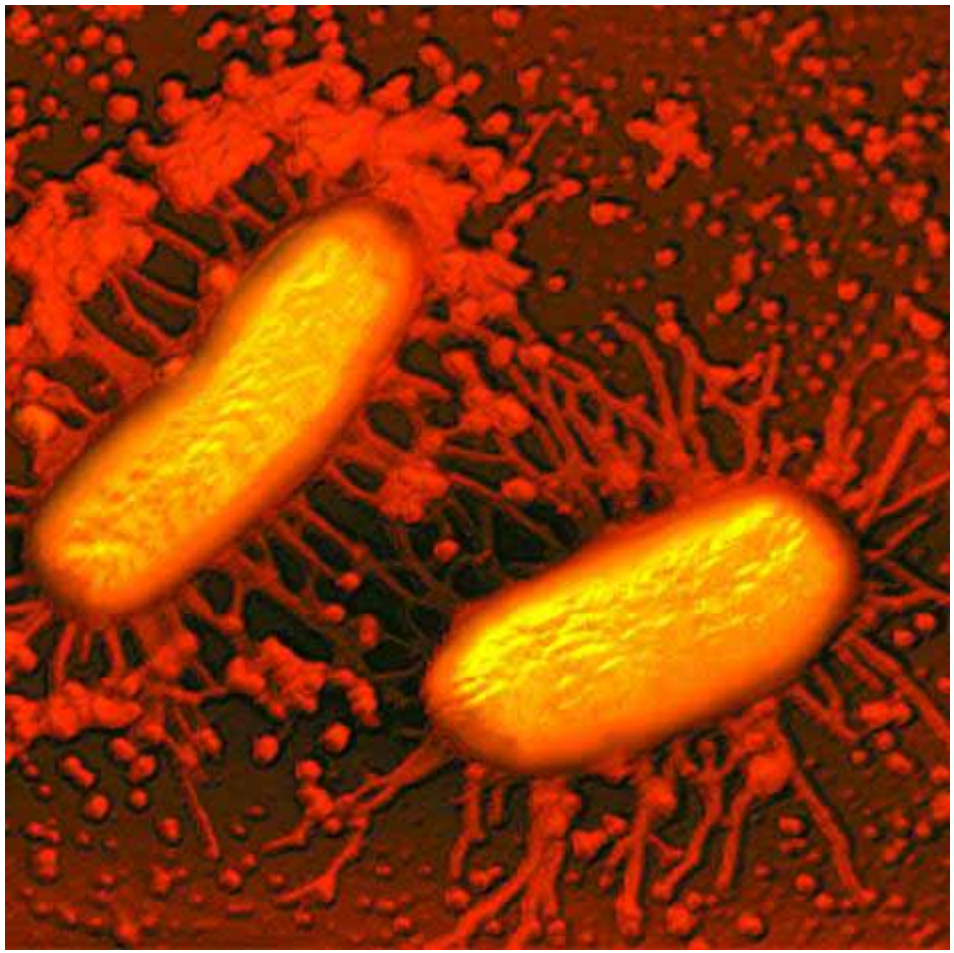
DNA image 500 nm scan

Angstroms can be resolved on Z axis



Single collagen I-III type molecules from rabbit skin scanned in air. On the right image is the height analysis of the line profile (white line on the left image). Note that small fractions of angstrom can be resolved by the height analysis.

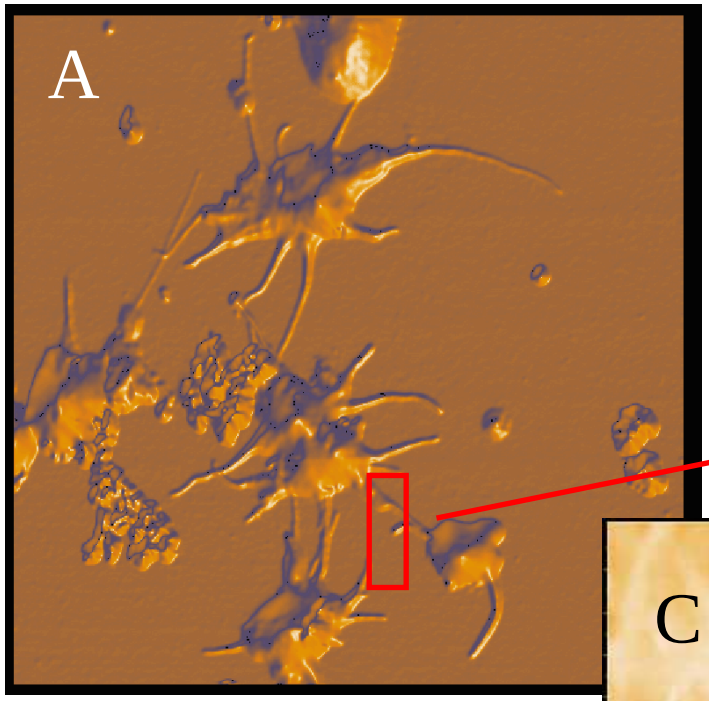
Microorganisms



E-coli enteric bacillus. Topography image in semicontact mode.

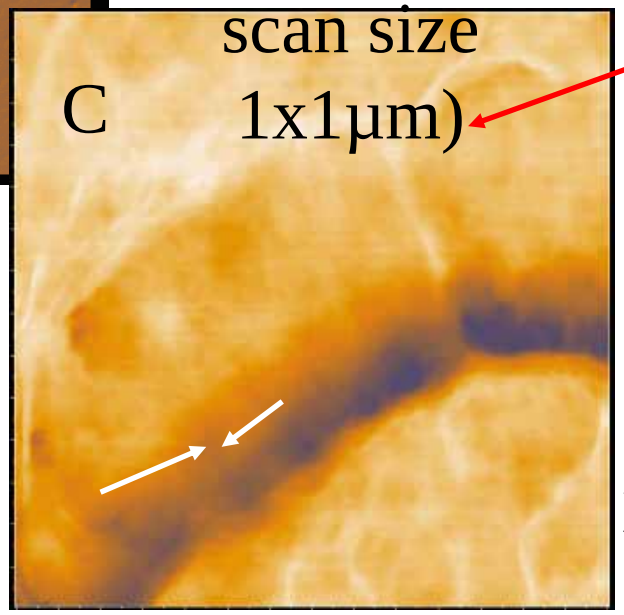
Scan size: 2.7x2.7µm.

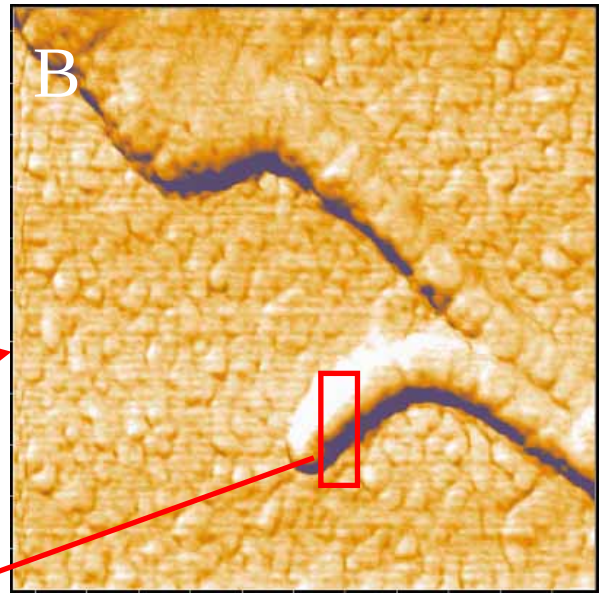
Ntegra is well suited for complex biological experiments



Upon activation single **thrombocytes** form very long protrusions (A, topography imaging, scan size: 14x14µm)

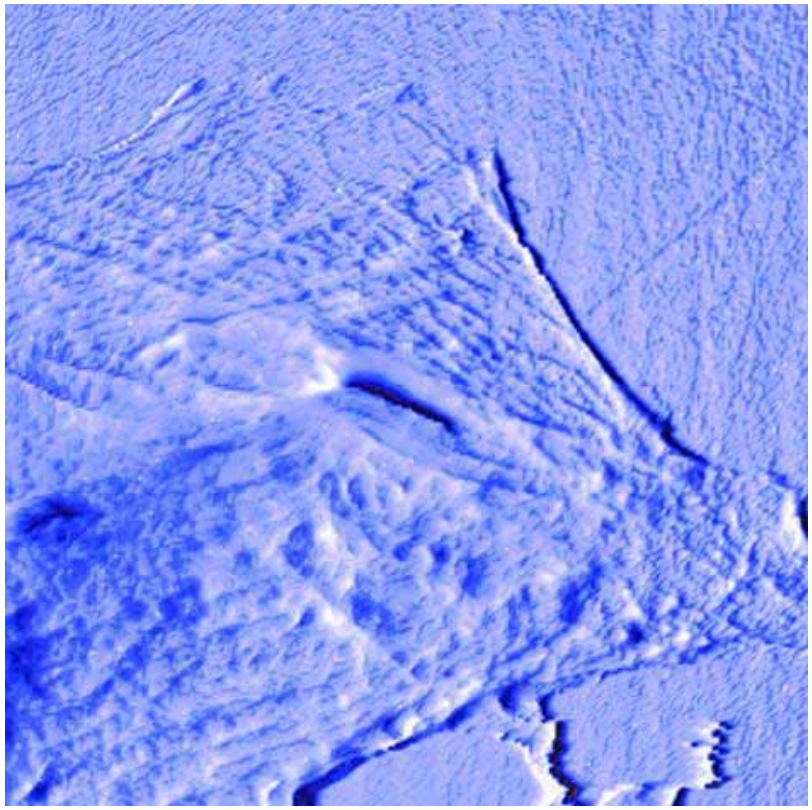
Neighboring cell may contact each other (B, phase imaging, scan size 1x1µm)





Fine analysis of the protrusion shows **actin filaments** (about **3 nm** thick) inside the cell that lay perpendicular to the long protrusion axis (C – arrows, phase imaging, size 250x250nm).

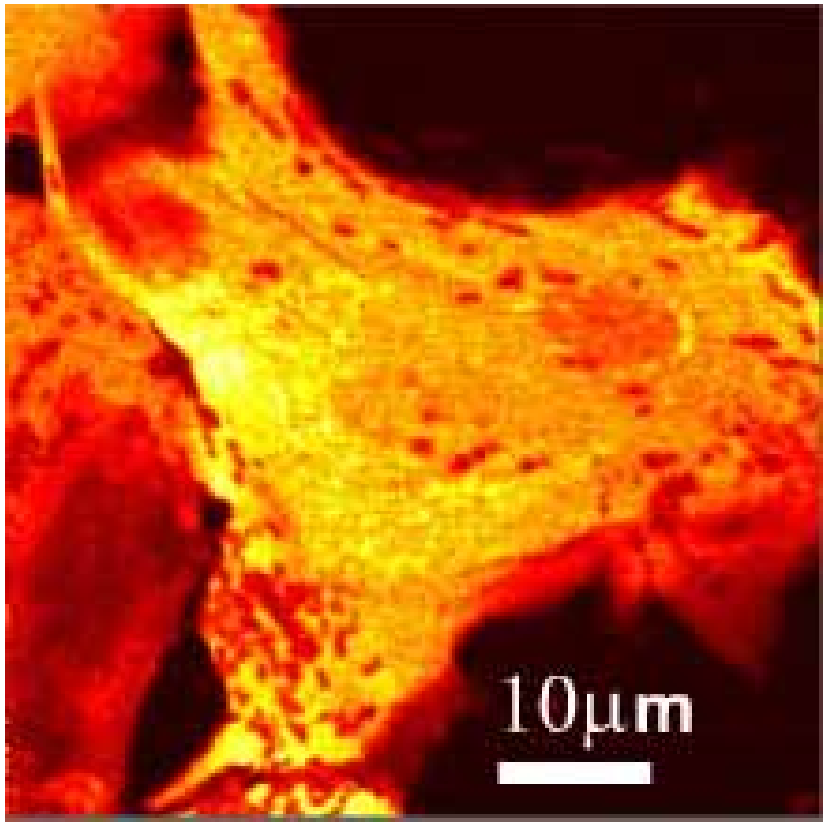
Measurements in liquid



Mouse fibroblast.
AFM image **in liquid**.
Scan size: 33x31x5µm.

NTEGRA Spectra

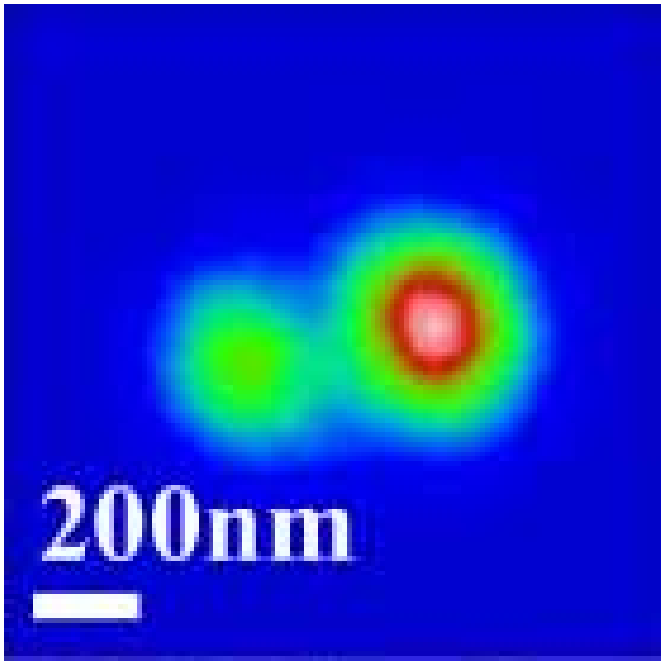
CONFOCAL FLUORESCENCE microscopy



Human cheek cell stained with Rhodamin-123 Fluorescence image in PMT mode

Image courtesy, Dr. I. Kudryashov, Tokyo Instrumen

Confocal Fluorescence: Polysterene beads



Polysterene beads [with coumarine dye "Fluoresbrite carboxy YG (Emission Yellow)].
Fluorescence image at 500-540 nm

NT-MDT demonstrates 200-250 nm resolution (depending on laser wavelength) as a standard acceptance test of the system

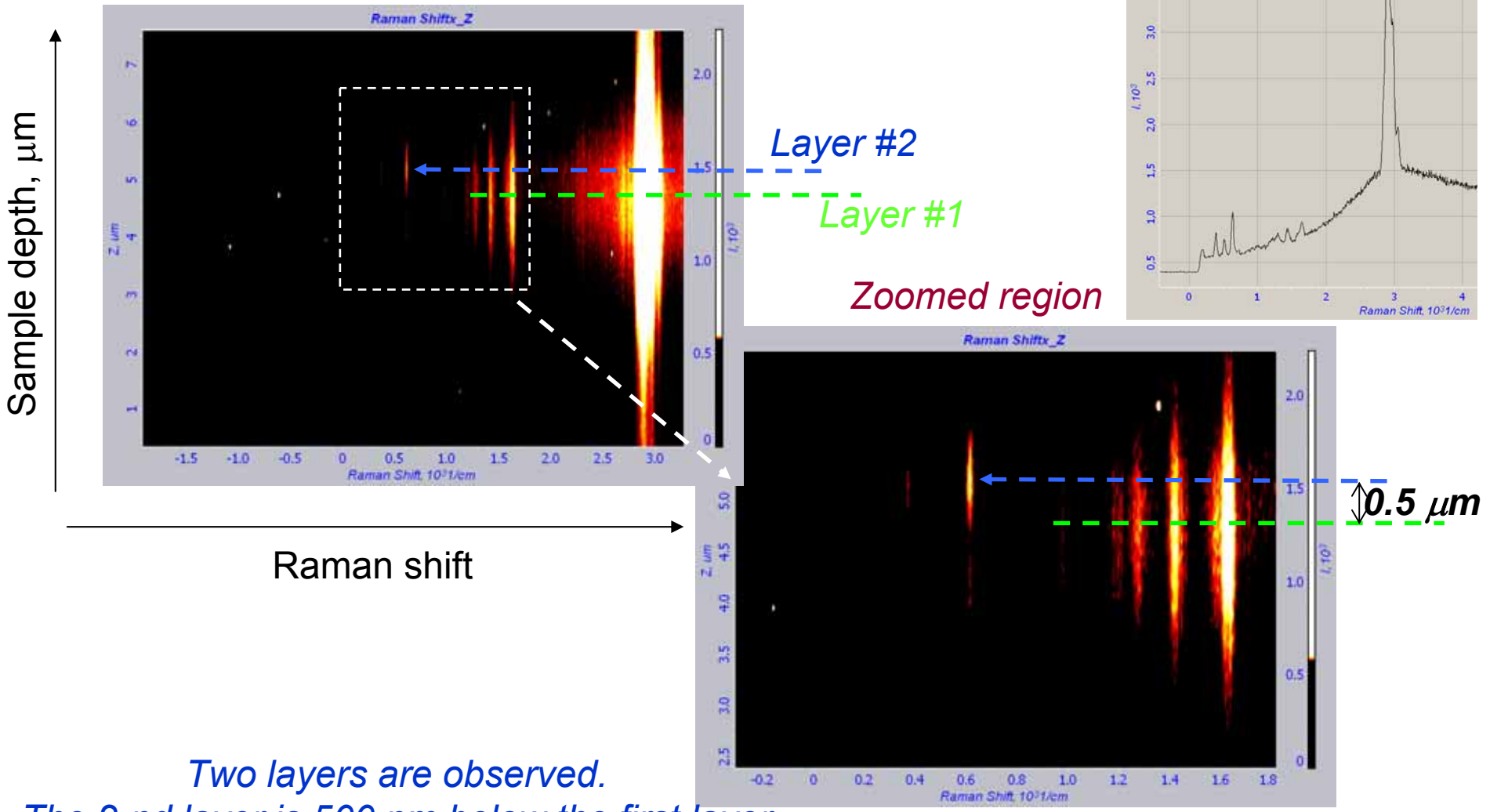
Image courtesy, Dr. I. Kudryashov, Tokyo Instruments

NTEGRA Spectra

Polymers

Polymer sample with protective cover layer - depth profile

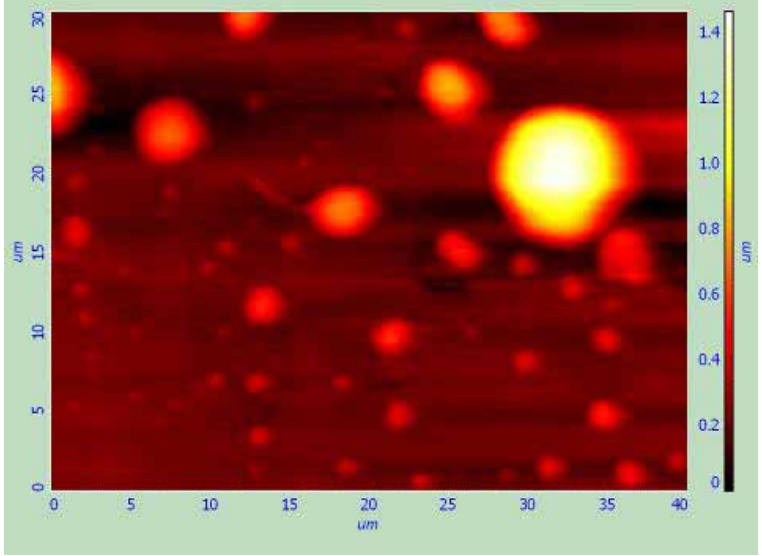
Raman spectrum versus sample depth



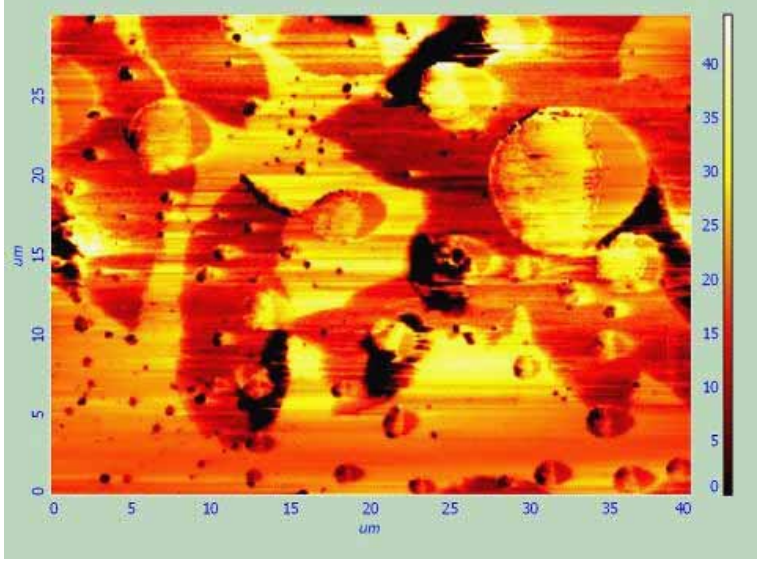
Two layers are observed.
The 2-nd layer is 500 nm below the first layer
and has a characteristic Raman line (620 cm^{-1})

Polymer blend

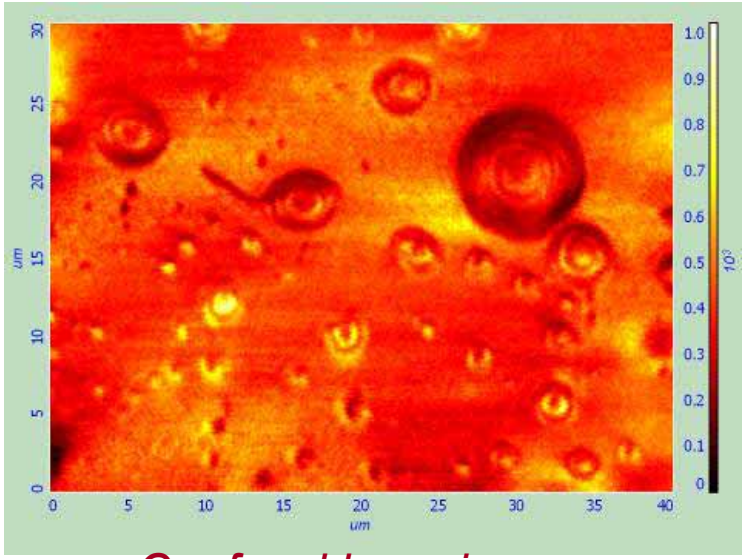
40x40 µm scans



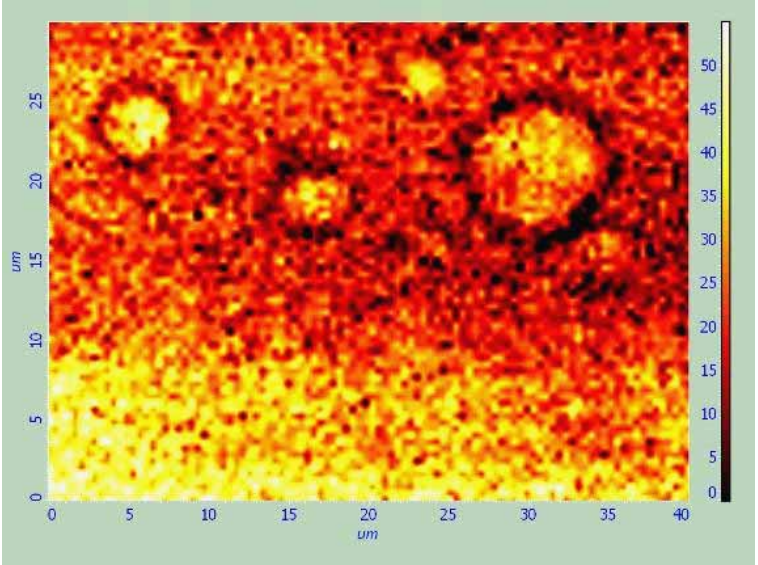
AFM topography



AFM phase

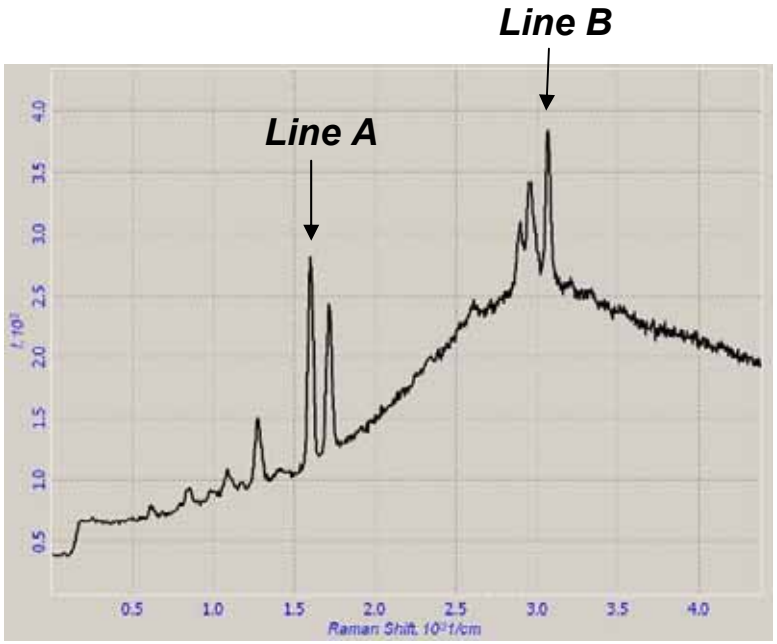


Confocal laser image

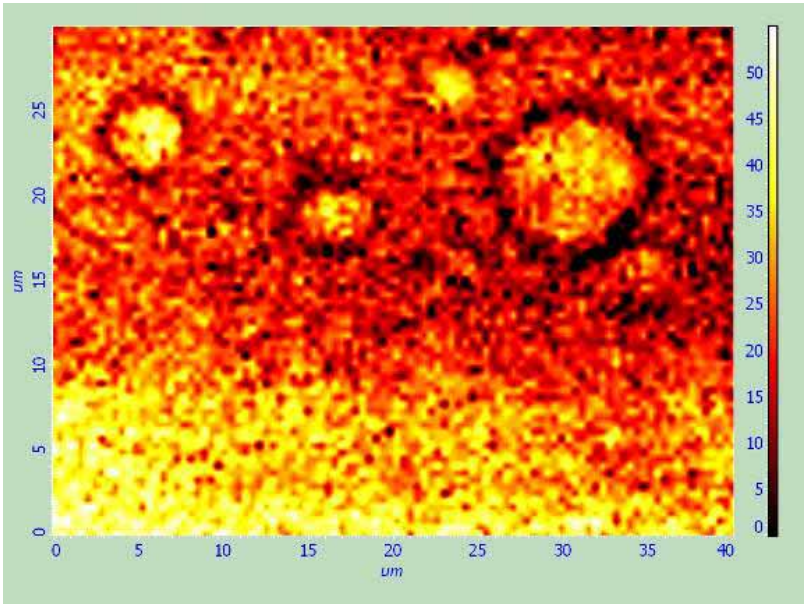


Raman map (Band A – next slide)

Polymer blend

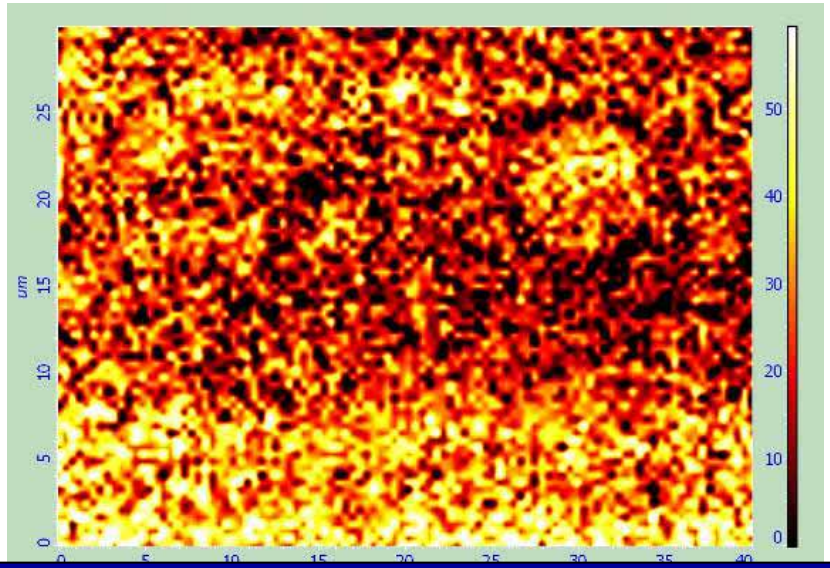


Line A



40x40 µm scans

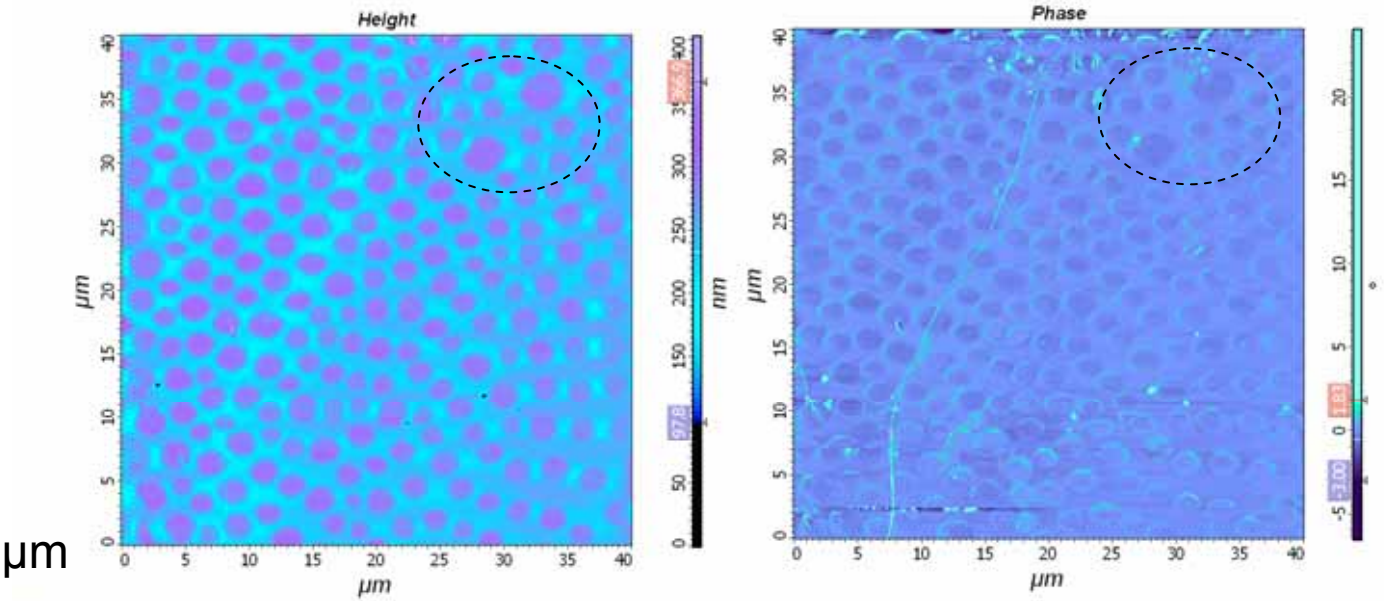
Line B



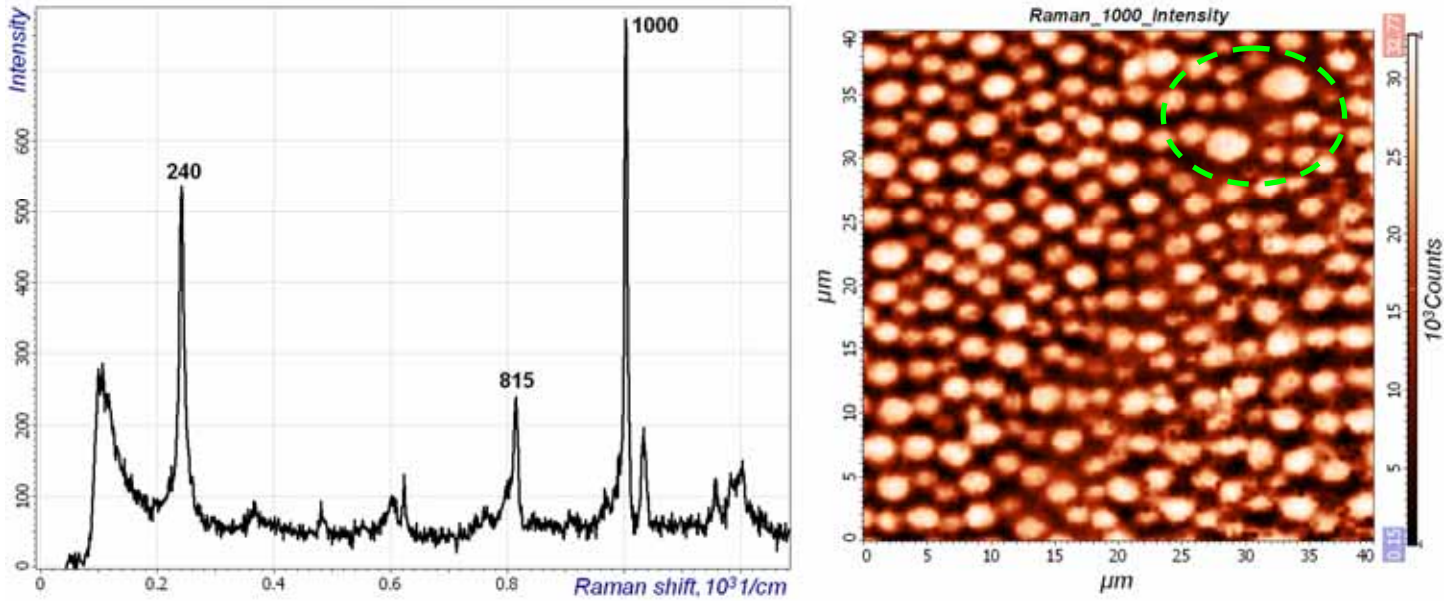
Polymer blend

AFM ->

Scan size: 40 x 40 μm

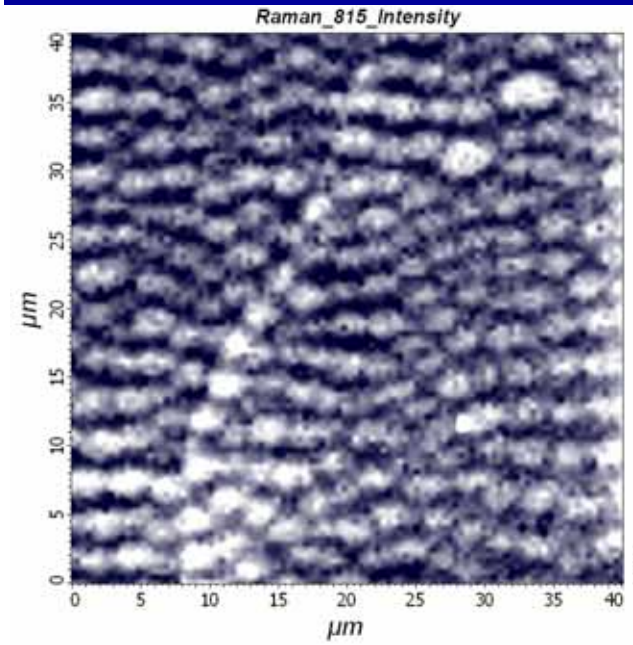


Raman ->

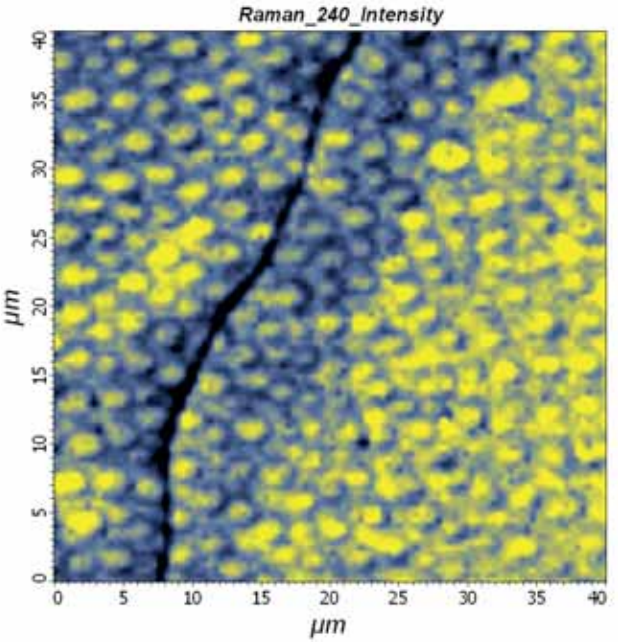


NT-MDT NTEGRA Spectra + Renishaw Raman microscope

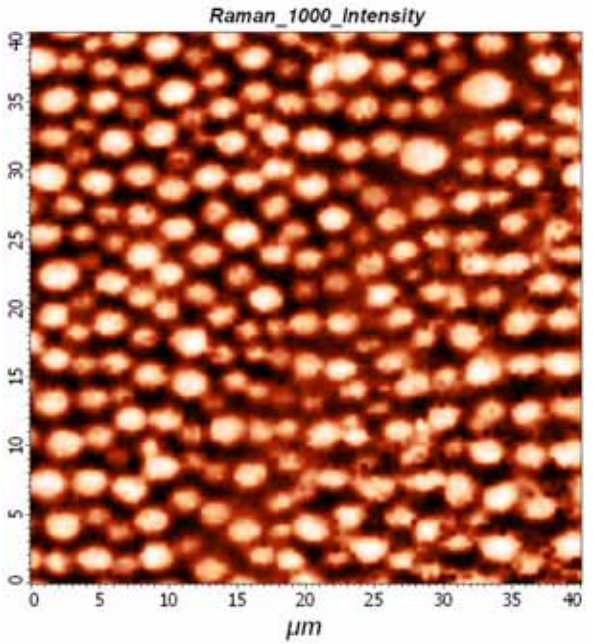
Polymer blend



815 1/cm



240 1/cm



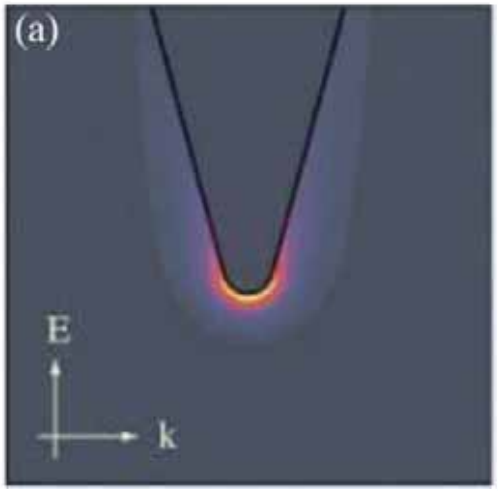
1000 1/cm

NT-MDT NTEGRA Spectra + Renishaw Raman microscope

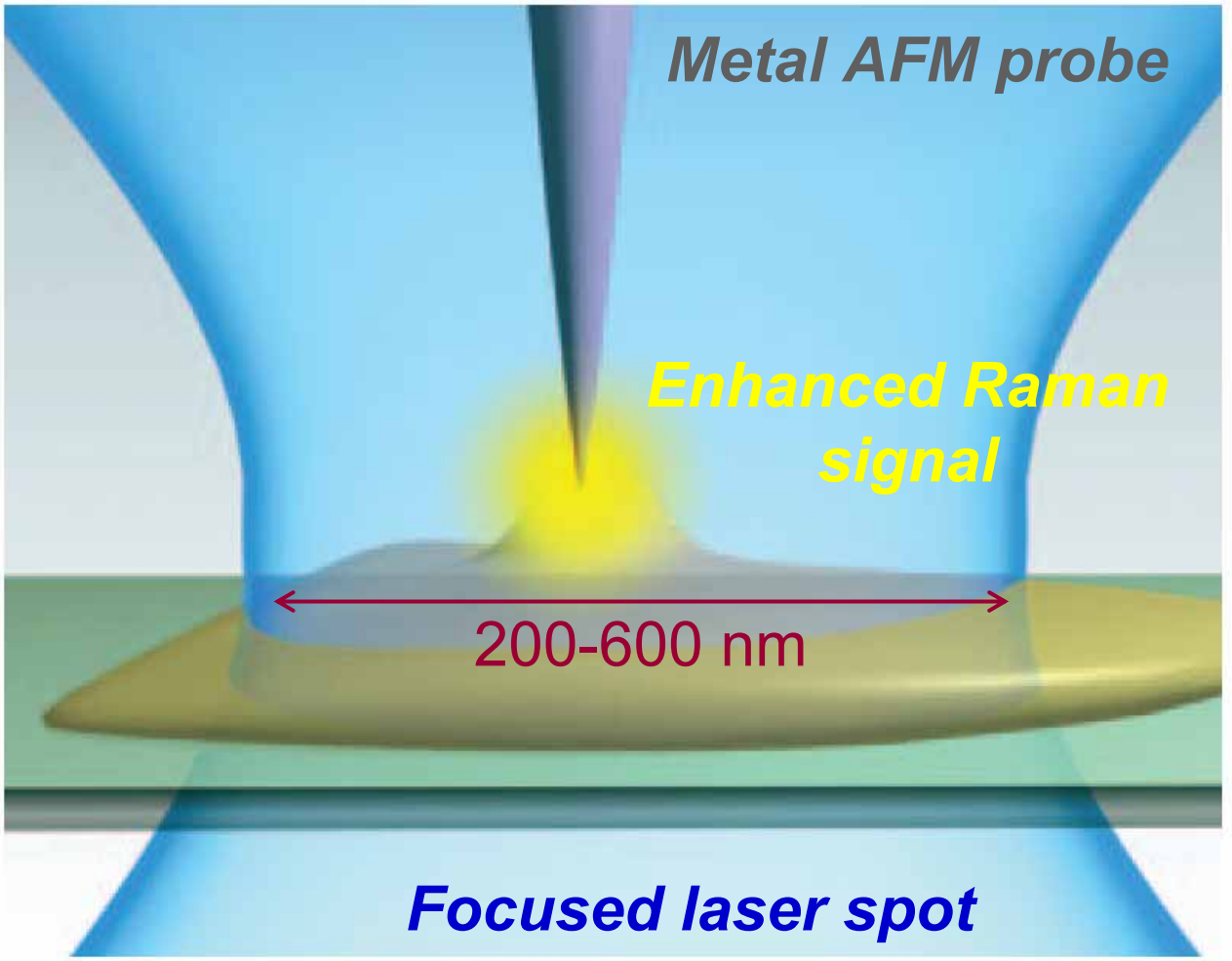
Tip Enhanced Raman Scattering (TERS)

A route to Raman microscopy with subwavelength spatial resolution and single molecule sensitivity

TERS – “inverted” SERS effect (scanning metal tip is a HOT SPOT)

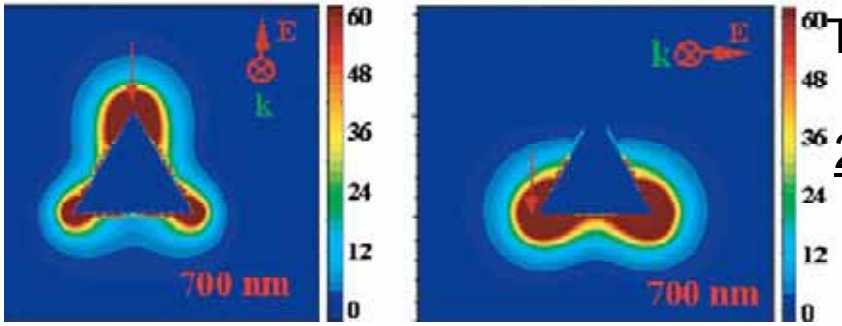


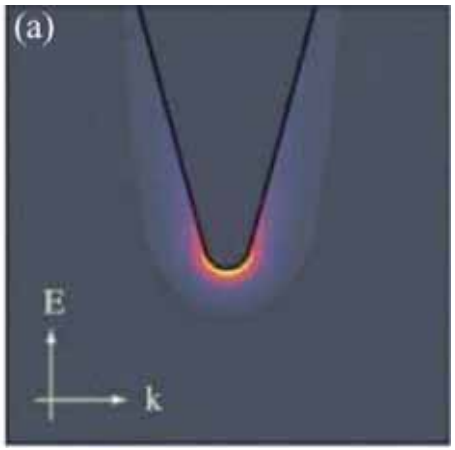
Electromagnetic field intensity around metal tip



Field enhancement mechanisms of asymmetrical nanoparticles

Taken from: E. Hao and G. C. Schatz, J. Chem. Phys. **120**, 357 2004





Electrical near-field of different Ag nanoparticles and Ag tip

Two interplaying field enhancement mechanisms:
1. Surface plasmon resonance
2. Lightning rod effect (concentration of electrical field at sharp edges)

The field can be enhanced as much as $k=E_{local}/E_0$ =100 times by those 2 mechanisms

This would give Raman enhancement $k^4=10^8$!!!
Additional "chemical enhancement" is believed to give another 10^2

Together this gives 10^{10} Raman enhancement !
Some researchers even claim 10^{14} !!!

**** NT-MDT produces AFM cantilevers with attached Ag nanoparticles coated with polymer. Those cantilevers are chemically stabilized and expected to provide high field enhancement required for TERS***

TERS: Importance of light polarization

"Z-polarized" light (with electrical field polarized along the tip axis) light experiences the largest enhancement at the tip apex

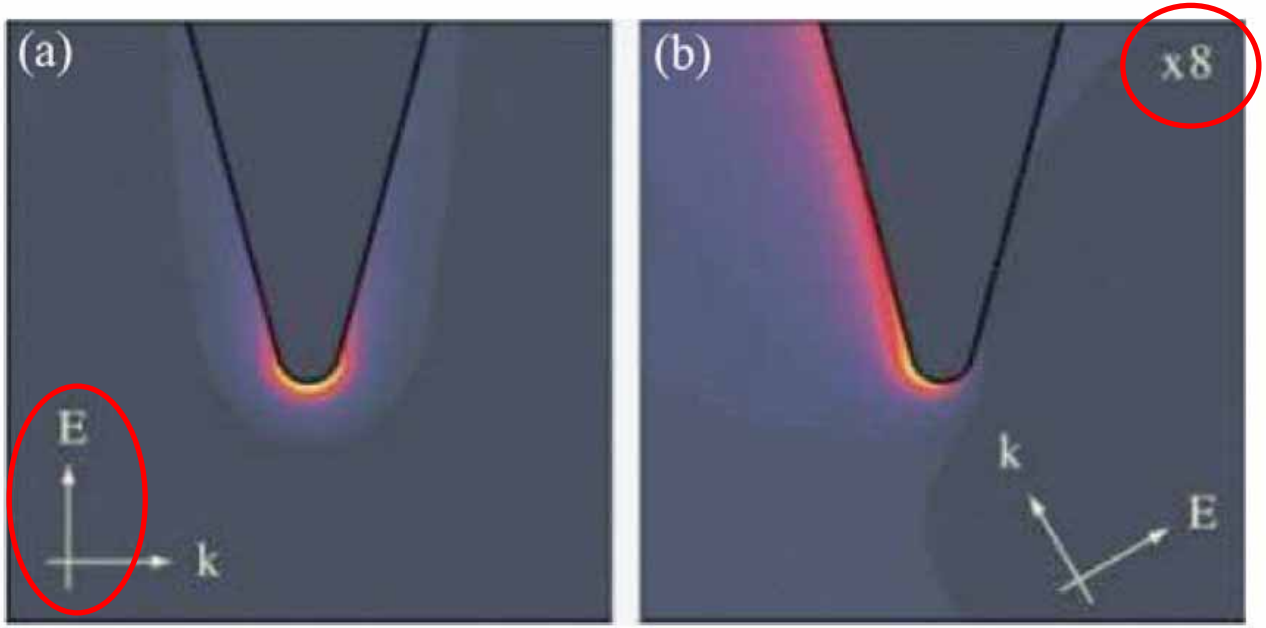
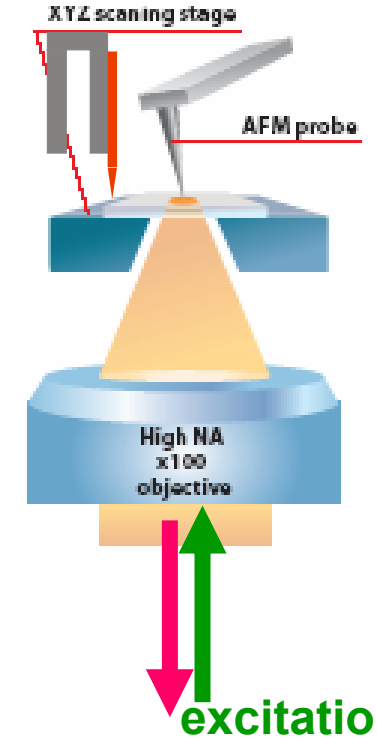


Fig. 1 Calculated field distribution at a sharp Au tip with a diameter of 5 nm. (a) Field distribution for an incident electric field vector parallel to the tip shaft showing localization of the electric field at the tip apex. (b) Field distribution for an incident electric field orientated nonparallel to the tip shaft. The field is no longer confined to the tip apex.

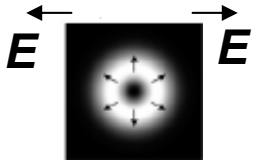
Taken from: N. Anderson, A. Hartschuh, L. Novotny, Materials Today (2005)

NT-MDT provides *all* possible AFM/Raman/TERS configurations

INVERTED



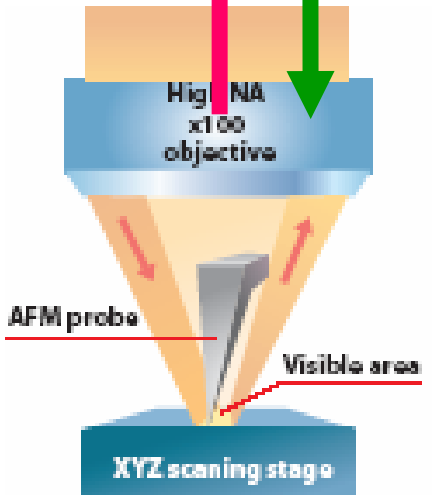
TERS collection



UPRIGHT

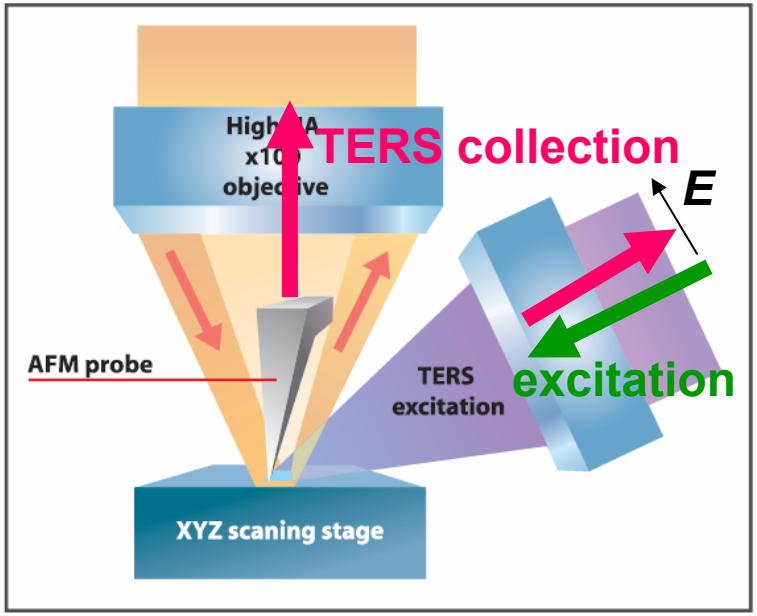
TERS collection

excitation



AFM or STM or Shear force

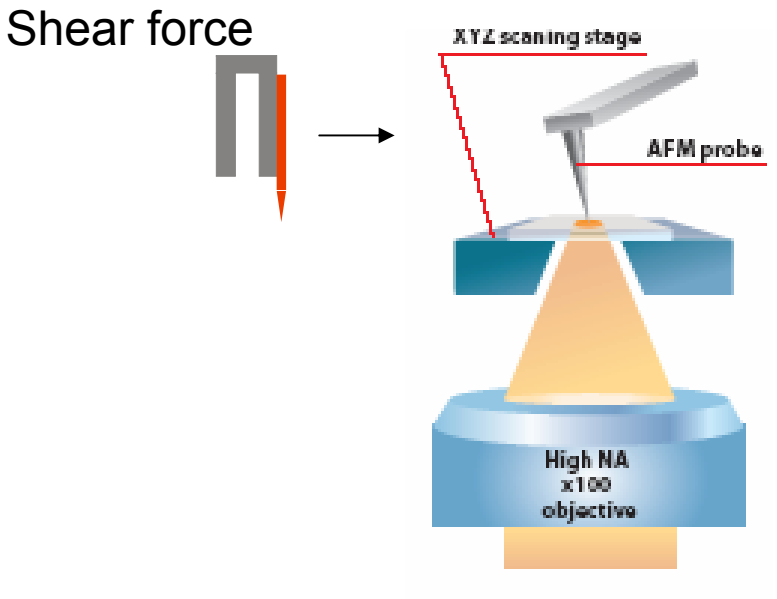
Side illumination + UPRIGHT



AFM or STM or Shear force

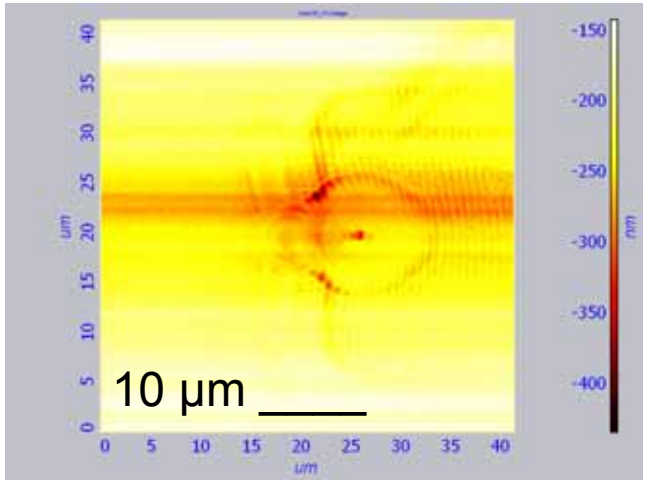
Tip Enhanced Raman

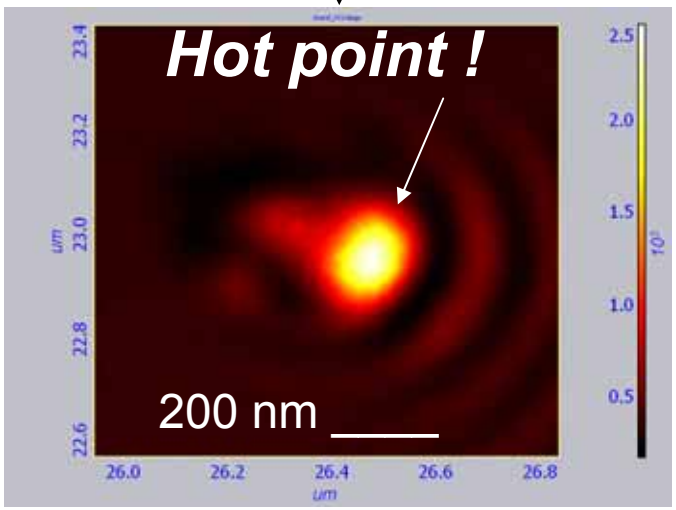
INVERTED geometry (transparent samples)



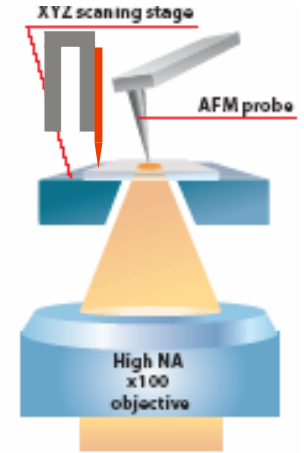
To find HOT POINT (Maximum enhanecement):

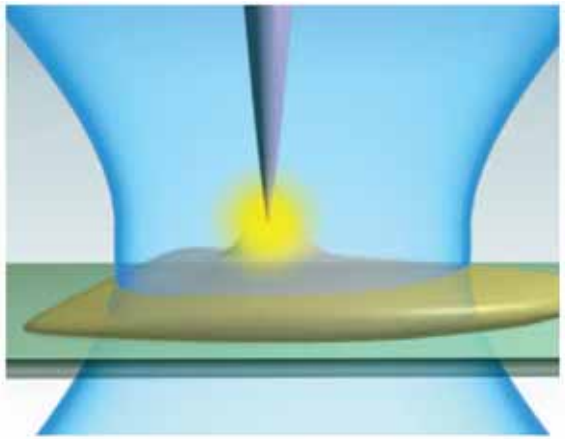
Scan - BY TIP; Measure - intensity of laser light scattered by the tip

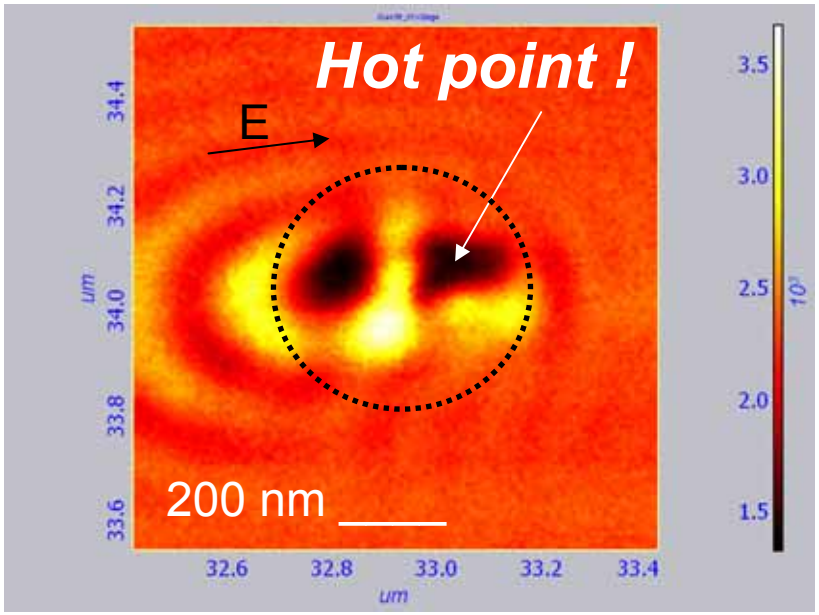




Au-coated cantilever





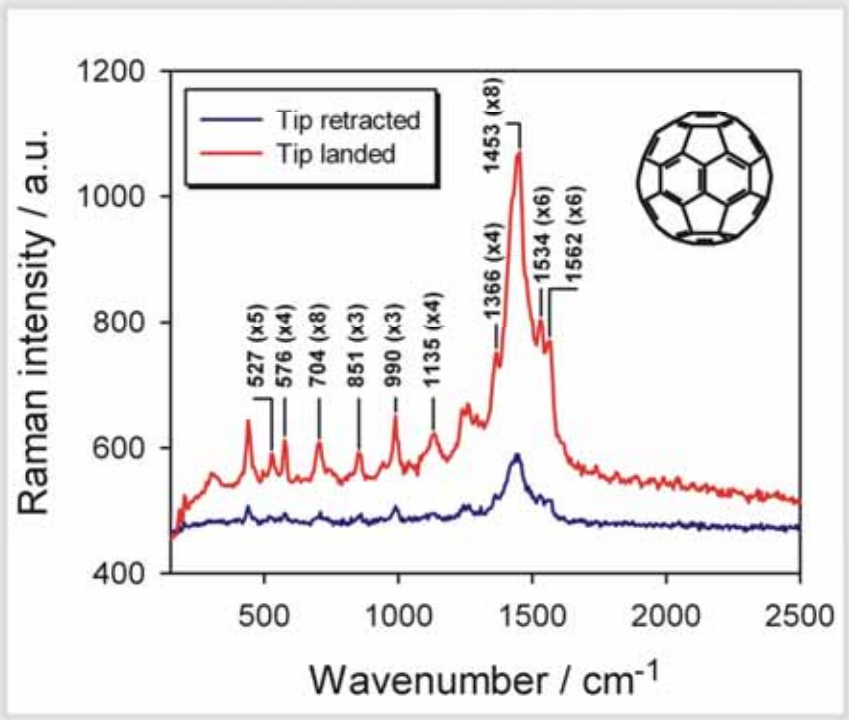


Etched Au wire

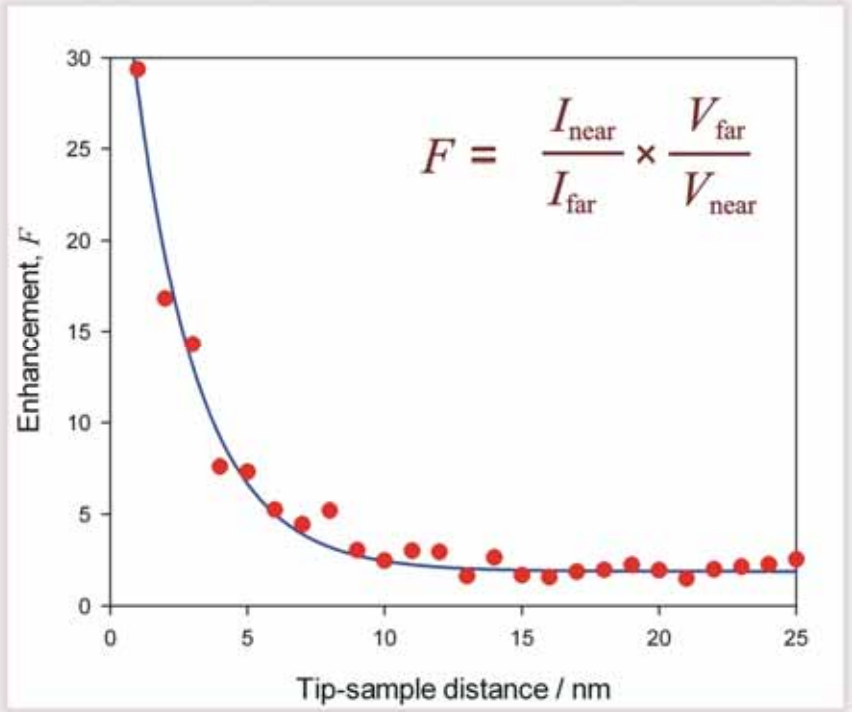
Data courtesy of S. Kharintsev, J. Loos, G. Hoffman, G. de With, TUE, the Netherlands and P. Dorozhkin, NT-MDT

TERS effect on fullerenes

The enhancement of Raman spectra of a fullerene thin film.
Exposure time 60sec. Laser power 100 μW.
Laser wavelength 632.8 nm.



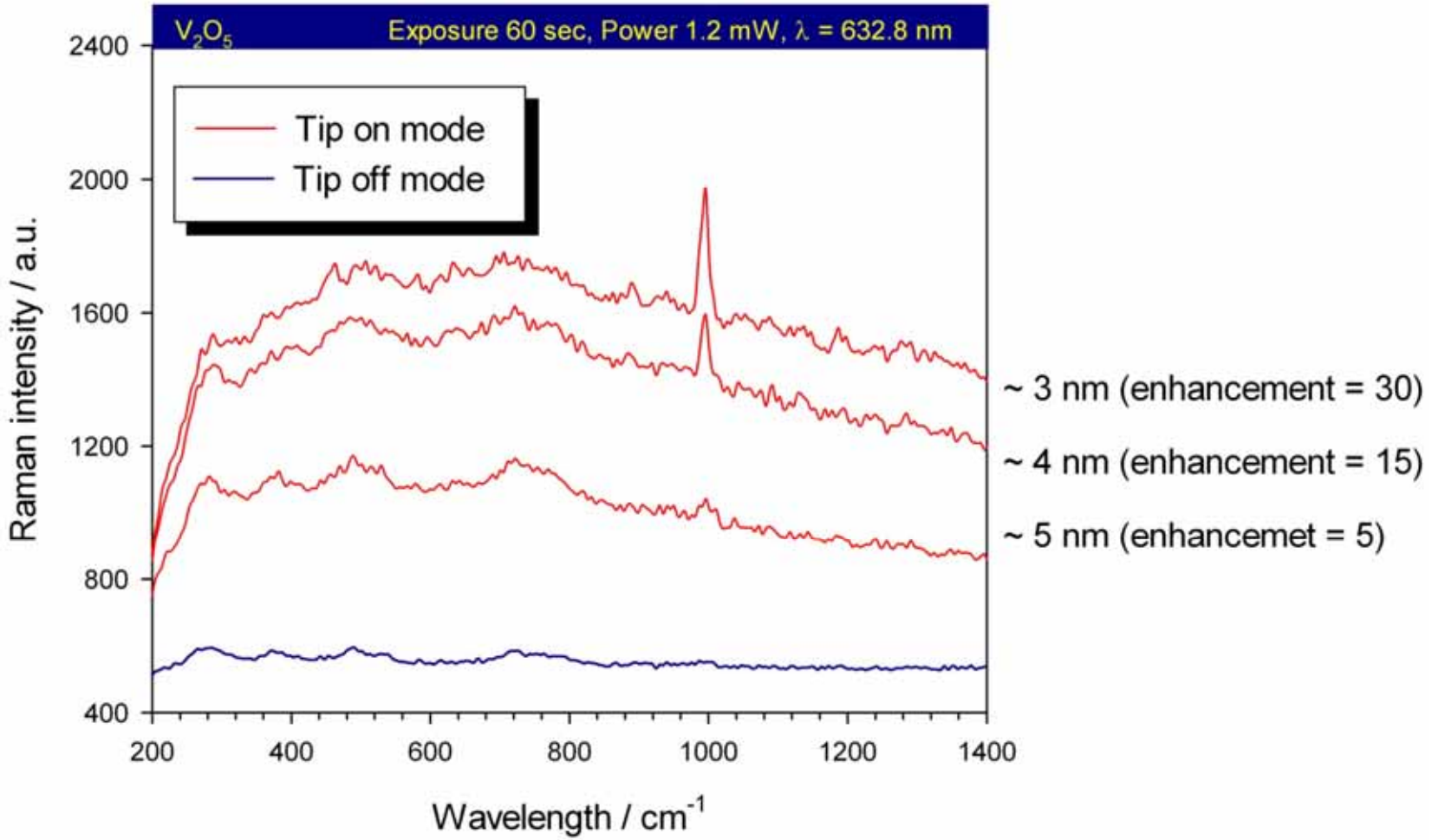
Signal enhances >10 times after tip is approached



Signal enhancement versus tip-sample distance: proof of plasmonic nature of the effect

Data courtesy of S. Kharintsev, J. Loos, G. Hoffman, G. de With, TUE, the Netherlands and P. Dorozhkin, NT-MDT

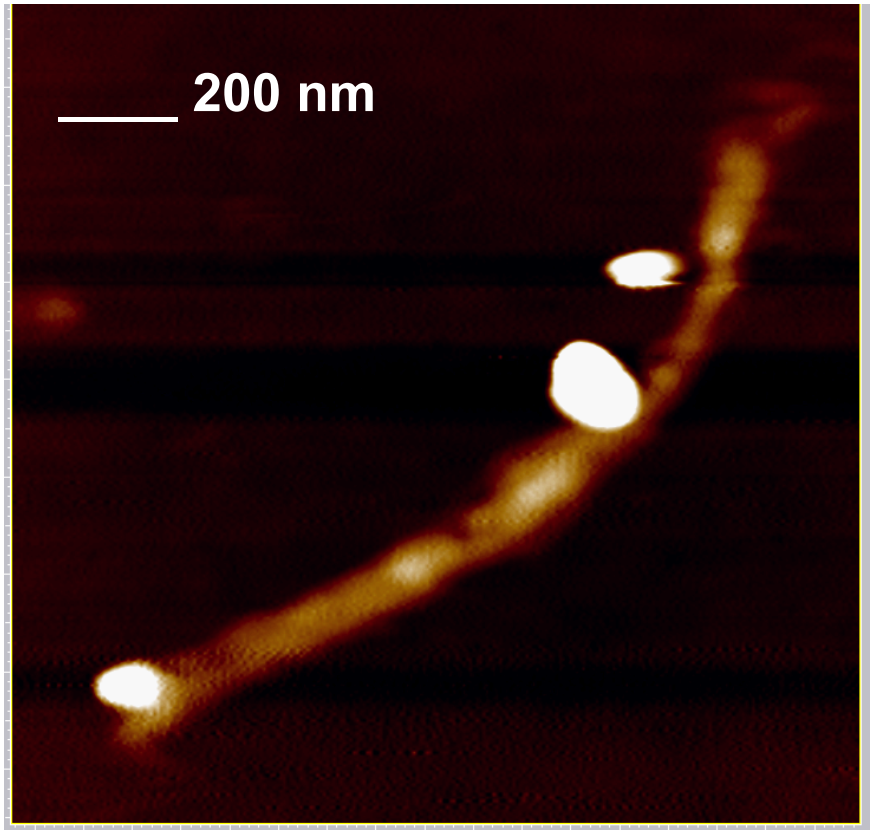
TERS on Vanadium Oxide uniform layer

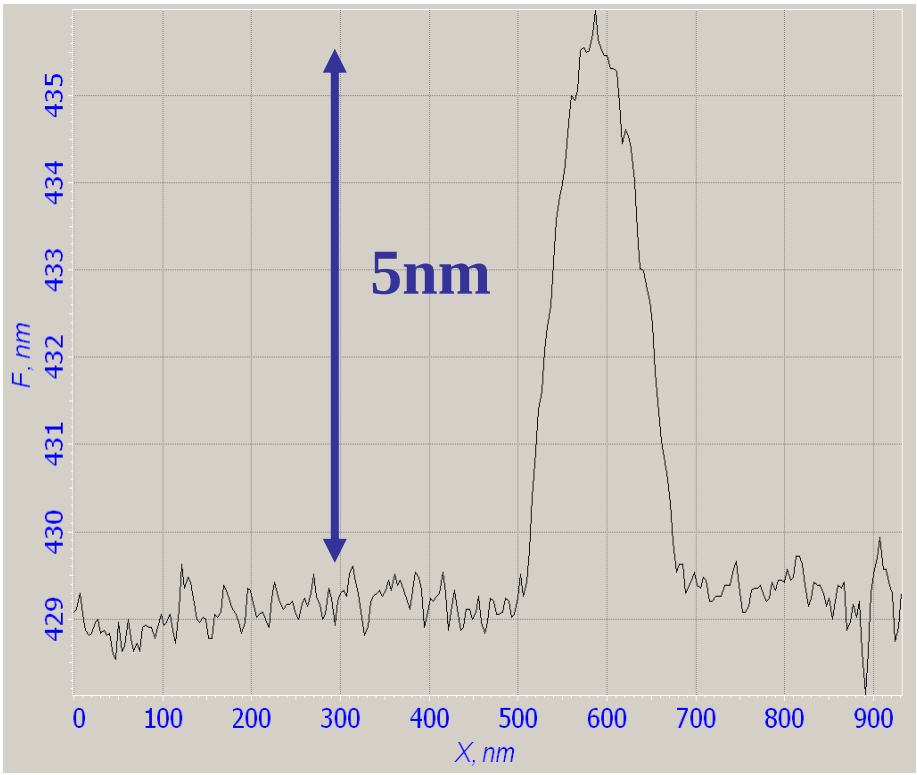


Signal enhancement versus tip-sample distance:
proof of plasmonic nature of the effect

S S Kharintsev[1,2], G G Hoffmann[1,3], P S Dorozhkin[4], G de With[1] and J Loos[1] Nanotechnology **18** (2007) 315502 (9pp)

TERS on Carbon nanotubes

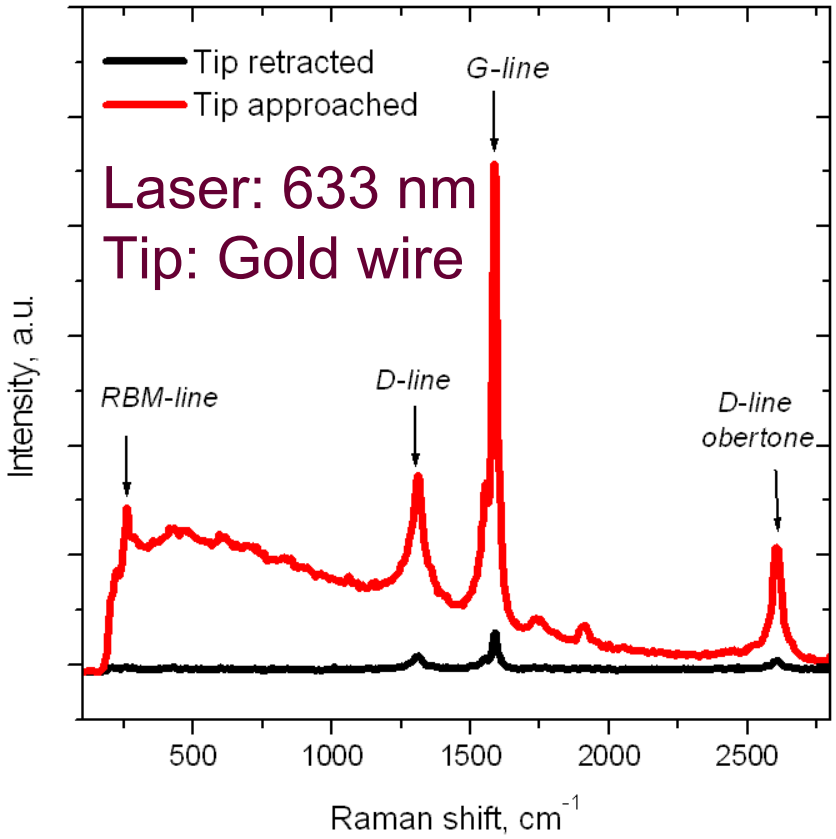




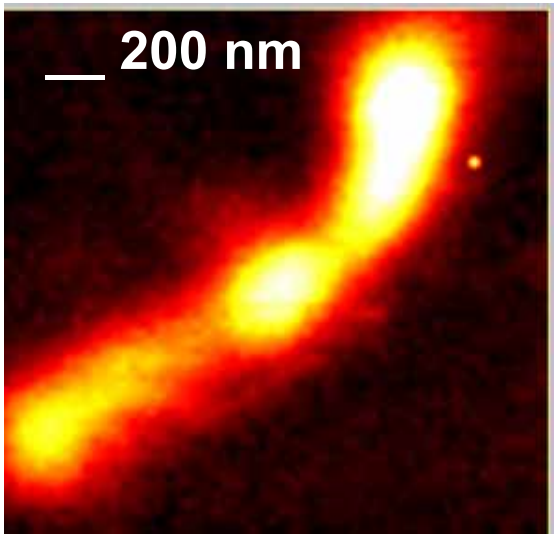
AFM topography and height cross-section of the nanotube bundle
The bundle is ~5 nm height

Data courtesy of S. Kharintsev, J. Loos, G. Hoffman, G. de With,
TUE, the Netherlands and P. Dorozhkin, NT-MDT

Breaking diffraction limit in optical resolution !



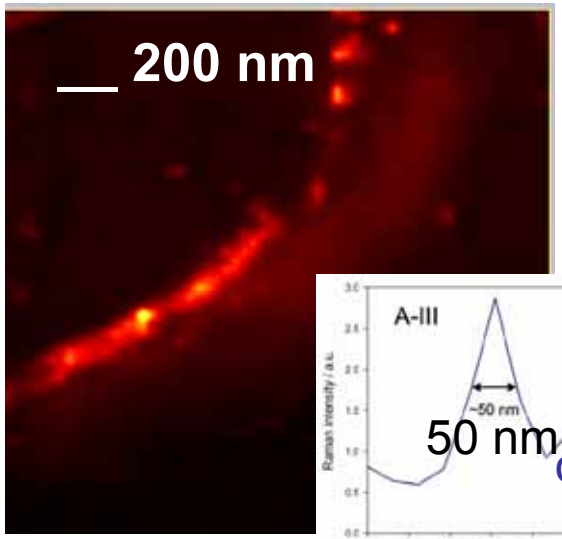
Data courtesy of S. Kharintsev, J. Loos, G. Hoffman, G. de With, TUE, the Netherlands and P. Dorozhkin, NT-MDT



Tip is away

Tube image width is ~250 nm (limited by wavelength of light)

G-line



Tip is approached

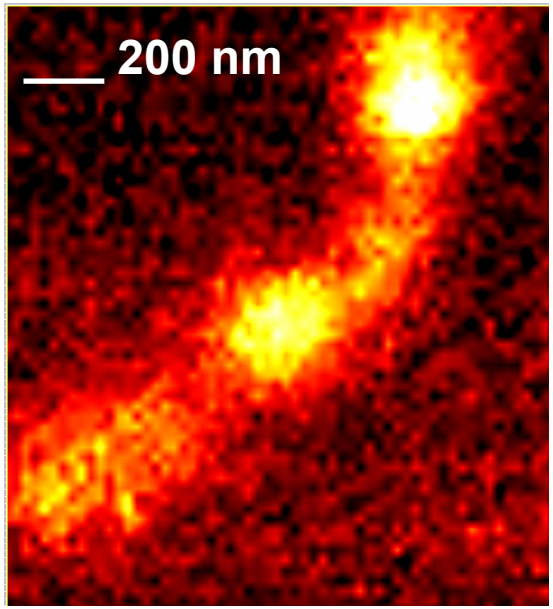
Tube image width is **~ 70 nm** (limited only by size of the tip)

Raman spectra and 2D confocal Raman maps (G-line) of carbon nanotube rope with and without enhancing AFM tip (GOLD wire)

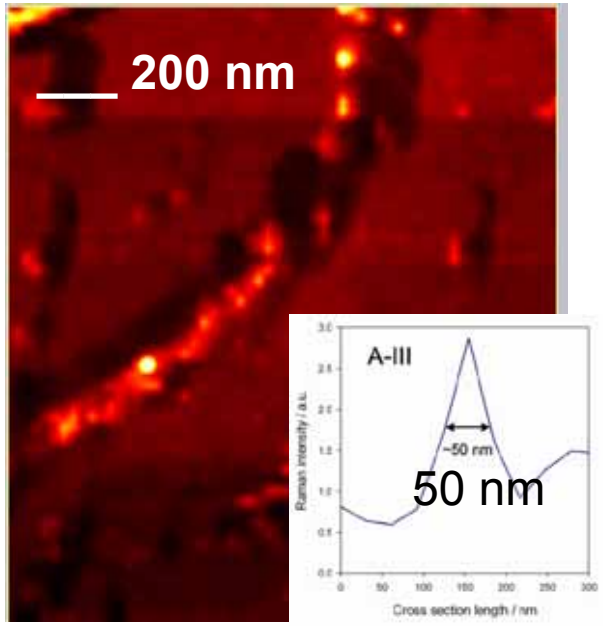
Breaking diffraction limit in optical resolution !

Laser: 633 nm, Tip: **Gold** wire

Radial breathing mode line

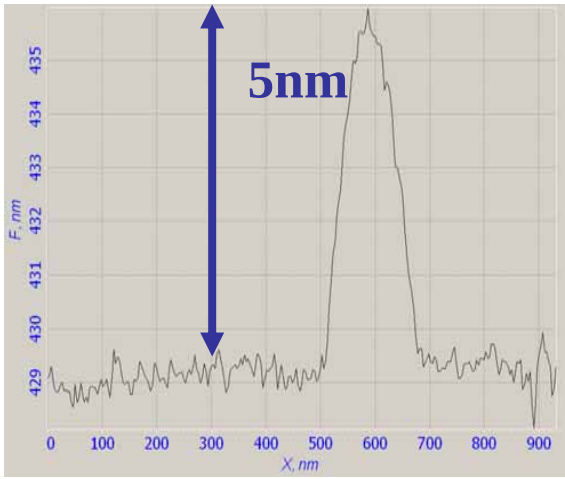


Tip is away.
Tube image width is ~250 nm
(limited by wavelength of light)



Tip is approached.
Tube image width is **~ 70 nm**
(limited only by size of the tip)

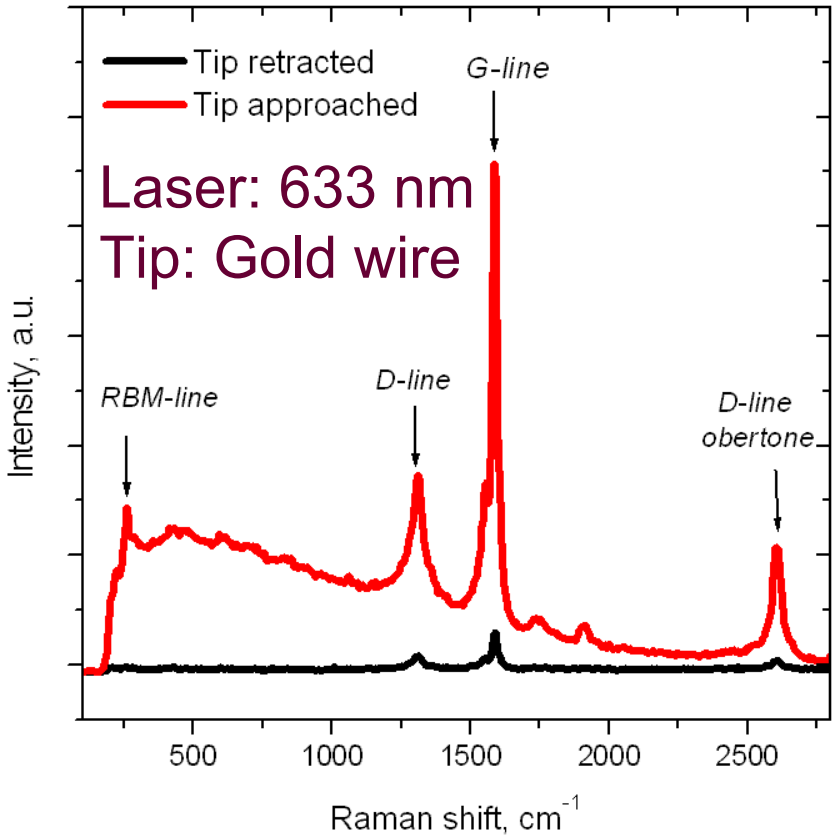
AFM topography



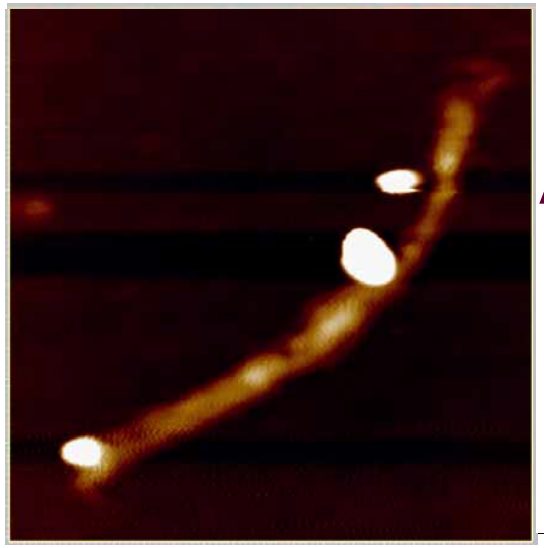
Raman spectra and 2D confocal Raman maps of nanotube rope with and without enhancing AFM tip

Data courtesy of S. Kharintsev, J. Loos, G. Hoffman, G. de With,
TUE, the Netherlands and P. Dorozhkin, NT-MDT

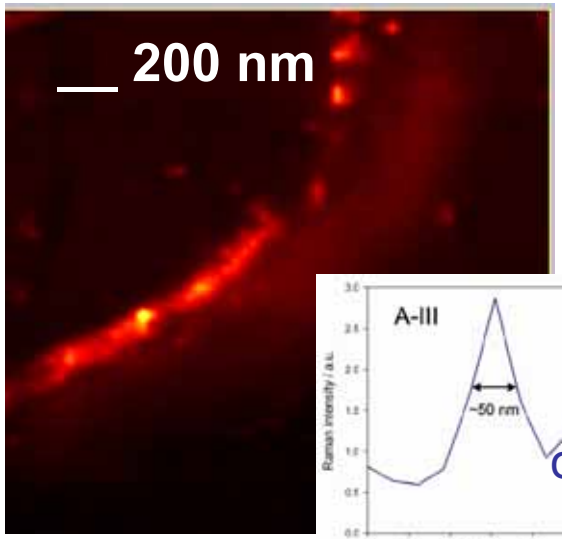
TERS imaging of single-walled CNT bundle



S.S. Kharintsev, G. Hoffmann, P.S. Dorozhkin,
G. de With, and J. Loos
Nanotechnology 18 (2007), 315502



AFM topography (height ~ 5 nm)



Raman map (G-line)

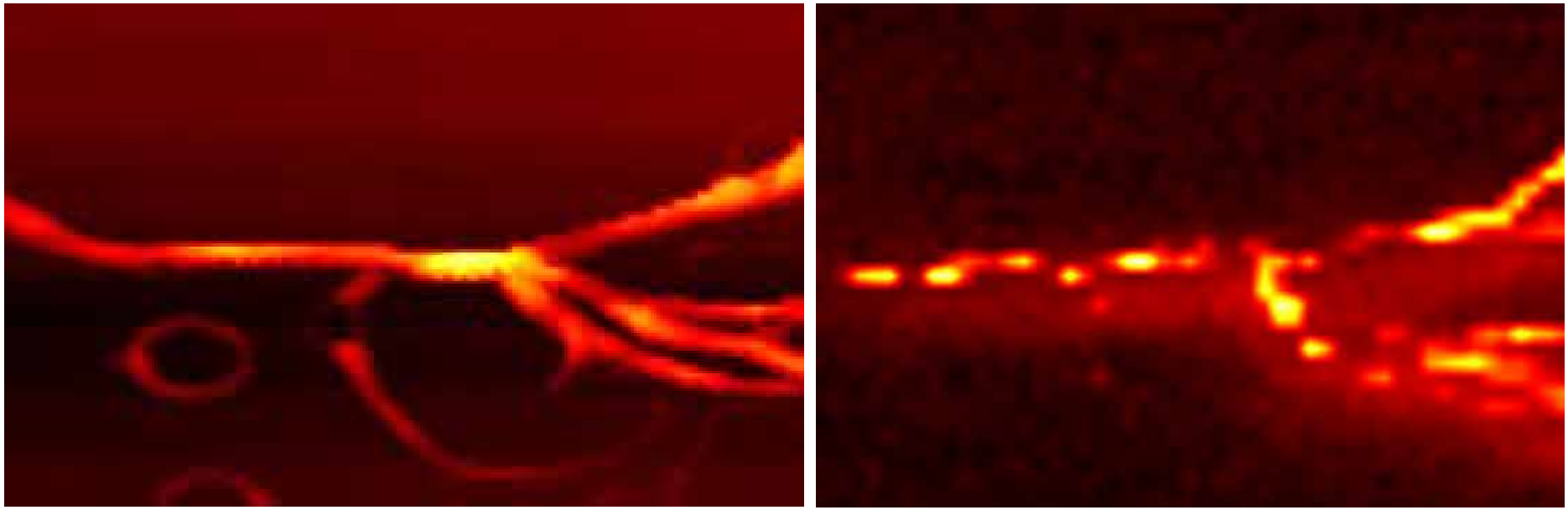
Tip is approached

Tube image width is **~50 nm** (limited only by size of the tip)

Raman spectra and 2D confocal Raman maps (G-line) of carbon nanotube rope with and without enhancing AFM tip (GOLD wire)

TERS with Silver coated cantilevers

Scan size: 2x3 micron

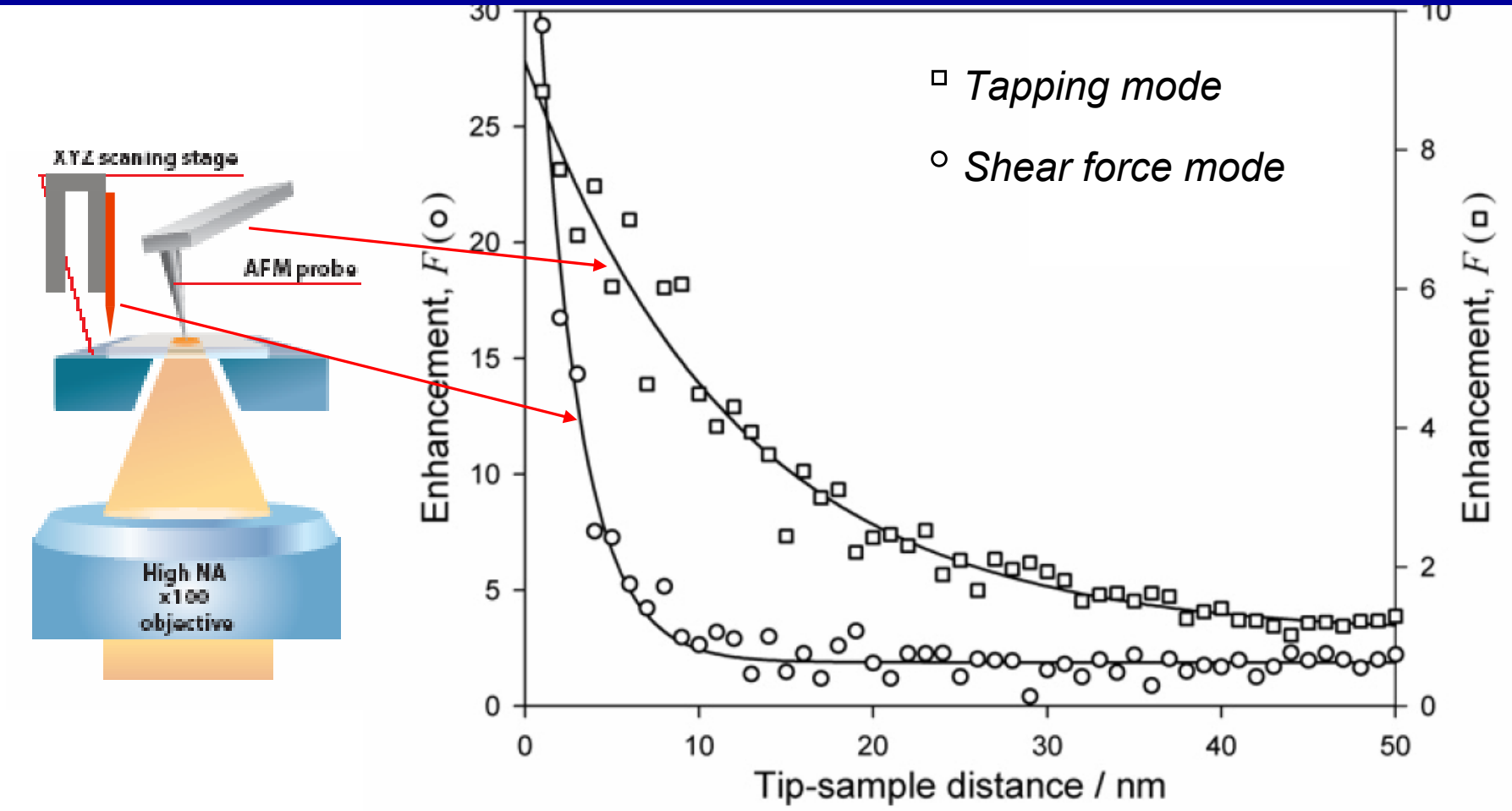


AFM image of carbon nanotube bundle

TERS image of the same bundle

Image courtesy: Jacon Jao, Renato Zenobi ETH Zurich, Switzerland; G. Hoffman, J. Loos, TUE, Eindhoven; and Pavel Dorozhkin, NT-MDT Russia

TERS Enhancement versus probe-sample distance



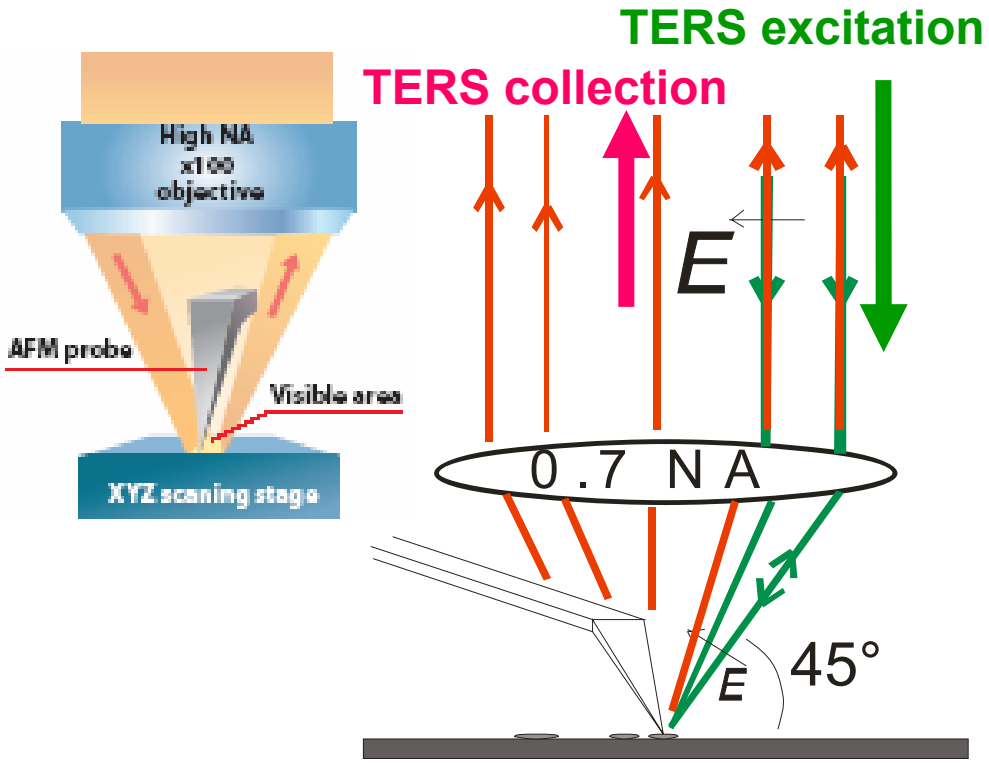
Signal enhancement versus tip-sample distance for cantilever in tapping mode (vertical oscillation and for metal wire in Shear force mode (horizontal oscillation)

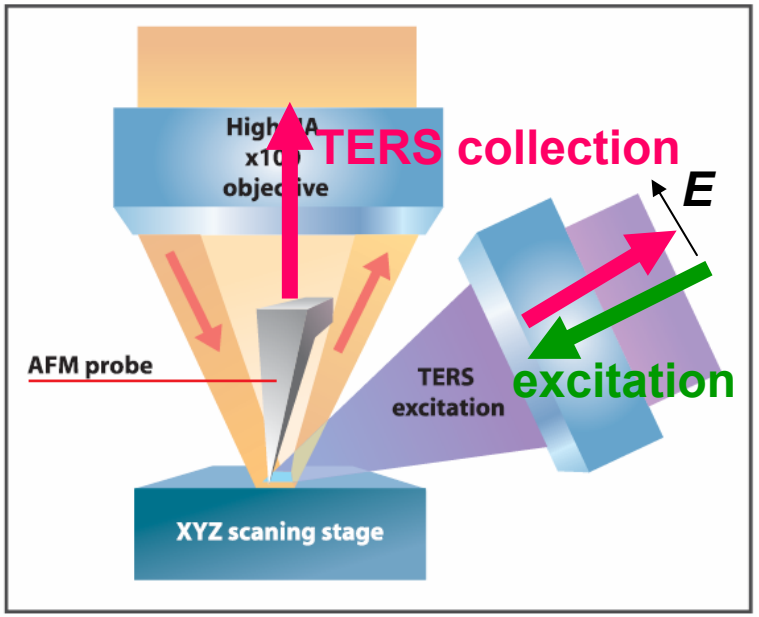
S.S. Kharintsev, G. Hoffmann, P.S. Dorozhkin, G. de With, and J. Loos
Nanotechnology 18 (2007), 315502

Tip Enhanced Raman

UPRIGHT geometry (non-transparent samples)

Data on real TERS with non-transparent samples is to be published soon. Request NT-MDT for further information





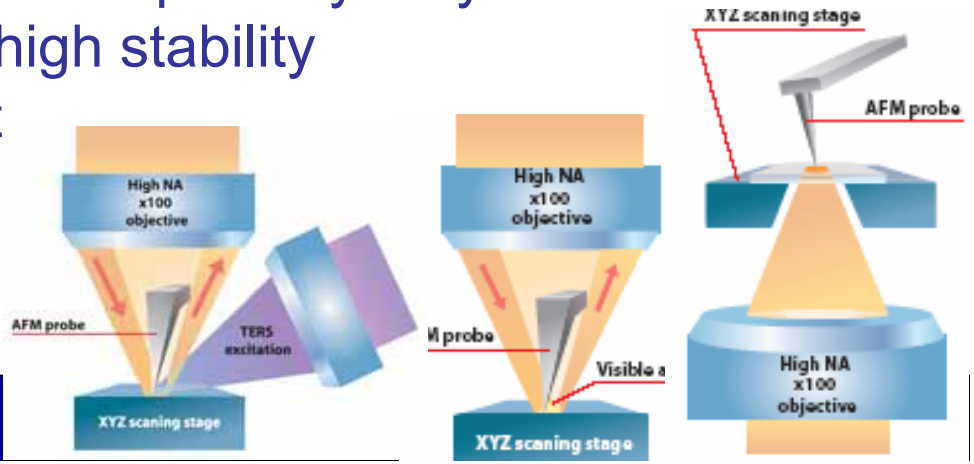
Successful Tip Enhanced Raman experiment: Major requirements to experimental setup (AFM – Raman combination):

1. Different geometry of AFM - Raman optics: bottom illumination/collection, top illumination/collection, side illumination/ top collection. All optics must have very high Numerical Aperture.

2. Independent scanning options: by laser beam, by sample, by AFM tip (at least 6 scanning coordinates required). All AFM and Raman control must be integrated into one software

3. Very low AFM noise (to keep TERS tip safely very close to sample), low drifts and high stability (to keep laser exactly on the hot spot – with 10 nm precision)

4. *Good TERS tip*



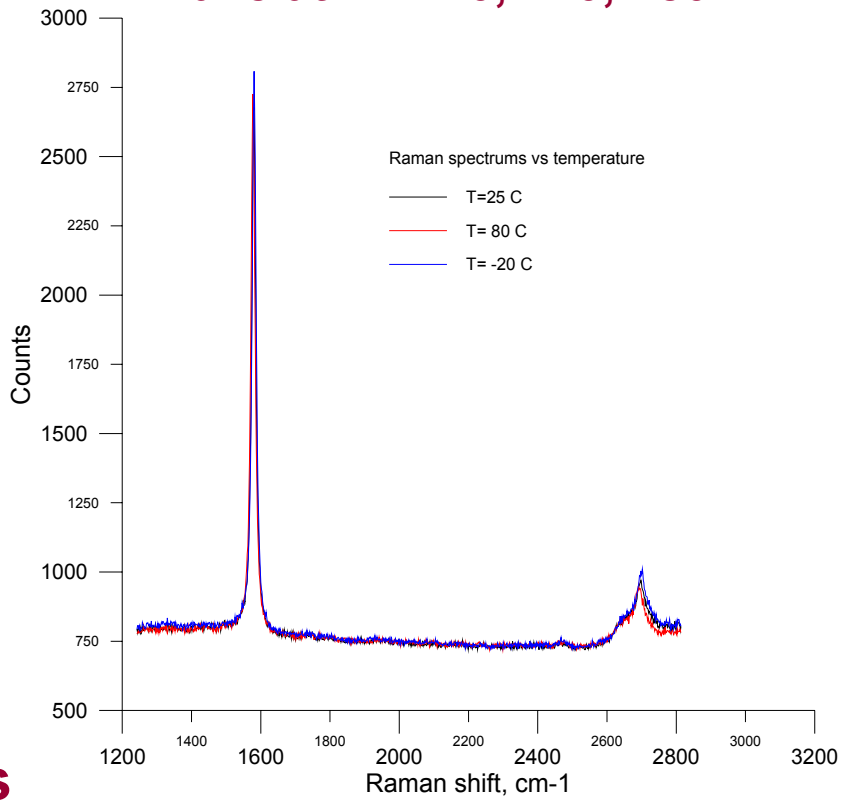
Ultrastable AFM – Raman – TERS measurements in wide temperature range

T = -30 - +80 ºC

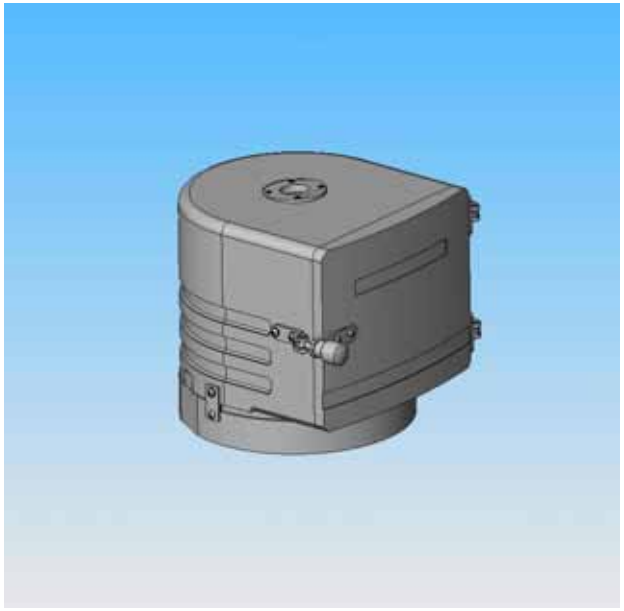
Drifts < 10 nm per 1ºC

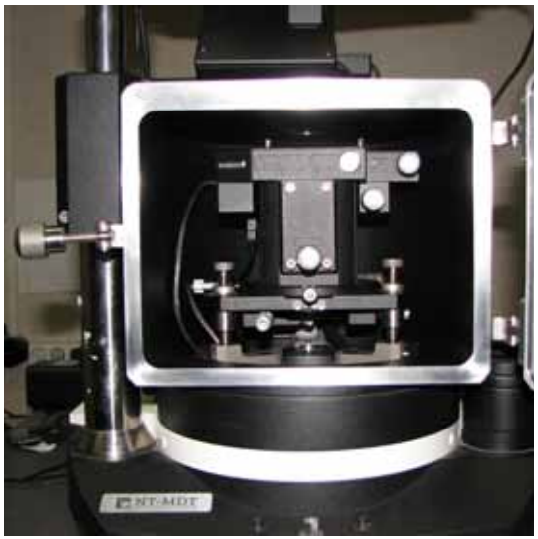
< 10 nm per hour at all temperatures

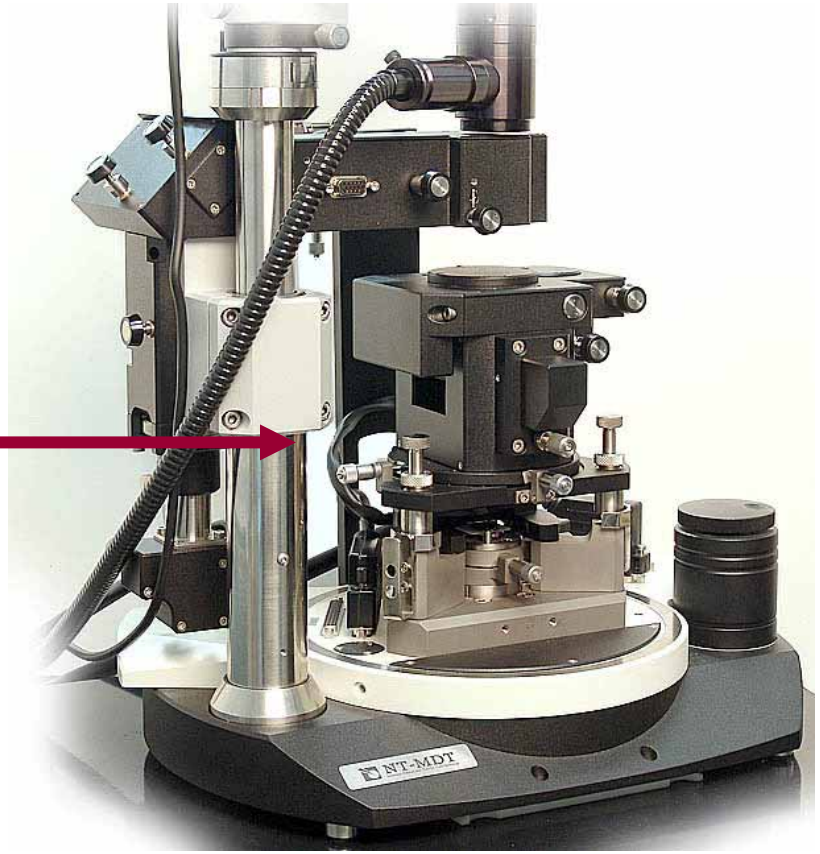
Raman spectra of graphene flake at T = -20, +20, +80 ºC



AFM-Raman-TERS in controlled atmosphere







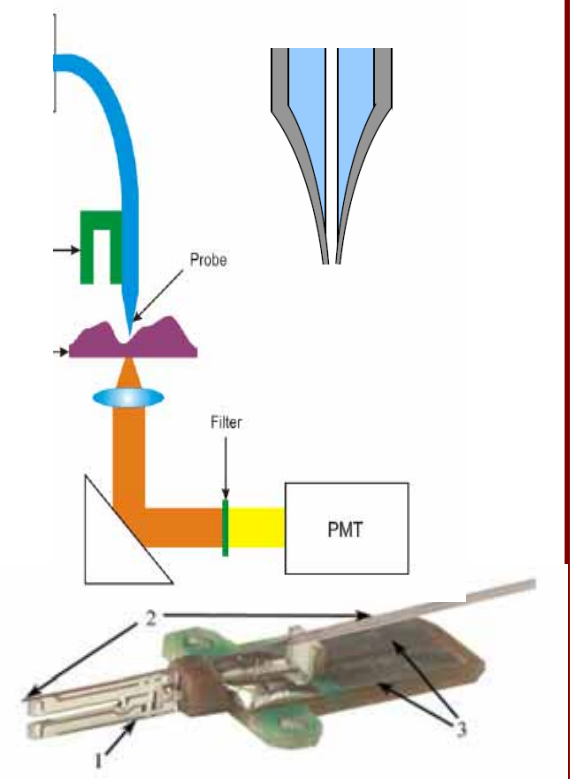
Controlled atmosphere chamber for AFM-Raman-TERS (controlled temperature, humidity, inert gases etc.)

NTEGRA Spectra

SNOM

NT-MDT supports all existing SNOM techniques

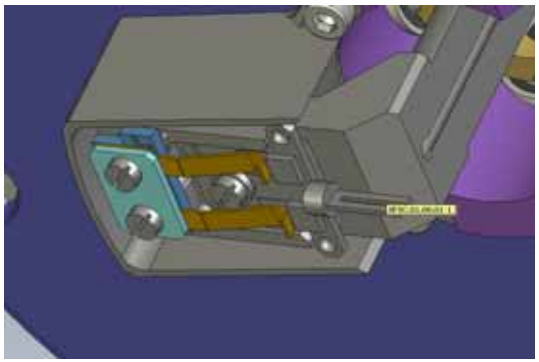
1. Straight quartz fiber (glued to tuning fork)



NT-MDT produces (for >10 years) both SNOM hardware and SNOM probes for various ranges of wavelengths (from UV to IR).

All SNOM modes are supported

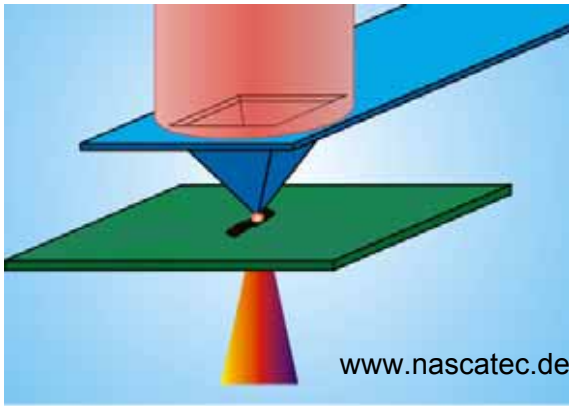
2. Bent quartz fiber (glued to tuning fork)

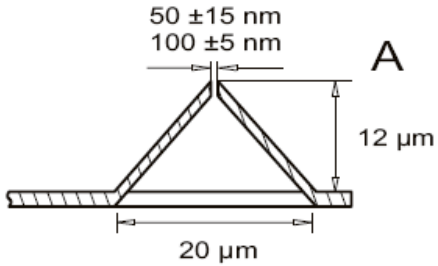


NT-MDT produces all hardware to work with such probes at all SNOM modes.

NT-MDT does not produce the probes – they have to be produced by customer or bought from another supplier

3. Silicon cantilevers with aperture

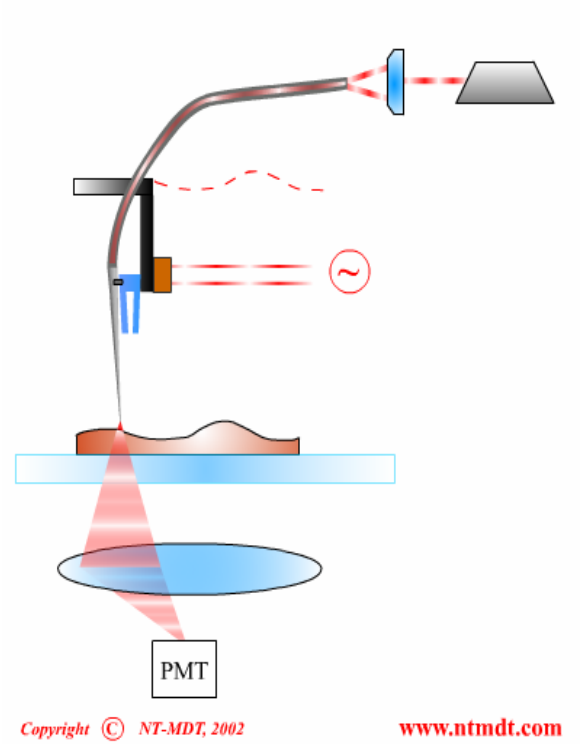




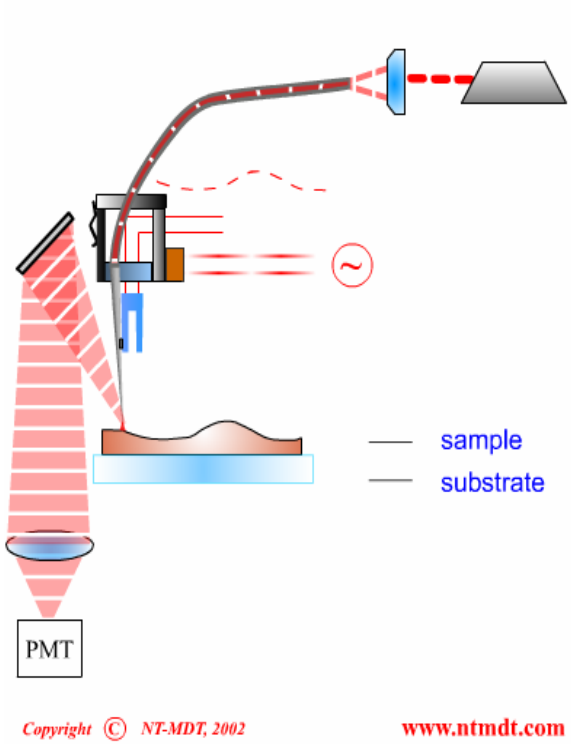
NT-MDT produces all hardware to work with such probes at all SNOM modes.

SNOM cantilever probes are produced by Nascatec, Germany

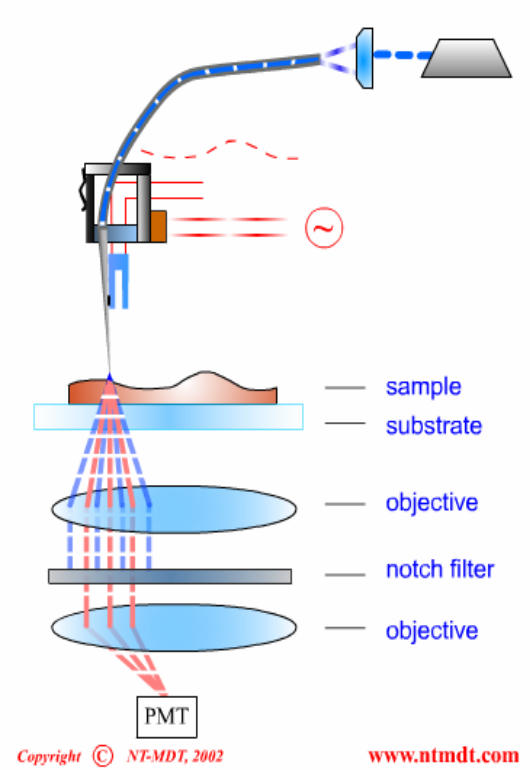
Example of some SNOM modes



Transmission



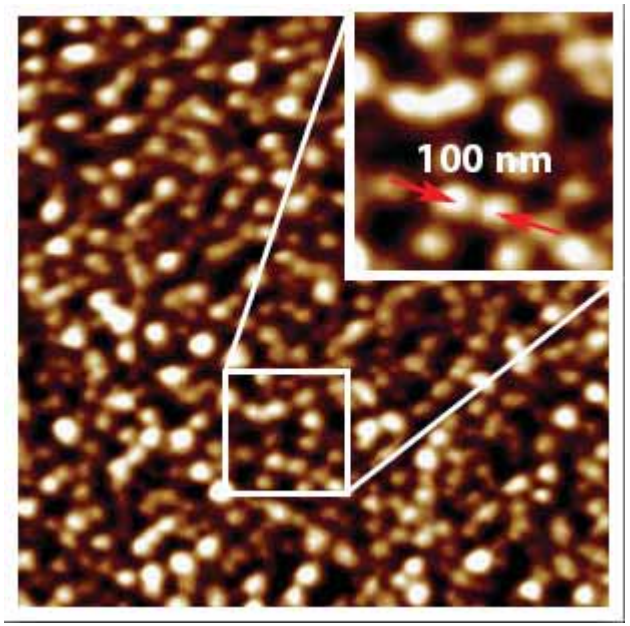
Reflection



Transmission
Fluorescence

All SNOM modes are available:
Collection, Transmission, Reflection
(for all signals/modes: *laser, fluorescence and spectroscopy*)

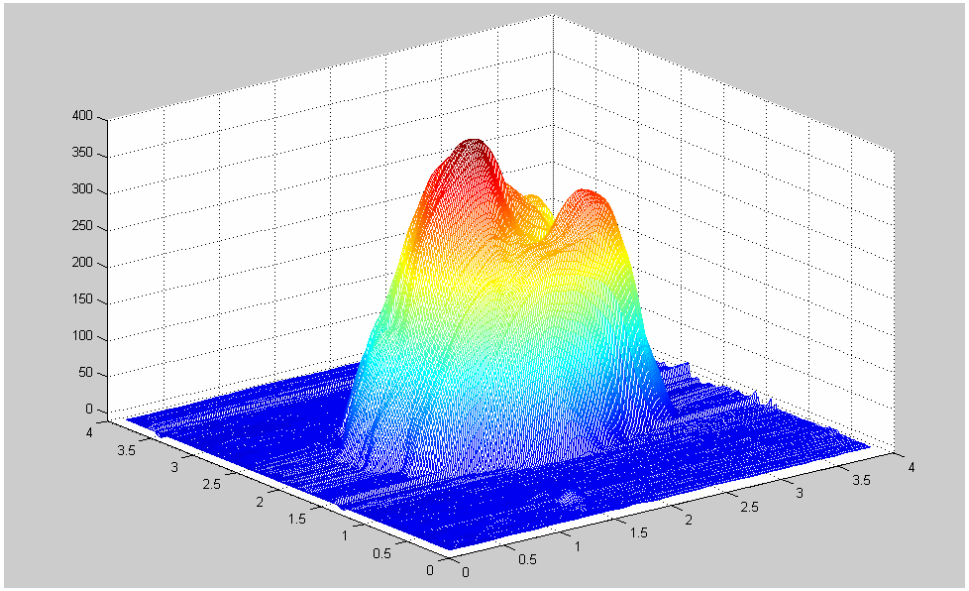
SNOM: transmission luminescence



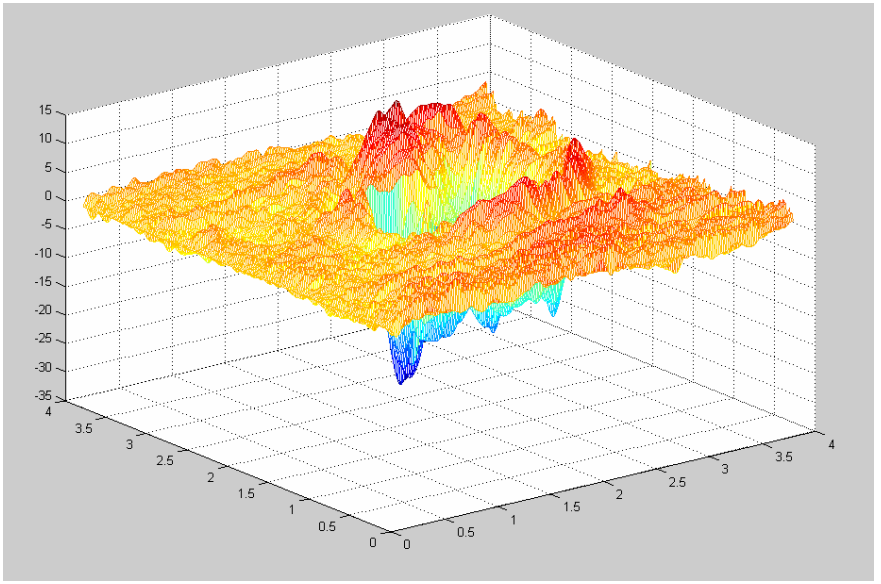
Near-field optical image of composite polymer with globular structure.
Particle size is about 30-40 nm.

When 3.5μm image is zoomed electronically (because initial pixel resolution is high enough) it is clear that particles of just the same size are resolved much and much better.

SNOM transmission: Single lipofuscin granule



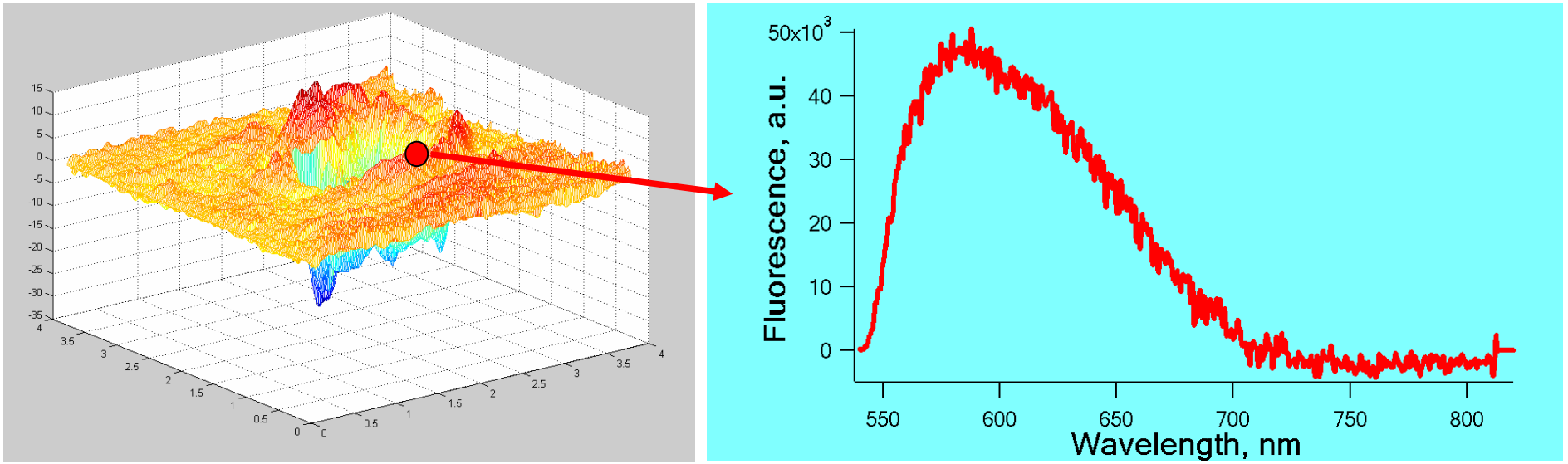
Shear force topography



SNOM transmission

Single lipofuscin granule 400 nm in height and 1.7 – 2.7 μm in diameter. Two "humps" can be seen as well at shear-force image (left one). On the right image transmission at 420 nm can be seen. Quartz substrate transmission was subtracted so negative values can be referred to sample absorption and positive ones (most probably) to sample fluorescence.

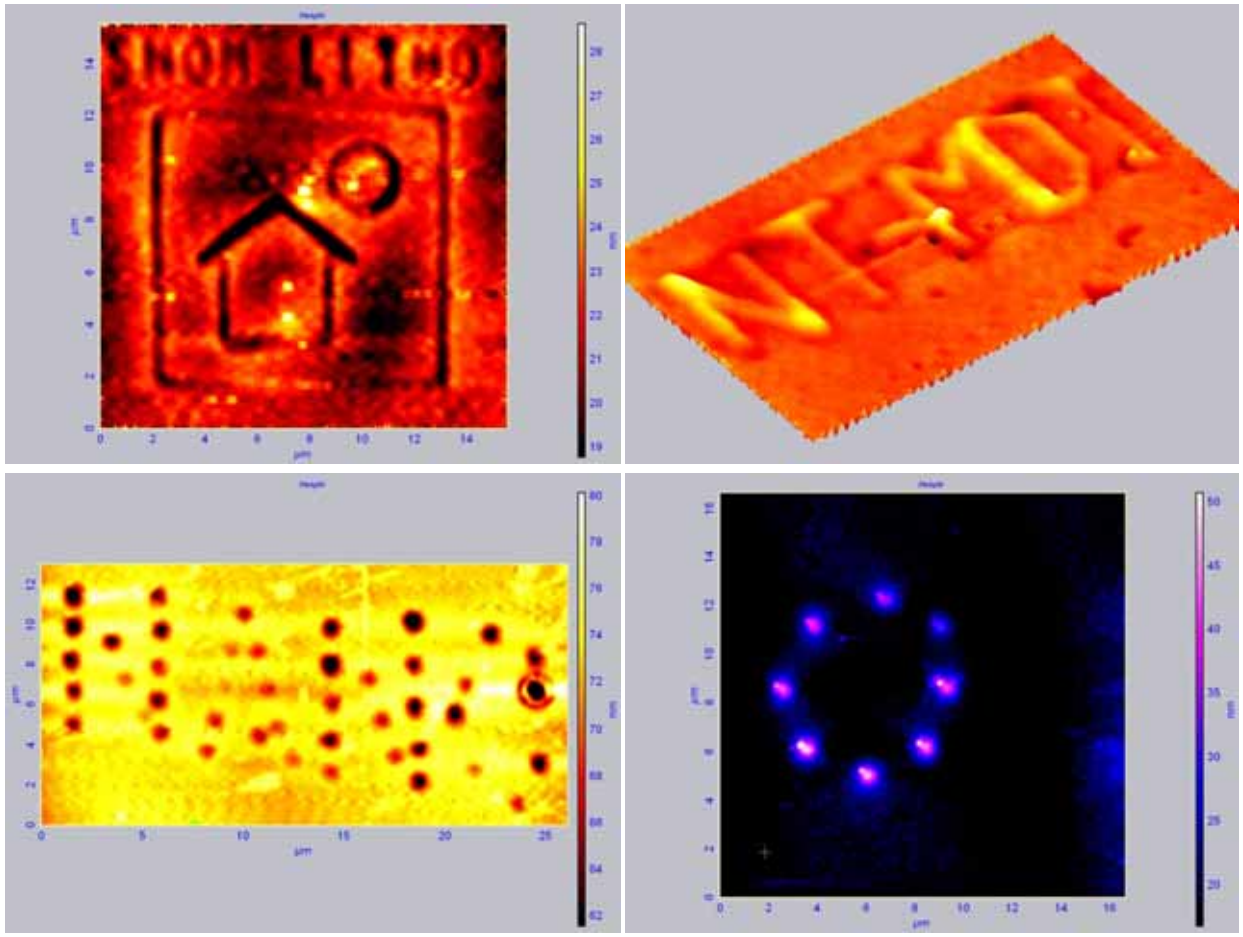
SNOM spectroscopy: Single lipofuscin granule

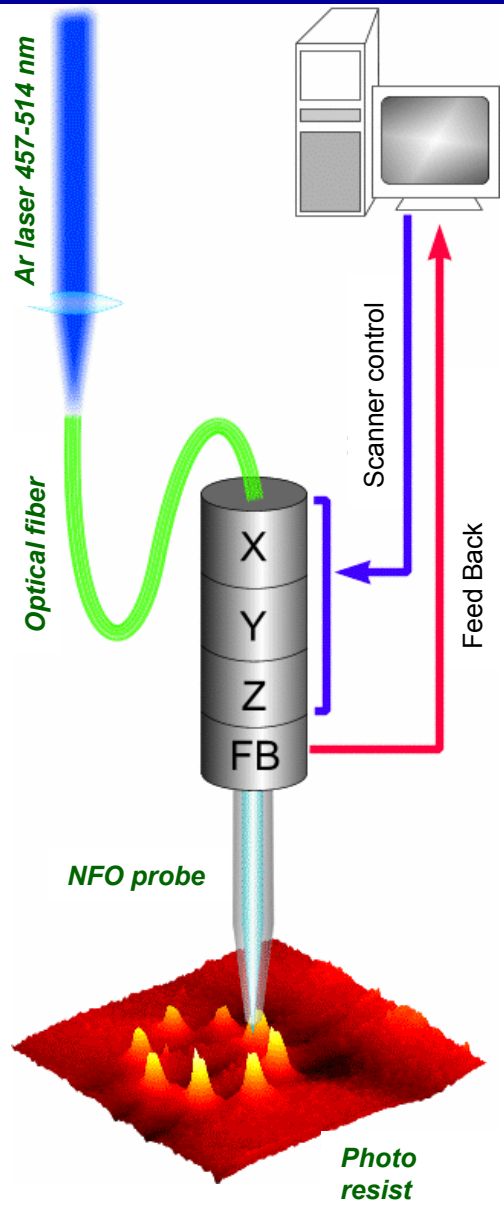


Point-localized spectroscopy of putative fluorescent region. The spectrum obtained corresponds well with the spectrum of pure A2E fluorophore thought to be the major cause of aging-related retina degeneration.

SNOM Lithography

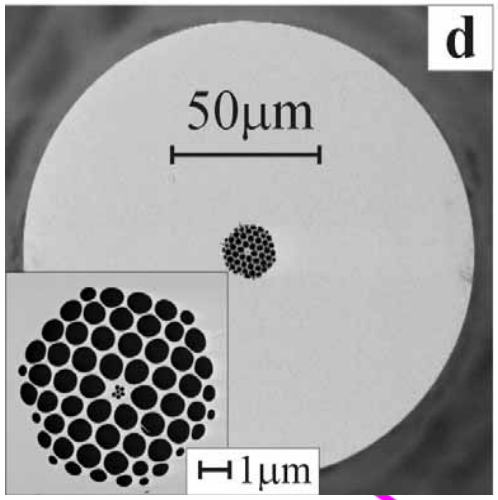
Sample : Positive photoresist FP 380 on Si substrate

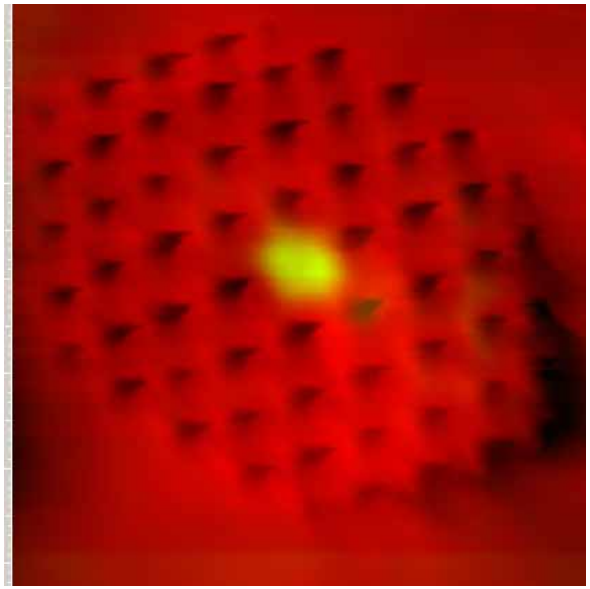


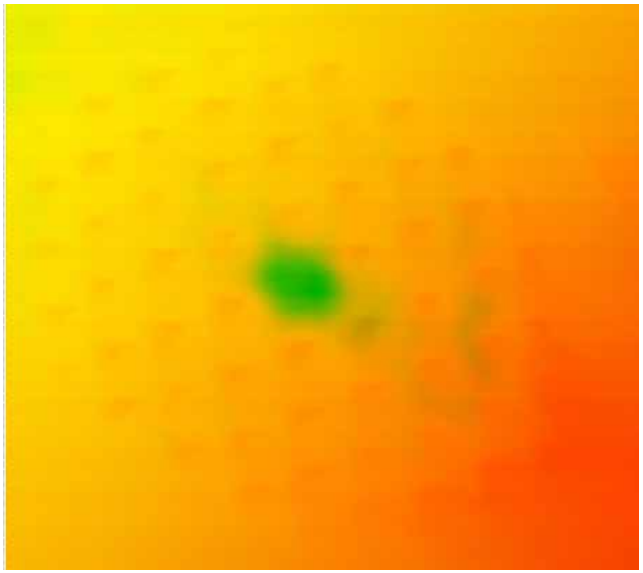


Shear Force image of SNOM lithography results. Lithography made using Ar laser.

SNOM on photonic crystal optical fibers





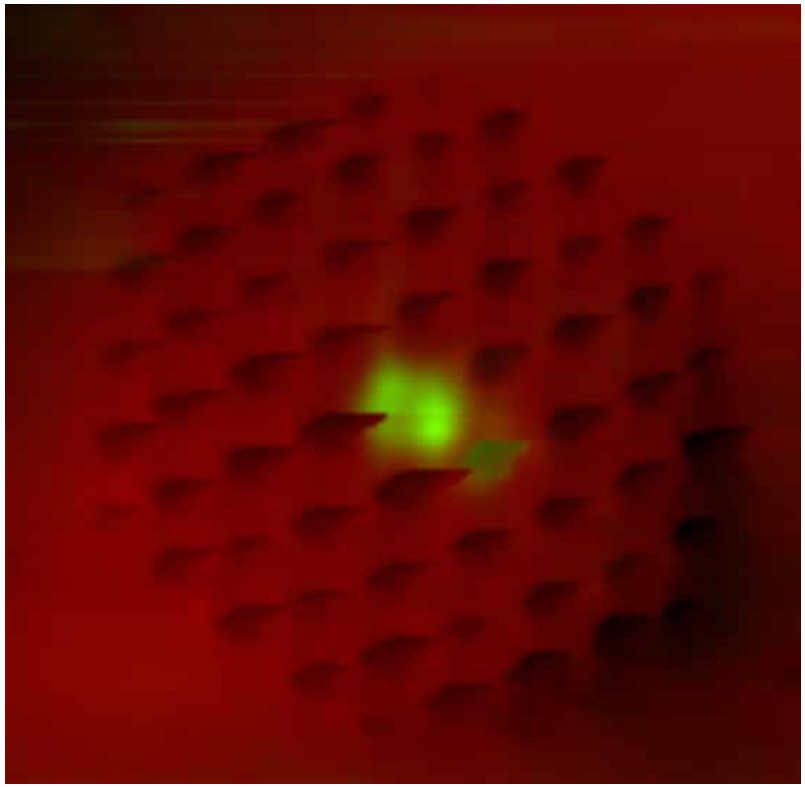


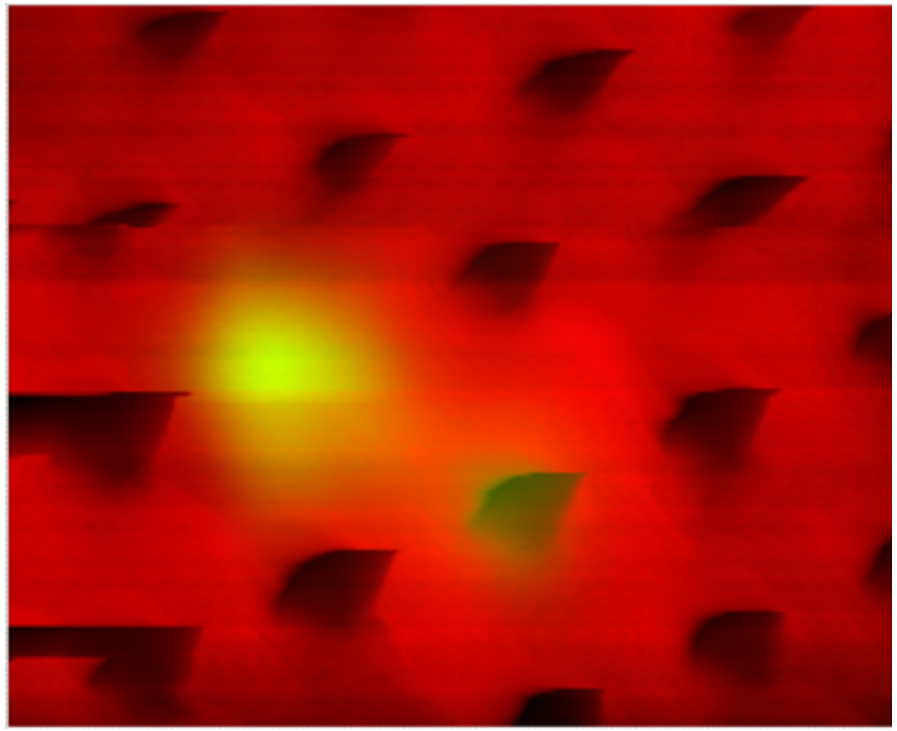
Overlay of simultaneously measured:
Sample topography (orange/red palette) and
SNOM intensity (green palette)

Launch light from outside of the NT-MDT system with particular sources

Sample courtesy:
Yinlan Ruan, Heike Ebendorff-Heidepriem, Tanya M. Monro
Centre of Expertise in Photonics, School of Chemistry & Physics, University of Adelaide, Adelaide, 5000 Australia

SNOM on photonic crystal optical fibers





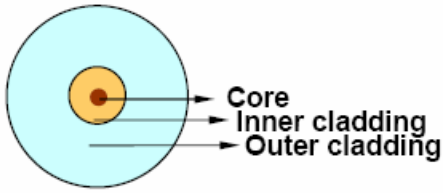
Overlay of simultaneously measured:
Sample topography (orange/red palette) and SNOM intensity (green palette)

Sample courtesy:
Yinlan Ruan, Heike Ebendorff-Heidepriem, Tanya M. Monro
Centre of Expertise in Photonics, School of Chemistry &
Physics, University of Adelaide, Adelaide, 5000 Australia

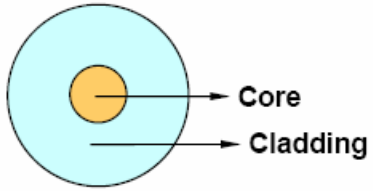
SNOM measurements (VIS & IR) : Cr:YAG optical fibers

Nanospectroscopy of Cr:YAG Double-clad Crystal Fiber

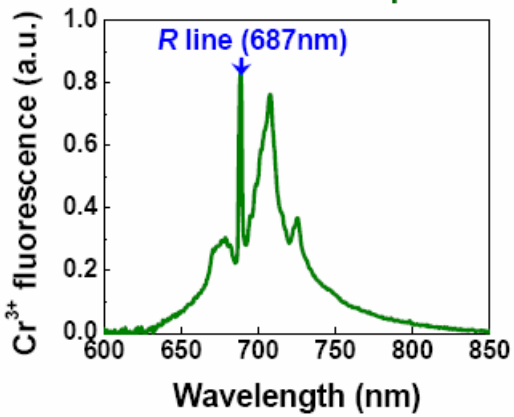
Chien-Chih Lai[1], Kuang-Yao Huang[1], Shi-Chang Wang[2], Yen-Sheng Lin[3], and Sheng-Lung Huang[1,4]
[1]Institute of Photonics and Optoelectronics, National Taiwan University, Taipei 106, Taiwan
[2]Department of Photonics, National Sun Yat-Sen University, Kaohsiung 804, Taiwan
[3]Department of Electronic Engineering, I-Shou University, Kaohsiung 840, Taiwan
[4]Department of Electrical Engineering, National Taiwan University, Taipei 10
Phone: +(8862)33663700 ext. 348, Fax: +(8862)33663692, Email: slhuang@cc.e

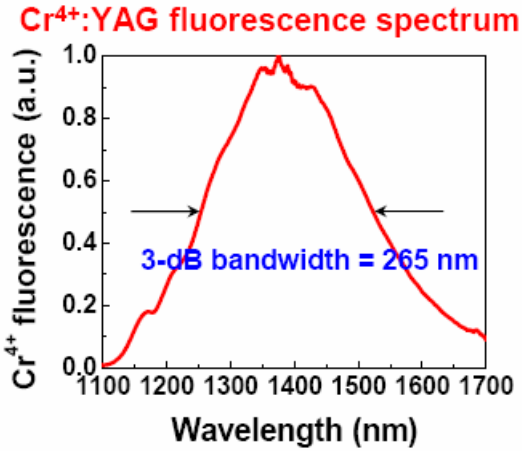


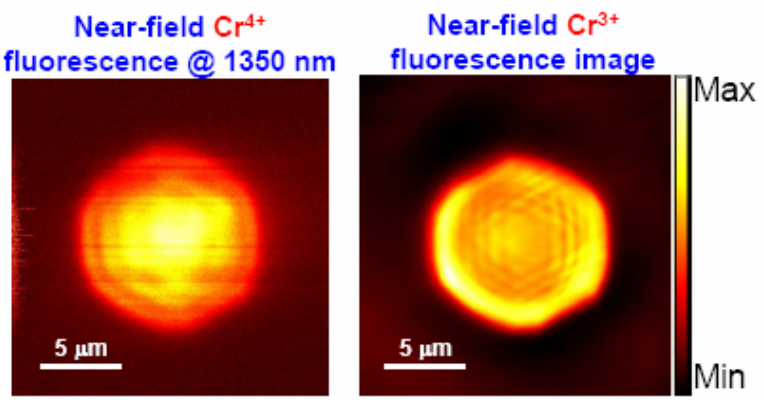
Double-clad structure

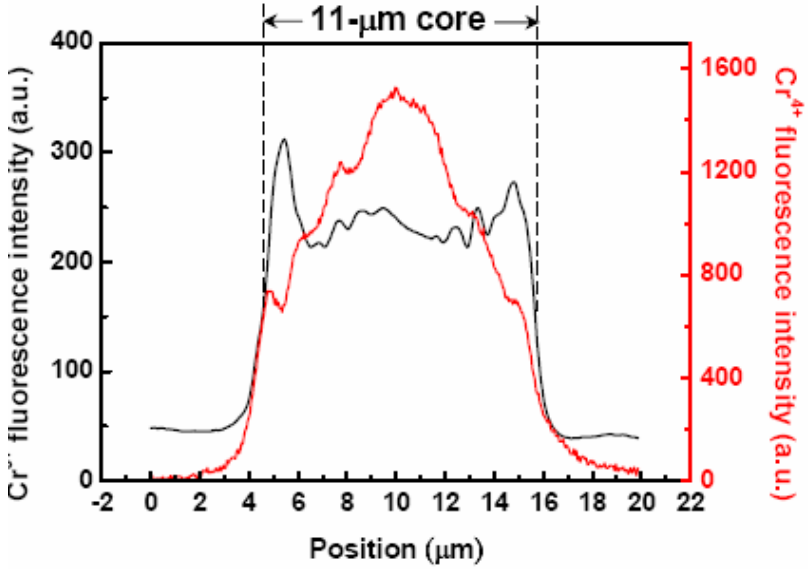


Single-clad structure



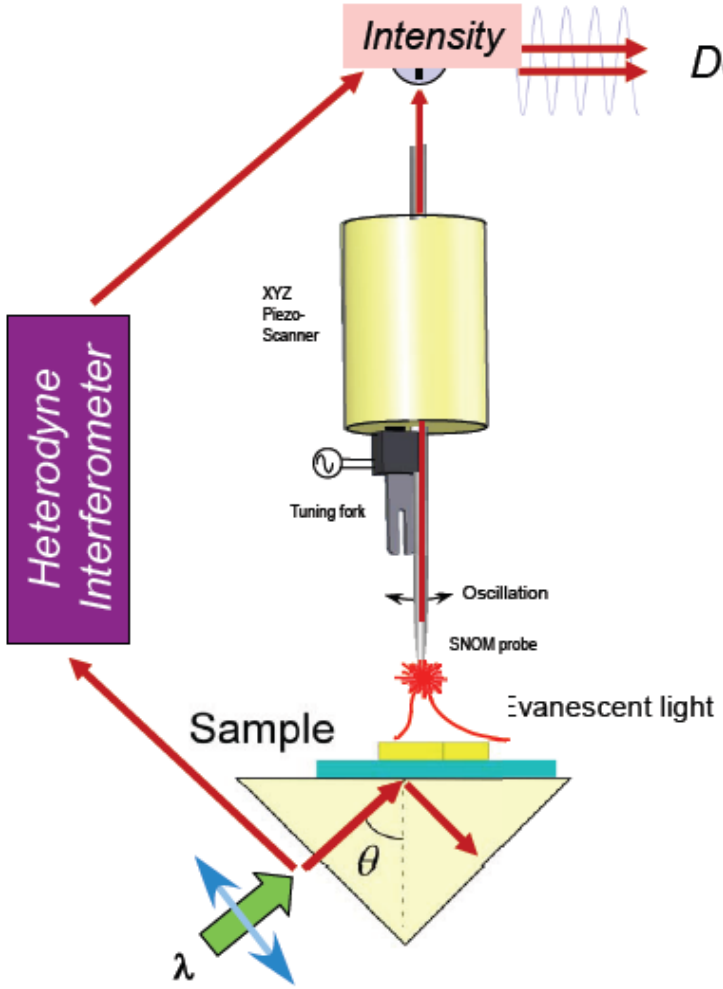






SNOM on Surface Plasmon Polaritons

Coherent Photon Scanning Tunneling Microscope



- PSTM = SNOM in collection mode
- Shear-force Atomic Force Microscope (AFM): topography.
- Usually Intensity recording only
- PSTM combined with a heterodyne interferometer) →

AMPLITUDE & PHASE

Data taken from:
Antonell Nesci and Olivier J.F. Martin,
EPFL, Lausanne, Switzerland
(NT-MDT SNOM system was used + home built Heterodyne interferometer)

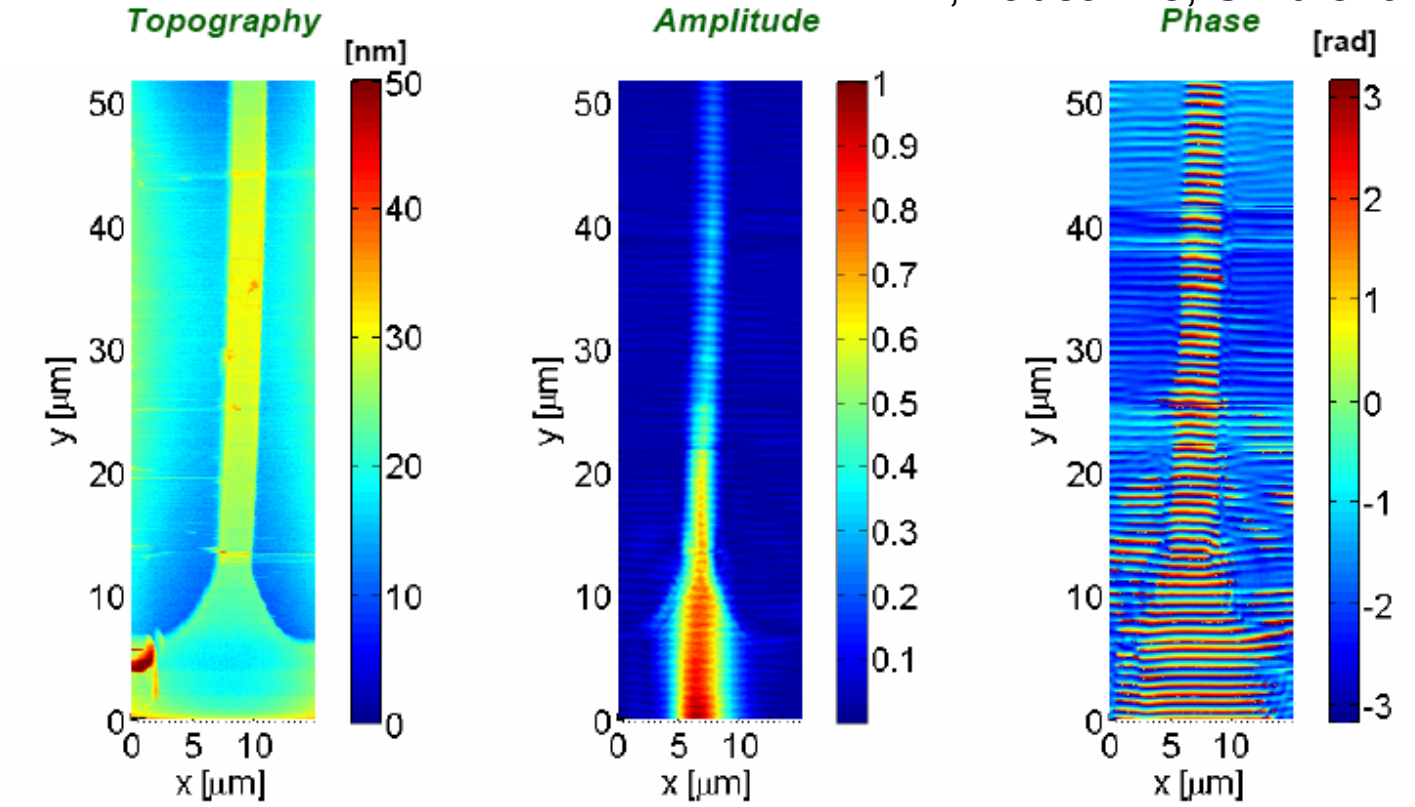
SNOM on Surface Plasmon Polaritons

Guided Plasmons on gold waveguides

3 μm wide WG

λ = 785 nm

Data from:
Antonell Nesci and Olivier J.F. Martin,
EPFL, Lausanne, Switzerland



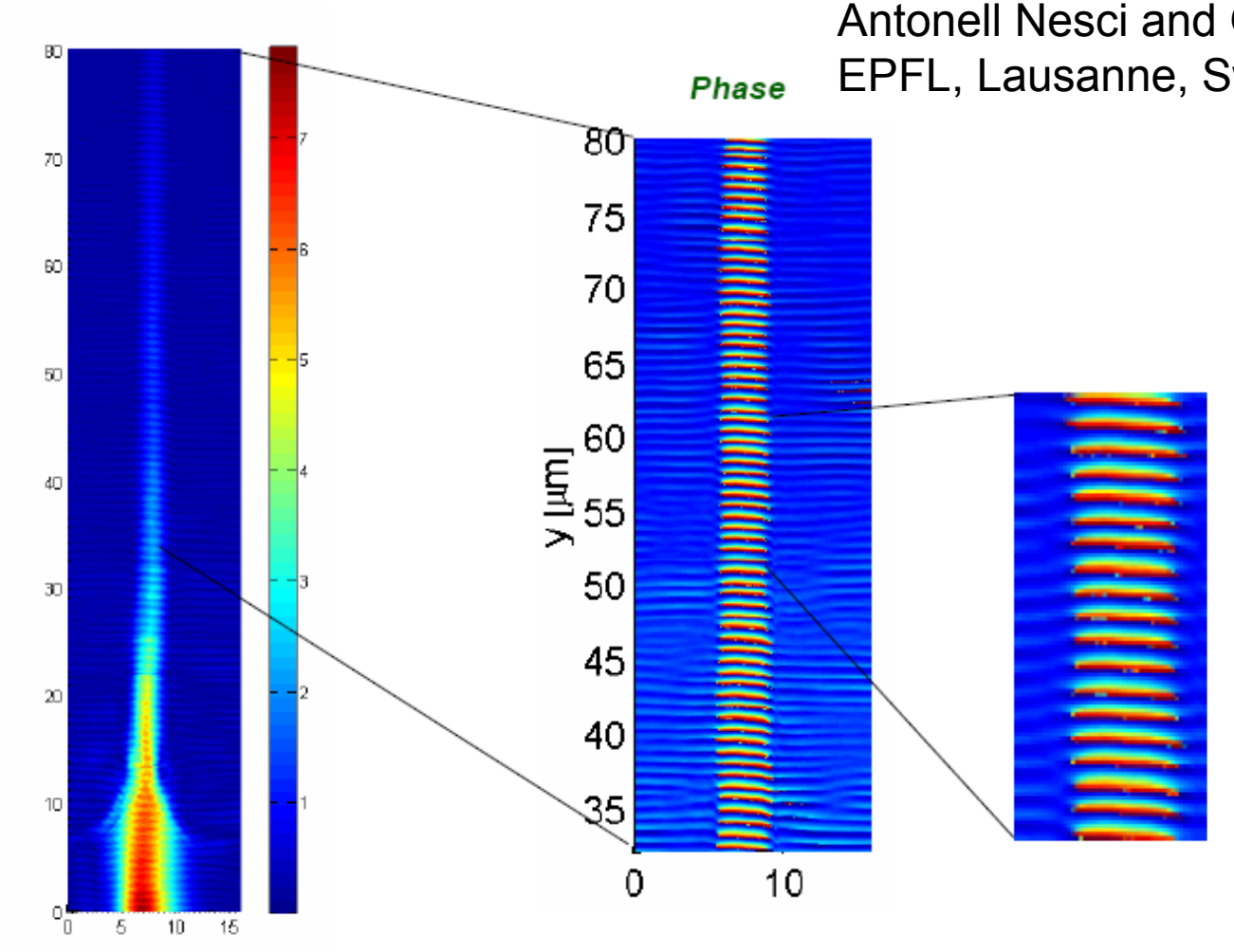
e.g. to address optically single molecules

SNOM on Surface Plasmon Polaritons

Guided Plasmons in gold waveguides

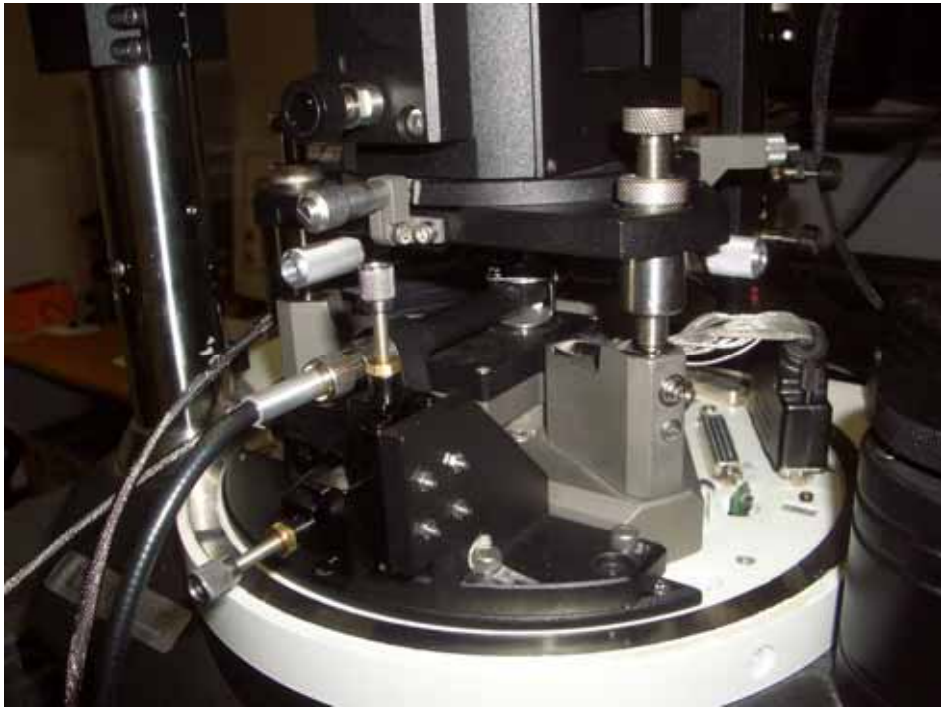
3 μm wide WG

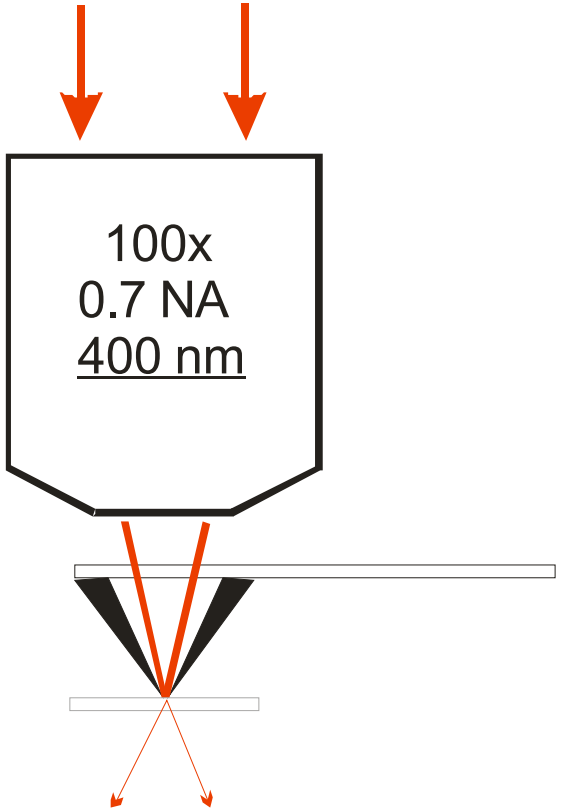
Data from:
Antonell Nesci and Olivier J.F. Martin,
EPFL, Lausanne, Switzerland



→ λ_{plas} = 756nm

SNOM on cantilevers with aperture



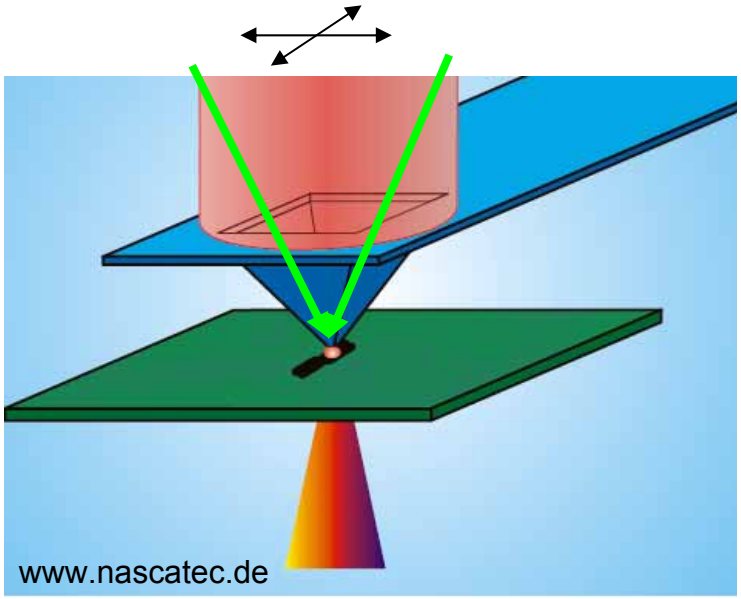


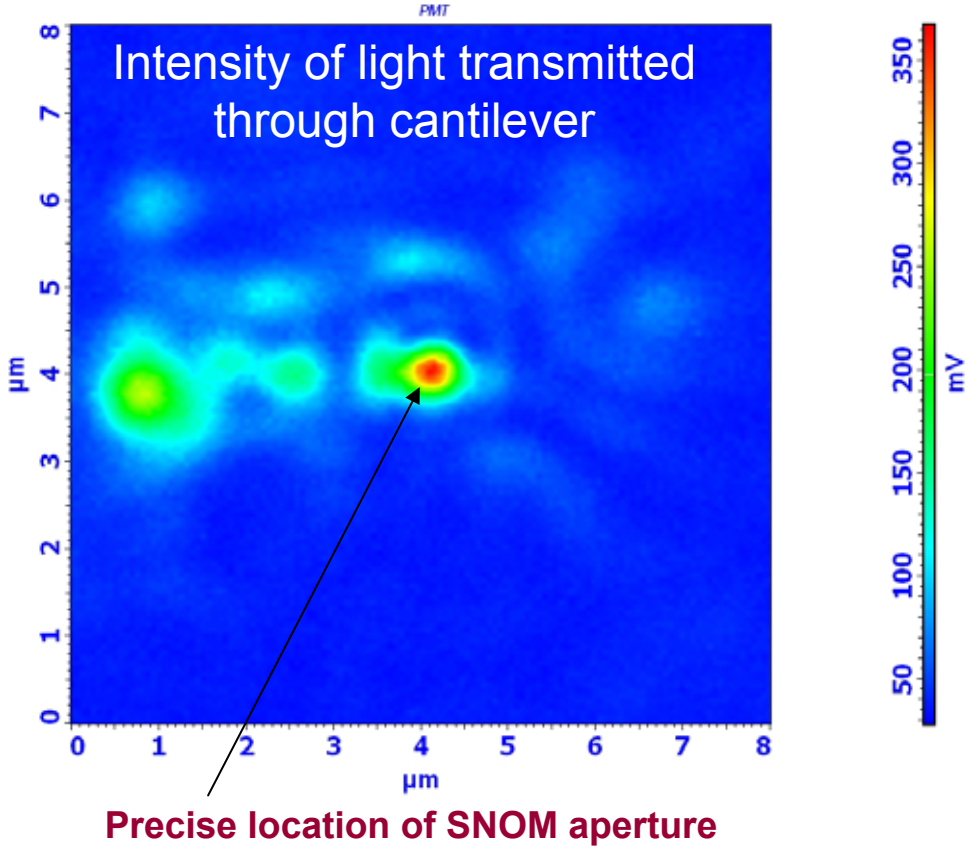
High resolution objective is used to focus light onto or collect light from the SNOM cantilever

Size of the light spot: 400 nm

SNOM on cantilevers with aperture

laser spot is scanned: x,y



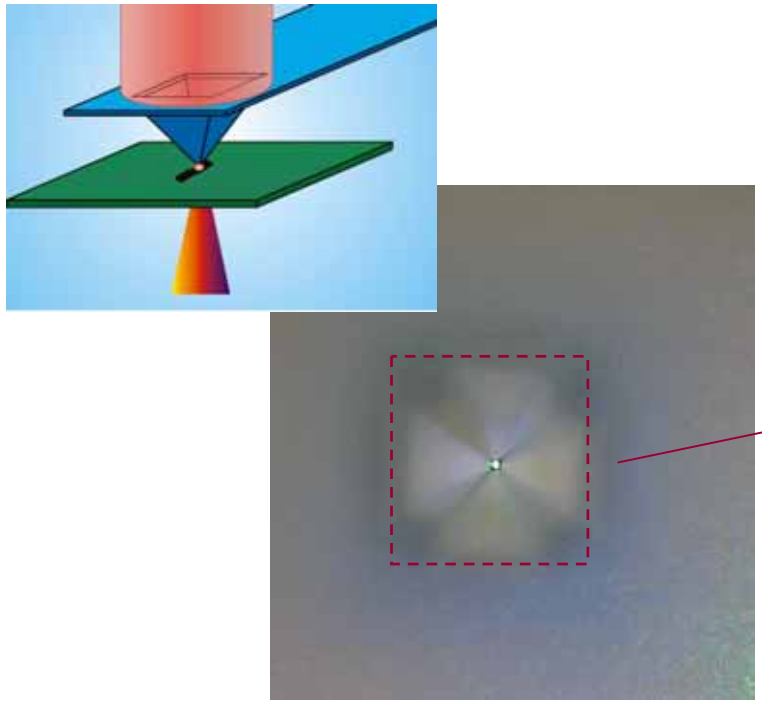


Precise location of SNOM aperture

Laser spot is scanned in *automatic regime* across SNOM cantilever and transmitted signal is measured – to locate the SNOM aperture with very high accuracy (<10 nm).

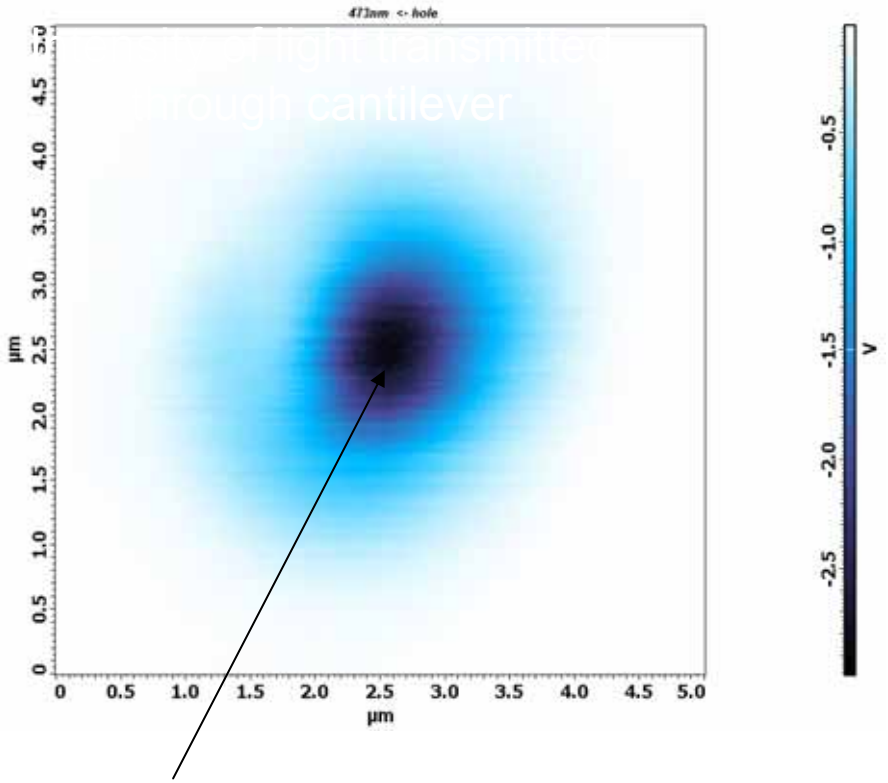
Afterwards, 400 nm size laser spot is focused exactly onto the aperture – to realize SNOM transmission regime with very high optical throughput.

SNOM on cantilevers with aperture



Optical view of cantilever with SNOM aperture in Transmission regime - laser is focused on the sample from the bottom, cantilever is viewed from above. Light transmitted through the aperture can be seen (in this case, SNOM aperture is quite large)

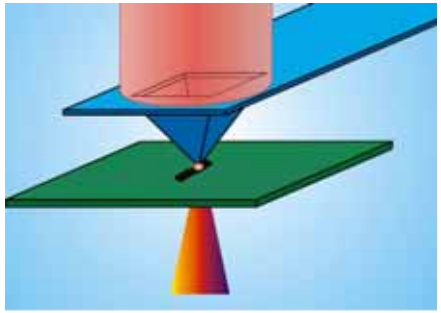
Note extremely high resolution of the image: it is done with optics 100x, 0.7 NA, 400 nm resolution



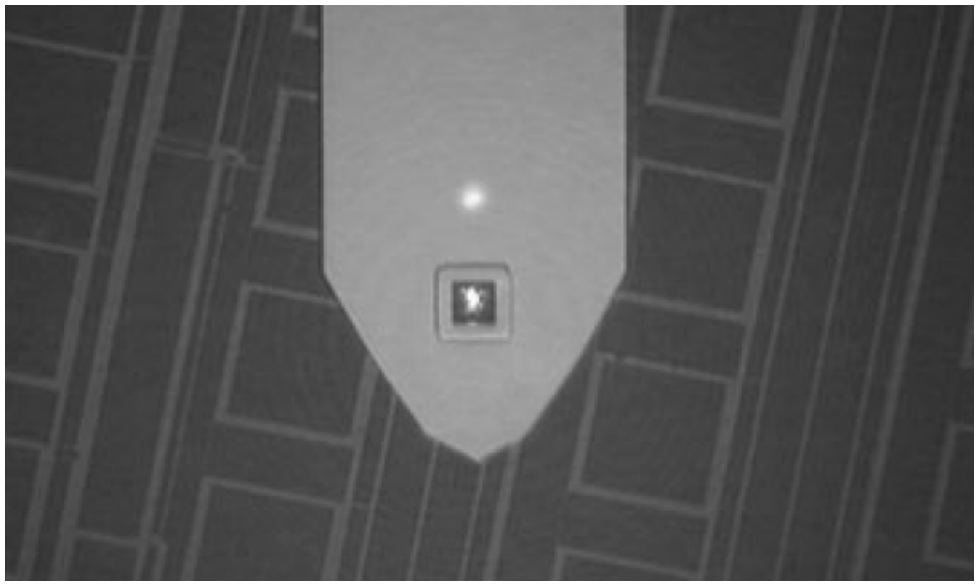
Precise location of SNOM aperture

Intensity distribution of light across the SNOM aperture (measured by automatic scanning of light collection area across the SNOM aperture)

Optical view of SNOM cantilever



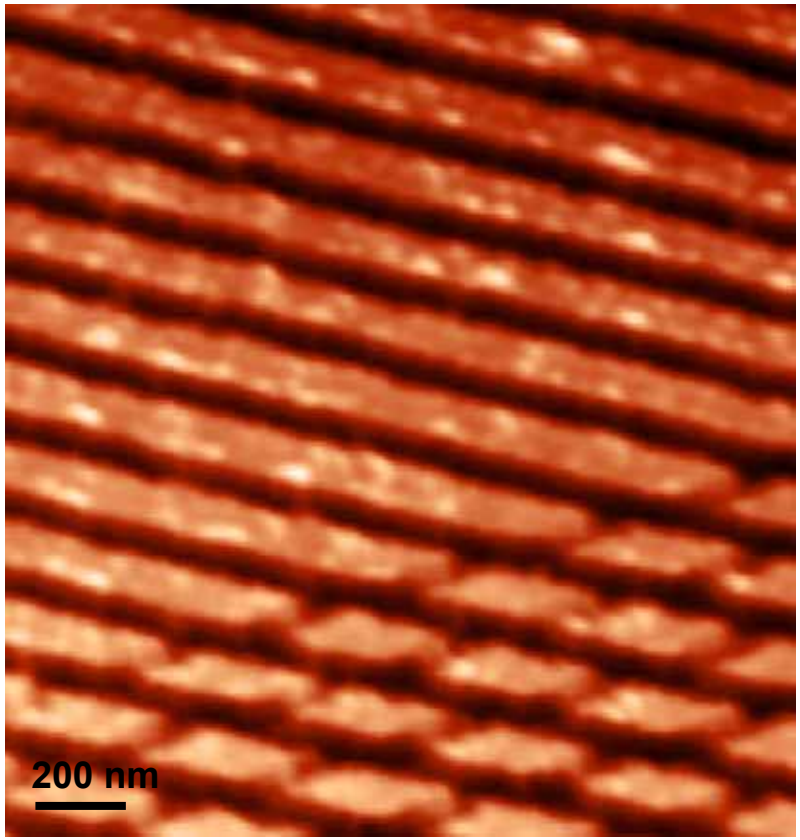
Optical image with HIGH resolution NT-MDT optics (400 nm resolution)



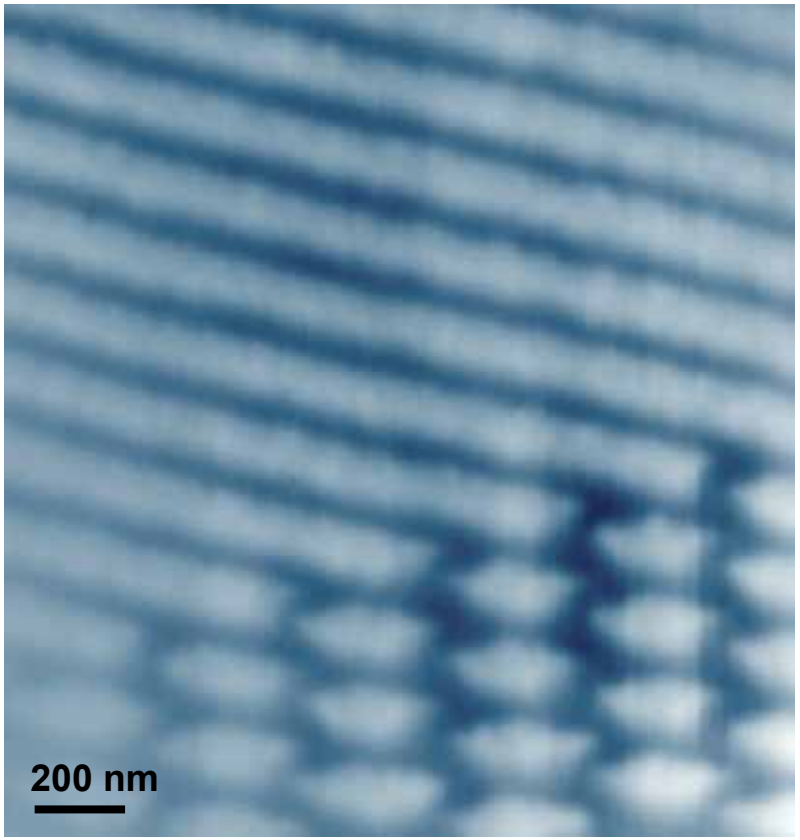
Standard optical image with low resolution optics of other commercial system (about 3 μm resolution image)

Experimental results

Sample: SERS substrate. Au nanodiamond arrays on quartz.



Topography

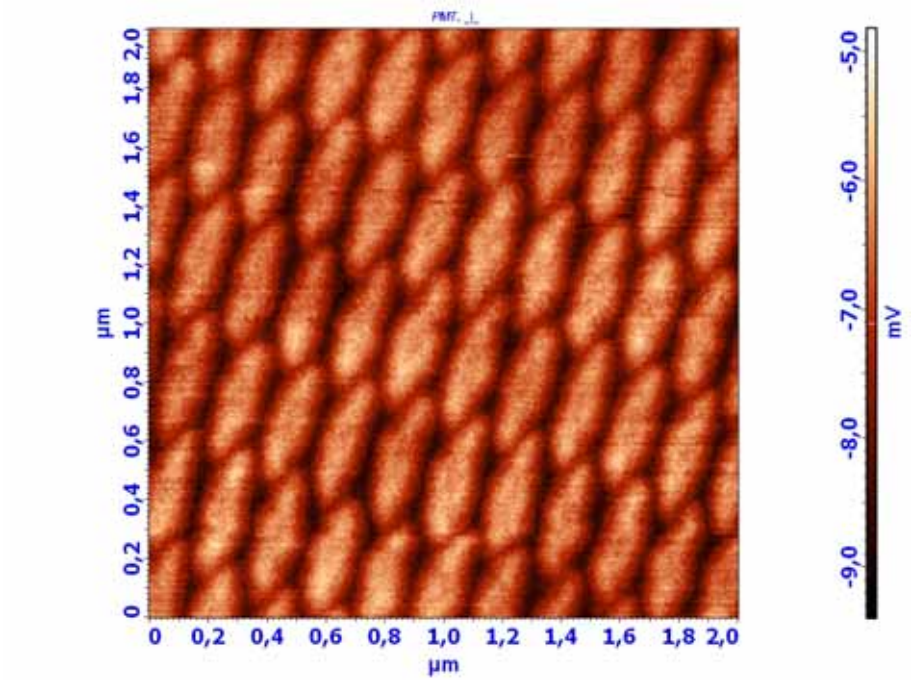


SNOM transmission

Period of the structure: 200 nm
SNOM resolution: < 70 nm

Sample courtesy: Dr. Henrik Schneidewind, Institute of Photonic Technology (IPHT Jena), Germany

Experimental results



SNOM transmission

Period of the structure: 200 nm
SNOM resolution: < 70 nm

Sample courtesy: Dr. Henrik Schneidewind, Institute of Photonic Technology (IPHT Jena), Germany

Unique features of NT-MDT SNOM on cantilevers with aperture

- VERY high resolution optics is used to focus/collect light onto/from SNOM aperture. Resolution and Spot Size: 400 nm !

- Precise automatic positioning of the laser spot onto the SNOM aperture by scanning laser spot across cantilever. Positioning precision: < 10 nm

- High AFM stability (Z-noise on sub-nm level)

Contact: Dr. Pavel Dorozhkin, NT-MDT Co. dorozhkin@ntmdt.com