AFM integration with Laser Spectroscopy: Challenges, Solutions, Advantages

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# Product Line

<table>
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<tr>
<th></th>
<th>SOLVER NANO</th>
<th>NEXT / TITANIUM</th>
<th>NTEGRA</th>
<th>NTEGRA SPECTRA II</th>
<th>NTEGRA IR</th>
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<tr>
<td><strong>AFM</strong></td>
<td>Compact desktop AFM/STM for both education and science</td>
<td>AFM/STM with exceptional level of automation</td>
<td>Modular high performance AFM/STM for wide range of applications</td>
<td>SPM</td>
<td>IR sSNOM system</td>
</tr>
<tr>
<td></td>
<td>Full set of AFM/STM modes</td>
<td>Fast, precise and low-noise closed-loop scanner</td>
<td>Low noise and high resolution</td>
<td>Automated AFM laser, probe and photodiode</td>
<td>High resolution AFM</td>
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<td>High AFM/STM performance</td>
<td>High resolution imaging due to extremely low noise and high stability</td>
<td>Full set of standard and advanced AFM/STM modes</td>
<td>Confocal Raman / Fluorescence / Rayleigh Microscopy</td>
<td>Stabilized CO₂ laser</td>
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<td>Closed-loop Scanner</td>
<td>AFM/STM for wide range of applications</td>
<td>HybriD Mode™</td>
<td>Tip Enhanced Raman Scattering (TERS)</td>
<td>HybriD Mode™</td>
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<td>TERS optimized system for all possible excitation/detection geometries</td>
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</table>
PIEZO SCANNING COORDINATES (CLOSED LOOP):

Mirror scanning (α,β)

AFM integration with LIGHT

OPTICAL DETECTION
- Confocal Raman/Fluorescence microscope
- Photon counting PMT, APD
- Lock-in detection (ω, 2ω, 3ω ...)
- Gated photon counting
- Time resolved (FLIM)
- Laser confocal microscopy

Tip, XYZ

Sample, XYZ

Objective, Z

Mirror scanning (α,β)
NTEGRA Spectra II in Upright, Inverted and Side illumination configuration

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>Light input from side</td>
<td>(with scanning mirror)</td>
</tr>
<tr>
<td>Top optics</td>
<td>(LED illuminator &amp; camera)</td>
</tr>
<tr>
<td>Light input from top</td>
<td>(with scanning mirror)</td>
</tr>
<tr>
<td>Optical AFM</td>
<td>(AFM probe + 100x objective on the top)</td>
</tr>
<tr>
<td>XYZ sample stage</td>
<td>(bottom illumination objective inside)</td>
</tr>
<tr>
<td>Light input from bottom</td>
<td>(with scanning mirror)</td>
</tr>
<tr>
<td>Bottom optics</td>
<td>(LED illuminator &amp; camera)</td>
</tr>
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</table>
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

Measurement parameters:
- Laser: 473 nm, 20 mW
- Objective: 100x, 0.95 NA
- Grating: 600 lines/mm
- Exposure time: 10 sec
- Number of exposures: 15

Si line, 1st order in saturation
Si line, 2nd order
Si line, 3rd order
Si line, 4th order

2nd order of Si: ~300 000 counts
4th order of Si: clearly resolved
Low wavenumbers Raman spectrum of sulfur. Cut-off at 10 \(1/\text{cm}\) 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

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
MoSe$_2$ flakes

**µ-Photoluminescence, ~ 800 nm**

- monolayer
- bilayer
- multilayer

**Raman, ~220-250 1/cm**

- monolayer
- bilayer
- multilayer

**KPFM (Surface Potential)**

**AFM Topography**

Wolfgang Mertin, Gerd Bacher, Artem Shelaev, Sergey Lemeshko, Universität Duisburg & NT-MDT
KPFM-Raman Studies of Polymer Blends

Polymer Blend PS-PVAC: Thick Film on ITO glass

**Polystyren**

**Poly(vinyl acetate)**

Raman Map (PVAC)

Raman Map (PS)

Height

Surface Potential

30μm×30μm
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 al // 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. ~8 mW of 473 nm laser used. Exposure time 1 s/points and 50x50 points scan size.

L. Eng, A. Shelaev & NT-MDT
Photocurrent mapping under localized optical excitation

Topography map

Local photoconductivity map

Raman map (μc-Si:H)

Microcrystalline (μc-Si:H) islands

Fully amorphous Si layer (a-Si:H)

Martin Ledinský, Antonín Fejfar, Aliaksei Vetushka and Artem Shelaev
Solar cell diagnostics by combination of Kelvin probe microscopy with local photoexcitation

Multijunction solar cell structure. Digits 1,2,3 show p-n junctions. Blue: n-type layers, pink: p-type layers, yellow: highly conductive layers

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

A. Ankoudinov, A. Shelaev Ioffe Institute & NT-MDT
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

A. Ankoudinov, A. Shelaev Ioffe Institute & NT-MDT
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

Raman mapping of a pharmaceutical tablet

AFM image topography
Total height variation: ~ 6 µm

Raman maps
WITH focus track

Paracetamol

Raman maps
WITHOUT focus track

Paracetamol

Size of images: 20x20 µm
Graphene, AFM + Confocal Raman

Real time simulation. Scanning area of 100x100 pixels, 50 sec scanning time
Graphene, AFM + Confocal Raman

- **Lateral Force Microscopy (friction)**
- **Electrostatic Force Microscopy (charge distribution)**
- **Force Modulation Microscopy (elasticity)**
- **Capacitance Microscopy**
- **AFM Topography**
  - Size: 30*30 µm
- **Raman Map, 2D Band position**
- **Confocal Rayleigh Microscopy**
- **Scanning Kelvin Probe Microscopy (surface potential)**
- **Raman Map, G-band Intensity**
Resolution and capabilities of different techniques

- Optical techniques (color imaging, physical & chemical analysis)
- Scanning probe microscopy (topography, mechanical, electrical, magnetic and other properties of the surface)
- AFM (STM) + Optical techniques = Dramatic increase of resolution and sensitivity
Super-resolution imaging using scanning optical antennas

Tip enhanced near-field optical microscopy
Light localization and enhancement by localized surface plasmon

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

\[ \varepsilon(\omega_{\text{res}}) = -2\varepsilon_d \]

(Fröhlich mode)

Drude model:

\[ \varepsilon'(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \]

\[ \omega_{\text{res}} = \omega_p / \sqrt{3} \]
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.

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

Data courtesy of S. Kharintsev, J. Loos, G. Hoffman, G. de With, TUE, the Netherlands
TERS on carbon nanotubes
All data – using NT-MDT instrument

Tip Enhanced Raman Scattering ("nano-Raman") imaging
TERS on carbon nanotubes

All data – using NT-MDT instrument

Resolution: ~ 50 nm
Resolution: ~ 100 nm
Resolution: <14 nm
Resolution: ~ 30 nm

Overlap of G-band (blue) and D-band (red)

200 nm


M. Zhang, J. Wang, Q. Tian, Optics Communications 315, 164 (2014)
TERS enhancement in different geometries (1D, 2D, 3D)

3D (bulk sample) 
- TERS Tip
- Laser spot
- TERS volume
- Confocal volume
- Sample (bulk)
- K ~ 1.1 – 1.5

2D (thin layer) 
- TERS Tip
- Laser spot
- TERS volume
- Confocal volume
- Sample (thin layer)
- K ~ 10

1D (nanotube/nanowire) 
- TERS Tip
- Laser spot
- TERS volume
- Confocal volume
- Sample (1D nanowire)
- K ~ 30-100

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 WS$_2$ flake

TERS on Graphene Oxide
AFM TERS cantilevers, HYBRID regime

Typical TERS resolution with AFM TERS probes: ~ 20 – 40 nm.
TERS ("nano-Raman") on periodic Si-Ge structure resolution ~50 nm

Lateral resolution of Raman maps: <50 nm

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

**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.

*More than 50 publications.*
Super-resolution imaging using scanning optical antennas

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

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

Slit structure in Au film (AFM image)

Excitation light polarization

Numerical simulation

Experiment

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

Topography (by SNOM fiber)

Near-Field Optical Beam Induced Photocurrent (NOB-IC) experiment

Correlation of local reflectivity, local light-current conversion and topography

Overlay of topography (3D) and local light to current conversion coefficient (color)

P. Tomanek, P. Skarvada et al., Adv. In Optical Technol., v.2010, 805325
NT-MDT cantilever SNOM: contact AND non-contact probes

1) Lever sizes and the pyramid position:

![Diagram of lever sizes and pyramid position with dimensions L = (200,500)]

Pyramid LxWxH = 20x20x13 (70 deg)

<table>
<thead>
<tr>
<th>Probe</th>
<th>Resolution</th>
<th>TR@ 473</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 contact</td>
<td>150 nm</td>
<td>~3*10^-4</td>
</tr>
<tr>
<td>1 contact</td>
<td>??</td>
<td>0.3*10^-4</td>
</tr>
<tr>
<td>1 noncontact</td>
<td>110 nm</td>
<td>~0.16*10^-4</td>
</tr>
<tr>
<td>2 noncontact</td>
<td>120 nm</td>
<td>~0.5*10^-4</td>
</tr>
<tr>
<td>3 noncontact</td>
<td>135 nm</td>
<td>~0.7*10^-4</td>
</tr>
<tr>
<td>4 noncontact</td>
<td>100 nm</td>
<td>~0.2*10^-4</td>
</tr>
<tr>
<td>5 noncontact</td>
<td>150 nm</td>
<td>~1.6*10^-4</td>
</tr>
</tbody>
</table>

2) Tip shape and aperture size:

![Diagram of tip shape and aperture size with dimensions and materials: Si, SiO2, Al, 400-600 nm, 4 um, 100 nm, 70 deg, FIB milled]

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

![Diagram of Al deposition on tip side FIB from pit side]

<table>
<thead>
<tr>
<th>Spring Constant (N/m)</th>
<th>Frequency (kHz)</th>
<th>Length (micron)</th>
<th>Width (micron)</th>
<th>Thickness (micron)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal</td>
<td>Min</td>
<td>Max</td>
<td>Nominal</td>
<td>Min</td>
</tr>
<tr>
<td>16.5</td>
<td>9.9</td>
<td>19.0</td>
<td>130</td>
<td>88</td>
</tr>
<tr>
<td>Contact</td>
<td></td>
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</tbody>
</table>

all sizes are expressed in um
SNOM of InP/GaInP quantum dots with GaInP cap layer

Cap layer only (QDs not visible)

2x2 µm scans

Simultaneously obtained topography (left) and SNOM maps of photoluminescence (PL) in 700-770 nm (center) and 800-810 nm (right) spectral regions. 100x100 pixels, 0.1 s/point

Images obtained by cantilever based SNOM in with excitation and collection via the same SNOM aperture

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

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

Simultaneously obtained topography (left) and SNOM maps of light whispering gallery modes in the ranges 753-757 nm band (center) and 732-735 nm (right). 100x100 pixels, 0.1 s/point

Images obtained by cantilever SNOM with side illumination

A. Mintairov, A. Ankoudinov, A. Shelaev, P. Dorozhkin, Ioffe Institute & NT-MDT
Laser emission in 3D studied by SNOM

Cantilever SNOM operation at near IR region (~1.1 μm)

Far field (propagating e-m radiation)

Surface (near field)

Ioffe Physical Institute; NT-MDT Co. & ITMO
Aperture SNOM applications (NT-MDT instrumentation)

- Lasers
- Quantum dots
- Polymers
- Photonic crystals
- E-m field in plasmonic structures
- Surface plasmon polaritons
- Optical fibers
- Photovoltaics
- Optical micro-devices

Photocurrent
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)**
  - 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, AFM cantilevers).

- **Aperture scanning near-field optical microscopy (SNOM)**
  - ~ $\lambda/10$ 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.

Controlled environment: liquid, gases, temperature, electrochemistry, magnetic field
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