

AFM integration with Laser Spectroscopy: Challenges, Solutions, Advantages

Shelaev Artem, application scientist shelaev@ntmdt-si.com

Product Line

AFM

AFM-Raman / IR / TERS









SOLVER NANO

NEXT / TITANIUM

NTEGRA

NTEGRA SPECTRA II NTEGRA IR

- Compact desktop AFM/STM for both education and science
- Full set of AFM/STM modes
- High AFM/STM performance
- Closed-loop Scanner

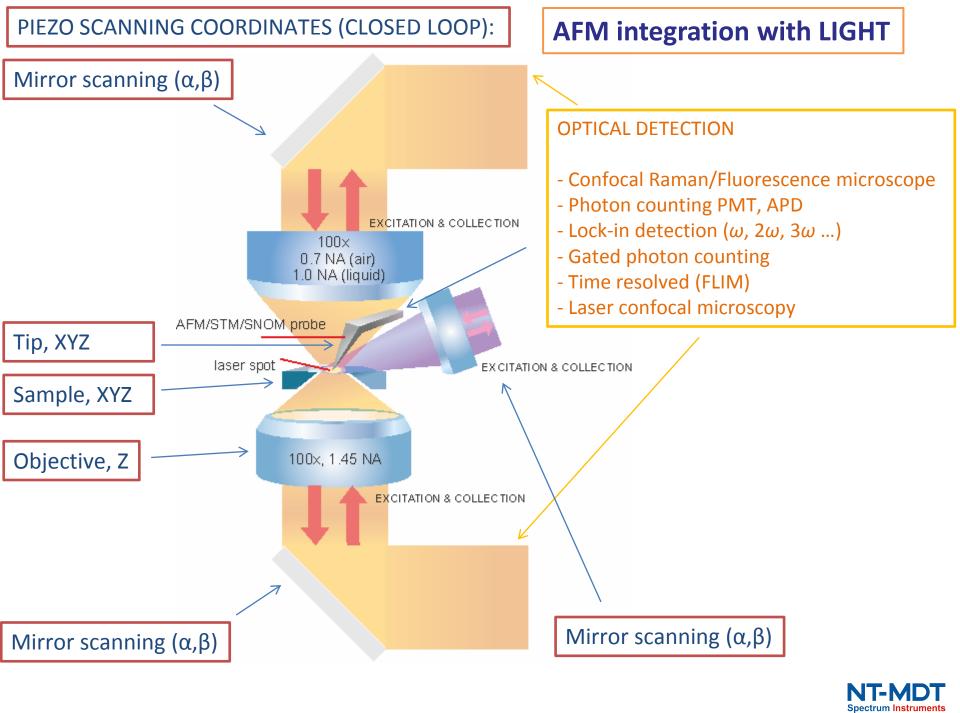
- AFM/STM with exceptional level of automation
- Fast, precise and low-noise closedloop scanner
- High resolution imaging due to extremely low noise and high stability
- Full set of standard and advanced AFM/STM modes
- HybriD ModeTM

- Modular high performance AFM/STM for wide range of applications
- Low noise and high resolution
- Full set of standard and advanced AFM/STM modes
- HybriD ModeTM

- SPM
- Automated AFM laser, probe and photodiode
- Confocal Raman / Fluorescence / Rayleigh Microscopy
- Tip Enhanced Raman Scattering (TERS)
- TERS optimized system for all possible excitation/detection geometries
- HybriD Mode[™]

- IR sSNOM system
- High resolution AFM
- Stabilized CO₂ laser
- HybriD Mode[™]





NTEGRA Spectra II in Upright, Inverted and Side illumination

Light input from side (with scanning mirror)

Top optics (LED illuminator & camera)

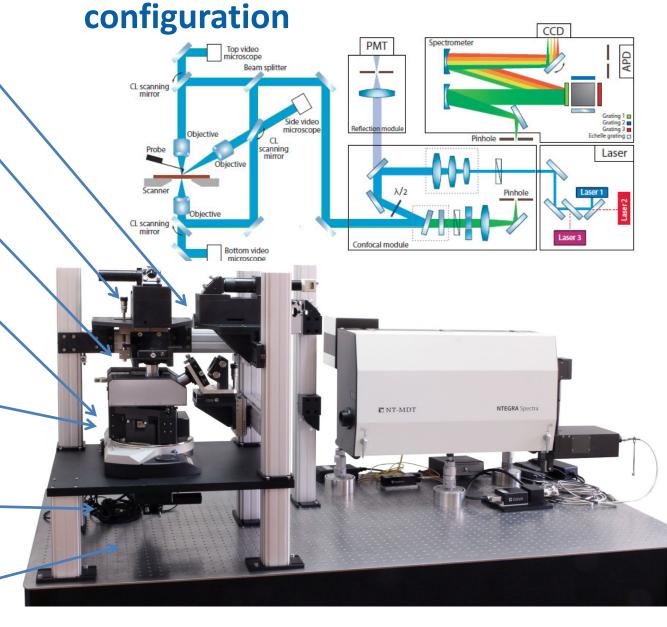
Light input from top (with scanning mirror)

Optical AFM (AFM probe + 100x objective on the top)

XYZ sample stage (bottom illumination objective inside)

Light input from bottom (with scanning mirror)

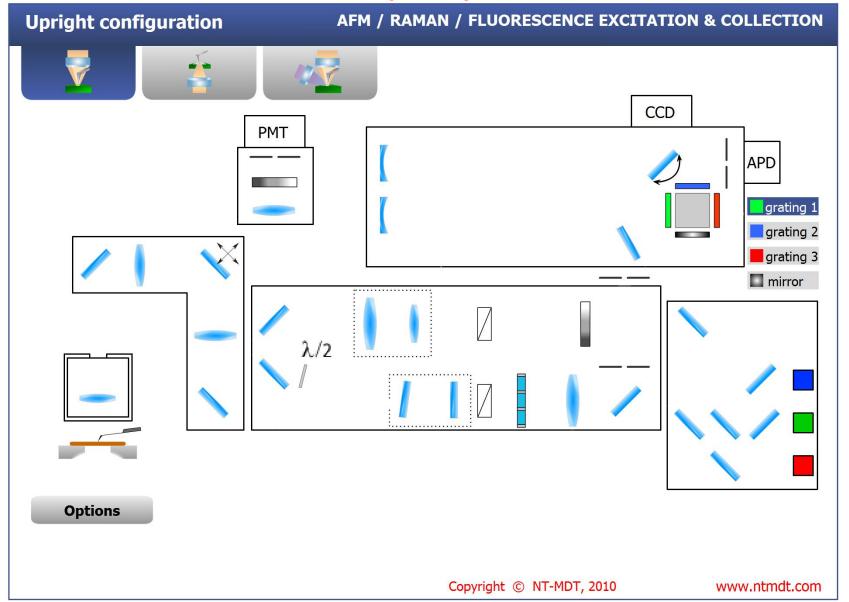
Bottom optics (LED illuminator & camera)





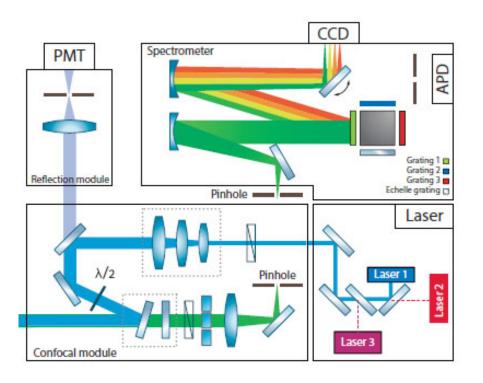
AFM – Confocal Raman / Fluorescence – SNOM – TERS

NTEGRA Spectra optical scheme





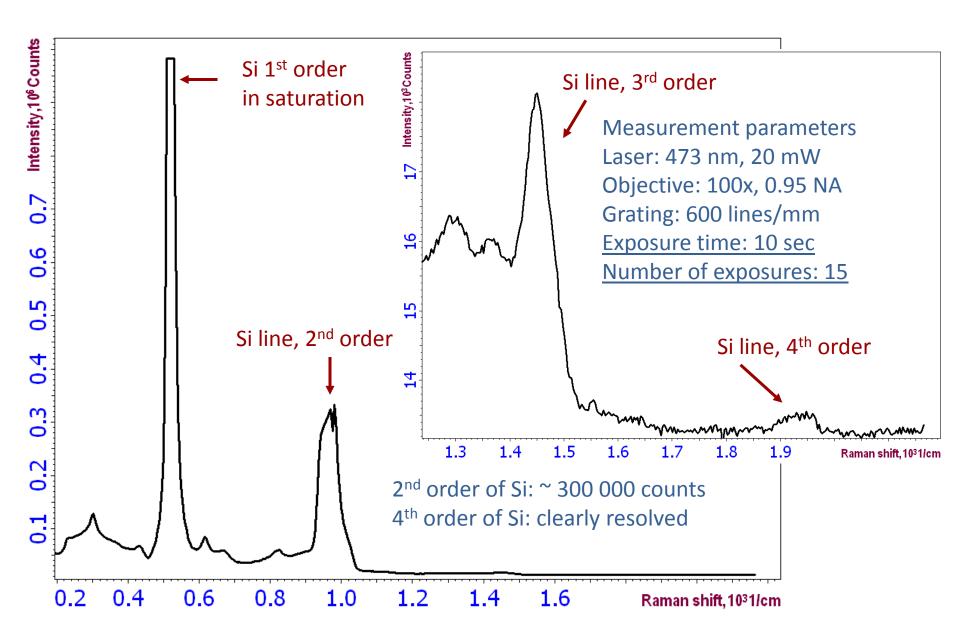
Optical scheme of Spectrometer



- True confocal design. Motorized confocal pinhole.
- Diffraction limited resolution guaranteed (e.g. 200 nm for blue laser, immersion optics)
- Extremely high optical throughput (~70-80 % for spectrometer, ~40-50% sample-to-detector)
- Fully motorized laser change (up to 3 / 5 lasers). UV VIS IR region
- Fully motorized: polarization optics, zoom beam expander, pinhole, 4 gratings
- Can be equipped by fastest and most sensitive detectors available (FI/BI CCD, EMCCD, DD-CCD etc.)
- Zoom beam expander to guarantee diffraction limited laser spot to every objective
- Three optical ports for detectors: two in monochromator, one in separate channel

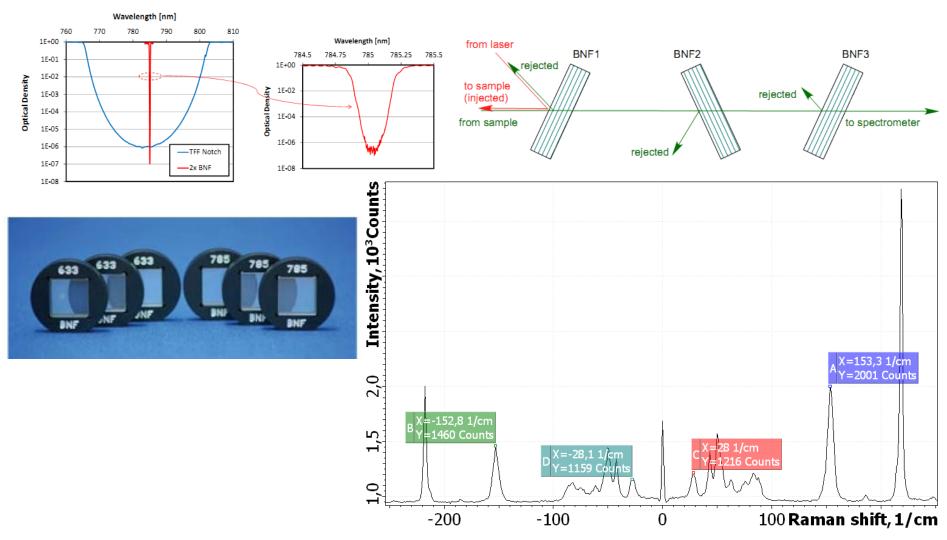


Sensitivity: 4th order of Si Raman band is clearly resolved





Low wavenumbers Raman spectra

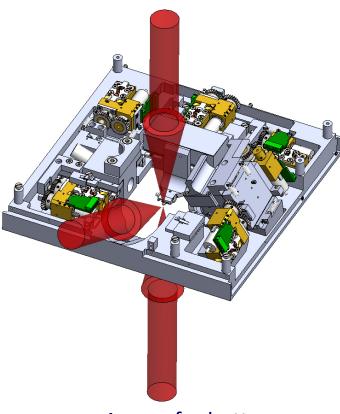


Low wavenumbers Raman spectrum of sulfur. Cut-off at 10 1/cm 488 nm laser, 1800 lines/mm grating.

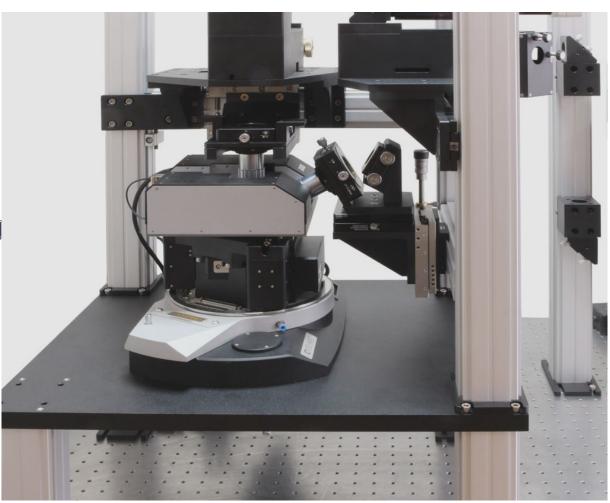


Optical access from Top, Bottom and Side

Access for **Mitutoyo** long working distance objective for top illumination

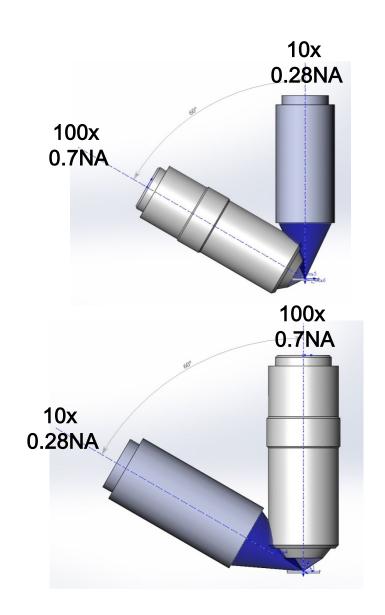


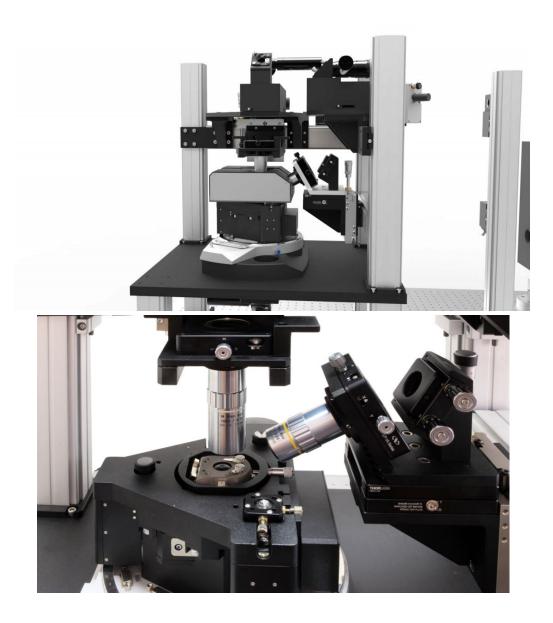
Access for bottom Illumination objective





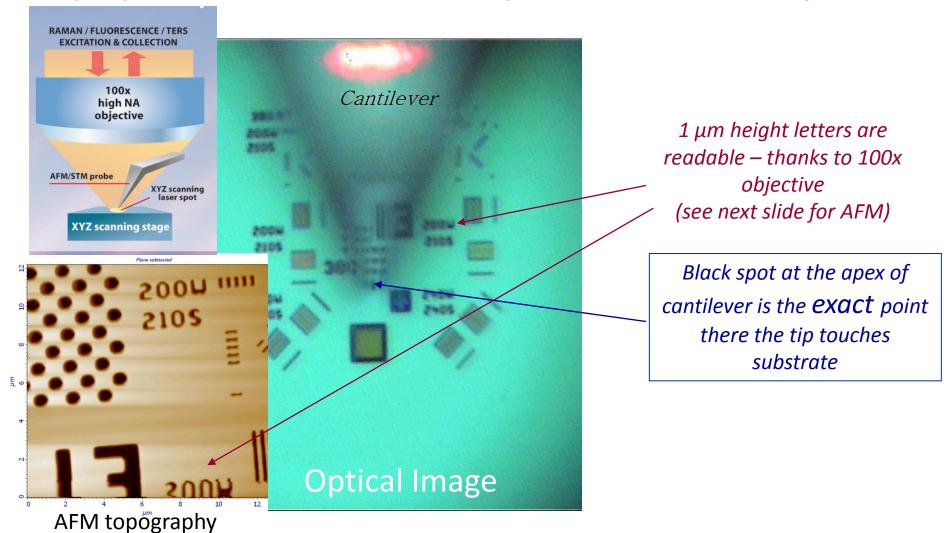
Excitation-collection configurations







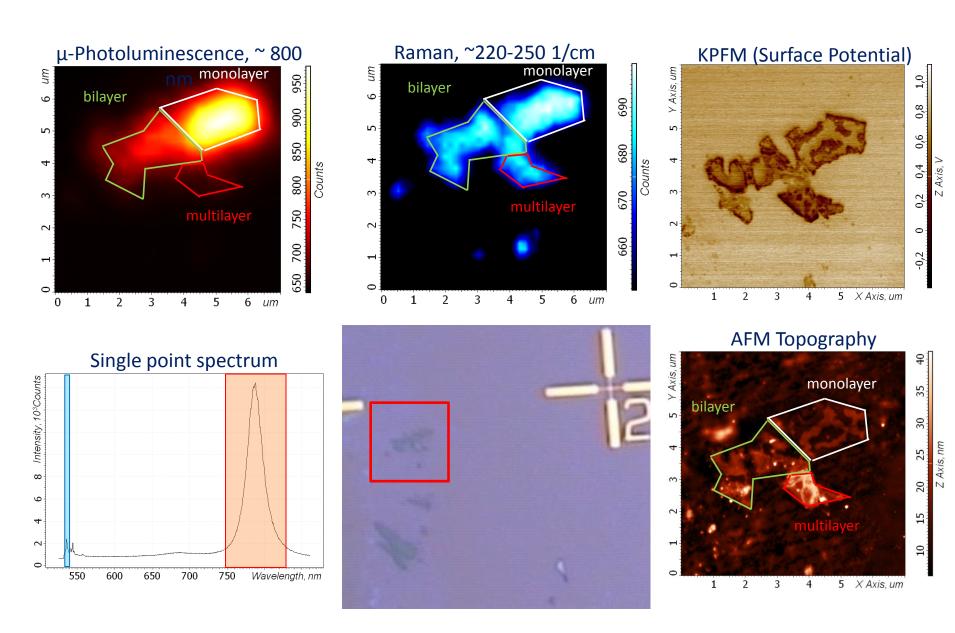
Top optical access to the AFM probe with 100x objective



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

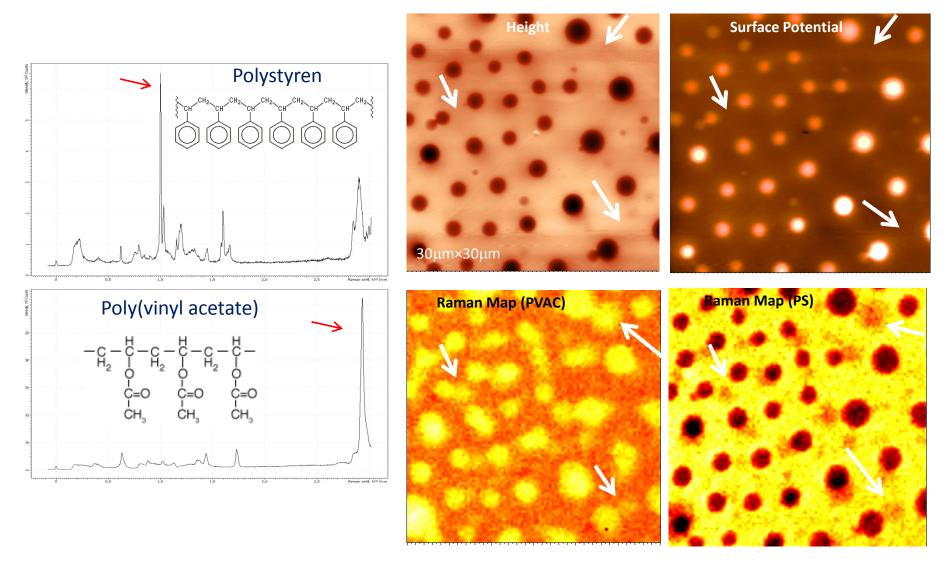


MoSe₂ flakes



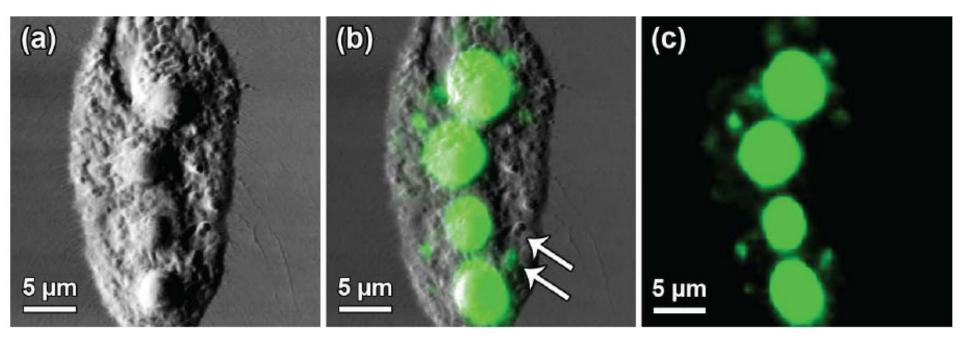
KPFM-Raman Studies of Polymer Blends

Polymer Blend PS-PVAC: Thick Film on ITO glass





Cyanobacteria biofilm: AFM and Raman mapping

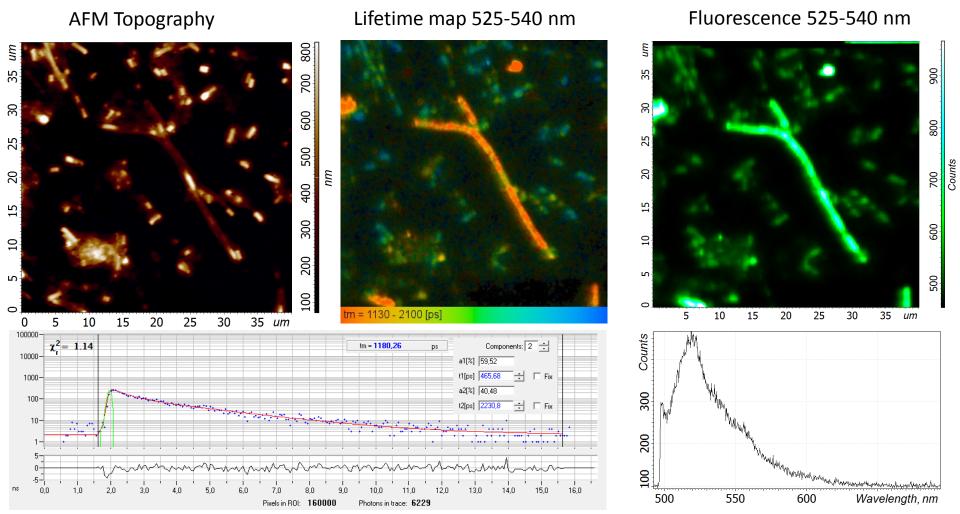


Combined study of cyanobacteria biofilm by means of atomic force microscopy and confocal Raman microscopy. AFM image in phase contrast (left) gives an image with nm resolution, however, does not contain any chemical information. Raman map (right) corresponds to the distribution of beta-carotene. Resolution Raman map is limited by the optical limit and is 400-500 nm. Beta-carotene is the pigment contained in cyanobacteria which perform photosynthesis. Overlay of two images (center) provides the chemical identity and relate it to the AFM image of high resolution.

Data courtesy: Thomas Schmid, Pawel L. Urban, Andrea Amantonico, Renato Zenobi ETH Zurich, Switzerland

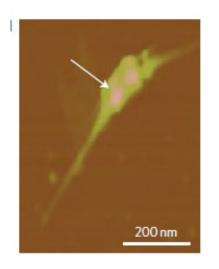


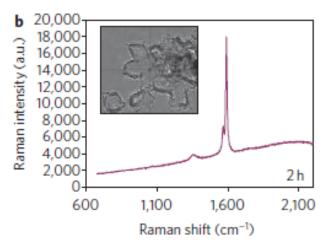
Topography and FLIM image of e-coli

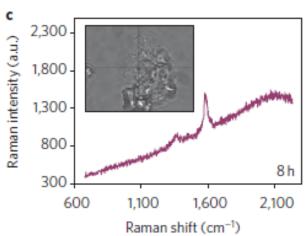


Topography (left) and FLIM mapping of 525-540 nm band (center) and fluorescence intensity (right). Decay curve on the bottom left image and fluorescence spectrum on the bottom right one. Different FLIM signals come from different fluorescent proteins, which produced by e-coli genetically modified in different ways. Spectrum shape is very similar. Intensity and lifetime is different. AFM + Spectrometer + FLIM provides sufficient information to identify different proteins in bacteria.

Biodegradation of carbon nanotubes







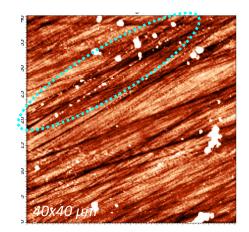
AFM image showing the capture of a single nanotube by living cell of immune system (neutrophils).

Raman spectra of neutrophil with IgG-nanotubes after 2 hours (b) and 8 hours (c). Reducing the intensity of G- and D-bands of carbon nanotube indicates biological degradation of single nanotubes. Thus, neutrophils were successfully processed and excreted objects such as carbon nanotubes

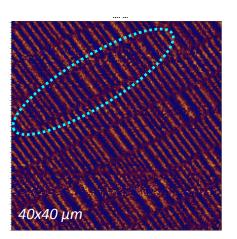
Y. Volkov et all // Carbon nanotubes degraded by neutrophil myeloperoxidase induce less pulmonary inflammation, Nature Nanotechnology, 2010



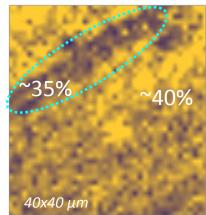
DLC Protective Layer of Hard Disk Drive



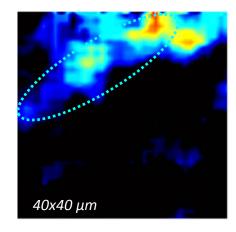
AFM topography
Nearly parallel scratches in
DLC protective layer are
produced by low-flying
magnetic head. Bumps are
signatures of erosion of Co
magnetic layer.



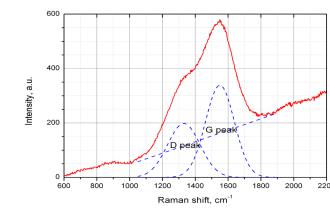
MFM image Magnetic domains are not damaged yet.



Raman map, sp3 (diamond-type) bonding fraction $\omega G = 1580$.

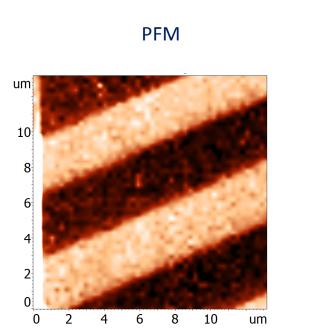


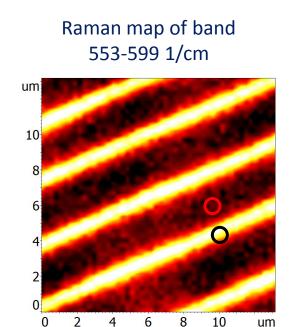
Raman map,
ID/IG ratio
Increased fraction of
sp2 bonds and
defects.

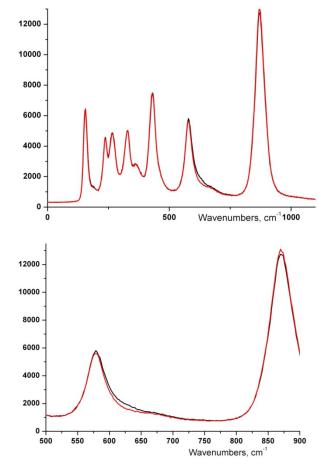




Simultaneous PFM and Raman mapping





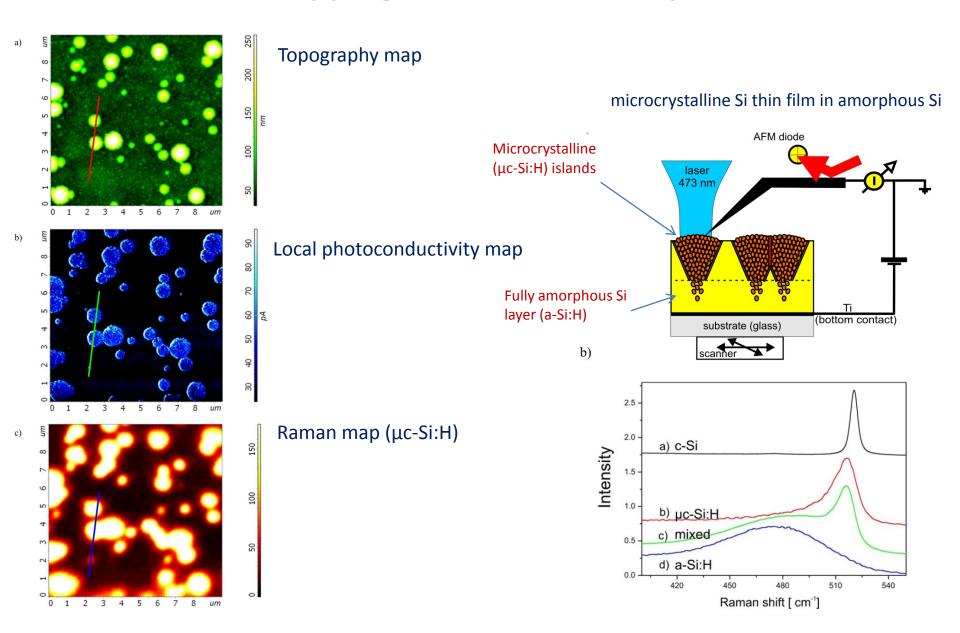


PFM mapping and Raman mapping of 553-599 1/cm band Lithium Niobate. Changes of Raman bands intensities appears on the border of domains

100x0,7 objective used. \sim 8 mW of 473 nm laser used. Exposure time 1 s/points and 50x50 points scan size.



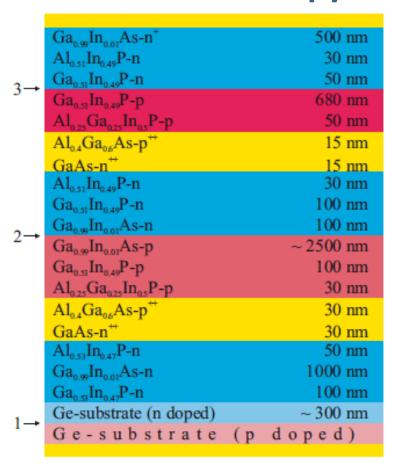
Photocurrent mapping under localized optical excitation





Solar cell diagnostics by combination of Kelvin probe microscopy with local photoexcitation

excitation laser spot



Optical image

Individual p-n junction is locally excited by a 400 nm laser spot. Variation of surface potential is measured by cantilever (Kelvin prove microscopy)

100x

high NA

objective

Multi-junction solar cell

Electrical AFM probe

Multijunction solar cell structure. Digits 1,2,3 show p-n junctions.

Blue: n-type layers, pink: p-type layers,

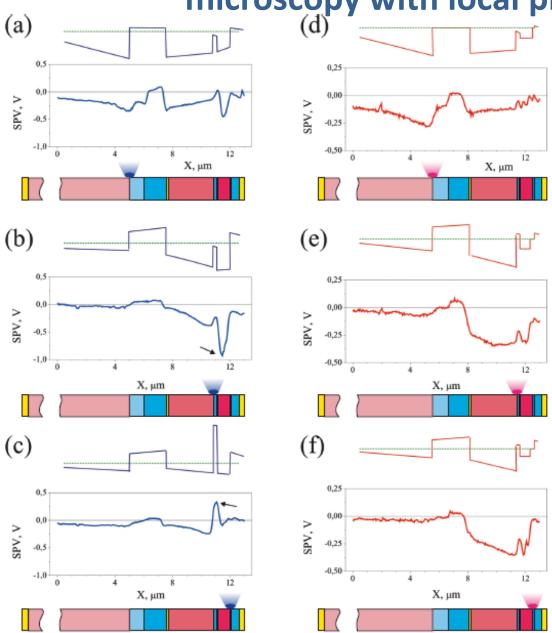
yellow: highly conductive layers



cantilever apex

Solar cell diagnostics by combination of Kelvin probe

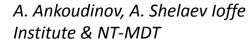
microscopy with local photoexcitation



Surface potential variation for local excitation by 473 nm laser (left row: a,b,c) and 785 nm laser (right row: d,e,f).

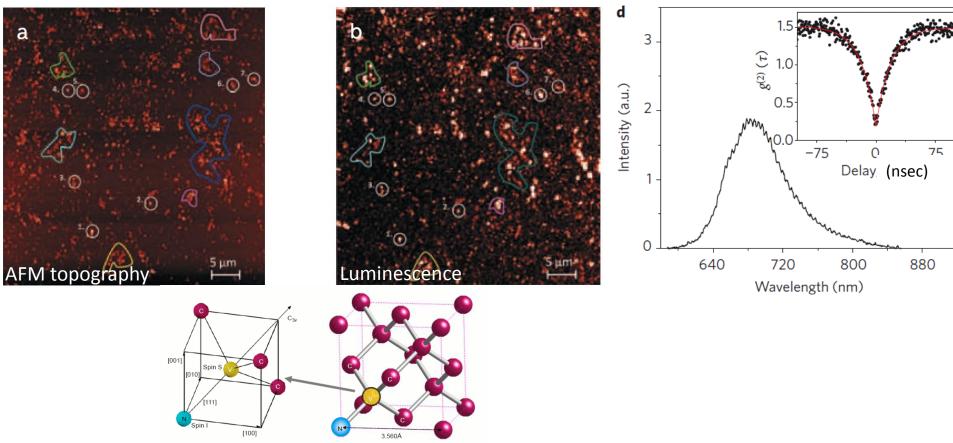
Different individual p-n junctions are locally excited.

Experimental results correspond well to numerical simulation





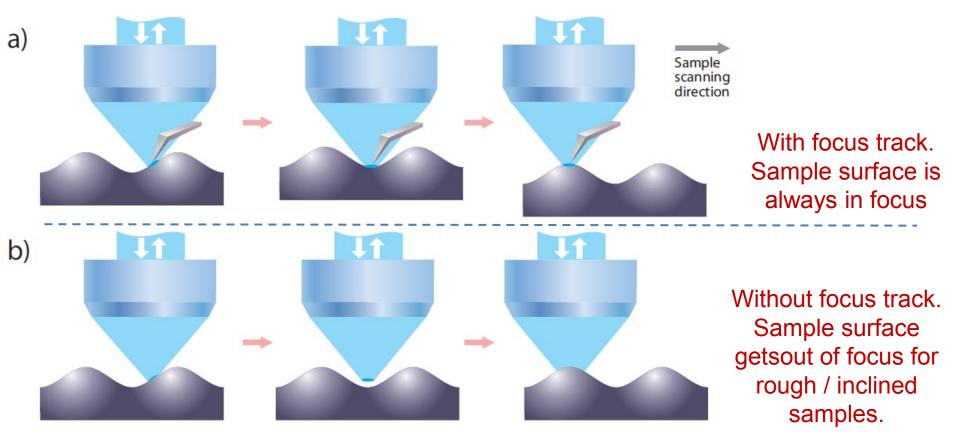
Nitrogen vacancy color centers in nanodiamonds



Observation of nitrogen-vacancy (NV) color centers in *discrete* detonation nanodiamonds (a) AFM topography image; smallest particles observed are discrete isolated nanodiamonds of ~5 nm size. (b) Confocal luminescence map of the same sample area; nitrogen-vacancy luminescence from isolated nanodiamonds is clearly seen. (c) Luminescence spectrum of individual NV center in a 5 nm crystal host.



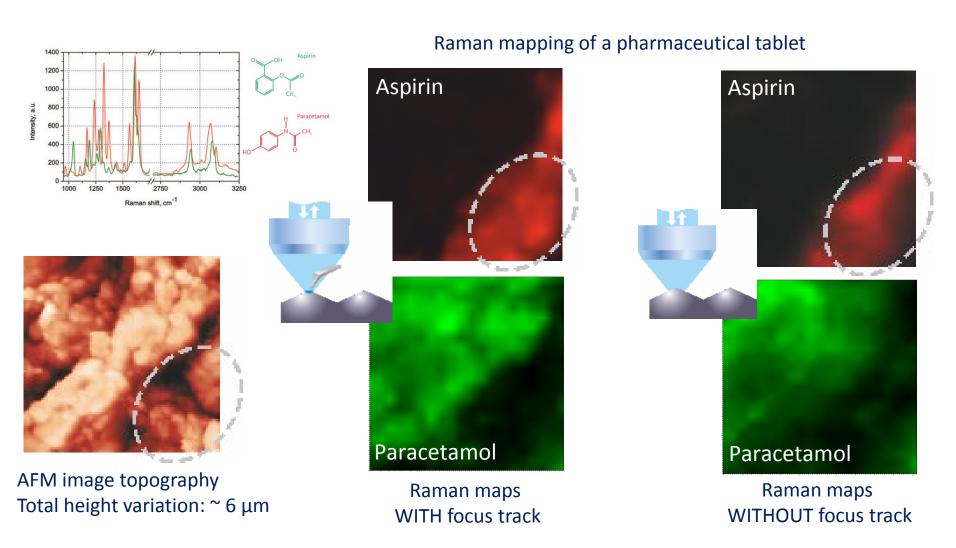
Focus track feature of integrated AFM - confocal Raman/fluorescence instrument



- (a) Integrated AFM-Raman instrument and its "focus track" feature. Sample surface always stays in focus due to AFM feedback mechanism. This provides true information about sample chemical composition even for very rough surfaces.
- (b) Standard confocal Raman/fluorescence imaging sample is scanned in X&Y directions; Sample gets out of focus, providing incorrect data about optical properties of the surface.



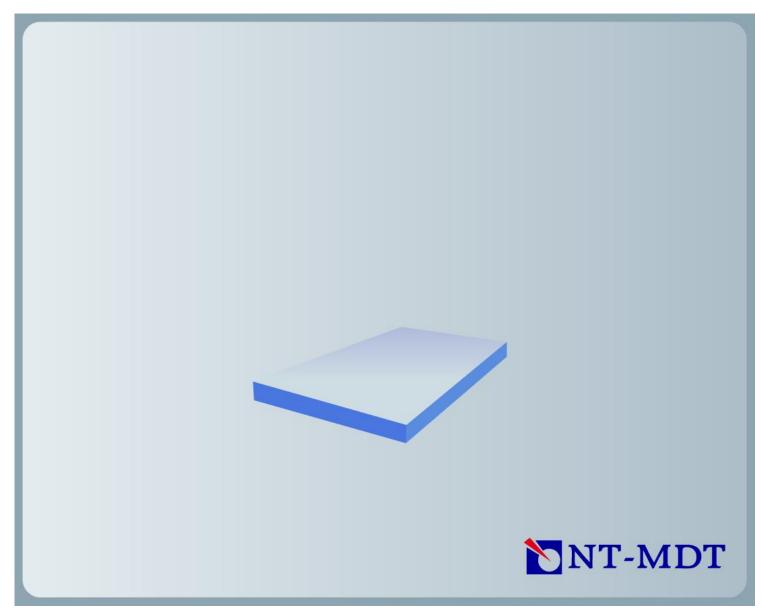
Focus track feature of integrated AFM - confocal Raman/fluorescence instrument



Size of images: 20x20 μm



Graphene, AFM + Confocal Raman





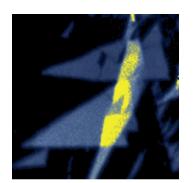
Graphene, AFM + Confocal Raman



Lateral Force Microscopy (friction)



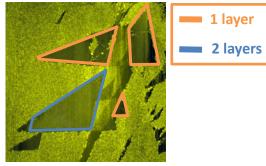
Capacitance Microscopy



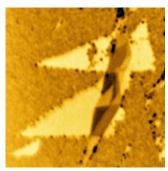
Raman Map, 2D Band position



Electrostatic Force Microscopy (charge distribution)



AFM Topography
Size: 30*30 μm



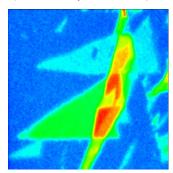
Confocal Rayleigh Microscopy



Force Modulation Microscopy (elasticity)



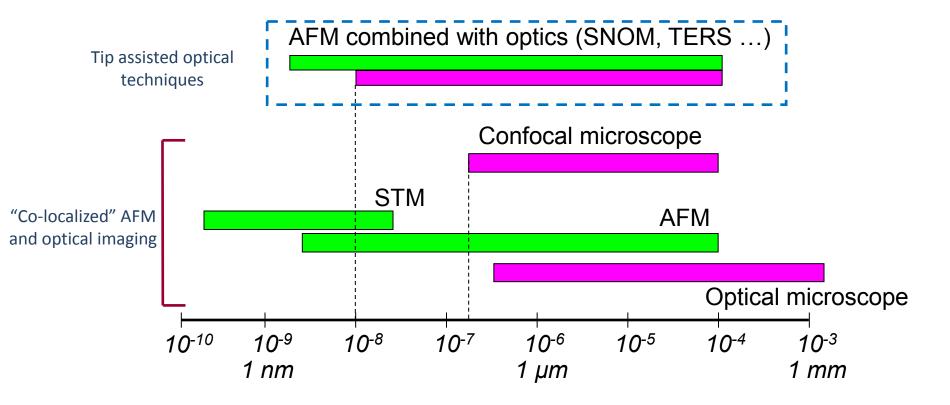
Scanning Kelvin Probe Microscopy (surface potential)

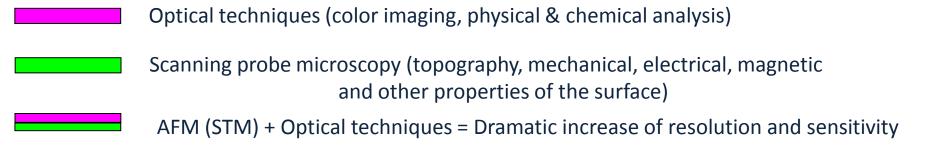


Raman Map, G-band Intensity



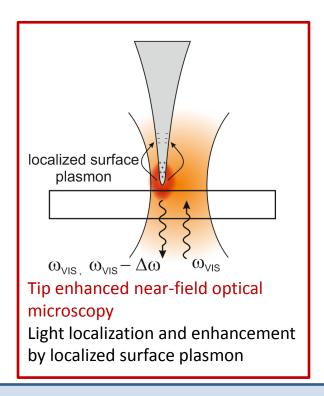
Resolution and capabilities of different techniques

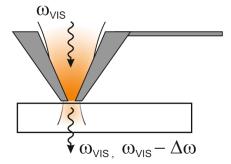






Super-resolution imaging using scanning optical antennas





Aperture scanning near-field optical microscopy (SNOM)
Light transmission through non-

ANTENNA

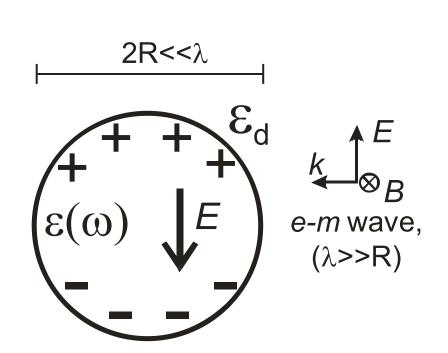
resonant subwavelength aperture

Optical antenna: a device designed to efficiently convert free-propagating optical radiation to localized energy, and vice versa.

- L. Novotny, N. van Hulst, Nature photonics 5, 89 (2011)
- P. Bharadwai, B. Deutch, L. Novotny, Adv. In Opt. Phot. 1, 438 (2009)
- Pohl D. W., Optics, Principles and Applications (World Scientific, 2000).



Localized surface plasmon resonance in metal nanoparticles (0D geometry)



$$\alpha = 4\pi R^3 \frac{\varepsilon(\omega) - \varepsilon_d}{\varepsilon(\omega) + 2\varepsilon_d}$$

Nanoparticle polarizability

Resonant interaction with light at:

$$\varepsilon(\omega_{res}) = -2\varepsilon_d$$

(Fröhlich mode)

metal spherical nanoparticle in dielectric medium

Drude model:
$$\varepsilon'(\omega) = 1 - \omega_n^2 / \omega^2$$

$$\omega_{pe} = \sqrt{\frac{4\pi n_e e^2}{m}} \quad \omega_{res} = \omega_p \, / \, \sqrt{3}$$



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

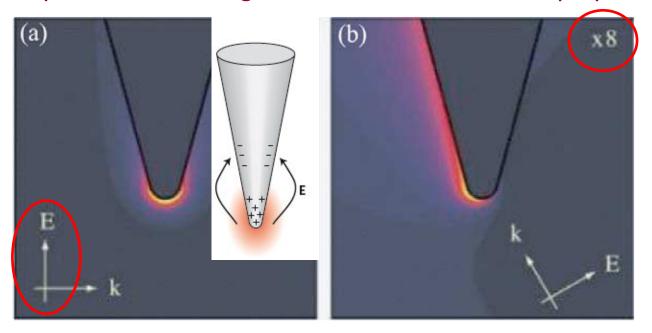


Fig. 1 Calculated field distribution at a sharp Au tip with a diameter of 5 nm. (a) Field distribution for an incident electric field vector parallel to the tip shaft showing localization of the electric field at the tip apex. (b) Field distribution for an incident electric field orientated nonparallel 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)



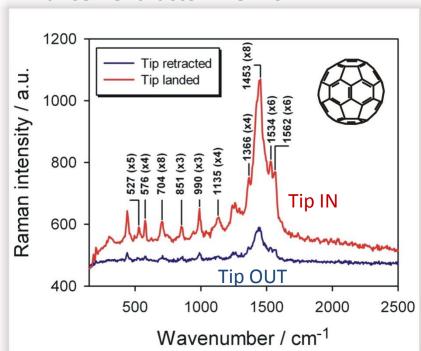
TERS enhancement factor as function of tip-sample distance Fullerene thin film

Laser: 633 nm

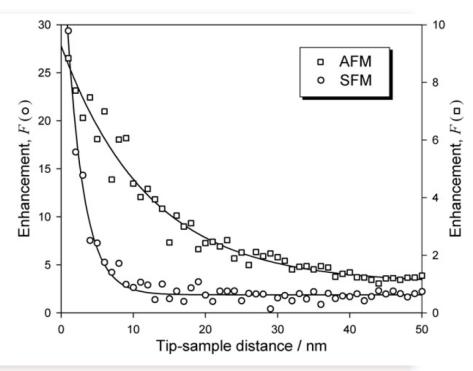
Tip: Au etched wire & Au coated cantilever

Mode: Shear force & non-contact mode

Enhancement factor: ~ 5–10x



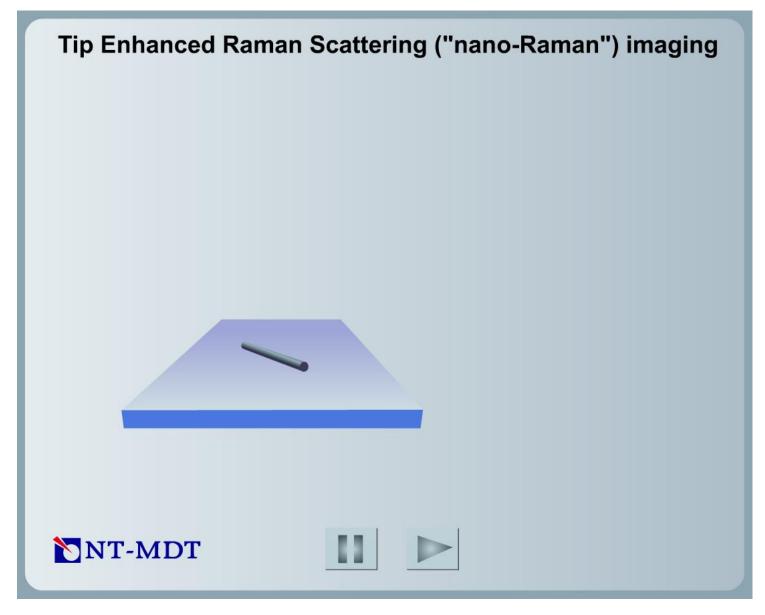
Signal enhances >10 times after tip is approached



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

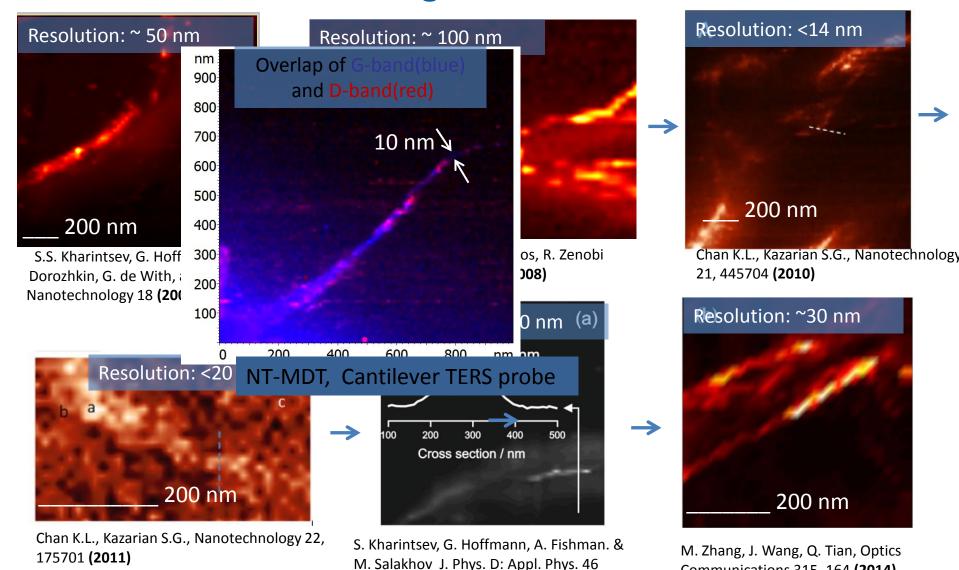


TERS on carbon nanotubes All data – using NT-MDT instrument





TERS on carbon nanotubes All data – using NT-MDT instrument

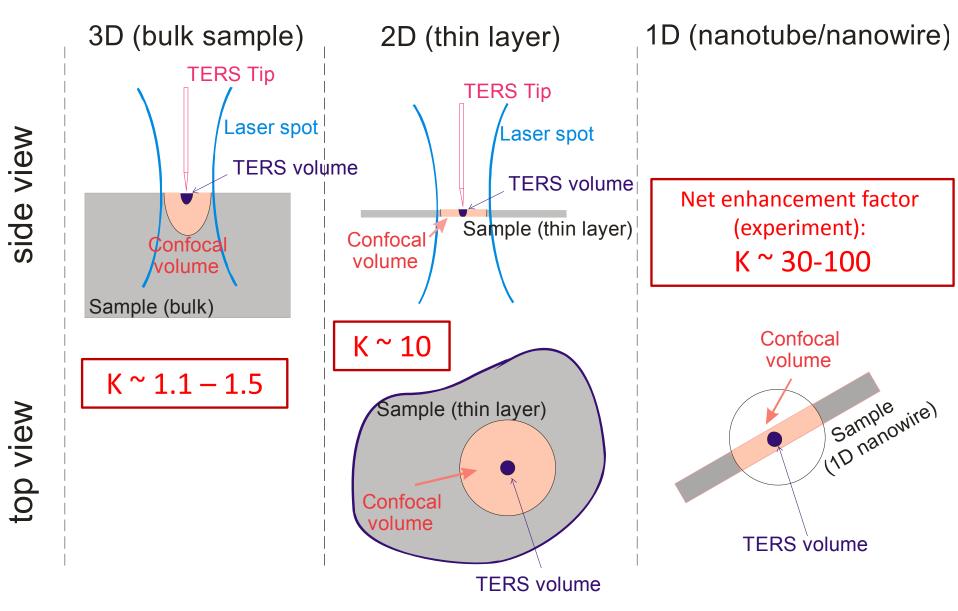


(2013) 145501



Communications 315, 164 (2014)

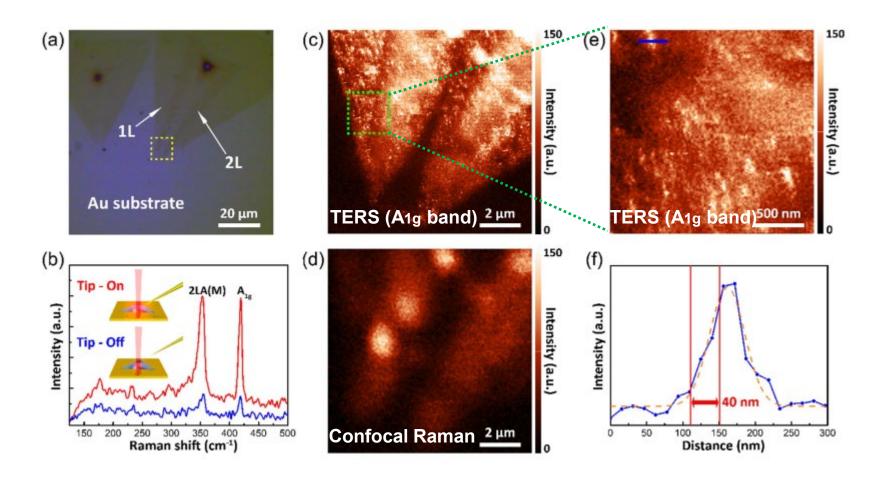
TERS enhancement in different geometries (1D, 2D, 3D)



Far field to near field volume ratio decreases with decreasing dimension – lower dimensions are more advantageous for TERS



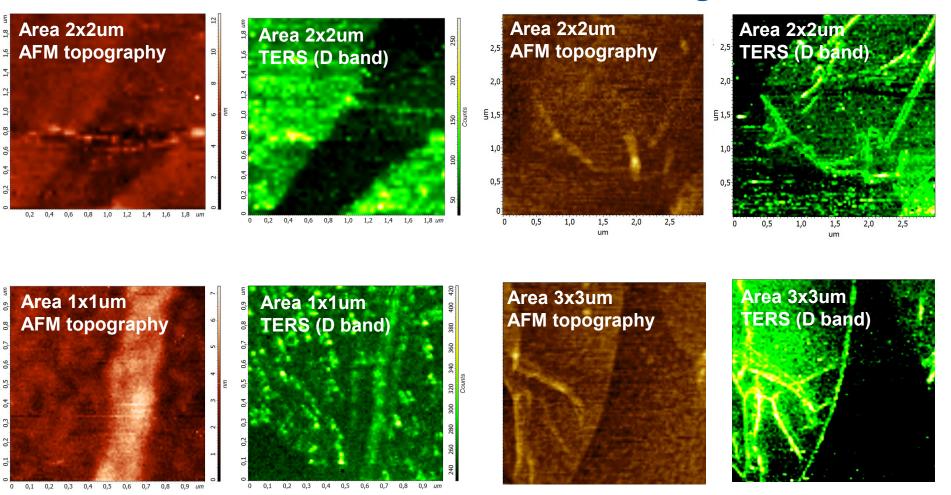
TERS spectra and images of mono/bilayer WS2 flake



C. Lee *et al.*, "Tip-Enhanced Raman Scattering Imaging of Two-Dimensional Tungsten Disulfide with Optimized Tip Fabrication Process," *Sci. Rep.*, vol. 7, no. September 2016, p. 40810, Jan. 2017.



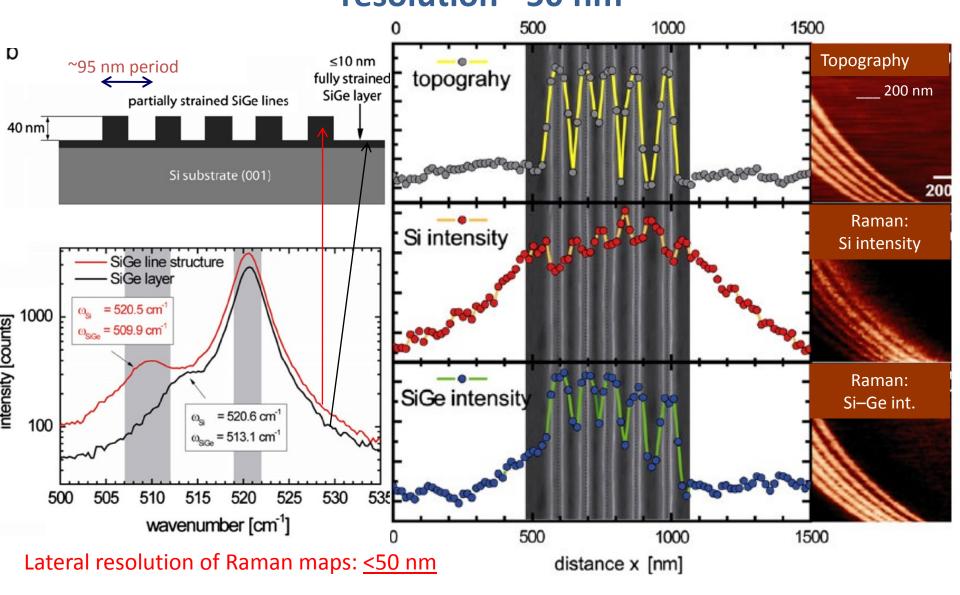
TERS on Graphene Oxide AFM TERS cantilevers, HYBRID regime



Typical TERS resolution with AFM TERS probes: $\sim 20 - 40$ nm.



TERS ("nano-Raman") on periodic Si-Ge structure resolution ~50 nm

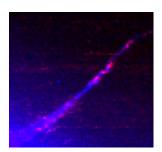


P.Hermann, M. Hecker, D. Chumakov, M. Weisheit, J. Rinderknecht, A.Shelaev, P. Dorozhkin, L.M.Eng, Fraunhofer CNT & AMD, Dresden; NT-MDT. Ultramicroscopy 111, 1630 (2011)

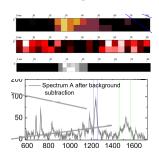


Tip Enhanced Raman Scattering

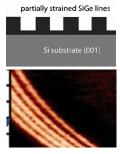
Various types samples. Proven by multiple publications by NT-MDT customers.



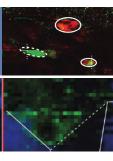
Carbon nanotubes
Resolution: ~10 nm
Nanotechnology, 2011
& ~10 other papers



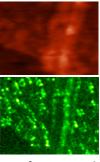
DNA molecule Resolution: ~15 nm Ang. Chem. Int., 2014, E. Lipiec et. al



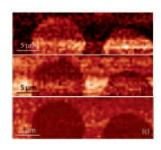
Si/SiGe structures
Resolution: <50 nm
Ultramicroscopy, 2011
P. Hermann et al.



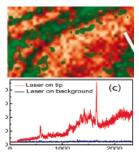
Graphene Resolution: ~12 nm ACS Nano, 2011 R. Zenobi et. al.



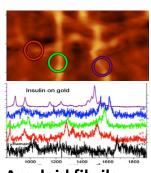
Graphene Oxide
Resolution: ~15 nm
A. Shelaev, et. al.,
2014



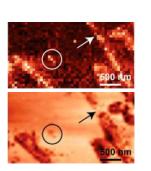
Thiol monolayers
Resolution: ~50 nm
Beilstein J. Nano, 2011
R. Zenobi et. al.



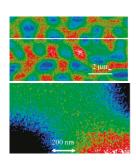
Thin molecular layers
Resolution: ~15 nm
NanoLett., 2010
R. Zenobi et. al.



Amyloid fibrils
Resolution: ~50 nm
Plasmonics, 2012
E. Di Fabrizio et. al.



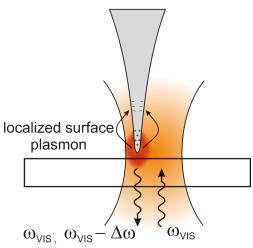
Peptide nanotapes Resolution: ~50 nm ACS Nano, 2013 R. Zenobi et. al.



Polymers Resolution: ~50 nm Macromol., 2011 G. Hoffmann et al.

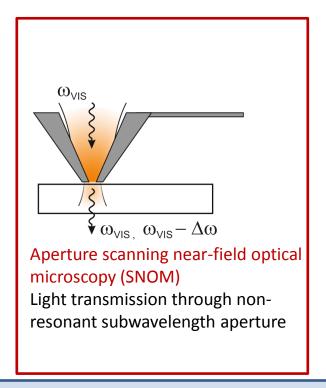


Super-resolution imaging using scanning optical antennas



Tip enhanced near-field optical microscopy

Light localization and enhancement by localized surface plasmon



ANTENNA

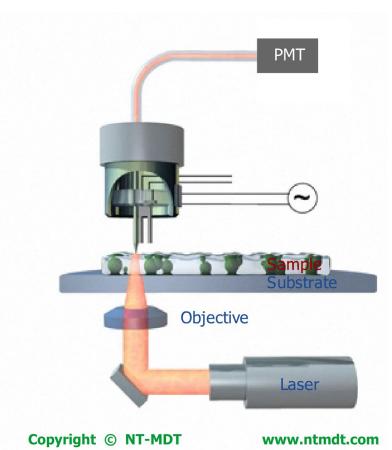
Optical antenna: a device designed to efficiently convert free-propagating optical radiation to localized energy, and vice versa.

- L. Novotny, N. van Hulst, Nature photonics 5, 89 (2011)
- P. Bharadwai, B. Deutch, L. Novotny, Adv. In Opt. Phot. 1, 438 (2009)
- Pohl D. W., Optics, Principles and Applications (World Scientific, 2000).



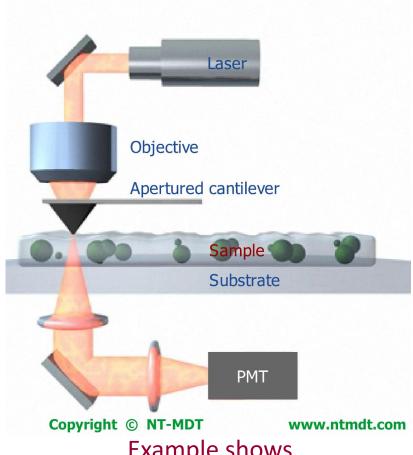
Two major types of SNOM

FIBER SNOM



Example shows
SNOM collection mode
(laser signal)

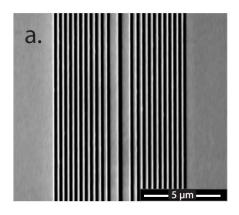
CANTILEVER SNOM



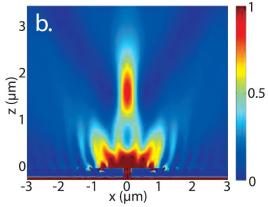
Example shows
SNOM Transmission mode
(laser signal)



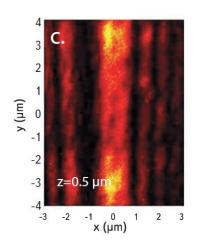
SNOM for focusing micro-devices

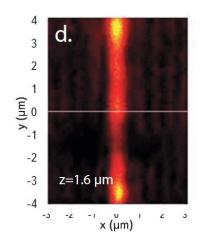


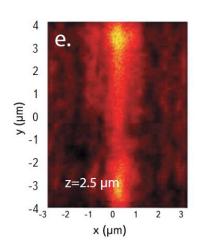
SEM image of a focusing plasmonic device

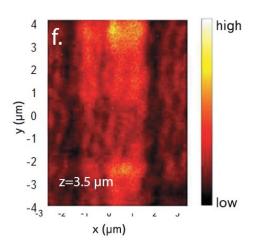


Intensity distribution of the transmitted/focused light (simulation)







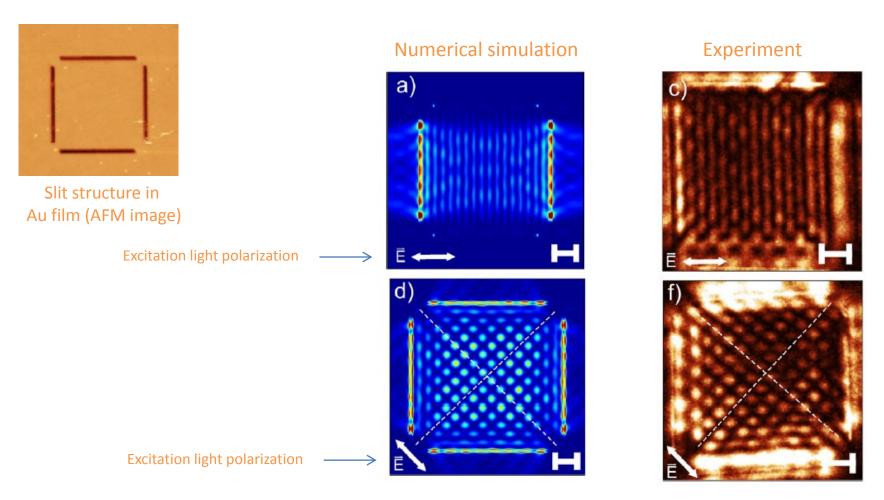


SNOM data: light intensity at different distances from the sample surface

Data from: Dr. Fenghuan Hao, Dr. Rui Wang and Dr. Jia Wang, OPTICS EXPRESS Vol. 18, No. 3, 15741-15746 (2010)



SPP interference studied by SNOM

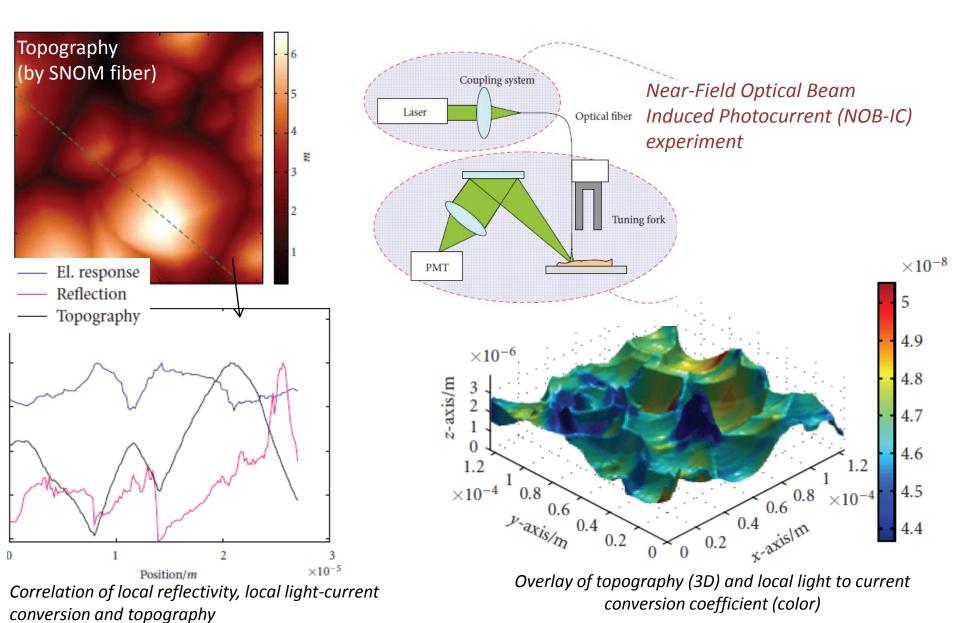


Near-field interference pattern of surface plasmon polaritons in a square-like slit structure in Au film

Control and Near-Field Detection of Surface Plasmon Interference Patterns. Petr Dvořák, Tomáš Neuman, Tomáš Šikola et al., Nano Letters 2013



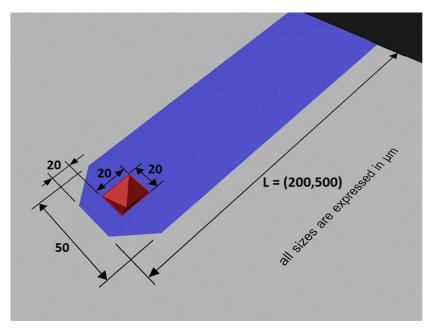
SNOM for localized optical excitation in photovoltaics





NT-MDT cantilever SNOM: contact AND non-contact probes

1) Lever sizes and the pyramid position:

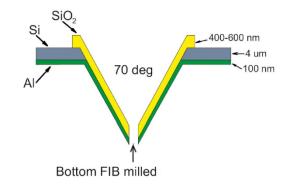


Pyramid LxWxH = 20x20x13 (70 deg)

	Spring Constant (N/m)			Frequency (kHz)			Length (micron)			Width (micron)			Thickness (micron)		
	Nominal	Min	Max	Nominal	Min	Max	Nominal	Min	Max	Nominal	Min	Max	Nominal	Min	Max
NonContact	16.5	5.9	39.0	130	88	180	200	190	210	55	54	57	4	3	5
Contact	1.01	0.41	2.30	20.8	15	27	500	490	510	55	54	57	4	3	5

Probe	Resolution	TR@ 473			
1 contact	150 nm	~3*10-4			
1 contact	???	0.3*10-4			
1 noncontact	110 nm	~0.16*10-4			
2 noncontact	120 nm	~0.5*10-4			
3 noncontact	135 nm	~0.7*10-4			
4 noncontact	100 nm	~0.2*10-4			
5 noncontact	150 nm	~1.6*10-4			

2) Tip shape and aperture size:



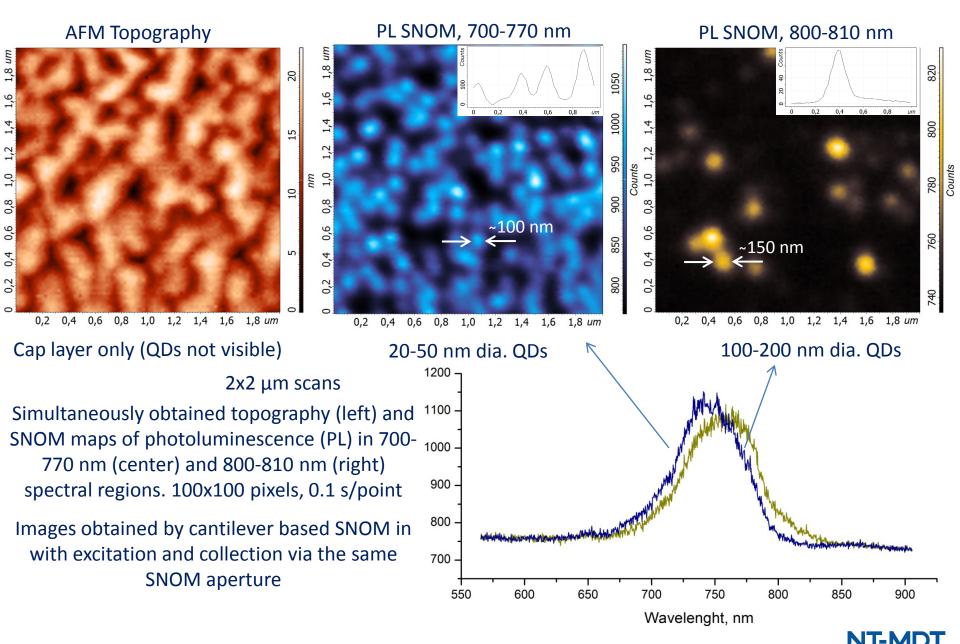
Pyramid (SiO2) thickness 400-600 nm

3) Coating: Al, about 100 nm, coating from bottom side. Bottom FIB milling is done after coating. Typical aperture diameter about 170 ±25nm.



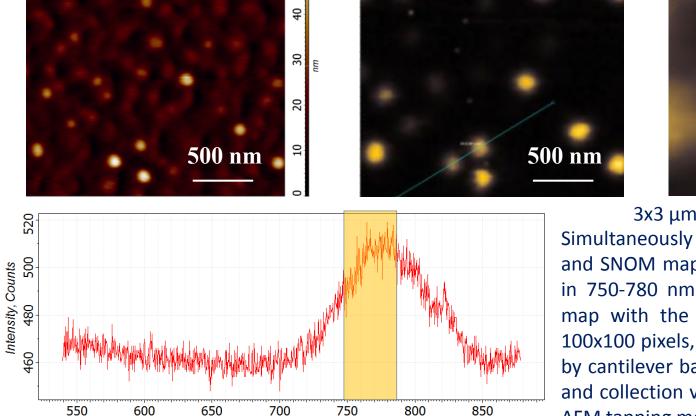


SNOM of InP/GaInP quantum dots with GaInP cap layer



QD SNOM spectroscopy and topography

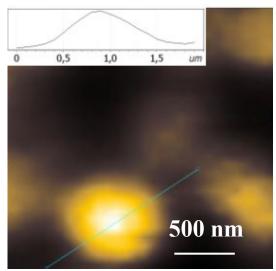
SNOM PL, 750-780 nm



Wavelength, nm

AFM Topography

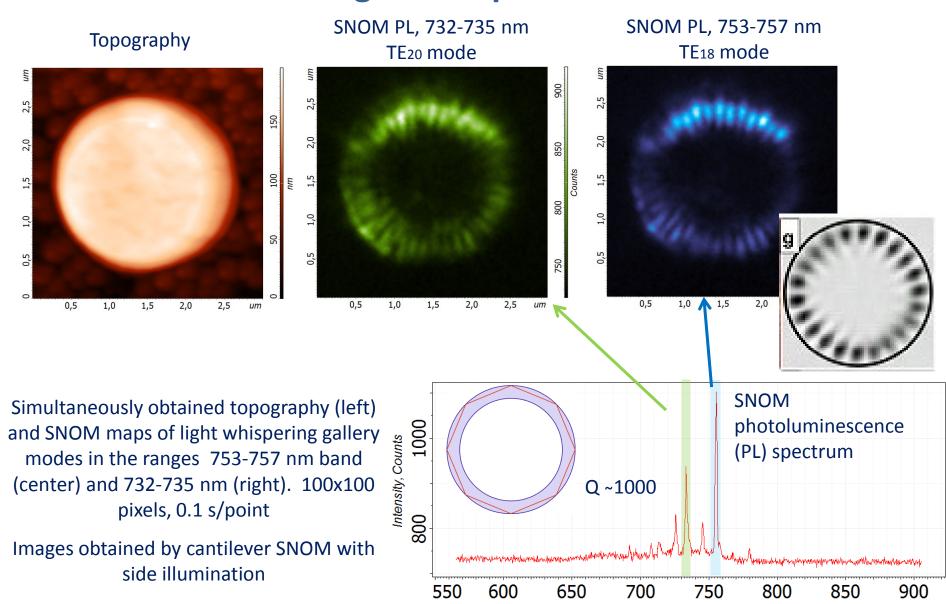
Confocal map, 750-780 nm



3x3 μm scans
Simultaneously obtained topography (left) and SNOM maps of photoluminescence (PL) in 750-780 nm band (center) and confocal map with the same spectral band (right). 100x100 pixels, 0.1 s/point. Images obtained by cantilever based SNOM in with excitation and collection via the same SNOM aperture. AFM tapping mode used.

Shelaev A. V., Mintairov A. M., Dorozhkin P. S., and Bykov V. A. Scanning near-field microscopy of microdisk resonator with InP/GalnP quantum dots using cantilever-based probes // J. Phys. Conf. Ser. 2016. Vol. 741. P. 12132.

Whispering gallery light modes in microdisks with InP/GaInP self-organized quantum dots



A. Mintairov, A. Ankoudinov, A. Shelaev, P. Dorozhkin, Ioffe Institute & NT-MDT

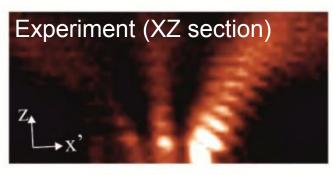
Wavelength, nm

Spectrum matruments

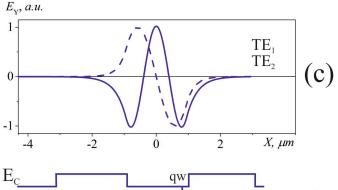
Laser emission in 3D studied by SNOM



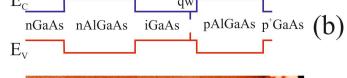
Cantilever SNOM operation at near IR region ($^{\sim}1.1 \mu m$)

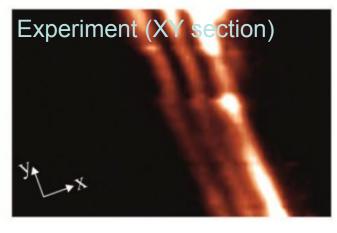


Comparison (Surface (near field)



Angie, degree





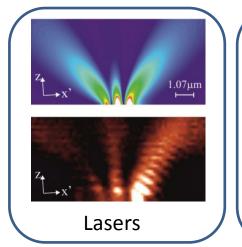
Surface (near field)

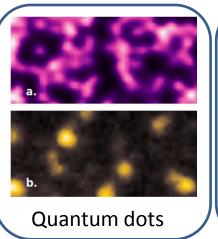


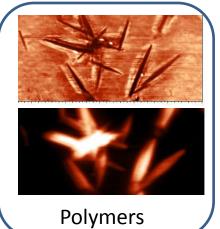
A.V. Ankudinov, P.S. Dorozhkin, A.A. Podoskin, A.V. Shelaev, S.O. Slipchenko, I.S. Tarasov, M.L. Yanul Ioffe Physical Institute; NT-MDT Co. & ITMO

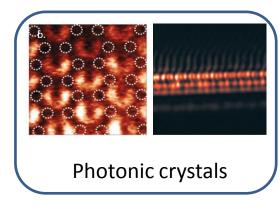


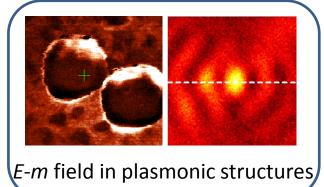
Aperture SNOM applications (NT-MDT instrumentation)

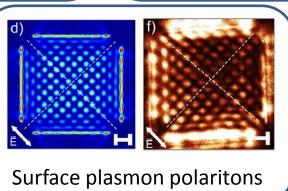


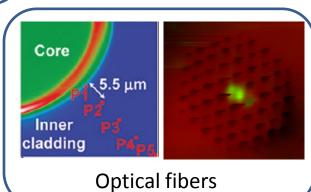


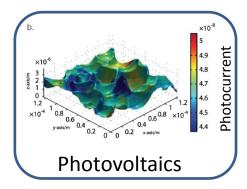


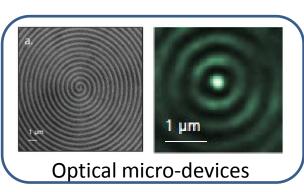














Physical and chemical characterization at the nanoscale: experimental approaches utilizing AFM probe

Co-localized AFM-Raman

- Comprehensive simultaneous physical (AFM) and chemical (Raman) sample characterization.
- Spatial resolution: AFM ~1 nm; Raman ~200-400 nm.
- Various excitation and collection geometries.
- Tip Enhanced Raman Scattering (TERS)

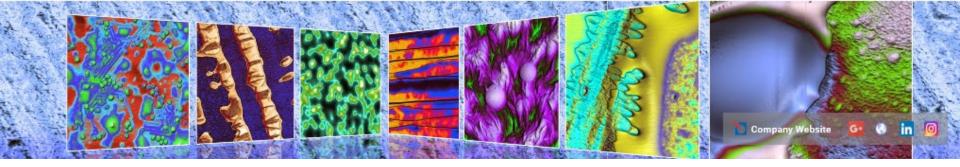
- Controlled environment: liquid, gases, temperature, electrochemistry, magnetic field
- Signal enhancement for weakly scattering samples.
- ~10 nm spatial resolution in Raman (chemical) imaging.
- Graphene and other carbon nanomaterials, polymers, thin molecular layers, semiconductor nanostructures, biological structures, DNA molecules etc.
- Advances in production of reproducible TERS probes (STM, tuning fork, <u>AFM cantilevers</u>).
- Aperture scanning near-field optical microscopy (SNOM)
- $\sim \lambda/10$ spatial resolution (~ 100 nm for NIR).
- Advances in cantilever SNOM manufacturing: contact & non-contact probes, improved signal collection efficiency.
- Plasmonics and nanophotonics structures, lasers, optical fibers, photovoltaics, QDs, etc.





Thank you for your attention!

www.ntmdt-si.com



Follow us in social networks! **#NTMDT**











